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ROZPRAWA DOKTORSKA

Tytuł rozprawy w języku polskim: **Adsorbenty do usuwania związków endokrynnie czynnych ze środowiska wodnego**

Tytuł rozprawy w języku angielskim: **Adsorbents for removing endocrine active compounds from the aquatic environment**

Promotor

dr hab. inż. Anna Schmidt, prof. PG

Gdańsk, 2026



OŚWIADCZENIE

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**Adsorbenty do usuwania związków endokrynnie czynnych ze środowiska wodnego
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OPIS ROZPRAWY DOKTORSKIEJ

Autor rozprawy doktorskiej: Dominika Nowacka

Tytuł rozprawy doktorskiej w języku polskim: Adsorbenty do usuwania związków endokrynnie czynnych ze środowiska wodnego

Tytuł rozprawy w języku angielskim: Adsorbents for removing endocrine active compounds from the aquatic environment

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Streszczenie rozprawy w języku polskim: Związki endokrynnie czynne (EAC) są uważane za jedno z największych zagrożeń dla środowiska w ostatnich dekadach. Przykładami takich substancji są przede wszystkim bisfenole, pestycydy, barwniki, farmaceutyki, często z grupy popularnych niesteroidowych leków przeciwzapalnych. Ich rozprzestrzenienie stanowi istotne wyzwanie dla współczesnych badaczy i skłania do poszukiwania nowych rozwiązań, które przede wszystkim będą opierały się na zasadach zielonej chemii i zrównoważonego rozwoju. Głównym problemem tych związków chemicznych jest to, że nawet w niezwykle niskich stężeniach (ng L^{-1} do $\mu\text{g L}^{-1}$) są w stanie spowodować duże spustoszenie w odniesieniu do organizmów żywych. Nie pomaga fakt, że są oznaczane nagminnie w praktycznie każdym źródle wody, np. w wodzie pitnej czy w teoretycznie oczyszczonych strumieniach ścieków wprowadzanych do wód powierzchniowych. Niestety, wiele sposobów radzenia sobie z tym problemem nie ma wystarczającej wydajności, na przykład konwencjonalne metody oczyszczania ścieków. Z tego właśnie powodu istnieje zapotrzebowanie na ciągle poszukiwanie i doskonalenie dostępnych adsorbentów, gdyż adsorpcja to sposób, który wyróżnia się na tle innych dostępnych technik w tym zakresie i pozwala na osiąganie wysokich wydajności usuwania EACs. Celem niniejszej rozprawy było krytyczne przedstawienie dostępnych źródeł zanieczyszczeń, ze szczególnym uwzględnieniem związków endokrynnych, omówienie dostępnych i wykorzystywanych obecnie sposobów oczyszczania wody i ścieków, ogólnego zarysu adsorpcji i charakterystyki ważniejszych adsorbentów. Ostatnim etapem było również zwrócenie uwagi na aspekty zrównoważonego rozwoju, które należy rozważyć, projektując materiały sorpcyjne. Ponadto fundamentem niniejszej pracy jest cykl sześciu publikacji naukowych – czterech oryginalnych prac badawczych i dwóch przeglądowych. Oryginalne prace badawcze stanowią o szeregu nowatorskich materiałów adsorpcyjnych, ich syntezie, charakterystyce, badaniach adsorpcyjnych i zastosowaniu w realnych warunkach środowiskowych bądź przemysłowych. Badania opierały się na materiałach wykonanych ze źródeł odnawialnych, polimerach na bazie cyklodekstryny, polimerach z nadrukiem molekularnym oraz możliwych modyfikacjach tych materiałów. Badania wykazały, że opracowane adsorbenty pozwalają na znaczące usunięcie wybranych modelowych zanieczyszczeń. Dla fioletu krystalicznego (CV), przedstawiciela barwników kationowych na poziomie wyższym niż 1000



mg g⁻¹, natomiast dla bisfenoli czy farmaceutyków na poziomie od kilkunastu do > 160 mg g⁻¹. Mechanizmy procesu adsorpcji oraz etapy limitujące zostały określone za pomocą modeli kinetycznych (między innymi pseudo-pierwiego i pseudo-drugiego rzędu, Webera-Morrisa, Elovicha) i izotermicznych (na przykład Langmuira, Freundlicha, Sipsa, Hilla). Mechanizmy reakcji są różne w zależności od adsorbowanego zanieczyszczenia i od struktury chemicznej adsorbentu. Jednak z pewnością nie można tutaj pominąć wiązań wodorowych, oddziaływań hydrofobowych, oddziaływań gość-gospodarz, które świadczą o tworzeniu kompleksów inkluzyjnych i innych. Należy pamiętać, że takie nowoczesne materiały często mają potencjał praktyczny, co jest również widoczne w tym przypadku. Poza tym porównując badane sorbenty z powszechnie stosowanym węglem aktywnym, uzyskuje się łatwiejszą regenerację oraz selektywność (np. wykorzystanie odcisku molekularnego). Jak wynika z danych uzyskanych w wyniku przeprowadzonych badań, zaawansowane materiały adsorpcyjne mogą być realnym zamiennikiem w przemyśle, gdyż cechują się biodegradowalnością, zdolnością regeneracji i zgodnością z założeniami gospodarki o obiegu zamkniętym.

Streszczenie rozprawy w języku angielskim: Endocrine disrupting compounds (EACs) are considered one of the greatest threats to the environment in recent decades. Examples of such substances include bisphenols, pesticides, dyes, and pharmaceuticals, often from the popular nonsteroidal anti-inflammatory drugs. Their proliferation poses a significant challenge for contemporary researchers and prompts the search for new solutions based primarily on the principles of green chemistry and sustainable development. The main problem with these chemicals is that even at extremely low concentrations (ng L⁻¹ to µg L⁻¹), they can cause significant damage to living organisms. This is further compounded by the widespread detection of these compounds in virtually every water source, including drinking water and supposedly purified wastewater streams discharged into surface waters. Unfortunately, many methods for addressing this problem lack sufficient efficiency, such as conventional wastewater treatment methods. For this reason, there is a need for continuous research and improvement of available adsorbents, as adsorption is a method that stands out from other available techniques in this field and allows for high EAC removal efficiency. This dissertation aimed to critically present available pollutant sources, with particular emphasis on endocrine compounds, discuss available and currently used water and wastewater treatment methods, provide a general overview of adsorption, and characterize the more important adsorbents. Finally, it also highlighted the aspects of sustainability that should be considered when designing adsorbent materials. Furthermore, this work is based on a series of six scientific publications – four original research papers and two review papers. These original research papers provide insight into a number of innovative adsorption materials, their synthesis, characterization, adsorption studies, and applications in real-world environmental or industrial conditions. The research was based on materials derived from renewable resources, cyclodextrin-based polymers, molecularly imprinted polymers, and possible modifications of these materials. Studies have shown that the developed adsorbents enable significant removal of selected model contaminants. For crystal violet (CV), a representative of cationic dyes, the removal levels exceeded 1000 mg g⁻¹, while for bisphenols and pharmaceuticals, the removal levels ranged from a dozen to >160 mg g⁻¹. The adsorption process mechanisms and limiting stages were determined using kinetic models (including pseudo-first and pseudo-second order, Weber-Morris, and Elovich models) and isothermal models (e.g., Langmuir, Freundlich, Sips, and Hill models). Reaction mechanisms vary depending on the adsorbed contaminant and the chemical structure of the adsorbent. However, hydrogen bonds, hydrophobic interactions, and host-guest interactions, which indicate the formation of inclusion complexes, among others, certainly cannot be ignored. It is important to remember that such modern materials often have practical potential, as is also evident in this case. Furthermore, comparing the tested sorbents with commonly used activated carbon results in easier regeneration and selectivity (e.g., using molecular imprinting). According to the data obtained from the conducted research, advanced adsorption materials can be a viable substitute in industry, as they are biodegradable, regenerable, and compliant with the principles of a circular economy.

List of publications forming the basis of the dissertation:

- [1] Efficient Water Pollutants Targeting: Novel Materials with Molecular Imprints for Textile Industry Use – *Industrial & Engineering Chemistry Research*, 2025, original article; DOI: <https://doi.org/10.1021/acs.iecr.5c00705>; IF: 3.9 (2025), quartile: Q1; MEiN points: 140.
- [2] Removal of nonsteroidal anti-inflammatory drugs and analgesics from wastewater by adsorption on cross-linked β -cyclodextrin – *Water Resources and Industry*, 2022, original article; DOI: 10.1016/j.wri.2022.100186; IF: 5.1 (2022), quartile: Q1; MEiN points: 200.
- [3] Cellulose and its derivatives, coffee grounds, and cross-linked β -cyclodextrin in the race for the highest sorption capacity of cationic dyes in accordance with the principles of sustainable development – *Journal of Hazardous Materials*, 2022, original article; DOI: 10.1016/j.jhazmat.2022.129588; IF: 13.6 (2022), quartile: Q1; MEiN points: 200.
- [4] Structural Adaptive, Self-Separating Material for Removing Ibuprofen from Waters and Sewage – *Materials*, 2021, original article; DOI: 10.3390/ma14247697; IF: 3.748 (2021), quartile: Q2; MEiN points: 140.
- [5] Recent Advancements in Cyclodextrin-Based Adsorbents for the Removal of Hazardous Pollutants from Waters – *Polymers*, 2022, review article; DOI: 10.3390/polym14122341; IF: 5.0 (2022), quartile: Q1; MEiN points: 100.

Other publications (not included in the dissertation):

- [1] Cyclodextrins functionalized polyvinylidene fluoride membranes: Strategies and diverse applications – *Tetrahedron*, 2025, review article; DOI: 10.1016/j.tet.2024.134385; IF: 2.2 (2024), quartile: Q1; MEiN points: 70.

International and National Conferences:

- [1] 1st International Online Conference on Separations; MDPI Separations; online conference; 15–17 October 2025; active participation (oral presentation): “Adsorption of Methylene Blue onto Waste Fractions of Cannabis sativa from CBD and Hemp Seed Oil Production.”
- [2] 5th International Conference on Strategies towards Green Deal Implementation – Water, Raw Materials & Energy in Green Transition; Polish Academy of Sciences; online conference; 27–29 November 2024; active participation (oral presentation): “Evaluation of leaf-based adsorbents for rapid dye removal from water.”



- [3] 43rd WEDC International Conference – Water and Climate Resilience; Loughborough University; online conference; 9–13 September 2024; active participation (poster presentation): “Nature-based solution: Adsorption of Methylene Blue on Powdered Leaves of Six Tree Species.”
- [4] 65th Congress of the Polish Chemical Society; Polish Chemical Society; Toruń; 18–22 September 2023; active participation (oral presentation): “Selektywne usuwanie zanieczyszczeń organicznych z roztworów wodnych przy użyciu nowatorskich materiałów z nadrukami molekularnymi.”
- [5] 65th Congress of the Polish Chemical Society; Polish Chemical Society; Toruń; 18–22 September 2023; co-author of an award-winning scientific poster: “Inteligentne Materiały Selektywne Usuujące Mikrozanieczyszczenia z Bałtyku.”
- [6] 7th European Cyclodextrin Conference (EuroCD); Budapest; 5–8 September 2023; active participation (poster presentation): “Adsorption Process Development: Targeted Removal of Water Pollutants Using New Materials with Molecular Imprints.”
- [7] 7th Interdisciplinary Scientific Conference on Environmental Protection (IAKOŚ); Gdańsk; 21–23 September 2023; active participation (poster presentation): “Nanostructured cyclodextrin materials for the removal of ibuprofen from water and wastewater.”

Science Popularization Activities

- [1] Participation in the preparation and presentation during the Baltic Science Festival at the Gdańsk University of Technology on 23-24.05.2024. The presentation and workshop title was “The Magic of Colors”.
- [2] Participation in the preparation and presentation during the National Open Days of the Gdańsk University of Technology on 21.03.2024. The presentation and workshop title was “Dyes Around Us”.
- [3] Participation in the preparation and presentation during the visit of students of the 1st Secondary School of the Philomaths of the Michałowo Land in Brodnica, at Gdańsk University of Technology on 26.01.2024. The presentation and workshop title was “Dyes Around Us”.
- [4] Oral presentation during the Gdańsk University of Technology Open Days on 22.03.2022. The title of the presentation was “Removal of pollutants from the aquatic environment using nanosponges obtained from renewable raw materials”.

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SYMBOLS AND ABBREVIATIONS

AC	–	Activated Carbon
ADONA	–	Ammonium 4,8-dioxa-3H-perfluorononanoate
AOP	–	Advanced Oxidation Process
BET	–	Brunauer–Emmett–Teller
BJH	–	Barrett–Joyner–Halenda
BPA	–	Bisphenol A
BPB	–	Bisphenol B
BPF	–	Bisphenol F
BPS	–	Bisphenol S
CC	–	Commercial microcrystalline cellulose
CD	–	Cyclodextrin
CD-1	–	β -Cyclodextrin polymer material (synthesized with Pyridine)
CD-2	–	β -Cyclodextrin polymer material (synthesized with <i>N,N</i> -Dimethylformamide)
CDP	–	Cyclodextrin polymer
CG	–	Coffee grounds
CGC	–	Cellulose from coffee grounds
CPB	–	Cetylpyridinium Bromide
CT	–	Modified cellulose
CTCD	–	Cellulose- β -Cyclodextrin material
CV	–	Crystal Violet
CV ⁺	–	Triphenylmethane cation
DI-CDP	–	Cyclodextrin polymer imprinted with Diphenylmethane
DPM	–	Diphenylmethane
DSC	–	Differential Scanning Calorimetry
DDT	–	Dichlorodiphenyltrichloroethane
DIC	–	Diclofenac
E1	–	Estrone
E2	–	17 β -Estradiol
EE2	–	17 α -Ethinylestradiol
EAC	–	Endocrine active compound
EDC	–	Endocrine disrupting compound
EDTA	–	Ethylenediaminetetraacetic Acid Disodium Salt Dihydrate
ER α , ER β	–	Estrogen receptors
EU WFD	–	European Union Water Framework Directive
FTIR	–	Fourier-transform infrared spectroscopy
GAC	–	Granulated activated carbon
H1–H5	–	Hypotheses 1–5

HMDI	–	Hexamethylene Diisocyanate
HPLC	–	High-performance liquid chromatography
IBU	–	Ibuprofen
IPCS	–	International Programme on Chemical Safety
KL	–	Langmuir constant (L mg^{-1})
KETO	–	Ketoprofen
KF	–	Freundlich constant ($\text{mg}^{(1-1/n)} \text{L}^{(1/n)} \text{g}^{-1}$)
KS	–	Sips constant ($\text{L}^{(1/n)} \text{mg}^{(-1/n)}$)
KD	–	Dissociation Constant (mg L^{-1})
LCV	–	Leucocrystal Violet
MB	–	Methylene Blue
MEiN	–	Ministry of Science and Higher Education
MG	–	Malachite Green
MICP	–	Molecularly imprinted cyclodextrin polymer
MIP	–	Molecularly imprinted polymer
NAPR	–	Naproxen
NF	–	Nanofiltration
NIP	–	Non-Imprinted polymer
NP	–	Nonylphenol
NSAID	–	Nonsteroidal anti-Inflammatory drug
OP	–	Octylphenol
OTC	–	Over-the-Counter
PAH	–	Polycyclic Aromatic Hydrocarbons
PAC	–	Powdered activated carbon
PCB	–	Polychlorinated Biphenyls
PFAS	–	Per- and Polyfluoroalkyl substances
PFOA	–	Perfluorooctanoic Acid
PFOS	–	Perfluorooctane Sulfonate
POP	–	Persistent Organic Pollutant
PVDF	–	Polyvinylidene Fluoride
PZC	–	Point of zero charge (isoelectric point)
q_e	–	Adsorption capacity at equilibrium (mg g^{-1})
q_{max}	–	Maximum sorption capacity (mg g^{-1})
q_t	–	Amount of pollutant adsorbed at time t (mg g^{-1})
RME	–	Removal efficiency (%)
SALI	–	Salicylic Acid
SEM	–	Scanning electron microscopy
Sips (n)	–	Heterogeneity factor
SPE	–	Solid-phase extraction
TBT	–	Tributyltin

TGA	–	Thermogravimetric analysis
t-Plot	–	Thickness plot method
TPM	–	Triphenylmethane
TDI	–	Toluene-2,4- and 2,6-Diisocyanate
TRAM	–	Tramadol
TRI-CDP	–	Cyclodextrin polymer imprinted with Triphenylmethane
UV	–	Ultraviolet
UV-Vis	–	Ultraviolet-visible spectroscopy
β -CD	–	β -Cyclodextrin
β -CD-M	–	β -Cyclodextrin nanosponge cross-linked by hexamethylene diisocyanate

THEORETICAL INTRODUCTION

1. Introduction to the Issue of Aquatic Environment Pollution

Water pollution is one of the most significant environmental problems and challenges of our time. The consequences for public health and aquatic and terrestrial ecosystems have been evident for years. Given that clean water is a basic requirement for life, this issue should be addressed with due commitment. However, despite increased awareness, pollution continues to grow. According to statistics, as much as 80% of sewage is not adequately treated before being released into environmental waters. This suggests a global problem affecting the entire world, Asia, Latin America, Africa, and beyond. Furthermore, it has been reported that approximately 1.8 billion people use contaminated drinking water due to incomplete purification. The scale of the problem is alarming, not only in terms of human life but also because the lives of many aquatic and terrestrial animals are at risk. Several factors contribute to this deterioration, including disproportionate industrialization in relation to environmental capabilities (such as emission control and water treatment), increased urbanization, and a growing population. This problem is particularly evident in developing countries, where differences have become apparent almost daily since the 1990s [1–3].

On the other hand, this problem can also be considered locally or regionally, citing Europe as an example. A lot of time has passed since the introduction of legal regulations regarding pollutants and their levels in water. However, according to recent reports assessing the criteria of the European Union's Water Framework Directive (EU WFD), only 29% of water bodies can boast good chemical status, and only 8% more than that have an ecological status rated as good or very good. The main reason is historical pollution, which is now banned (e.g., polychlorinated biphenyls), and unfortunately, their effects are still visible today due to their persistence, stability, and accumulation. The assessment of the standards generally shows that most water bodies do not meet the criteria imposed by the European Union, as evidenced by water blooms, animal extinctions, or epidemics related to water pollution [4,5].

These global and regional perspectives only confirm the importance of continuous improvement in this area and the streamlining of current research and related processes.

In addition to standard pollutants, micropollutants such as endocrine disruptors, microplastics, personal hygiene products, and pharmaceuticals, which pose environmental hazards, have also become a significant issue in recent years. These trace compounds are still detectable later on, including in tap water, rivers, and groundwater, because current water purification systems are not completely developed to remove them. This raises the crucial question of the future consequences of such a safety issue [6,7].

To address these challenges, international and governmental organizations are coming up with new proposals for implementing safeguards and countermeasures to help eliminate dangerous consequences. A prime example is the United Nations, whose sustainable development goals include treatment and reuse of wastewater, and its assumption is improving water quality and reducing the impact of contaminants (Goal 6.3) [8]. The consequences of such proposals will undoubtedly include infrastructure changes, the introduction of certain innovations,

and intensified scientific and engineering work to implement solutions and ideas. One of the most universal and encouraging solutions is adsorption, which has no limitations in its effectiveness, even at very low concentrations [9].

Considering the above information, which forms the basis for a more detailed analysis, the following subsections discuss sources of water pollution (section 1.1), the types of water pollution (section 1.2), and the problem of endocrine-active compounds in the environment (section 1.3).

1.1 Sources of Water Pollution

Water pollution sources can be broadly divided into two types: point and non-point (Figure 1). The first type, the simplest to monitor and regulate, includes easily identifiable wastewater from treatment plants and pipelines from various industries. The second type, non-point, unlike point sources, has no specific point of emission, and can cover large areas, be dispersed, and therefore less traceable and more difficult to monitor and regulate. Specific examples include sewage runoff from agricultural fields, contaminated with fertilizers, and urban runoff [10].

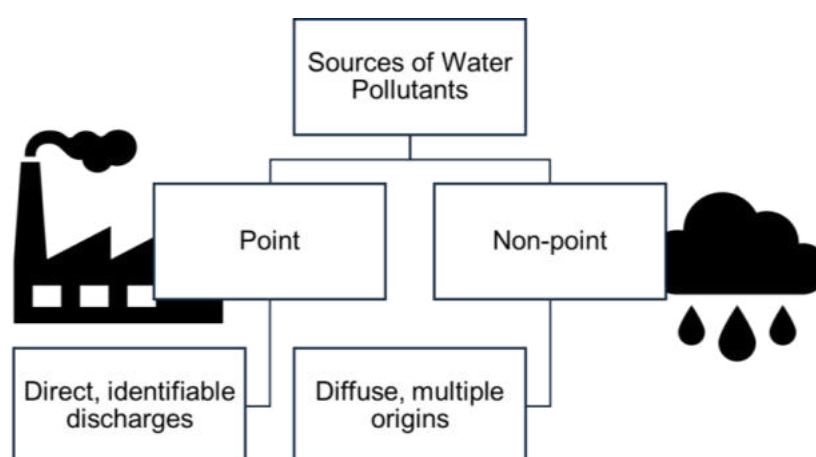


Figure 1. Division of water pollution sources.

Municipal sewage is one of the most commonly cited sources of water pollution in literature. Because it is so pervasive, it is a global issue. Wastewater contains not only fecal matter but also household detergents, food scraps, personal hygiene products, and over-the-counter (OTC) medications. In developed countries, emergency shutdowns pose a significant problem, bypassing some or all of the treatment steps due to technical failure. Shutdown can also happen due to excessive load, or ongoing maintenance, not only due to the failure reason. On the other hand, in developing countries, the problem is completely different. Lack of infrastructure and the frequent inaccessibility of wastewater treatment systems result in contaminated streams being released into rivers or coastal waters. Furthermore, inadequate treatment increases the risk of pathogens' presence (viruses, bacteria, parasites), which can pose a real threat to humans and animals. Other consequences of insufficient efficiency of the treatment process may include algal blooms associated with high nitrogen and phosphorus levels, or reduced access to oxygen due to large discharges of organic matter [11].

The second major source of pollution is agriculture, which primarily causes this through the high use of nitrate and phosphate fertilizers, herbicides, and pesticides. An example is the Mississippi River basin, which supplies nutrients to the Gulf of Mexico, which is annually deprived of oxygen, and the eutrophication occurring there creates a "dead zone". This problem also exists in many European seas and lakes, including the Baltic Sea. Another component is livestock farming, which undoubtedly contributes to the problem [12,13].

Another significant source of pollution is industry (textile, chemical, mining, petrochemical, electronics, electroplating, etc.). Depending on the type of industry, various hazardous substances originating from it can be distinguished, such as organic compounds, heavy metals, oils and fats, dyes, and carcinogenic or endocrine-disrupting substances. Due to inadequate approaches to the treatment of effluents, these hazardous compounds can affect the hydrobionts and humans who consume contaminated water and/or aquatic animals. A further prime example of this type of problem was Minamata Bay in Japan, contaminated by mercury originating from a plastics factory, which resulted in an epidemic of poisoning, causing neurological disorders. Regardless of the legal regulations introduced, system failures sometimes occur, causing serious pollution, but this is certainly more common in countries with weak oversight nowadays. During such contamination events, a serious problem is that the hazardous pollutants can settle in the bottom sediment and be released undetected under appropriate conditions [14,15].

Another polluting factor is runoff from urban areas. The rain washes roads and buildings, carrying contaminants with it. These substances include automotive fuels and oils, deicing compounds, wastes, and brake dust containing copper and lead. A serious consequence of this is the accumulation of pollutants and their transport along with rainwater through storm sewers to water reservoirs, which can lead to sudden changes in the concentration of harmful compounds. Additionally, episodic hydrological stress can be observed during rainfall, which can lead to the destruction of plants, aquatic habitats, and bank erosion [16–18].

Additional and equally important factors reducing water quality include mining, which causes acid rain and heavy metal distribution, and atmospheric pollutants, which cause lake acidification and mercury bioaccumulation in aquatic organisms. Another important aspect is deforestation caused by urbanization, which is the reason for water turbidity and reduced biodiversity [19].

It is worth noting, in the context of this dissertation, that all of the above-described sources emitting water pollutants may also release endocrine active compounds (EACs), also known as endocrine disrupting compounds (EDCs), into the environment. For example, municipal, industrial, or agricultural wastewater, in addition to standard components, may also contain pharmaceuticals, pesticides, hormones, cosmetics, and their derivatives that negatively impact the hormonal system in multiple ways, demonstrating its endocrine activity. The major branches impacting the water quality, such as EDCs pollution sources, are presented in Figure 2.

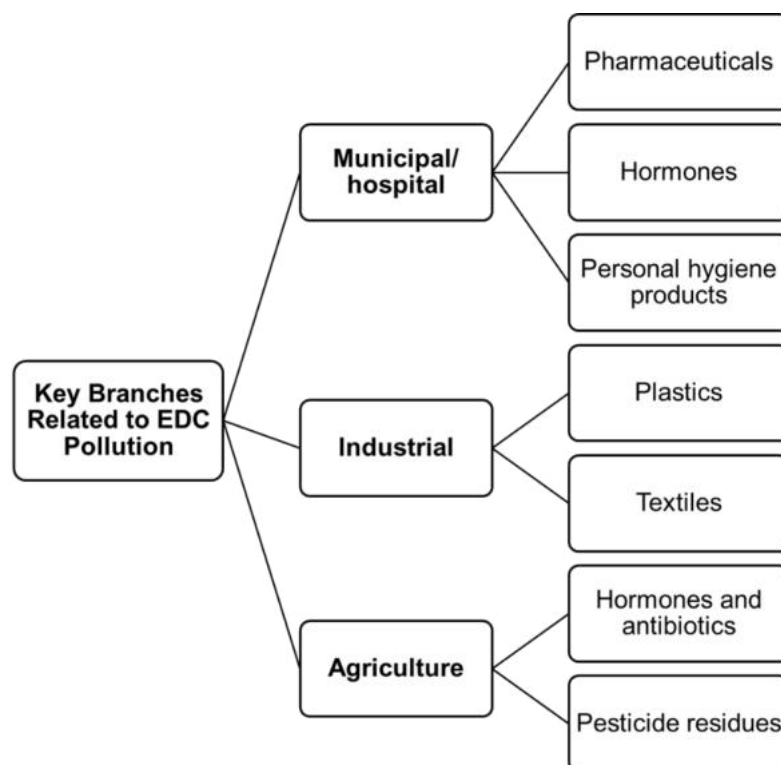


Figure 2. Key branches related to EACs pollution.

In summary, there are many sources of water pollution, divided primarily into point and non-point sources. Classifying them allows for effective control of their spread. While the former is easier to limit through the introduction of various regulations and legal acts, the second one should be eliminated as much as possible through best practices implemented within agricultural or urban areas (e.g., runoff management). Furthermore, the correct identification of sources of hazardous substances, such as EACs, can be the basis for recognizing and eliminating them from the environment [20].

1.2 Types of Water Pollutants

There are many classifications of aquatic pollutants. One involves the identification of five categories: nutrients, microbial pathogens, heavy metals and inorganics, organic pollutants, and emerging ones (Figure 3). Representatives of the first category include nitrates and phosphates, which can originate from sewage or fertilizers, leading to eutrophication, algal blooms, or the formation of dead zones [21,22]. The second group, microbial pathogens (e.g., *E. coli*) originating from sewage, urban runoff, or agricultural runoff, can cause serious disease epidemics [23]. Additionally, heavy metals (Hg, As, Cd, etc.) and inorganic compounds (acids, ammonia, etc.) from industry or fuel combustion also contribute massively to aquatic pollution due to their toxicity (also neurotoxicity) or bioaccumulation in aquatic wildlife or bottom sediments [24]. Importantly, the next category includes persistent organic pollutants – POPs like pesticides (herbicides, insecticides), solvents, hydrocarbons from the petroleum industry, and industrial chemicals (e.g., flame retardants, polychlorinated biphenyls). They can originate from various sources and cannot be ignored due to their harmfulness, carcinogenicity, and general adverse effects on flora

and fauna [25,26]. Furthermore, there is another category, most important for this work: emerging pollutants, which include personal care products, dyes, pharmaceuticals, microplastics, and, in general, the entire group of EDCs. These compounds occur at very low concentrations in the environment and pose a significant risk, primarily because they persist in water even after supposedly being purified in sewage treatment plants or other purification systems. They are increasingly encountered in nature, which is why they have recently become a target of researchers and ecologists.

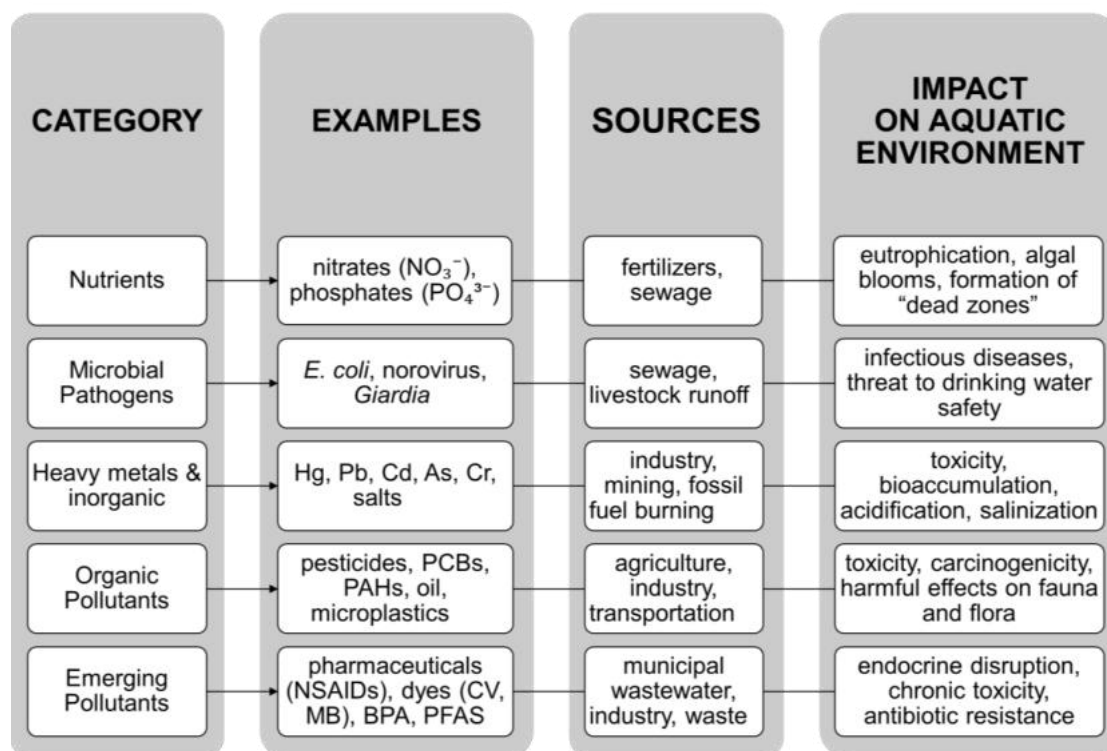


Figure 3. Categories of water pollutants with examples, sources, and their impact on the aquatic environment.

1.3 Importance of Endocrine Active Compounds in the Aquatic Environment

In the past few decades, endocrine active chemicals have emerged for their specific mechanisms of action and are recognized as particularly hazardous. Their impact is not limited to one species but affects all levels of the food chain, including humans and animals, where they wreak havoc on organisms by affecting the endocrine system, including reproductive function, growth and development, metabolic problems, basic organ function, the development of hormone-related cancers, and feminization [27–31]. The difficulty with these chemicals is that high concentrations are not required to exert a destructive effect. Furthermore, their spread is increasing year by year, and these hazardous compounds are detected in almost every reservoir, like rivers, lakes, groundwater, tap, and glacial waters of the distant Arctic [32]. As mentioned in Section 1.1, many industries generate EDCs, which do not favor prospects given their tendency to be stored in tissues [33,34]. Their ecological and public health repercussions are also associated with biodiversity loss, altered sexual function in fish, and the development

of various defects [35,36]. As mentioned earlier in this chapter, systemic requirements exist to limit the distribution and minimize the occurrence of water pollutants, but unfortunately, in the case of EACs, the regulations leave much to be desired [37]. Moreover, lists containing information on whether a given chemical is considered or suspected of being an EAC vary from country to country, so the issue should continue to be monitored and harmonized. Importantly, the problem of these compounds should also be considered at the level of compound degradation and their possible transformation into potentially poisonous endocrine active substances [38]. The main categories of EACs, their exemplary effects, and representatives are placed in Table 1.

Table 1. The main categories of EACs, with examples and the mechanism of action [31,39,40].

Category	Examples	Effects	Ref.
Hormones (natural & synthetic)	Natural (estradiol (E2), estrone (E1), progesterone, testosterone)	Impaired fertility and reproduction in humans, feminization of males in fish	[41]
	Synthetic (17 α -ethinylestradiol (EE2), progestins)	Intersexuality, decreased population size of one sex relative to the other	
Pharmaceuticals	Analgesics/NSAIDs (diclofenac, ibuprofen, naproxen)	Thyroid dysfunction	[42]
	Antiepileptics/psychoactives (carbamazepine, valproate)	Nervous system disruption	[43]
Industrial Chemicals	Plastics and additives (bisphenol A, B, S, F, phthalates)	Mimicking the action of natural estrogens, disruption of androgen function, metabolic disorders	[44,45]
	Persistent pollutants (PCBs, dioxins, brominated and chlorinated flame retardants)	Thyroid dysfunction and nervous system disruption	[46,47]
Agrochemicals (pesticides, herbicides, fungicides, insecticides)	Atrazine, Dichlorodiphenyltrichloroethane (DDT), Tributyltin (TBT), endosulfan, organotins	Feminization in frogs, impairing the structure of important organs in snails, and disrupting androgen function	[39,48–50]
Personal Care Products & Household Chemicals	Alkylphenols (octylphenol, nonylphenol), parabens (methylparaben, ethylparaben, propylparaben), triclosan, UV-filters (octocrylene, oxybenzone)	Thyroid dysfunction, reproductive, and fertility effects	[51–53]
Dyes and Textile Additives	Cationic dyes (crystal violet, malachite green, brilliant green)	Teratogenic, mutagenic, anti-estrogenic effect, genotoxicity, cancerogenicity	[54–56]
	Azo dyes with hormonal activity (Tartrazine (E102), Erythrosin B (E127))	Leading to feminization, impaired larval development (e.g., mollusks), and developmental neurotoxicity	[57–59]
Natural Analogues	Phytoestrogens (genistein, daidzein, coumestans, lignans)	Reproductive and fertility effects, antiandrogenic effects	[60,61]
Metalloestrogens	Cadmium, Arsenic, Cobalt, Copper, Nickel, etc.	Cancerogeneity, reproductive disorders	[62–64]

Category	Examples	Effects	Ref.
Per- and polyfluoroalkyl substances (PFAS)	Perfluorooctanoic acid (PFOA), Perfluorooctane sulfonate (PFOS), Ammonium 4,8-dioxa-3H-perfluorononanoate (ADONA)	Delayed puberty, thyroid effects, and reproductive problems	[65]

2. Characteristics of Endocrine Active Compounds (EACs)

2.1 Definition and Mechanisms of Action of EACs

The definition of endocrine disrupting compounds (EDCs) depends on the source, but according to the World Health Organization (International Programme on Chemical Safety - IPCS), EDCs are compounds that affect the elimination, synthesis, transport, secretion, action, and binding of hormones. These substances are defined as exogenous (unnatural) and disrupt homeostasis, causing negative effects on the body. Furthermore, they often affect the reproduction, behavior, or development of the individual exposed to such a substance [66].

The mechanism of action of EDCs can take several forms (Figure 4). The first involves binding to the receptor and directly exerting hormone activity. The other one involves receptor occupancy, which leads to inhibition of endogenous hormone action, and the next involves interfering with hormonal signaling pathways. Such a situation results in incorrect transmission of endocrine signals, which have even wider consequences, such as the already mentioned reproductive problems, hormone-dependent cancers, reproductive system defects, etc. [67]. Interestingly, even EDCs (BPA and phthalates) concentrations of ng L^{-1} or $\mu\text{g L}^{-1}$ show lasting changes in mouse and rat models, according to the scientific research [68–70].

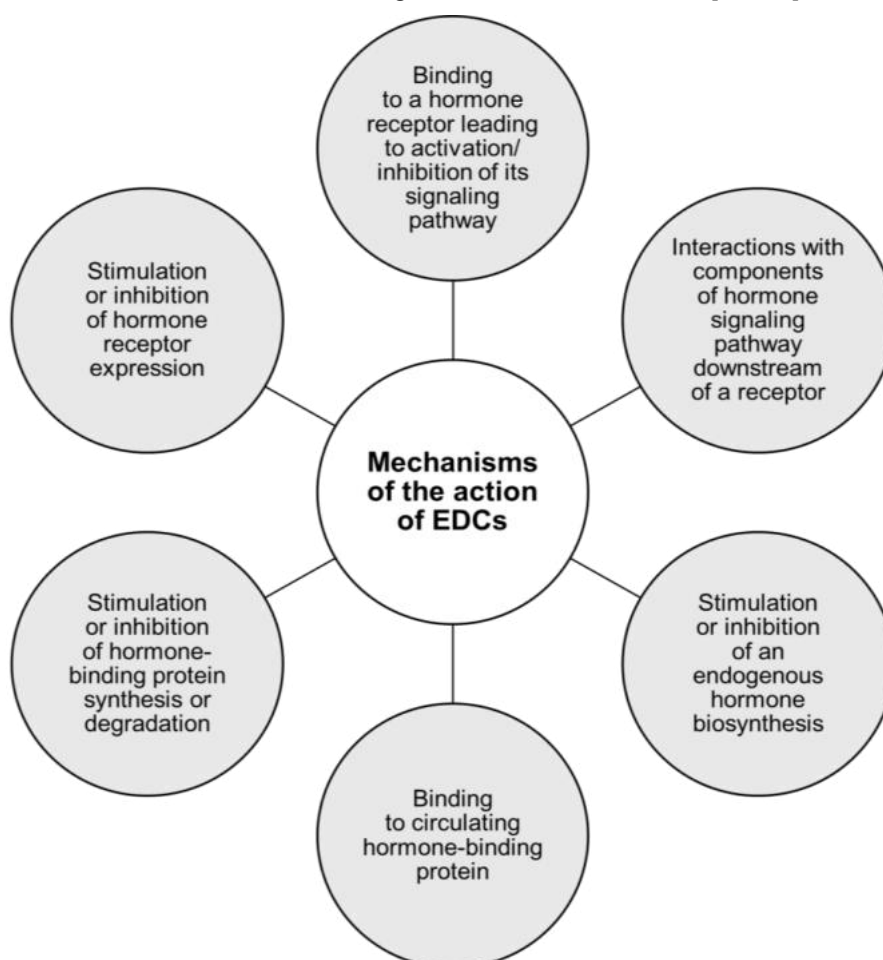


Figure 4. Possible mechanisms of action of EDCs [71].

2.2 Sources and Occurrence of EACs in the Aquatic Environment

Sources of EDCs pollution include both point and diffuse (non-point) sources. As shown in Figure 2, the most critical sources of EDCs are municipal sewage, hospital wastewater, industrial wastewater, and agricultural wastewater.

Municipal sewage has a highly complex composition, which can also become more complex due to the use of many medications by humans nowadays. For example, 17 α -ethinylestradiol (EE2), estrone (E1), and 17 β -estradiol (E2) are commonly detected in waters due to the widespread use of contraceptives. It is worth noting that EE2 was detected in previously treated waters in Europe (France) at concentrations of about 1 ng L⁻¹, which may be associated with feminization of males [72]. Other examples include over-the-counter (OTC) medications and anti-inflammatory or analgesic drugs in general, such as ibuprofen, naproxen, diclofenac, and ketoprofen. Cosmetics and other personal hygiene products also constitute a significant amount. A prime example is the ingredients of recently popular UV filters – oxybenzone, octocrylene, and triclosan [53,73–75].

Another significant source of pollution is industrial wastewater. Plastic production contributes to the release of many substances, such as bisphenol A and its analogues BPS and BPF. Globally, this problem is evident when measuring concentrations in nearby waters relative to industrialized areas. Such concentrations can reach up to 991.9 ng L⁻¹ for BPA (China) and 1364 ng L⁻¹ (Poland) or 406 ng L⁻¹ (Canada) for triclosan [76]. Every industry contributes to the spread of EDCs. For instance, the cosmetic industry can be combined with UV filters and parabens, the pharmaceutical industry with NSAIDs and hormones, and the textile and paper industry with dyes and detergents [77,78]. Nonylphenol (e.g., 4-nonylphenol) and octylphenol (e.g., 4-*tert*-octylphenol), which belong to the alkylphenols and their derivatives like ethoxylated alkylphenols (alkylphenol ethoxylates, APEs), may be highlighted as important compounds here. All of these chemicals have been linked to negative hormonal effects [78–80].

The agricultural industry and its runoff can be linked to veterinary drugs (including antibiotics), pesticides (atrazine, chlorpyrifos), and hormones (testosterone, progesterone). For example, contamination from poultry farms can reach up to 0.022 μ g L⁻¹ of natural estrogens [81].

To further illustrate the problem of these hazardous substances in the aquatic environment, exemplary concentrations of EDCs found in various types of water (freshwater, wastewater, seawater, drinking water) and in various regions of the world are presented in Table 2 [82].

Table 2. Concentration of the EDCs in the different water matrices and areas [82].

Water Matrix	EDC	Concentration [ng L ⁻¹]	Country
Freshwater	E1	2.6-3	Italy
	E2	0.33-5	Hungary
	EE2	0.8-1.7	Portugal
	BPA	3310-15700	Africa
	Alkylphenols	30-337	Spain
	Metformin	3100	Germany
Seawater	BPA	10.6-52.3	Greece
	NP	1.3-21.3	Germany
	E1	1.43	China
	E2	0.7	China
	EE2	0.6	China
Wastewater	Diclofenac	4869	Greece
	Ketoprofen	793	Greece
	Naproxen	3581	Greece
	Paracetamol	27.7	Greece
	Carbamazepine	6822	Greece
	Ciprofloxacin	591	Greece
	Sulfamethoxazole	507	Greece
	BPA	6.8	Serbia
	NP	4.9	Serbia
	OP	1.9	Serbia
Drinking water	BPA	140	Korea

Water Matrix	EDC	Concentration [ng L ⁻¹]	Country
	NP	3.1	Serbia
	OP	1.7	Serbia
	E1	5.9	Serbia
	E2	7.2	Serbia
	Ketoprofen	3	Taiwan
	Triclosan	8-103	Taiwan
	Sulfamethoxazole	13	Taiwan
	Phthalates	2-316	Taiwan
	Erythromycin	11	Taiwan

2.3 Examples of Endocrine Active Compounds and Their Characteristics

2.3.1 Bisphenols

A prime example of EDCs is bisphenols, once considered safe and used industrially as a monomer in the production of plastics (polycarbonates and epoxy resins), a substrate for thermal paper production, and a component of varnishes. However, it is now known that BPA, along with its analogues BPB, BPS, and BPF, poses a threat and causes numerous hormonal and metabolic disruptions. The chemical structures of the most well-known bisphenols are presented in Figure 5. BPA exhibits estrogenic activity, meaning it mimics the natural hormone E2 and binds to it, causing a range of adverse effects, as confirmed by in vitro and in vivo studies. Obesity, diabetes, hormone-dependent cancers, and fertility issues have all been connected to it. Because BPA and its analogs leach from common plastic waste, packaging, and industrial streams, they can be found in surface water, sediments, and municipal sewage [83–85]. Depending on the region and type of water tested, bisphenols are detected at levels ranging from several thousand to several dozen thousand ng L⁻¹ (Table 2) [82]. Moreover, according to literature reports, BPA is found in municipal wastewater at levels of approximately 62 ng L⁻¹. Extraordinarily, BPS and BPF, which began to be used much later as a BPA replacement in bisphenol A-free products, are currently detected at levels of approximately 55 ng L⁻¹ (BPS) and 128 ng L⁻¹ (BPF) in the same type of water [86].

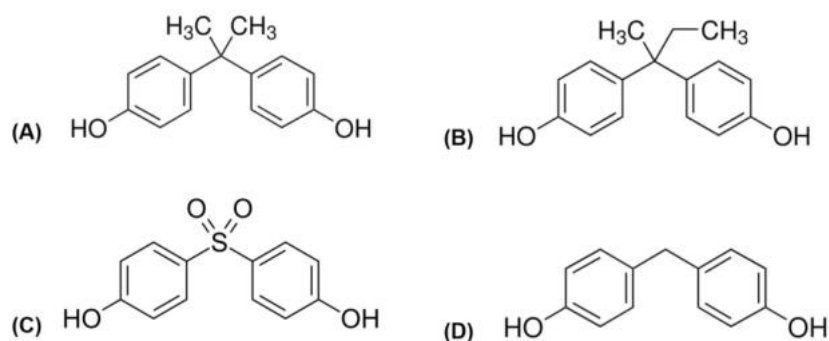


Figure 5. Chemical structures of: (A) bisphenol A, (B) bisphenol B; (C) bisphenol S, (D) bisphenol F.

2.3.2 Dyes

In recent years, a growing number of dyes have been considered endocrine disrupting or potentially endocrine active (Figure 6). Classic examples include azo dyes and triphenylmethane dyes [55,59]. The primary sources of these dyes are the textile, paper, food, and leather industries. Some triphenylmethane dyes have also been used as a coloring agent in histological laboratories (crystal violet, CV) or for treating fungal infections in aquatic animals (malachite green, MG) [87,88]. Studies on CV have also shown it to be genotoxic, teratogenic, and carcinogenic, similar to MG, which also inhibits thyroid hormones in fish. For this reason, they have been regulated and withdrawn from general use. However, this group of dyes is prone to bioaccumulation in sediments and fish tissues, which poses a serious ecological problem. The gravity of the situation is further heightened by the fact that these compounds and their leucoforms are highly persistent and non-biodegradable [89–91]. This is supported by studies demonstrating significant levels of CV and its reduced form, leucocrystal violet (LCV), in the tissues of eels inhabiting polluted waters in Germany, where LCV was found to be the predominant form. The total concentration was $6.7 \mu\text{g kg}^{-1}$ of the animal's body weight [92]. Furthermore, some azo dyes (e.g., Tartrazine, Reactive Yellow 18, Reactive Blue 19) also exhibit harmful effects after long-term exposure. These effects include organ damage, including liver damage, and reproductive disorders. Changes in sex ratio or irreversible changes to reproductive organs are common, resulting in infertility and reduced biodiversity [59,93].

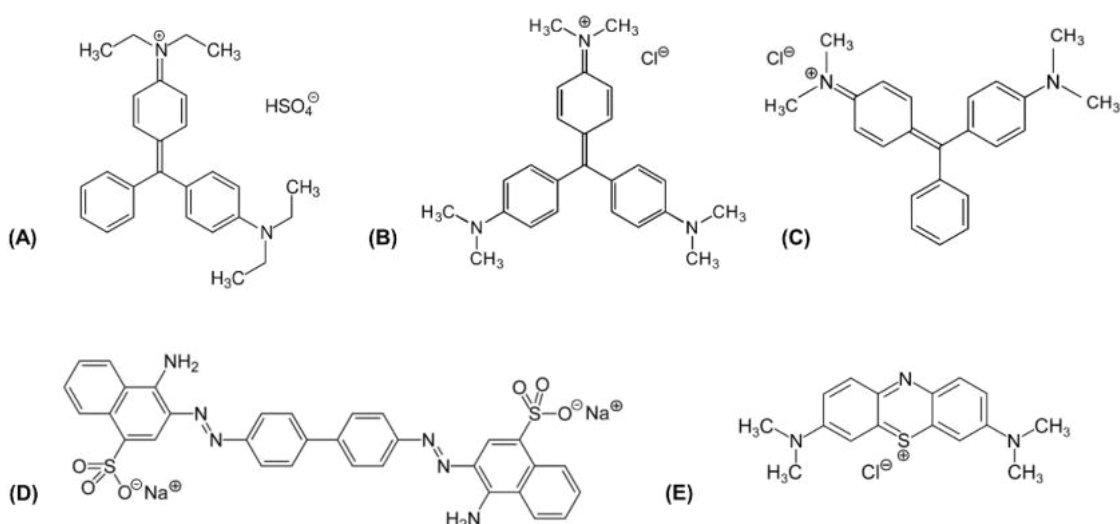


Figure 6. Chemical structures of selected dyes indicated in the literature as endocrine active or potentially endocrine active. (A) Brilliant Green, (B) Crystal Violet, (C) Malachite Green, (D) Congo Red, (E) Methylene Blue.

2.3.3 Pharmaceuticals

In addition to the flagship bisphenols and hazardous dyes, pharmaceuticals are also an important group of EDCs (Figure 7). The most common pharmaceutical with widely documented effects is EE2 – 17 α -ethinylestradiol, an oral contraceptive. Its effect is binding to estrogen receptors ($\text{ER}\alpha$, $\text{ER}\beta$), and endocrine effects may include menstrual disorders, fertility disorders, or the development of female characteristics in males (declining fish populations) [94,95]. It is worth noting that not only hormones but also common analgesics and anti-inflammatory drugs (e.g., ketoprofen, ibuprofen, diclofenac) have similar effects [96]. For example, in male fish, exposure to them has been observed to induce the female protein vitellogenin, as is the case with EE2 [97]. Furthermore, ibuprofen also has a destructive effect on spermatogenesis [98]. In general, NSAIDs (nonsteroidal anti-inflammatory drugs) act within the hypothalamic-pituitary-gonadal axis, which can lead to indirect effects on many hormones, as confirmed by studies in fish [99]. However, what raises the greatest concern is that pharmaceuticals exert this effect at very low concentrations, on the order of $0.1\text{--}1\text{ ng L}^{-1}$, and are found at levels of hundreds of ng L^{-1} in surface waters and even thousands of ng L^{-1} in wastewater (Table 2) [82].

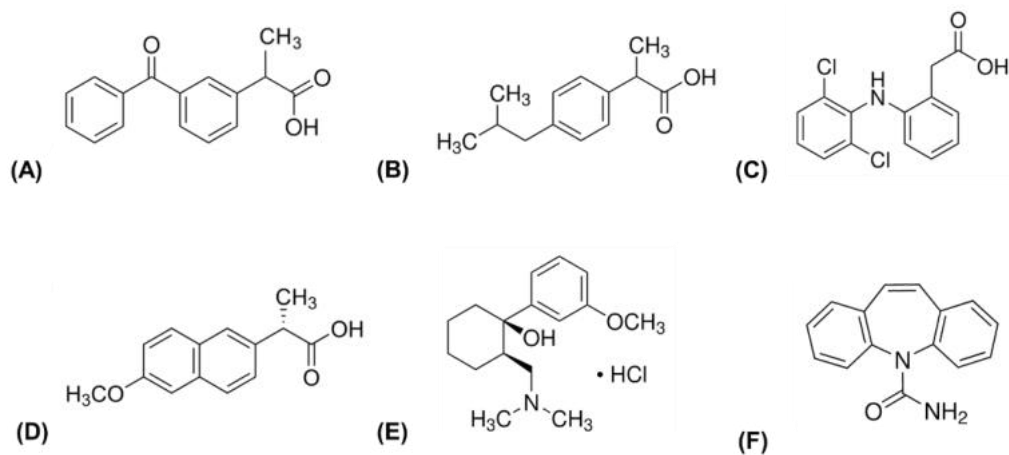


Figure 7. Chemical structures of selected pharmaceuticals indicated in the literature as endocrine active or potentially endocrine active. (A) ketoprofen, (B) ibuprofen, (C) diclofenac, (D) naproxen, (E) tramadol, (F) carbamazepine.

3. Review of Water and Wastewater Treatment Methods (with Emphasis on Adsorption)

3.1 Conventional Water and Wastewater Treatment Methods

Conventional water and wastewater treatment methods can be divided into three types: physical, chemical, and biological (Figure 8). Physical methods are effective for removing solid contaminants, which are often associated with increased water turbidity. These methods include mechanical filtration using various types of filter media (most commonly sand), sedimentation, and membrane-based processes such as microfiltration and ultrafiltration. However, these processes have limited usefulness in removing EDC from water. Chemical methods (just like physical ones) are ineffective against EDC and other organic compounds, but they are perfect for liquidating heavy metals and dangerous pathogens. The second group includes chlorine disinfection, coagulation, and precipitation. At the same time, biodegradable organic contaminants are efficiently removed by biological methods. Here, the use of bioreactors and activated sludge can be mentioned, which are also able to influence EDCs to a certain extent, partially removing them (e.g., by adsorption in activated sludge). However, despite the use of a combination of these conventional methods, we can still find endocrine chemicals in treated wastewater streams, mainly at the level of several to several dozen ng L^{-1} , which indicates incomplete removal of these micropollutants and the constant need to develop new solutions [82,100–103].

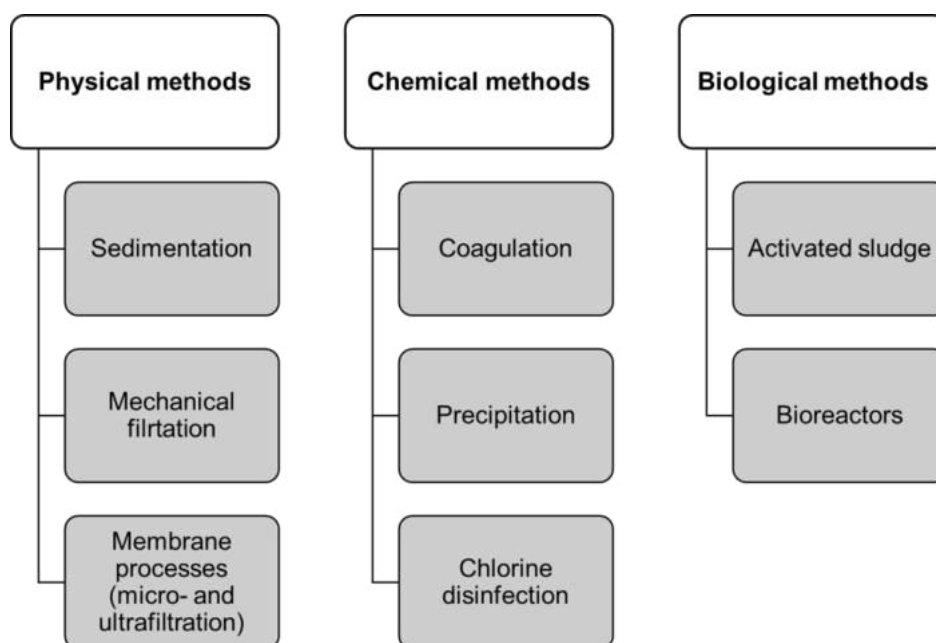


Figure 8. Conventional water and wastewater treatment categories.

3.2 Advanced Treatment Methods

Due to the insufficient elimination of environmentally persistent organic compounds and their derivatives from water, advanced methods are constantly being developed to remove them

efficiently. Such modern techniques include ozonation, photooxidation (UV/H₂O), and Fenton reactions, which are classified as advanced oxidation processes (AOPs) considered among the most effective methods. By exposing selected contaminants to highly reactive radicals ($\bullet$ OH), they degrade them [104–106]. The efficiency of these processes is 95–97% for steroid hormones and even exceeds 90% for organic compounds [107]. Nevertheless, it is impossible to ignore their drawbacks, such as the possibility that byproducts produced during AOPs could be just as dangerous to the environment as the pristine substance. In addition, the cost of energy and reagents required for these processes is not among their benefits. Furthermore, precise conditions often need to be maintained during the process to achieve the desired results [104,106].

Membrane technologies also accomplish similar levels of efficiency to the previous group of methods. Nanofiltration (NF) and reverse osmosis (RO) achieve removal efficiencies above 90% and effectively eliminate micropollutants such as ibuprofen and diclofenac [107]. However, like their predecessors, they have numerous drawbacks, including the requirement for prior preparation of the treated medium to prevent fouling and the cost of equipment. Another problem arising from the use of membrane technologies can be the disposal of the retentate, which contains the removed contaminants [108,109].

Additionally, ion exchange, particularly useful for polar ionic compounds, and adsorption on powdered materials (e.g., the popular activated carbon) are also worth mentioning [110].

Furthermore, combining various advanced purification methods is also an important approach. For example, photocatalysis and electrooxidation used together during purification can demonstrate a synergistic effect [111]. Other examples include advanced oxidation with membrane processes, the use of adsorption with bioreactors, and adsorption with ozonation. Such combinations can somewhat reduce the risk of failures associated with individual methods [112–114].

In summary, advanced water and wastewater treatment methods demonstrate exceptionally high results, as mentioned above. Still, they also carry the risk of creating secondary pollutants and have drawbacks, such as high operating costs.

3.3 Adsorption as a Water Treatment Technique (Advantages and Significance)

Adsorption is a well-established method for removing trace contaminants from water. It is versatile enough to successfully eliminate a wide range of contaminants (including EDCs and other organics) from the treated medium. Its simplicity of operation and low costs distinguish it from previously described methods, such as AOPs. Another benefit of adsorption processes may be the absence of any secondary substances (by-products) due to the binding of contaminant molecules to the adsorbent, rather than their elimination by converting them into other compounds, as occurs, for example, in free-radical reactions. Furthermore, adsorption achieves high maximum sorption capacities at trace concentrations in the ng L⁻¹, facilitating the purification of highly diluted EDCs in water. In practice, due to these advantages, adsorption is ideal for final water purification (after the actual purification in wastewater treatment plants),

protecting surface waters from harmful substances. In general, the most commonly used adsorbent in industrial practice is powdered or granular activated carbon. However, recently, there has been a demand for new materials that can target specific contaminants or possess other specialized properties. In summary, due to the combination of numerous advantages, adsorption processes can be considered a key technique in water purification technology, even in demanding situations (Figure 9) [115–118]. More information about adsorption and adsorbents is provided in Chapters 4-7.

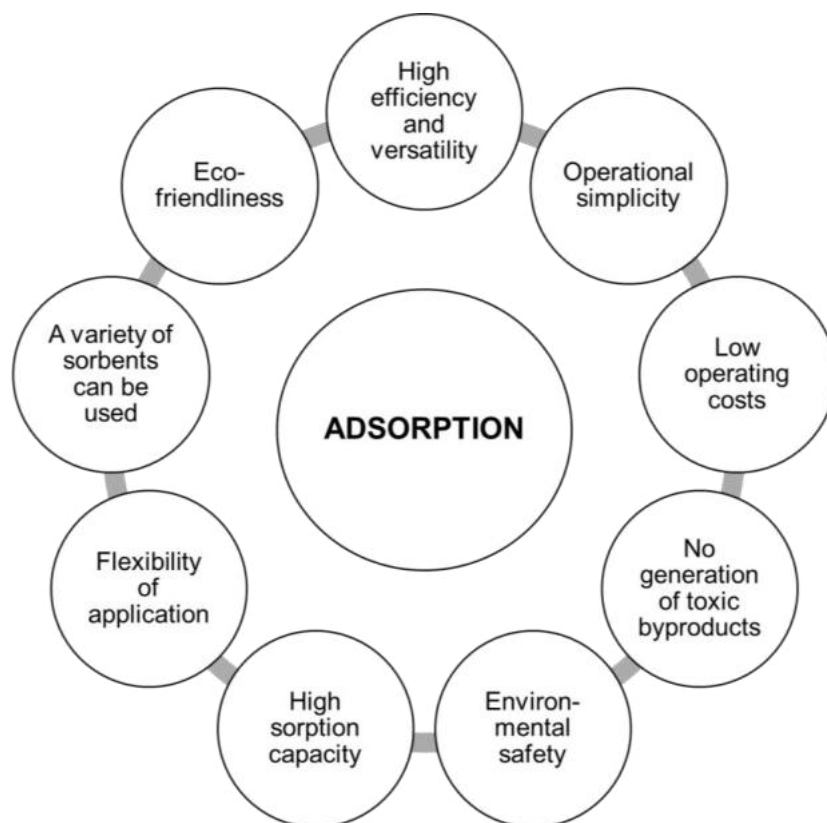


Figure 9. The advantages of adsorption.

4. Adsorption as a Technique for Removing EACs

4.1 Adsorption Mechanism

In general, adsorption is the process of attaching adsorbate molecules (e.g., contaminants) to the surface of a solid adsorbent material. Both the adsorbent and the adsorbate influence the process mechanism. The chemical structure and hydrophobicity of both sides, as well as the porosity of the material, have a significant impact. Physisorption, which operates on the principle of weak interactions (intermolecular or van der Waals forces), is an example of one of the mechanisms that occurs after an adsorbed substance reaches the adsorbent surface. Unusually, certain factors, such as solution pH or temperature, can reverse the physisorption process. The stronger and more selective chemisorption, which involves covalent or ionic bonds, is the second available option and is less likely to be reversed than the first-described physisorption (Figure 10) [119,120].

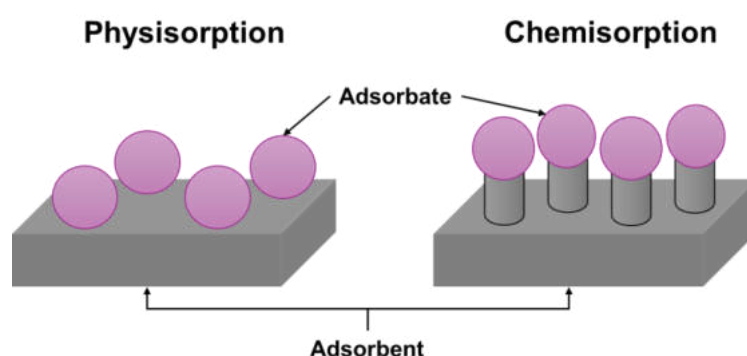


Figure 10. Mechanism of physisorption and chemisorption.

For instance, the adsorption of EDCs is predominantly governed by the polarity of the respective compounds. More polar or ionic substances (pharmaceuticals, natural hormones, some pesticides like atrazine, and anionic phenols) require an adsorbent structure that allows for hydrogen bonding or electrostatic interactions. This can be achieved by creating a material holding special functional groups that will interact well with the adsorbate. On the other hand, less polar substances (PCBs, organochlorine pesticides like DDT, lindane) utilize hydrophobic interactions or van der Waals forces to bind to a more hydrophobic material, such as an activated carbon surface. From a practical perspective, adsorption typically does not rely on these two easily described mechanisms; it is a very complex process that can involve many steps and limiting points. It may involve the formation of inclusion complexes or represent alternating or overlapping chemisorption and physisorption processes. Therefore, each case should be thoroughly and adequately examined before discussing its mechanism [120].

Importantly, the complete adsorption process typically consists of three key stages: film diffusion, intraparticle diffusion, and surface binding. Film diffusion involves the transport of adsorbate to the adsorbent surface, intraparticle diffusion refers to transport into the pores, and

the final stage is simple physisorption or more complex chemisorption (e.g., the formation of host-guest complexes) [120–122].

There is also the concept of the rate-limiting step, which refers to the slowest stage of adsorption that controls the entire process. It is most often combined with intraparticle diffusion. Identifying this step is crucial because it helps in the development of the process, for instance, by selecting optimal mixing to accelerate the transport of substances into the pores or by selecting special types of adsorbents with appropriate porosity, depending on which step is rate-limiting [123].

4.2 Adsorption Kinetics

The optimum adsorption time needed to reach equilibrium and adsorbent saturation, the rates of each process step, and the mechanism of contaminant removal are all determined by adsorption kinetics. The limiting step, which is essential to process design, can also be found using kinetic models. Adsorption kinetics of endocrine active compounds can be fitted to many mathematical models, but the most commonly chosen are pseudo-first order, pseudo-second order, Elovich, intraparticle diffusion (Weber–Morris), film diffusion, Bangham's pore diffusion, and Avrami fractional order model [124–126]. Their main assumptions are presented in Figure 11 and equations in Table 3.

Pseudo-first order	Adsorption rate is proportional to the number of unoccupied sites and assumes monolayer physisorption dominated by weak van der Waals forces.
Pseudo-second order	Adsorption rate depends on the square of unoccupied sites or assumes chemisorption involving valence forces (electron sharing/exchange).
Elovich	Assumes a heterogeneous surface with exponentially decreasing adsorption energy as surface coverage increases. Linked to activated chemisorption.
Weber–Morris intraparticle diffusion	Overall adsorption rate may be controlled by the diffusion of molecules inside pores. q_t is linearly related to $\sqrt{t}$.
Film diffusion	Mass transfer resistance across the thin stagnant liquid film around adsorbent particles controls the overall rate.
Bangham's pore diffusion	Focuses on micropore diffusion as the controlling step. Adsorption rate described by logarithmic relation with time.
Avrami fractional order	Assumes adsorption proceeds via multiple simultaneous mechanisms (diffusion + surface reaction). Rate follows a stretched exponential function.
Modified Freundlich	Assumes fractional reaction order, reflecting surface heterogeneity and combined diffusion-chemisorption mechanisms.

Figure 11. Overview of adsorption kinetic models and their main assumptions [126–128].

Literature reports indicate that adsorption initially occurs at sites that are readily accessible to the adsorbate. This faster phase is then followed by a more time-consuming diffusion process into the material pores, which are less accessible to the model pollutants [129]. Despite the many complex models available to describe adsorption, the pseudo-second order model usually provides the best fit for endocrine active compounds (including pharmaceuticals), a finding confirmed by numerous researchers [130–132]. An example is ibuprofen and its adsorption onto a cyclodextrin polymer, which, after kinetic studies and calculations, showed the best fit to the pseudo-second order model ($R^2 > 0.999$) [133]. Furthermore, typical EDCs, such as the steroid hormones estradiol and progesterone, can also be mentioned here [134]. In short, this means that these processes are not controlled by diffusional resistance, but rather by the binding step on the adsorbent surface (usually referred to as chemisorption). However, both the Elovich and modified Freundlich models, in addition to this model, can confirm the dominance of the chemisorption step, provided a satisfactory fit is achieved [135,136]. In practical terms, kinetics is invaluable for two reasons. Firstly, understanding the optimal contact time between the adsorbent and adsorbate. Secondly, identifying steps that can be improved (accelerated or enhanced). Examples include changing the adsorbent to one with a different porosity based on kinetic conclusions or overcoming the time-limiting external transport process by intensifying mixing [123].

Table 3. Kinetic models with mathematical equations and their parameters.

Model	Equation	Parameters	Ref.
Pseudo-first order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	k_1 – rate constant (min^{-1})	[137]
Pseudo-second order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	k_2 – rate constant ($\text{g mg}^{-1} \text{ min}^{-1}$)	[137]
Elovich	$\frac{dq_t}{dt} = \alpha e^{\beta q_t}$	α – initial rate ($\text{mg g}^{-1} \text{ min}^{-1}$) β – desorption constant (g mg^{-1})	[136]
Weber–Morris intraparticle diffusion	$q_t = k_{id}t^{1/2} + C$	k_{id} – diffusion rate constant ($\text{mg g}^{-1} \text{ min}^{-1/2}$) C – boundary layer effect	[138]
Film diffusion (boundary layer)	$\ln\left(1 - \frac{q_t}{q_e}\right) = -k_f t$	k_f – film diffusion rate constant (min^{-1})	[139]
Bangham's pore diffusion	$\log\left[\frac{c_0}{c_0 - q_t m}\right] = \log(k_b m) + a \log t$	k_b, α – pore diffusion constants	[140]
Avrami fractional order	$q_t = q_e(1 - e^{-(k_{av}t)^n})$	k_{av} – Avrami rate constant n – Avrami exponent (reaction order)	[141]
Modified Freundlich	$\frac{dq_t}{dt} = k_F(q_e - q_t)^n$	n – fractional kinetic order	[135]

c_0 – initial pollutant concentration (mg L^{-1}), q_e – amount of pollutant adsorbed at equilibrium (mg g^{-1}), q_t – amount of pollutant adsorbed at time t (mg g^{-1}), t – time (min).

4.3 Adsorption Isotherms

One of the key studies describing the relationship between the amount of adsorbed substance and pollutant concentration in solution is the adsorption isotherm. Isotherms studied at constant temperature provide information on a material's maximum adsorption capacity, the adsorption mechanism, and the potential formation of adsorbate layers on the surface. Various models can also clarify aspects of the adsorption process, including interactions between adsorbed molecules (e.g., the Hill model) and the heterogeneity of the adsorbent surface. Several key models are primarily used in studies on endocrine compounds. Their main assumptions are presented in Figure 12 [119,124,126]. Furthermore, their mathematical formulas and parameters are also included in Table 4.

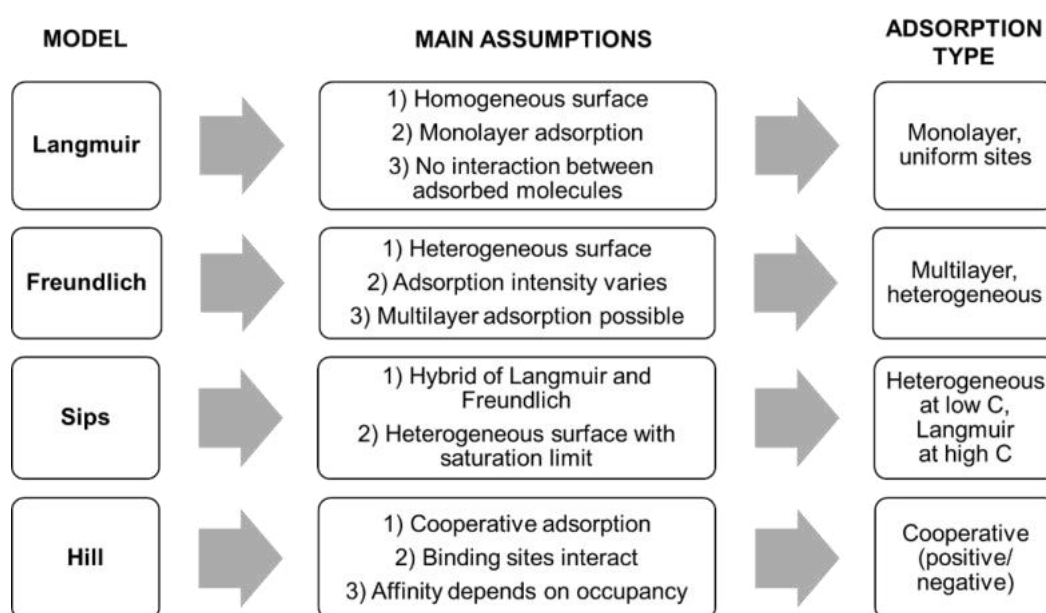


Figure 12. Isothermal models with the main assumptions [142–145].

Table 4. The most commonly used adsorption isotherm models.

Model	Equation	Reference
Langmuir	$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e}$	[142]
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	[143]
Sips	$q_e = \frac{q_{max}K_S C_e^{\frac{1}{n}}}{1 + K_S C_e^{\frac{1}{n}}}$	[144]
Hill	$q_e = \frac{q_{max}C_e^{n_H}}{K_D + C_e^{n_H}}$	[145]

q_{max} - maximum adsorption capacity (mg g⁻¹); q_e - adsorption capacity at equilibrium (mg g⁻¹); C_e - adsorbate concentration at equilibrium (mg L⁻¹); K_F - Freundlich constant (mg^(1-1/n) L^(1/n) g⁻¹); K_L - Langmuir constant (L mg⁻¹); K_S - Sips constant (L^(1/n) mg^(-1/n)), K_D - dissociation constant (mg L⁻¹), n - heterogeneity factor; n_H - Hill coefficient.

An example of the application of isotherm results is the determination of adsorption characteristics obtained by analyzing parameters derived from isotherms, such as the Langmuir constant (K_L), the heterogeneity factor (n), or the maximum sorption capacity ($q_{\max}$). Importantly, in scientific practice, it is also possible to obtain thermodynamic data using the isothermal data obtained at various temperatures. Important clues from these analyses may indicate the spontaneity of the process or the nature of adsorption (chemisorption is associated with the endothermic nature of adsorption, while physisorption is associated with the exothermic nature of adsorption) [146,147].

Based on the literature reports, the Langmuir isotherm fit (monolayer adsorption) is often repeatable for cyclodextrin polymer adsorbents, which achieve substantial adsorption capacities for EDC. For instance, for cyclodextrin polymer β -CDP, researchers obtained $q_{\max}$ of 126.16, 145.81, and 118.05 mg g⁻¹ for E2, EE2, and BPA, respectively [148]. Nevertheless, heterogeneity-indicating Sips is often chosen as the best-fitting model. In fact, Sips is a combination of Langmuir and the Freundlich models, which are usually the basis for the prime factorization of adsorption characteristics in general [144]. For example, according to literature reports, Sips determines a $q_{\max}$ of 86.21 mg g⁻¹ for β -CD-M and 87.50 mg g⁻¹ for 2-hydroxypropyl- β -cyclodextrin polymer in the case of ibuprofen adsorption [133]. For other NSAIDs, higher results can also be obtained according to the Sips isotherm – for example, ketoprofen adsorbed by β -CD-HMDI at the level of 162.60 mg L⁻¹ [149]. Furthermore, high capacities according to the Hill model (which indicates cooperation of adsorbate molecules) were also obtained for dyes (CV), exceeding 1000 mg g⁻¹, demonstrating the potential of advanced adsorbents and the diversity of the process behavior [150].

4.4 Factors Influencing EAC Adsorption

Several factors contribute to changes in the effectiveness of the adsorption process. These include fluctuations in pH, temperature, the properties of the adsorbed substance, and changes in the surrounding environment, such as the presence of other contaminants in the adsorption medium, the presence of ions, and natural organic matter (Figure 13) [151].

The degree of ionization of the functional groups of the adsorbent material and the pollutant being removed depends directly on the pH of the solution. Whether EDCs exist in a neutral or dissociated form depends on pH, as most of them are weak acids or bases. Simultaneously, adsorbents can also behave in two ways due to their surface charge. Below their isoelectric point (point of zero charge), they are positively charged, and above, they are negatively charged. A solution with a pH < pH_{PZC} is ideal for the adsorption of anionic contaminants (e.g., phenols in the form of phenolates), while the reverse situation (pH > pH_{PZC}) favors the adsorption of cationic pollutants (e.g., crystal violet in the form of the triphenylmethane cation CV⁺). At more alkaline pHs, phenolate adsorption will be reduced, as will CV⁺ adsorption at more acidic pHs. However, a more acidic or more alkaline pH does not always improve process efficiency. Finding the optimal point is often crucial. An example is BPA and its adsorption

on activated carbon. In such a situation, a slightly acidic pH is most favorable (the material is not strongly negative on its surface, and BPA is then neutral) [152–154].

The second factor that determines adsorption efficiency is temperature. This process is exothermic, especially in the case of EDCs. According to Le Chatelier's principle, as temperature increases, the reaction equilibrium shifts toward desorption, resulting in a decrease in the maximum adsorption capacity. Furthermore, there is a relationship between temperature and the kinetic energy of the molecules. The higher the temperature, the greater the probability of contaminant molecules "detaching" from the adsorbent surface due to the increase in the kinetic energy of the molecules with temperature. Importantly, in practice, this problem can be ignored in most cases, as adsorption processes are primarily conducted at ambient temperature. An exception may be, for example, the treatment of hot industrial wastewater streams. A solution to the reduced efficiency in this case may be to increase the adsorbent amount or add a stream cooling step before the actual adsorption treatment process [155].

In addition to the above-mentioned factors, temperature and pH, the presence of other contaminants, ions, or natural organic matter also influences adsorption and its efficiency. The literature often mentions that humic or fulvic acids found in real environmental matrices can act as pore blockers, preventing actual contaminants in the form of EDCs from entering them. Furthermore, various metal ions often form complexes with organic contaminants, which can also reduce their interaction with adsorbents. Moreover, inorganic ions can also cause changes in the surface charge of the adsorbent, reducing the availability of groups capable of binding contaminants and reducing the process's efficiency. There are also reports of competition from other contaminants, if present in the solution being treated. They can interfere with sorbents and utilize active sites that were previously intended for another contaminant [156–158].

Furthermore, the adsorbate itself (the substance being adsorbed) is an important factor. Its molecular size, polarity, ability to form bonds (e.g., hydrogen bonds), and ionizability are all extremely important in terms of its suitability for adsorption. Molecular size determines its fit within the adsorbent's pores (if it is too large, materials with larger pores will be required to achieve good results). The importance of hydrogen bonding can be evident, for example, in the case of phenols, which are easier targets for materials designed to possess donor groups such as -OH or -NH₂. Furthermore, electrostatic interactions also play a significant role, but this depends on the ionizability of the contaminant, as mentioned above. Importantly, the higher the initial contaminant concentration, the greater the adsorption driving force (concentration gradient), resulting in faster utilization of the sorbent's active sites, but also a lower RME percentage. Typically, a higher initial EDC concentration is also associated with a higher adsorption capacity (mg g⁻¹) [159–161].

Last but not least, the initial contaminant concentration and the mass of the adsorbent used in the process also play a role in achieving a high percentage of model EDC removal. The more material used, the more active sites will be available for occupation, and consequently, the greater the removal rate. However, it is important to remember that optimality is crucial, as using too much material is not economical and environmentally friendly [162].

Most importantly, before the actual adsorption studies or adsorbent usage, the optimal adsorbent-to-contaminant ratio and sufficient contact time between them (to achieve equilibrium) are usually determined. These parameters are selected during kinetic and isothermal studies (discussed in subsections 4.2 and 4.3) [162].

In summary, there are many factors that can influence the overall adsorption process. However, each case should be considered individually, taking into account the specific interactions that may occur between the adsorbent and the adsorbed substance. None of these parameters should be omitted from the analysis if high efficiency is intended during process design.

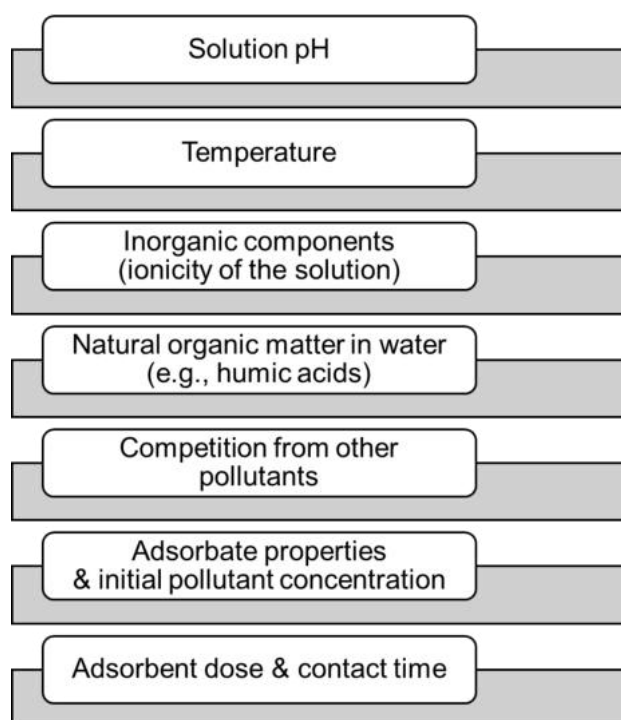


Figure 13. Key factors impacting the adsorption process and its efficiency [163,164].

5. Review of Adsorbents for EAC Removal

5.1 Natural Adsorbents

Natural adsorbents include the most common activated carbon (PAC – powdered, GAC – granulated), but also promising alternatives such as zeolites (e.g., clinoptilolite), waste-based, agricultural-based materials, and biochars.

Activated carbon is known primarily for its large specific surface area and high porosity. Its surface area ranges from 500 to 1500 m² g⁻¹. It is produced by carbonization or chemical/physical activation. Various materials, such as nutshells, peat, wood, and coal, are used for its production. It is known for its reliability in removing different types of contaminants, including EDCs such as pesticides, PCBs, pharmaceuticals, and dyes. The combination of its specific properties helps it achieve high removal rates. These include a vast number of micropores on their surface, as well as basic and acidic functional groups and additional hydrophobic groups that interact perfectly with non-polar compounds, which translates into versatility. However, a key aspect worth mentioning is their problematic regeneration and disposal. This process is often unprofitable and environmentally unfriendly (thermal firing is required) [165,166].

Aluminosilicates with a crystalline structure, or zeolites, can be found in volcanic tuffs, among other places. They are capable of ion exchange due to their negatively charged skeleton and neutralized by cations (such as Na⁺ and Ca²⁺). Furthermore, they have an extremely regular microporous structure, which is their hallmark. According to the literature, they are effective in removing heavy metals, ammonium, and radionuclides, but in their original form, they may have limited effectiveness in removing EDCs due to their polar structure. [167,168]. This, however, is not a major obstacle due to the possible modifications associated with the cationic group. These groups can be replaced with surfactants or other organic cations to obtain organozeolites. Organozeolites show better adsorption properties for more hydrophobic substances, such as BPA, than those in their native form. This was also demonstrated by a study of BPA adsorption on clinoptilolite modified with CPB (cetylpyridinium bromide). According to the literature, the material achieved 49.3 mg g⁻¹ for BPA adsorption. Comparing it to unmodified zeolite, it was observed that the unmodified material did not remove any negligible amounts of BPA, demonstrating the effectiveness of organozeolites [169].

The current trend is to produce biochar and other related materials that can be obtained from biomass. Pyrolysis is the primary process for obtaining this type of adsorbent. It is carried out under anaerobic conditions, and the substrate used for transformation can be various types of waste, such as rice husks, straw, agricultural waste like corn leaves, tree bark, fruit, or vegetable peels. Biochar is essentially chemically very similar to activated carbon, as it is rich in elemental carbon content and has a highly porous structure. Additionally, there are numerous phenolic, carbonyl, and carboxyl groups on its surface. This sustainable, inexpensive, and readily available material has already been tested for the adsorption of many EACs, with positive results. Unmodified biochars often have lower $q_{\max}$ values than, for example, targeted sorbents, but they can always be modified or activated chemically, such as with steam, to intensify the process.

An example of this group of sorbents is modified biochar from rice straw, for which atrazine adsorption is at the level of 95%. Furthermore, the same biodegradable sorbent from rice straw also effectively eliminates typical hormones, such as 17 β -estradiol (46.22 mg g⁻¹), according to the Freundlich isotherm (heterogeneity). Furthermore, referring to literature reports, pomelo peel achieves a maximum adsorption capacity of 256.5 mg g⁻¹, which is not among the lowest values. Other biochars, such as pepper stem, achieve even higher values (569.6 mg g⁻¹) for ibuprofen removal. The most important advantage of biochars is that they bind carbon from waste biomass, meaning they achieve a positive carbon balance, which is extremely important for sustainable development [170].

In addition to biochars, adsorption can also be performed directly on natural materials without prior treatment. Loffredo & Taskin reported that using plant-derived materials, such as spent coffee grounds or tea leaves, and composted humic acid, is well-suited for removing certain EAC groups. Removal of Octylphenol (OP), E2, and two pesticides (Fenuron and Carbaryl) was assessed as effective by all tested sorbents, and most importantly, environmentally friendly. Coffee grounds achieved the best adsorption for OP, with spent tea leaves showing slightly lower adsorption. However, spent leaves showed better sorption for one of the pesticides (carbaryl). Furthermore, composted humic acid proved to be the most versatile, with no preference for any contaminant. For example, comparing the sorption capacity of coffee grounds and biochar, it can be safely stated that the sorption capacity is much higher for the former, as confirmed by the $q_{\max}$ values reported by the researchers [171].

Interestingly, the pronounced sorption properties of coffee grounds can be attributed to their complex chemical composition. The presence of cellulose and hemicellulose, which are rich in hydroxyl (–OH) groups, together with lignin containing phenolic rings, provides a high density of active sites capable of interacting with and binding various contaminants. Furthermore, it is possible to process such natural materials and extract what is needed from them, for example, cellulose, which, due to its numerous hydroxyl groups, offers a variety of binding possibilities. Furthermore, natural cellulose itself can be subjected to various modifications, changing its properties, as discussed in more detail in the next subsection [150,172,173].

5.2 Modified Adsorbents

A prime example of title adsorbents is modified activated carbons. Modification refers to changes in the sorbent's structure that intensify the adsorption process or target specific contaminants. Modifications can be divided into chemical and physical. One possible process is impregnating the surface of unmodified carbon with polar compounds, which increases the potential for electrostatic binding. This form of carbon better adsorbs ionized phenols and estrogenic phenolates, among others. Furthermore, it also increases the deposition of acid-base residues. Examples of agents that can be used for this type of reaction include amines and metal oxides – iron or manganese. In addition, another modification is possible, which allows for simultaneous degradation with adsorption. Impregnation should be carried out using a redox

catalyst (e.g., iron (III)), which subsequently aids in the decomposition of the adsorbate, at least partially [174,175].

The second group of modified sorbents are carbon nanomaterials. These include nanotubes and graphene. They are primarily used as material composites that are deposited on a suitable matrix, as they are difficult to operate without one (they aggregate and do not separate from water). As reported in the literature, examples of such materials include nanotubes deposited on a silica or polymer matrix. The advantage of such modifications is the ease of separation of the sorbent material and an increase in the specific surface area of the sorbent. These modified carbon nanomaterials are effective in removing PCBs and organochlorine pesticides – hydrophobic and aromatic substances that pose a threat to the environment [176,177]. An additional example of successful operation is the 100% effective removal of bisphenol A from water by a graphene-based material based on cyclodextrin [178]. Reflecting on the principles of green chemistry, it is important to note that the materials described above are expensive and may encounter certain challenges in scaling the modification idea, including due to their non-biodegradability.

Interestingly, the properties of clay minerals (bentonite) also encourage certain modifications to their structure. Montmorillonite, which in its native form is not a very efficient sorbent for nonpolar compounds, is primarily used in research. As with organozeolites, the surface (interlayer spaces) of these substances can be transformed into a more hydrophobic one. Modifiers used by researchers include quaternary ammonium salts, polymers, or surfactants [179]. The product of this type of structural modification will be organobentonites. In addition to bentonites, silicas and aluminosilicates can also be modified in this way [180]. Scientific research has documented attempts to remove well-known pesticides (atrazine and chlorpyrifos) that resulted in the successful use of modified composite materials based on cellulose and bentonite [181].

As previously mentioned, there are many reports on the modification of coffee grounds, tea, corn, and tree leaves. An example is the extraction of a polysaccharide composed of β -D-glucopyranose subunits, i.e., cellulose. Cellulose can be subjected to further modifications, such as oxidation, the formation of composites, or the introduction of additional functional groups, which could theoretically improve its selectivity or generally increase its sorption capacity [150,182,183].

An example from the literature is the study of the adsorption of the most known BPA by functionalized cellulose fibers originating from Spanish broom. The results showed that equilibrium was achieved within 1 hour at pH 5, and maximum adsorption capacity was equal to 4.86 mg g⁻¹. Despite the relatively low $q_{\max}$ value, cellulose fiber efficiency remained unchanged even after three uses. Importantly, when switching from ultrapure water to wastewater, RME values decreased only slightly, from 77% to 64% removal [184].

The second example is a more advanced modification involving the creation of a β -cyclodextrin-modified magnetic rice husk-derived cellulose composite. Adsorption capacity in this case was significantly higher – 266.2 mg g⁻¹ for Pb (II), and 412.8 mg g⁻¹ for BPA. Besides

the relatively short operating time (30 minutes), other advantages include easy separation (using magnetic particles) and promising regeneration with a small decrease in efficiency [185].

The materials in this subsection represent a unique combination of versatile natural materials, which lack selectivity but are inexpensive, and specialized, more expensive, but more effective synthetic materials.

5.3 Polymeric Adsorbents

A separate group that deserves attention is polymer adsorbents, examples of which include polymer resins, or more precisely, a special group of them – adsorption resins, which operate by binding chemical compounds. The most well-known example is Amberlite XAD – a polystyrene-divinylbenzene resin with controlled pore size. Its specific surface area is impressive, reaching several hundred $\text{m}^2 \text{g}^{-1}$, but that is not its only advantage – it also boasts easier regeneration than activated carbon through solvent washing and is more durable than activated carbon. In addition to easy regeneration and chemical resistance, polymer adsorbents are also characterized by high purity (no dust formation, unlike activated carbon or natural-based biochar). Another important aspect of this group is the ease with which surface chemistry can be tailored to current needs [186]. Selected functional monomers can be incorporated into the polymer structure, thus targeting the desired group of chemical compounds for removal. According to scientific reports, adsorption resins such as XAD-4 and Dow Marathon A demonstrate higher RME results compared to granular activated carbon for PFOA removal [187]. Modifications to adsorption (nonionic) resins also exist, as reported in the literature. For example, the polymeric adsorbent Amberlite XAD-7 impregnated with quaternary amine Aliquat 336 was studied, yielding BPA adsorption values of q_{max} of 11 mg g^{-1} [188]. An additional example that fits perfectly into this group is cross-linked polymers with dendritic structures and hyper-cross-linked polymers (HCPs). As already published, the hyper-cross-linked polymer resin (NDA-701) achieved results of maximum adsorption capacity higher than Amberlite XAD-4 and granulated activated carbon for the adsorption of toxic 4-nitrophenol, which only confirms their potential [189,190].

5.4 Molecularly Imprinted Polymers (MIP)

Molecularly imprinted polymers (MIPs) are a special group of polymers capable of targeted adsorption. This type of material is created by reacting with a matrix (template), which serves as a template that shapes the interior of a porous adsorbent. The template can be the substituent being removed (model contaminants) or a structurally similar compound. This ensures a good fit of the adsorbate molecules to the cavity of the modeled polymer. The pores of the sorbent prepared in this way have a similar shape and arrangement of functional groups tailored to the target molecule, resulting in increased adsorption. The principle of operation during the preparation of this type of material is that the pores and the entire system of voids in the adsorbent adapt to the matrix during polymerization. In this situation, the monomeric units arrange themselves to adapt to the structure of the selected matrix, and after the entire process, the

template is removed, with the final structure being perfectly adapted to capture the contaminant, like a key in a lock. These custom-designed sorbents, due to their selective locations, excel at selectively removing a given substance even in the presence of other substances in solution, which is often crucial when working with complex wastewater matrices or water from natural reservoirs containing other chemical entities [191–193].

An example from the literature about the selective binding of EDCs is a MIP designed using a 17 β -estradiol template, which performs well in solutions with hormone concentrations of 2 $\mu\text{g L}^{-1}$. Its competitiveness was also tested, and it was shown that it only effectively removes 17 β -estradiol, even in the presence of estrone, 19-nortestosterone, epiandrosterone, and cholesterol [194]. In another study combining a molecularly imprinted polymer (MIP) with photodegradation, the E2-templated MIP achieved 73% efficiency in desorbing contaminants using acetone, whereas the unimprinted material reached only 46%. This highlights the superiority of MIPs not only in adsorption but also in regeneration. [195]. These kinds of sorbents have also been studied for the targeted adsorption of pesticides (nonylphenol), BPA, other hormones, and pharmaceuticals, with positive results [196].

However, the potential problems of this type of material cannot be overlooked, including a lack of universality, stepwise and complex synthesis, and sometimes the lack of availability of active sites capable of binding contaminants.

In addition, various modifications of MIPs have been developed, including their immobilization on a matrix (porous support), which increases the number of active sites and, consequently, the maximum sorbent capacity. Practical applications of MIPs also extend to analytical techniques, where they are increasingly used as components of SPE column cartridges, valued for their process selectivity. [197]. Adsorption on MIPs is sometimes combined sequentially with other processes, such as UV irradiation, which can aid in the removal and decomposition of previously adsorbed contaminants [198]. It is also important to note that renewable raw materials, such as cyclodextrins, can also be used in MIPs. Such cases have been reported in the literature since the 1990s. The chart of molecular imprinting polymerization for the formation of molecularly imprinted cyclodextrin polymers (MICPs) is shown in Figure 14 [199,200].

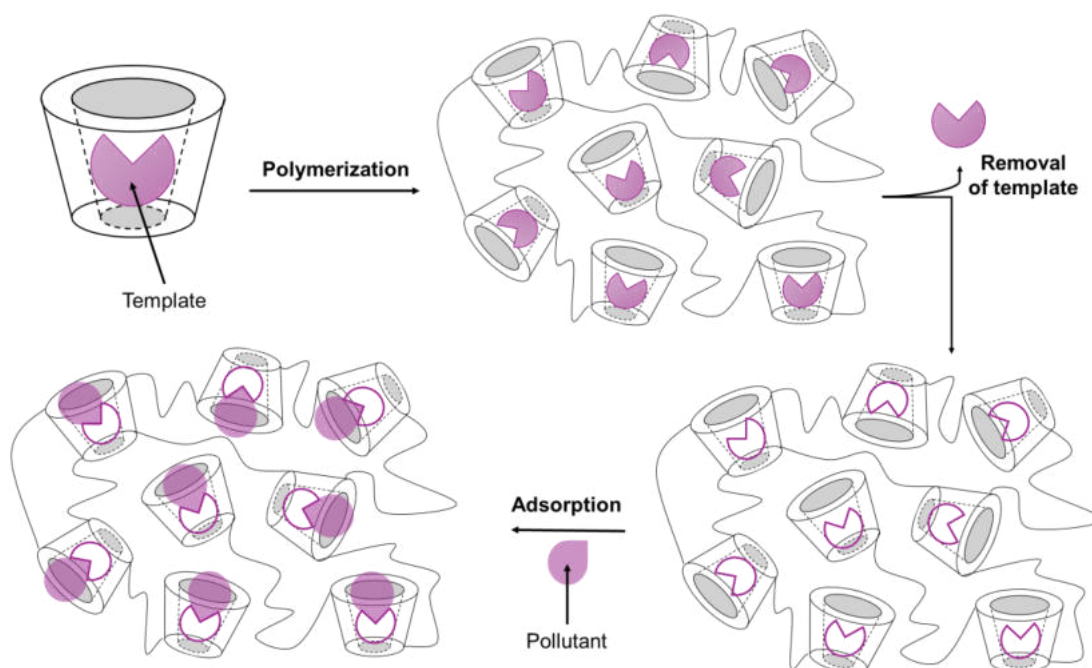


Figure 14. Schematic representation of imprinting polymerization for cyclodextrin nanosponges.

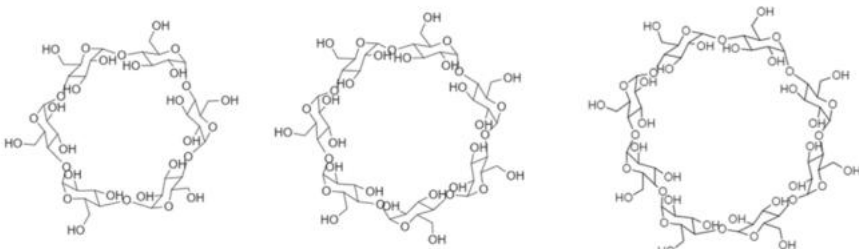
For example, according to the author's research, the adsorption of the triphenylmethane dye CV by cyclodextrin MIPs was almost twice as high as by non-imprinted material (NIP). Studies have also shown that MIPs adsorb CV more efficiently even in the presence of phenolic compounds (BPA and BPB). The more advanced the mixture, the better the CV adsorption observed [201].

In summary, MIPs are highly valuable for their selectivity, enabling the capture of target molecules without affecting other substances present in the aqueous matrix. As confirmed by research, in addition to this benefit, their stability during use and after regeneration also deserves mention.

5.5 Cyclodextrin-Based Adsorbents

Cyclodextrin adsorbents, including cyclodextrin nanosponges, are a group of adsorbents attracting increasing interest year after year. Cyclodextrins (CDs), from which these sorbents are composed, are oligosaccharides composed of glucopyranose subunits. The most popular are α , β , and γ -cyclodextrin, which differ in the number of glucopyranose building blocks. The key properties of them are shown in Table 5 [202,203].

Table 5. The most important cyclodextrins and their properties [202,204].

Property	α -Cyclodextrin (α -CD)	β -Cyclodextrin (β -CD)	γ -Cyclodextrin (γ -CD)
Number of glucose units	6	7	8
Cavity diameter (Å)	4.7–5.3	6.0–6.5	7.5–8.3
Outer diameter (Å)	14.6	15.4	17.5
Molecular height (Å)	7.9		
Molecular weight (g mol ⁻¹)	972	1135	1297
Water solubility (25 °C) (g L ⁻¹)	145	18.5	232
Cavity volume	Small (fits low-molecular-weight hydrophilic molecules)	Medium (suitable for many pharmaceuticals, phenols, bisphenols, dyes)	Large (accommodates bulky hydrophobic molecules (steroids, macrolides, EDC mixtures))
Stability constant (guest–host complexes)	Generally lower (weak inclusion)	Moderate to high (strongest interactions for many aromatics)	Moderate (better for larger molecules but weaker binding per unit)
Cost and availability	Moderate	Cheapest and most widely available	Expensive (industrial-scale still limited)
Relevance to adsorption studies	Limited due to small cavity	Widely studied and numerous CD-polymers and MIPs based on β -CD for EAC removal	Promising for larger EACs but less common due to cost
Chemical structure			

β -Cyclodextrin (β -CD) is the most commonly used cyclodextrin in practice due to its medium-sized cavity, which allows it to form inclusion complexes with relatively small organic compounds, including pharmaceuticals, bisphenols, and dyes, across a range of CD-to-pollutant ratios. The structure of cyclodextrins is indeed unusual, as they possess amphiphilic properties (a hydrophobic cavity and a hydrophilic surface), which provide numerous binding opportunities for many types of molecules (phenols, dyes, pharmaceuticals, and other EDCs). In practice, a molecule can be adsorbed both inside the cyclodextrin torus and outside via hydroxyl groups [205–207]. Despite these many advantages, native CDs cannot be used as sorption materials due to their water solubility. For this reason, scientists have suggested polymerizing them, which ensures their insolubility. Nanostructured particles after such

polymerization can be considered as cyclodextrin-based nanosponges. The scheme with CD structure and cross-linking reaction is presented in Figure 15 [208,209].

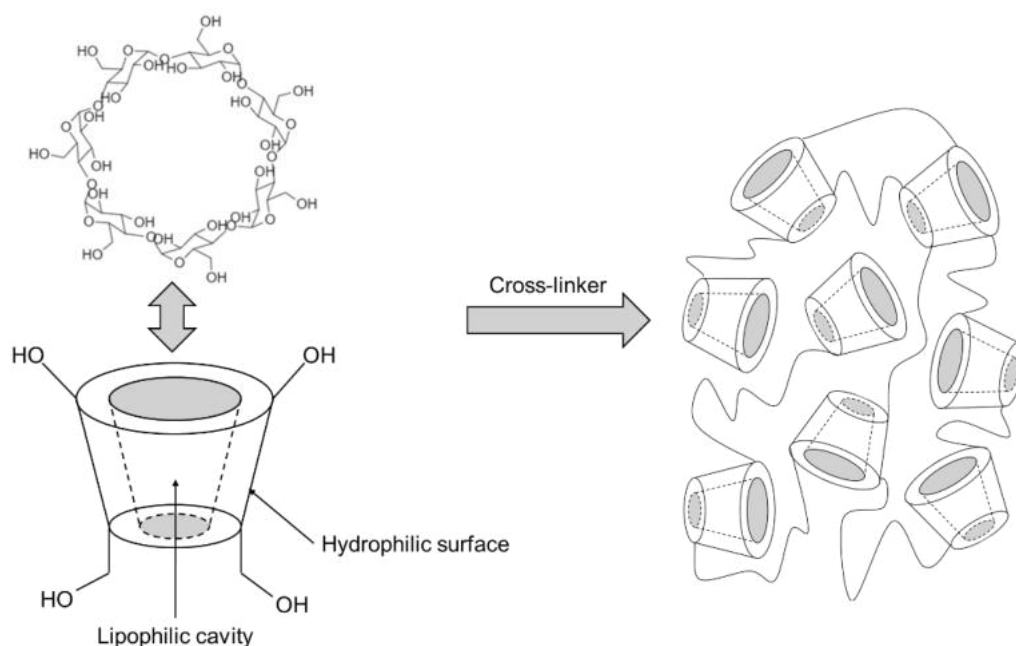


Figure 15. The schematic representation of the CD structure and cross-linking reaction [121].

Highly cross-linked materials typically exhibit rapid adsorption kinetics due to their dense network structure. During polymerization, reaction conditions and the choice of cross-linking agents can be adjusted to tune the properties of the resulting sorbent. Furthermore, the resulting polymers can be further modified – for example, by incorporating magnetic nanoparticles to facilitate separation using a magnet. An example is the use of aromatic diisocyanates (e.g., TDI (toluene-2,4- and 2,6-diisocyanate)), which allows for the creation of larger and stiffer pores in the adsorbent structure. Similar changes can be achieved by modifying the reaction time, the cross-linker to CD ratio, or the temperature. The most used cross-linkers in CD polymerization are presented in Figure 16 [133,149,208,209].

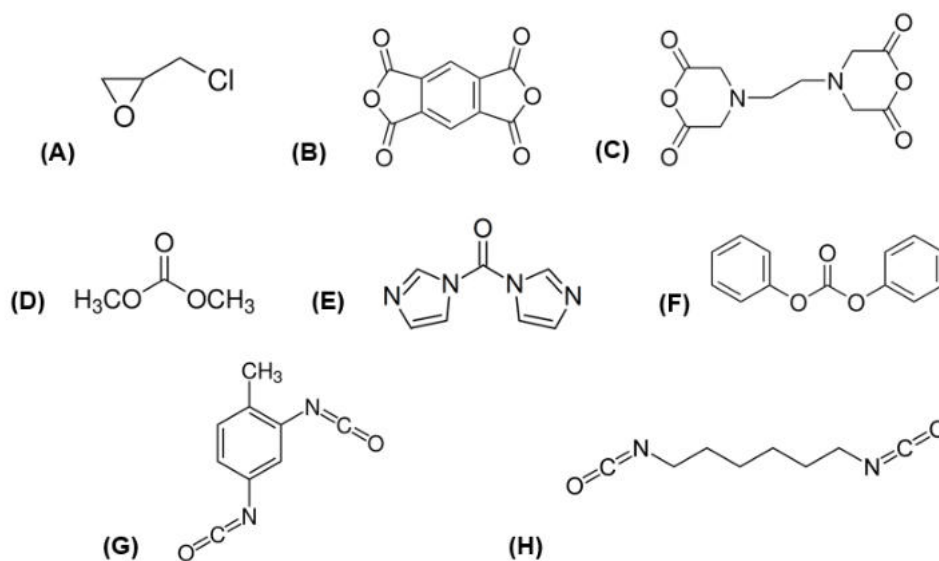


Figure 16. Chemical structures of popular cross-linkers for CD polymerization. (A) Epichlorohydrin; Anhydride linkers: (B) Pyromellitic Dianhydride, (C) EDTA Dianhydride; Carbonyl linkers: (D) Dimethyl Carbonate, (E) Carbonyl Imidazole, (F) Diphenyl Carbonate; Diisocyanate linkers: (G) Toluene Diisocyanate (TDI), (H) Hexamethylene Diisocyanate (HMDI) [121].

According to literature reports, a $q_{\max}$ of 47.75 mg g⁻¹ was achieved for the adsorption of bisphenol A by β -cyclodextrin nanosponge. After the regeneration process, the adsorption efficiency was calculated as more than 99%, while before it was reported as 95.51%. Unusually, the researchers in this study did not use the standard solvents for regeneration, but supercritical CO₂-based regeneration was employed [210]. Other researchers have reported β -cyclodextrin polymer crosslinked with epichlorohydrin RMEs of >99% for BPA and hormones, and RMEs of >85% for diclofenac and ibuprofen, which is a very satisfying result, especially considering they were working on a pilot solution, knowing that scalability sometimes does not yield the same results as those obtained in the laboratory-scale studies [211].

Moreover, desorption and regeneration studies are often performed alongside CD polymer adsorption studies. Many studies indicate that these materials are capable of maintaining the same level of performance even after several desorption and regeneration cycles preceded by adsorption of the selected contaminant. Alsbaiee et al. reported that even after five cycles of methanol regeneration (following BPA adsorption), it is possible to maintain the original sorption capacity [212].

In summary, the key to this group of sorbents is the optimal design of a material that, after appropriate processing, can even surpass the properties of commonly used, traditional adsorbents. Remarkably, this group also stands out for its environmental friendliness, as it is based on natural sugars, from which CDs are composed. From the natural benefits, it can also be mentioned that they represent mechanical and chemical stability and have ease of regeneration in a mild environment [213].

6. Sustainable Development and Biodegradability of Adsorbents

6.1 Sustainable Adsorbents

As the name suggests, sustainable adsorbents align with the requirements of sustainable development, which is currently considered paramount. When selecting the right eco-friendly adsorbent, it must have the smallest possible environmental footprint, not generate additional waste, and ideally be manufactured using only renewable raw materials. The circular economy is also playing a crucial role, as waste materials or leftovers intended for utilization are reused, reducing negative environmental impact. Biochars made from agricultural wastes or biopolymers based on renewable raw materials such as cellulose, starch, or cyclodextrins, as described above, can be reported as an example of that kind of material. The advantages of such sorbents include their cost, which makes them a viable competitor to commonly used industrial sorbents. Furthermore, beyond the source and environmental friendliness of the substrates used to create this type of adsorbent, it is also critical that the synthesis process itself be as optimized as possible. It cannot consume excessive amounts of energy or excessive use of hazardous chemicals, as this generates costs related to, for example, the use of high-temperature activation and others. Following the principles of green chemistry in adsorbent production involves modifying certain processes or their components, such as replacing catalysts with natural alternatives, using polymerization in water, or steam activation. After the production process, it is also important that the sorbents reveal sufficiently high sorption capacity when used in the process. This impacts several key aspects: primarily, the amount of material used, which transforms into a mass of waste to be disposed of. The higher the capacity, the less sorbent will be required [214–216].

For example, the $q_{\max}$ parameter obtained for a novel sulfhydryl-rich β -cyclodextrin (cyclodextrin polymer) was equal to 288 mg g⁻¹ during BPA removal [217]. Compared to the same parameter for BPA, AC-40 Activated Carbon achieves a result of 94 mg g⁻¹ [218]. This means that for the first sorbent based on renewable raw materials, we will use approximately three times less energy for its production and disposal, and at the same time, we will use less raw material during the adsorption process, achieving the same result as for AC [216].

In summary, sustainable sorbents require a balance between the three most important stages of their life cycle – production, use, and end-of-life. The most important requirements needed to meet the principles of sustainable development are presented in Figure 17, along with the corresponding phases of the material life cycle.

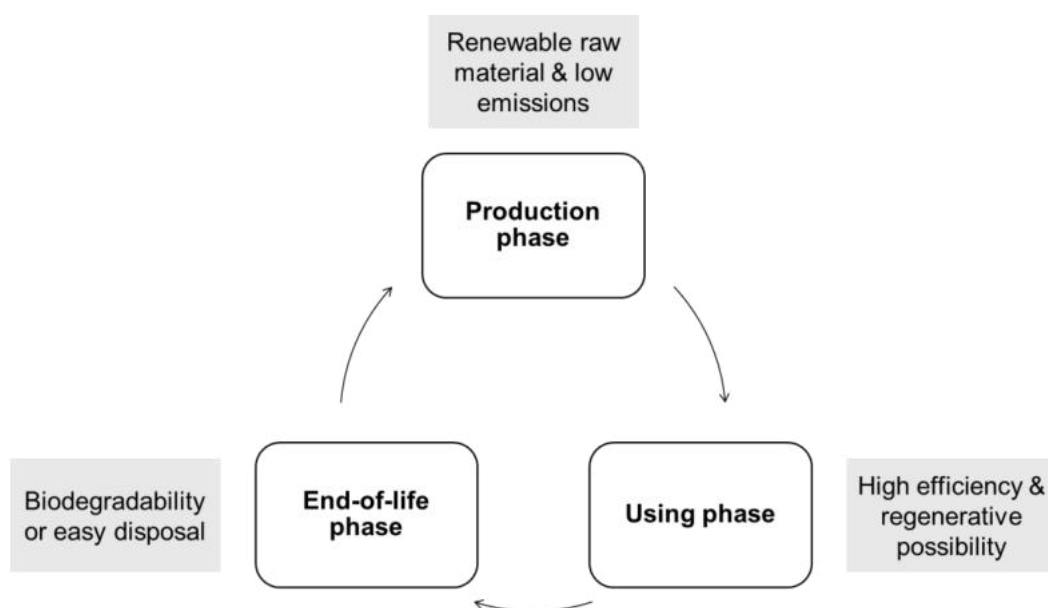


Figure 17. Life cycle of a sustainable adsorbent [219,220].

6.2 Biodegradability

Another important aspect of the new generation of adsorbents is their biodegradability. This process of decomposition allows for the degradation of materials in an environmentally safe manner, using microorganisms. Currently, significant emphasis is placed on maintaining a clean and environmentally friendly end-of-life stage for sorbents. Scientists are referring to the proper disposal of used materials, for example, using incineration with energy recovery or composting. For example, composting can lead to the formation of harmless substances such as CO₂, water, and biomass. It is important to avoid the generation of secondary products during this process. Moreover, it is worth noting that not every sorbent is able to be biodegraded. Importantly, it is crucial to remember that some known and currently used materials will remain in the environment if not treated in the appropriate way [221]. For example, polymeric adsorbents such as Amberlite XAD can be mentioned here [222]. Hence, the current trend of researchers is engaging in the development of sorbents based on natural resources. In addition to the aforementioned in the previous chapters, biodegradable cyclodextrins and cellulose, alginate (derived from algae), and chitosan (derived from crustacean shells) are also currently used [182,223,224]. Their use in materials preparation allows for a higher percentage of biodegradable material by weight. In addition to the adsorbents described above, inorganic sorbents (such as clay minerals) can also be safely disposed of [225]. They are environmentally neutral, so they can be returned to the environment after regeneration and removal of hazardous contaminants previously adsorbed on their structure. It is also worth mentioning that the safest method is always to first remove (deactivate) the contaminants and then transfer the materials directly to the soil or use composting, which significantly reduces the undesirable release of adsorbed contaminants into the environment [226–228]. It is important to consider not only the degradation of sorbents but also the elimination of the adsorbate. Interestingly, there are also studies confirming that, for

example, hazardous dyes are capable of biodegrading under the influence of microorganisms such as bacteria, actinomycetes, yeasts, and fungi. Their degradation mechanism is primarily based on enzymatic transformations, which is also a solution that could contribute to a sustainable approach [229]. Additionally, controlled biodegradation is also possible. It utilizes specific conditions, such as environment and temperature, or involves pre-designed bonds intentionally introduced into the material to improve degradation [230]. This is an important approach for industrial practice, where we aim to operate in a closed loop [227].

For example, for naturally derived materials such as cellulose or coffee, as well as CD-based materials, degradation has been observed to be possible in the presence of baker's yeast. Furthermore, this not only leads to biodegradation, but its presence also promotes the desorption of previously adsorbed dyes, which is an additional advantage for the entire process [150,231].

6.3 Regeneration and Reuse

Sustainable adsorption can be achieved by developing materials that are capable of regeneration and reuse. Ideally, after adsorption of contaminants, the material should also be able to desorb pollutants and be reused with similar efficiency. According to expert knowledge and literature, many sorbents possess this property to keep the performance at a similar level to the initial one, even after several to a dozen regeneration cycles [210,231,232]. There are adsorbents not as readily regenerated as others, such as activated carbon. To regenerate it, high temperatures and calcination are necessary, or the contaminants must be rinsed with hot steam or solvents. Unfortunately, such extreme conditions can often result in the release of oxidation products into the environment, negatively impacting the life and health of flora, fauna, and humans [233,234]. On the other hand, when examining polymeric adsorbents (e.g., cyclodextrin-based), which are relatively stable, it can be observed that even using relatively mild conditions, such as rinsing with solvents (or water-alcohol mixtures) or changing the solution's pH, they can be sufficiently regenerated. Materials prepared this way after adsorption of pharmaceuticals or bisphenols can be used for at least another 5 cycles without significant losses in the RME [149,201].

Regeneration and reuse of sorbents can offer many advantages, including reducing the amount of waste for disposal, lower operating costs due to fewer operational interruptions (the bed requires less frequent replacement), and the use of a smaller amount of sorbent. Despite the advantages described, there is, of course, the possibility of irreversibly contaminating the adsorbent pores through the accumulation of substances that cannot be removed [235]. Furthermore, chemical degradation (often after thermal treatment) or physical degradation (abrasion during the mixing process) is also possible. However, despite this, literature reports that for cyclodextrin polymers, for example, for ibuprofen removal, the adsorption capacity remains virtually unchanged even after 10 regeneration cycles, hence it proves that some sorbents are still possible to be used after many cycles of adsorption-desorption [236]. Furthermore, imprinted

cyclodextrin polymers tested for dibutyl phthalate (DBP) adsorption retained 93% of their initial efficiency even after 4 regeneration cycles [237].

Beyond the essence of the regeneration process itself – obtaining a ready-to-use sorbent – there is another aspect extremely important to maintaining a green approach: the treatment of contaminants removed from the material. Common methods for dealing with this stage of the process include oxidation (e.g., ozonation) or incineration of the contaminant along with the sorbent [112,238]. An example of the first method is the previously mentioned photodegradation of hormones (E1, E2, and EE2) after adsorption and acetone extraction of the sorbent pores [195]. Moreover, the second method is often used with activated carbon, followed by subsequent purification of the resulting gases in a cyclone.

Taking all this into consideration, it is important to remember that ultimately, the most important thing is to prevent hazardous contaminants from escaping the adsorption system, either as residue after desorption from the material or through improper storage of the contaminated sorbent [235].

In conclusion, research so far suggests that there is a genuine chance of success in creating and managing sustainable adsorbents, even knowing the obstacles like cost-effectiveness and scalability. Combining the majority of the options mentioned above, such as biodegradation, regeneration, reuse, and green design concepts (process non-toxicity and renewability), is crucial to reach success [235].

PUBLICATION CYCLE

7. Dissertation Assumptions

7.1 Research objectives

This doctoral dissertation aimed to design, synthesize, prepare, and test modern adsorption materials. The primary focus was on adsorbents based on cyclodextrins, particularly β -cyclodextrin, and renewable raw materials, which would demonstrate effective adsorption of hazardous contaminants. The model contaminants studied included dyes, pharmaceuticals, NSAIDs, and other drugs, as well as bisphenols, all examples of endocrine-active compounds. The primary goal was to establish that appropriate design and targeted performance of materials can improve both the maximum sorption capacity ($q_{\max}$) and, in some cases, selectivity for the contaminants to be adsorbed. The specific objectives are presented below:

1. Synthesis (cross-linking) of cyclodextrin-based polymers (including MIP synthesis with imprinted template molecules) and the preparation and potential modification of natural polymers (cellulose) and waste materials (coffee grounds).
2. Characterization of the obtained adsorption materials through physicochemical analysis, including information on the surface area, structure, and elemental composition of the adsorbents.
3. Analysis of the interactions between the sorbent and adsorbate and determination of the predicted mechanism of the adsorption process.
4. Examination of the sorption capacity of the prepared sorbents towards selected model pollutants (dyes, NSAIDs, analgesics, bisphenols) using various conditions, including the initial concentration of the adsorbate and adsorbent, contact time, and the presence of various other substances in the solution. Comparison of sorption capacity with sorbents traditionally used in industry.
5. Evaluation of the potential for regeneration and reuse of the designed sorbents. Specifically, in the case of cyclodextrin polymers, the determination of whether sorbents adapt after contact with contaminants and whether the structural reorganization effect can be maintained after subsequent regeneration cycles.
6. Use of low-cost (including waste) renewable raw materials (e.g., coffee grounds, cellulose) to prepare effective sorbents and verify their suitability for highly efficient contaminant removal, while maintaining sustainable development principles and minimizing environmental impact through their potential biodegradability.
7. Synthesis of the current knowledge on cyclodextrin adsorbents for the removal of various types of environmental contaminants, identifying potential directions requiring further research, and assessing the suitability of the materials studied for industrial applications.

Taking the above into account, this doctoral thesis aims to provide new scientific knowledge on the combination of sorption efficiency and ecological aspects. It aims to demonstrate that it is possible to maintain biodegradability (even partial), the possibility of regeneration/degradation, or the use of waste/renewable raw materials while simultaneously

integrating these features with functionality and sometimes selectivity towards the removal of difficult-to-remove hazardous substances from water and sewage.

7.2 Research Hypotheses

Based on the research objective, available literature, and preliminary research results, the following hypotheses were formulated:

Hypothesis 1 (H1): Designed β -cyclodextrin polymers, also with molecular imprints or other modifications, will selectively and highly efficiently remove selected endocrine-active contaminants from water. Furthermore, it is assumed that the present supramolecular interactions and the presence of amphiphilic cyclodextrin structures will result in above-average adsorption capacity and rapid kinetics compared to other available, studied, and described cyclodextrin sorbents and traditional adsorbents.

Hypothesis 2 (H2): Cyclodextrin-based materials will remember the shape of the contaminant and adapt their structure to it after the first adsorption cycle (after initial exposure). This reorganization will result in materials that will adsorb the contaminant more easily and efficiently in subsequent cycles.

Hypothesis 3 (H3): Adsorbents containing naturally derived materials (such as cyclodextrins), waste (coffee grounds), or low-cost raw materials (cellulose) will demonstrate comparable or even higher adsorption capacity than traditional sorbents. At the same time, they will also demonstrate lower cost and have minimal environmental impact. Furthermore, it is assumed that additional modifications to these natural or semi-natural materials will affect regeneration stability and adsorption efficiency, resulting in $q_{\max}$ values reaching several hundred mg g^{-1} .

Hypothesis 4 (H4): All designed and developed adsorption materials will be effective under real-world conditions, both for removing contaminated water samples from the Baltic Sea and the Vistula River, as well as for eliminating industrial wastewater, if applicable. Despite the presence of typical naturally occurring co-occurring substances and variable pH, no reduction in the removal efficiency of the model contaminants is expected. Furthermore, in some cases, it is postulated that the sorption capacity will be higher than in tests conducted with distilled water.

Hypothesis 5 (H5): A thorough literature review of the research topic will help identify research gaps and allow for the selection of the path and specific focus of the research that is the subject of this dissertation. It is assumed that this review will help integrate existing knowledge and identify potential opportunities for researchers to advance the important issue of removing emerging pollutants from water.

7.3 Scope of the Work

The scope of work related to this doctoral dissertation covers two primary areas – experimental and theoretical. These concern the design, synthesis, and characterization of new adsorption materials, as well as their usefulness in real-world water and wastewater treatment processes. This dissertation was based on a collection of thematically related publications, each

of which provides a unique component to the overall topic. The entire dissertation consists of five articles – four original and one review, published between 2021 and 2025 in peer-reviewed international journals. All publications are inextricably linked to the topic of this doctoral dissertation, concerning adsorbents for removing endocrine-active compounds from the aquatic environment. Table 6 provides details of the articles mentioned above, including the title, authors, their contributions, Ministry of Science and Higher Education (MEiN) points, and DOI. Moreover, the general scope of the aforementioned works was:

Publications 1-4 (research) – design, synthesis, and/or modification of various types of adsorbents (using cyclodextrin, cellulose, or waste materials such as coffee grounds), examination of their sorption capacity based on studies on the model contaminant EDC, determination of their regenerative or degradative capabilities, and verification of their potential for use in real-world conditions.

Publication 5 (review) – synthesis of information found in the latest literature reports on the subject of research. This publication provides context for the conducted research in light of gaps in current knowledge. This work is based on an objective presentation of the multitude of cyclodextrin adsorbents used to remove dyes, drugs, heavy metals, and endocrine-active compounds. The methods for synthesizing these materials are also described in detail. Integrating these aspects allowed for a new understanding of the record-breaking sorption capacities of some of them, as well as modern approaches to materials regeneration, among other things.

To sum up, the substantive scope of the research focused on three main subjects: the development of new materials, their characterization, and the study of the sorption process, which also included environmental and industrial research. Furthermore, incorporating the principles of sustainable development and green chemistry is an integral and crucial part of this work.

Table 6. Overview of the articles included in the dissertation.

No.	Title/ Journal	Year	Type	DOI	MEIN points	IF (year)/ Quartile	Author contributions	Ref.
1	Efficient Water Pollutants Targeting: Novel Materials with Molecular Imprints for Textile Industry Use – Ind. Eng. Chem. Res.	2025	Research	https://doi.org/10.1021/acs.iecr.5c00705	140	IF: 3.9 (2025); Q1	D. Nowacka (60%), A. Schmidt (30%), B. Łęska (5%), R. Pankiewicz (5%)	[201]
2	Removal of nonsteroidal anti-inflammatory drugs and analgesics from wastewater by adsorption on cross-linked β -cyclodextrin – Water Resources and Industry	2022	Research	10.1016/j.wri.2022.100186	200	IF: 5.1 (2022); Q1	A. Skwierawska (60%), D. Nowacka (30%), K. Kozłowska-Tylingo (10%)	[149]
3	Cellulose and its derivatives, coffee grounds, and cross-linked β -cyclodextrin in the race for the highest sorption capacity of cationic dyes in accordance with the principles of sustainable development – J. Hazard. Mater.	2022	Research	10.1016/j.jhazmat.2022.129588	200	IF: 13.6 (2022); Q1	A. Skwierawska (60%), M. Bliźniewska (5%), K. Muza (5%), A. Nowak (6%), D. Nowacka (15%), S.E.Z. Syeda (2%), M.S. Khan (2%), B. Łęska (5%)	[150]
4	Structural Adaptive, Self-Separating Material for Removing Ibuprofen from Waters and Sewage – Materials	2021	Research	10.3390/ma14247697	140	IF: 3.748 (2021); Q2	A. Skwierawska (40%), D. Nowacka (20%), P. Nowicka (15%), S. Rosa (15%), K. Kozłowska-Tylingo (10%)	[133]

No.	Title/ Journal	Year	Type	DOI	MEIN points	IF (year)/ Quartile	Author contributions	Ref.
5	Recent Advancements in Cyclodextrin-Based Adsorbents for the Removal of Hazardous Pollutants from Waters – Polymers	2022	Review	10.3390/polym14122341	100	IF: 5.0 (2022); Q1	S.E.Z. Syeda (25%), D. Nowacka (25%), M.S. Khan (25%), A.M. Skwierawska (25%)	[204]

8. Research Materials and Methods

8.1 Sorption materials

During the research on the topic of this doctoral dissertation, novel materials were developed and studied, undergoing various modifications and exhibiting different properties during the adsorption process. The most important group consists of β -cyclodextrin-based materials (so-called cyclodextrin nanosponges), formed by cross-linking native cyclodextrins with various cross-linking agents, such as isocyanates, e.g., hexamethylene diisocyanate, which are widely used in research. In addition to conventional cyclodextrin polymers, MIPs were also synthesized – molecularly imprinted cyclodextrin polymers formed using di- and triphenylmethane. These DI-CDP and TRI-CDP materials were designed for the removal of specific triphenylmethane dyes and bisphenols due to their structural similarity. In addition to materials based on cyclodextrins and their cross-linked structures, low-cost materials such as cellulose (a polysaccharide) and biowaste such as used coffee grounds were also studied. Microcrystalline cellulose, in addition to being tested in its native form, was also examined after modification to improve its sorption properties and after creating a composite material combining cyclodextrin with a cellulose carrier. All starting materials used are readily available, biodegradable, and contain many functional groups capable of reacting with contaminants and the material.

8.2 Characterization of sorbents

Once the adsorbents are obtained, they must be subjected to physicochemical tests to correlate their structure and specific characteristics with the adsorption process. One of the most important tests is scanning electron microscopy (SEM), which visualizes the morphology and allows for the estimation of sorbent particle size. Fourier transform infrared spectroscopy (FTIR) is used to identify functional groups characteristic of a given material and to confirm the occurrence of certain chemical reactions, such as the observation of a band associated with the formation of the -NH-CO- bond after the synthesis of cyclodextrin nanosponges. Thermogravimetric analysis (TGA) and the associated differential scanning calorimetric (DSC) were used to determine the thermal stability of the adsorption materials and to understand the thermal effect during each of the transformations. BET (Brunauer–Emmett–Teller), BJH (Barrett–Joyner–Halenda), and t-Plot (thickness plot method) analyses are also integral parts of adsorbent analysis. These analyses provide information on the pore distribution, specific surface area, and overall texture and porosity of the sorbents. Parameters related to these analyses are determined based on nitrogen sorption isotherms. In addition to the above tests, zeta potential analysis is also performed – this method is used to determine surface charge. Performed at various solution pHs, it helps determine the potential electrostatic interactions between the adsorbent and adsorbate. The final key technique for sorbent characterization is elemental analysis, which is responsible for determining the chemical composition and potential calculation of the degree of cross-linking

(for example, the percentage of nitrogen can indicate the presence of groups formed after cross-linking with isocyanates).

8.3 Adsorption test procedures

Adsorption experiments constituted a fundamental part of all studies. They were conducted in a static system – so-called batch adsorption studies in a standardized format. Each time, a known amount of sorbent was weighed and added to solutions with known concentrations of the model pollutant or a mixture of pollutants. Thermodynamic studies were conducted at controlled temperature, while other studies were conducted at room temperature using a shaker to ensure continuous contact between the adsorbent and the adsorbate. Kinetic studies were analyzed by the contaminant concentration decrease over time, previously collecting solution samples at specified time intervals (usually lasting up to 60–120 minutes for the materials covered in this dissertation). Concentration measurements for dyes and bisphenols were performed spectrophotometrically using a UV-Vis spectrophotometer (the absorbance of the characteristic absorption maximum for a given contaminant was measured). For pharmaceuticals, a different analytical technique was used: HPLC (high-performance liquid chromatography with UV detection). The concentration change determined by these methods was used to calculate the amount of EDC adsorbed per unit mass of sorbent (q , mg g^{-1}), as well as the removal rate (%). To fit the data to the kinetic models, models such as pseudo-first order, pseudo-second order, Weber-Morris, and Elovich were used, identifying the rate-limiting process of adsorption (e.g., chemical bonding or pore diffusion). Furthermore, to determine the q_{max} parameter, the maximum sorption capacity, an attempt was made to fit the data obtained from the isothermal experiments to isothermal models, such as the classic Langmuir and the Freundlich models, as well as more complex ones, such as Sips, Hill, Jovanovic Monolayer, and Halsey. The isothermal experiment itself was performed by adding a constant amount of sorbent to a series of solutions with different initial EDC concentrations to achieve equilibrium. These calculated parameters each provided a measure of the materials' effectiveness and were used for comparison.

8.4 Real-world testing, regeneration, and utilization

After basic adsorption testing, the performance and efficiency of adsorbents can also be verified after use, as well as their suitability for use in real-world conditions, such as in wastewater or environmental matrices. To verify the effectiveness of materials in such conditions, the sorption process is tested using real water/wastewater samples (e.g., model industrial wastewater or doped samples from water reservoirs). The testing process for such samples begins with preliminary filtration and separation of large pollutant particles. Selected model pollutants are then doped, and the sorption process is conducted as described in section 8.3. Such tests aid in the initial verification of sorbents and the selection of those truly suitable for use in conditions close to real-world conditions, whether the presence of co-occurring matrix components hinders adsorption, and how they are affected by variables such as pH, ionic

strength, and the presence of organic substances such as humic acids. Furthermore, cyclic adsorption-desorption tests allow for the assessment of economic viability and stability. Such tests are conducted by conducting normal adsorption, i.e., saturation of the material with contaminants, followed by regeneration, for example, by washing it out with a solvent such as methanol or ethanol. This yielded positive results for all sorbents tested in this study. Such tests provide valuable information for evaluating sorbent performance, for example, by helping to estimate the possible cycles in which a given adsorbent can be used, the efficiency in each cycle, and whether the materials can be easily and cost-effectively disposed of (e.g., after removing the contaminants) through composting. Degradation tests can be performed for materials based on natural components (e.g., cyclodextrin or cellulose). In the case of the publication cycle for the tested materials from Publication 3, such tests were carried out by exposing the material to baker's yeast. The effect was positive, and in addition to degradation, an improvement in the removal of the model contaminant – crystal violet – from the surface of the materials was also observed.

9. Guide to the Publication Cycle

Chapter 9 provides a brief description of the publications that form the basis of this doctoral dissertation, along with the purpose and scope of each work, key findings, and the scientific innovations found in each. For ease of reference, articles are numbered 1 to 5, as shown in Table 6, which also provides bibliographic information for each.

9.1 Publication 1 – *Efficient Water Pollutants Targeting: Novel Materials with Molecular Imprints for Textile Industry Use* (Ind. Eng. Chem. Res., 2025 – original research paper) [201]

Purpose and Scope

The main goal of Publication 1 was to determine whether molecular imprints on cyclodextrin polymers would enable highly efficient, selective removal of contaminants typical of the textile industry from water. Of particular note in this work are hazardous organic dyes, such as crystal violet and other trienylmethane dyes, as well as a group of bisphenols. The hypothesis adopted was that creating a molecular imprint using diphenylmethane (DPM) and triphenylmethane (TPM) would allow better matching of bisphenol and dye molecules to sorbents than using a polymer without the imprint (CDP). The prepared imprinted sorbents were designated DI-CDP and TRI-CDP, and the adsorption process for CV, BPA, and BPB was studied (Figure 18).

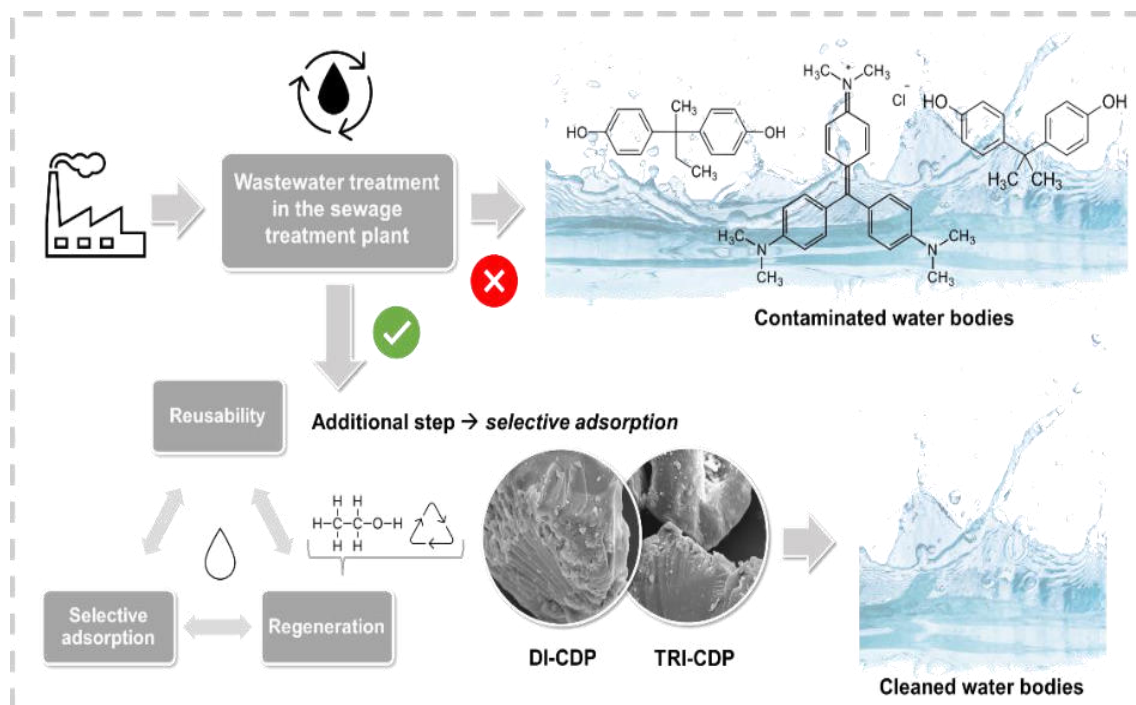


Figure 18. Graphical representation of the purpose of Publication 1.

Key Findings

The tested sorbents achieved unexpectedly high sorption capacity for the CV dye. Adsorption reached equilibrium after just 1 minute for crystal violet, indicating complete removal of the contaminant in a very short time. Simultaneously, sorption isotherms using the Hill model showed that the maximum adsorption capacity for DI-CDP, a polymer imprinted with diphenylmethane, was as high as 1075.8 mg g^{-1} . Conversely, for TRI-CDP, a polymer imprinted with triphenylmethane, it was 1005.8 mg g^{-1} , while for CDP it was only 594 mg g^{-1} . These results confirmed that the designed imprinting was superior to CD polymers without this modification, demonstrating the validity of the study. Moreover, after testing the regeneration of the materials, it was found that the sorption efficiency remained unchanged up to five cycles. Importantly, this study was conducted using mild conditions and in a virtually waste-free manner, and no disruption of the polymer structure was observed after the whole testing. Furthermore, the competitiveness test demonstrated that the DI- and TRI-CDP materials preferentially and selectively bound the target CV even when other organic compounds were present in the solution. For example, it was observed that despite the presence of bisphenols and dye in the mixture, the sorbents targeted the adsorption of violet, achieving the same or better results for CV than when it was present alone in the tested solution. At the same time, for some multicomponent mixtures, a decrease in bisphenol removal efficiency was also observed, while the CV removal efficiency was increased. The preferential dye binding effect was observed not only in the competitiveness test but also in real water samples and model textile wastewater studies. This showed that targeted adsorption of a selected group of contaminants resulted from the addition of molecular imprinting to the synthesis step. This work demonstrates that the designed sorbents achieve some of the highest q_{max} values for this type of dye. Furthermore, the materials offer a new level of reusability while maintaining unchanged effectiveness, which is crucial for practical applications and cost-effective adsorbent operation.

Novelty and Significance

Publication 1 presents for the first time MICP materials intended for dye removal from wastewater. Previous reports have primarily synthesized information on the adsorption of smaller organic molecules by this type of cyclodextrin-based adsorbents. Furthermore, it is extremely important and significant that over 1 g of dye adsorption per 1 g of sorbent was achieved during the study, indicating a record value for this type of adsorbent-contaminant interaction. Furthermore, the possibility of targeted contaminant removal was demonstrated, even from highly complex matrices like textile wastewater and contaminated water bodies. Considering that standard treatment methods often fail in various plants, the possibility of using the tested materials as filters or sorption cartridges was also suggested, which would selectively act in the final stages of textile wastewater treatment.

9.2 Publication 2 – Removal of nonsteroidal anti-inflammatory drugs and analgesics from wastewater by adsorption on cross-linked β -cyclodextrin (Water Res. Ind., 2022 – original research paper) [149]

Purpose and Scope

Publication 2 was primarily intended to present a study of the adsorption of single- and multi-component mixtures containing common pharmaceutical contaminants by a β -cyclodextrin-based polymer. The primary goal of the research included in the article was to evaluate the binding of individual drugs by the sorbent, particularly nonsteroidal anti-inflammatory drugs (NSAIDs), but also analgesics, which are increasingly detected in municipal wastewater and water bodies in general, thus posing a serious environmental and social problem. The model contaminants studied included diclofenac (DIC), ketoprofen (KETO), ibuprofen (IBU), tramadol (TRAM), salicylic acid (SALI), and naproxen (NAPR), and the structures of some of them are presented in Figure 7. The properties and structures of these model drugs are important here. All, except tramadol, exhibit weakly acidic properties and are hydrophobic aromatic molecules. TRAM, on the other hand, is an amine with basic properties. This allows for a broader picture of the designed sorbent's performance and efficiency. In addition to standard studies such as isotherms and kinetics (single- and multi-component), the adsorbent's behavior under challenging conditions was also examined. The example of the tested conditions was high salinity and low pH, which are often observed in process wastewater in the pharmaceutical industry.

Key Findings

The designed material was shown to be suitable for the simultaneous removal of the tested pharmaceutical compounds, being highly effective and therefore also universal. The tests conducted showed that after contact with the material, the concentrations of all six model pharmaceutical contaminants tested decreased, and after establishing optimal process conditions, it was also found that the RME exceeded 90%, particularly for DIC, IBU, KETO, and NAPR. Stability and ease of regeneration are also advantages of this adsorbent, as in the case of the material from the previous publication. Most remarkably, this cyclodextrin polymer exhibits an increase in sorption capacity after subsequent regeneration cycles. This is explained by the fact that the material underwent a certain structural reorganization upon initial contact with the drugs and memorized the shape of the molecules it removed, making subsequent contact much easier and, consequently, more efficient than before (the so-called shape-memory effect). In the case of kinetic studies, a good fit to the pseudo-second-order model was obtained, indicating relatively rapid achievement of equilibrium. The fit to this model indicates the possible dominance of inclusion interactions or chemisorption. For example, for ketoprofen, described in detail and its behavior in multicomponent mixtures, this publication indicates that several dozen minutes are needed to achieve kinetic equilibrium sorption. Furthermore, the maximum sorption capacity for ketoprofen was also reported, which was 162.6 mg g⁻¹. Considering the complexity of the solution in which adsorption was studied, this value is a very good result and indicates that this sorbent

is insensitive to unfavorable and extreme conditions, such as the previously mentioned low pH, intended to simulate acidic leachates. Its properties also remain unchanged when exposed to high salt concentrations – in saline environments, it can reach approximately 90% of the initial RME. It is worth noting that these conditions were tested because they frequently occur in real drug production processes, where streams can reach truly extreme pH values and varying ionic strengths. Overall, the studies proved that the designed material exhibits versatility with respect to the tested contaminants. Furthermore, during the mechanism analysis, it was determined that supramolecular interactions within the cyclodextrin cavities, i.e., the formation of inclusion complexes, are of primary importance. At the same time, other binding sites cannot be ruled out, for example, in the polymer network formed during synthesis (Figure 19).

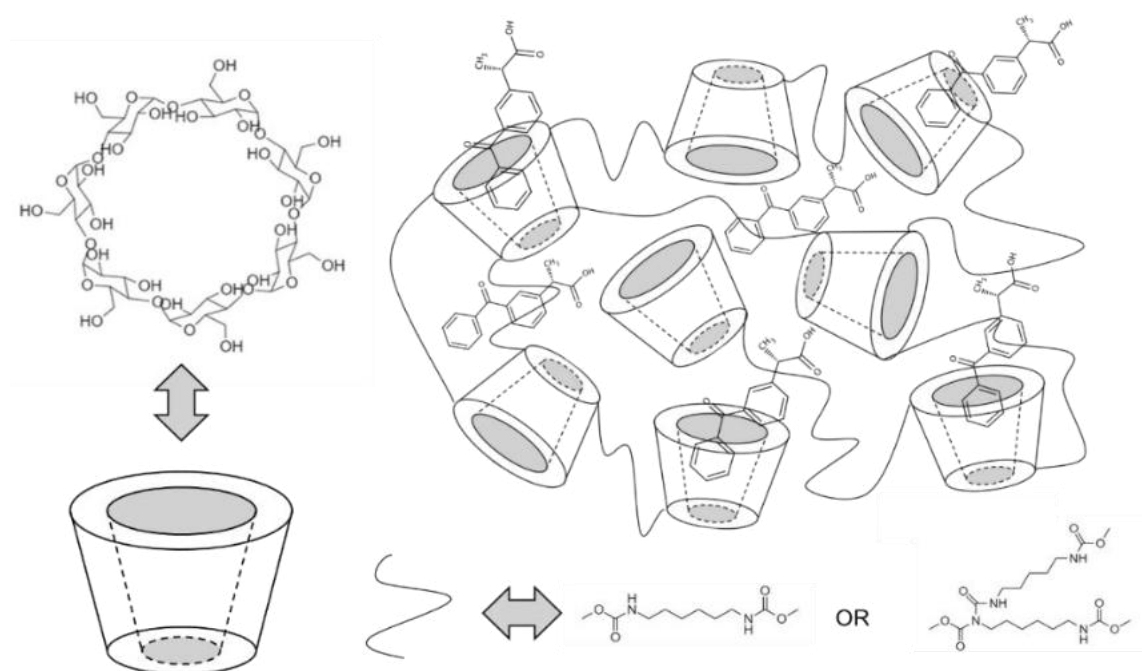


Figure 19. Adsorption mechanism on the example of KETO.

Novelty and Significance

The main novelty of this work is the demonstration of the possibility of simultaneous removal of a multicomponent drug mixture using a single cyclodextrin-based material. This is one of the first studies to focus on a broader approach, rather than focusing on a single substance, as is the case with other publications on similar cyclodextrin-related adsorption topics. Furthermore, the proven effectiveness and durability under harsh wastewater conditions provide a basis for pilot studies using this adsorbent, for example, as a packing material for continuous columns (in accordance with closed-loop requirements). Furthermore, research on this material suggested that it possesses shape memory properties, and after initial structural arrangement with contaminant molecules, its efficiency can be significantly increased. All these features suggest that, from a practical perspective, this adsorbent has real potential for use in on-site wastewater treatment plants. Furthermore, the operating cost of such a sorbent should also

be considered, suggesting a relatively inexpensive solution, taking into account its ease of regeneration and insensitivity to pH or other interfering factors. In summary, this innovative approach demonstrates that cyclodextrin materials with unique properties exist and can provide a highly efficient method for treating wastewater from multiple contaminants simultaneously.

9.3 Publication 3 – Cellulose and its derivatives, coffee grounds, and cross-linked β -cyclodextrin in the race for the highest sorption capacity of cationic dyes in accordance with the principles of sustainable development (J. Hazard. Mater., 2022 – original research paper) [150]

Purpose and Scope

Publication 3 focuses primarily on presenting a study of environmentally friendly adsorbents for the removal of dyes from water. In line with the principles of sustainable development, this research aimed to evaluate the adsorption efficiency of modern cyclodextrin-based polymers with representatives of biosorbents (natural and waste materials) in relation to cationic dyes. The study focused on three main groups of materials and one model pollutant – CV (Table 7, Figure 20). The first group of sorbents consisted of cellulose and its derivatives – microcrystalline cellulose, cellulose obtained from coffee grounds, and cellulose modified to potentially achieve better compatibility with pollutants. The second group consisted of used coffee grounds, which are an example of reusable waste and possess favorable functional groups due to their structure of lignin, cellulose, hemicellulose, etc. The third group consisted of cyclodextrin-based polymers synthesized using two different syntheses. The study aimed to test all seven materials and their adsorption of dyes such as crystal violet (triphenylmethane dyes) and to select the most promising ones (highest $q_{\max}$, speed, stability) from a practical and green chemistry point of view.

Table 7. Materials that are the subject of the study, with abbreviations and explanations.

Abbreviation	Explanation
CC	Cellulose microcrystalline
CD-1	Sorbent obtained in the reaction of cyclodextrin with toluene-2,4-di-isocyanate conducted in a pyridine medium
CD-2	Sorbent obtained in the reaction of cyclodextrin with toluene-2,4-di-isocyanate conducted in a dimethylformamide medium
CG	Coffee grounds
CGC	Cellulose obtained from coffee grounds
CT	Cellulose sorbent obtained in the reaction of microcrystalline cellulose with toluene-2,4-di-isocyanate in a pyridine medium
CTCD	Sorbent obtained in the reaction of microcrystalline cellulose and cyclodextrin with toluene-2,4-di-isocyanate in a pyridine medium

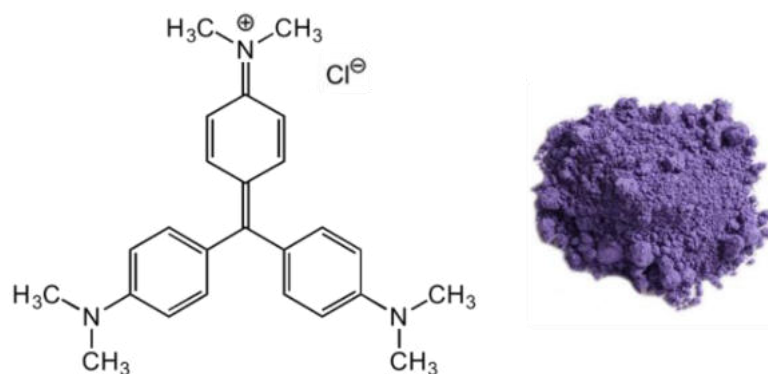


Figure 20. The main model pollutant studied in Publication 3.

Key Findings

Studies have shown that all designed materials have exceptionally high sorption capacities for CV removal. $q_{\max}$ values were proven to be many times higher than those of standard traditional materials such as activated carbon. For example, for the Langmuir and Sips isotherms, depending on the adsorbent, sorption capacity values for the tested materials ranged from 1092.2 to 1235.3 mg g⁻¹. This means that they are capable of sorption of >1 g pollutant per 1 g of their mass. This confirms that both biosorbents, in their native and modified states, are a safe and effective alternative to their synthetic counterparts. The highest adsorption capacity was obtained for the cross-linked β -cyclodextrin polymer (designated CD-2), but for the rest of the materials, such as cellulose or coffee grounds, they did not differ significantly, as evidenced by the $q_{\max}$ range given above. Larger differences are seen in the adsorption kinetics – for the cyclodextrin polymers, equilibrium was established much faster, within 1 minute, while for coffee grounds, adsorption equilibrium was achieved the slowest, within 20 minutes. The rest of the materials (e.g., cellulose-based materials) achieved a rate of several minutes, thus intermediate in relation to the other two groups. It is worth noting that the 20-minute kinetics for coffee grounds, compared to other materials available in the literature, especially waste-based materials, is still an excellent result. In particular, it is worth noting the 90% CV removal rate achieved by this biosorbent after this time, which demonstrates the extremely dynamic nature of the process. As with the material from Publication 2, after regeneration of some adsorbents, it turned out that the CV sorption capacity increased with subsequent adsorption/desorption cycles. This may indicate additional surface activation in the initial regeneration cycles, resulting in higher values. Methanol was used for this process, which can be later purified and recycled back to the process during subsequent cycles, indicating that the designed process can be used in a nearly waste-free procedure. Furthermore, Publication 3 also mentions that each of the biosorbents, such as coffee grounds or cellulose, can be recycled/degraded because it is a cheap material that can be easily and cost-effectively replaced and does not require repeated regeneration. Furthermore, degradation through composting helps avoid the problem of waste management after adsorption. Last but not least, examination of real water samples doped with dye contaminants was also done. It was demonstrated that even in such a complex, real-world matrix, the tested sorbents performed

exceptionally well, achieving almost complete removal of contaminants. Therefore, further advantages of the tested adsorbents include practicality and stability even when exposed to complex solutions.

Novelty and Significance

Of particular note in Publication 3 is the presentation of a cross-section of materials that can be used as examples of sustainable adsorbents. The paper addresses the topic for the first time in such a broad comparative context and provides practical guidance. It was demonstrated that an excellent waste biosorbent, such as coffee grounds, provides such a high sorption capacity (more than 1g of pollutant can be removed using 1g of sorbent). Importantly, such a high capacity has not been reported before. Furthermore, it was shown that natural, relatively inexpensive cellulose, one of the most well-known biopolymers, can also outperform ion exchange resins in its efficiency. Another innovative quality was the comparison of a large cross-section of different materials and the provision of numerous studies characterizing the adsorbents themselves and the adsorption process. Regeneration and potential disposal were also considered. It has been verified not only that we are dealing with cheap, environmentally friendly, and fast-acting materials, but also that they surpass traditional adsorbents in their environmental friendliness while simultaneously presenting no complications. As in previous works (Publications 1 and 2), the potential for use as a filter for dye wastewater can also be demonstrated, which can significantly reduce costs and, of course, be consistent with the principles of green chemistry. Another important aspect is the proposed complex mechanism of the adsorption process for each sorbent, indicating, among other things, the presence of -OH and -COOH groups in cellulose, and tannins and polyphenols in coffee grounds. Moreover, what was controversial and doubtful in previous works – regeneration – is explained here step by step, and the procedure proposed seems to be a perfect solution in the face of subsequent regulations imposed by the European Union.

9.4 Publication 4 – *Structural Adaptive, Self-Separating Material for Removing Ibuprofen from Waters and Sewage* (Materials, 2021 – original research paper) [133]

Purpose and Scope

Publication 4 contains research on the adsorption of ibuprofen, a difficult-to-degrade, toxic NSAID, by a material with adaptive properties. As previously mentioned in the theoretical section, ibuprofen is one of the most frequently detected over-the-counter drugs in surface waters and therefore poses an extremely high risk. Therefore, the goal of Publication 4 was to design a suitable adsorbent that would aid in the removal of this contaminant while also being preferably, at least partially, biodegradable and easily separable from purified water after the process. A β -cyclodextrin-based material was chosen due to previous literature reports on the formation of inclusion complexes between CD cavities and small drug molecules such as ibuprofen, and their natural origin. The synthesis of the developed β -cyclodextrin material was carried out in the presence of pyridine, and hexamethylene diisocyanate (HMDI) was the crosslinking agent chosen

for the polymerization reaction (Figure 21). During the sorbent design, it was assumed that such a material would have a sufficiently "semi-rigid" structure that, if necessary, would allow the pore shape of the host (β -CD-M) to be adjusted to the structure of the model pollutant (guest) upon contact. Following synthesis, the material was characterized based on spectroscopic and microscopic studies. Thermal analysis was also performed, followed by an examination of the adsorption process itself. Various factors influencing the process were optimized, including solution pH, the presence of other conditions that could interfere with sorption, sorbent amount, contact time, and others. A practical aspect was also assessed: the adsorbent's separability, enabling easy separation after drug removal, for example, through sedimentation or filtration. Last but not least, regeneration was also assessed to minimize waste production and the possibility of preserving the activity (reuse) of the polymer.

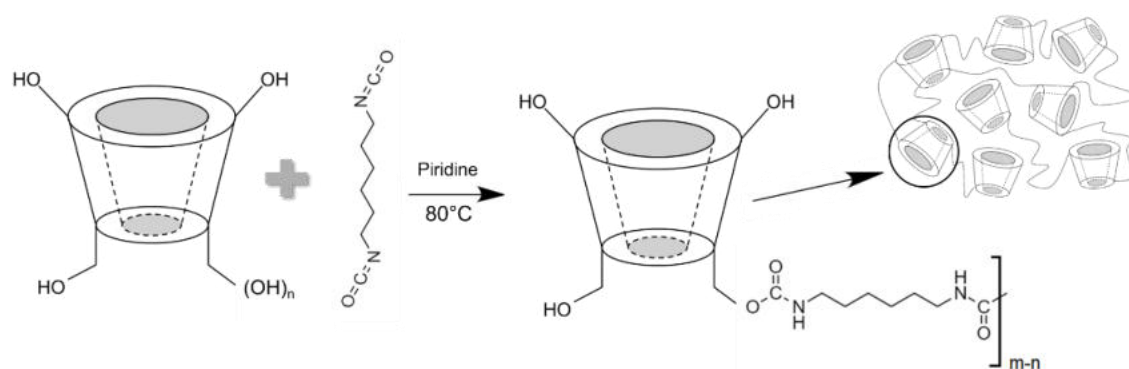


Figure 21. The schematic representation of β -CD-M synthesis.

Key Findings

After testing, it was determined that, thanks to the well-thought-out cross-linking, the material met the above-described assumptions but also demonstrated other unique properties. Using the Sips isothermal model, the maximum adsorption capacity ($q_{\max}$) for ibuprofen was calculated

to be 86.2 mg g^{-1} . Despite the significant leap from dye removal materials, the material discussed in Publication 4 should not be considered of inferior quality. It should be noted that characteristics such as ibuprofen's low molecular weight and hydrophilicity influence $q_{\max}$ values. Furthermore, comparing literature data, this value is significantly high for ibuprofen and other smaller molecules (e.g., over-the-counter medications). The kinetics of the process are best described by a pseudo-second-order model, a typical model for this type of contaminant. In terms of process rate, full kinetic equilibrium is achieved in approximately 1 hour, with 50% removal achieved within just a few minutes. From a practical perspective, this sorbent performs remarkably well at very low concentrations (e.g., around 1 mg L^{-1}), which is crucial for the ecology and protection of water bodies. An interesting phenomenon was also observed in the study with the addition of ions (Na^+ and Ca^{2+}), which are almost always available under real-world environmental conditions. Hydrophobic contaminant-adsorbent interactions were intensified in the presence of these salts, and in some cases, the RME of the contaminant was also slightly increased. Besides the adsorbent's excellent ability to handle these accompanying salt compounds, the presence

of humic acids (10 mg L^{-1}) also demonstrated synergy, achieving 66% better results in their presence than without their addition. Electrostatic changes likely occur in the reaction mixture, or due to competition for the active site, the IBU structure is favored by the sorbent. These preliminary studies confirmed that this material is suitable for use in real-world wastewater conditions, which was further investigated and confirmed. Wastewater samples containing $2\text{-}3 \text{ }\mu\text{g L}^{-1}$ IBU were purified by the polymer by 84-100%, depending on the initial concentration. It was also observed that the adsorbent does not swell upon contact with water and is easily separated from the solution (purified water) after the adsorption process because it does not form a colloid or gel, which would be difficult to separate. Like the materials described above, the one subject of Publication 4 also demonstrates high stability (it does not degrade during the adsorption or regeneration processes, nor does it leach components) and high regeneration potential after treatment with methanol. Furthermore, it is worth mentioning that the key finding is the structural self-adaptation of this cyclodextrin-based material. By undergoing reorganization, its structure changes form after the first contact with the contaminant and does not return to its initial state after desorption. This results in a better fit and a higher q_{max} after subsequent uses of the adsorbent. This characteristic of the adsorbent also confirms hypothesis H2 described in section 7.2 Research Hypotheses.

Novelty and Significance

Publication 4 examined a material that was the first in the literature to be created using HMDI in these proportions and with pyridine during synthesis. Furthermore, a significant contribution from this publication stems from demonstrating the existence of a self-adapting adsorbent upon contact with contaminant particles, which is characterized by a shape memory effect. This feature helps maintain the adsorbent's full functionality not during a single adsorption, but over many repeated cycles, rather than undergoing degradation as with other sorbents. In addition to this important feature, there are other characteristics that can describe this material. The first is self-separability, which is possible through deep cross-linking (high degree of polymerization). The second feature may be biodegradability, at least partially due to the significant presence of cyclodextrin as a monomer in the material, which is natural and capable of full biodegradation. Generally, cyclodextrin-based materials, according to the literature, are capable of being degraded by microorganisms (e.g., fungi), meaning that the presented material will not pose an environmental burden to the same extent as non-degradable plastics [239]. Its ability to withstand harsh conditions, such as salinity or the presence of substances competing for active sites, supports the conclusion that pharmaceutical wastewater treatment could be a potential application, where, for example, other sorbents fail.

9.5 Publication 5 – *Recent Advancements in Cyclodextrin-Based Adsorbents for the Removal of Hazardous Pollutants from Waters* (Polymers, 2022 – review paper) [204]

Nature of work and scope

Publication 5 is a review that synthesizes the latest information gathered from the literature on the most important developments (as of 2022) in the field of cyclodextrin adsorbents used to remove emerging pollutants such as drugs, EDCs, heavy metals, and dyes (Figure 22). The work contains comprehensive information not only on cyclodextrin materials in their native form but also with certain modifications, up to the most complex ones, such as composites, CDs immobilized on solid surfaces, or cyclodextrin nanosponges. Furthermore, it is worth noting the multitude of topics covered in this work and the detailed state of research – it includes reviews of syntheses and modifications, as well as descriptions of the mechanisms of adsorption processes, along with their yields (including the selectivity of some of the presented adsorbents). Recent trends in this field have also been addressed, such as the use of nanomaterials to create multifunctional sorbents (e.g., graphene or iron nanoparticles). As mentioned in previous works, attention was paid to the regeneration and reuse of sorbents.

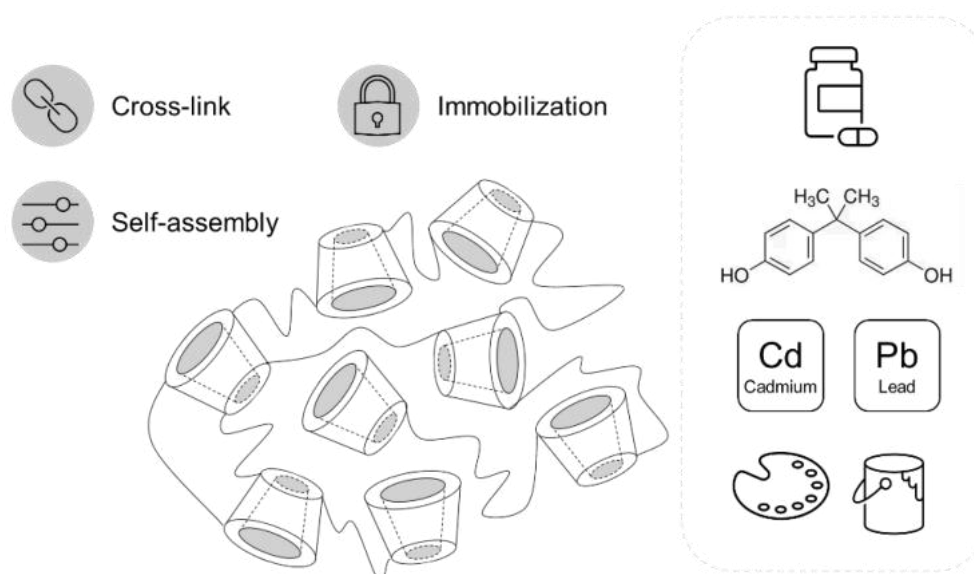


Figure 22. Graphical representation of the scope of Publication 5.

Key Content of the Review

Publication 5 begins with an introduction to the growing problem of water pollution and a presentation of the importance of adsorption compared to other described techniques. As discussed in the theoretical introduction to this dissertation, adsorption demonstrates a prototypical and economical approach. The subsequent chapters of the review present basic information on cyclodextrins, such as their structure, the ability of the CD torus to react and make complexes with contaminants, and the solubility of native cyclodextrins compared to cross-linked ones. Native cyclodextrins cannot be used for adsorption due to their water solubility. The use

of cross-linking reactions demonstrates the potential for cyclodextrins to serve as sorbents for wastewater treatment by forming solid forms. However, the most crucial part of the review is the presentation of specific solutions to the current environmental problem. For example, for heavy metals, examples of cyclodextrin modification with chelating groups (thiol- and amino-) were found, which are known for their ability to bind metal ions, such as heavy metals, which are the main focus of this work. Magnetic nanoparticles are also frequently mentioned here, demonstrating their significant assistance in post-process sorbent separation. The second group of contaminants, dyes, has been linked to the solid removal efficiency of β -CD polymers, as publications have been found in which, despite their low specific surface area, results comparable to those of activated carbons were achieved – this is all due to the exceptional matching of the pore sizes of these unusual polymers to the contaminant molecules. However, these are not the only CD-based adsorbents that interact effectively with harmful dyes – cyclodextrins embedded on solid supports such as silica were also mentioned, making their handling significantly easier. The last two groups of contaminants, pharmaceuticals and EDCs (such as PFAS and pesticides), are also discussed with numerous examples. Polyurethane adsorbents for the removal of perfluorocarbons and CD nanosponges for the removal of organophosphate pesticides seem promising. A solution was also presented, using cyclodextrin ion exchange resins, which are excellent for both phenols and common pharmaceuticals found in water. Of course, it is important to note that all of these materials have been tested for regeneration – they vary, but the general trend is that many of them are reusable, which puts these materials in a favorable position. Summarizing the collected data, it can be noted that although many CD-based solutions already exist, there is still growing scientific interest in this type of adsorbent, primarily because they combine unique features stemming from supramolecular chemistry (the ability to engineer interactions) with simplicity and effectiveness against many model contaminants. An integral part of this work is also an indication of the challenges facing scientists and potential future directions that could be developed. The following were mentioned: checking the scalability of the syntheses and sorption process of these materials, stability tests (long-term use tests), continuous improvement in order to achieve full biodegradability and assessment of their life cycle but also increasing their specific surface area.

Importance of the Review

Review publication 5 summarizes the current state of knowledge and confirms that following the latest literature trends is crucial in the process of developing adsorbents. However, this discussion primarily served to place our results (Publications 1-4) in a broader perspective, demonstrating that the developed materials are at the forefront compared to other available materials, notably due to their sorption capacities, which often exceed 1000 mg g⁻¹. Publication 5 also highlights the unique conclusions drawn from the studies on the designed sorbents (self-adaptability, structure memory, and biodegradability). The studies described in the previous publications fit perfectly into the issues described in a literature review, also drawing attention to their pioneering approach. Moreover, thanks to the critical approach to the article analysis,

it was possible to notice that one of the most important aspects, both theoretically and practically, is the reusability and regeneration itself, as well as the associated procedure. This confirms that the assumptions made during the goal-setting stage were correct. The novelty of this publication also suggests what still needs to be investigated to obtain a complete picture of the materials described, making it a guide for future research. However, the main idea of the review is consistent: CD-based sorbents are a constantly and rapidly developing group of adsorption materials, used globally to improve water and wastewater treatment methods.

10. CONCLUSIONS, SCIENTIFIC NOVELTY, AND PRACTICAL SIGNIFICANCE [133,149,150,201]

Pollution of water bodies with hazardous substances is a serious problem, not only because of the devastation it wreaks on aquatic life, but also because of the consequences this poses to humans. This work aimed to develop innovative sorbents targeted at the adsorption of endocrine-active compounds. These substances are extremely hazardous even at ultralow concentrations, and still, they are not sufficiently removed from streams flowing into water bodies, such as rivers. The technique chosen to address this problem, adsorption, is characterized by its versatility, potential ease of implementation, relatively low cost, and the possibility of regeneration, which further enhances its importance compared to other techniques.

This work combines a theoretical part with the design of new materials – adsorbents, thus providing a critical perspective on the subject of adsorption. Moreover, this dissertation is based on a series of publications (four original research papers and one review paper). The results obtained from this work demonstrated high efficiency and unique properties for newly designed and comprehensively tested materials, primarily based on β -cyclodextrin, but also on waste and natural raw materials. Based on the results discussed in the above study and in publications 1 to 5, the following conclusions were made:

1. An increase in sorption capacity and process efficiency was observed using rational molecular design of sorbents. This method contributed to the creation of selective binding sites and a shape tailored to the target molecule. This resulted in a nearly two-fold improvement in preferential contaminant removal compared to materials synthesized without imprinting. This occurred not only when removing a single dye but also when other co-occurring substances were present in solution. This situation was observed in the case of the CV dye, where the imprinted cyclodextrin polymer achieved a maximum sorption capacity of 1000 mg g^{-1} , significantly higher than traditional adsorbents and other cyclodextrin sorbents available in literature. As indicated above, this material is also capable of reducing the adsorption of co-occurring substances other than the dye while simultaneously increasing its ability to remove CV. This study confirms that MIP sorbents, if well-designed, can selectively capture particles.
2. Cross-linked β -cyclodextrin nanosponges proved to be a universal method for removing many types of contaminants and are also extremely resistant to any of the factors tested. A study of the adsorption of six different analgesics and NSAIDs demonstrated an exceptionally high RME (mostly $>90\%$) for each of them, even when only one material was used. Another important aspect is the variable and harsh environment, such as high salinity and acidity. This makes it an exceptionally good candidate for use in the treatment of wastewater from the pharmaceutical industry. Consequently, hypothesis H1 was confirmed – using a single, well-designed adsorbent, it is possible to remove multiple contaminants with different structures and properties.
3. A groundbreaking discovery is that the resulting materials possess a property known as shape/structure memory. This stems from the fact that, after initial contact with a model

contaminant, the material's structure rearranges and adapts to it. This improves the process in subsequent cycles and increases the RME. This phenomenon, rarely mentioned by researchers, indicates the adaptive properties of the material and indicates that, unlike other materials, instead of losing its properties during the process, this one further improves them and becomes more contoured by learning how to bind individual molecules. Importantly, this also confirms the established hypothesis H2 – that the material can self-adapt depending on the contaminant being removed, fastening and developing the process path.

4. Furthermore, it has been proven that, in addition to typical cyclodextrin-based materials, other 100% natural materials, such as cellulose, or waste materials such as coffee grounds, can provide a comparable base for the removal of organic compounds. In some studies, even better results were observed than with conventional sorbents. Importantly, their use does not impose any additional environmental burden. It is crucial that even minor modifications can achieve high values, such as approximately 1.1-1.2 g g⁻¹ of sorption capacity – this was the case with cheap and renewable cellulose after chemical modification (CV removal). Waste materials whose disposal can be problematic can also be a useful source of sorption material, offering high RME. Similar values to those for modified cellulose were obtained for used coffee grounds (> 1 g g⁻¹). Natural materials as adsorbents therefore perform well even with larger molecules such as dyes – this confirms hypothesis H3. Furthermore, regeneration, reuse, and potential degradation are further advantages of choosing low-cost natural materials. Overall, the results provided by Publication 3 suggest that it is possible to use sustainable technologies without any ecological compromises. From a practical perspective, these biosorbents, which are part of a global trend, are an ideal alternative to expensive activated carbon and synthetic resins, while also avoiding toxic process waste and disposal issues, which can pose another serious environmental problem.
5. Another conclusion drawn from the research concerns the effectiveness of the sorbents under real-world conditions. All materials were tested for this purpose and found to achieve high efficiency in both industrial and municipal wastewater, as well as using water from well-known bodies of water (the Vistula River and the Baltic Sea). Numerous coexisting factors, such as other chemical compounds, variable pH, and salinity, do not appear to significantly impede adsorption, and in some cases, even the presence of salts can aid the process. This conclusion is exemplified by DI- and TR-CDP, which achieved almost 100% dye removal from prototype textile wastewater. Another prominent example is β -CD-M, which achieved 100% ibuprofen removal from municipal wastewater, which is crucial for the scalability of the process. In accordance with the assumptions of hypothesis 4, it is observed in the research that real conditions do not threaten the effectiveness of the developed materials. Even in changing conditions, they work flawlessly, which confirms the validity of the hypothesis.

6. A key advantage of the designed adsorbents is their simple, waste-free regeneration and, importantly, their potential for repeated use. No loss of activity was demonstrated even after a minimum of five adsorption-desorption cycles using methanol or ethanol for regeneration, which also confirms their chemical and mechanical durability. Developing a regeneration procedure that minimizes the release of post-regeneration waste into the environment is one of the greatest achievements, as it eliminates one of the greatest drawbacks of conventional adsorbents. Furthermore, the example of ibuprofen also highlights the economic viability criterion – the methanol used in the process can be recovered via distillation, reducing the operating costs associated with purchasing a new solvent. Furthermore, the material's longevity also reduces the cost of purchasing a new adsorbent.
7. In addition to the above, it is also worth noting that the literature review of the latest reports and global trends in cyclodextrin adsorption materials has made a significant contribution to the field of adsorbents. This was particularly important for providing a broader perspective and a basis for comparison with the designed materials that are the subject of this work. This helped to assess that the materials synthesized and studied are consistent with these literature trends and often exceed the current state of knowledge in certain respects. Furthermore, it is not without reason that an increase in research on CD-based materials is currently observed – these kinds of sorbents are selective if this is the intended characteristic, non-toxic, and also capable of a wide variety of modifications. This doctoral thesis brings with it many new findings regarding practical applications and sorption capacity but also resolves many inconsistencies regarding the mechanisms of adsorption. As mentioned above, the boundaries of knowledge have been expanded here, including in terms of shape memory, record-high absorption capacities, and the use of waste materials for dye removal. As a result of this research, traditional water purification techniques are gaining a promising new alternative in the form of cyclodextrin adsorbents and biosorbents.

Taking all of the above into account, this doctoral dissertation fully demonstrated the achieved goals and confirmed the proposed hypotheses. Innovative sorbents were developed, characterized, and evaluated. Their high efficiency, selectivity, and regeneration potential confirmed their suitability for removing model EDCs, specifically selected for this thesis. The obtained results and proposed solutions are fully consistent with improving and developing sustainable water treatment technologies.

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I, the undersigned, Dominika Nowacka, hereby declare that I contributed to the preparation of the following publications:

1. Efficient Water Pollutants Targeting: Novel Materials with Molecular Imprints for Textile Industry Use, *Industrial & Engineering Chemistry Research* (2025), DOI: 10.1021/acs.iecr.5c00705.

My contribution included: conceptualization, methodology, investigation, formal analysis, validation, visualization, writing original draft, writing, review, and editing.

2. Removal of nonsteroidal anti-inflammatory drugs and analgesics from wastewater by adsorption on cross-linked β -cyclodextrin, *Water Resources and Industry* 28 (2022) 100186, DOI: 10.1016/j.wri.2022.100186.

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3. Cellulose and its derivatives, coffee grounds, and cross-linked β -cyclodextrin in the race for the highest sorption capacity of cationic dyes in accordance with the principles of sustainable development, *Journal of Hazardous Materials* 439 (2022) 129588, DOI: 10.1016/j.jhazmat.2022.129588.

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4. Structural Adaptive, Self-Separating Material for Removing Ibuprofen from Waters and Sewage, *Materials* 2021, 14, 7697, DOI: 10.3390/ma14247697.

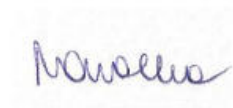
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1. Efficient Water Pollutants Targeting: Novel Materials with Molecular Imprints for Textile Industry Use, *Industrial & Engineering Chemistry Research* (2025), DOI: 10.1021/acs.iecr.5c00705.
My contribution included: conceptualization, design of sorbent materials, materials synthesis, methodology, investigation, formal analysis, validation, writing original draft, visualization, review, and editing.
2. Removal of nonsteroidal anti-inflammatory drugs and analgesics from wastewater by adsorption on cross-linked β -cyclodextrin, *Water Resources and Industry* 28 (2022) 100186, DOI: 10.1016/j.wri.2022.100186.
My contribution included: conceptualization, design and synthesis of sorbent materials, methodology, investigation, formal analysis, validation, writing original draft, visualization, review & editing.
3. Cellulose and its derivatives, coffee grounds, and cross-linked β -cyclodextrin in the race for the highest sorption capacity of cationic dyes in accordance with the principles of sustainable development, *Journal of Hazardous Materials* 439 (2022) 129588, DOI: 10.1016/j.jhazmat.2022.129588.
My contribution included: conceptualization, design of sorbent systems, methodology, investigation, formal analysis, validation, writing original draft, visualization, review & editing.
4. Structural Adaptive, Self-Separating Material for Removing Ibuprofen from Waters and Sewage, *Materials* 2021, 14, 7697, DOI: 10.3390/ma14247697.
My contribution included: conceptualization, design and synthesis of materials, methodology, software, validation, formal analysis, investigation, resources,

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5. Recent Advancements in Cyclodextrin-Based Adsorbents for the Removal of Hazardous Pollutants from Waters, *Polymers* 2022, 14, 2341, DOI: 10.3390/polym14122341.

My contribution included: writing, reviewing, and editing, supervision, project administration, and funding acquisition.

6. Cyclodextrin functionalized polyvinylidene fluoride membranes: Strategies and diverse applications, *Tetrahedron* 170 (2025) 134385, DOI: 10.1016/j.tet.2024.134385.

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1. **Efficient Water Pollutants Targeting: Novel Materials with Molecular Imprints for Textile Industry Use**, *Industrial & Engineering Chemistry Research* (2025), DOI: [10.1021/acs.iecr.5c00705](https://doi.org/10.1021/acs.iecr.5c00705).

My contribution included **funding acquisition**.

2. **Cellulose and its derivatives, coffee grounds, and cross-linked β -cyclodextrin in the race for the highest sorption capacity of cationic dyes in accordance with the principles of sustainable development**, *Journal of Hazardous Materials* 439 (2022) 129588, DOI: 10.1016/j.jhazmat.2022.129588.

My contribution included **funding acquisition, review & editing**.

I confirm that **MSc Eng. Dominika Nowacka's** contribution to the above publications was significant and independent.



Poznań, 26.09.2025

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1. **Efficient Water Pollutants Targeting: Novel Materials with Molecular Imprints for Textile Industry Use**, *Industrial & Engineering Chemistry Research* (2025), DOI: [10.1021/acs.iecr.5c00705](https://doi.org/10.1021/acs.iecr.5c00705).

My contribution included **funding acquisition**.

I confirm that **MSc Eng. Dominika Nowacka's** contribution to the above publication was significant and independent.


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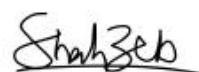
1. **Cellulose and its derivatives, coffee grounds, and cross-linked β -cyclodextrin in the race for the highest sorption capacity of cationic dyes in accordance with the principles of sustainable development**, *Journal of Hazardous Materials* 439 (2022) 129588, DOI: 10.1016/j.jhazmat.2022.129588.

My contribution included: **investigation, review & editing.**

2. **Recent Advancements in Cyclodextrin-Based Adsorbents for the Removal of Hazardous Pollutants from Waters**, *Polymers* 2022, 14, 2341, DOI: 10.3390/polym14122341.

My contribution included **conceptualization and writing the original draft.**

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1. **Cellulose and its derivatives, coffee grounds, and cross-linked β -cyclodextrin in the race for the highest sorption capacity of cationic dyes in accordance with the principles of sustainable development**, *Journal of Hazardous Materials* 439 (2022) 129588, DOI: 10.1016/j.jhazmat.2022.129588.

My contribution included: **investigation, review & editing.**

2. **Recent Advancements in Cyclodextrin-Based Adsorbents for the Removal of Hazardous Pollutants from Waters**, *Polymers* 2022, 14, 2341, DOI: 10.3390/polym14122341.

My contribution included **conceptualization and writing the original draft.**

I confirm that **MSc Eng. Dominika Nowacka's** contribution to the above publications was significant and independent.

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1. **Removal of nonsteroidal anti-inflammatory drugs and analgesics from wastewater by adsorption on cross-linked β -cyclodextrin, *Water Resources and Industry* 28 (2022) 100186, DOI: 10.1016/j.wri.2022.100186.**

My contribution included **formal analysis and validation (HPLC)**.

2. **Structural Adaptive, Self-Separating Material for Removing Ibuprofen from Waters and Sewage, *Materials* 2021, 14, 7697, DOI: 10.3390/ma14247697.**

My contribution included **HPLC analysis and associated aspects, including methodology, validation, formal analysis, investigation, resource provision, and review & editing.**

I confirm that **MSc Eng. Dominika Nowacka's** contribution to the above publications was significant and independent.

Signature



ARTICLES

- [1] Efficient Water Pollutants Targeting: Novel Materials with Molecular Imprints for Textile Industry Use – *Industrial & Engineering Chemistry Research*, 2025, original article; DOI: <https://doi.org/10.1021/acs.iecr.5c00705>; IF: 3.9 (2025), quartile: Q1; MEiN points: 140.
- [2] Removal of nonsteroidal anti-inflammatory drugs and analgesics from wastewater by adsorption on cross-linked β -cyclodextrin – *Water Resources and Industry*, 2022, original article; DOI: 10.1016/j.wri.2022.100186; IF: 5.1 (2022), quartile: Q1; MEiN points: 200.
- [3] Cellulose and its derivatives, coffee grounds, and cross-linked β -cyclodextrin in the race for the highest sorption capacity of cationic dyes in accordance with the principles of sustainable development – *Journal of Hazardous Materials*, 2022, original article; DOI: 10.1016/j.jhazmat.2022.129588; IF: 13.6 (2022), quartile: Q1; MEiN points: 200.
- [4] Structural Adaptive, Self-Separating Material for Removing Ibuprofen from Waters and Sewage – *Materials*, 2021, original article; DOI: 10.3390/ma14247697; IF: 3.748 (2021), quartile: Q2; MEiN points: 140.
- [5] Recent Advancements in Cyclodextrin-Based Adsorbents for the Removal of Hazardous Pollutants from Waters – *Polymers*, 2022, review article; DOI: 10.3390/polym14122341; IF: 5.0 (2022), quartile: Q1; MEiN points: 100.

Publication 1

Efficient Water Pollutants Targeting: Novel Materials with Molecular Imprints for Textile Industry Use – *Industrial & Engineering Chemistry Research*, 2025

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Efficient Water Pollutants Targeting: Novel Materials with Molecular Imprints for Textile Industry Use

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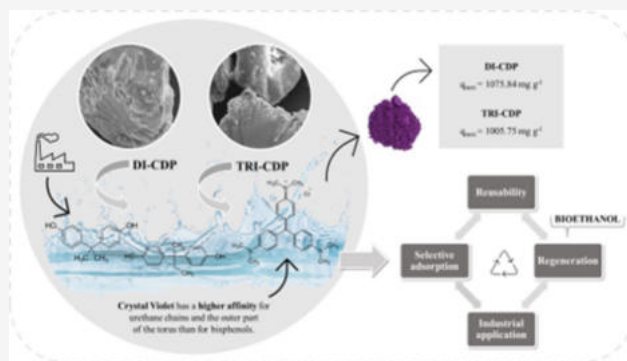
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ABSTRACT: In this study, the effect of diphenylmethane and triphenylmethane templates on the adsorption capacity of materials obtained by reacting β -cyclodextrin with hexamethylene diisocyanate was investigated. The obtained materials were evaluated as adsorbents for the removal of bisphenol A (BPA), bisphenol B (BPB), and crystal violet (CV) from aqueous solutions and wastewater. All materials showed selective interaction with CV, which was adsorbed within 1 min. The adsorption kinetics followed a pseudo-second-order model. According to the Hill isotherm model, the maximum adsorption capacities for CV were 594.89 mg g⁻¹ (CDP), 1075.84 mg g⁻¹ (DI-CDP), and 1005.75 mg g⁻¹ (TRI-CDP). The significantly increased adsorption capacity of molecularly imprinted polymers (MIP) confirmed their superiority over nonimprinted polymers (NIP). The adsorption capacity remained stable after five cycles of virtually waste-free regeneration. Selective adsorption of CV over BPA and BPB was observed in both model and real wastewater samples, including those from the textile industry.



1. INTRODUCTION

The textile industry's exponential growth leads to 92 million tons of annual waste, causing severe environmental repercussions.¹ Harmful compounds from textiles persist in oceans, soils, and even polar ice, endangering ecosystems and health.² Notable culprits include dyes like crystal violet and substances like bisphenols (BPA and BPB), known for health risks ranging from endocrine disruption to neurological issues.³ The challenge also involves durable textile removal and subsequent environmental release of not completely purified effluents.⁴ To tackle this, wastewater treatment plants often employ various methods like filtration, biological processes, and chemical treatments to remove pollutants.⁴ However, some persistent and harmful compounds can remain in the effluent, posing risks to the environment and human health. Adsorption, especially using advanced molecularly imprinted materials, may act as a supplementary step to effectively target and capture these persistent contaminants.⁵ Integrating adsorption into on-site treatment plants as a final treatment stage makes it possible to selectively capture and remove specific pollutants that conventional treatments might miss. Imprinted materials, tailored to recognize and adsorb particular contaminants, offer a promising solution due to their high selectivity and efficiency in removing trace amounts of pollutants from water and their relatively low cost.⁶ This step can significantly enhance the wastewater treatment overall efficiency, reducing the release of harmful compounds into surrounding ecosystems. It is a proactive approach toward environmental

protection, ensuring that the effluents discharged are of a higher quality and pose fewer risks.⁷ Additionally, intercepting these residual harmful compounds before discharge can also potentially prevent the contamination of larger water bodies like rivers, lakes, and seas, thereby safeguarding aquatic ecosystems and minimizing the spread of pollutants in the environment.⁸

This study presents the design and synthesis of three β -cyclodextrin-based materials: one nonimprinted polymer (CDP) and two molecularly imprinted polymers, DI-CDP and TRI-CDP, engineered for the selective adsorption of the hazardous cationic dye crystal violet (CV). In contrast to conventional cyclodextrin-based adsorbents, such as non-imprinted CDP, the imprinted materials incorporate structural memory by using diphenylmethane (DPM) and triphenylmethane (TPM) as template molecules during the imprinting process (Figure 1).⁹ By combining molecular imprinting with the host–guest inclusion capability of β -cyclodextrin within a recyclable and environmentally friendly polymer matrix, this study addresses a key challenge in the development of

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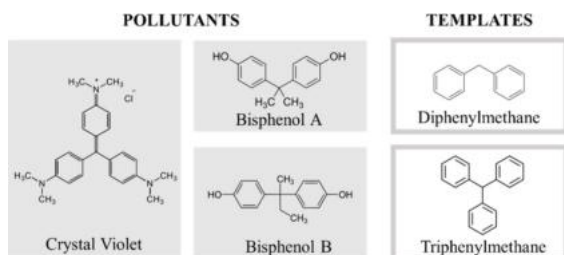


Figure 1. Comparison of the structures of templates and model pollutants.

biobased adsorbents.¹⁰ The resulting materials exhibit high selectivity toward CV, even in the presence of competing pollutants, such as bisphenol A (BPA) and bisphenol B (BPB),

and offer regeneration capability over multiple adsorption–desorption cycles.

2. EXPERIMENTAL SECTION

2.1. Materials. Hexamethylene diisocyanate (1,6-HMDI $\geq 99\%$), β -cyclodextrin (β -CD $\geq 97\%$), bisphenol A (BPA $\geq 99\%$) and bisphenol B (BPB $\geq 98.0\%$), diphenylmethane (DPM = 99%), triphenylmethane (TPM = 99%), crystal violet (CV $\geq 96\%$), eriochrome black T (EB; ACS reagent grade; C.I. 14645), brilliant green (BG $\geq 98.0\%$), methylene blue (MB $\geq 97\%$), bromocresol purple sodium salt (BP $\geq 90\%$), Congo red (CR $\geq 85\%$; C.I. 22120), toluidine blue (TB $\geq 80\%$; C.I.52040), malachite green (MG $\geq 90\%$; C.I. 63163); 2-chlorophenol (2-CP $\geq 99\%$), 4-aminophenol (4-AP; USP), 4-hydroxybiphenyl (4-HBP $\geq 99\%$), 3-aminophenol (3-AP $\geq 98\%$), 4-bromophenol (4-BP $\geq 99\%$), 4,4'-dihydroxybiphenyl

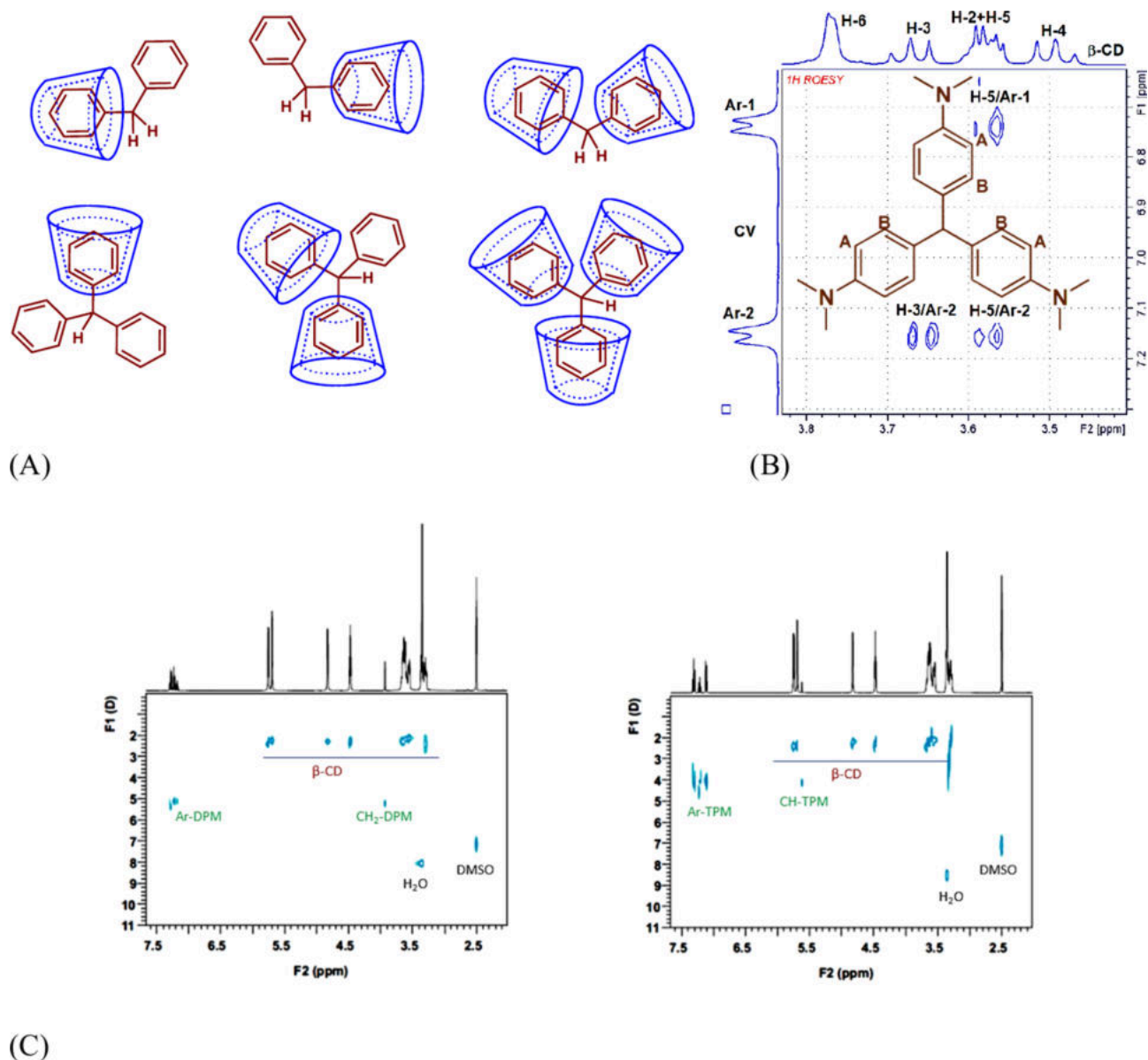


Figure 2. (A) Hypothetical effect of matrices on the arrangement of cyclodextrin molecules before the cross-linking step; (B) 400 MHz ROESY spectrum of the CV β -CD inclusion complex with the selected regions expanded to evaluate the interactions between CV and β -CD in D_2O ; (C) 500 MHz DOSY spectra of a mixture of β -CD and DPM and a mixture of β -CD and TPM in d -DMSO.

(4,4'-biphenol; 4,4'-BP $\geq 97\%$), 2,4-dichlorophenol (2,4-DCP $\geq 99\%$), 4-Chloro-2-nitrophenol (4-C-2-NP $\geq 97.0\%$), and 2,6-bis(hydroxymethyl)-4-methylphenol (2,6-BHMP $\geq 95\%$) were purchased from Sigma-Aldrich (Poland). Acetone (CH_3COCH_3 , 100%), dimethylformamide (DMF; ACS reagent), methanol (CH_3OH $\geq 99.8\%$), sodium and calcium chlorides (ACS reagents, $\geq 99.0\%$), as well commercial humic acids contain 50% of humic acids and 50% fulvic acids (HA, 90% dry matter) were purchased from POCH (Poland). Potassium bromide (KBr spectroscopy grade) was delivered by Fisher Scientific and dried before use. All chemicals were used without further purification. Hach cuvette tests (Poland) were used to determine BOD₅, COD, total nitrogen, and phosphorus. All chemicals were used without further purification. Water purified by a Hydrolab system was used to prepare the stock solutions (HLP-SPRING, Poland, temperature 22 °C, $\kappa \geq 2.70 \mu\text{S}$).

2.2. Synthesis. Cyclodextrin materials imprinted with diphenylmethane (DI-CDP) or triphenylmethane (TRI-CDP), as well as without imprinting (CDP), were synthesized following the procedure previously reported, with significant modifications.^{11–16}

2.2.1. Synthesis of CDP, DI-CDP, and TRI-CDP. DMF (100 mL) was added to a flask containing 1 g of the matrix compound: diphenylmethane (5.95 mmol) for DI-CDP or triphenylmethane (4.09 mmol) for TRI-CDP. The stage of adding the matrix was omitted in the case of CDP. The contents of the flask were stirred at 80 °C until dissolved. Then, 10 g of β -CD (8.81 mmol) was added in one portion. After 20 min with vigorous stirring, the slow dropwise addition of a solution of 1,6-HMDI (8.48 mL in 10 mL of DMF; 52.93 mmol) was started. The reaction was continued for an additional 6 h. The molar ratios of β -cyclodextrin:matrix:1,6-HMDI in the respective syntheses were equal to 1.00:0.00:6.01 for CDP, 1.00:0.68:6.01 for DI-CDP, and 1.00:0.46:6.01 for TRI-CDP. After cooling to room temperature, 200 mL of acetone was poured into the reaction mixture. Although the reaction forms a highly viscous, solid-like mass, acetone was added to reduce the solubility of the polymer in the DMF medium and promote complete precipitation. The precipitate was filtered off and then transferred to a flask containing 200 mL of chloroform and stirred for 0.5 h to remove residual matrix and solvents. After separation, the precipitate was dried at room temperature. It was then quantitatively transferred to a beaker containing 500 mL of distilled water and stirred for 0.5 h to remove unreacted cyclodextrin and possible residual DMF. The precipitate was filtered off, rinsed with ethanol, placed in a Soxhlet thimble, and extracted with ethanol for 8 h. After initial drying at room temperature, the product was placed in a moisture analyzer and dried at 120 °C until a constant weight was obtained. The product was then ball-milled, sieved, and stored in a desiccator. The final yield of the reaction mixture was 16.24 g (85.2%) CDP, 16.25 g (81.0%) DI-CDP, and 17.34 g (86.4%) TRI-CDP.

2.3. Methods. The materials and adsorption process characterization methods are listed in the [Supporting Information](#) in section S1 called "Materials characterization and adsorption characterization methods".

3. RESULTS AND DISCUSSION

3.1. Morphology, Structure, and Properties. In this work, three green organic adsorbents were synthesized following a sustainable approach based on biodegradable,

nontoxic β -cyclodextrin, with demonstrated reusability over five regeneration cycles and minimal secondary waste production, to purify wastewater or water polluted with hazardous compounds selectively. The DI-CDP and TRI-CDP materials were prepared by cross-linking β -CD with hexamethylene diisocyanate and were synthesized with a diphenylmethane and triphenylmethane template, respectively, to remove targeted impurities specifically ([Figure 1](#)). At the same time, CDP (without a template) was synthesized to compare the results and prove the usefulness and effectiveness of DI- and TRI-CDP.

Very large groups of persistent environmental micro-pollutants are aromatic compounds. One way to remove them from water is by adsorption. Adsorbents can be tailor-made using elements ideally sized for the phenyl substituents, while ensuring their proper arrangement by using the appropriate molecular fingerprint. The β -CD molecules meet the first assumption, and the DPM and TPM matrices potentially take care of the preorganization before the cross-linking step. A large excess of β -CD compared to the template hypothetically allows the formation of inclusion complexes with different stoichiometry ([Figure 2A–C](#)). The determined arrangement of the tori shapes the size of the pores and their subsequent accessibility to pollutants at the adsorption stage. Comparing the geometry of the matrix molecules, a universal character is expected in the case of TPM. The crystalline form matrices used vary considerably, probably also when dissolved in dimethylformamide. The structure of DPM is of the helical type, with ring torsion angles of 63.9° and 71° and a central C–C–C bond angle of 112.5°. TPM consists of two types of molecules. Both have phenyl rings in a propeller configuration, with cis-H–Csp₃–C–C–C torsion angles of 54.9° (6), 34.8° (7), and 31.9° (6)° and –50.0° (7), –39.5° (7), and –20.1° (7)° for type 1 and type 2 molecules, respectively. The central C–C–C bond angles range from 111.5° to 113.6°. The DPM matrix likely favors the formation of a more ordered structure due to the arrangement of the phenyl substituents. In the case of TPM, the internal structure of the material may be more chaotic, which consequently makes it easier to adapt during the adsorption processes.

Matrices that would allow dynamic inclusion by the cyclodextrin molecule were being sought. A theoretically good fit was intended while simultaneously maximizing the residence time of the guest (or its fragment) inside the β -CD cavity. Indeed, the differences in particle size are not impressive, but considering that the volume of the β -CD cavity is about 262 Å³ in the dry state and probably changes slightly in DMF solution at 80 °C, it is reasonable to assume that in the case of DPM, the inclusion is facilitated.¹⁹ Undeniably, diphenylmethane is slightly more polar and thus shows better solubility in aprotic polar solvents such as DMF.²⁰ The slightly polar character is due to the arrangement of substituents around the –CH₂– bridge, the presence of which enables interactions with, for example, the polar carbonyl group of DMF.²¹ The resulting moderate dipole–dipole and dispersion-type interactions make the solvation relatively efficient. Triphenylmethane is nearly nonpolar and, in addition, more steric. In this case, solvation occurs mainly through dispersion (van der Waals) forces.²² The larger structure makes DMF less capable of uniformly "covering" the TPM. Solvation still occurs, but is less efficient per surface area than diphenylmethane. Solvation further increases the volume of guest molecules, resulting in a significant reduction in the

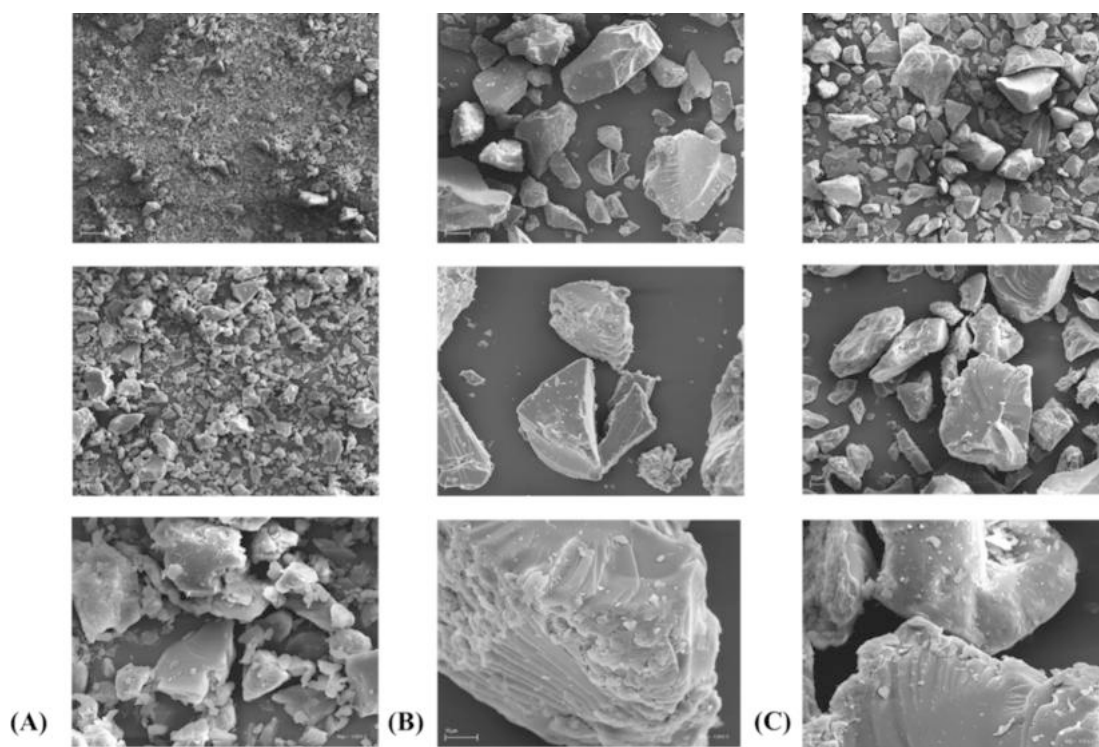


Figure 3. SEM photographs of CDP (A), DI-CDP (B), and TRI-CDP (C) materials recorded in magnification 300 $\times$, 1000 $\times$, and 4000 $\times$ (from up to down, respectively).

thermodynamic strength of the inclusion.²³ In water, the inclusion is strongly driven by the hydrophobic effect; the host sheds water and surrounds the hydrophobic guest.²⁴ In DMF, the hydrophobic effect is greatly reduced or absent because DMF dissolves hydrophobic molecules well, in this case, water molecules inside the host.²⁵ Tracking the dynamics of the complexation process of DPM and TPM by β -CD by magnetic resonance using the DOSY method, it can be seen that even at 15 $^{\circ}\text{C}$, the complexes formed are very unstable.²⁶ During the reaction carried out at 80 $^{\circ}\text{C}$ for 6 h, the amplitude of the inputs and outputs of guest molecules from the host cavity is undoubtedly impossible to determine. Nevertheless, in the end, the materials obtained with the mobile matrix have almost twice the adsorption capacity compared with the product of the reaction carried out without the addition of matrices.

The morphology of the adsorbents was reviewed by using the SEM (scanning electron microscope) technique. As shown in Figure 3A–C, the surface of the obtained adsorbents seems to be grainy, dense, and irregular. The varied jagged structure of the particles can support the adsorption process by increasing the specific surface area. On the surface of all materials, characteristic wrinkles and roughness are visible. Comparing the particle cross sections of the two materials with templates, it can be seen that DI-CDP has a more ordered interior with a multilayer character. The distances between the layers can be a determining factor during the adsorption process. The materials consist of particles that differ in size and structure, despite using the same grinding and sieving methods. CDP contains particles from 0.9 to 35.2 μm , DI-CDP from 30.0 to 455.9 μm , and TRI-CDP from 26.4 to 277.1 μm . The average particle size values for CDP, DI-CDP, and TRI-CDP were 18.1, 155.5, and 50.1 μm , respectively.

The specific surface areas determined by the BET (Brunauer–Emmett–Teller) method in the classical mode during nitrogen adsorption and desorption on dried adsorbents are small, amounting to 1.52 $\text{m}^2 \text{g}^{-1}$, 1.92 $\text{m}^2 \text{g}^{-1}$, and 1.43 $\text{m}^2 \text{g}^{-1}$ for CDP, DI-CDP, and TRI-CDP, respectively. The larger value of the BET surface area for the DI-CDP is not surprising when we return to the SEM images of this material, which show rather dense layers that are probably more easily accessible to gas than in the case of the TRI-CDP. On the other hand, CDP probably compensates for the BET surface by smaller particle sizes visible on SEM, resulting in an equal surface area as DI-CDP. Cross-linking β -CD with HMDI naturally results in materials with relatively low BET surface areas. For instance, a study reported a BET surface area of 7.31 $\text{m}^2 \text{g}^{-1}$ for β -CD-HMDI polymers, indicating a dense network structure that may limit porosity.²⁷ Therefore, the obtained materials may be suitable for certain applications, such as the adsorption of relatively small molecules. The BET isotherms obtained for all materials indicate type II. This shape is the result of the successive overlapping of unlimited monolayers up to a high $p/p_0 = 1$. The average pore size of 13.91 nm for CDP, 10.82 nm for DI-CDP, and 10.08 nm for TRI-CDP, respectively, places the materials among the mesoporous (2–50 nm).²⁸ What distinguishes the materials is the content of the β -CD units capable of forming supramolecular complexes. A routine test with phenolphthalein^{29–31} revealed the content involved in complexes β -CD was 27.14%, 39.33%, and 45.24% for CDP, DI-CDP, and TRI-CDP, respectively (Table S2), which may be due to the spatially more suitable matrix in the latter case, as it was predicted above from the geometry of the TPM used. Additionally, FTIR and elemental analyses were applied to characterize the degree of CD substitution (Table S3). The studies point out a single substitution of the

monomeric unit (anhydroglucose), which may be associated with a high degree of cross-linking.³² Adsorbents tend to retain water. Their wet weight increased by 113% (CDP), 124% (DI-CDP), and 174% (TRI-CD), respectively (Table S4). Soaking in water does not change the appearance of the materials. The materials do not change their volume and do not swell, which may indicate a high degree of cross-linking. Regardless of the similar and high degrees of substitution across all materials, the cross-linking density (ν_c) decreased from CDP, through DI-CDP to TRI-CDP (Table S3), indicating a transition from a more rigid to a looser network structure. This means that TRI-CDP forms a more open and flexible structure with greater swelling capacity. The hydrophobicity indexes (HI) determined by the static method have a low value and are 0.16, 0.11, and 0.12 for CDP, DI-CDP, and TRI-CDP, respectively, which means that the adsorption materials will perform well during adsorption processes carried out in aqueous solutions. The details on the hydrophobicity indexes (HI) determination method are placed in the Supporting Information.^{33,34}

Fourier transform infrared (FTIR) spectrometry was used to study the surface functional groups of the synthesized adsorbents, which showed high similarity (Figure S3). Figure 4 also shows β -CD and the material called CDP, obtained

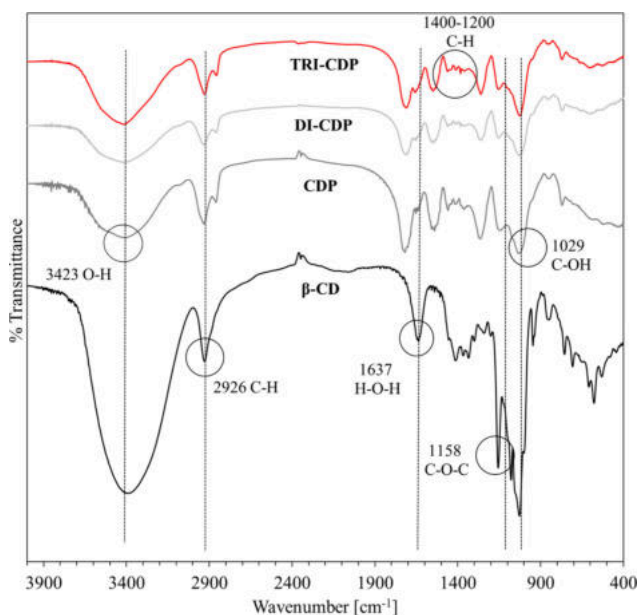


Figure 4. FTIR spectra of investigated materials in comparison with those of CDP (cyclodextrin material obtained without template) and β -CD (β -cyclodextrin).

without a template and described in the literature.³⁵ Adsorption bands located in similar regions indicate the presence of the same functional groups in the tested materials. As clearly shown in Figures 4 and S3, DI-CDP and TRI-CDP have the same infrared absorption bands around 3420 cm^{-1} ($-\text{OH}$ stretching vibration), 1640 cm^{-1} ($\text{H}-\text{O}-\text{H}$ strain, bending of water molecules), 1400–1200 cm^{-1} ($\text{C}-\text{H}$ bands of deformation vibrations in primary and secondary hydroxyl groups), such as β -CD and CDP. The FTIR spectra of the tested adsorbents obtained in condensation reactions with hexamethylene diisocyanate (HMDI) do not contain the bands 2275–2250 cm^{-1} , which suggests the transformation of isocyanate groups into urethane groups (approximately 1715

cm^{-1}). For more information about FTIR spectra, see Supporting Information section S2, Materials characterization results.

Information about the surface chemistry of the materials was completed by analyzing the pH of the zero-charge point (pH_{pzc}). The results obtained show that the isoelectric point of the DI-CDP is at a pH value equal to 3.05. At pH values above pH_{pzc} , the negatively charged surface of the material is predominantly present. At pH values lower than 3.05, the surface charge can mainly be positive. In contrast, the situation with the TRI-CDP material is a bit more complex. It is observed that its surface is charged alternately, once positively and then negatively. TRI-CDP has 5 isoelectric points at the following pH values: 2.42, 5.88, 6.63, 8.02, and 10.40. In the case of DI-CDP, there is a clear demarcation between the positive and negative charges of the adsorbent surface through the designated isoelectric point, while in the case of TRI-CDP, there is a greater oscillation at zero potential with two distinct distances from 0 mV ($\text{pH} = 2.42\text{--}5.88$; $\text{pH} = 8.02\text{--}10.40$). The observed fluctuations in zeta potential suggest an inhomogeneous distribution of surface charge across the material.³⁶ In the case of TRI-CDP synthesized using TPM as a template, this behavior likely reflects nonuniform surface functionalization. The bulky and symmetric structure of TPM may sterically hinder the uniform reaction of β -cyclodextrin hydroxyl groups with HMDI, resulting in irregular cross-linking and heterogeneous surface coverage.³⁷ Furthermore, due to the weak host–guest interactions between TPM and β -cyclodextrin, particularly in aprotic polar solvents such as DMF, the template is not consistently incorporated into the CD cavities.³⁸ This leads to a disordered pore architecture and uneven presentation of polar and nonpolar moieties on the material's surface, which further contributes to the variability in surface charge as reported in the previous articles.³⁹ The distribution of material charges depending on pH is shown in Figure S14 and Figure S15 for DI-CDP and TRI-CDP, respectively. In addition, problems were encountered during the measurement of the zeta potential; problems were encountered due to the too large particles of the materials and the stability of the mixture prepared for the measurement. However, after recrushing the substance, the results presented in this paper were evaluated.

Thermogravimetric analysis of all materials was carried out under a nitrogen atmosphere. A two-step degradation can be observed in the TGA/DSC plot (Figures S16, S17, and S18). The onset of degradation occurs at over 300 $^{\circ}\text{C}$, which is quite a high result compared to conventional polyurethanes that generally begin to degrade at approximately 200 $^{\circ}\text{C}$, as evidenced by prior research.⁴⁰ The better thermal stability of the nanosponge can be attributed to the cross-linked nature of the material. Cross-linking leads to an improvement in the thermal stability. Weight loss is maximum (more than 50%) during the first step of thermal degradation, which is due to cleavage of the urethane bond and volatilization of degradation byproducts. The various thermal changes taking place when the sample was heated at a specific rate were recorded with a differential scanning calorimeter. Phase transitions up to 250 $^{\circ}\text{C}$ were also observed, suggesting a glass transition. Such a transition results from the need for stronger cross-linking of the material. On the other hand, the graph shows the exothermic peak of oxidative decomposition at a temperature of about 350 $^{\circ}\text{C}$.

3.2. Adsorption Experiments. **3.2.1. Effect of the Adsorbent Mass.** The adsorption of BPA, BPB, and CV was investigated by changing the amount of the adsorbent in the test solution and maintaining the initial concentration of the adsorbates. Figure 5A–C illustrates the study, which showed that the percent removal of contaminants increased with adsorbent dosing. The reason for such a phenomenon may be the increasing number of adsorbent sites along with an increase in mass. A similar trend was observed by Crini et al.⁴¹ All materials for BPA and BPB were in equilibrium with the adsorbents at a concentration of 4 g L⁻¹, while in the case of CV adsorption by DI- and TRI-CDP, they were in equilibrium with a concentration of 0.2 g L⁻¹. The exception was the situation of CDP, for which equilibrium was obtained at 3 g L⁻¹, and then the q_t values declined. The highest removal efficiency for each amount of adsorbent used was found in TRI-CDP, while CDP is slightly less effective, and DI-CDP is the least effective. Using TRI-CDP at a concentration of 0.2 g L⁻¹ showed BPA, BPB, and CV removal of 72, 70, and 91%, respectively.

3.2.2. Effect of the Contact Time and Adsorption Kinetics. Several tests were carried out to determine the optimal time of contact of adsorbents with pollutants (Figure 5D–I), stating that this process is most dynamic in the first minute. For CV adsorption by CDP and DI- and TRI-CDP, equilibrium is obtained in 1 min, in contrast to the results reported by Tian et al. for the other β -cyclodextrin-based adsorbent, where it is reached at 320 min.⁴² For bisphenols, the q_t is almost three times higher for TRI-CDP than for DI-CDP due to structural fit, while CDP q_t values are placed in the middle. Perhaps due to the easier formation of the inclusion complex between bisphenols and DI-CDP and the subsequent rapid desorption, a more negligible adsorption effect can be observed over time. The reason may be the lower process stability and dynamic exchange of impurities while using DI-CDP. In contrast to literature reports where adsorption equilibrium for bisphenols typically requires 180–200 min, our materials achieved equilibrium within just 25 min, reaching a q_t limit of 7.12 mg g⁻¹ for BPA and 7.48 mg g⁻¹ for BPB during adsorption on TRI-CDP.⁴³ What is noteworthy is the very quick adsorption of the tested dye and bisphenols on the materials. CV equilibrium stabilizes at the start of the test, and q_t values remain constant throughout the process, with maximum CV adsorbed by DI-CDP at 4.97 mg g⁻¹ and by TRI-CDP at 4.91 mg g⁻¹, undoubtedly contributing to the lower concentration of the dye used and the better structural fit of the phenyldimethylamine residues to the interior of the CD. Figure 2B shows a fragment of the ROESY spectrum of an equimolar mixture of β -CD and CV in deuterated water. The recorded cross peaks indicate the inclusion of the dye inside the tori, which is consistent with earlier observations described by Garcia-Rio et al.⁴⁴ Interestingly, two types of complexes are visible. The first is formed when the dye is incorporated from the side of the smaller rim, then only the H-5/A-2 signal is visible, and the second is formed when it is introduced from the opposite side, then it penetrates deeper, resulting in two signals, H-5/A-1 and H-3/A-2. Based on the obtained results, it can be concluded that TRI-CDP is a more universal material (Figure 5). It is, therefore, worth attempting to determine the order of the nature and mechanism of the adsorption process using the appropriate models: pseudo-first-order and pseudo-second-order, Weber and Morris, Elovich, and Avrami. The results obtained from the kinetic tests, along with the estimated

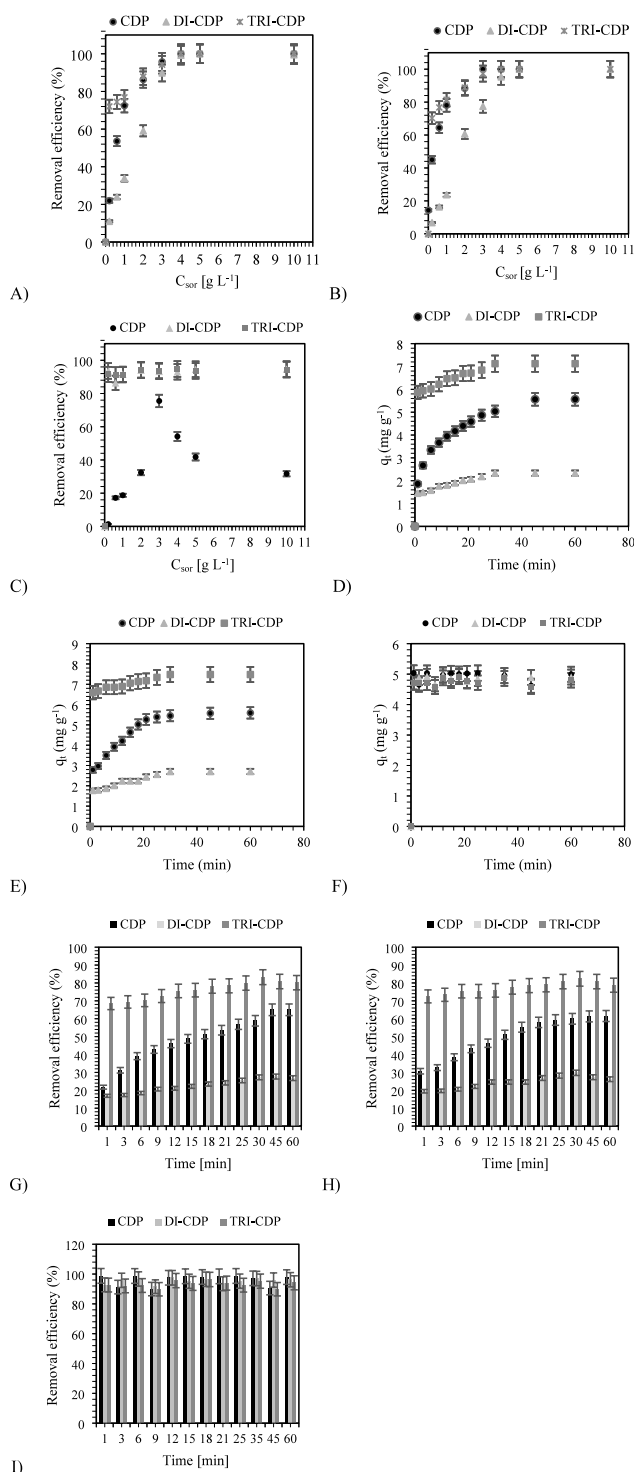


Figure 5. Effect of adsorbent concentration on removal efficiency of (A) BPA ($C_0 = 17.12$ mg L⁻¹), (B) BPB ($C_0 = 18.17$ mg L⁻¹), and (C) CV ($C_0 = 10.20$ mg L⁻¹) for all experiments; $C_{\text{sor}} = 0.2$ – 10 g L⁻¹ and $t_{\text{contact}} = 20$ min. Influence of time on adsorption capacity of (D) BPA ($C_0 = 17.12$ mg L⁻¹, $C_{\text{sor}} = 2$ g L⁻¹), (E) BPB ($C_0 = 18.17$ mg L⁻¹, $C_{\text{sor}} = 2$ g L⁻¹), and (F) CV ($C_0 = 10.20$ mg L⁻¹, $C_{\text{sor}} = 0.2$ g L⁻¹). Influence of time on removal efficiency of (G) BPA ($C_0 = 17.12$ mg L⁻¹, $C_{\text{sor}} = 2$ g L⁻¹), (H) BPB ($C_0 = 18.17$ mg L⁻¹, $C_{\text{sor}} = 2$ g L⁻¹), and (I) CV ($C_0 = 10.20$ mg L⁻¹, $C_{\text{sor}} = 0.2$ g L⁻¹).

BPA, BPB, and CV adsorption rate constants, are presented in Table S10. After modeling attempts among the above-

mentioned first- and second-order models, the pseudo-second-order equation was finally selected for all the tested systems ($R^2 \geq 0.90$). The main reasons were higher values of linear regression coefficients and strong agreement between calculated and experimental adsorption capacities (q_e and q_t) for each of the systems. This model operates under the premise that the step determining the rate is chemical adsorption or chemisorption. It forecasts the behavior across the entire spectrum of adsorption. This chemisorption-dominated pseudo-second-order model behavior has been reported in several studies.^{45–47} Under these circumstances, the rate of adsorption relies on the adsorption capacity rather than on the concentration of the adsorbate. To better understand the nature of the studied adsorption, the Elovich model (developed by Zeldowitsch) was applied in the next step. The model allows for consideration of mass and surface diffusion, activation, and deactivation energies. It was originally used for the adsorption of gases, but has also proven to be suitable for wastewater. The solute adsorption rate is assumed to decrease exponentially as the amount of the adsorbed substance increases. Moreover, according to this model, solid surfaces are energetically inhomogeneous, which means that neither desorption nor interactions between the adsorbed substances can significantly influence the adsorption kinetics at low surface coverage, as supported by existing literature.⁴⁸ All pollutants tested based on the R^2 coefficient (each above 0.93) show a good fit to this model and, at the same time, show a relatively high value of α , which is the baseline indicator. It can therefore be assumed that the process of chemical adsorption involving heterogeneous surfaces is observed. In addition, a fractional Avrami order model was also calculated. This model fits well with BPA, BPB, and CV when adsorbed by CDP and TRI-CDP, and for CV adsorbed by DI-CDP. In addition, all materials tested, but particularly CDP, revealed the largest magnitude of CV interactions with adsorption sites, which is due to the value of n , and then indicates a much better match between the dye structure and the adsorbent structure. As previously reported, there is a possibility that the dye released from the salt will eventually be incorporated into the structure of the adsorbent, which, due to its limited solubility, precipitates and settles on the material.⁴⁹ The Weber–Morris model, which is widely used, was chosen to determine the step controlling the adsorption rate. The results showed an average fit of this model. However, the C values were greater than zero, so it can be concluded that intramolecular diffusion is a velocity control step because the higher the C value, the greater the influence of the layer boundary on the adsorption process.

3.2.3. Adsorption Equilibrium. Information on the adsorption equilibrium was obtained based on the Freundlich, Harkins–Jura, Temkin, Hill, Redlich–Peterson, and Toth models. The parameters of the isotherms are listed in Table S11.

Adsorption of the tested pollutants by CDP, DI-, and TRI-CDP is best suited to the Hill model, which assumes that adsorption is a cooperative phenomenon in which the ability to bind a ligand at one site on the adsorbent can affect different binding sites on the same adsorbent. This is because calculated values have the best match to the experimental values, and the R^2 coefficients are exceptionally high ($R^2 \geq 0.93$). In addition, by analyzing the n_{hi} factor, it is possible to distinguish the type of bonding between different molecules with homogeneous surfaces. For example, if $n_{hi} = 1$, the bond is noncooperative, and when $n_{hi} > 1$, the bond is positively cooperative, and

negative when $n_{hi} < 1$. CDP and TRI-CDP for CV, and DI-CDP for all pollutants indicate a binding relationship that has positive cooperation. This may indicate the preorganization of the material during adsorption. In addition, the results obtained for the Freundlich model also present a good fit ($R^2 \geq 0.89$) for all systems. This model describes multilayer, nonideal, and reversible adsorption and can be applied to multilayer formation, with nonuniform distribution of heat and affinity adsorption on a heterogeneous surface. Due to the value of the coefficient n , the adsorption process can be regarded as favorable. Nevertheless, Toth's isotherm (preferred for heterogeneous adsorption systems meeting both low and high concentration limits) shows a good match to the adsorption of BPA, BPB, and CV. Toth's model reduces to the equation of the Langmuir isotherm when $n = 1$. When n is less than unity, the system is considered heterogeneous, as seen in the case of almost all models except CV+DI-CDP and CV+TRI-CDP. In those two exceptional situations, adsorption probably consists of complex behaviors or cooperative interactions ($n > 1$).

However, one cannot ignore the interaction defined by the Redlich–Peterson model, which includes the assumptions of the Langmuir isotherm with some additions of mechanical contact between the desorbing and adsorbing molecules. The postulates of this model can be applied to both mobile and single-layer localized adsorption without side interactions. Fitting is visible in all systems except BPA+CDP and BPB+CDP.

Taking the above into account, the calculated q_{max} values from the Hill model for BPA were 137.52, 13.98, and 64.33 mg g^{−1}, for BPB, 147.58, 27.83, and 79.30 mg g^{−1}; and for CV, 594.89, 1075.84, and 1005.75 mg g^{−1} for CDP, DI-CDP, and TRI-CDP, respectively. These findings show that using molecular imprinting in DI-CDP and TRI-CDP increased the maximum adsorption capacity for CV, while also decreasing the adsorption of bisphenols. This selective behavior highlights the effective imprinting of CV in both DI- and TRI-CDP materials, which encourages targeted dye adsorption at the cost of reduced affinity for bisphenols A and B.

For a better perspective, Tables 1 and 2 present a comparison of the obtained values of the maximum adsorption

Table 1. Comparison of Adsorption Capacities of Different Adsorbents for Bisphenol A

adsorbent	q_{max} (mg g ^{−1})	ref
CDP	137.52	this work
DI-CDP	13.98	this work
TRI-CDP	64.33	this work
β -CD/CMC-EGDE	14.15	S3
β -CD-BTCAD	40.64	S2
β -CD-PEGDE	49.31	S6
β -CD-divinyl sulfone	69.17	S4
β -CD-EGDE	78.53	S3
β -CD-tetrafluoroterephthalonitrile	87.89	S5

capacity for different materials in the case of BPA and CV, respectively. All materials presented in the following tables were obtained by synthesizing β -cyclodextrin with a cross-linking agent without any other additives. For CV, it can be seen that the materials described in this paper are in the lead in terms of q_{max} values, increasing the least effective material by as

Table 2. Comparison of Adsorption Capacities of Different Adsorbents for Crystal Violet

adsorbent	$q_{\max}$ (mg g ⁻¹)	ref
CDP	594.89	this work
DI-CDP	1075.84	this work
TRI-CDP	1005.75	this work
β -CD-CA	30.30	50
EPI- β -CD	41.61	57
EDTA- β -CD	114.23	
EDTA-CDP	599.73	58
CD-1	1137.70	59
p(NIPAM-co-MAA)/ β -CD	1253.78	51

much as 20, 36, and 33 times for CDP, DI-CDP, and TRI-CDP, respectively.⁵⁰ However, one can also find better performing adsorbents, such as p(NIPAM-co-MAA)/ β -CD, which have disadvantages that our materials do not have. For comparison, the mentioned material reaches equilibrium after 400 min at 25 °C, while our materials for CV reach it in just 1 min without losing much of their maximum adsorption capacity.⁵¹ On the other hand, for BPA, among the materials tested, the highest value of the maximum adsorption capacity was reported for nonimprinted CDP (137.52 mg g⁻¹), which is much higher than the values reported for other β -CD-based adsorbents, such as β -CD/CMC-EGDE (14.15 mg g⁻¹), β -CD-BTCAD (40.64 mg g⁻¹) or β -CD-PEGDE (49.31 mg g⁻¹). Even compared to more advanced structures, such as β -CD-tetrafluoroterephthalonitrile (87.89 mg g⁻¹) or β -CD-EGDE (78.53 mg g⁻¹), the obtained result is much higher.^{52–55} This makes CDP a promising candidate for applications in the removal of organic BPA from aqueous solutions. Moreover, modifications in the form of matrix addition in the case of DI-CDP and TRI-CDP resulted in a decrease of $q_{\max}$ to 13.98 mg g⁻¹ and 64.34 mg g⁻¹, which may be due to changes in the porous structure of the material, limiting the availability of binding sites. It is worth adding that although TRI-CDP is characterized by a lower adsorption capacity than CDP, its efficiency still exceeds many other, more complex, β -CD-based materials.

Additionally, both an experimental comparison with two commercial adsorbents (Norit SX Plus and Organosorb 200-C303) and a literature-based benchmark against widely used industrial adsorbents (such as activated carbons, natural clays, and zeolites) were carried out to better contextualize the performance of the synthesized materials. The cyclodextrin-based MIPs outperformed high-surface-area materials often due to their rapid adsorption kinetics and superior adsorption capacities for crystal violet, even though they had a low surface area (Tables S13 and S14, Supporting Information).

3.2.4. Thermodynamic Analysis. To determine whether the adsorption by the obtained materials is a spontaneous process, thermodynamic analysis was used. The parameters required for this were calculated using the van't Hoff equation. As can be seen in Table S12, the processes discussed in this paper are exothermic ($\Delta H^0 < 0$) for DI- and TRI-CDP. Adsorption of model pollutants used in the research by imprinted adsorbents is a process leading to an increase in orderliness at the solid–liquid interface ($\Delta S^0 < 0$). Negative values obtained for ΔS^0 indicate decreased randomness. When the value of ΔG^0 is negative, this means that adsorption may occur spontaneously, which is evident in almost all cases presented. The determined thermodynamic parameters provided additional information

on the adsorption processes involving both materials. Adsorption of bisphenols and crystal violet by DI-CDP and TRI-CDP materials indicates exothermic processes. Most of the ΔG^0 values calculated for them are negative, which indicates spontaneous and thermodynamically favorable processes. Positive values of Gibbs-free enthalpy are observed for the highest tested temperature in almost all cases, which is related to the nonspontaneity.

In addition, considering the obtained results for unmodified CDP material, it can be concluded that the adsorption of all contaminants onto CDP is clearly an endothermic process, which is confirmed by the positive enthalpy values ($\Delta H^0 = 91.59$, 61.20, and 65.85 kJ mol⁻¹ for BPA, BPB, and CV, respectively). The entropy changes are positive ($\Delta S^0 = 318.45$ to 235.38 J K⁻¹ mol⁻¹), indicating the growth of disorder at the interface where the process takes place. What is more, it indicates that the nonimprinted variant behaves in an opposite manner to the imprinted ones. Moreover, the adsorption of bisphenols and dye is spontaneous and thermodynamically favorable since the Gibbs free energy (ΔG^0) values for CDP are negative. Surprisingly, ΔG^0 decreases with increasing temperature, suggesting that the main driving force for adsorption onto CDP is entropy and not enthalpy.

Additionally, both types of adsorption processes, endothermic and exothermic, have been previously reported in articles for the various molecularly imprinted cyclodextrin-based materials. This calls attention to the highly important influence of modeled pollutants, adsorption process conditions, or synthesis strategy on the thermodynamic variability.^{60–63}

Unfortunately, mere knowledge of the enthalpy resulting from the binding energy is not sufficient to identify this process as physical or chemical adsorption. To define interaction as either physical or chemical, we must also consider other parameters, including charge transfer and bond distance.

3.2.5. Effect of pH, Ionic Strength, and Humic Acids Concentration. The impact of pH on pollutant adsorption was studied (Figure 6A–C). Textile effluent pH typically falls between 7 and 9. Testing pollutants at pH levels from 2 to 11 revealed that pH alters the adsorbent surface charge, affecting adsorption. For CV, a similar trend was observed by Tcheka et al. concluding that the higher pH enhanced removal efficiency, which is consistent with prior studies.^{64,65} Zeta potential measurements indicated pH-induced charge shifts on the adsorbent surface, influencing the dye adsorption. DI-CDP showed a positive surface charge at acidic pH, turning negative with higher pH, enhancing the removal. TRI-CDP displayed a similar trend, and pH-induced charge fluctuations might have affected the measurements. Above pH 8, TRI-CDP's shift to a positive charge (near $pH_{PZC} = 8.02$) slightly decreased the removal efficiency. BPA and BPB adsorptions were stable in acidic to neutral pH but decreased at pH 8–9 due to repulsive interactions between negatively charged impurities and the adsorbent. Although the trend of the effect of pH on the adsorption of bisphenols is similar to that observed in the literature for other materials, our results indicate a more variable and irregular response, which may indicate specific properties of the adsorbents used.⁶⁶ The material without a matrix, CDP, shows intermediate BPA removal efficiency, lower than TRI-CDP but higher than DI-CDP. Additionally, it is more sensitive to pH fluctuations, as can be seen in the Figures. Even at neutral pH, significant differences can be seen, which indicate the lack of comparable stabilization of the material to adsorbents synthesized with matrices. For CV

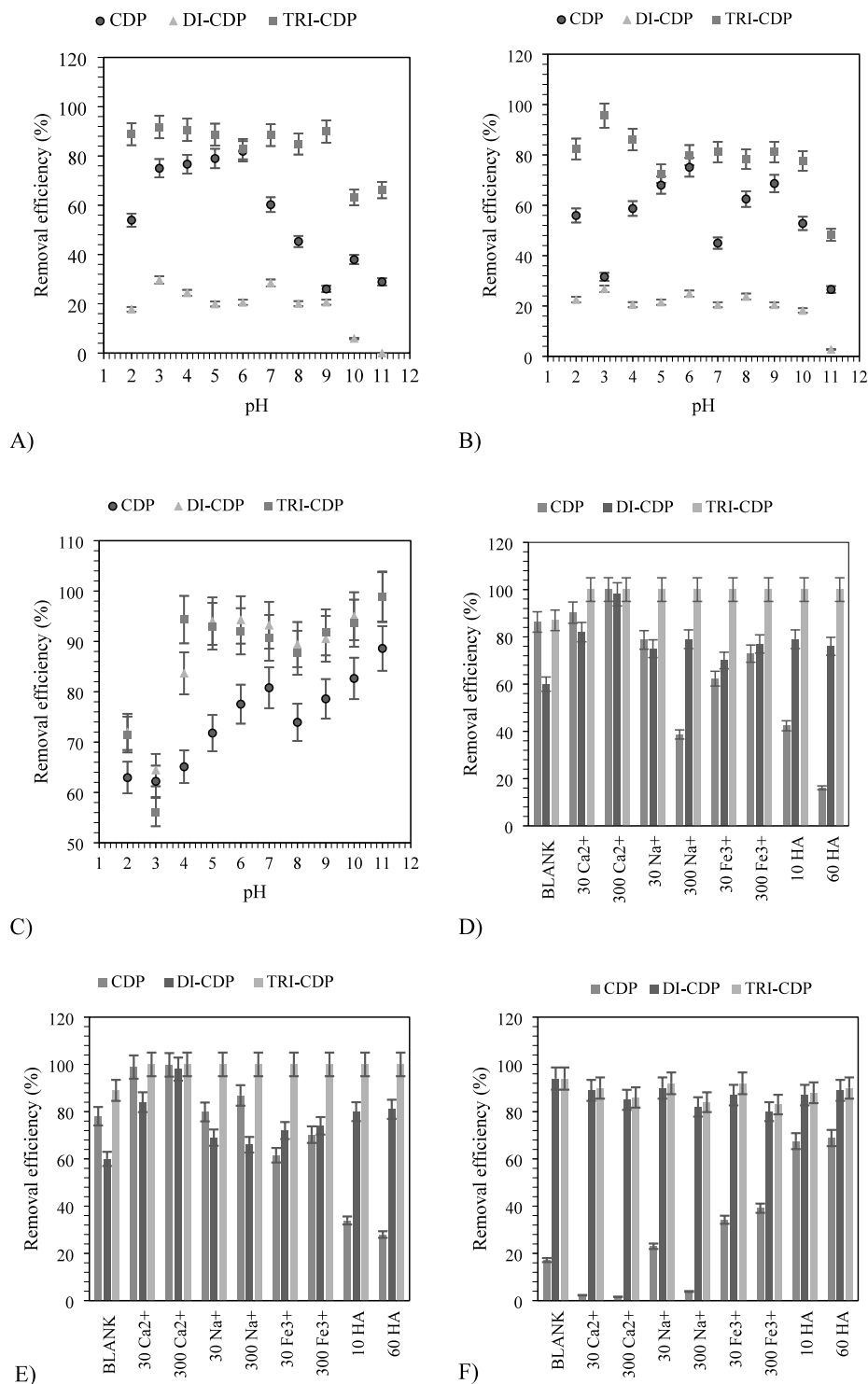


Figure 6. Effect of (A) pH for BPA, (B) pH for BPB, (C) pH for CV, (D) salts and humic acids concentration on adsorption of BPA, (E) salts and humic acids concentration on adsorption of BPB, (F) salts and humic acids concentration on adsorption of CV ($c_{\text{BPA}} = 17.12 \text{ mg L}^{-1}$, $c_{\text{BPB}} = 18.17 \text{ mg L}^{-1}$, $c_{\text{CV}} = 10.20 \text{ mg L}^{-1}$, $c_{\text{sor}} = 2 \text{ g L}^{-1}$) by adsorbents ($t_{\text{contact}} = 20 \text{ min}$). 30 Na^{+} and 300 Na^{+} ($C_{\text{NaCl}} = 76.05 \text{ mg L}^{-1}$; $C_{\text{NaCl}} = 760.50 \text{ mg L}^{-1}$); 30 and 300 Ca^{+} ($C_{\text{CaCl}_2} = 83.25 \text{ mg L}^{-1}$; $C_{\text{CaCl}_2} = 832.50 \text{ mg L}^{-1}$); 10 HA and 60 HA ($C_{\text{humic acids}} = 10 \text{ mg L}^{-1}$; $C_{\text{humic acids}} = 60 \text{ mg L}^{-1}$).

removal by CDP, the trend is similar to that of the other tested materials, but the efficiency is lower by an average of 15% RME.

Salts present in wastewater can significantly affect the adsorption of water pollutants (Figure 6D–F). The presence of calcium, sodium, and iron chlorides in the studied

concentration range affected the RME values differently, depending on impurities and materials used. The presence of humic and fulvic acids is typical for surface waters and can be of great importance in removing pollutants from waters. Their addition influenced adsorption efficiency, often enhancing it (e.g., calcium ions), but reducing it in some cases, particularly

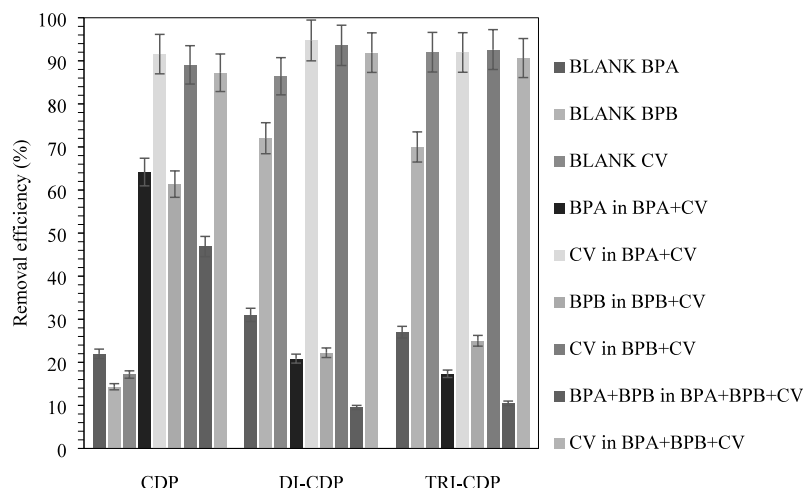


Figure 7. Removal efficiency from a complex model mixture ($c = 2.5 \times 10^{-5} \text{ mol L}^{-1}$, $c_{\text{sor}} = 0.2 \text{ g L}^{-1}$, $t = 20 \text{ min}$).

for CDP. Salts increase the ionic strength of the solution, which can affect the surface charge of the adsorbent material and adsorbate molecules. This change in ionic strength, likely in the case of DI-CDP and TRI-CDP, reduced the electrostatic repulsion between the adsorbent and adsorbate, promoting better interaction and easier adsorption in some cases. Additionally, the presence of ions can shield charges on the adsorbent surface, allowing better access to binding sites for contaminants. Additionally, some salts, especially metal salts such as ferric chloride and natural organic matter like humic acids, may form complexes with the adsorbate molecules. Depending on the system tested, these complexes may either enhance or impede adsorption. In addition, humic acids can also facilitate the adsorption process by improving transport or associating these contaminants with active sites in the adsorbent material. At the same time, in the case of CDP, they often caused lowered adsorption. Moreover, in the adsorption of bisphenols A and B, TRI-CDP consistently showed the highest efficiency (RME = 100%) under all tested conditions. Calcium ions have generally been reported in the literature to exert a limited effect on BPA adsorption, but in this study, they significantly improved adsorption for all materials, especially at 300 mg L^{-1} (e.g., BPA 98% for DI-CDP, 100% for CDP, and TRI-CDP).⁶⁷ Additionally, Fe^{3+} and humic acids had a weaker or even negative impact, particularly for CDP. For example, BPA removal by CDP lowered from 86% to 16% at 60 mg L^{-1} HA, and BPB from 78% to 28%. Despite these influences, TRI-CDP maintained 100% adsorption even in the presence of Fe^{3+} and HA, confirming its superior stability and applicability. In the adsorption of CV, TRI-CDP and DI-CDP showed high stability across all tested conditions (RME $\geq 80\%$), while CDP remained highly susceptible to interference. Ca^{2+} ions caused the strongest suppression for CDP, reducing efficiency from 17% to 1.6% at 300 mg L^{-1} . In contrast, TRI-CDP maintained RME at the level of 86–90% in the presence of calcium and sodium ions and 90% even at 60 mg L^{-1} humic acid. Additionally, boosted adsorption favorability is often linked to the simultaneous presence of humic acids and dyes, which has been reported in previous studies.^{68,69} Iron ions also affected CDP (RME = 39%), but results for TRI-CDP remained unchanged (92–83%), confirming its validity toward interfering ions and organic matter.

3.2.6. Adsorption Selectivity: The Influence of Coexisting Components in the Mixture. The presence of additional impurities in the test solution increases the efficiency of the CV removal from model mixtures (Figure 7). Two- and three-component models were used to check the selectivity of materials to the tested impurities. The removal enhancement effect is strongest with a mixture of bisphenol A and crystal violet, where the violet is removed with a removal efficiency of 95%, which is higher than that obtained in the absence of other impurities. During the observed removal with higher dye removal efficiency, a decrease in bisphenol removal can also be noted when using the mixtures. The observed increase in CV adsorption while reducing BPA and BPB adsorption is an undisputed advantage of DI- and TRI-CDP materials and has the potential to be used in the treatment of multicomponent wastewater to remove a selected dye (e.g., crystal violet or similar structures) when treating wastewater.

In the case of CDP, no distinct selectivity toward crystal violet (CV) is observed, in contrast to DI-CDP and TRI-CDP, which exhibit a marked preference for this compound. The removal efficiency (RME) of bisphenols (both BPA and BPB) is significantly higher for CDP, by up to 50%, compared to those of the other materials. This confirms that the incorporation of additional matrices during the synthesis of DI- and TRI-CDP induced selective adsorption behavior.

Furthermore, as shown in section 3.2.5 on the effect of pH, DI-CDP and TRI-CDP exhibit a high RME of crystal violet in the pH range found in textile industry wastewater, and the process is extremely fast (1 min), which means that these materials should be considered when selecting an adsorbent for selective applications, CV removal from postproduction wastewater. Especially since it copes well with even very high CV concentrations during its adsorption, as can be seen in Figure S19.

3.2.7. Textile Industry Effluents Prototype Application. The study evaluated the adsorption capacities of DI-CDP and TRI-CDP for the removal of bisphenol A, bisphenol B, crystal violet, and their various mixtures from textile wastewater prototypes. The study revealed varying adsorption efficiencies for target pollutants and their combinations (Figure 8). The results obtained are slightly worse than those obtained for distilled water, but they still show a high adsorption capacity. Notably, DI-CDP and TRI-CDP materials showed significant

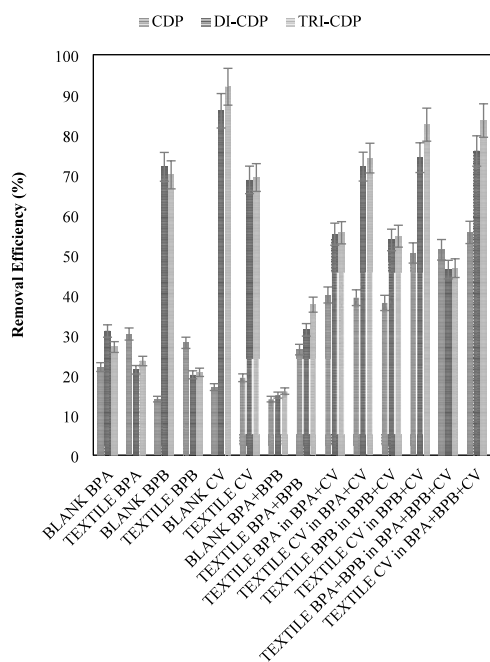


Figure 8. Removal efficiency of BPA, BPB, and CV from a textile effluents prototype ($c = 2.5 \times 10^{-5} \text{ mol L}^{-1}$, $c_{\text{sor}} = 0.2 \text{ g L}^{-1}$, $t = 20 \text{ min}$). BLANK with the usage of distilled water, and TEXTILE with the usage of textile effluents prototype. BPA+BPB is a mixture of bisphenol A and B; BPA+CV is a mixture of bisphenol A and crystal violet; BPB+CV is a mixture of bisphenol B and crystal violet; BPA+BPB+CV is a mixture of bisphenol A, bisphenol B, and crystal violet.

effectiveness in removing individual contaminants under various conditions, with TRI-CDP showing higher percentages of removal of BPA, BPB, and CV compared to DI-CDP, which was expected due to its more versatile character demonstrated earlier and the greater amount of cyclodextrin available. Additionally, in the case of mixed contaminants, TRI-CDP showed excellent adsorption performance for each combination, in particular, for BPA and CV, which have higher results than those in the absence of additional contaminants. For example, when using TRI-CDP and the BPA+BPB+CV mixture, 84% for CV was obtained, while the adsorption of a single pollutant from textile wastewater showed 69% removal. What is important in terms of the purification process on an industrial scale is that, as can be seen in Figure 8, along with the efficiency of adsorption of CV from textile wastewater, the efficiency of adsorption of BPA and BPB also increases (regardless of whether it is a two- or three-component mixture). The results highlight the potential application of these adsorbents in the context of postproduction wastewater treatment from the textile industry, highlighting their effectiveness in mitigating the presence of pollutants before their discharge into natural water bodies, thereby solving complex environmental problems.

In comparison, CDP, lacking the additional polymer matrix, demonstrated a notably lower performance across most test conditions. Nevertheless, the CDP showed slightly improved RME ($\text{RME}_{\text{BPA+BPB}} = 51\%$; $\text{RME}_{\text{CV}} = 56\%$) in the BPA+BPB+CV mixture compared to the single-component one. This suggests that although CDP is less efficient overall, synergistic effects in more complex multicontaminant mixtures could possibly support its adsorption efficiency to a limited extent.

3.2.8. Environmental Application: The Case of the Vistula River. Under environmental conditions, we can encounter many undesirable, harmful substances in water, which get into it, among others, through the insufficient treatment of postproduction wastewater from textile manufacturers. To illustrate how the adsorbents we designed work under real conditions, environmental tests were carried out, the results of which are presented in Figure 9 from A to C for the case of the Vistula River (Table S1). During its flow across the country, the Vistula, the largest river in Poland, meets various environments, including those that can be described as related to the production plants. Therefore, this river was selected to check whether and how co-occurring substances influence the adsorption process. Higher results for the RME parameters were obtained in the case of samples prepared from water from the Vistula River, and the higher the concentration of the tested pollutant, the more difficult it was to remove it, regardless of its type. In the case of BPA and BPB adsorption, there is a correlation that leads to an increase in the RME for removing impurities from water for DI-CDP for the used Vistula water, and a decrease in this value for TRI-CDP when using Vistula water compared to the use of distilled water. When it comes to crystal violet, we do not see such a relationship - the results are comparable to those for distilled water, with a decrease in RME for higher concentrations. The highest removal efficiency values for all three pollutants and imprinted materials are about 95% (most often at a concentration of about 10 mg L^{-1}).

In this study, CDP showed significantly lower adsorption efficiency compared to the other materials over the whole concentration range. For example, for BPA, BPB, and CV at a concentration of about 2 mg L^{-1} , the RME for CDP was 69%, 59%, 79%, while for imprinted materials, it exceeded 90% in most cases. The observed trend is not surprising, given the results of previous studies, which also showed a significantly lower RME for CDP (e.g., in the presence of salt and variable pH). Considering this, it can be stated that CDP shows lower stability and adsorption efficiency compared to those of DI-CDP and TRI-CDP in complex environmental systems.

3.2.9. Adsorption of Various Phenolic and Dye Compounds. DI-CDP, TRI-CDP, and reference material CDP were tested for adsorption of selected phenolic compounds and dyes considered to be endocrine active substances (Figure 10A, B). Their chemical structures are presented in Figures S1 and S2. The highest removal efficiency ($>96\%$) was obtained across all adsorbents for methylene blue, toluidine blue, and crystal violet. High efficiency of MB and TB may result from structural matching and low steric hindrance. CV was characterized by better adsorption than dyes with a similar structure, which may be due to the presence of an additional dimethylamino group.

In the case of phenolic compounds, only DI-CDP (76%) and TRI-CDP (99%) showed increased adsorption efficiency of 4-bromophenol, a relatively small compound with a substituent in the para position. CDP achieved significantly lower values (39%), which emphasizes the importance of imprinting. CV achieved the highest RME regardless of the adsorbent used.

3.2.10. Regeneration Experiments. The practical potential of adsorptive materials relies on their ability to be regenerated for reuse, a cost-effective option in material use (Figure 11). Evaluating CDP, DI-CDP and TRI-CDP for reusability involved multiple adsorption/desorption cycles. CDP and

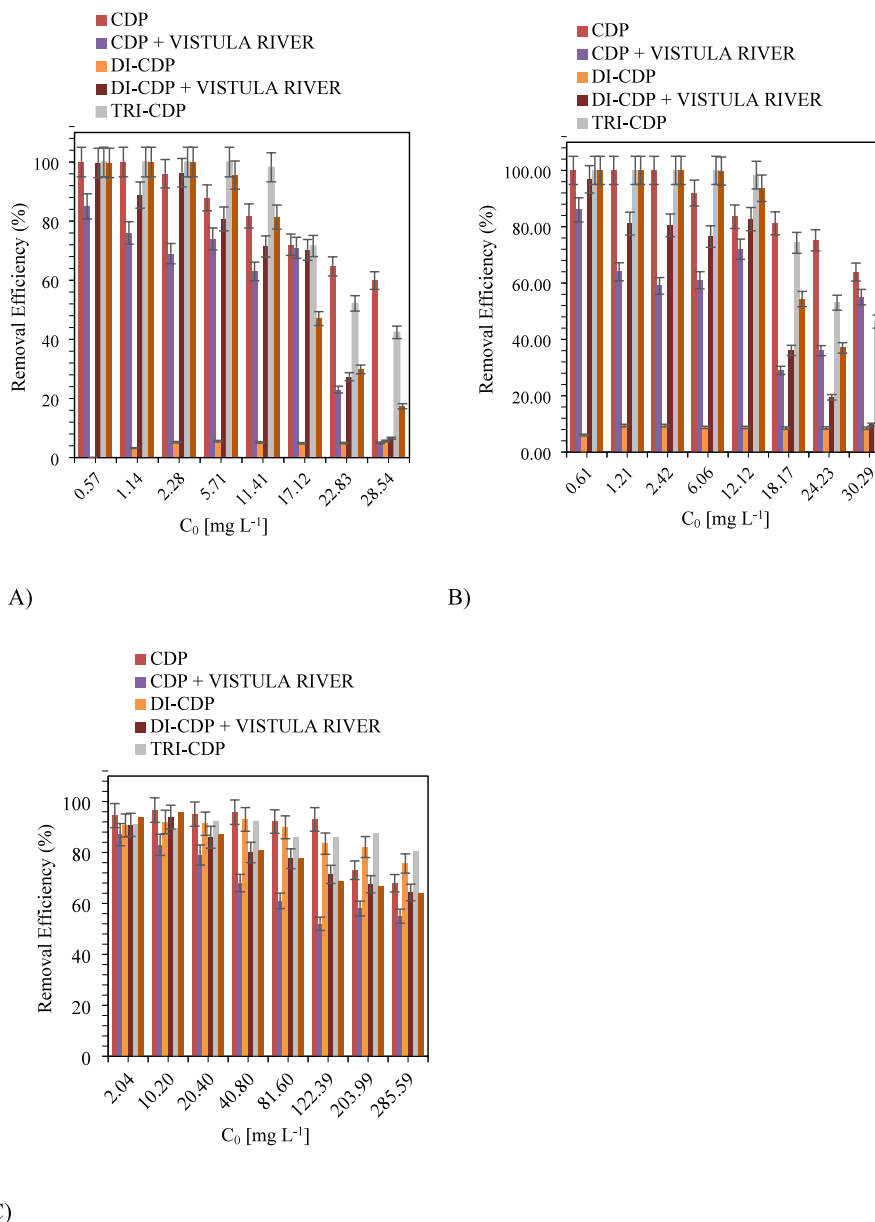


Figure 9. Effect of different concentrations of the solution prepared with the water samples from the Vistula River on the removal efficiency of (A) BPA, (B) BPB, and (C) CV. The parameters used are as follows: $c_{\text{sor}} = 0.2 \text{ g L}^{-1}$, $t = 20 \text{ min}$.

TRI-CDP maintained consistent removal efficiency for BPA (and potentially BPB) across five cycles, ensuring its potential for reuse. DI-CDP showed efficiency fluctuations but eventually reached 100% in the fourth cycle for all of the pollutants. This follows the pattern observed in previous literature, where high recovery rates of 97.23–99.21% were reported for other cyclodextrin-based MIPs after BPA removal.⁷⁰ All materials exhibited increasing efficiency with each cycle for crystal violet, reaching 100% by the fifth cycle; the exception is CDP, which was stable across all cycles performed. Notably, the regeneration process efficiently separates bioethanol for potential reuse, presenting economic benefits. Regenerated bioethanol holds industrial value, serving as a solvent and precursor for plastics production, aligning with closed-loop production principles.

3.3. Proposed Mechanism of Adsorption. The adsorption process, which is crucial for the removal of BPA,

BPB, and CV, relies on complex interactions between contaminants and adsorption materials. Assuming a mechanism based solely on the attachment of guest molecules to the interior of tori, the maximum adsorption capacity would be 142.79 mg g^{-1} (CV), 79.90 mg g^{-1} (BPA), 84.81 mg g^{-1} (BPB) for DI-CDP, each gram of which contains 0.35 mmol CD, and 163.19 mg g^{-1} (CV), 91.32 (BPA) and 96.92 mg g^{-1} (BPB) for TRI-CDP, each gram of which contains 0.4 mmol CD. From the above data, it appears that in the case of bisphenols, even complete filling of the CD rings is not achieved. The reason for this is probably the instability of the resulting complexes due to mismatching and a lack of additional stabilization. The effective adsorption of crystal violet is almost certainly largely due to simple statistics. The CV molecule consists of three theoretically identical elements, which greatly increases the probability of supramolecular interactions. An additional advantage is the presence of

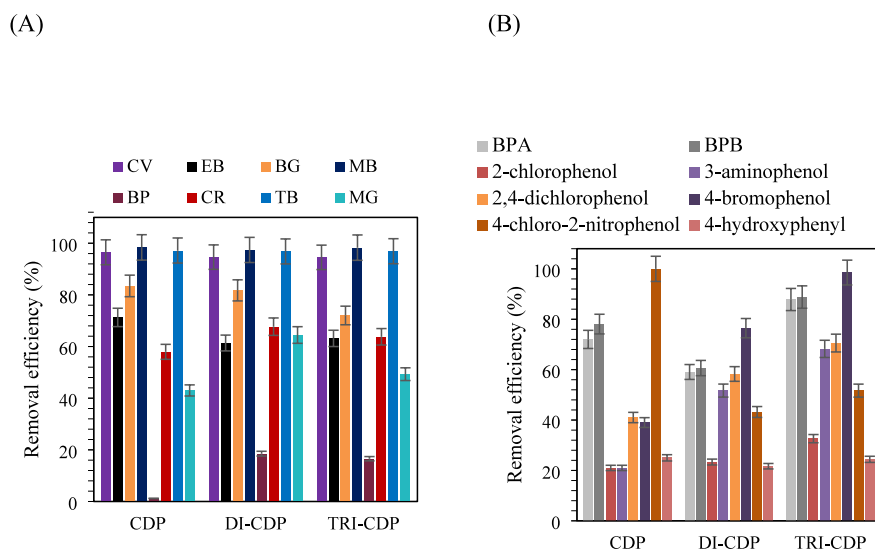


Figure 10. (A) Comparison of adsorption efficiency of various dyes ($c_0 = 2.5 \times 10^{-5} \text{ mol L}^{-1}$, $c_{\text{sor}} = 2 \text{ g L}^{-1}$, and $t = 20 \text{ min}$). (B) Comparison of adsorption efficiency of various phenolic compounds ($c = 2.5 \times 10^{-5} \text{ mol L}^{-1}$, $c_{\text{sor}} = 2 \text{ g L}^{-1}$, $t = 20 \text{ min}$).

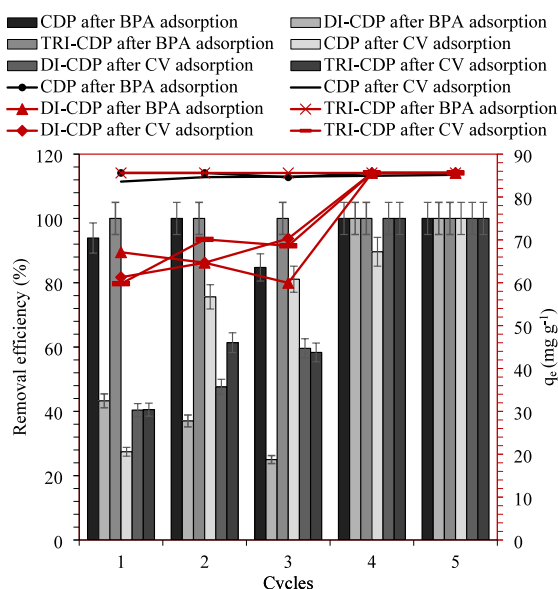


Figure 11. Average efficiency of BPA ($c_{\text{BPA}} = 17.12 \text{ mg L}^{-1}$, $c_{\text{sor}} = 20 \text{ g L}^{-1}$) and CV ($c_{\text{CV}} = 10.20 \text{ mg L}^{-1}$, $c_{\text{sor}} = 20 \text{ g L}^{-1}$) removal by DI-CDP and TRI-CDP after consecutive regeneration cycles.

dimethylamine groups, which also have a partial positive charge. The surface urethane groups are likely to be discriminating factors in the adsorption process. Interactions between impurities and the adsorbent surface largely depend on the chemical composition of the functional groups. It is well-known that electron-rich groups, such as amide, ester, or urethane groups, have a higher affinity for positively charged impurities such as metal ions or cationic dyes. Note also that the adsorption materials were synthesized in the presence of two different matrices. It is reasonable to assume that a greater effect of molecular imprinting on the distribution of urethane chains was obtained for TPM, assuming the inclusion of only one aromatic ring inside of the CD torus. In an aqueous environment, the materials fill with water with different intensities, which may indicate different availability of

functional groups involved in hydrogen bonding and thus in the stabilization of hydrated, complexed, etc., new systems. Consequently, the final effect is seen in the maximum values of adsorption capacity, which are about 4,000 times higher for CV than BPA (DI-CDP) and 17 times higher for CV than BPA (TRI-CDP).

4. CONCLUSIONS

In this study, novel biobased materials DI-CDP and TRI-CDP were synthesized using β -CD molecular imprinting, exhibiting heterogeneous structures rich in active β -CD content ($\geq 39\%$). These materials exhibit a preference for common textile industry aromatic compounds, notably ionic ones, across a wide pH range (4–9), ideal for the textile industry. Their effectiveness in removing organic pollutants increases in the presence of typical water components, such as salts and humic acids, promising practical applicability. Surface analysis reveals heterogeneous adsorption, while their high regenerative capacity and easy separation add to their appeal. Testing in environmental conditions, using river waters from the Vistula, sustains or enhances the pollutant removal efficiency. Both imprinted materials exhibit selectivity for crystal violet removal from multicomponent mixtures. Notably, their adsorption process is exceptionally rapid, making them suitable for the final quick treatment stage of partially treated streams discharged from sewage treatment plants into environments like rivers. A potential green light for the use of our materials in industry was also provided by research using synthetic textile sewage, which showed excellent pollutant removal properties, especially when it comes to mixtures and no single compounds, which is extremely important in industry, where individual streams can combine into one during wastewater treatment in on-site wastewater treatment plants or after use. Finally and importantly, efficient adsorption can be achieved during the treatment of model and real wastewater samples, even with a prototype effluent from the textile industry. We can assume that we have partially developed an effective adsorption process for selectively removing model pollutants (especially crystal violet among the tested pollutants) from water and wastewater, with a potential application to the textile industry.

Considering the above findings, the experimental results successfully confirmed the assumption that both DI-CDP and TRI-CDP adsorption materials selectively remove crystal violet and exhibit a higher adsorption capacity than toward bisphenol A and B. This is confirmed by the reference material (CDP), which does not show this selective interaction toward CV, even using the mixtures of BPA, BPB, and CV. This outcome can be attributed to the dye's stronger affinity for the urethane chains and the external toroidal surface of the cyclodextrin-based polymeric materials imprinted by DPM and TPM. Furthermore, the two adsorption materials demonstrated efficient adsorption in the treatment of both model and real wastewater samples. Remarkably, high adsorption efficiencies were achieved even for prototype effluents from the textile industry, showcasing the versatility and practicality of DI-CDP and TRI-CDP materials. These findings highlight the potential of DI- and TRI-CDP adsorbents for practical applications in removing dyes and other contaminants from industrial wastewater. At the same time, CDP did not work as well as the imprinted adsorbents in model wastewater and textile studies. This statement confirms that the gap in adsorption studies was filled, as native cyclodextrin-based materials do not achieve such results as those that can be obtained by imprinted ones.

■ ASSOCIATED CONTENT

Data Availability Statement

Data will be made available on request.

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.5c00705>.

Several sections detailing the investigated materials' characterization, adsorption studies, and practical applications, i.e., materials characterization and adsorption characterization methods, adsorption experiments, textile industry effluents prototype application, environmental applications, regeneration of adsorbents, materials characterization results, adsorption characterization results, and adsorption mechanism analysis (PDF)

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript. Dominika Natalia Nowacka: conceptualization, methodology, investigation, formal analysis, validation, visualization, writing—original draft, writing—review and editing. Anna Maria Schmidt (formerly Anna Maria Skwierawska): conceptualization, methodology, investigation, formal analysis, validation, writing—original draft, visualization, writing—review and editing. Bogusława Łęska: funding acquisition. Radosław Pankiewicz: funding acquisition.

Notes

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■ ABBREVIATIONS

2-CP, 2-chlorophenol; 2,4-DCP, 2,4-dichlorophenol; 2,6-BHMP, 2,6-bis(hydroxymethyl)-4-methylphenol; 3-AP, 3-aminophenol; 4-AP, 4-aminophenol; 4-BP, 4-bromophenol; 4-C-2-NP, 4-chloro-2-nitrophenol; 4-HBP, 4-hydroxybiphenyl; 4,4'-BP, 4,4'-dihydroxybiphenyl; BG, brilliant green; BET, Brunauer–Emmett–Teller; BP, bromocresol purple sodium salt; BPA, bisphenol A; BPB, bisphenol B; CDP, cyclodextrin material obtained without template; CR, Congo red; CV, crystal violet; DI-CDP, the cyclodextrin material obtained against the diphenylmethane template; DMF, dimethylformamide; DPM, diphenylmethane; EB, eriochrome black T; HA, humic acids; HMDI, hexamethylene diisocyanate; KBr, potassium bromide; MB, methylene blue; MG, malachite green; RME, removal efficiency; SEM, scanning electron microscope; TB, toluidine blue; TPM, triphenylmethane; TRI-CDP, the cyclodextrin material obtained against the triphenylmethane template

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SUPPORTING INFORMATION

Efficient Water Pollutants Targeting: Novel Materials with Molecular Imprints for Textile Industry Use

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S1. Materials characterization and adsorption characterization methods

The final form of each adsorbent was obtained after drying the material in a moisture analyzer (MA50/1.R, Radwag, Poland) and grinding in a ball mill (Pulverisette 7 classic line, Fritsch, Poland). Fourier transform infrared (FT-IR) spectra were performed on a Thermo Nicolet iS10 (Thermo Fischer Scientific, Poland) using the KBr pellet method (spectral resolution was 4 cm^{-1} and the scanning range was from 400 to 4000 cm^{-1}). The specific surface area was measured by the Brunauer–Emmett–Teller (BET) method ¹. Pore size distribution (PSD) was measured using the classical Barrett–Joyner–Halenda (BJH) model ². Scanning electron microscopy (SEM) was studied on a Quanta FEG 250 (Thermo Fisher Scientific, Poland) scanning electron microscope operating at 10 kV . The elemental analyzer FLASH 2000 (Thermo Fisher Scientific, Poland) operating in the dynamic separation technique was used to measure the content of carbon, hydrogen, and nitrogen. The degree of substitution (DS) was estimated with respect to the monomeric unit (anhydroglucose) using elemental analysis ^{3,4}, FTIR spectroscopy ⁵ and additionally for systems containing β -CD, phenolphthalein complexation ^{6–8}. The swelling experiments determined cross-linking density (v_e) according to Flory–Rehner Theory ⁹. PZC was conducted according to the titration procedures described in previous papers ^{10–14}. The water regain analysis was determined in a manner typical for this type of material ¹⁵.

Determination of the β -CD content

The content of β -CD in the synthesized materials was determined by spectrophotometric titration using phenolphthalein as the calibrant. Samples were prepared by adding 10 mg of adsorption material (CDP, DI-CDP, TRI-CDP) to 5 mL of phenolphthalein solution ^{16,17}. The absorbance of these solutions was analyzed at 550 nm and compared with the standard curve, which was prepared as in previous studies ¹⁸. The amount of β -CD involved in complexation was calculated using the following equation:

$$\beta - \text{CD content} = \frac{VC_{\beta\text{-CD}}}{mM_{\beta\text{-CD}}} \quad (1)$$

where V (mL) is a sample solution volume, $C_{\beta\text{-CD}}$ is the concentration of $\beta\text{-CD}$ (mg mL⁻¹) calculated based on the standard curve, m (g) is the mass of the adsorption material, and $M_{\beta\text{-CD}}$ is the molecular weight of $\beta\text{-CD}$ (g mol⁻¹).

Water regain analysis

Water regain analysis can be used to investigate the hydrophilicity of a material. 100 mg of each material was dispersed in deionized water for 24 hours to reach the swelling equilibrium state. After that time, the wet polymer was drained through filter paper. The collected material was additionally blotted using dry filter paper and then weighed. These experiments were carried out 5 times. Next, the water regain was calculated by the following equation:

$$\text{Water regain} = \frac{W_w - W_d}{W_d} \quad (2)$$

where W_d (mg) and W_w (mg) represent the mass of material in dry and wet form, respectively.

Hydrophilic and Hydrophobic Characteristics of Materials

The assessment of hydrophilic and hydrophobic properties of the adsorbents was carried out through two experimental procedures. In the first one, approximately 300 mg of each material was placed in a 10 mL open glass vial and then sealed inside chambers containing either 200 mL of water or toluene. The setup was maintained at 25 °C for 24 hours. This procedure was repeated three times. The adsorption capacity of each solvent was evaluated based on the weight increase of the adsorbents. Furthermore, the hydrophobicity index (HI_{static}) was calculated by taking the ratio of the toluene uptake to the water uptake.

In the second method, a biphasic system of water and toluene was employed. Equal volumes (10 mL) of both liquids were transferred into beakers placed on magnetic stirrers. A single 30 mg portion of the adsorbent was then introduced, and the time it took to settle was recorded. Following a 2-minute rest period, the mixtures were stirred vigorously for 15 minutes. After stirring, the system was allowed to separate into distinct phases. The progress and outcome of the experiment were documented photographically.

Cross-linking density (v_e) according to Flory–Rehner Theory

To determine the cross-linking density (v_e) of the CDP, DI-CDP, TRI-CDP materials, swelling experiments were performed in distilled water at room temperature. The study was performed by immersing 300 mg of dry powder in deionized water (5 mL) and mixing it for 20 min. After 72h, the polymer volume fraction in the swollen state (v_2) was used in the Flory–Rehner equation ⁹.

$$v_e = -\frac{1}{V_1} \cdot \frac{\ln(1-v_2)+v_2+\chi v_2^2}{v_2^{1/3}-\frac{v_2}{2}} \quad (3)$$

where:

v_e – cross-linking density (mol cm⁻³),

V_1 – molar volume of water (18.01 cm³ mol⁻¹),

v_2 – polymer volume fraction in the swollen state,

χ – Flory-Huggins interaction parameter.

The Flory–Huggins interaction parameter (χ) between the polymer and water was assumed to be **0.473** for all materials, based on literature values for dextran ¹⁹.

Adsorption experiments

The adsorption performance of CDP, DI-CDP, and TRI-CDP has been tested by BPA, BPB, and CV as model organic pollutants. Batch adsorption experiments were performed in vials shaken on a centrifugal mixer at 700 rpm at room temperature. All samples were filtered through 0.22 μ m inorganic membrane filters. Residual concentrations of pollutants in water were determined by using UV–Vis spectrophotometer. The detection wavelengths of BPA, and BPB were 276 nm and 591 nm for CV. All experiments were repeated three times in parallel.

Adsorption kinetics

100 mg of CDP, DI-CDP, and TRI-CDP were added to 50 mL of shaken aqueous solutions of BPA, BPB, and CV with a concentration of 17.12, 18.17, and 10.20 mg L⁻¹, respectively. Then, samples were taken by a syringe at specific intervals. The removal efficiency of model pollutants was calculated by the following equation:

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (4)$$

where c_0 (mg L⁻¹) and c_t (mg L⁻¹) represent the initial and the residual concentrations of the pollutants in the initial solution and the filtrate at a certain time, individually. The adsorption capacity of pollutants by adsorbents was calculated by the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (5)$$

where q_t (mg g⁻¹) is the amount of pollutant adsorbed per gram of adsorbent at the given time, V (L) and m (g) are the volume of the pollutant solution and the mass of adsorbent, respectively.

Adsorption isotherms

The adsorbent (0.2 g L⁻¹) was added into BPA, BPB, and CV solution (with initial concentrations ranging from: 0.57 to 28.54 mg L⁻¹; 0.61 to 30.29 mg L⁻¹; 2.04 to 407.98 mg L⁻¹, respectively) and was shaken on a digital vortex mixer at 700 rpm at 25 °C for 20 min. The supernatant was then sampled and filtered. The equilibrium adsorption concentration of each of them was determined. Langmuir, Freundlich, Harkins-Jura, Jovanovic-Monolayer, Temkin, Hill, Jovanovic-Multilayer, Redlich-Peterson, Sips, and Toth models were used to fit adsorption isotherms (Table S10).

Thermodynamic analysis

The following equations were used to determine the key thermodynamic parameters ²⁰:

$$\ln(K_e^0) = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (6)$$

$$\Delta G^0 = -RT \ln(K_e^0) \quad (7)$$

$$K_e^0 = \frac{KM_a C_a^0}{\gamma} \quad (8)$$

where ΔH^0 , ΔS^0 , ΔG^0 are standard enthalpy, entropy, and free energy, and K_e^0 is a dimensionless thermodynamic equilibrium constant, which is calculated from the best isotherm fitted K (L g⁻¹), M_a and C_a^0 are molecular weight and standard concentration of the adsorbate (1 M), and γ is the coefficient of activity, respectively.

Effects of the dosage of the adsorbent, pH, humic acid, and salts

The effect of adsorbent dosage was studied by the addition of the adsorbent ($0.2 - 2 \text{ g L}^{-1}$) to the BPA, BPB, and CV solutions (17.12 , 18.17 , and 10.20 mg L^{-1} , respectively) and shaken on a digital vortex mixer at 700 rpm at 25°C for 20 min . Then the supernatant liquid was sampled and filtered. The adsorption equilibrium concentration of each sample was measured spectrophotometrically. The influence of ionic strength was investigated analogously, using pollutants solutions enriched with appropriate salts, humic, and fulvic acids, and the pH was adjusted to the appropriate value in the range from 2 to 11 with 0.1 N HCl and 0.1 N NaOH .

Adsorption selectivity

To determine the rivalry between individual pollutants during adsorption, mixtures of bisphenols and crystal violet (initial concentration of pollutant was $2.5 \cdot 10^{-5} \text{ mol L}^{-1}$). The adsorbent concentration 0.2 g L^{-1} was used. The mixtures were shaken on a digital vortex mixer at 700 rpm at 25°C for 20 min . The supernatant was then sampled and filtered. The Removal Efficiency Parameter (RME) of each sample of the binary or ternary mixture was measured and compared to the RME value of the single-component mixture.

Textile industry effluents prototype application

To determine the quality of work of adsorbents in water from the textile industry, bisphenols and crystal violet and their mixtures were used as model pollutants (the initial concentration of the pollutant was $2.5 \cdot 10^{-5} \text{ mol L}^{-1}$, adsorbent concentration 0.2 g L^{-1}). To obtain a prototype of textile sewage after pre-treatment, solutions with the following parameters were prepared:

pH	-	6	
BOD	-	180	
COD	-	200	
Total alkalinity	-	500	(mg L^{-1})
Total Kjeldahl nitrogen	-	75	(mg L^{-1})
Sulfides	-	5	(mg L^{-1})
Sulfates	-	398	(mg L^{-1})

Chloride	-	35	(mg L ⁻¹)
Potassium	-	30	(mg L ⁻¹)
Sodium	-	5	(mg L ⁻¹)
Zinc	-	3	(mg L ⁻¹)
Coppe	-	2	(mg L ⁻¹)
Chromium	-	2	(mg L ⁻¹)
Nickel	-	1	(mg L ⁻¹)

The characteristics of the textile sewage water prototype after initial treatment were developed based on literature data ²¹.

The mixtures were shaken on a digital vortex mixer at 700 rpm. at 25°C for 20 minutes. A sample of the supernatant was then taken and filtered. The removal efficiency (RME) parameter of each binary or three-component mixture sample was measured and compared to the RME of the single-component mixture.

Environmental applications

Due to the coexistence of various other phenols and dyes (Figure S1 and S2) in the water environment along with BPA, BPB, and CV, the effectiveness of their removal by prepared adsorbents was tested ^{22,23}. For this purpose, adsorbents (2 g L⁻¹) were added to the prepared solutions of dyes or phenols (2.5·10⁻⁵ M). The mixtures were placed on a shaker for 20 min (700 rpm). The residual concentration of model compounds was tested spectrophotometrically at appropriate wavelengths. In addition, the possibility of using the obtained CDP, DI-CDP, and TRI-CDP materials in real samples was recognized. Water was collected from the Vistula (the main river of Poland), as there have been reports of these harmful chemicals in the past ²⁴. The procedure described above was followed, but BPA, BPB, and CV solutions were prepared based on samples collected from the Vistula River (Mikoszewo). The concentrations of the solutions were as follows for BPA 17.12 mg L⁻¹, BPB 18.17 mg L⁻¹, and for CV 10.20 mg L⁻¹. The characteristics of waters from the Vistula River are presented in Table S1.

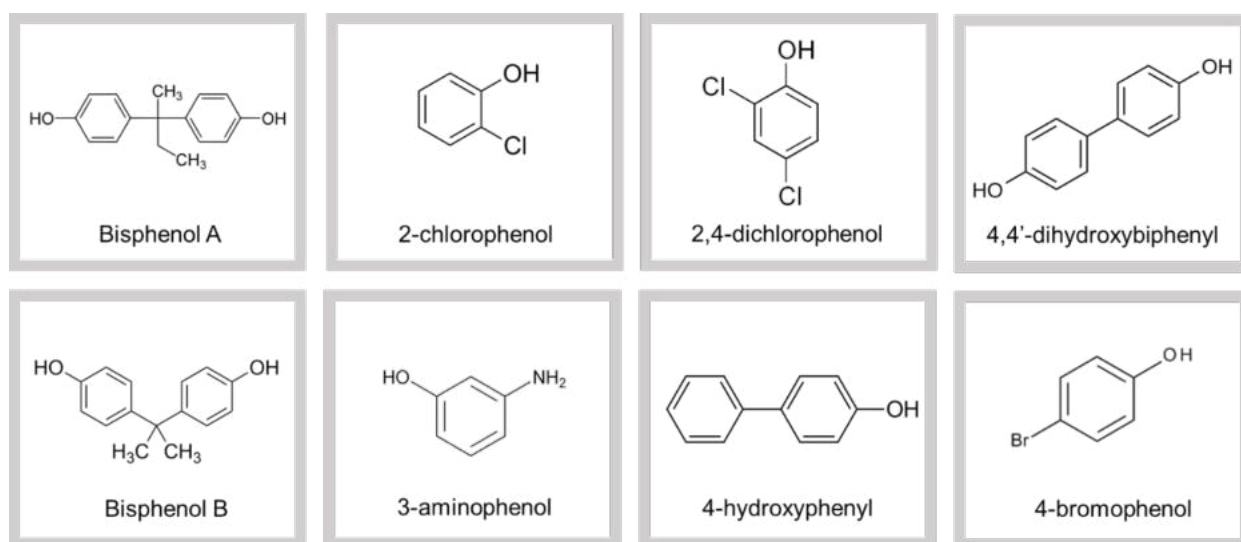


Figure S1. Chemical structures of phenolic compounds tested in the adsorption study described in Section 3.2.9 of the Manuscript.

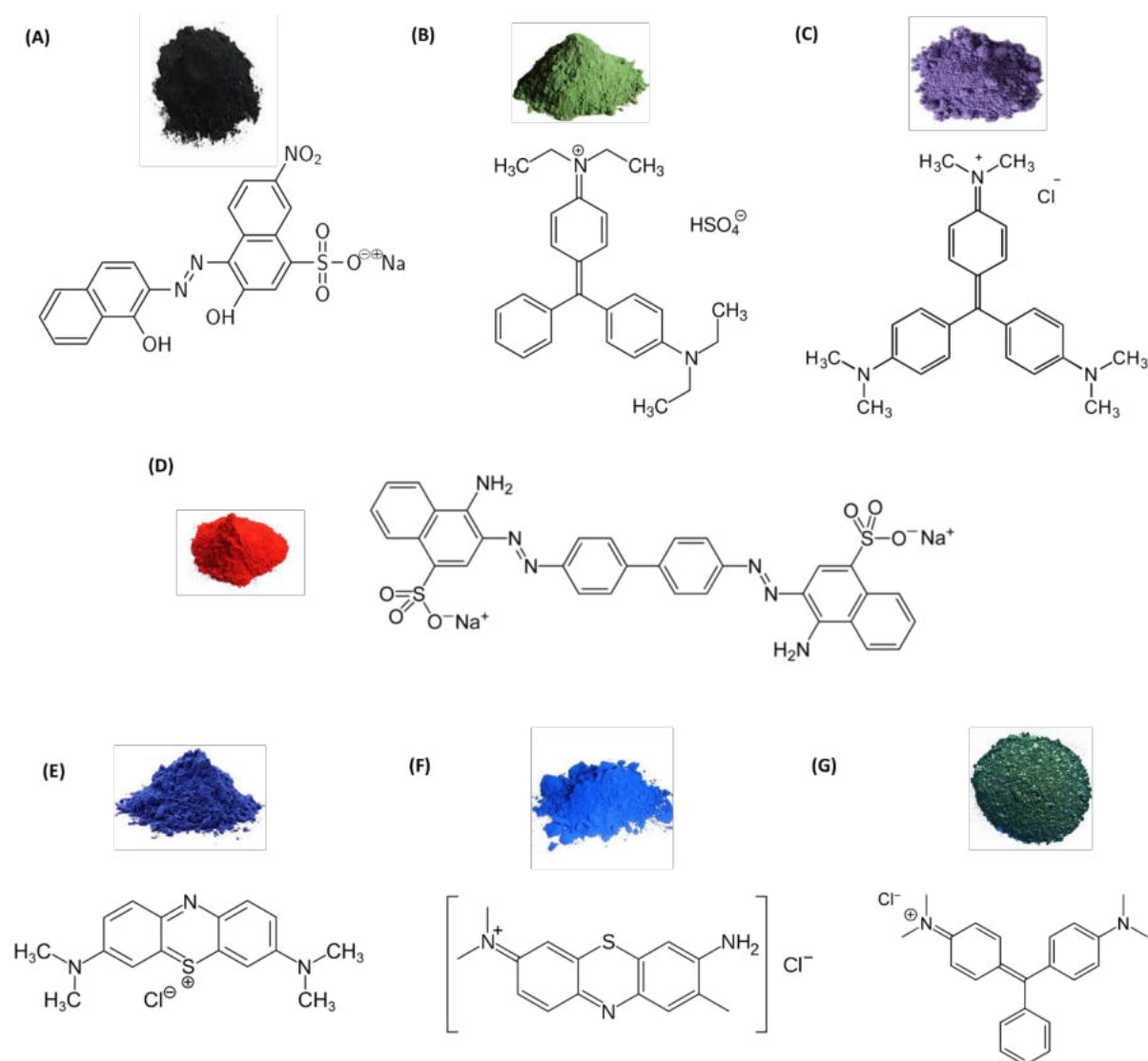


Figure S2. Chemical structures of dyes used in the adsorption experiments presented in Section 3.2.9 of the Manuscript: (A) Eriochrome Black T, (B) Brilliant Green, (C) Crystal Violet, (D) Congo Red, (E) Methylene Blue, (F) Toluidine Blue, (G) Malachite Green.

Table S1. The characteristics of waters from the Vistula River.

Parameter	Vistula River
pH	8.45
Salinity (psu)	2.40
Total nitrogen ($\mu\text{mol L}^{-1}$)	225.00
$\text{NH}_4\text{-N}$ ($\mu\text{mol L}^{-1}$)	4.90
Total phosphorus ($\mu\text{mol L}^{-1}$)	8.35
Biochemical oxygen demand (BOD_5) ($\text{mg O}_2 \text{ L}^{-1}$)	9.70
Chemical oxygen demand (COD) ($\text{mg O}_2 \text{ L}^{-1}$)	12.15

Regeneration

100 mg of material was added to the vial containing 50 mL of the BPA, BPB, and CV solutions (17.12, 18.17, and 10.20 mg L^{-1}). The mixtures were shaken in a digital vortex mixer at 700 rpm (25°C, 20 min). After five minutes, the solution was decanted from the surface of the precipitate, and in its place, 20 mL of bioethanol was added, soaking for 20 minutes. The procedure was repeated until no BPA, BPB, or CV were found in the filtrate, and finally, the precipitate was washed with distilled water (20 mL). The adsorption-desorption experiment was performed five times.

S2. Materials characterization results

FTIR spectrum of CDP, DI-CDP, TRI-CDP

FTIR (CDP) cm^{-1} : 3423 ($\nu_{\text{O-H}}$), 2933, 2860 ($\nu_{\text{C-H}}$), 1718 ($\nu_{\text{C=O}}$), 1653 ($\delta_{\text{H-O-H}}$), 1541 ($\delta_{\text{C-N-H}}$), 1458 ($\delta_{\text{C-H}}$), 1411 ($\delta_{\text{C-H}}$), 1364 ($\delta_{\text{C-H}}$), 1263 ($\delta_{\text{C-H}}$), 1137 ($\delta_{\text{O-H}}$), 1026 ($\nu_{\text{C-O}}$)

FTIR (DI-CDP) cm^{-1} : 3423 ($\nu_{\text{O-H}}$), 2929, 2858 ($\nu_{\text{C-H}}$), 1720 ($\nu_{\text{C=O}}$), 1684 ($\delta_{\text{H-O-H}}$), 1544 ($\delta_{\text{C-N-H}}$), 1458 ($\delta_{\text{C-H}}$), 1411 ($\delta_{\text{C-H}}$), 1383 ($\delta_{\text{C-H}}$), 1259 ($\delta_{\text{C-H}}$), 1155 ($\delta_{\text{O-H}}$), 1024 ($\nu_{\text{C-O}}$)

FTIR (TRI-CDP) cm^{-1} : 3423 ($\nu_{\text{O-H}}$), 2923, 2856 ($\nu_{\text{C-H}}$), 1712 ($\nu_{\text{C=O}}$), 1655 ($\delta_{\text{H-O-H}}$), 1551 ($\delta_{\text{C-N-H}}$), 1460 ($\delta_{\text{C-H}}$), 1410 ($\delta_{\text{C-H}}$), 1384 ($\delta_{\text{C-H}}$), 1259 ($\delta_{\text{C-H}}$), 1150 ($\delta_{\text{O-H}}$), 1022 ($\nu_{\text{C-O}}$)

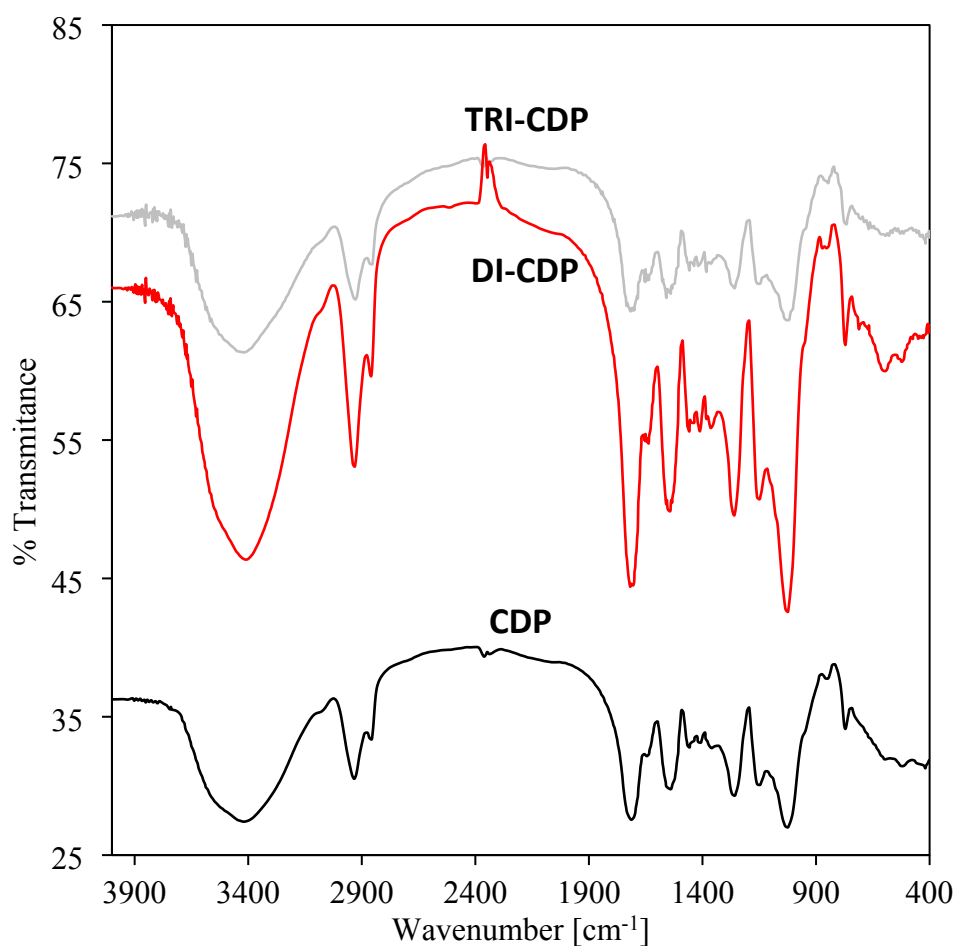


Figure S3. FTIR spectra of investigated materials CDP, DI-CDP, and TRI-CDP.

Determination of β -CD content in the materials

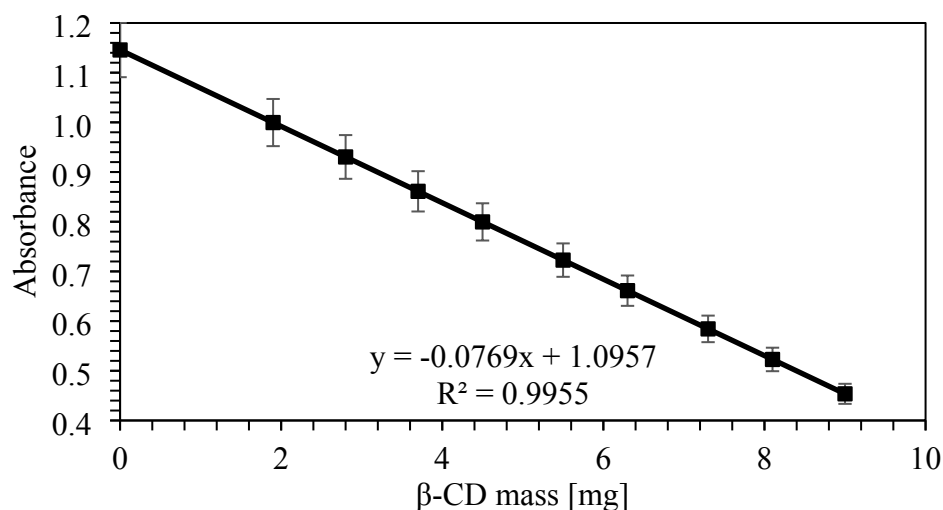


Figure S4. Spontaneous decrease in absorbance of phenolphthalein solution ($\lambda = 550$ nm).

Table S2. Elemental analysis results for tested materials.

Sample	Elemental content (wt.%)				β -CD content	
	C (% $\pm$	H (% $\pm$	N (% $\pm$	O (% $\pm$	(wt.%) $\pm$	(mmol/g) $\pm$
	SD)	SD)	SD)	SD)	SD	SD
CDP	48.26 $\pm$	7.51 $\pm$	6.94 $\pm$	37.29 $\pm$	27.14 $\pm$	2.83 $\pm$ 0.07
(C ₃₀₀ H ₅₅₆ N ₃₇ O ₁₇₄)	0.23	0.08	0.06	0.28	0.15	
DI-CDP	48.53 $\pm$	7.37 $\pm$	7.35 $\pm$	36.75 $\pm$	39.33 $\pm$	4.03 $\pm$ 0.06
(C ₂₈₅ H ₅₁₆ N ₃₇ O ₁₆₂)	0.21	0.06	0.04	0.18	0.12	
TRI-CDP	48.57 $\pm$	7.43 $\pm$	7.41 $\pm$	36.59 $\pm$	45.24 $\pm$	4.57 $\pm$ 0.04
(C ₂₈₃ H ₅₁₆ N ₃₇ O ₁₆₀)	0.19	0.05	0.05	0.20	0.10	

Table S3. Other physical and chemical properties of the obtained adsorbents.

Material	CDP	DI-CDP	TRI-CDP
----------	-----	--------	---------

The degree of substitution			
DS (C%)	0.8994	0.9092	0.9107
DS (N%)	0.9749	0.9742	0.9741
DS (FTIR)	0.9512	0.9710	0.9859
The cross-linking density			
v_e [mol cm ⁻³]	0.0436	0.0307	0.0228
Network tightness	Rigid	Flexible	Loose
Temperature			
Loss of surface water [°C]	101.3	100.9	101.6
The onset of intense thermal decomposition [°C]	302.5	321.8	318.2

Water regain, pore size, pore volume, and surface area of CDP, DI-CDP, TRI-CDP

Table S4. Water regain, pore volume, and surface area of CDP, DI-CDP, TRI-CDP.

Sample	H ₂ O	Dry	Dry pore	S _{BET} ^[3]	S _{Langmuir} ^[4]	S _{BJH-}	S _{BJH-}	S _{t-Plot}
	regain	pore	volume ^[2]	(m ² g ⁻¹)	(m ² g ⁻¹)	adsorption	desorption	(m ²
	(wt%)	size ^[1]	(cm ³ g ⁻¹)	¹)		(m ² g ⁻¹)	(m ² g ⁻¹)	g ⁻¹)
		(nm)						
CDP	113	13.91	0.004	1.52	2.32	1.14	1.29	2.17
DI-CDP	124	10.82	0.004	1.92	3.19	1.42	0.93	3.05
TRI-CDP	174	10.08	0.002	1.43	2.18	1.57	0.94	2.09

[1] BJH adsorption average pore diameter (4V/A).

[2] BJH adsorption cumulative volume of pores between 1.7 nm and 300 nm in diameter.

[3] BET surface area obtained from N₂ adsorption-desorption isotherms.

[4] Langmuir Surface Area from N₂ adsorption-desorption isotherms.

Specific surface area and pore size distribution

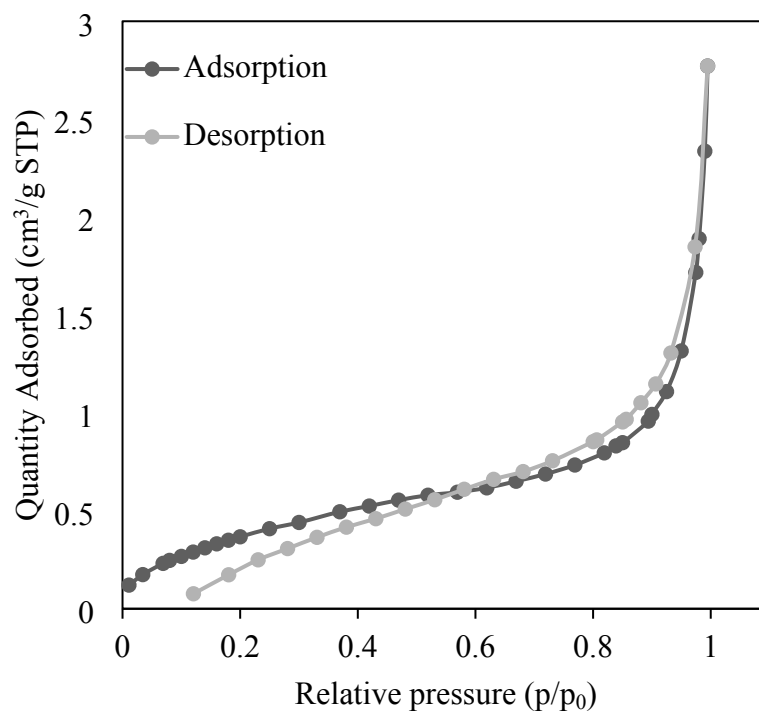


Figure S5. N₂ adsorption-desorption isotherms for CDP.

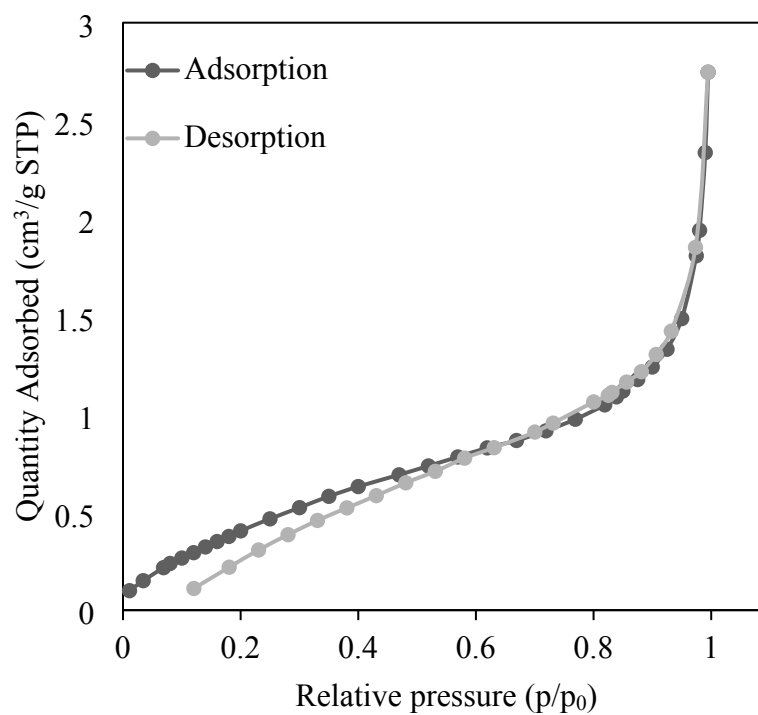


Figure S6. N₂ adsorption-desorption isotherms for DI-CDP.

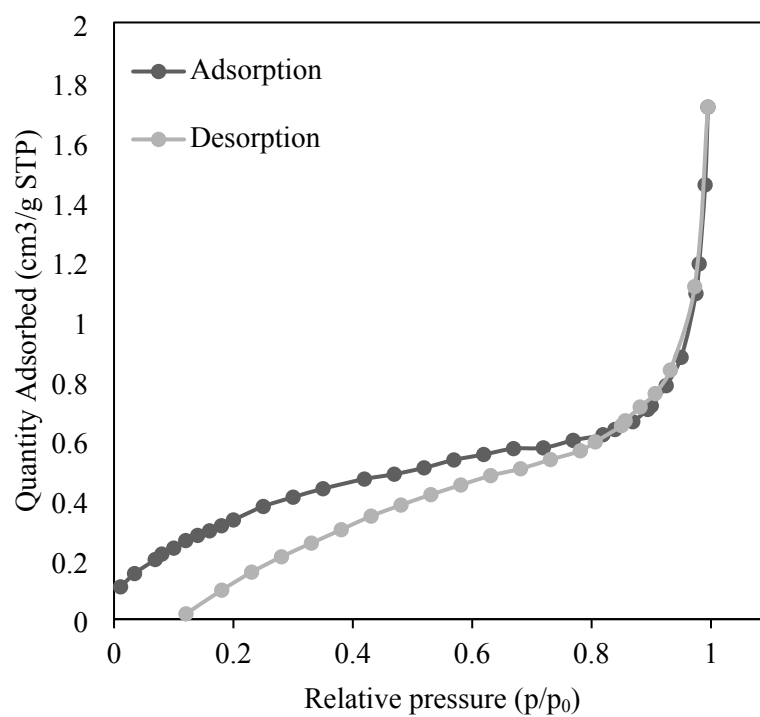


Figure S7. N₂ adsorption-desorption isotherms for TRI-CDP.

Table S5. BET and Langmuir Surface Area Report for CDP, DI-CDP, and TRI-CDP.

Parameters	BET			Langmuir		
	CDP	DI-CDP	TRI-CDP	CDP	DI-CDP	TRI-CDP
Surface Area	1.5248 ± 0.0154 m ² /g	1.9192 ± 0.0402 m ² /g	1.4299 ± 0.0201 m ² /g	2.3222 ± 0.0906 m ² /g	3.1935 ± 0.1844 m ² /g	2.1767 ± 0.0672 m ² /g
Slope	2.715719 ± 0.028422 g/cm ³ STP	2.059881 ± 0.046965 g/cm ³ STP	2.867956 ± 0.042236 g/cm ³ STP	1.874564 ± 0.073130 g/cm ³ STP	1.363162 ± 0.078729 g/cm ³ STP	1.999914 ± 0.061737 g/cm ³ STP
Y-Intercept	0.139220 ± 0.004400 g/cm ³ STP	0.208373 ± 0.007270 g/cm ³ STP	0.176425 ± 0.006538 g/cm ³ STP	136.075229 ± 7.671264 mmHg·g/cm ³ STP	177.117869 ± 8.255004 mmHg·g/cm ³ STP	161.516106 ± 6.470180 mmHg·g/cm ³ STP
C or b	20.506658 1/mmHg	10.885568 1/mmHg	17.255921 1/mmHg	0.013776 1/mmHg	0.007696 1/mmHg	0.012382 1/mmHg
Qm	0.3503 cm ³ /g STP	0.4409 cm ³ /g STP	0.3285 cm ³ /g STP	0.5335 cm ³ /g STP	0.7336 cm ³ /g STP	0.5000 cm ³ /g STP

Correlation Coefficient	0.9996169	0.9981855	0.9992418	0.995465	0.990141	0.997153
Molecular Cross- Sectional Area	0.1620 nm ²					

Table S6. Porous property of CDP.

Average Diameter (Å)	Cumulative Pore Volume (cm ³ /g)	Cumulative Pore Area (m ² /g)
2302.611826	0.000702568	0.012204718
1185.898706	0.001434902	0.036906108
857.7464707	0.001717429	0.050081428
472.6091485	0.002391926	0.107168526
306.2575718	0.002741454	0.152819966
224.4232005	0.002935662	0.187434617
194.8360125	0.002994831	0.19958209
151.9759707	0.003174903	0.246976962
128.9840164	0.003199504	0.254606155
116.7857901	0.003257965	0.274629617
95.06005524	0.003356183	0.315958103
76.12303248	0.003428036	0.353714415
62.98957569	0.003484075	0.389300812
53.31266575	0.003537655	0.42950097
45.84594055	0.003566375	0.454559202
39.87008617	0.003580444	0.468673772
34.95205815	0.003621328	0.51546313
30.8118573	0.00367668	0.587320602
27.24016149	0.00372919	0.664427478
23.3881677	0.003840735	0.855198685
20.2512892	0.003895695	0.96375483
17.73544087	0.003975114	1.142874143

Table S7. Porous property of DI-CDP.

Average Diameter (Å)	Cumulative Pore Volume (cm ³ /g)	Cumulative Pore Area (m ² /g)
2297.4321	0.000662886	0.011541329
1183.1586	0.001311711	0.033476696
857.38244	0.001524022	0.043381794
472.6433	0.002060577	0.088790644
305.77175	0.002320889	0.122843737
223.29262	0.002469569	0.149477841
175.44275	0.00257477	0.173463149
144.01168	0.002673368	0.200849254
128.10524	0.002726256	0.217363182
115.98101	0.002796685	0.241652842
94.281794	0.002920507	0.294185831
75.364406	0.003021196	0.347626827
62.22263	0.00310434	0.401075963
52.548028	0.003164803	0.447100861
45.087741	0.003247832	0.520761057
39.113148	0.003331366	0.606188804
34.198414	0.003414485	0.70340851
29.155479	0.003522503	0.851605202
25.220193	0.003616121	1.000085413
22.218147	0.003728033	1.201564339
19.496781	0.003832894	1.416699419

Table S8. Porous property of TRI-CDP.

Average Diameter (Å)	Cumulative Pore Volume (cm ³ /g)	Cumulative Pore Area (m ² /g)
2348.1897	0.000421058	0.007172463
1185.7801	0.00085412	0.021780981
862.47773	0.001017629	0.0293642
474.10933	0.00137464	0.05948476
306.40896	0.001531384	0.079946857
223.9864	0.001643888	0.100038129
194.3784	0.001664254	0.104228978
167.01879	0.001732268	0.120517988
135.41377	0.00177183	0.132204369
116.25642	0.001799639	0.14177231
94.519693	0.00182268	0.151523345
75.571799	0.001862734	0.172723483
53.378746	0.001897458	0.198744519
45.903958	0.001929913	0.227025407
39.928125	0.001983875	0.281084753
35.014542	0.002025054	0.32812649
30.86818	0.002053287	0.364712574
26.507096	0.002119004	0.463880661
23.028604	0.002179282	0.568582776
20.309369	0.00224532	0.69864669
17.793035	0.002349033	0.931800222

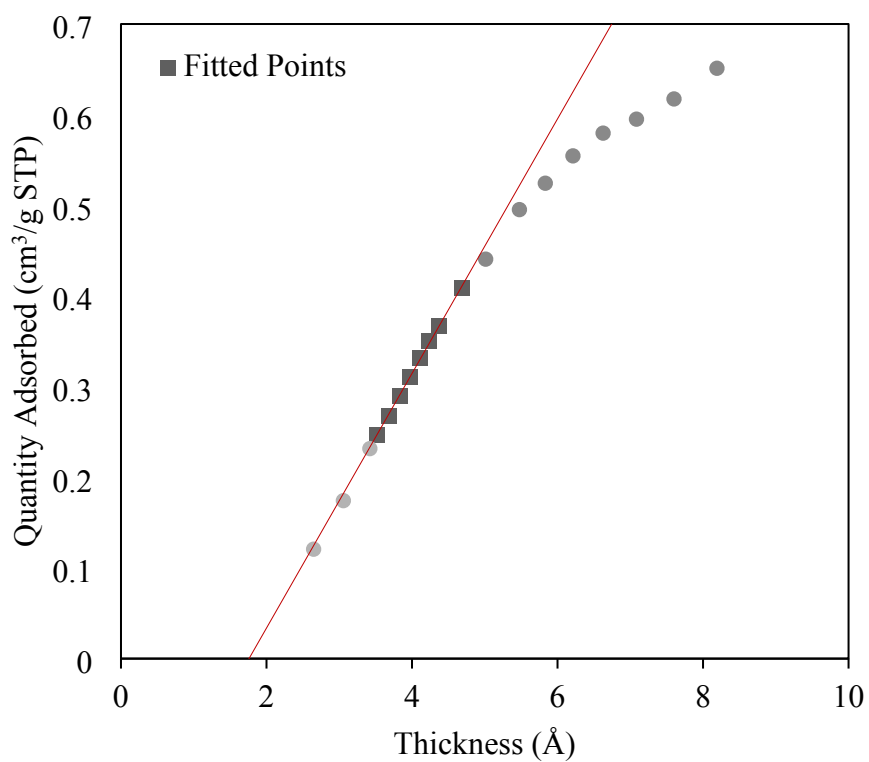


Figure S8. Harkins and Jura t-Plot for CDP.

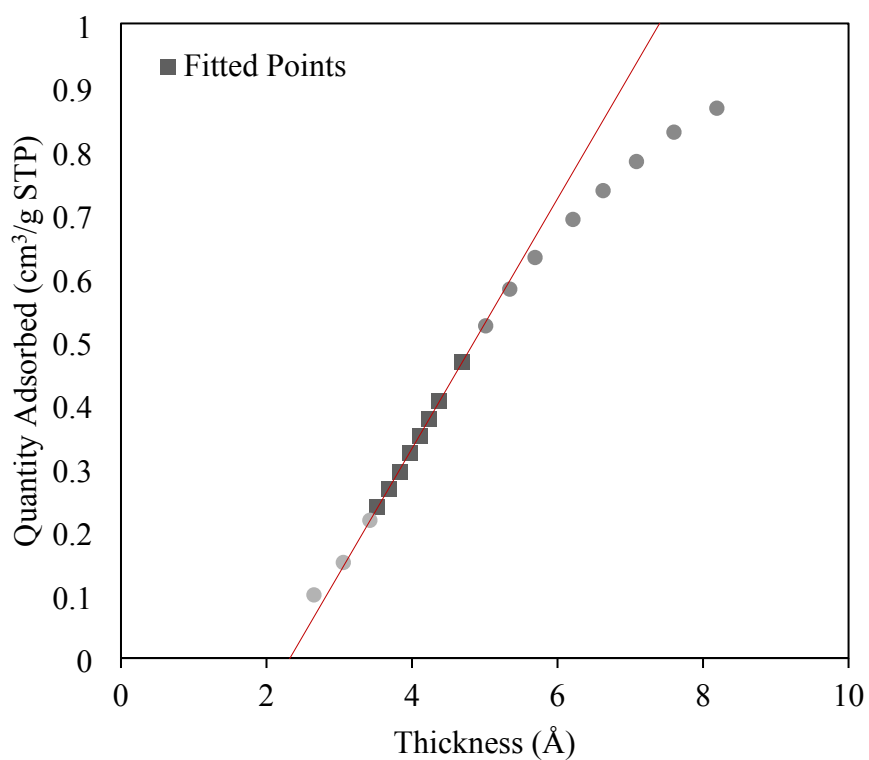


Figure S9. Harkins and Jura t-Plot for DI-CDP.

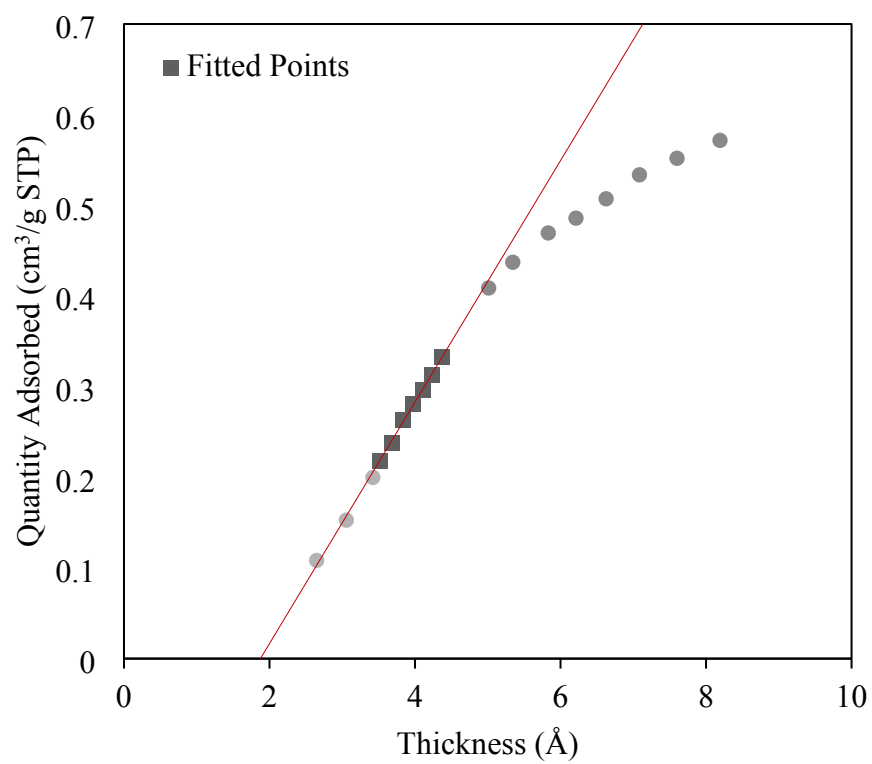


Figure S10. Harkins and Jura t-Plot for TRI-CDP.

Table S9. t-Plot Report for CDP, DI-CDP, and TRI-CDP.

Parameter	CDP	DI-CDP	TRI-CDP
Micropore Volume	-0.000382 cm ³ /g	-0.000707 cm ³ /g	-0.000397 cm ³ /g
Micropore Area	*	*	*
External Surface Area	2.1719 m ² /g	3.0452 m ² /g	2.0880 m ² /g
Slope	0.140411 ± 0.001852 cm ³ /g·Å STP	0.196873 ± 0.002069 cm ³ /g·Å STP	0.134986 ± 0.002083 cm ³ /g·Å STP
Y-Intercept	-0.247111 ± 0.007531 cm ³ /g STP	-0.457344 ± 0.008412 cm ³ /g STP	-0.256705 ± 0.008468 cm ³ /g STP
Correlation Coefficient	0.999478	0.999669	0.999286
Surface Area Correction Factor	1.000	1.000	1.000
Density Conversion Factor	0.0015468	0.0015468	0.0015468
Total Surface Area (BET)	1.5248 m ² /g	1.9192 m ² /g	1.4299 m ² /g
Thickness Range		3.5000 Å to 5.0000 Å	
Thickness Equation		Harkins and Jura	

*The micropore area is not reported because either the micropore volume is negative or the calculated external surface area is larger than the total surface area.

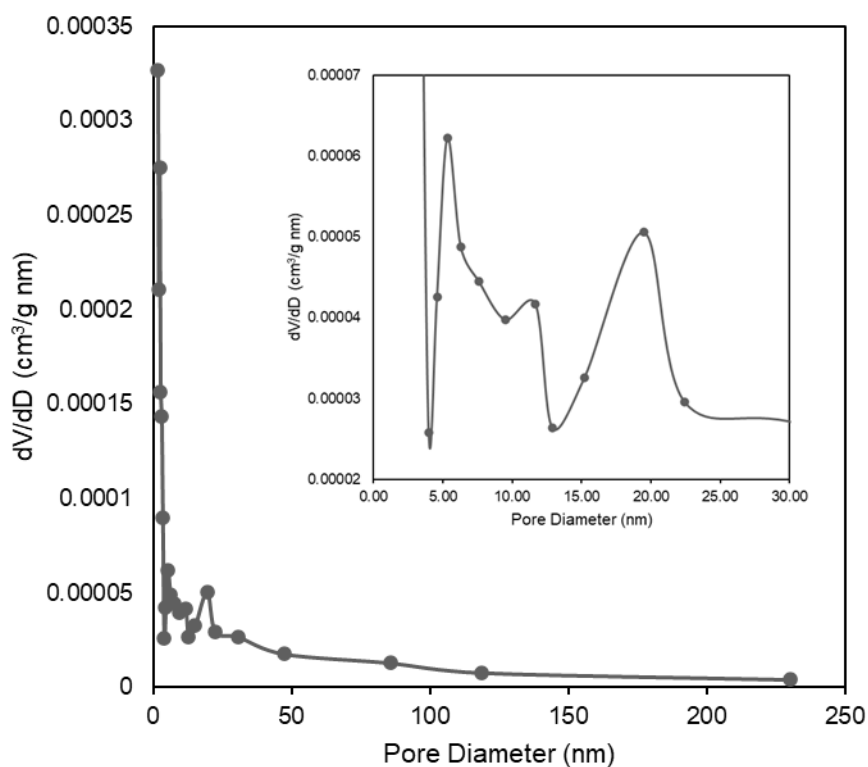


Figure S11. Barrett-Joyner-Halenda (BJH) pore size distribution from N_2 adsorption isotherm expressed as pore volume for CDP.

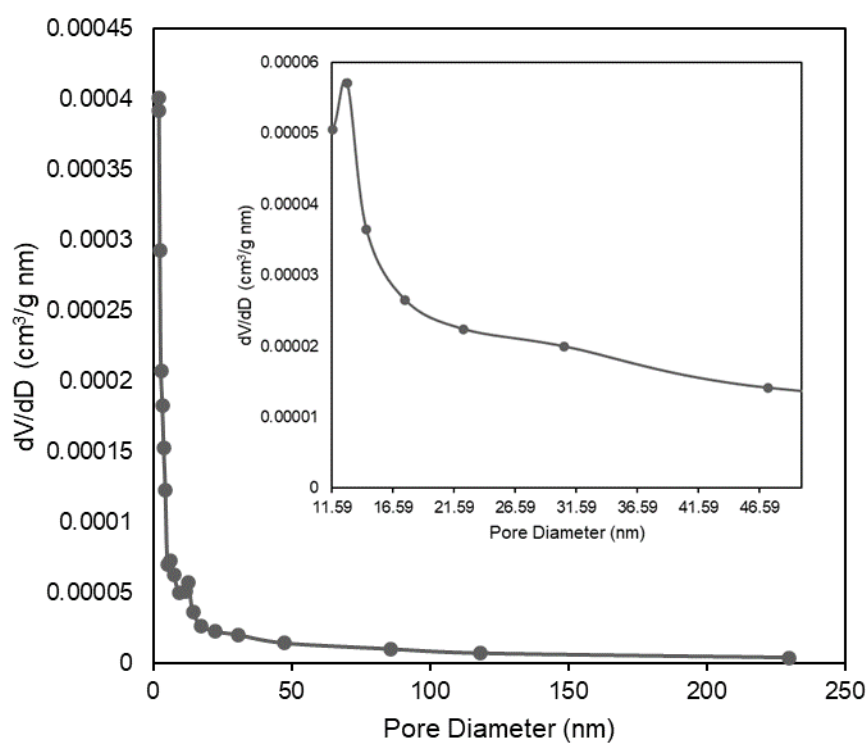


Figure S12. Barrett-Joyner-Halenda (BJH) pore size distribution from N₂ adsorption isotherm expressed as pore volume for DI-CDP.

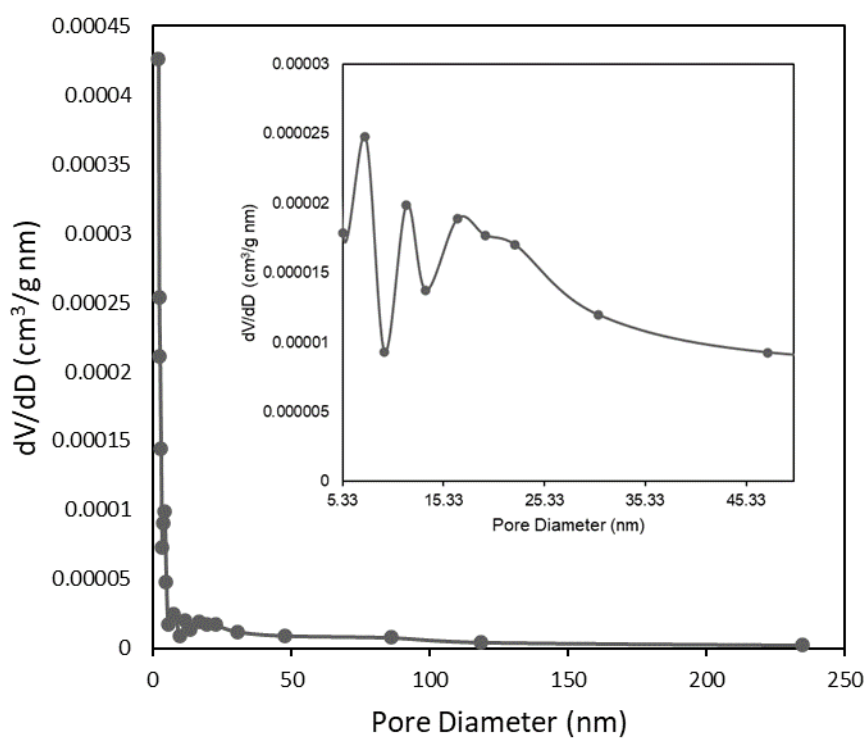


Figure S13. Barrett-Joyner-Halenda (BJH) pore size distribution from N₂ adsorption isotherm expressed as pore volume for TRI-CDP.

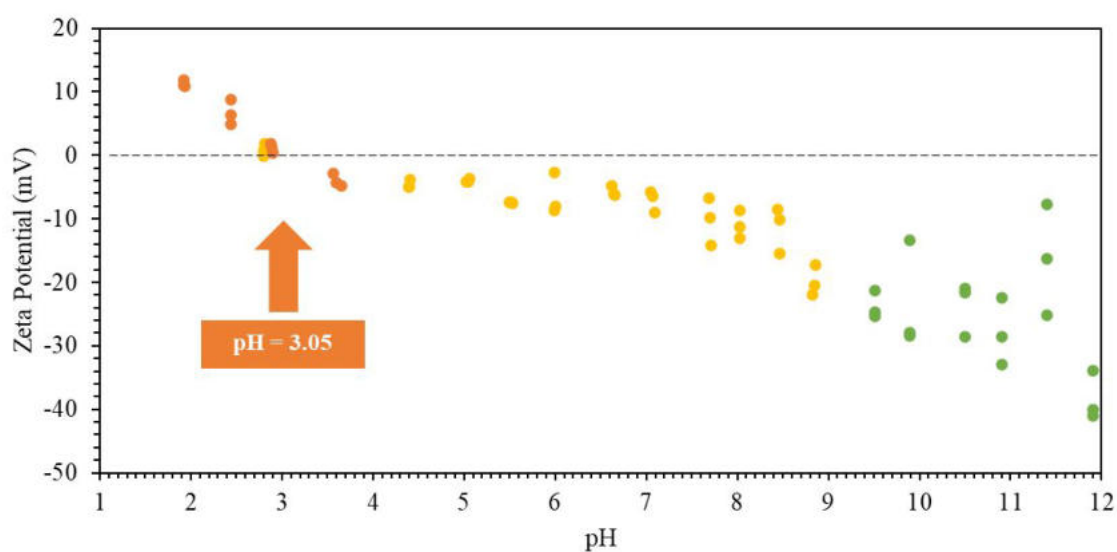


Figure S14. Potential Zeta plot of DI-CDP depending on the pH.

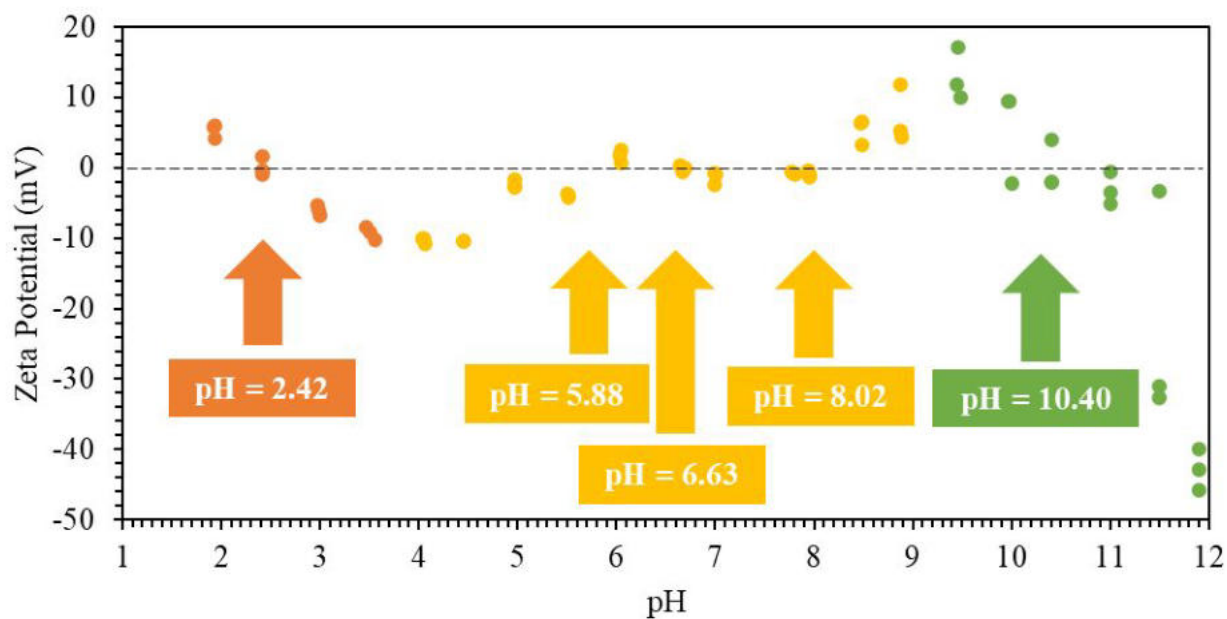


Figure S15. Potential Zeta plot of TRI-CDP depending on the pH.

Thermogravimetric Analysis of CDP, DI-CDP, TRI-CDP

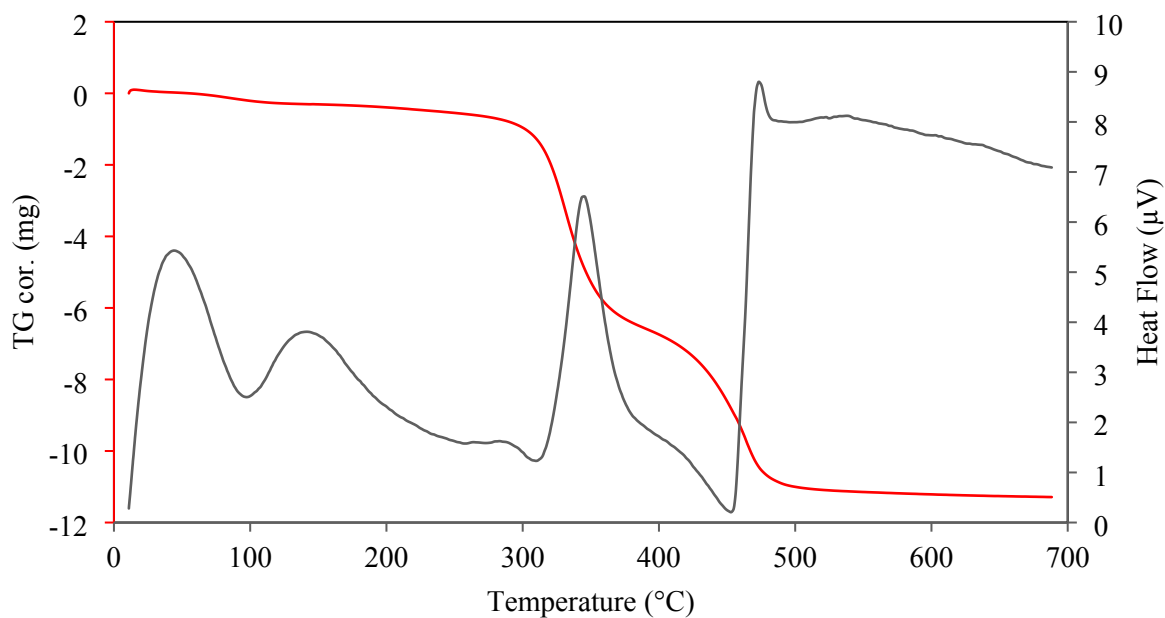


Figure S16. Thermogravimetric analysis of CDP under nitrogen atmosphere.

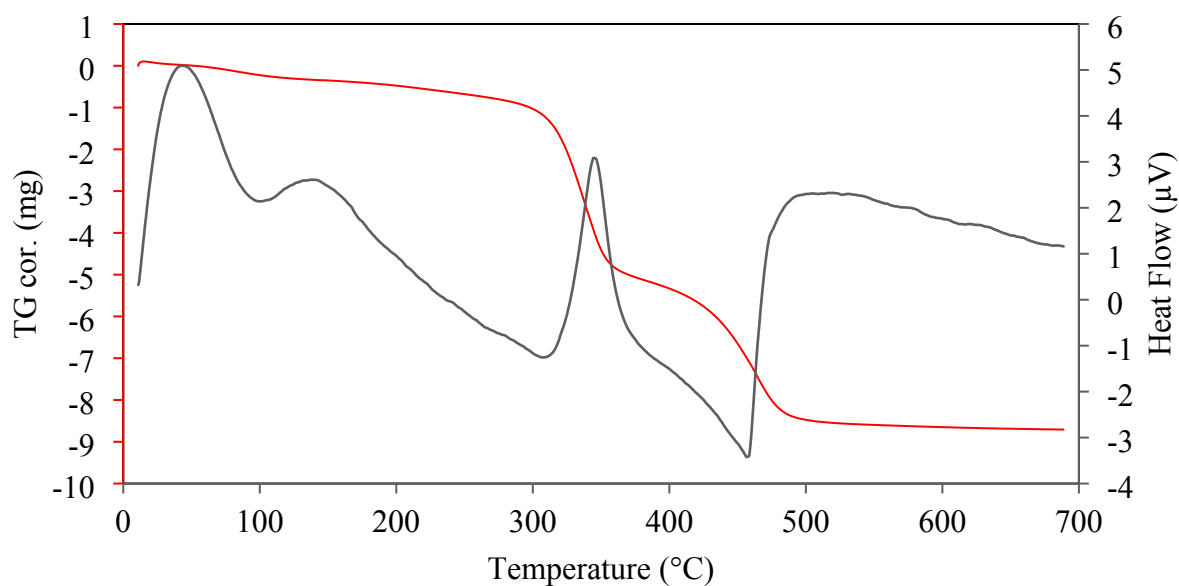


Figure S17. Thermogravimetric analysis of DI-CDP under nitrogen atmosphere.

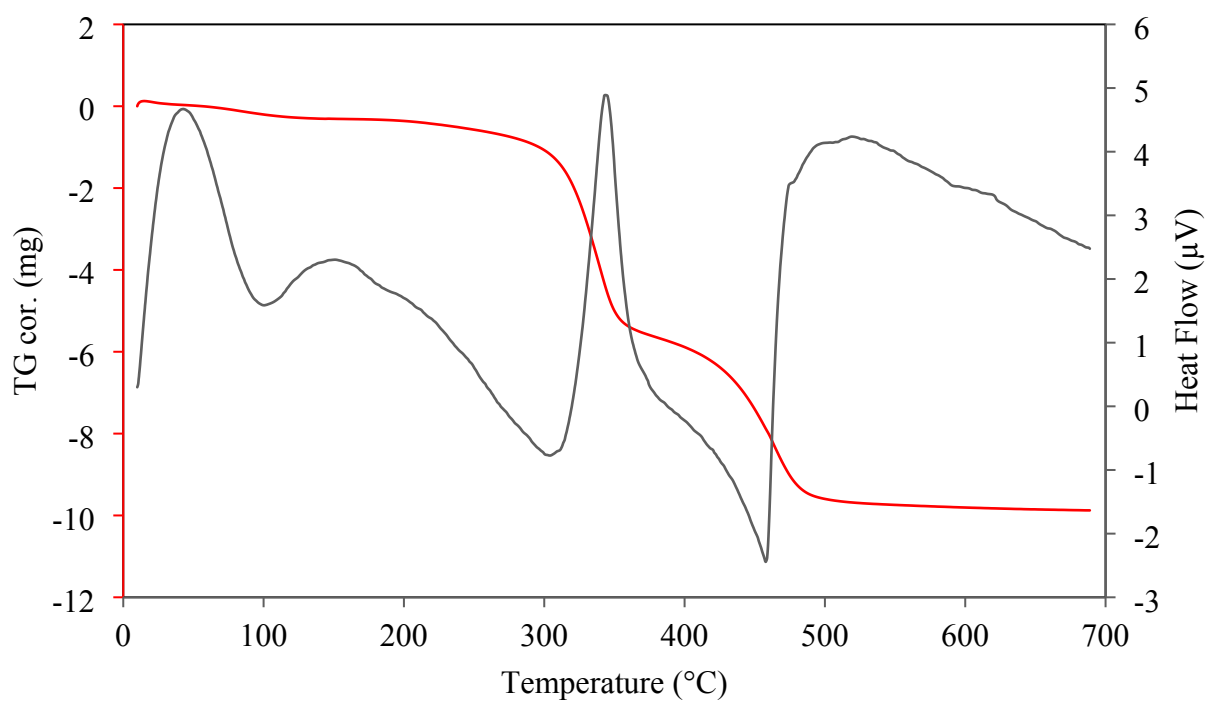


Figure S18. Thermogravimetric analysis of TRI-CDP under nitrogen atmosphere.

S3. Adsorption characterization results

Adsorption kinetics

Table S10. Parameters obtained from kinetics models fitted to experimental data.

Material	CDP			DI-CDP			TRI-CDP		
Pollutant	BPA	BPB	CV	BPA	BPB	CV	BPA	BPB	CV
Pseudo-first order									
Equation	$\ln(q_e - q_t) = \ln q_e - k_1 t$								
q _l (mg g ⁻¹)	4.97	5.19	4.91	2.00	2.28	4.87	6.58	7.09	4.75
k ₁ (min ⁻¹)	0.18	0.23	28.10	0.98	1.32	3.53	2.19	2.64	5.03
R Pearson	0.9596	0.9373	0.9923	0.9038	0.9273	0.9983	0.9822	0.9933	0.9971
R ²	0.9025	0.8477	0.9846	0.8164	0.8599	0.9965	0.9647	0.9867	0.9941
Adj. R ²	0.8830	0.8172	0.9816	0.7797	0.8318	0.9958	0.9576	0.984	0.993
SQE	2.8984	4.6455	0.3476	0.8504	0.7881	0.0758	1.4514	0.6212	0.1229
RMSE	0.4722	0.5978	0.1635	0.2558	0.2462	0.0764	0.3341	0.2186	0.0972
Marquardt (%)	20	22	4130	33	62	489	405	534	691

MSE	0.2230	0.3573	0.0267	0.0654	0.0606	0.0058	0.1116	0.0478	0.0095
Hybrid	9.3137	13.3112	0.6718	4.2426	3.3846	0.1471	2.0671	0.8036	0.2416
χ^2	1.8017	3.1656	0.0731	0.4402	0.349	0.0156	0.2208	0.0877	0.0259
Pseudo-second order									
Equation	$\frac{t}{q_t} = \frac{1}{K_2} q_e^2 + \frac{t}{q_e}$								
q ₂ (mg g ⁻¹)	5.59	5.63	4.91	2.16	2.41	4.88	6.72	7.17	4.76
k ₂ (g min ⁻¹ mg ⁻¹)	0.05	0.07	9451.56	0.48	0.68	6.82	0.73	1.21	15.84
R Pearson	0.9829	0.9625	0.9923	0.9485	0.957	0.9982	0.9889	0.9957	0.9971
R ²	0.9627	0.9221	0.9846	0.8990	0.9157	0.9965	0.9779	0.9913	0.9943
Adj. R ²	0.9552	0.9065	0.9815	0.8788	0.8988	0.9958	0.9735	0.9896	0.9931
SQE	1.1105	2.3769	0.3476	0.468	0.4744	0.0772	0.9074	0.4046	0.1205
RMSE	0.2923	0.4276	0.1635	0.1897	0.191	0.0771	0.2642	0.1764	0.0963
Marquardt (%)	19	42	6869050	40	90	4873	963	1847	10797
MSE	0.0854	0.1828	0.0267	0.036	0.0365	0.0059	0.0698	0.0311	0.0093
Hybrid	3.6790	6.6170	4719.0551	2.4177	2.0475	0.3846	1.3061	0.5547	1.3982

χ^2	0.5634	1.0333	0.0708	0.2832	0.2271	0.0160	0.1408	0.0575	0.0257
Weber and Morris									
Equation	$q_t = K_{wm} t^{1/2} + C$								
$K_{wm} (\text{mg g}^{-1} \text{ min}^{-1/2})$	0.67	0.65	0.32	0.24	0.24	0.32	0.56	0.54	0.31
C (mg g ⁻¹)	1.27	1.71	3.33	0.87	1.14	3.25	3.89	4.45	3.20
R Pearson	0.9430	0.8982	0.5134	0.8584	0.7777	0.5336	0.6713	0.6088	0.309
R ²	0.8893	0.8067	0.2636	0.7368	0.6048	0.2847	0.4506	0.3706	0.5222
Adj. R ²	0.8672	0.7681	0.1163	0.6842	0.5258	0.1416	0.3407	0.2448	0.2727
SQE	3.2913	5.8944	16.6483	1.2194	2.2224	15.6684	22.5743	29.3613	0.1272
RMSE	0.5032	0.6734	1.1317	0.3063	0.4135	1.0978	1.3178	1.5029	15.2495
Marquardt (%)	3822739659	5165708816	10030157450	26381389	34502635	98084040	117194796	134100545	1
MSE	0.2532	0.4534	1.2806	0.0938	0.171	1.2053	1.7365	2.2586	96631717
Hybrid	1461333853	2668454763	10060405857	6959779	11904322	96204799	137346213	179829574	1.173
χ^2	1.6386	2.2982	4.6525	1.1398	1.5649	4.4842	5.2196	6.0293	93376897

Elovich									
Equation	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$								
α (mg min ⁻¹ g ⁻¹)	4.49	12.16	45631157.23	30.52	254.54	673555.00	262014.00	569347.00	695598.00
β (mg g ⁻¹)	0.99	1.15	4.43	3.78	4.30	3.57	2.45	2.38	3.66
R Pearson	0.9981	0.9852	0.9743	0.9868	0.9794	0.9739	0.9954	0.99	0.9704
R ²	0.9962	0.9706	0.9490	0.9738	0.9593	0.948	0.9904	0.9795	0.9413
Adj. R ²	0.9954	0.9647	0.9388	0.9685	0.9511	0.9376	0.9885	0.9754	0.9295
SQE	0.1131	0.8978	1.1537	0.1216	0.2291	1.1399	0.3942	0.9571	1.2313
RMSE	0.0933	0.2628	0.2979	0.0967	0.1327	0.2961	0.1741	0.2713	0.3078
Marquardt (%)	105	337	752495717	890	7640	10350714	6102177	10858133	10425173
MSE	0.0087	0.0691	0.0887	0.0094	0.0176	0.0877	0.0303	0.0736	0.0947
Hybrid	0.2788	2.1343	56624982.4573	0.6429	1.5009	1071375	372366	1178992	1086844
χ^2	0.0317	0.2417	0.4834	0.0725	0.1022	0.5689	0.2604	0.4862	0.5957
Avrami									

Equation	$q_t = q_e(1 - e^{-(k_{avr}t)n_{avr}})$								
q_{avr} (m g ⁻¹)	4.97	5.19	4.91	2.00	2.28	4.87	6.58	7.09	4.75
k_{avr} (l min ⁻¹)	0.33	1.33	1.57	1.01	0.80	0.15	0.81	3.63	0.06
n_{avr}	0.54	0.17	1507.38	0.98	1.65	22.97	2.71	0.73	77.83
R Pearson	0.9596	0.9373	0.9923	0.9038	0.5014	0.9983	0.9822	0.9933	0.9971
R ²	0.9025	0.8477	0.9846	0.8164	0.2469	0.9965	0.9647	0.9867	0.9941
Adj. R ²	0.8700	0.7969	0.9795	0.7553	0.0355	0.9954	0.9529	0.9822	0.9922
SQE	2.8984	4.6455	0.3476	0.8504	0.7881	0.0758	1.4514	0.6212	0.1229
RMSE	0.4722	0.5978	0.1635	0.2558	0.2563	0.0764	0.3341	0.2186	0.0972
Marquardt (%)	21	23	368601	35	14	513	424	560	725
MSE	0.2230	0.3573	0.0267	0.0654	0.0657	0.0058	0.1116	0.0478	0.0095
Hybrid	10.2456	14.6423	14.3238	4.667	4.1367	0.1618	2.2738	0.8839	0.2657
χ^2	1.8019	3.1656	0.0709	0.4403	0.3490	0.0156	0.2208	0.0877	0.0259

Adsorption isotherms

Table S11. Parameters obtained from adsorption models fitted to experimental data.

Material	CDP			DI-CDP			TRI-CDP		
Pollutant	BPA	BPB	CV	BPA	BPB	CV	BPA	BPB	CV
Freundlich									
n	2.52	2.68	3.45	0.98	0.92	2.45	10.81	10.55	2.35
K_F ($\text{mg}^{1-1/n}$ $\text{L}^{1/n} \text{g}^{-1}$)	32.01	41.62	145.95	0.25	0.38	130.96	51.30	56.34	134.22
R^2	0.9852	0.9640	0.9077	0.9943	0.9983	0.9202	0.8945	0.9042	0.8549
Adj. R^2	0.9792	0.9496	0.8769	0.9920	0.9976	0.8936	0.8523	0.8659	0.8066
χ^2	698.90	1884.58	238.78	0.26	0.13	264.61	28.59	32.91	433.44
Harkins-Jura									
A_{hj}	3432.19	6095.61	263856.91	7.05	24.53	415794.50	8091.00	9314.66	438144.10
B_{hj}	2.89	2.97	5.87	3.41	3.44	5.55	4.55	4.42	5.41
R^2	0.8891	0.8952	0.6901	0.8800	0.8773	0.6682	0.7660	0.7873	0.6038
Adj. R^2	0.8447	0.8532	0.5868	0.8320	0.8283	0.5576	0.6725	0.7022	0.4717

χ^2	30.56	32.68	585.54	3.60	6.39	1016.50	44.76	46.94	1289.28
Temkin									
b_t (J mg ⁻¹)	765.2394	665.1179	26.9647	1398.6900	767.9000	15.4900	774.4700	703.4400	14.4000
K_t (L mg ⁻¹)	5679977.8777	38346326.8636	4.6296	0.9400	0.9400	1.6600	47776509.0000	46102750.0000	1.5500
R^2	0.6221	0.7620	0.9663	0.8463	0.8140	0.8948	0.9256	0.9247	0.8208
Adj. R^2	0.4710	0.6668	0.9550	0.7848	0.7396	0.8598	0.8958	0.8946	0.7610
χ^2	13.7403	46.6675	10.5930	0.9500	3.5000	5.7800	28.0000	33.9600	143.6400
Hill									
q_{hi} (mg g ⁻¹)	137.52	147.58	594.89	13.98	27.83	1075.84	64.33	79.30	1005.75
K_{hi} (L mg ⁻¹)	3.32	2.78	5.98	40.75	50.45	28.66	0.09	0.26	1975.03
n_{hi}	0.6491	0.7251	1.0294	1.0896	1.1158	1.0900	0.2816	0.2100	2.6100
R^2	0.9901	0.9702	0.9921	0.9692	0.9704	0.9900	0.9340	0.9262	0.9711
Adj. R^2	0.9826	0.9478	0.9873	0.9461	0.9482	0.9770	0.8844	0.8708	0.9538
χ^2	31819.89	436231.92	13.21	0.60	0.74	53.57	28.01	34.23	17146.81
Redlich-Peterson									

K _{rd1} (L g ⁻¹)	-	-	112.61	826.06	527236.23	32.37	16238045.00	20863435.00	28.80
K _{rd2} (L mg ⁻¹)	-	-	0.22	3241.76	1388347.25	0.01	278178.90	335283.90	0.001
n _{rd}	-	-	0.9709	0.0173	0.0812	1.2800	0.9800	0.9600	1.8600
R ²	-	-	0.9926	0.9943	0.9983	0.9908	0.9340	0.9262	0.9831
Adj. R ²	-	-	0.9881	0.9900	0.9970	0.9853	0.8846	0.8708	0.9730
χ ²	-	-	17.52	0.26	0.13	78.02	28.01	34.24	105.13
Toth									
q _{to} (mg g ⁻¹)	44.45	66.45	506.34	0.27	0.49	9313.10	58.37	62.23	3411324.00
b _{to} (L mg ⁻¹)	0.44	0.79	4.63	6.30	17.64	119.17	3.16	2.33	1623.16
n _{to}	0.8537	0.8944	0.9826	0.0002	0.0000073	1.1800	0.9900	0.9800	1.5800
R ²	0.9885	0.9681	0.9927	0.9942	0.9967	0.9913	0.9340	0.9262	0.9825
Adj. R ²	0.9799	0.9442	0.9883	0.9898	0.9942	0.9860	0.8846	0.8708	0.9720
χ ²	4227108.44	23637699.40	17.46	0.26	0.10	73.26	28.01	34.24	101.79

Thermodynamic analysis

Table S12. Thermodynamic analysis for BPA, BPB, and CV adsorption by CDP, DI-CDP, and TRI-CDP

Material	CDP			DI-CDP			TRI-CDP		
Pollutant	BPA	BPB	CV	BPA	BPB	CV	BPA	BPB	CV
ΔH^0 (kJ mol ⁻¹)	91.59	61.20	65.85	-419.72	-452.73	-128.43	-293.22	-291.95	-231.2
ΔS^0 (J K ⁻¹ mol ⁻¹)	318.45	220.81	235.38	-1281.4	-1369	-408.8	-843.11	-838.93	-717.82
ΔG_{297}^0 (kJ mol ⁻¹)	-2.93	-2.49	-4.36	-48.58	-52.28	-8.18	-43.1	-43.01	-18.49
ΔG_{313}^0 (kJ mol ⁻¹)	-5.48	-10.29	-5.09	-8.19	-22.06	-1.36	-35.99	-36.11	-11.62
ΔG_{333}^0 (kJ mol ⁻¹)	-16.00	-11.03	-14.13	1.37	2.23	8.29	-8.5	-8.57	10.88
R pearson	0.9313	0.8876	0.8700	0.9496	0.9983	0.9951	0.9545	0.9531	0.9568
R ²	0.8674	0.7879	0.7569	0.9017	0.9965	0.9903	0.9111	0.9084	0.9154

Effect of pollutant concentration on the RME parameter for CDP, DI- and TRI-CDP

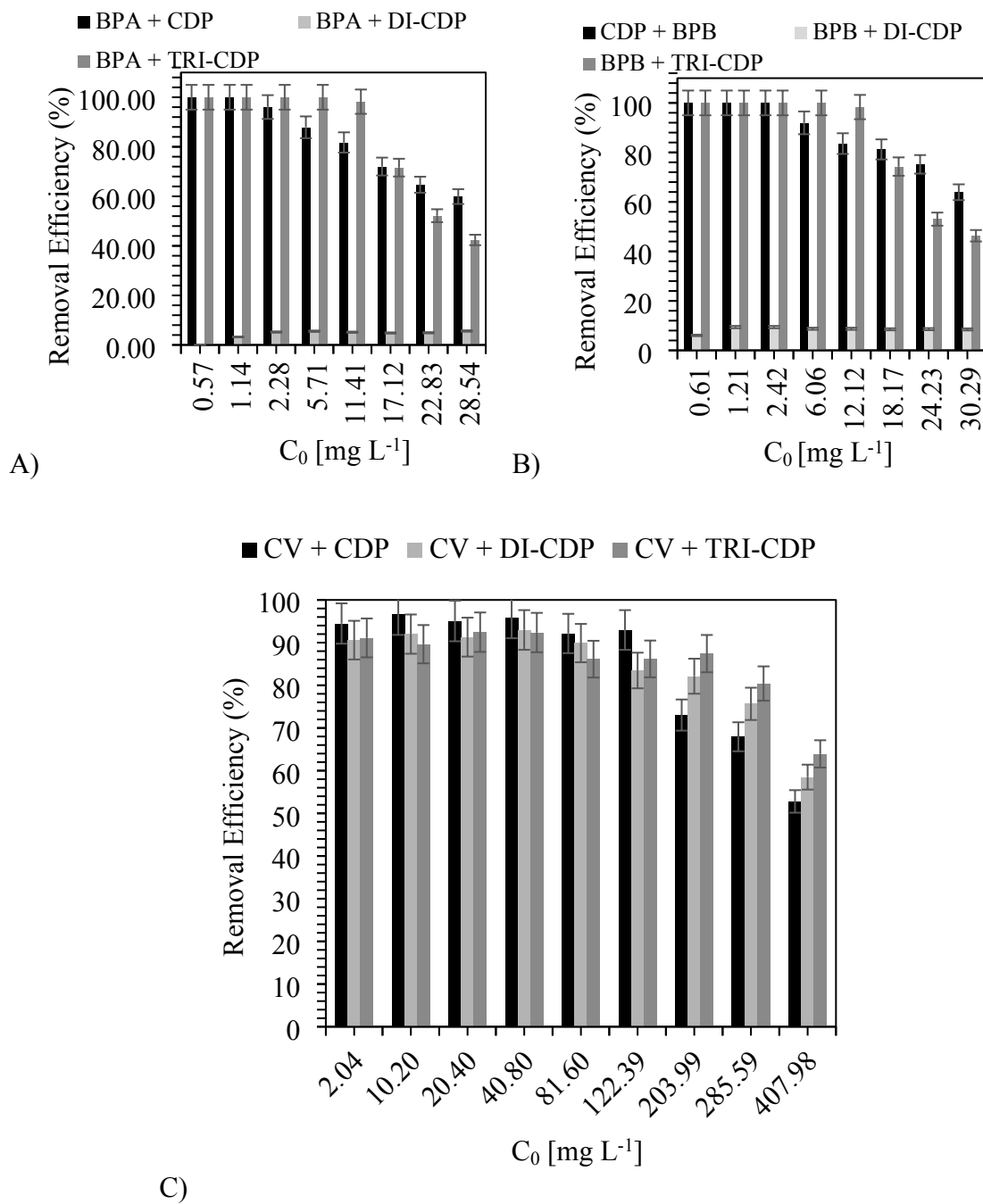


Figure S19. Effect of: A) BPA different concentrations on removal efficiency; B) BPB different concentrations on removal efficiency; C) CV different concentrations on removal efficiency of CDP, DI-CDP, and TRI-CDP. The parameters used are as follows: $c_{\text{sor}} = 0.2 \text{ g L}^{-1}$, $t = 20 \text{ min}$.

Adsorption mechanism

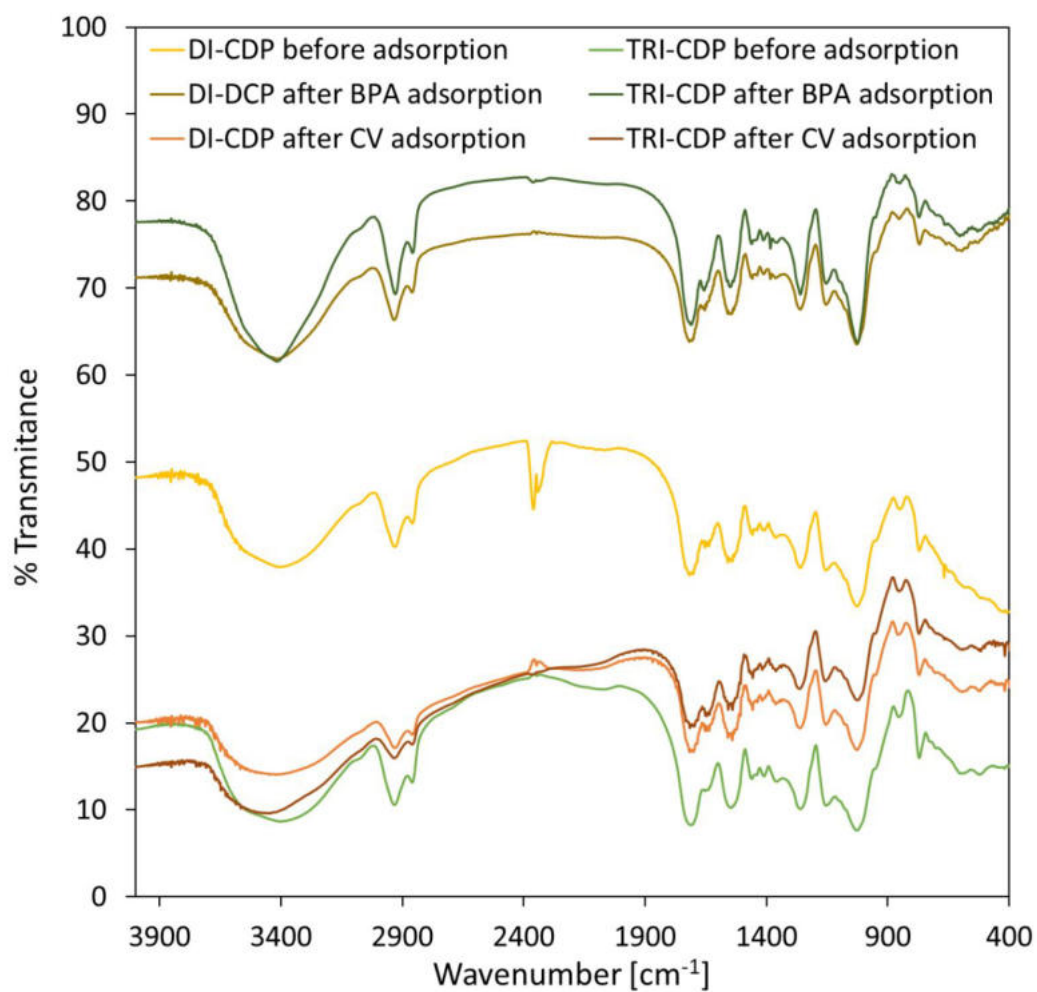


Figure S20. The comparison of FTIR spectra (KBr pellet) of DI-CDP, and TRI-CDP before and after adsorption of BPA and BPB.

Comparison of CDP, DI-CDP, and TRI-CDP with industrial adsorbents

Table S13. Summary of experimental adsorption results (this work) for Crystal Violet (CV), Bisphenol A (BPA), and Bisphenol B (BPB) using β -cyclodextrin polymer adsorbents (CDP = non-imprinted polymer (NIP); DI-CDP and TRI-CDP = molecularly imprinted polymers (MIPs)) and two commercial activated carbons (Norit SX+ and Organosorb 200-C303). Each adsorbent's BET surface area, adsorption equilibrium time, and maximum adsorption capacity ($q_{\max}$) for each pollutant are given. These results show the high selectivity and capacity of the imprinted CD-based polymers for CV, despite their very low surface areas.

Adsorbents		Surface	Equilibrium		$q_{\max}$ (mg g ⁻¹)		
		Area	time (min)				
		(m ² g ⁻¹)	BPA, BPB	CV	BPA	BPB	CV
NIP	CDP	1.52	25	1	137.52	147.58	594.89
MIP	DI-CDP	1.92	25	1	13.98	27.83	1075.84
MIP	TRI-CDP	1.43	25	1	64.33	79.30	1005.75
INDUSTRIAL ADSORBENTS	Norit -SX+	1000	25	10	68.14	61.64	868.20
	Organosorb 200-C303	1290	25	10	67.00	63.35	983.24

Table S14. Comparative adsorption performance of selected industrial/commercial adsorbents for removing Crystal Violet (CV) and bisphenols from water (environmental/textile wastewater context). Data consist of the adsorbent type, target pollutant, BET surface area, reported $q_{\max}$, and typical adsorption equilibrium time. These examples illustrate that conventional high surface area

adsorbents like activated carbons achieve good capacities but can require longer contact times, whereas novel adsorbents (e.g., clays) offer varying performance.

Adsorbent (Type)	Target Pollutant	BET	$q_{\max}$ (mg g ⁻¹)	Equilibrium	Ref.
		Surface Area (m ² g ⁻¹)		Time (min)	
AC-40 Activated					
Carbon (bituminous-coal AC, extruded)	BPA	1201	94	2880	25
Spectrogel®					
Organoclay (bentonite modified with quaternary ammonium)	BPA	3	56	1200-1920 (depending on concentration)	26
Amberlite XAD-7					
<i>impregnated</i> with Aliquat 336 (polymeric adsorbent + quaternary amine)	BPA	62	11	120	27
Activated Carbon					
(Commercial GAC, granular)	BPA	1050	16	40-60	28

Activated Carbon					
Norit® SAE SUPER (Commercial PAC, powder)	BPA	851	368	120	29
Zeolite Y	BPA	505	111	4	30
Commercial activated carbon (CAC)	CV	1050- 1150	2000	180	31
Montmorillonite Clay (natural clay)	CV	74	500	240	32
Sepiolite Clay (natural silicate)	CV	297	150	30	33
Zeolite A	CV	19	11	45	34
ZSM-5	CV	330	142	20	35

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Publication 2

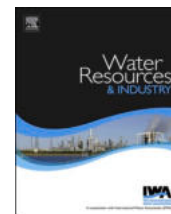
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Removal of nonsteroidal anti-inflammatory drugs and analgesics from wastewater by adsorption on cross-linked β -cyclodextrin

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ABSTRACT

We present a method using the material in the form of cross-linked β -cyclodextrin (CD) showing high efficiency in the simultaneous removal of hazardous pollutants from sewage, such as diclofenac (DIC), ibuprofen (IBU), ketoprofen (KETO), naproxen (NAPR), salicylic acid (SALI) and tramadol (TRAM). The material is stable and particularly easy to regenerate. The sorbent probably remembers the shape of the contaminants, which increases its sorption capacity after the second use. The kinetics of the KETO adsorption process from one-, two- and three-component solutions are well described by the pseudo-second-order model. The maximum polymer capacity was 162.60 mg g^{-1} . The interactions of KETO with CD were investigated, indicating that the main sorption mechanism is based on supramolecular interaction and uptake by a polymer network. The material is not sensitive to low pH and high salinity, so it can be used for the treatment of DIC, IBU, and KETO post-production wastewaters.

1. Introduction

Pharmaceutical industry wastewaters are high variability of composition due to the wide spectrum of manufactured drugs [1,2]. Moreover, the wastewater streams generated during production are characterized by relatively high concentrations of pharmacologically active substances (API) [3]. Often, they have a very low or high pH. Usually, before entering the activated sludge chambers, their composition is averaged by mixing in a homogenizer and pH correction in a neutralizer [4]. At this stage, many pharmaceuticals precipitate out and become less bioavailable [5]. This phenomenon can be counteracted by subjecting the post-production streams to preliminary treatment. The most commonly used are Advanced Oxidation Processes (AOP) [6–10], membrane [11–14], and adsorption methods [15–17]. In the first case, mineralization is very rarely achieved. Typically, the drug is converted into other derivatives that may be less environmentally friendly than the native substance [18,19]. The use of appropriate membranes seems to be a better resolution. Disregarding the high cost, the contaminants are obtained in a form that is easier to dispose of due to the significantly reduced volume [20,21]. Adsorption produces give a similar effect with much less investment. In the pharmaceutical industry, activated carbon (AC) is most often used, both in the product purification stage and in the removal of impurities from waste streams [22–33]. The most important advantages of AC include a large specific surface area and the ability to bind both organic and inorganic compounds. The disadvantages include separation and regeneration problems, especially when using AC in powder form, and final disposal [34]. Waste AC usually undergoes combustion [35]. This process is difficult to carry out due to the lack of volatile

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components and therefore a supply of steam and oxygen is required, thus creating the conditions for gasification [36]. The described procedure is far from green technology and requires the implementation of new ones. A solution that is currently very popular is organic adsorbents derived from renewable raw materials [37–39]. This group includes both dried and shredded plant waste [40,41] as well as cellulose [42–44], chitosan [45–48], and cyclodextrins (CD) [49–51]. The latter is quite soluble and requires appropriate modification. The selection of appropriate cross-linking agents enables the synthesis of an adsorbent tailored to the size of a single or a group of pollutants [52–54]. The basis of sorption is supramolecular interactions produced by van der Waals forces, hydrogen bonds, and molecular fit of guest (pollutant molecule) to host (CD) [53,55]. CDs are cyclic compounds composed of 6, 7, or 8 glucose units linked by α -1,4-acetal bonds [56,57]. The torus is hydrophobic on the inside and hydrophilic on the outside [58]. The hydrophobic parts of the organic compounds are contained inside the torus or, if the structure of the polymer allows it, also in the resulting network. Usually, the materials are durable, regeneration is simple [59–61], and the spent polymer can potentially be broken down during composting, for example [62,63].

This paper presents the possibility of removing ketoprofen directly from post-production wastewater streams. Subsequent experiments show that the composition of wastewater has a significant impact on the efficiency of drug removal. This research can help manage streams going to the homogenizer in industrial wastewater treatment plants. The presented material may also find application in the treatment of municipal wastewater from non-steroidal anti-inflammatory drugs (NSAID) and painkillers.

2. Materials and methods

2.1. Reagents and techniques

Hexamethylene diisocyanate (1,6-HMDI $\geq 99\%$), β -cyclodextrin (β -CD $\geq 97\%$), pyridine (anhydrous $\geq 99.8\%$), diclofenac (DIC), ibuprofen (IBU), ketoprofen (KETO), naproxen (NAPR), paracetamol (PARA), salicylic acid (SALI), tramadol (TRAM) (drugs meet USP testing specifications) were delivered by Sigma-Aldrich. Acetonitrile (HPLC-grade), methanol ($\text{CH}_3\text{OH} \geq 99.8\%$), sodium and calcium chlorides ($\text{NaCl} \geq 99.8\%$, $\text{CaCl}_2 \geq 99.8\%$), as well commercial humic acids contain 50% of humic acids and 50% fulvic acids (HA, 90% dry matter) were purchased from Chempur and Agraplant, respectively. All chemicals were used without their further purification. Water purified by Hydrolab-system was used to prepare the stock solutions (HLP-SPRING, temp. 22 °C, $\kappa = 2.70 \mu\text{S}$). The characteristic of effluents from the local municipal sewage treatment plant is presented in the supplementary material (SM, Table S2).

The final form of the adsorbent was obtained after drying material in a moisture analyzer (MA50/1.R, Radwag) and grinding in a ball mill (Pulverisette 7 classic line, Fritsch, GmbH). Fourier transform infrared (FT-IR) spectra were performed on a Thermo Nicolet iS10, using the KBr pellet method. The spectral resolution was 4 cm^{-1} and the scanning range was from 400 to 4000 cm^{-1} . The specific surface area was estimated by the Brunauer-Emmett-Teller (BET) method [64] and pore size distribution (PSD) was measured using the classical Barrett-Joyner-Halenda (BJH) model [65] and the Harkins and Jura t-Plot method [66,67]. The surface charge properties of the adsorbents were investigated by Zeta potential measurements, which were conducted at a different equilibrium pH using a Nano-ZS Zetasizer (Malvern Instruments Inc. UK). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was performed on β -CD-HMDI using a Mettler-Toledo TGA/DSC thermogravimetric analyzer. Samples were heated from 0 °C to 1000 °C at the rate of 10 °C/min under the air atmosphere (flow rate: 10 ml min^{-1}). The surface morphology β -CD-HMDI was studied using scanning electron microscopy (SEM) on a Quanta FEG 250 scanning electron microscope operating at 10 kV . The elemental FLASH 2000 analyzer operating in the dynamic separation technique was used to measure the content of carbon, hydrogen, and nitrogen. The oxygen content analysis was performed by the device in the pyrolysis mode.

2.2. Synthesis of β -CD-HMDI

To a flask containing 150 ml of dry pyridine at 80 °C, 10 g of CD and 5.93 g of 1,6-HMDI were added simultaneously over 2 h with vigorous stirring. Reactions were continued for an additional 8 h . After cooling to room temperature, 300 ml of acetone was poured into the reaction mixture to precipitate the product. The precipitate was filtered and air-dried. Unreacted cyclodextrin and residual pyridine were removed during liquid/solid extraction with water and hydrochloric acid, respectively. The precipitate was filtered and washed with distilled water until the pH of the filtrate was neutral, and then the precipitate was allowed to dry at room temperature. The product was placed in a moisture analyzer and dried at 120 °C until solid. The product thus dried was ground and stored in a desiccator. The final reaction yield was 11.15 g [68].

2.3. Methods

To determine the adsorption mechanism, the interactions between β -CD and API were analyzed through proton nuclear magnetic resonance. ^1H NMR spectra were recorded in D_2O on a Bruker Advance III HD 400 MHz spectrometer at 25 °C.

The concentrations of API were determined by ultraviolet spectra, detected by high-pressure liquid chromatography (HPLC Agilent Technologies 1200 Series, USA). The analytical method for DIC, IBU, KETO, and NAPR was obtained from the reported literature [69–74]. The samples were injected at a volume of $1 \mu\text{L}$ each time. The flow rate of a mobile phase (using acetonitrile: acetate buffer pH 3.2, ratio 60: 40) through the C-18 column (Zorbax Eclipse PAH, $4.6 \times 100 \text{ mm}$, $3.5 \mu\text{m}$, Agilent Technologies) was set at 1.0 ml min^{-1} . The concentration was measured by the UV detector at the wavelength of 220.8 (ref. 360 ± 100) nm. TRAM, SALI and PARA were separated on the column XDB C18 Eclipse ($4.6 \times 150 \text{ mm}$, $5 \mu\text{m}$, Agilent Technologies, using mixture of deionize water (A): 0.05% TFA in acetonitrile (B) as a mobile phase, with flow rate 1.2 ml min^{-1} in gradient: $0 \text{ min} - 85\%$ (A) to $11 \text{ min} - 40\%$ (A), and back to the

initial conditions (12–17 min - 0% (A)). The samples were injected at a volume of 40 μL . The concentration of analytes was measured by the UV detector at the wavelength of 200.8 (ref. 360 ± 100) nm. All experiments were carried out in triplicate ($n = 3$) and, the maximum standard error was 2.1%. API removal efficiency (RME) was determined by Eq. (1),

$$RME (\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where the RME (%) was the efficiency of API removal, C_0 (mg L^{-1}) and C_t (mg L^{-1}) were the initial concentration and concentration at time t of API in the sample.

2.4. Adsorption procedure

The experiments were performed at room temperature on a digital vortex mixer (OHAUS VXHDDG) at 700 rpm. After shaking, the adsorbent was separated from the solution by filtration (Whatman Grade 540 filter paper) and the concentration of the filtrate (c_e) was determined. The influence of the adsorbent quantity was initially investigated. For this purpose, β -CD-HMDI in an amount of 1–100 mg was added to 5 ml of KETO solution in plastic Falcon tubes (7 ml). Then, the influence of electrolytes and humic acids, as well as pH 2 to 10 (corrected with NaOH or HCl), was investigated using a previously selected dose of the adsorbent. Each time, three sets of experiments were carried out at the KETO (20 mg L^{-1} , the contact time of 60 min).

2.5. Kinetic, equilibrium studies, and thermodynamic analysis

Kinetic and equilibrium experiments were performed under optimal experimental conditions. In the first one, the KETO (20 mg L^{-1}) solution was used, and in the second - KETO ($1\text{--}100 \text{ mg L}^{-1}$). The adsorption equilibrium and kinetics data were analyzed using the models presented in Tables S4 and S6. The tables also show the relevant mathematical relations of these models, the parameters to be valued, and the dependable references. The reliability of the results was considered based on the analysis of variance (Anova test).

2.6. Real wastewater treatment

2.6.1. API's post-production effluents

Many methods for synthesizing ketoprofen can be found in the literature [75–80]. However, not all of them are suitable for industrial purposes, which explains the continued use of the syntheses described in patents from the past century [75,81,82]. Fig. 1 shows two examples of the reactions carried out under industrial conditions.

Their common feature is usually an alkaline hydrolysis step carried out in an organic solvent environment, which is then distilled. The resulting drug is in the form of a salt from which it is released. The resulting solution of the drug in the solvent is washed repeatedly with water and solutions of different pH. The combination of these streams produces saline and usually acidic wastewater. A similar situation is observed during the production of diclofenac [83]. The exception is the ibuprofen system, which is considered to be waste-free [84]. The information in the literature has become a determinant of the composition of model post-production leachates (EP) which were prepared by dissolving DIC, IBU, and KETO (0.4 mmol L^{-1}) in a hydrochloric acid solution of sodium chloride ($\text{pH}=2$; 763 mg L^{-1}).

2.6.2. Wastewaters

Model wastewater was obtained by dissolving individual APIs (0.4 mmol L^{-1}) in treated municipal wastewater (MW), the description of MW is shown in Table S1. The resulting mixtures can successfully mimic the feedstock for the next treatment step based on adsorption.

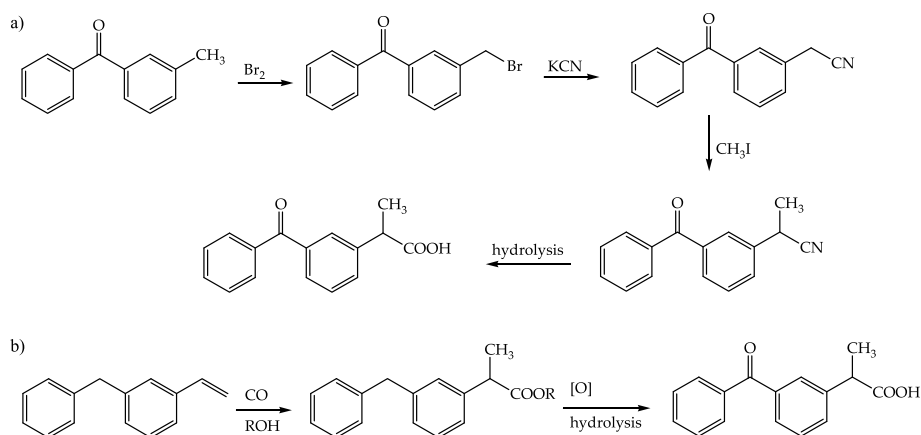
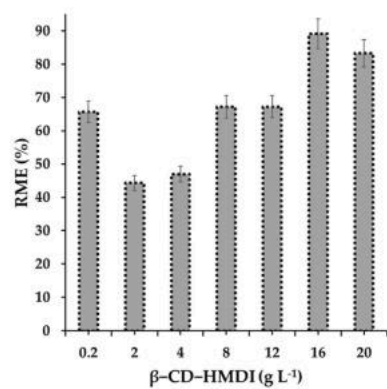
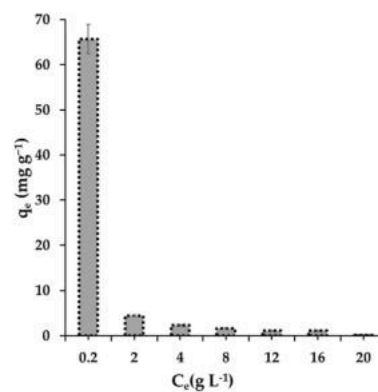


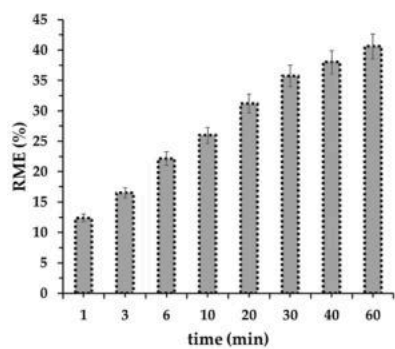
Fig. 1. Industrial methods of ketoprofen synthesis.



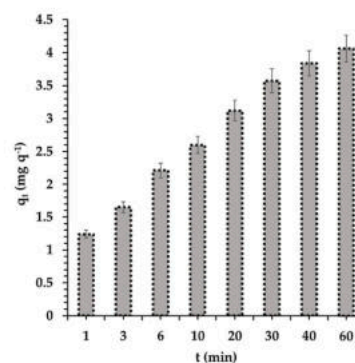
a)



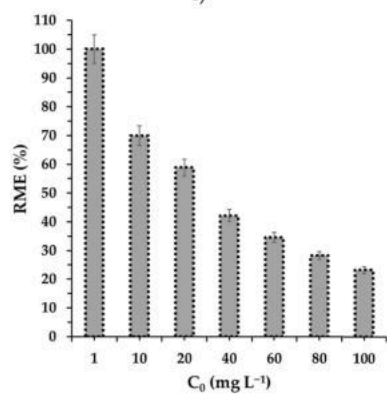
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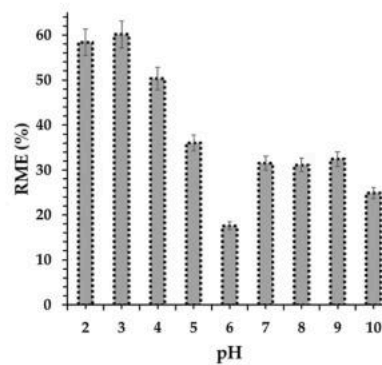
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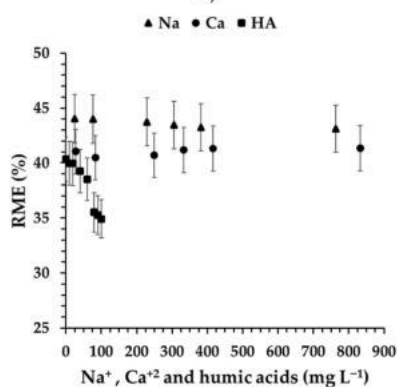
d)



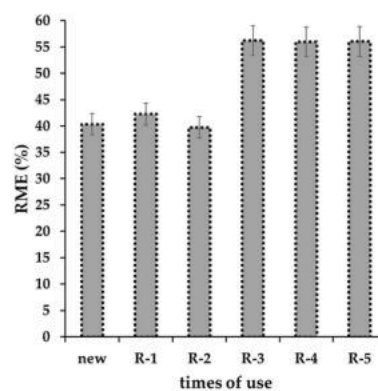
e)



f)



g)



h)

(caption on next page)

Fig. 2. a) Effect of adsorbent mass on removal efficiency, ($C_{\beta\text{-CD-HMDI}} = 0.2\text{--}20 \text{ g L}^{-1}$; $C_0 = 20 \text{ mg L}^{-1}$, $t = 60 \text{ min}$, temp. 25°C); b) Effect of adsorbent mass on adsorption capacity, ($C_{\beta\text{-CD-HMDI}} = 0.2\text{--}20 \text{ g L}^{-1}$; $C_0 = 20 \text{ mg L}^{-1}$, $t = 60 \text{ min}$, temp. 25°C); c) Effect of the time on removal efficiency, ($C_{\beta\text{-CD-HMDI}} = 0.2\text{--}20 \text{ g L}^{-1}$; $C_0 = 20 \text{ mg L}^{-1}$, $t = 60 \text{ min}$, temp. 25°C); d) Effect of time on adsorption capacity (q_t), ($C_{\beta\text{-CD-HMDI}} = 2 \text{ g L}^{-1}$; $C_0 = 20 \text{ mg L}^{-1}$, $t = 0\text{--}60 \text{ min}$, temp. 25°C); e) Effect of KETO initial concentration on removal efficiency, ($C_{\beta\text{-CD-HMDI}} = 0.2 \text{ g L}^{-1}$; $C_0 = 10\text{--}100 \text{ mg L}^{-1}$, $t = 60 \text{ min}$, temp. 25°C); f) Effect of pH = 2–10 value on KETO removal efficiency, ($C_{\beta\text{-CD-HMDI}} = 2 \text{ g L}^{-1}$; $C_0 = 20 \text{ mg L}^{-1}$, $t = 60 \text{ min}$, temp. 25°C); g) API Effect of salt and fulvic and humic acids (F&H) on API removal efficiency, ($C_{\beta\text{-CD-HMDI}} = 2 \text{ g L}^{-1}$; $C_0 = 20 \text{ mg L}^{-1}$, $t = 60 \text{ min}$, temp. 25°C , $C_{\text{NaCl}} = 25.42\text{--}703.00 \text{ mg L}^{-1}$, $C_{\text{CaCl}_2} = 27.75\text{--}832.50 \text{ mg L}^{-1}$, $C_{\text{F\&H}} = 10\text{--}100 \text{ mg L}^{-1}$); h) Comparison of the removal efficiency of KETO using a new and sequentially regenerated adsorbent, ($C_{\beta\text{-CD-HMDI}} = 2 \text{ g L}^{-1}$; $C_0 = 20 \text{ mg L}^{-1}$, $t = 60 \text{ min}$, temp. 25°C). The symbols C_e and q_e denote equilibrium concentrations of KETO in solution and adsorbent, while C_0 and $C_{\beta\text{-CD-HMDI}}$ represent initial concentrations of KETO and adsorbent.

2.6.3. Multicomponent wastewaters (mix)

Ternary blends were prepared by mixing equal volumes of the respective DIC, IBU, and KETO solutions in MW. Seven-component effluents were obtained analogously by mixing all the solutions of the drugs under study.

The aforementioned model effluents (50 ml) were poured into Falcon-type plastic tubes containing 50 mg each of $\beta\text{-CD-HMDI}$. The vials were sealed tightly, and the mixtures were shaken in a digital vortex mixer at 700 rpm for 1 h at 25°C . The supernatant was then collected and filtered. The concentration at adsorption equilibrium of each was measured by HPLC.

2.7. Regeneration

100 mg of $\beta\text{-CD-HMDI}$ was added to 50 ml of KETO solution initial (20 mg L^{-1}). The mixture was shaken in a digital vortex mixer at 700 rpm (25°C , 1 h). After 1 h, the solution was decanted from the surface of the precipitate and in its place, 20 ml of methanol was added, soaking for 15 min. The procedure was repeated in distilled water. The adsorption-desorption experiment was performed five times.

3. Result and discussion

The synthesized material is characterized by a high degree of cross-linking. The basic sorbent unit consists of three $\beta\text{-CD}$ molecules. In a single $\beta\text{-CD}$, a total of 21 primary hydroxyl groups are available, 16 of which are substituted. Significantly, only 14 are embedded in urethane bonds and two in allophanate bonds. The resulting material is amphiphilic having both rigid and flexible elements (Fig. S13) so it can easily adapt to the structure of the adsorbed drug. The BET surface area of $\beta\text{-CD-HMDI}$ is $7.31 \text{ m}^2 \text{ g}^{-1}$. The average pore size is 16.8 nm and the total pore volume is 3.08 ml g^{-1} . The average particle size of $\beta\text{-CD-HMDI}$ varieties is from 270 to 600 μm , valued by SEM (Fig. S2). The particles have a divergent porous structure. The material is thermally stable at temperatures below 250°C , after which decomposition follows. The final weight loss is observed at 333°C (61.82%). The Zeta potential (ξ) of $\beta\text{-CD-HMDI}$ in the pH range from 2 to 11 is 0 for pH = 2.53, and above this value, it is constantly negative. The material does not permanently retain water and does not tend to swell. More information on the sugar adsorbent can be found in the publication [68].

3.1. Adsorption experiments

The adsorption studies were carried out conventionally, examining the influence of individual parameters on the course of the process. The obtained results are discussed in subsequent subsections.

3.1.1. Effect of adsorbent mass

It can be considered that overall, an increase in the mass of the sorbent ($0.2\text{--}20 \text{ g L}^{-1}$) is accompanied by an increase in the degree of removal of API from the solution, which is certainly typical. Nevertheless, in the case of KETO, it reaches minimums and maximums, which indicate probably the formation of new equilibria (Fig. 2a). A significant excess of API in the solution compared to the initial amount of $\beta\text{-CD-HMDI}$ causes a rapid equilibrium state where the q_e limits of 65.42 mg g^{-1} (Fig. 2b). Therefore, to be able to investigate the kinetics of the sorption process, no minimum amount of material, but 10 mg was used in the next stage. The pH of the API solutions (20 mg L^{-1}) was not corrected.

3.1.2. Effect of contact time

The adsorption processes are required to run efficiently in a relatively short time to reduce the cost of the unit operation. The time in which the maximum removal of the desired component from solution was achieved depends on the kinetics of the process, which is predominantly influenced by the physicochemical properties of the adsorbent and adsorbate. In the KETO question, the required state was achieved in between 5 min and 24 h, depending on the material used [85–87]. Two compartments can be distinguished in the analyzed system. The first one, lasting 30 min, is dynamic, then it slows down significantly. The result is a 40.62% removal of KETO in 60 min (Fig. 2c).

3.1.3. Effect of API initial concentration

The initial concentration is the driving force needed to overcome the resistance to mass transfer between the aqueous and solid phases. At the first moment of contact, $\beta\text{-CD-HMDI}$ has the largest number of centers capable of interacting with the components of the liquid phase, which usually results in a high adsorption efficiency observed at the lowest concentration of 1 mg L^{-1} . A higher

concentration may create an additional barrier to overcome in the form of already accumulated KETO particles, or API transfer from solution to solid. Hence, the involvement of deeper structures is partial, and consequently, the ineffectiveness of API removal is observed. The concentration of 20 mg L^{-1} was selected for further research (Fig. 2e).

3.1.4. Effect of pH

KETO contains a pH-sensitive carboxyl group. In a solution with $\text{pH} = 3$, the degree of API removal is the highest and amounts to almost 61% (Fig. 2f), then it gradually decreases with increasing pH, assuming the lowest value for $\text{pH} = 6$ ($\text{RME} = 17.55\%$), after which, when exceeded, there is an almost two-fold increase to $\text{pH} = 9$. The electrokinetic potential of the various dispersed phases depends largely on the concentration of hydrogen ions. In the case of the tested material, the electrokinetic potential is zero at $\text{pH} = 2.53$, this value corresponds to the highest degree of KETO removal (Fig. S3). This is an area close to the complete disappearance of anticoagulant electrostatic repulsion. Considering that the final pH of the effluent from KETO production is acidic and the drug content is at the level of several dozen mg, the resulting material can potentially be used to remove the drug from this stream before it is sent to the on-site sewage treatment plant [81]. However, to restore normal adsorption conditions, the pH of the KETO solutions was not adjusted in further tests and was 4.21.

3.1.5. Effect of salts, humic and fulvic acids

The salts present in the wastewater can significantly affect the sorption of drugs. In the case of KETO, both sodium and calcium chloride increase the removal efficiency of the drug by several percent. Even high salinity mustn't adversely affect the sorption process, which means that $\beta\text{-CD-HMDI}$ can potentially be used during the treatment of neutralized post-production wastewater. The presence of humic and fulvic acids is typical for surface waters and may be of great importance when removing KETO from the natural environment. These compounds have little effect on the value of the RME parameter in the range of low concentrations, the effect increases with increasing concentration, resulting in a reduction in the degree of KETO removal by 5% (Fig. 2g).

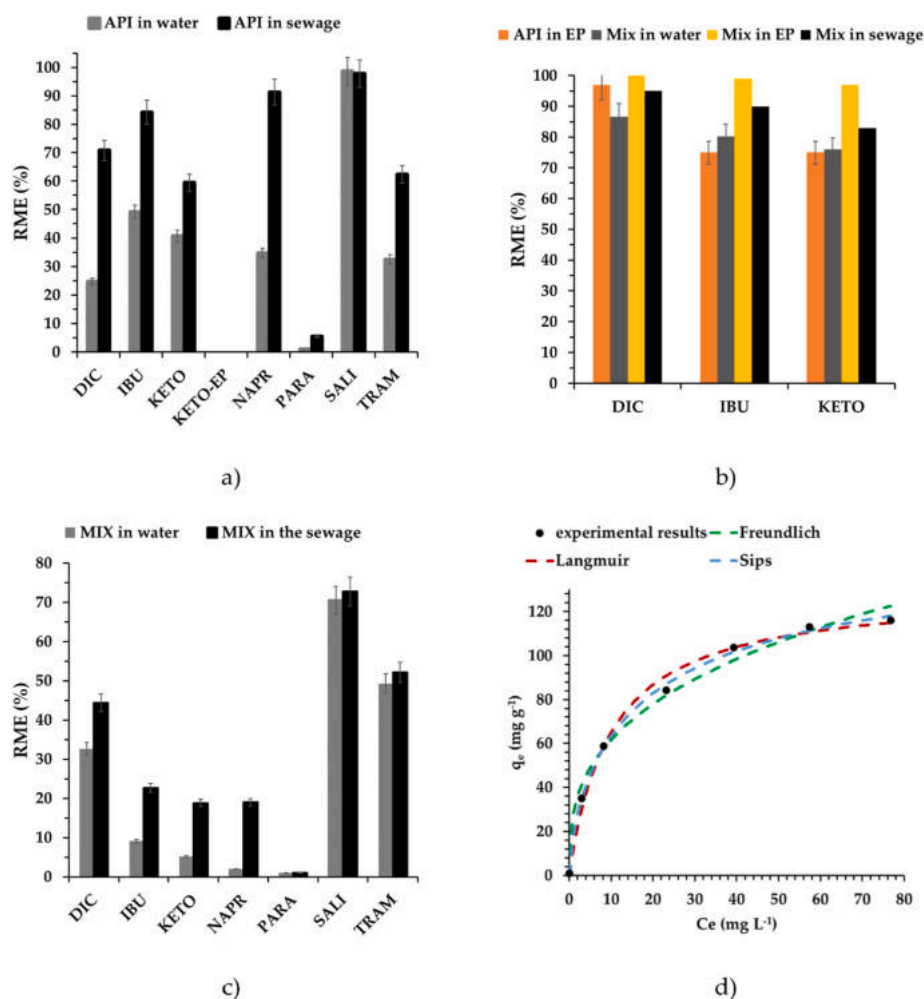


Fig. 3. a) The removal efficiency of single API from water and municipal wastewater; b) Removal of drugs from three-component mixtures in water, post-production effluent (EP), and municipal wastewater; c) Removal of drugs from seven-component mixtures in water and municipal sewage. In all cases $C_{\text{API}} = 0.3 \text{ mmol L}^{-1}$, $C_{\beta\text{-CD-HMDI}} = 1.25 \text{ g L}^{-1}$ contact time 60 min, temp. 25°C ; d) Equilibrium adsorption isotherm of KETO ($C_0 = 0.001 - 0.1 \text{ g L}^{-1}$, $C_{\beta\text{-CD-HMDI}} = 0.2 \text{ g L}^{-1}$, contact time 60 min, temp. 25°C).

3.1.6. Regeneration

The presented material contains elements of different elasticity, enabling a better adjustment of the material structure to the shape of the adsorbate. The initial structure of β -CD-HMDI was formed by a pyridine matrix which was removed in the purification step. During the first sorption, the material is reorganized and arranged according to the structure of the guest molecule. The new system is not fully formed but does not fail under mild methanol desorption conditions. During the next two cycles (adsorption-desorption), the new polymer system is remembered and the process becomes more efficient (Fig. 2h). The low boiling point of alcohol and the lack of azeotropes with water make the regeneration stage relatively cheap and waste-free. The regeneration process must be very effective and simple. In industrial conditions, it is enough to place the sorbent in the mixer with post-production effluents. After an appropriate time, it is enough to drain the treated sewage and replace it with methanol, after only 15 min, the solvent phase can also be drained and sent to the distillation tower, and the material itself can be washed with water. The operation does not need to be repeated. Aqueous washings can also be used repeatedly after removing residual methanol (Scheme S1).

3.1.7. Removal of pollutants from a complex model mixture

The presence of additional drugs such as DIC and IBU increases the removal efficiency of the individually tested API from model solutions. This effect is strongest with DIC, which is removed from the solution with an efficiency of 24.7% in the absence of other drugs. In the case of a mixture containing all tested pharmaceuticals, the effectiveness increases up to 86.6%. The observed synergism of these drug adsorption is an unquestionable advantage of β -CD-HMDI and has the potential to be used in the treatment of combined post-production wastewater from the simultaneous manufacture of these medicines (Fig. 3a and b and Scheme S1).

3.1.8. Adsorption of pharmaceuticals present in biologically treated sewage of municipal type and post-productions streams

The composition of the wastewater depends on the source of its formation. Two cases of mixtures containing API were included in the research. The first one with the pH = 2 and sodium chloride (763 mg L^{-1}) is the simulation of the KETO adsorption process from post-production effluents [81]. The second is the removal of drugs from municipal wastewater. First, the effect of the matrices on the removal efficiency of single APIs was determined, followed by mixtures containing three or seven drugs (concentration 0.3 mmol L^{-1} each). Components of municipal wastewater have a positive effect on the removal of API from wastewater containing single pharmaceuticals (Fig. 3a). The degree of KETO removal is similar to that in the presence of salt and humic acids. The phenomenon of low PARA adsorption is difficult to explain, especially as it complexes with β -CD (Fig. S10), like other studies (Figs. S6, S7, S8, S9, S11, S12) [88,89]. Perhaps interactions under environmental conditions are unstable or the matrix contains more attractive substances.

The three-component mixtures (DIC, IBU, and KETO) are noteworthy as they indicate the synergism of the mentioned compounds also under environmental conditions, which effectively eliminates the influence of the matrices. The result is a high removal rate for each drug, slightly higher than that of distilled water solutions (Fig. 3b). The efficiency of removing these APIs from synthetic production wastewater is impressively high for single production streams as well as their mixtures (Fig. 3b). Cyclodextrin materials do not have functional groups sensitive to low pH, and the hydrophobic interior is not attractive to salt, hence the lack of sensitivity to the high salinity of the formed supramolecular complexes. This could be expected based on the previously conducted studies on the effect of pH and sodium chloride on the sorption efficiency of the drug (Fig. 2f and g). β -CD-HMDI is a material whose action is based primarily on the formation of supramolecular complexes, characterized by various durability. It is no wonder that for more complex systems we can see completely different results, such as for mixtures formed by dissolving DIC, IBU, KETO, NAPR, PARA, SALI, and TRAM in water or wastewater, respectively. The APIs used for comparison also belong to the group of hazardous pollutants commonly found in the natural environment, which justifies the choice [90–93]. The presence of seven pharmaceuticals in the mixture significantly reduced the influence of the matrix on adsorption compared to the one-component systems. The strongest interactions with the β -CD-HMDI surface are observed in the case of SALI and TRAM, which are removed with an efficiency of 72.7% and 52.1%, respectively. Unfortunately, the degree of removal of the remaining ones decreased in a relatively high concentration range (Fig. 3c).

3.1.9. Adsorption isotherms

The isotherm shown in Fig. 3d corresponds to type I. The course of the isotherm reflects the basic assumptions of Langmuir's theory that the adsorbent surface has many active sites, and only one adsorbate molecule can adsorb to one active site. The amount of adsorption initially increases in proportion to the concentration of the adsorbate, then the increase gradually decreases and the adsorption becomes constant. All active places are occupied and a monolayer is formed. A larger amount of the adsorbate particles cannot be adsorbed on the adsorbent surface. Using the nonlinear and linear form of the Langmuir equation, the maximum adsorption capacity (q_{max}) was determined, amounting to 129.70 mg L^{-1} and 131.23 mg L^{-1} , respectively. This value is higher than that resulting from the β -CD content in the polymer structure (54%) [68], which indicates the existence of non-supramolecular interactions. An important addition to the Langmuir isotherm is the dimensionless separation factor R_L . The calculated value shows the privileged course of the process $0 < R_L < 1$ (Table S4). The Freundlich model was also used to eliminate or confirm multilayer adsorption involving inhomogeneous surfaces with non-uniform heat distribution of adsorption. The parameter n , which is decisive for the quality of the adsorption process, was estimated based on its linear form. When its value is in the range of 1–10, the process is preferable in that case. However, the determined statistical coefficients indicate a worse fit of the experimental points to the model (Table S5). The Sips model is a sense of balance to those described and works well for localized adsorption without adsorbate-adsorbate interaction [94, 95]. As C_e approaches a low value, the Sips isotherm transforms into Freundlich, and at high C_e into Langmuir. The Sips isotherm equation is also characterized by the dimensionless heterogeneity coefficient n , which can be used to describe the heterogeneity of the system if the value of n is from 0 to 1. In the case under consideration, $n = 0.71$ (nonlinear) and $n = 1.43$ (linear). The linear model may show a relationship between adsorbent and adsorbed molecules. The β -CD-HMDI - KETO system is perfectly suited to the Sips model as

evidenced by the error analysis and the value of the linear regression coefficient (Table S5). Based on the nonlinear and linear form of the Sips isotherm, the value of $q_{max} = 161.13 \text{ mg L}^{-1}$ and $q_{max} = 162.60 \text{ mg L}^{-1}$ was determined, which is higher than that resulting from the Langmuir equation. This obtained q_{max} value was compared with the maximum sorption capacity of other sorbent materials for KETO reported in the literature and presented in Table 1. Of these, only nitrogen-doped reduced graphene has a higher q_{max} than β -CD-HMDI. It should be noted that in the case of β -CD-HMDI the adsorption process is more efficient considering the short adsorption time and five times the lower specific surface area. In addition, β -CD-HMDI maintains a constant sorption capacity in subsequent cycles and the regeneration itself is fast and simple.

3.1.10. Thermodynamic analysis

The obtained negative value of ΔH° means that the process is exothermic and proceeds with energy release. Negative ΔG° values point to unprompted and thermodynamically favorable processes as well as an affinity of the adsorbate for the adsorbent [101]. Positive values of ΔS° specify a high preference for the adsorbate molecules on the adsorbent surface [102] (Table S5).

3.2. Kinetic models

Seven classical models of adsorption kinetics were used to fit the data: pseudo-first order, pseudo-second order, Elovic, modified Freundlich, Weber Morris (intramolecular diffusion), Bangham pore diffusion, and liquid layer diffusion (Table S5). Considering the fit to the model based on the statistical analysis, it can be concluded that the pseudo-first-order model best describes the adsorption of KETO, $R^2 > 0.998$ (Table S7). Nevertheless, the value of q_e estimated based on this model deviates significantly from the experimental value (Fig. 2d), which is close to q_e calculated from the pseudo-second-order model (Table S6). Three more models were used to determine the limiting stage of the process. The results obtained after fitting the experimental data to these models indicate that the diffusion of the boundary layer (film) and inside the surface of solid particles (pores), substances dissolved in the solution, are equally important. A long time to reach the adsorption equilibrium (approx. 1 h) may indicate that internal diffusion dominates the overall adsorption kinetics. To confirm unequivocal information about the reaction rate limitation, the assumptions of Weber and Morris based on an internal diffusion model [103,104] were used. This model describes the equation shown in Table S6, the k_{id} is the intra-particle diffusion rate constant and C is the layer thickness. The higher the value of C, the greater the influence of the boundary layer on the adsorption process. If the rate-limiting factor is diffusion inside the particles, then the dependence of the square root function q_t on the time $t^{1/2}$ is a straight line passing through the origin of the coordinate system, i.e. $C = 0$. In the case under consideration, $C = 1.05$, which markers that the rate-limiting factor is the boundary layer (film) controlled by the diffusion process (Table S7). Additional applied Elovic and modified Freundlich models during fitting experimental data were linear over the entire range, and the slopes describing the modified Freundlich kinetic model significantly below the value of unity confirm the chemisorption of KETO at a concentration of 20 mg L^{-1} (Table S7).

The presence of additional APIs results in a better fit to the pseudo-second-order kinetic model of each of the drugs under consideration (Table S8). Two-component mixtures are characterized by a significantly higher rate of removal of organic compounds and better use of the specific surface area of the material (Fig. S5). In the case of three-component mixtures, the highest degree of drug removal is observed as well as adsorption rates (Fig. S5 and Table S8). DIC pseudo-second-order reaction constant k_{2-DIC} increases almost 581-fold, k_{2-IBU} 7.7-fold, and k_{2-KETO} 72-fold, respectively. Conceivably this phenomenon is accompanied by changes in the structure of the material, which make it possible to significantly accelerate the adsorption of the most spatial molecules, i.e. DIC.

3.3. Mechanism of adsorption

To put it simply, all tested pharmaceuticals form supramolecular complexes with β -CD both in the solid phase and in aqueous solutions [88,105–108], so they should also be retained in the β -CD-HMDI structure. Six out of seven do. The exception is paracetamol, which forms a 3: 2 stoichiometry complex with CD in aqueous solutions (Fig. S10). The formation of a multi-component complex requires the appropriate mutual arrangement of the molecules that make up the compound. Cross-linking significantly reduces the number of degrees of freedom of the β -CD rings and requires a different arrangement. Consequently, the interactions are so weak that PARA is equally quickly adsorbed and desorbed. In the sorption process, the stoichiometry of the resulting complex is not the only

Table 1
Examples of adsorbents used to remove KETO from waters.

Adsorbent type	$Q_{max} \text{ (mg g}^{-1}\text{)}$	pH	Temp. (°C)	Time (h)	Specific surface area (m ² g ⁻¹)	Reference
Sonicated activated carbon	40.0	2.0	25	2	640.9	[27]
Montmorillonite	67.0	6.4	25	2	32.0	[96]
Carbon nanotubes	99.0	4.5	25	24	170.9	[97]
Activated carbon prepared from effluent treatment plant sludge of the beverage industry	105.9	4.0	25	3	642	[98]
activated carbon prepared from winery wastes	146.4	3	25	6	227.16	[99]
β-CD-HMDI	(161.13) 162.60	4.2	25	1	7.3	This work
Nitrogen-doped reduced graphene oxide modified by Fe ₃ O ₄	468.0	6.8	25	24	38.20	[100]

significant component. SALI in aqueous solutions also forms 3: 2 complexes with β -CD (Fig. S11) and, interestingly, shows the highest affinity for the material in both aqueous solutions and sewage. The explanation should be sought in the arrangement of the functional groups. Most likely, the aromatic rings of the acid are located in the β -CD tori, while its functional groups, located in the ortho position to each other, are involved in the formation of a network of hydrogen bonds with other elements of the sorbent structure. The remaining APIs show greater lipophilicity due to the presence of aliphatic or aromatic substituents, thereby increasing the number of possible structures (Fig. S6-S12 and S13). For example, the phenolic substituent KETO is complexed through the interior of the CD, the second ring interacts with the aliphatic chain of the lattice, and the carboxyl group is involved in hydrogen bonding with the urethane or allophanate moiety (Fig. S13).

4. Conclusions

The paper presents a material that, contrary to the commonly used activated carbons in the form of a powder, is easily separated and regenerated. It is durable and can work in environmental conditions. The sorption capacity remains unchanged after the next five regeneration cycles. Despite the small specific surface area of the material, a high degree of KETO removal from model post-production effluents is achieved during the simultaneous removal of diclofenac, ibuprofen, and ketoprofen, even in concentrations much higher than those found in the natural environment, which allows it to be used in industrial conditions. The outflow of streams from municipal wastewater treatment plants containing the above-mentioned drugs can be successfully purified, achieving efficiencies in removing diclofenac, ibuprofen, and ketoprofen of 95%, 82%, and 78%, respectively. Even higher efficiency of the pre-treatment can be obtained in industrial conditions by combining the streams of the above-mentioned APIs (100% DIC, 99% IBU, and 97% KETO). The presence of additional other NSAIDs and analgesics in the wastewater modifies the adsorption profile, and the preferred adsorbent compounds are mainly salicylic acid, tramadol, and diclofenac, for which the removal efficiencies are 72%, 52%, and 44%, respectively.

CRediT authorship contribution statement

Anna Skwierawska: Conceptualization, Methodology, Investigation, Formal analysis, Validation, Writing - original draft, Visualization, Writing - review & editing.

Dominika Nowacka: Investigation, Writing - review & editing.

Katarzyna Kozłowska-Tylingo: Formal analysis, Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wri.2022.100186>.

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Supplementary Material

**Removal of nonsteroidal anti-inflammatory drugs and analgesics from
wastewater by adsorption on cross-linked β -cyclodextrin**

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Supplementary Material

Basic information about the tested APIs and β -CD-HMDI

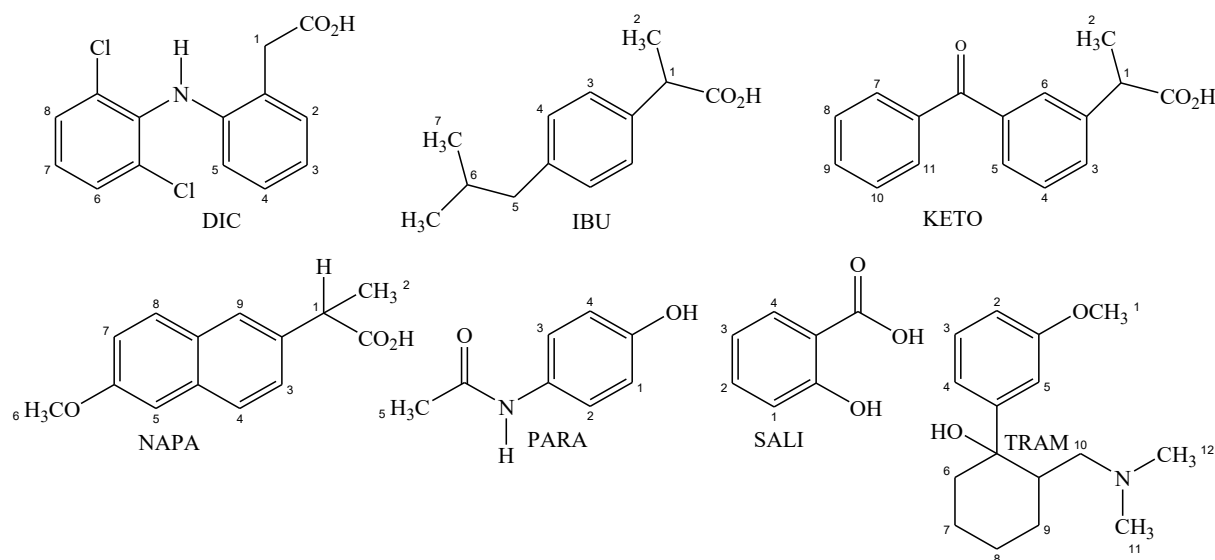


Fig. S1 Structural formulas of investigated drugs. The numbers describe the signals in the ^1H NMR spectra.

Table S1 Main information about used in studies pharmaceuticals.

API name	API	structure	molar mass (g mol ⁻¹)
diclofenac	DIC	C ₁₄ H ₁₀ Cl ₂ NO ₂ Na	318.14
ibuprofen	IBU	C ₁₃ H ₁₈ O ₂	206.29
ketoprofen	KETO	C ₁₆ H ₁₄ O ₃	254.28
naproxen	NAPR	C ₁₄ H ₁₄ Cl ₂ O ₃	230.26
paracetamol	PARA	C ₈ H ₉ NO ₂	151.17
Salicylic acid	SALI	C ₇ H ₆ O ₃	138.12
tramadol	TRAM	C ₁₆ H ₂₅ NO ₂ xHCl	272.88

β -CD-HMDI material

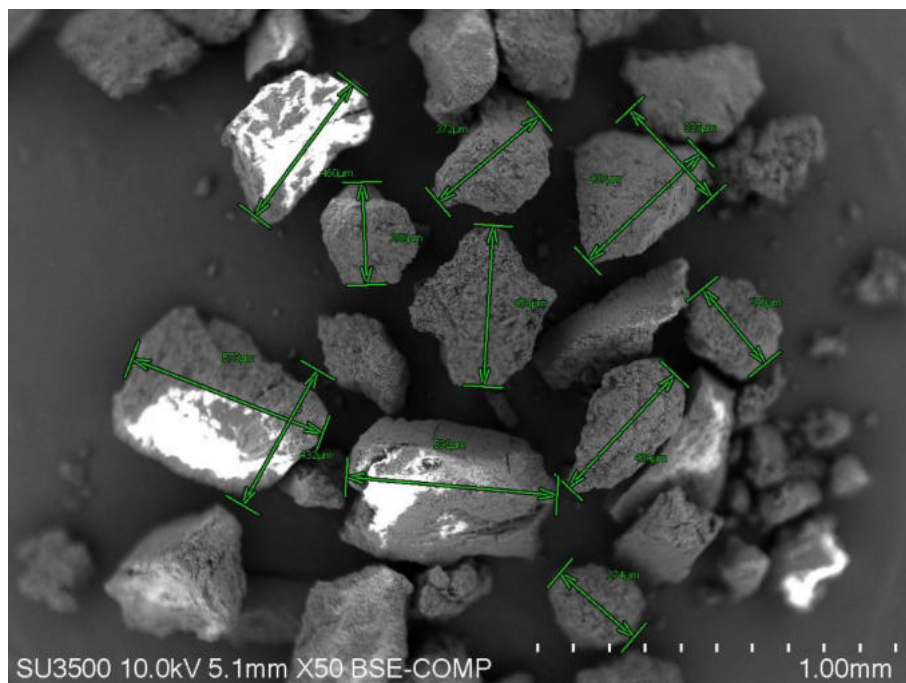


Fig S2 SEM image of β -CD-HMDI.

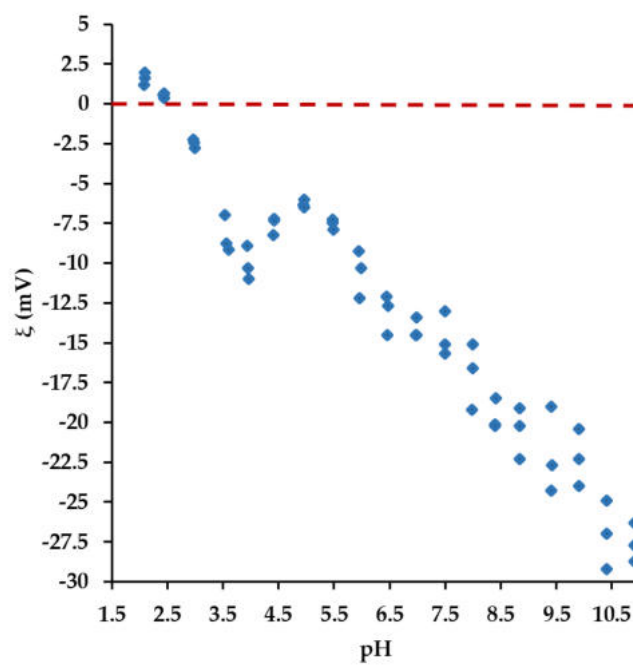
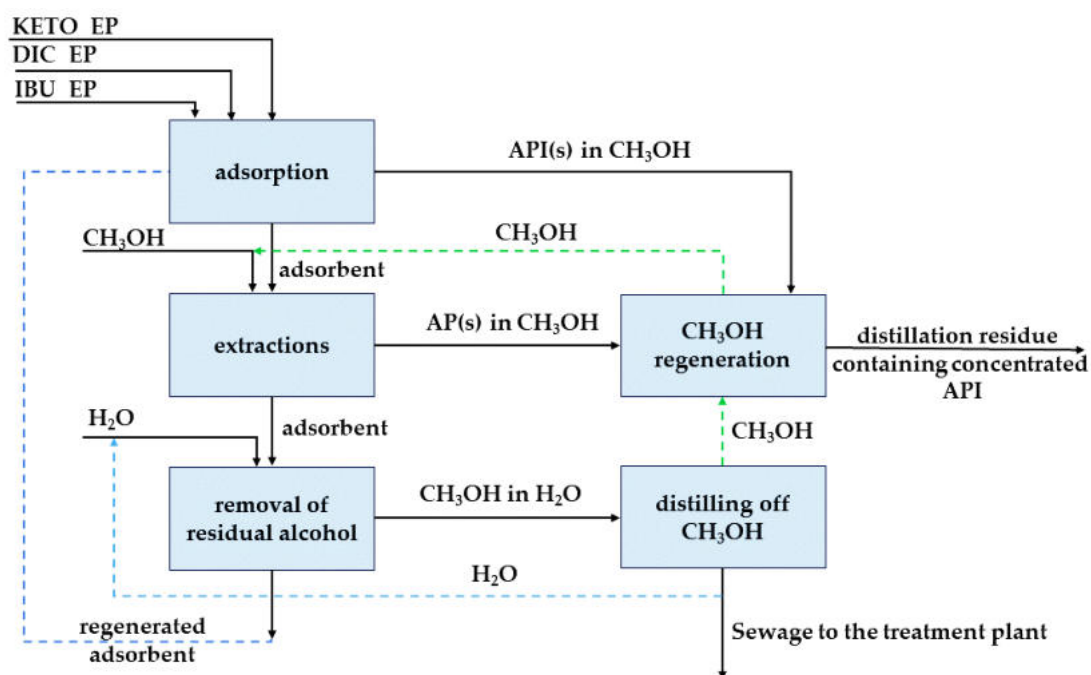


Fig. S3 Zeta Potential changes during titration of the range of pH 2 -11.

Supplementary Material

Table S3 Characterization of effluents from municipal sewage treatment plant.

Effluents			
parameter	value	parameter	value
BOD ₅	40 mg L ⁻¹ O ₂	Total nitrogen	20 mg L ⁻¹
		total phosphorus	0.5 mg L ⁻¹
COD	120 mg L ⁻¹ O ₂	Conductivity	1200 μS cm ⁻¹
TOC	2.2 mg L ⁻¹ C	pH	5.6
Total suspended solids	50 mg L ⁻¹		



Scheme S1 Improving the process of removing drugs from post-production (EP) wastewater.

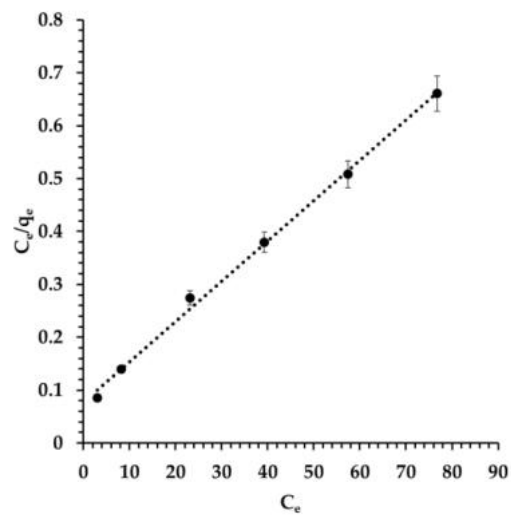
Equilibrium and kinetic studies, and thermodynamic analysis

Table S4 List of adsorption isotherms models and applied plots.

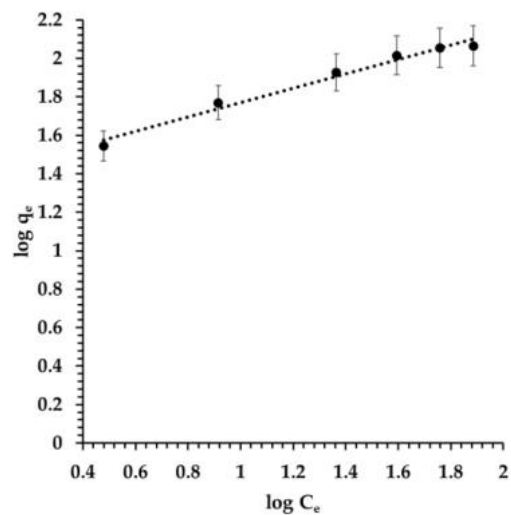
Model*	Model in Linear form*	Plot	Ref.
Langmuir			
$q_e = \frac{q_{max}K_L C_e}{1 + bC_e}$ (10)	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$	$\frac{C_e}{q_e} \text{ vs } C_e$	[1]
Freundlich			
$q_e = K_F C_e^{\frac{1}{n}}$ (11)	$\log q_e = \ln K_F + \frac{1}{n} \log C_e$	$\log q_e \text{ vs } \log C_e$	[2]
Sips			
$q_e = \frac{q_{max} K_S C_e^{\frac{1}{n}}}{1 + K_S C_e^{\frac{1}{n}}}$ (14)	$\frac{1}{q_e} = \frac{1}{q_{max} K_S} \left(\frac{1}{C_e} \right)^{\frac{1}{n}} + \frac{1}{q_{max}}$	$\frac{1}{q_e} \text{ vs } \left(\frac{1}{C_e} \right)^{\frac{1}{n}}$	[3]
thermodynamic parameters			
	$\ln(K_e^0) = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R}$ $\Delta G^0 = -RT \ln(K_e^0)$ $K_e^0 = \frac{K M_a C_a^0}{\gamma}$	$\ln(K_e^0) \text{ vs } \frac{1}{T}$	[4]

* q_{max} —maximum adsorption capacity (mg g^{-1}); K_L —adsorption equilibrium constant (L mg^{-1}); R_L —the separation factor; K_F —adsorption capacity constant ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$); K_S —Sips equilibrium constant [$(\text{mg L}^{-1})^{-1/n}$], n —heterogeneity factor. ΔH^0 , ΔS^0 , ΔG^0 are standard enthalpy, entropy and free energy and K_e^0 is dimensionless thermodynamic equilibrium constant, which is calculated from the best isotherm fitted K (L g^{-1}), M_a and C_a^0 are molecular weight and standard concentration of the adsorbate (1 M), and γ is coefficient of activity.

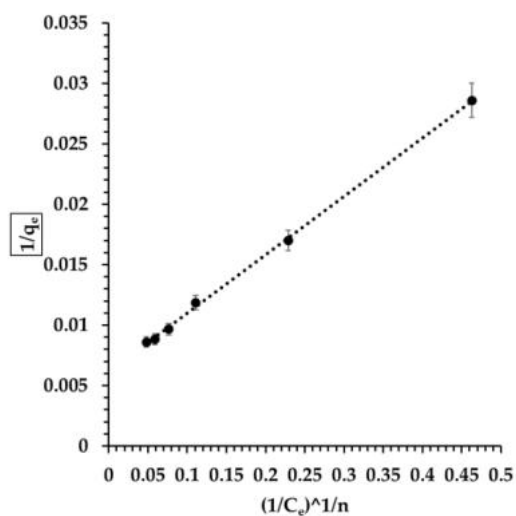
Adsorption linear model fitting isotherms



(a)



(b)



(c)

Fig. S4. Equilibrium adsorption linear model fitting: (a) Langmuir; (b) Freundlich; (c) Sips

Supplementary Material

Table S5 Parameters of the equilibrium sorption models and of linear (R^2) regression coefficient.

Isotherm model	Parameters	value	Parameters	value
Langmuir	K_L (L mg ⁻¹)	0.098	R^2	0.99855
	q_{max} (mg g ⁻¹)	131.23	Adj. R^2	0.99639
	Slope	0.00762	Slope SE	2.05247E-4
	Intercept	0.007739	Intercept SE	0.00892
	K_L (L mg ⁻¹)	0.0101	R^2	0.99347
	q_{max} (mg g ⁻¹)	129.70	Adj. R^2	0.99020
			χ^2	7667.65
$R_L = \frac{1}{1 + K_L C_0}$	R_L	0.093 - 0.911	RSS	6.98416E-4
Freundlich	n	2.67	R^2	0.98999
	K_F (mg ^{1-1/n} L ^{1/n} g ⁻¹)	24.95	Adj. R^2	0.9751
	Slope	0.3739	Slope SE	0.02665
	Intercept	1.39708	Intercept SE	0.03788
		RSS	0.00415	
	n	2.98	R^2	0.98919
	K_F (mg ^{1-1/n} L ^{1/n} g ⁻¹)	28.40	Adj. R^2	0.98379
			χ^2	2.0128
Sips	K_s (mg L ⁻¹) ^{-1/n}	0.1271	R^2	0.99957
	q_{max} (mg g ⁻¹)	162.60	Adj. R^2	0.99892
	n	1.43	RSS	2.59776E-4
	Slope	0.04839	Slope SE	7.11075E-4
	Intercept	0.00615	Intercept SE	1.56411E-4
	K_s (mg L ⁻¹) ^{-1/n}	0.0541	R^2	0.99830
	q_{max} (mg g ⁻¹)	161.13	Adj. R^2	0.99659
	n	0.71	χ^2	164.1213
Thermodynamic parameters	ΔH^0 (kJ mol ⁻¹)	-9.15	Intercept	4.06329
	ΔS^0 (J K ⁻¹ mol ⁻¹)	33.78	Intercept SE	0.35776
	ΔG_{297}^0 (kJ mol ⁻¹)	-19.33	Slope	1100.61316
	ΔG_{313}^0 (kJ mol ⁻¹)	-19.66	Slope SE	111,58891
	ΔG_{333}^0 (kJ mol ⁻¹)	-20.43	R^2	0.9949
	RSS	0.00105	Adj. R^2	0.97965

Supplementary Material

Kinetic

Table S6 Description of the kinetic models used in the calculations.

Kinetic model	Linear form	Plot	Ref.
Pseudo-first order	$\ln(q_e - q_t) = \ln q_e - k_1 t$ (3)	$\ln(q_e - q_t) \text{ vs } t$	[5]
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{K_2} q_e^2 + \frac{t}{q_e}$ (4)	$\frac{t}{q_t} \text{ vs } t$	[6]
Liquid film diffusion	$\ln \left(1 - \frac{q_t}{q_e}\right) = -K_{lf} t$ (6)	$\ln \left(1 - \frac{q_t}{q_e}\right) \text{ vs } t$	[7]
Bangham diffusion	$\log \log \left\{ \frac{c_0}{c_0 - m q_t} \right\} = \log \left\{ \frac{m K_B}{2.303 V} \right\} + \delta \log q_t$ (7)	$\log \log \left\{ \frac{c_0}{c_0 - m q_t} \right\} \text{ vs } \log t$	[8]
Elovic	$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln(t)$ (8)	$q_t \text{ vs } \ln(t)$	[9]
Modified Freundlich	$\ln q_t = \ln(k_f c_0) + \frac{1}{m} \ln t$ (9)	$\ln q_t \text{ vs } \ln t$	[10]

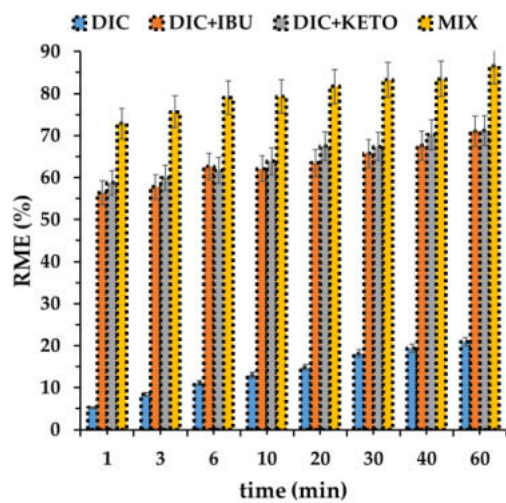
* q_e (mg g⁻¹); k_1 (min⁻¹), k_2 (g min⁻¹ mg⁻¹); δ ; K_B (mL L⁻¹ g⁻¹); K_{lf} (g mg⁻¹ min⁻¹); β (g mg⁻¹); α (g mg⁻¹ min⁻¹); $1/m$; k_F (L g⁻¹ min⁻¹)

Supplementary Material

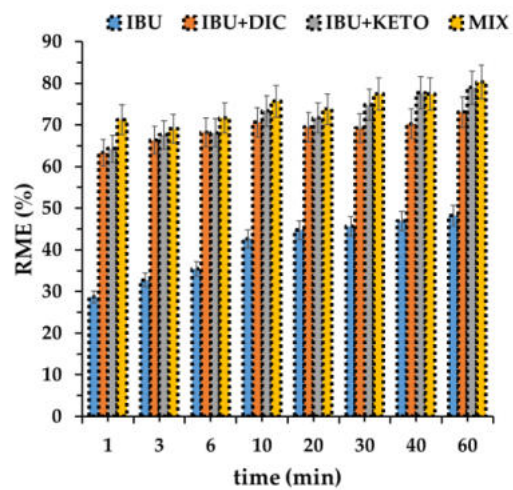
Table S7 Kinetic model constants of single-component mixtures and their error analysis.

Isotherm model	Parameters	value	Parameters	value
First-order kinetic model	q_e (mg g ⁻¹)	2.98	R ² /Adj. R ²	0.99822/0.99585
	k_1 (min ⁻¹)	0.057	RSS	0.03559
	Slope	-0.05735	Slope SE	0.0014
	Intercept	1.09054	Intercept SE	0.04031
Second-order kinetic model	q_e (mg g ⁻¹)	4.33	R ² /Adj. R ²	0.99688/0.99274
	k_2 (g min ⁻¹ mg ⁻¹)	15.06	RSS	1.00944
	Slope	0.2305	Slope SE	0.00745
	Intercept	1.24972	Intercept SE	0.21465
Bangham's pore diffusion model	δ	0.303	R ² /Adj. R ²	0.99629/0.99136
	K_B (mL L ⁻¹ g ⁻¹)	0.312	RSS	0.00177
	Slope	0.30296	Slope SE	0.01068
	Intercept	-3.56774	Intercept SE	0.1277
Weber and Morris Intraparticle diffusion model	C	1.05	R ² /Adj. R ²	0.98089/0.95584
	K_{id-1} (g mg ⁻¹ min ^{-1/2})	0.43	RSS	0.28425
	Slope	0.43002	Slope SE	0.03482
	Intercept	1.04733	Intercept SE	0.16051
Liquid film diffusion	K_{lf} (g mg ⁻¹ min ⁻¹)	0.057	R ² /Adj. R ²	0.99822/0.99585
			RSS	0.03559
	Slope	-0.05735	Slope SE	0.0014
	Intercept	-0.33256	Intercept SE	0.04031
Elovich	β (g mg ⁻¹)	1.36	R ² /Adj. R ²	0.99122/0.97961
	α (g mg ⁻¹ min ⁻¹)	2.92	RSS	0.13125
	Slope	0.7334	Slope SE	0.03993
	Intercept	1.01091	Intercept SE	0.10993
modified Freundlich	$1/m$	0.303	R ² /Adj. R ²	0.99629/0.99135
	k_F (L g ⁻¹ min ⁻¹)	0.062	RSS	0.00939
	Slope	0.30278	Slope SE	0.01068
	Intercept	0.21966	Intercept SE	0.02941

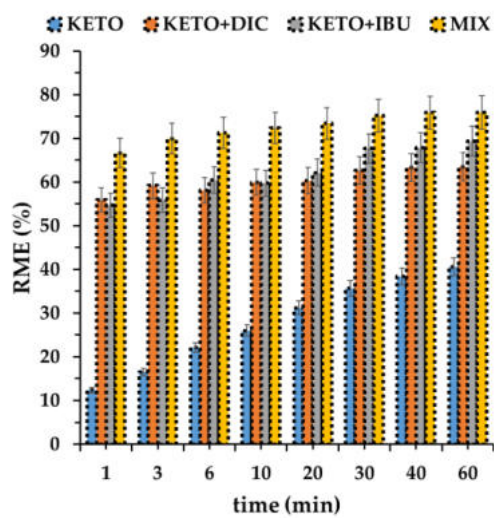
Multicomponent systems



a)



b)



c)

Fig. S5 Influence of the presence of other drugs on the kinetics of the adsorption process of each of them.

Supplementary Material

Table S8 Second-order kinetic model constants of two and three-component mixtures and their error analysis.

component	Parameters	DIC	IBU	KETO
Single API	q_e	2.36	4.91	4.34
	k_2 (g min ⁻¹ mg ⁻¹)	1.568	71.87	15.06
	R^2	0.99799	0.99898	0.99688
	RSS	1.48673	0.08961	1.00944
DIC + IBU	q_e (mg g ⁻¹)	7.08	7.25	
	k_2 (g min ⁻¹ mg ⁻¹)	301.458	738.34	-
	R^2	0.99898	0.99955	
	RSS	0.12421	0.05153	
DIC + KETO	q_e (mg g ⁻¹)	7.16		6.39
	k_2 (g min ⁻¹ mg ⁻¹)	410.29	-	507.17
	R^2	0.99968		0.99987
	RSS	0.03838		0.01871
IBU + KETO	q_e (mg g ⁻¹)		7.93	7.00
	k_2 (g min ⁻¹ mg ⁻¹)	-	529.82	298.30
	R^2		0.99946	0.99942
	RSS		0.05202	0.07222
DIC + IBU+KETO	q_e (mg g ⁻¹)	8.64	8.01	7.64
	k_2 (g min ⁻¹ mg ⁻¹)	910.81	695.35	1086.15
	R^2	0.99968	0.99956	0.99995
	RSS	0.02636	0.04149	0.00519

^1H NMR studies on API complex formation

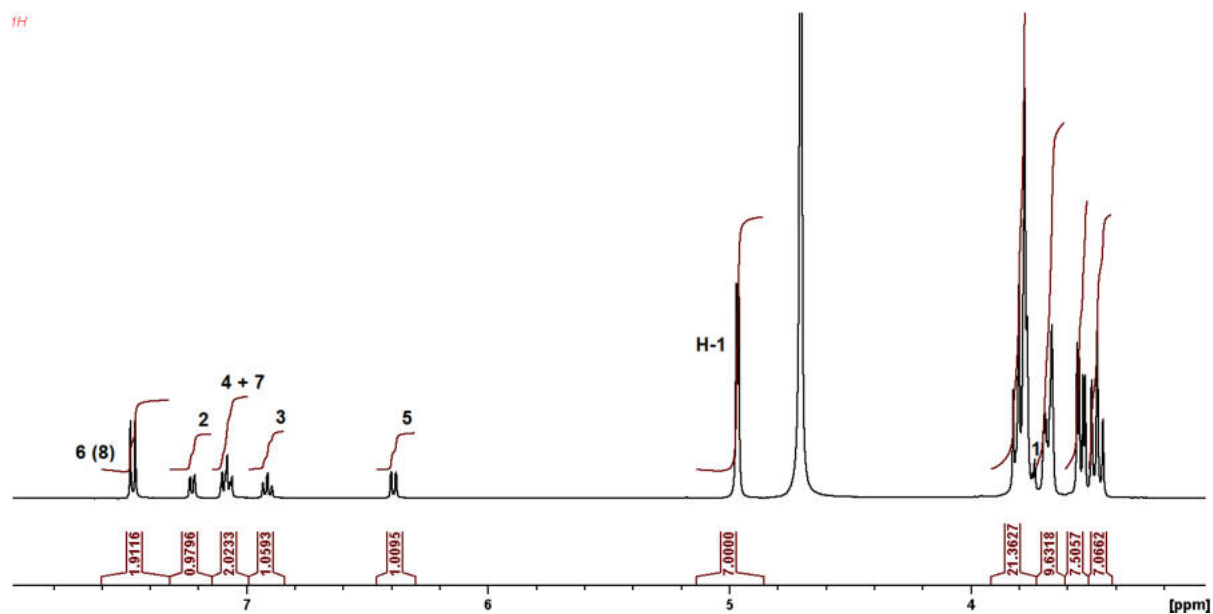


Fig. S6. ^1H NMR (400 MHz, δ) spectra of DIC complex with β -CD in D_2O .

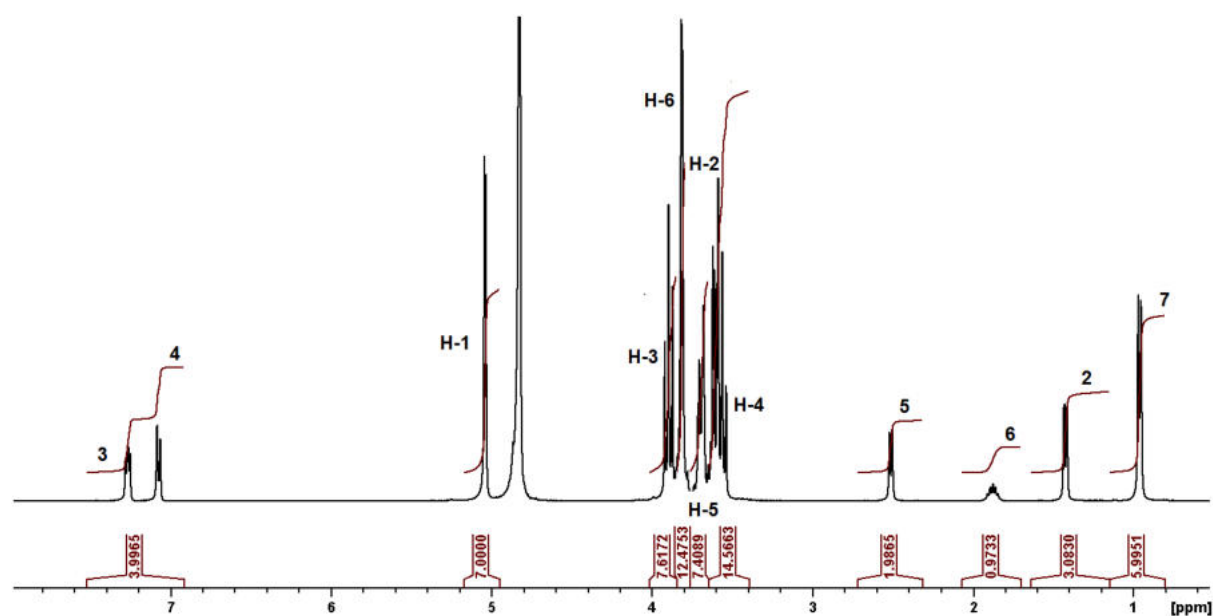


Fig. S7. ^1H NMR (400 MHz, δ) spectra of IBU complex with β -CD in D_2O .

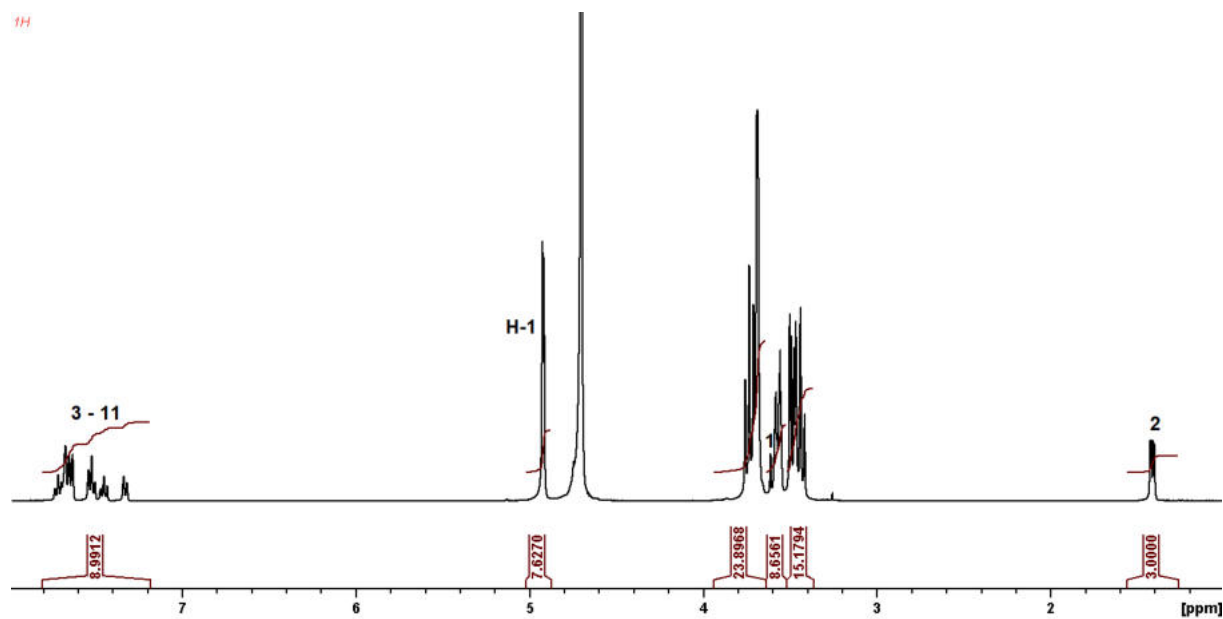


Fig. S8. ¹HNMR (400 MHz, δ) spectra of KETO complex with β -CD in D₂O.

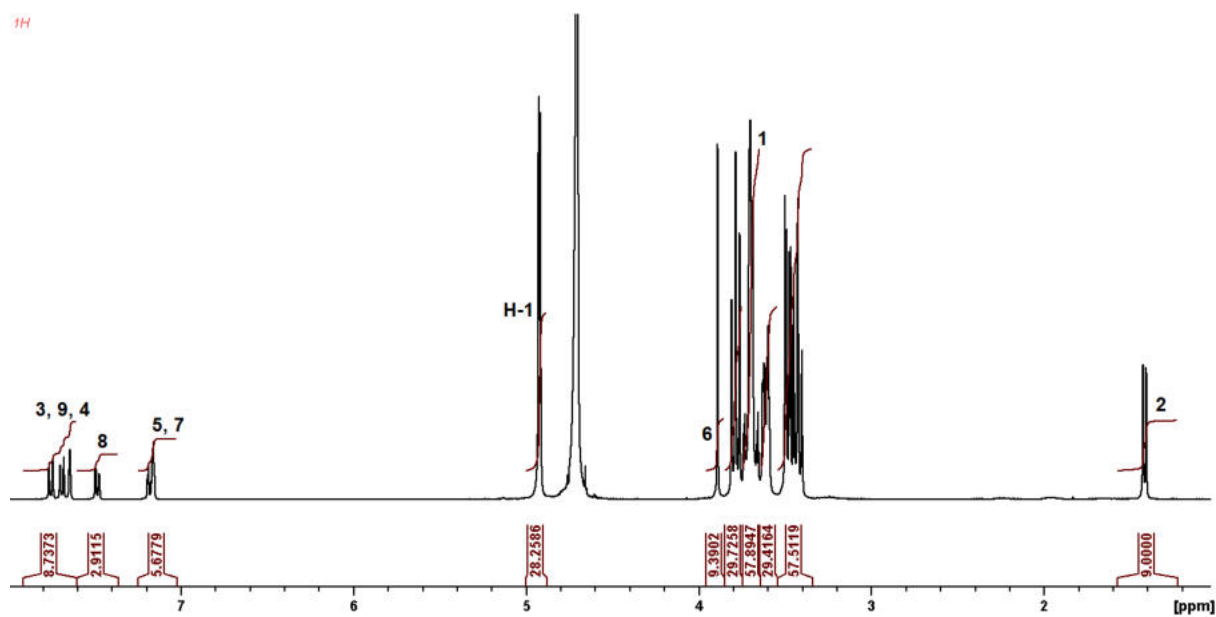


Fig. S9. ¹HNMR (400 MHz, δ) spectra of NAPR complex with β -CD in D₂O.

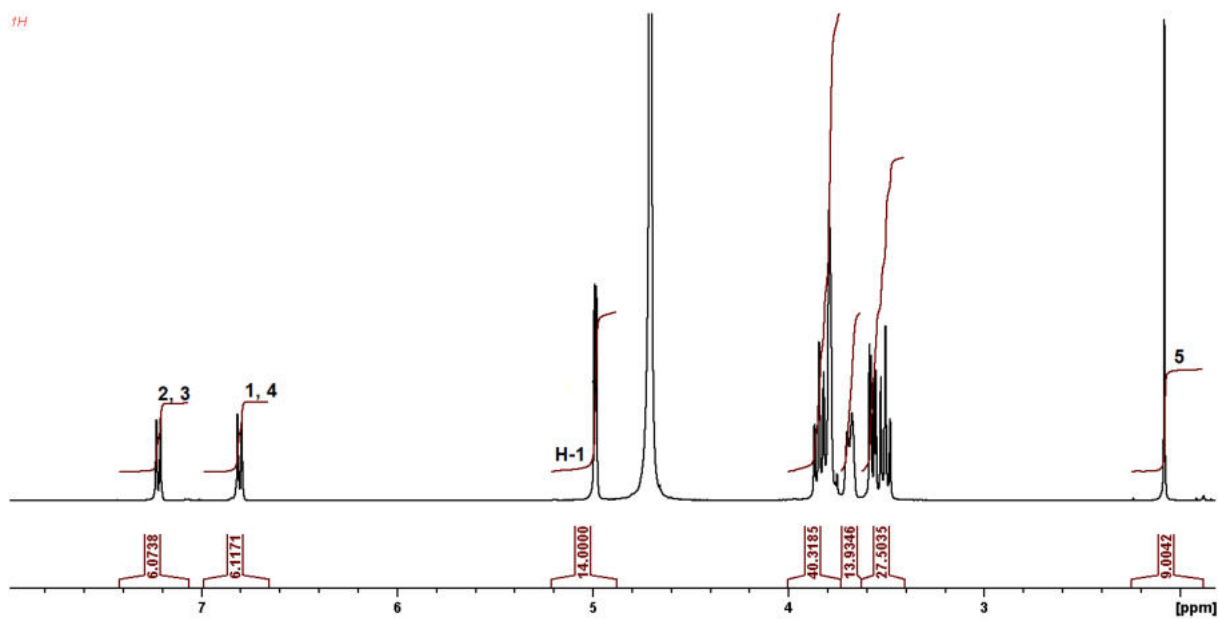


Fig. S10. ¹H NMR (400 MHz, δ) spectra of PARA complex with β -CD in D₂O.

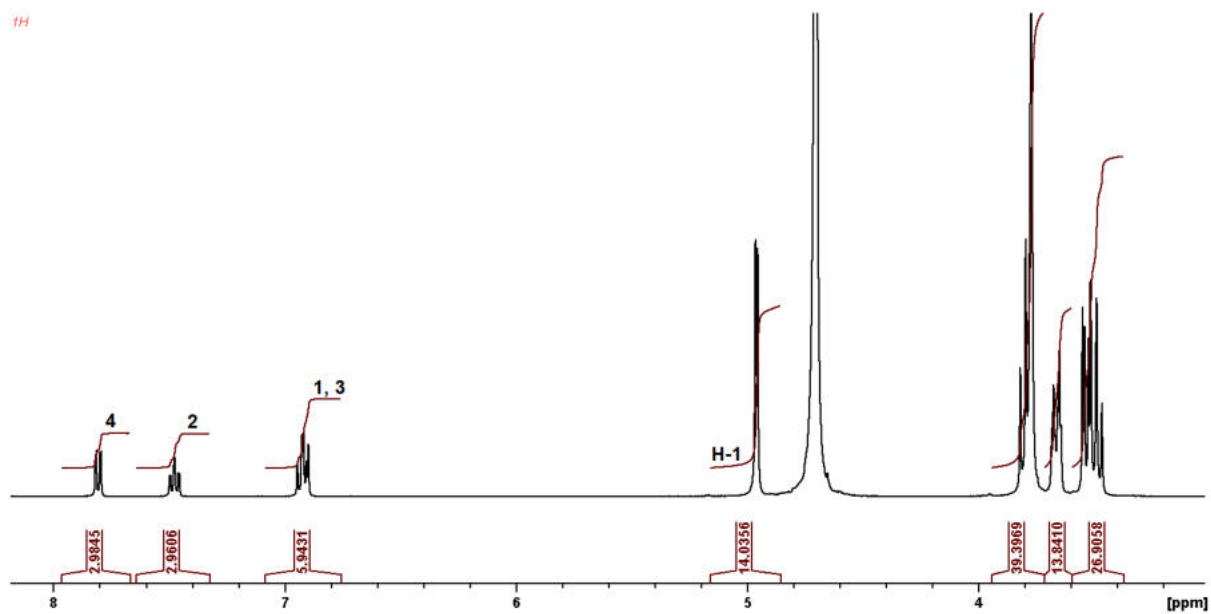


Fig. S11. ¹H NMR (400 MHz, δ) spectra of SALI complex with β -CD in D₂O.

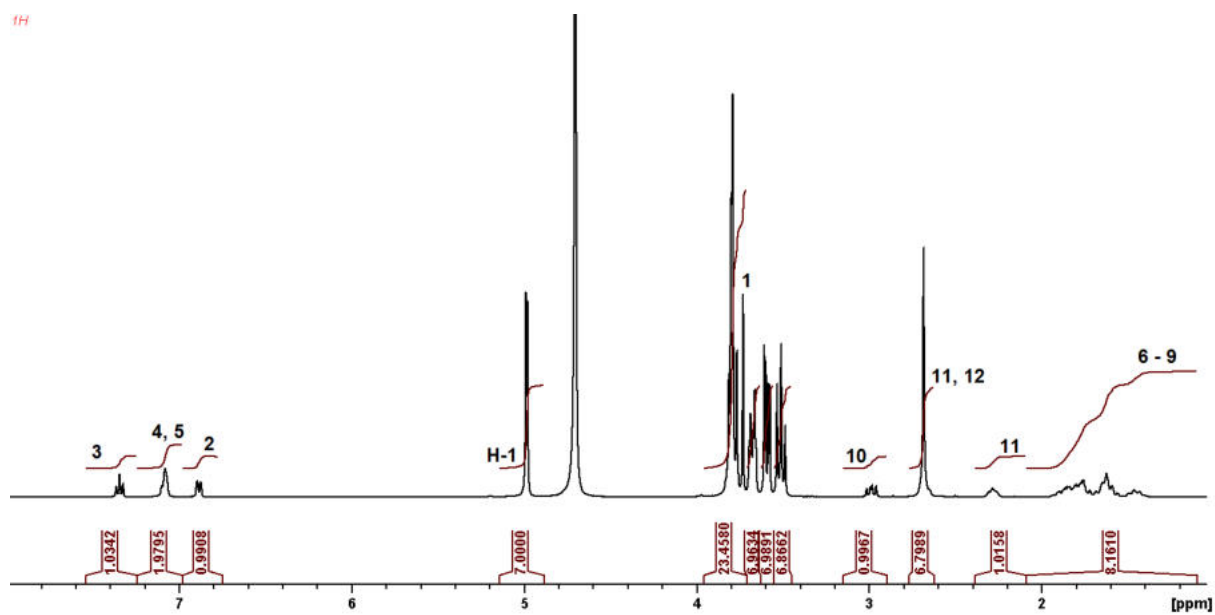


Fig. S12. ^1H NMR (400 MHz, δ) spectra of TRAMA complex with β -CD in D_2O .

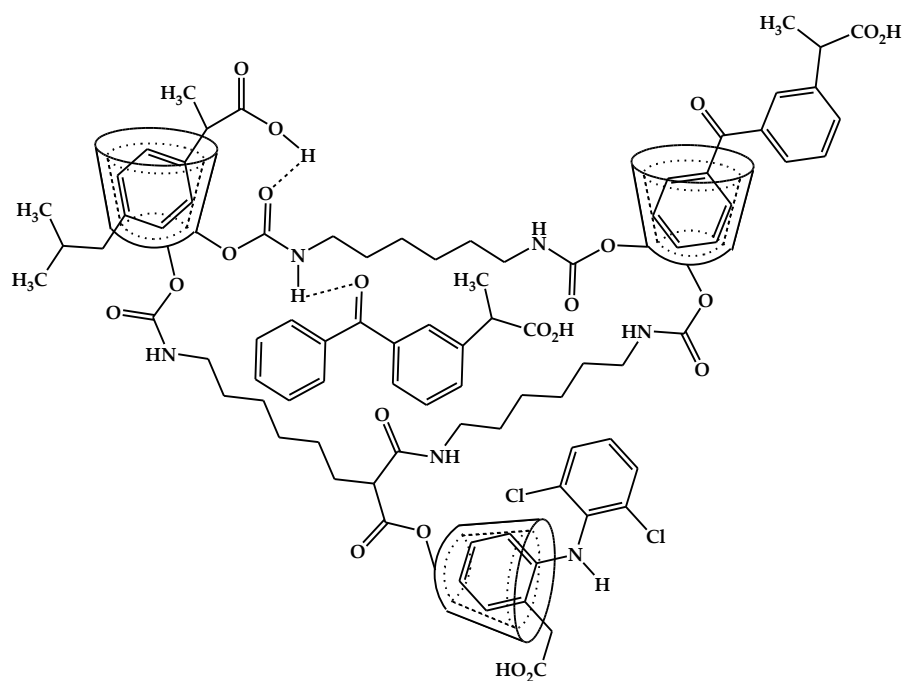


Fig. S13. Possible interactions of β -CD-HMDI with DIC, IBU and KETO.

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Publication 3

Cellulose and its derivatives, coffee grounds, and cross-linked β -cyclodextrin in the race for the highest sorption capacity of cationic dyes in accordance with the principles of sustainable development – *Journal of Hazardous Materials*, 2022

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Research Paper

Cellulose and its derivatives, coffee grounds, and cross-linked, β -cyclodextrin in the race for the highest sorption capacity of cationic dyes in accordance with the principles of sustainable development

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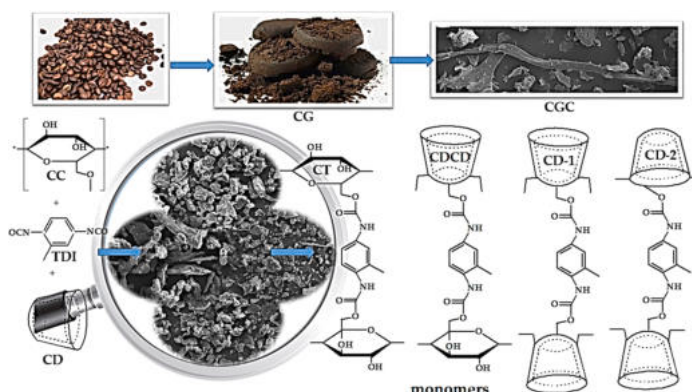
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HIGHLIGHTS

- Natural or semi-natural sorption materials which are better?
- The reaction solvent shapes the sorption properties of the polymers.
- Pollutant shape memory as the basis for the stability of sorbent efficiency.
- Waste-free regeneration of adsorbents.
- Possible decomposition of used adsorbents by composting.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, seven different materials were analyzed and includes coffee grounds (CG), two types of cellulose (CGC and CC), two types of modified cellulose (CT and CTCD), and cross-linked β -cyclodextrin (CD-1 and CD-2) were tested as adsorbents for the removal of dyes from the wastewater. The composition, morphology, and presence of functional groups in the obtained sorption materials were characterized by elemental analysis, SEM, TG/DTA, and FTIR spectroscopy. The sorption processes of the model contaminant, crystal violet (CV), were

Abbreviations: BG, brilliant green; BP, bromocresol purple sodium salt; CC, cellulose microcrystalline; β -CD, β -cyclodextrin; CD-1, sorbent obtained in reaction of cyclodextrin with toluene-2,4-di-isocyanate conducted in a pyridine medium; CD-2, sorbent obtained in reaction of cyclodextrin with toluene-2,4-di-isocyanate conducted in a dimethylformamide medium; CG, coffee grounds; CR, Congo red; CT, cellulose sorbent obtained in reaction microcrystalline cellulose with toluene-2,4-di-isocyanate in a pyridine medium; CTCD, sorbent obtained in reaction of microcrystalline cellulose and cyclodextrin with toluene-2,4-di-isocyanate in a pyridine medium; CV, crystal violet; DMF, dimethylformamide; EB, eriochrome black; HA, a mixture of humic acids 50% fulvic acids; MB, methylene blue; TB, toluidine blue; TDI, Itoluene-2,4-di-isocyanate.

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Shape memory
Yeast

studied by kinetics and equilibrium models. The results showed, that using CTCD, the dye was adsorbed rapidly in 1 min and the slowest adsorption occurred in 20 min by CG. The time evolution was adjusted using a two-model, pseudo second-order model (CG and CGC) and pseudo first-order model in the rest adsorbents. According to the Langmuir and Sips isotherm models, the maximum adsorption capacities were very high in each case ranging from 1092.24 to 1220.40 mg g⁻¹. Moreover, the adsorption capacity of the near-natural materials remained even higher after five regeneration cycles. The regeneration is almost waste-free and the materials used can be decomposed during composting. In addition, almost complete removal of cationic dyes was observed during the treatment of real wastewater samples.

1. Introduction

1.1. Natural origin adsorbents

Currently, a lot of attention is being paid to organic adsorbents (Marincas et al., 2016), seeing the possibility of final degradation through biodegradation (Karoyo et al., 2018). These adsorbents can be divided into four groups. The first is chemically unmodified, it includes various types of plant waste such as shells (Bulut and Aydin, 2006; Ferrero, 2007; Queirós et al., 2020), skins (Trends et al., 2021), fruits (Harshananda et al., 2020; Sathishkumar et al., 2015), leaves and barks (Ayalew and Aragaw, 2020; Futalan et al., 2019; Ibiyinka et al., 2021; Kim and Kim, 2020; Oliveira et al., 2008; Pavan et al., 2008). However, completely crude form was quite difficult to use, the plant raw material was first grounded and dried to a constant weight, and physically processed to remove undesirable components. Thus, the group of adsorbents obtained in this way includes coffee grounds and tea leaves (Lafi et al., 2014; Loulidi et al., 2021), citrus and banana peels, and nut shells (Rafatullah et al., 2010). The nature-compatible form of the adsorbent enables biological decomposition at a rate appropriate for a given plant (Chalker-scott, 2021; Kalemelawa et al., 2012; Raimondo et al., 2018; Scroll and For, 2012). The second group consists of adsorbents obtained from the above-mentioned raw materials as a result of chemical or biotechnological reactions (Brinchi et al., 2013; Kim et al., 1997; Liu et al., 2016; Rajput et al., 2016; J. Zhang et al., 2019; Zhong, 2020). These are the main plant components, i.e. cellulose, hemicellulose, and lignin, but also chitin and cyclodextrin (Militao et al., 2021; Shahnaz et al., 2021). The third group consists of adsorbents containing components of natural origin incorporated into the structure of the material by means of chemical reactions (Ding et al., 2020; A.M. Elgarahy et al., 2019, 2021; Ahmed M. Elgarahy et al., 2019; Elwakeel, 2009; Elwakeel et al., 2021b, 2021a, 2020; Erdős et al., 2020; Soares et al., 2019; Yang et al., 2020). The last one consists of various types of carbons obtained during the pyrolysis of various natural resources (Tomul et al., 2020; Yi et al., 2019). To practice the principles of sustainable development during the preparation of the adsorbents, following should consider the reduction of energy consumption and emission of gases, waste, and sewage during its production, regeneration, and disposal, which were quite difficult to achieve. Therefore, the basic problem is to keep the technological moderation that allows obtaining the cost-effective adsorbent in the least number of preparatory steps, but with a high sorption capacity.

1.2. Dye adsorption

Dye was checked using simple devices for adsorption purposes in the wastewater. Due to the increase in anthropogenic activities, there is an exponential increase in dye contaminants around the world. Additionally, the production of dyes and dyeing processes are an example of an industry that generates a large amount of wastewater containing organic substances (Katheresan et al., 2018; Liu, 2020; Shindhal et al., 2021). Dyes are a real environmental threat because they are not biodegradable (Garg and Chopra, 2022; Lellis et al., 2019) and the colored sewage hinders the growth of microorganisms and plants responsible for phytoremediation of waters. In factories and dye works, various solutions

are used to reduce the emission of dyes to the natural environment. The most frequently used methods to remediate dye pollutants from the environment are physical, chemical and biological (Dutta et al., 2021). None of the above-mentioned methods are fully effective; therefore, new solutions are constantly sought, including organic adsorbents. Dyes are designed in a way that allows permanent interaction with the colored surface. In the case of cotton and modified cellulose fibers, where dyes are often used and bind with the material through hydrogen bonding and van der Waals forces. The weak interactions are compensated by the multitude of free hydroxyl groups present in the glucose monomers. An example of such dye is triarylmethane derivatives containing amino groups. Furthermore, using cellulose adsorbents is an effective approach to remove these dyes from wastewater, but the problem is regeneration, which uses too many extractions. A potential solution may be the use of β -cyclodextrin polymers that selectively interact with dyes of this group by inclusion of one of the rings inside the torus. Similarly, the resulting supramolecular complex can be easily broken down which makes the desorption process easier.

In this study, seven adsorbents were intentionally selected: spent coffee grounds (CG), cellulose obtained from coffee grounds (CGC), commercial microcrystalline cellulose (CC); and four materials derived from the condensation of toluene-2,4-diisocyanate with microcrystalline cellulose (CT); a mixture of microcrystalline cellulose and β -CD (CTCD) and β -CD alone (CD-1 and CD-2). From the comparison of the first two, it was expected to obtain a result indicating the validity of the production of technical cellulose used in the removal of dyes from the environment. The choice of microcrystalline cellulose was aimed at highlighting the structural differences with respect to CGC affecting the durability of the obtained connections and the resulting problems during regeneration. Moreover, the synthesis of CT and CTCD was also a deliberate procedure. First, the modification with toluene-2,4-diisocyanate changes the hydrophobicity of cellulose. Secondly, in the case of CT, a more ordered structure and a greater likelihood of the emergence of $\pi - \pi$ interactions were to be expected. The addition of β -CD to the system made it possible to determine the importance of selective interaction with a specific dye. Knowing the influence of β -CD on the sorption capacity of the two-component material, it was still necessary to determine the flow of the arrangement of groups acting as linkers.

2. Experimental procedure and methods

2.1. Materials

Toluene-2,4-di-isocyanate (TDI $\geq 95\%$), Congo red (CR, C.I. 22120) eriochrome black, (EB, C.I. 14640), bromocresol purple sodium salt (BP, $\geq 90\%$), toluidine blue (TB, C.I.52040), crystal violet (CV $\geq 96\%$), brilliant green (BG $\geq 98\%$), methylene blue (MB $\geq 97\%$), β -cyclodextrin (CD $\geq 97\%$), cellulose microcrystalline (CC - for thin-layer chromatography, USP), and pyridine (anhydrous ≥ 99.8) were purchased from Merck. Dimethylformamide (anhydrous DMF ≥ 99.8), sodium hydroxide (NaOH $\geq 99\%$ and 0.1 N solution), hydrochloride acid (0.1 N HCl), and 30% aqueous solution of hydrogen peroxide were supplied by Chempur. Methanol (CH₃OH $\geq 99.8\%$), sodium and calcium chlorides (NaCl $\geq 99\%$ and CaCl₂ $\geq 99\%$) as well commercial humic acids containing 50% of humic acids and 50% fulvic acids (HA, 90% dry matter)

were purchased from Chempur and Agraplant, respectively. Potassium bromide (KBr spectroscopy grade) was delivered by Fisher Scientific and dried before use. Coffee grounds 100% Arabica were obtained from a local cafe as waste obtained from an espresso machine. All chemicals were used without further purification. Water purified by a Hydrolab-system was used to prepare the stock solutions (HLP-SPRING, temp. 22 °C, $\kappa = 2.70 \mu\text{S}$). The treated effluents were obtained from the Gdansk East sewage treatment plant. The final form of each adsorbent was obtained after drying material in a moisture analyzer (MA50/1. R, Radwag) and grinding in a ball mill (Pulverisette 7 classic line, Fritsch).

2.2. Instrumental analyzes

Fourier transform infrared (FT-IR) spectra were performed on a Thermo Nicolet iS10 using the KBr pellet method. The spectral resolution was 4 cm^{-1} and the scanning range was from 400 to 4000 cm^{-1} . The specific surface area was measured by the Brunauer–Emmett–Teller (BET) method (Brunauer et al., 1938), and pore size distribution (PSD) was measured using the classical Barrett–Joyner–Halenda (BJH) model (Barrett et al., 1951). The simultaneous TG–DTA curves were obtained with a heating rate of 10 °C min^{-1} in temperature range of 30 – 700 °C . The experiments were carried out under nitrogen atmosphere at a flow rate of 50 mL min^{-1} , in a SETSYS - 1200 (TG–DTA 1600 °C) system. The surface morphology of adsorbents was studied using scanning electron microscopy (SEM) on a Quanta FEG 250 scanning electron microscope operating at 10 kV . The surface charge properties of the adsorbents were investigated by Zeta potential measurements conducted at a different equilibrium pH using a Nano-ZS Zetasizer (Malvern Instruments Inc.). The elemental FLASH 2000 analyzer operating in the dynamic separation technique was used to measure the content of carbon, hydrogen, and nitrogen. The oxygen content analysis was performed by the device in the pyrolysis mode. The determination of surface functional groups was based on the Boehm titration method (Boehm, 1966). The degree of substitution (DS) was estimated with respect to the monomeric unit (anhydroglucose) using elemental analysis (Qin et al., 2017; Zhang et al., 2021), FTIR spectroscopy (Li et al., 2019) and additionally for systems containing β -CD phenolphthalein complexation (Cadena et al., 2009; Goel and Nene, 1995; Mohamed et al., 2012). PZC was evaluated according to titration procedures described in the literature (Abu-Danso et al., 2019; Kyzas, 2012; Leone et al., 2018; Luo et al., 2019; Oliveira et al., 2008). The water holding capacity (WHC) was determined in a manner typical for this type of material (Ballesteros et al., 2014).

2.3. Preparation and characterization of adsorbents

2.3.1. Coffee grounds (CG) preparation

Air-dried Arabica coffee grounds (100 g) were extracted three times with distilled water ($3 \times 0.5 \text{ L}$) at boiling point for 30 mins each time. The grounds were then filtered off under reduced pressure and dried at 120 °C for 4 h in the dryer and then they were kept for 4 h in the moisture dryer. The obtained dark powder (80 g) was stored in tightly closed containers.

2.3.2. Preparation of cellulose from coffee grounds (CGC)

CG (30 g) was quantitatively transferred to a flask containing 1% (w/v) H_2O_2 solution (1.5 L). The suspension was adjusted to pH 11.5 with NaOH and allowed to stir gently at room temperature (25 °C) for the indicated length of time (48 h). Subsequently, pH corrections were made during the reaction in the first hour. The insoluble residue was collected by filtration, washed with distilled water until the pH of the filtrate was neutral, and then dried at 120 °C for 4 h in a laboratory dryer and another 4 h in a moisture analyzer. The yield obtained was dark yellow, and weighed 14 g.

Table 1

Models of adsorption isotherms and applied plots in the research.

Model *		Ref.
Langmuir	$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e}$	(Langmuir, 1917)
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	(Freundlich, 1906)
Sips	$q_e = \frac{q_{\max} K_s C_e^n}{1 + K_s C_e^n}$	(Sips, 1948)

* $q_{\max}$ —maximum adsorption capacity (mg g^{-1}); K_L —adsorption equilibrium constant (L mg^{-1}); K_F —the separation factor; K_s —adsorption capacity constant ($\text{mg}^{1-1/n} \text{ L}^{1/n} \text{ g}^{-1}$); n —heterogeneity factor.

2.3.3. Synthesis of modified cellulose (CT), cellulose- β -cyclodextrin material (CTCD), and β -cyclodextrin material (CD-1)

Polymers were prepared according to the described procedure (Huang et al., 2012) with a few modifications. CC (10 g) or CD (10 g) or their mixture 1: 1 (5 g CD and 5 g CC) were suspended in dry pyridine (100 mL) at 80 °C . Then, TDI (9.7 g) was added dropwise over an hour. After being magnetically stirred at 80 °C for 3 h, the mixtures were cooled to room temperature and 300 mL of acetone was poured. The precipitates were filtered off and after drying were purified in Soxhlet apparatuses with ethanol for 8 h. The obtained materials were dried in an oven at 120 °C , ground, and dried again in a balance drier at 120 °C .

2.3.4. Synthesis of β -cyclodextrin material (CD-2) synthesis

CD-2 polymer was synthesized according to the reported method with one modification by changing the molar ratio of TDI:CD from 10:6:1. (Anne et al., 2018).

2.4. Adsorption experiments

2.4.1. Analytical method of pollutant concentration determination

The concentrations of CV were measured spectrophotometrically, (UV-Vis, model Hach Lange dr 6000). The effect of pH and aquatic environment on calibration curves and $\lambda_{\max} = 591 \text{ nm}$ were studied. Each of the determinations was repeated at least three times. The reliability of the results was considered on the basis of the analysis of variance (Anova test). Dye removal efficiency (RME) was determined by the Eq. (1),

$$\text{RME}(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where the RME (%) was the efficiency of CV removal, C_0 (mg L^{-1}) and C_t (mg L^{-1}) were initial concentration and concentration at time t of dye in the sample.

2.4.2. Adsorption isotherms

1 mg of the adsorbent was added into the 5 mL of CV solution (with initial concentration ranging from 2.45 to 407.98 mg L^{-1}) and shaken on digital vortex mixer at 700 rpm at 25 °C for 20 min. Then the supernatant liquid was sampled and filtered. The adsorption equilibrium concentration of each was measured. Three isotherm equations were used in the analysis of experimental data, Langmuir, Freundlich, and Sips (Table 1).

2.4.3. Thermodynamic analysis

The key thermodynamic parameters of adsorption were determined on the basis of the below Eq. (2)–(4).

$$\ln(K_e^0) = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R}, \quad (2)$$

Table 2

Description of the kinetic models used in the calculations.

Kinetic model		Ref.
Pseudo-first order	$q_t = q_e e^{(-k_1 t)}$	(Bello et al., 2021)
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$	(Wang et al., 2021)
Avrami fractional-order model	$q_t = q_e (1 - e^{-(k_{AV} t)^n})$	(Sivarajasekar et al., 2018)
Elovic	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$	(Martín et al., 2019)

$$\Delta G^0 = -RT \ln(K_e^0), \quad (3)$$

$$K_e^0 = \frac{KM_a C_a^0}{\gamma}, \quad (4)$$

where ΔS^0 , ΔH^0 , ΔG^0 standard enthalpy, entropy and free energy and K_e^0 is a dimensionless thermodynamic equilibrium constant, which is calculated from the best isotherm fitted K ($L \cdot g^{-1}$), M_a , and C_a^0 are molecular weight and standard concentration of the adsorbate (1 M), and γ is the coefficient of activity, respectively (Lima et al., 2019).

2.5. Adsorption kinetics in batch experiments

100 mg of adsorbent was added to three plastic vials containing 50 mL of CV solution (10.20 mg L^{-1}). The vials were shaken on digital vortex mixer at 700 rpm at 25 °C. The supernatant liquids were sampled at different times (0, 1, 3, 6, 10, 15, 20, 30, 45, and 60 min) and filtered using Whatman Grade 540 filter paper. The amount of CV bound to the adsorbent was determined by Eq. (5).

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (5)$$

where the m (mg) is the adsorbent dosage and the V (mL) is the solution volume used in the study. In further calculations, four kinetic models were used to determine kinetic constants using graphical methods (Table 2).

2.6. Effects of the dosage of the adsorbent, pH humic acid, and salts

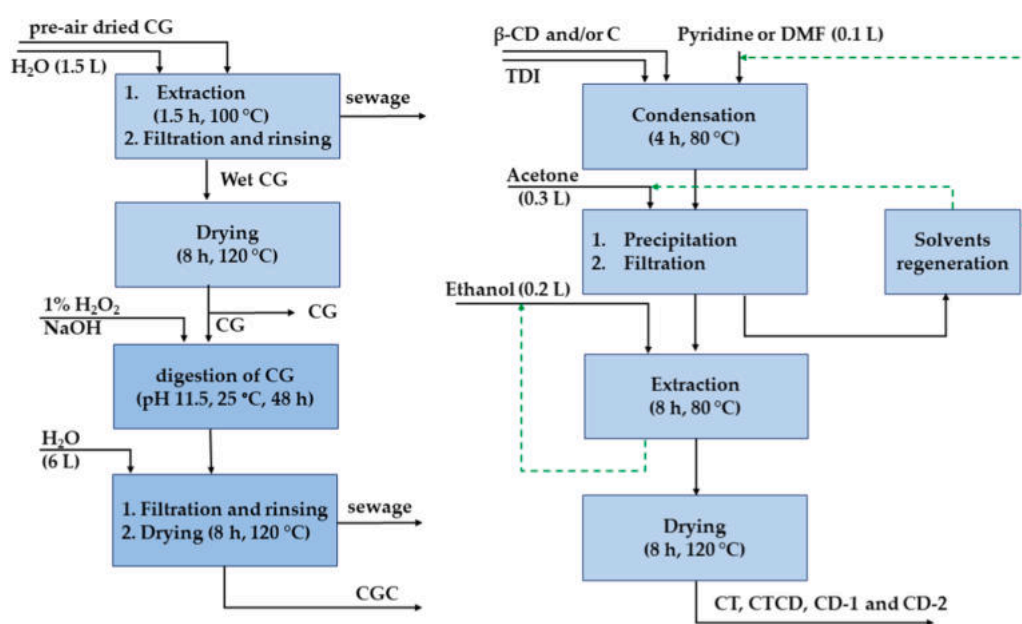
The effect of adsorbent dosage was studied by the addition of the adsorbent (1–100 mg) to the plastic vials (5 mL) containing CV solution (10.20 mg L^{-1}) and shaken on a digital vortex mixer at 700 rpm at 25 °C for 20 min. Then the supernatant liquid was sampled and filtered. The adsorption equilibrium concentration of each was determined colorimetrically. The influence of ionic strength was investigated analogously, using drug solutions enriched with appropriate salts, humic and fulvic acids, and the pH was adjusted to the appropriate value in the range from 2 to 11 with 0.1 N HCl and 0.1 N NaOH.

2.7. Real wastewater treatment

The wastewater was used to make solutions of dyes (Table S11). Relatively high concentrations of dyes, compared to those determined in the natural environment, were used intentionally as a simulation of an industrial sewage system. The adsorption procedure was the same as for model water samples with one difference; the wastewater was used to prepare the solutions instead of pure water. The 5 mL of dye ($0.025 \text{ mmol L}^{-1}$) solutions were added to plastic vials containing 10 mg of adsorbent, individually. The vials were sealed and the mixtures were shaken on digital vortex mixer at 700 rpm for 20 min at 25 °C. Then the supernatant liquid was sampled and filtered. The adsorption equilibrium concentration of each was measured.

2.8. Regeneration

100 mg of material was added to the vial containing 50 mL of the CV solution (10.20 mg L^{-1}). The mixture was shaken in a digital vortex mixer at 700 rpm (25 °C, 20 min). After five minutes, the solution was decanted from the surface of the precipitate and in its place, 20 mL of methanol was added, soaking for 10 min. The procedure was repeated until no CV was found in the filtrate, and finally, the precipitates were washed with distilled water (20 mL). The adsorption-desorption experiment was performed five times. Scheme 1.



Scheme 1. Simplified schematic diagrams showing the preparation of CG, CGC, CT, CTCD CD-1, and CD-2 adsorbents.

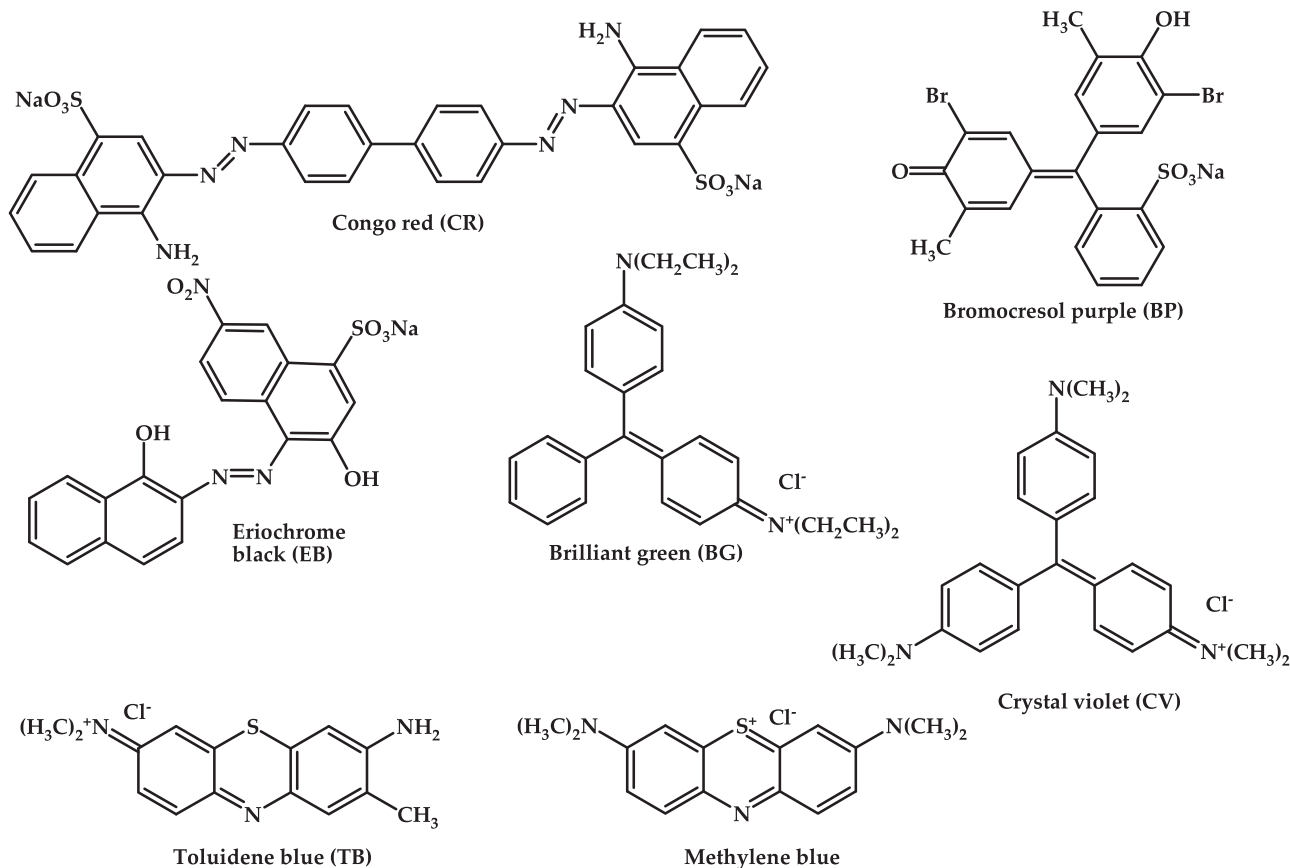


Fig. 1. Chemical formulas of studied pollutants.

3. Results and discussion

3.1. Material design and characterization

The study attempts to take a holistic approach to the production of organic sorbents with potential use in the treatment of wastewater containing dyes. First of all, attention was paid to reducing the number of unit operations, and thus the resulting waste. Nutritional waste such as CG has already been used for dyes adsorption in raw and pretreated forms (Ahalya et al., 2014; Ayalew and Aragaw, 2020; Kyzas, 2012; Oliveira et al., 2008), with different results. In this work, CG was subjected to extraction with boiling water to diminish its amount. As a consequence, the content of water-soluble components was reduced, obtaining a material that was more durable in subsequent cycles. Therefore, the processing of organic waste into new adsorbents is only justified in the case of obtaining a significantly higher degree of contamination removal from aqueous solutions. The CG was transformed into a material enriched with cellulose fibers (CGC) by a bleaching process. The bleaching processes generate large amounts of wastewater, characterized by high values of total organic carbon (TOC) and inorganic compounds (Börjesson and Ahlgren, 2015; Brännvall, 2009; Mohit et al., 2014). Microcrystalline cellulose (CC) was used in the research in its basic form and modified in the condensation reaction with TDI. This modification was aimed at reducing hydrophilicity and obtaining additional π - π interactions with aromatic dyes.

It was time effective to synthesize materials containing CD, which is known for the formation of supramolecular complexes with aromatic compounds. The incorporation of CD molecules usually increases the sorption capacity of the system. Thus, the cross-linked systems resulting from the reaction of TDI with cellulose and (or) CD were also synthesized.

In summary, seven adsorbents were obtained, based on D-glucose

oligomers and polymers, modified to a different extent. The mild CG bleaching conditions were designed to remove free phenolic groups while retaining others (Table S1). The goal was achieved, the content of phenolic groups was reduced by almost 60% while not significantly lowering the content of carboxyl and basic groups. The obtained material differed significantly from commercial microcrystalline cellulose. All raw materials used in the research contain free primary and secondary hydroxyl groups. By using an appropriate solvent, the selectivity of the substitution of these groups can be influenced. A simple system to investigate this phenomenon is CD, which has been modified in pyridine, which supports the selective substitution of primary hydroxyl groups, and in DMF, which does not. Such subtle changes lead to materials with varying degrees of cross-linking and properties.

FTIR spectroscopy is an inexpensive and widely available technique that enables the analysis of sparingly soluble organic compounds in water and organic solvents. Via FTIR, basic functional groups and hydrogen bonds can be identified. The proportion of crystalline and amorphous forms and the water content can be determined and was important for adsorption. Fig. 1 shows the spectra recorded during the FTIR analysis of the discussed materials in two forms: before after five uses. The comparisons show that the materials do not change after five adsorption-regeneration cycles. At first glance, the FTIR CD and CC spectra appear very similar. However, when analyzing more closely, differences are noticed, which are the result of the different spatial arrangement of monomer (glucose) molecules in the cyclic oligomer and the linear polymer and are within the wavenumber range 1630–1440 cm^{-1} (Figs. 2a and 2b).

The peaks at 1636.38 cm^{-1} (CD) and 1637.27 cm^{-1} (CC) were responsible for the vibrations of adsorbed water molecules; 1412.06 cm^{-1} (CD) and 1431.49 cm^{-1} (CC) were related to the degree of crystallinity while 896.43 cm^{-1} (CC) to the degree of amorphousness (Åkerholm et al., 2004). Comparing the CG and CGC spectra, it was seen

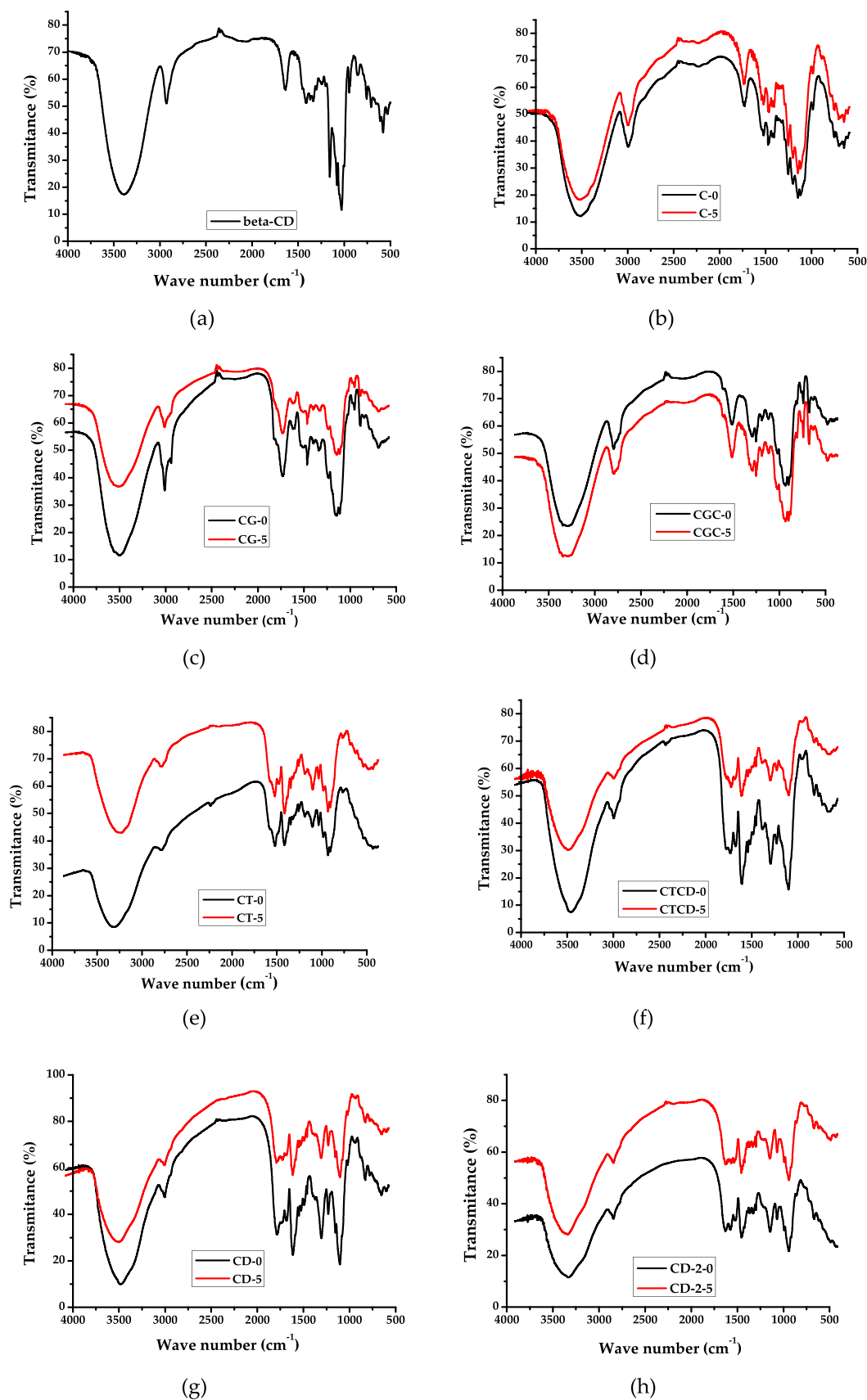


Fig. 2. Recorded FTIR spectra of sorbents in KBr. The adsorbents not used are marked in black, and the adsorbents after the fifth regeneration cycle are marked in red.

that CG contained more adsorption water, and the carboxyl groups, the presence of which was confirmed in Boehm's method, were probably in the deprotonated form (1542.59 cm^{-1}) (Figs. 2c and 2d). A higher proportion of the crystal structure guarantees a higher degree of order and better mechanical properties. The intensity of the bands described with wave numbers proximate the range of $1420 - 1430\text{ cm}^{-1}$ and 898 cm^{-1} corresponds to the content of the crystalline and amorphous structure in cellulose, as was mentioned (Åkerholm et al., 2004). The ratio between the two bands determines the empirical index of crystallinity proposed by Nelson and O'Connor (Nelson and O'Connor, 1964) as the lateral order index, which is correlated to the overall degree of order in the cellulose (LOI). The ratio of the bands at 1372 and 2900 cm^{-1} is the total crystal indicator of cellulose (TCI) (Nelson and O'Connor, 1964). The intensity of hydrogen bonding (HBI) of cellulose is closely related to the crystal system as well as the amount of bound water and can be determined from the ratio of absorbance bands at 3400 and 1320 cm^{-1} (Oh et al., 2005). The comparisons in Table S2 clearly showed that CC had the most ordered structure. The bleaching process slightly improved the order of particles in the material, while the attachment of β -CD cyclic spatial systems to the CC fiber gave the opposite effect. Modification of CC with isocyanate significantly increased the value of the total crystal indicator of cellulose, thus radically reducing the intensity of hydrogen bonds formed. The amount and strength of hydrogen bonds significantly affected the sorption capacity of the material, containing cellulose fibers, so they should be carefully examined. CTCD showed the lowest hydrogen bond energy at 3567 cm^{-1} , probably due to the amount of weakly bound water, enclosed in CD tori. On the other hand, CT and CG showed higher values of hydrogen bond energies at the same wavenumber, which may be the result of the formation of multiple intramolecular hydrogen bonds between adjacent urethane (CT) and phenolic groups in lignin (CG). Hydrogen bond energies for the bands 3423 cm^{-1} and 3342 cm^{-1} are highest for CG and CT. The energy values at 3278 cm^{-1} and 3221 cm^{-1} in relation to allomorphic forms of cellulose indicate a much greater proportion of intermolecular hydrogen bonds occurring in triclinic I_{α} cellulose (3221) than in monoclinic cellulose I_{β} (Table S3).

The FTIR spectra of the adsorbents obtained in the C and CD condensation reactions with TDI and it did not contain the $2275\text{--}2250\text{ cm}^{-1}$ bands, which proves the transformation of isocyanate groups into urethane groups (about 1715 cm^{-1}). All urethane derivatives were further characterized by determining the degree of substitution. The various techniques used gave quite convergent results, showing a single substitution of the monomeric unit (anhydroglucose) indicating a high degree of cross-linking (Table S4).

It is customary for adsorbents to determine BET isotherms to determine the specific surface area. Measurements were carried out at low temperature using nitrogen. The BET theory assumes that the adsorption energy was independent of the gas molecules' adsorption sites, which interact only in the vertical direction, while the side effects between adjacent adsorbed molecules were negligible (Brunauer et al., 1938). The BET isotherms obtained for CGC, CT, CTCD, and CD-1 belonged to type III (Fig. S1). The determined CC coefficients were less than one, and in the case of CGC and CTCD, they were even negative. These results specify the formation of a multilayer, with no asymptote on the curve. CG, C, and CD-2 gave type IV isotherms suitable for partial capillary condensation of nitrogen at a pressure less than the saturation pressure of the gas (Fig. S1). In areas of lower pressure, a monolayer was formed, followed by a multilayer system. This is typical of BET surfaces of mesoporous materials including CG, C, and CD-2. When plotting the BET equation, the plot should be linear with a positive slope. If such a graph is not obtained, the BET method is insufficient to determine the surface area of the material. Therefore, the determination of the CTCD BET surface area was not possible and in this case of CT and CD-2 were not entirely reliable (Table S5.) The next method developed by Barrett, Joyner, and Halenda, BJH assessments the pore size distribution (PSD) on the basis of the isothermal physisorption equilibrium state. The BJH

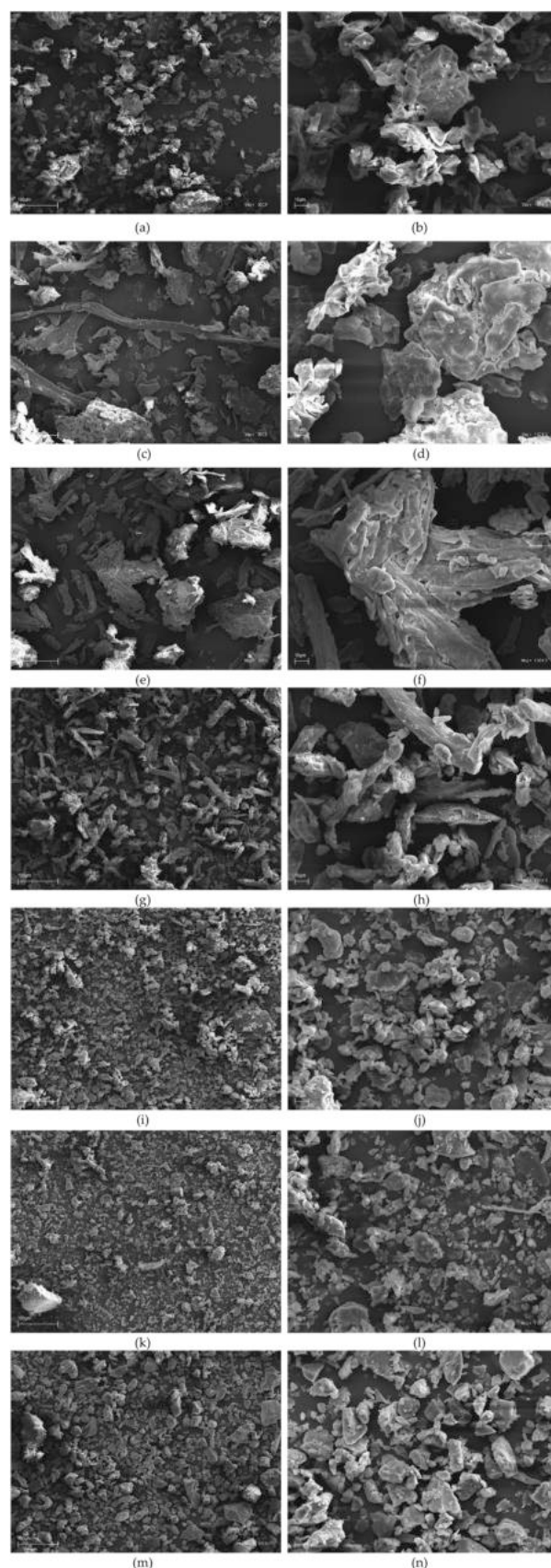


Fig. 3. SEM images of the obtained materials, recorded at mag. 300x and mag. 1000x: CG (a, b); CGC (c,d); CC (e, f); CT (g, h); CTCD (i, j); CD-1 (k, l); CD-2 (m, n).

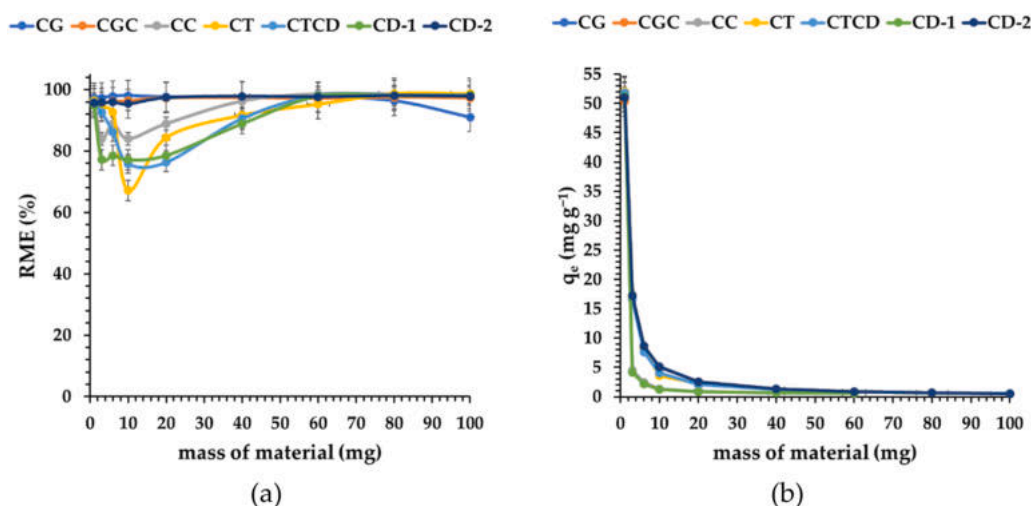


Fig. 4. Effect of the adsorbent mass on the removal efficiency (a) and adsorption capacity (b); $t_{\text{contact}} = 20$ min, $C_{\text{CV}} = 10.20 \text{ mg L}^{-1}$, $V_{\text{CV}} = 5 \text{ mL}$ and $m_{\text{CVsorbent}} = 1 - 100 \text{ mg}$.

theory implements follow basic rule book; first, the shape of the pores was cylindrical, and second, the amount adsorbed was due to both physical adsorption on the walls of the pores and capillary condensation at mesopores (Barrett et al., 1951). All adsorbents were mesoporous. In the case of CGC, macropores also have a large share (Table S5). All materials retain water in their structure and swell (Table S6). The CGC changed the most, fibers became larger which was accompanied by a more than threefold increase in material volume. This phenomenon was often observed with cellulose-containing materials and not only (Ballesteros et al., 2014; Ferro et al., 2014; Hoti et al., 2021; Pagalan et al., 2020; Zheng et al., 2018).

Each adsorbent viewed under an electron microscope was a cluster of particles differing in size and structure, despite the use of the same grinding and screening method. CG CGC contained the longest monofilaments of cellulose $154.55 \mu\text{m}$ (Figs. 3a) and $472.73 \mu\text{m}$ (Fig. 3c), and particles with a very diverse structure and size of $3.16 - 60.02 \mu\text{m}$ and $7.27 - 247.27$, respectively. Microcrystalline cellulose was a mixture of particles ranging in size from $10.91 \mu\text{m}$ to $190.91 \mu\text{m}$. (Figs. 4e and 4f). CT was a cluster of particles with an oval shape and size of $76.36 \times 56.36 \mu\text{m}$ and oblong about dimensions $163.36 \times 21.82 \mu\text{m}$. (Fig. 3g), and those containing CD were the most fragmented (Fig. 3i-n). CTCD mainly contained relatively small particles $2.73 \mu\text{m}$ and a few bigger ones ($101.82 \mu\text{m}$). The smallest particles with a length of $1.82 \mu\text{m}$ form CD-1 and CD-2, with the difference that the second one contained the greater proportion of particles with a length of $94.55 \mu\text{m}$.

The materials differ essentially in the pH values at which the zero charge points were determined and arranged in the series $\text{CD-1} > \text{CD-2} > \text{CT} > \text{CGC} > \text{CC} > \text{CTCD} > \text{CG}$. The differences were quite large between the extreme materials and amount to three units (Fig. S2 and Table S7). The large size and tendency to swell did not allow to determine the zeta potential of the most fibrous materials (CG and CGC). CD-1, despite its small dimensions, did not form sufficiently stable suspensions in aqueous solutions, which also made it impossible to perform the measurement. For the remaining materials, isoelectric points were determined and the distribution of charges was specified. Each of the adsorbents had two isoelectric points, which define the ranges of the charge distribution. Interestingly, the CTCD surface charge in almost the entire range of the tested pH2–11 is negative (Fig. S3).

All materials were thermally stable. At temperatures up to 150°C , they lose water (Table S8). The share of unstably bound water was the largest, which is removed below 100°C . The proper decomposition began above 250°C and mainly had the nature of endothelial transformation, only in the case of sorbents containing β -cyclodextrin, exothermic peaks were recorded. Figures exhibited the TG and DTA

curves and a detailed description was included in the [supplementary materials](#) (Fig. S4 and Table S9). An attempt was also made to determine the hydrophobic properties of the obtained materials. In the two-phase tests carried out, consisting of toluene and distilled water, only microcrystalline cellulose immediately found itself in the inorganic phase, in which it also remained after mixing. The remaining materials initially stopped at the interface. After intensive mixing, they fell into the water phase. The exception was CT, which was completely dispersed in the organic phase. Based on the estimated hydrophobicity index, the materials can be arranged in the following series: $\text{CT} > \text{CTCD} > \text{CG} > \text{CGC} > \text{CD-1} > \text{CD-2} > \text{CC}$ (Table S10).

3.2. Adsorption studies

3.2.1. Effect of the adsorbent mass

CV adsorption is one of the fastest processes. Using the constant concentration of the adsorbate and the variable adsorbent, the maximum degree of dye removal from the solutions were obtained for the value of 1 mg. This was due to the largest excess of dye in relation to the weight of the adsorbent used. The RME value for CGC and CD-2 in the entire range of tested masses is practically constant. In the case of CG, it also initially decreased after exceeding the value of 80 mg. In other cases, the dependence of RME on the mass of the material follows a different course. The maximum value was achieved for the smallest weights and the lowest for 10 mg of materials, followed by an increase in the RME value to the original cutoff value. The adsorbate excess for 1 mg of the adsorbent is tenfold, for 10 mg it is 1.05, and in the extreme case 0.105. Reducing the concentration increases the number of degrees of freedom in filling the surface without the need to penetrate deeper structures of the materials, as a result, the surface of the materials is only partially used (Fig. 4). The study indicated that the most reasonable adsorbent concentration during the determination of isotherms would be the value of 0.2 g L^{-1} . For this concentration, very similar values of the RME parameter and q_e were obtained for all materials. The use of uniform conditions in our opinion allows a better comparison of materials. The literature describes adsorption processes in which the authors used very low sorbent concentrations with success (Badruddoza et al., 2017; Bhadra et al., 2017; Ching et al., 2020; Liu et al., 2020; J. wei Wang et al., 2021; Younis et al., 2020). In the case of cyclodextrin materials, it is even desirable to be able to use every element of the structure and not just the interiors of the torus. During the first stage of sorption, supramolecular complexes are formed (Hemine et al., 2020). If the adsorbate concentration is high enough, subsequent molecules locate outside the torus (Huang et al., 2020). In the case of removal of

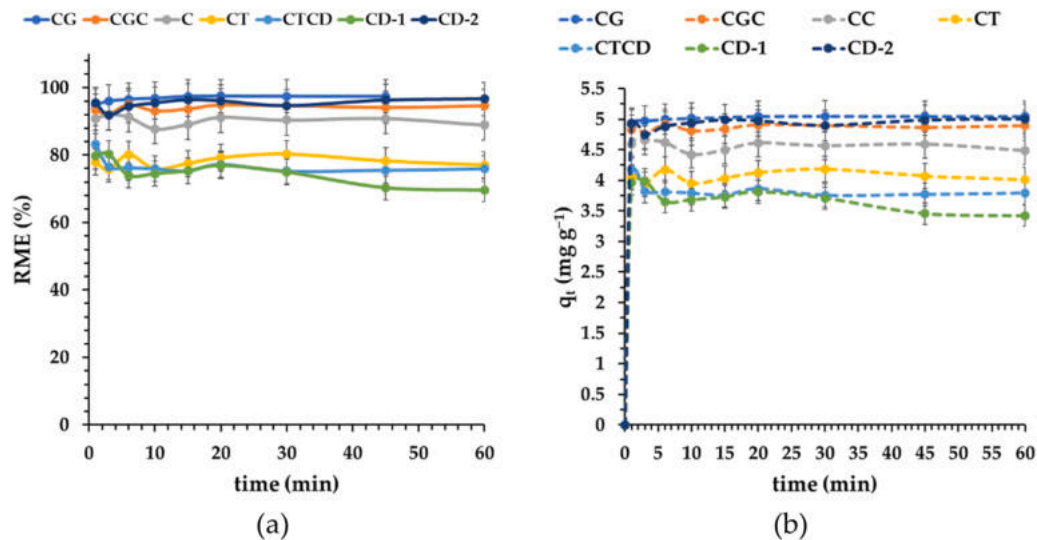


Fig. 5. Effect of the time on the removal efficiency ($t_{\text{contact}}=60$ min), (a) adsorption capacity (b); $C_{\text{CV}} = 10.20 \text{ mg L}^{-1}$, and $m_{\text{CV sorbent}} = 10 \text{ mg}$.

Table 3

Kinetic model constants of single-component mixtures and their error analysis.

Parameters	CG	CGC	CC	CT	CTCD	CD-1	CD-2
Pseudo –first order							
q_e (mg g^{-1})	5.02	4.86	4.56	4.06	3.84	3.71	4.93
k_1 ($\text{g min}^{-1} \text{mg}^{-1}$)	3.79	5.05	221.76	249.40	263.91	272.92	205.04
R	0.9998	0.9995	0.9987	0.9978	0.9942	0.9870	0.9988
R^2	0.9997	0.9980	0.9975	0.9956	0.9885	0.9742	0.9976
R_{adj}	0.9996	0.9980	0.9968	0.9943	0.9853	0.9669	0.9969
X^2	0.0016	3.881	0.01	0.0153	0.0380	0.0837	0.0101
Pseudo –second order							
q_e (mg g^{-1})	5.04	4.86	4.56	4.06	3.84	3.72	4.93
k_2 ($\text{g min}^{-1} \text{mg}^{-1}$)	6.74	38.78	55.02	55.02	90.67	96.14	38.60
R	0.9999	0.9994	0.9987	0.9987	0.9940	0.9867	0.9989
R^2	0.9999	0.9990	0.9974	0.9974	0.9879	0.9736	0.9978
R_{adj}	0.9999	0.9987	0.9966	0.9966	0.9844	0.9661	0.9970
X^2	0.0154	0.0052	0.0116	0.0116	0.0466	0.0918	0.0104
Avrani							
q_e (mg g^{-1})	5.02	4.86	4.56	4.06	3.84	3.71	–
k_{AV} ($\text{g min}^{-1} \text{mg}^{-1}$)	0.262	2.70	3.29	4.32	17.93	1.68	–
n	14.47	1.87	67.33	57.78	14.72	162.58	–
R	0.9999	0.9995	0.9987	0.9977	0.9943	0.9870	–
R^2	0.997	0.9985	0.9975	0.9956	0.9885	0.9742	–
R_{adj}	0.9996	0.9977	0.9962	0.9934	0.9828	0.9614	–
X^2	0.0016	3.88	0.0098	0.0154	0.0380	0.0837	–
Elovich							
β (g mg^{-1})	13,433.32	16,789.27	18,607.0	14,948.86	21,237.29	26,062.84	1624.08
α ($\text{g mg}^{-1} \text{min}^{-1}$)	2.60	2.74	2.97	3.30	3.62	3.82	2.70
R	0.9527	0.9509	0.9387	0.9481	0.9148	0.8909	0.9528
R^2	0.9068	0.9037	0.8808	0.8983	0.8366	0.7935	0.9073
R_{adj}	0.8757	0.8762	0.8467	0.8693	0.7899	0.7935	0.8808
X^2	0.9617	0.303	0.8998	0.6980	0.9598	1.0947	0.8247

micropollutants, only a minimal amount of adsorbent ensures its full utilization (Hu et al., 2020; Erdős et al., 2020; Yang et al., 2019).

3.2.2. Effect of the contact time and adsorption kinetics

To determine the appropriate contact time between sorption material and dye, a set of experiments were carried out (Figs. 5a and 5b). It was observed that in a minute equilibrium for CTCD is achieved; two more minutes were needed for CC and CD-1. CT and CGC take twice as long. The steady-state was most slowly reached by CD-2 (15 min) and CG (20 min). The amount of dye adsorbed at equilibrium time was the lowest for CD-1 and the highest for CG and amounts to 3.99 mg g^{-1} and 5.04 mg g^{-1} , respectively. To investigate the mechanism controlling the adsorption process: pseudo-first, pseudo-second, and Avrami fractional order kinetic models were studied for the experimental data (Fig. S5). In

the kinetic tests, 10 mg of the adsorbent was used per sample. The obtained parameters for the models are shown in Table 3. In the case of the tests performed for CC, CT, CTCD, CD-1, and CD-2, it seems that the dominant model was in the form of pseudo-first order kinetics. This might suggest that the mechanism of inclusion complex formation by inserting one ring inside the CD was a rate-controlling process in this system. The estimated CV adsorption rate constant is high and amounts to over $200 (\text{g min}^{-1} \text{mg}^{-1})$ (Table 3). The pseudo-second order model provides a better description of the interaction between CG (CGC) and the dye. A fairly good fit to the Avrami model indicated that a phase transition may take place in the adsorption process. It is possible that the dye released from the salt is finally incorporated into the sorbent structure, which, due to its limited solubility, precipitates and is deposited on the material. Another explanation could be the reaction of

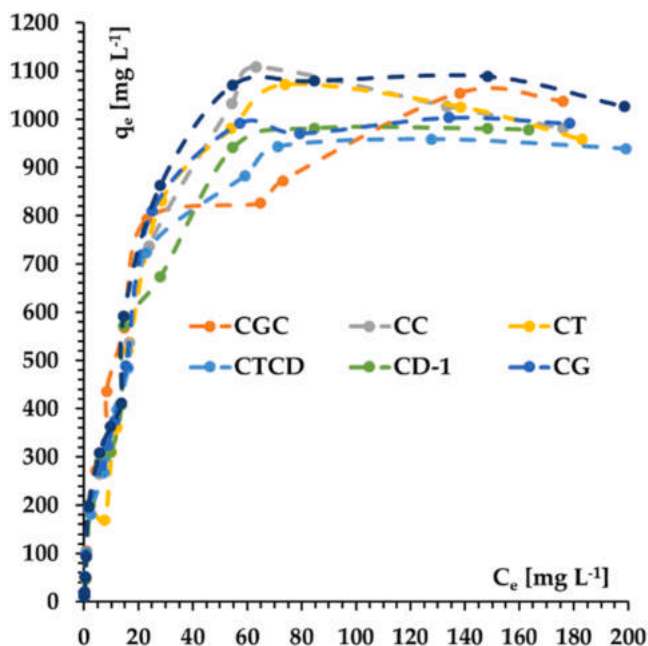


Fig. 6. Equilibrium adsorption isotherms of CV; $t_{\text{contact}} = 20$ min, $C_{\text{CV}} = 2.45 - 407.98 \text{ mg L}^{-1}$, $V_{\text{CV}} = 5$ mL and $m_{\text{CVsorbent}} = 1$ mg.

methine carbon which is a C-acid and can coordinate groups of a nucleophilic nature. Perhaps a necessary condition for this type of phenomenon is the presence of unsubstituted secondary hydroxyl

groups. It can be proved by the lack of fit of this model for CD-2, which was the only one obtained in a non-selective manner. The adsorbate was chemisorbed onto a solid surface without desorbing the products and the rate of adsorption decreased over time due to increased surface coverage. The model which described this type of chemisorption was the Elovich equation in which α is the initial rate; the parameter β is related to the range of surface coverage and the activation energy for chemisorption. In this case, a worse fit of the model was obtained. Nevertheless, the parameter values can lead to chemisorption.

3.2.3. Adsorption equilibrium

For each sorbent, a better fit of the experimental data (Fig. 6. and Fig. S6) of the Langmuir than the Freundlich models were obtained (Table 4.) in terms of the R^2 coefficient. These results suggested that adsorption mainly proceeds with monolayer formation over a relatively uniform surface. The Langmuir model assumed that adsorption occurred at specific and localized sites and that all adsorption sites were energetically identical (Langmuir, 1916). Homogeneous sites were found by analyzing the SEM images (Fig. 3).

The Freundlich isotherm was used to describe multilayer adsorption and non-homogeneous surfaces with non-uniform heat distribution of adsorption. In the isotherm equation, the value of the n parameter, which determines the quality of the adsorption process, is extremely important (Lessa et al., 2018). The process is favorable when it is between 1 and 10. Among the tested adsorbents all meet this condition. The Sips model bridges the gap between the isotherms described so far and works well for localized adsorption without adsorbate-adsorbate interaction (Mohamed et al., 2012; Usman et al., 2021). As C_e approaches a low value, the Sips isotherm is efficiently reduced to Freundlich, while at high C_e it predicts the sorption properties of the

Table 4

The isotherm parameters for the adsorption of CV by studied sorbents.

Parameters	CG	CGC	CC	CT	CTC	CD-1	CD-2
Langmuir							
K_L (L mg^{-1})	0.056	0.074	0.055	0.0467	0.0567	0.055	0.056
q_{max} (mg g^{-1})	1168.14	1092.24	1220.40	1226.24	1100.37	1137.71	1235.32
R	0.9875	0.9906	0.9833	0.9772	0.9911	0.9908	0.9853
R^2	0.9743	0.9809	0.9667	0.9548	0.9821	0.9813	0.9706
Adj. R^2	0.9700	0.9777	0.9612	0.9473	0.9791	0.9782	0.9657
χ^2	298.13	118.99	197.08	359.22	132.86	133.70	190.05
Freundlich							
K_F ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$)	181.22	181.22	187.51	168.68	170.02	164.35	199.204
n	2.78	2.79	2.77	2.66	2.79	2.66	2.87
R	0.9617	0.972	0.9487	0.9416	0.9599	0.9677	0.9508
R^2	0.919	0.9418	0.8930	0.8801	0.9144	0.9305	0.8966
Adj. R^2	0.9060	0.9321	0.8751	0.8601	0.9002	0.9189	0.8793
χ^2	471.08	464.04	580.60	658.69	486.74	465.30	662.20
Sips							
K_S [(mg L^{-1}) $^{-1/n}$]	0.0673	0.0612	0.0651	0.0645	0.0652	0.0551	0.067
n	1.36	0.86	1.344	1.17	1.22	1.001	1.29
q_{max} (mg g^{-1})	1073.07	1168.54	1123.99	1036.28	1034.34	1137.25	1157.18
R	0.9905	0.9910	0.9871	0.9920	0.9929	0.9908	0.9879
R^2	0.9768	0.9822	0.9711	0.9771	0.9838	0.9813	0.9731
Adj. R^2	0.9705	0.9773	0.9632	0.9709	0.9794	0.9762	0.9657
χ^2	1566.29	91.528	978.97	24,794.63	412.58	134.23	675.83
Thermodynamic parameters							
ΔH^0 (kJ mol^{-1})	39.46	133.55	38.86	4.23	6.59	2.23	6.77
ΔS^0 ($\text{J K}^{-1} \text{mol}^{-1}$)	227.3	505.75	221.92	119.17	126.56	56.56	127.08
ΔG_{293}^0 (kJ mol^{-1})	-27.14	-14.63	-26.16	-30.69	-30.50	-31.52	-30.45
ΔG_{313}^0 (kJ mol^{-1})	-31.70	-24.75	-30.60	-33.08	-33.02	-33.86	-33.00
ΔG_{333}^0 (kJ mol^{-1})	-36.24	-34.86	-35.05	-35.46	-35.55	-36.13	-35.55
R^2	0.99677	0.99963	0.99642	0.99842	0.98453	0.99289	0.99788
RSS	0.01032	0.00742	0.01323	6.8958E-5	0.00168	8.78268E-5	2.36836E-4
Adj. R^2	0.98709	0.99932	0.98571	0.99369	0.9386	0.97167	0.99155
Intercept	27.34106	60.83148	26.69261	14.33415	15.22238	13.8634	15.28478
Slope	-4746.21068	-16063.54095	-4673.54845	-508.74196	-793.07671	-269.50657	-814.21906
Intercept SE	1.22734	0.95234	1.27208	0.09183	0.45079	0.10364	0.17019
Slope SE	382.58742	296.86606	396.53433	28.62621	141.14505	32.30614	53.05127

Table 5

Maximum adsorption capacity of natural and semi-natural adsorbents given in the literature for CVs and their regeneration methods.

Sorbent	Adsorption capacity (mg g ⁻¹) at 25 °C	Desorption conditions	References
EDTA-Cross-Linked β -Cyclodextrin	0.11	Ethanoic solution of acids, precipitate, rising with water to pH= 7	(Zhao et al., 2015)
Lignin-Rich Adsorbent	10.05	2 M solution of NaOH; HCl addition to pH= 2, precipitate rising with water to pH= 7	(Menkiti and Aniagor, 2018)
nanosilica-supported poly β -cyclodextrin sorbent	34.50	1 M HCl, ethanol and water	(Chen et al., 2018)
β -cyclodextrin carbon-based nanoparticles with	87.87	No data	(Younis et al., 2020)
Avocado seed powder	95.9	No data	(Bazzo et al., 2016)
Coffee waste	125.00	No data	(Lafi et al., 2014)
supramolecular hydrogels in form of cyclodextrin pseudorotaxane and clay	199.00	No data	(Zhang et al., 2019)
grapefruit peel	254.16	1 M NaOH, precipitate rising with water to pH= 7	(Saeed et al., 2010)
CGC	1092.24	Methanol	This work
CG	1168.14	Methanol	This work
CD-2	1235.32	Methanol	This work
CC	1220.40	Methanol	This work
CT	1226.24	Methanol	This work
CTCD	1100.37	Methanol	This work
CD-1	1137.71	Methanol	This work
β -cyclodextrin modified electrospinning fibers	1049.88	Ethanol, pH= 4	(Jia et al., 2019)

Langmuir monolayer. The Sips isotherm equation was characterized by a dimensionless heterogeneity coefficient n , which was used to describe a system inhomogeneity if the value of n is between 0 and 1. When $n = 1$, the Sips equation became the Langmuir equation and represented the homogeneity of the adsorption process. All sorbents represent a good fit to the Sips model. The parameter n for six of the seven sorbents was greater than one which might indicate that sorption of one (first) CV molecule increased sorption of more others. These values of the obtained q_{max} were very high and in any case. These results indicated that the correct choice of materials was made. Nevertheless, from the point of view of the adsorption process itself, used coffee grounds were the best choice because they were waste and the cost of their preparation is low. Table 5 presented a list of adsorbents derived from renewable raw materials described in the literature. Among them, only β -cyclodextrin modified electrospinning fibers had q_{max} values at the same level, when using a sorbent concentration twice as high. All our β -cyclodextrin materials maintained a constant sorption capacity in the next five cycles, while the fibers lose 20% after four cycles.

3.2.4. Thermodynamic analysis

The thermodynamic parameters obtained from Eq. (2)–(4) provided supplementary information on the adsorption process (Table 5). The obtained positive values of ΔH° for each material meant that the processes were endothermic and proceeded with energy absorption. The most endothermic processes were those in which both dye and water are

retained in the structure of the material. This phenomenon was accompanied by structural changes in the adsorbent resulting, inter alia, from an increase in volume. Cellulose modification significantly reduced the interaction with water, which was reflected in the reduction of the needed energy. Negative ΔG° values point to spontaneous and thermodynamically favorable processes as well as a high affinity of the adsorbate for the adsorbent (Bergmann and Machado, 2015). Positive values of ΔS° specified a high preference of the adsorbate molecules on the adsorbent surface. The highest values of ΔS° were determined for systems with structural changes (Lima et al., 2019).

3.2.5. Effect of pH salts, and humic acids on removal efficiency

The pH of a solution often has a significant impact on the adsorption efficiency of contaminants present in solutions, particularly during the treatment of industrial wastewater, which is sometimes extremely acidic or alkaline. In studies of the sorption process, CV solutions with pH ranging from 2 to 11 were used (Fig. 7a). In each case, a significantly lower dye removal efficiency was observed for pH= 2 of 9.3% (CC), 38% (CTCD), 43% (CGC), 48% (CG), 52% (CD-1), 54% (CT), and 55% (Cd-2).

Crystal violet is an alkaline dye containing three nitrogen atoms. Of the three salts, two are stable at very low pH while the third is even in alkaline media (Fig. 7b) (Adams et al., 1914). Thus, in a solution at pH2 there are organic cations ($2.5 \cdot 10^{-5} \text{ mol L}^{-1}$), protons (0.01 mol L^{-1}), an equivalent amount of chloride ions and a sorbent. The surface of the material regardless of the pH of the solution can be neutral, positively or negatively charged (Liu et al., 2020; Fröhlich et al., 2019; Streit et al., 2021). Very often the charge is the driving force of the adsorption process. In the system under consideration, if it is negative, electrostatic attraction of cations will occur very quickly. The concentration of protons is 400 times higher than that of organics. In addition, protons are small, light and very mobile, so they reach the surface of the adsorbent first. If the surface of the material is positive, the first interaction that will occur will be electrostatic repulsion toward the cations present there and attraction of chloride anions. The surface of the CC is consistently negative in the acidic range up to pH= 5.6. As the hydrogen ion concentration decreases, there is a slow increase in the degree of CV removal from 25% for pH 3, 49% for pH 4 and 88% for pH 5 for which we finally have a predominance of organic cations. The CTCD surface is also negative in acidic media but unlike CC it has two additional structural elements namely: aromatic and cyclodextrin rings, which are not attractive to protons but are to the dye which explains the better removal rate of 38% for pH 2 and 47% for pH 3. Positive surface charge (for example, CT and CD-1) in the low pH range is less of a hindrance to the adsorption process. It is not excluded that the dye is adsorbed as an ion pair and not as a free cation, which significantly nullifies the electrostatic repulsion. Less processed CG and CGC materials contain acidic and alkaline components that buffer the pH of the environment to some extent, so the degree of dye removal is much higher compared to crystalline cellulose in pH 2. In a neutral environment, the dye removal efficiency is high and ranges from 92% to 98%. Undoubtedly, the dye in the cationic form ($pK_a = 8.64$) is involved in the interaction with the material surface. A further increase in pH no longer has such a significant effect on the process.

The effect of salt by adding sodium or calcium chloride was also investigated, using rather high concentrations found in dye-house effluents (Fig. 7c) (Dutta et al., 2021). Among the seven materials, as many as six can successfully work in conditions of high salinity. The exception was microcrystalline cellulose. The presence of calcium ions in a lower concentration also negatively influenced the sorption capacity of CT, CTCD, and CD-1 and CD-2. Perhaps it was related to the easier migration of ions to mesopores and their filling. However, the biggest problem was humic acids present in high concentration, which happens in the case of surface water (Rodrigues et al., 2009; Tungsudjawong et al., 2018; Zhang et al., 2020). In this case, the degree of CV removal from the model wastewater was reduced by half for CC, CT, CTCD, and CD-1 (Fig. 7b). Nevertheless, these are only two-component solutions,

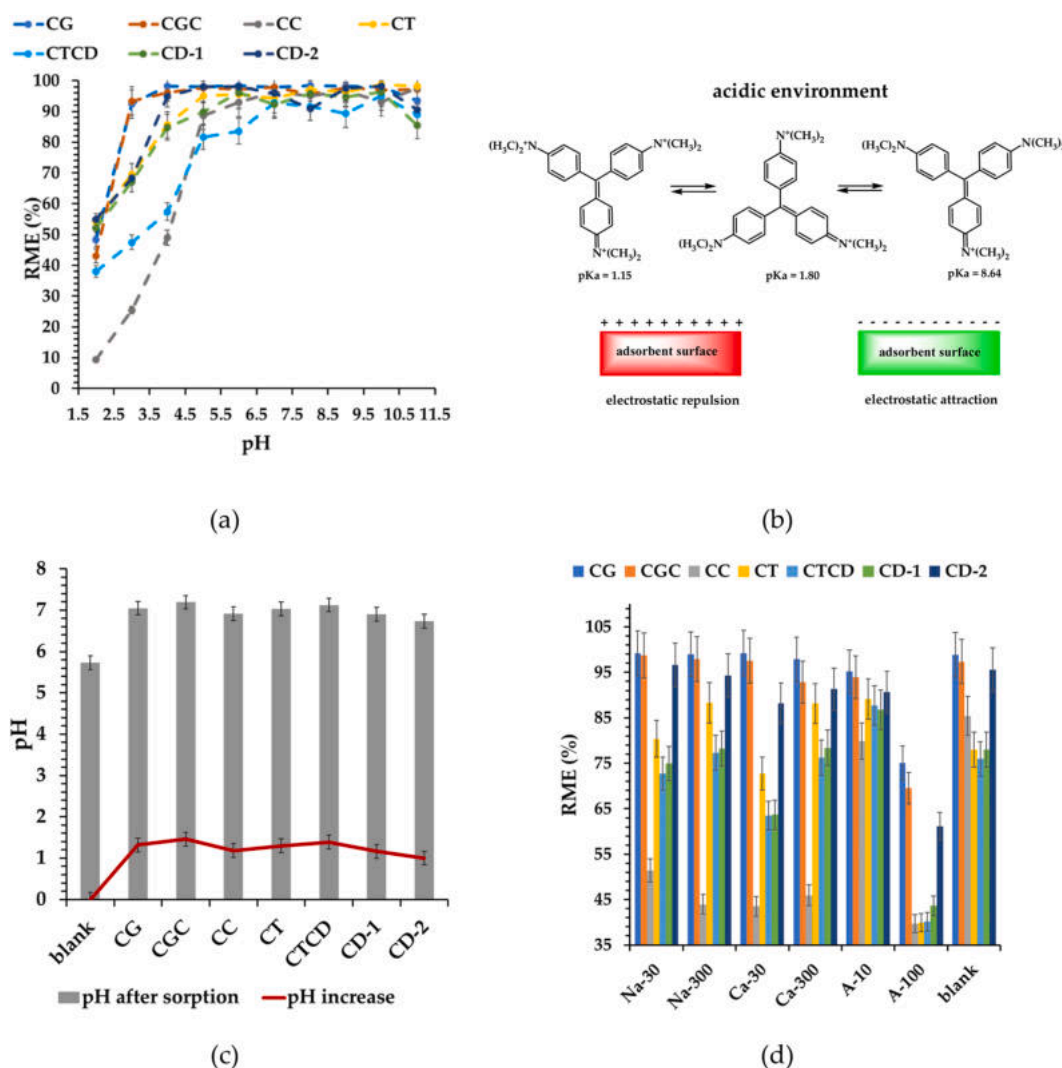


Fig. 7. Effect of (a) pH (b) Possible interactions of the adsorbent surface with the dye, (c) adsorption on the change of the pH of the solution; (d) salts and humic acids concentration on adsorption of CV (C_{CV} = 10.20 mg L⁻¹, pH = 5.7, m_{sor} = 10 mg) by sorbents (t_{contact} = 20 min). Na-30 and Na-300 (C_{NaCl} = 76.05 mg L⁻¹; C_{NaCl} = 760.50 mg L⁻¹); Ca-30 and Ca-300 (C_{CaCl₂} = 83.25 mg L⁻¹; C_{CaCl₂} = 832.50 mg L⁻¹); A-10 and A-100 (C_{humic acids} = 10 mg L⁻¹; C_{humic acids} = 100 mg L⁻¹).

containing salt and CV or humic acids and CV. The matrix of real wastewater was much richer, which, paradoxically, may give a completely different effect on the dye sorption process.

3.2.6. Environmental applications

In environmental research, treated sewage from municipal sewage treatment plant containing organic and inorganic compounds in dissolved and suspended form was used. This choice was dictated by the use of a matrix that allows to simulate the situation when sewage treatment plants leave sewage containing undecomposed dyes (Fig. 1). So, the sewage was used to prepare dye solutions (Table S11). The results were compared with those obtained in model systems (Fig. 8.), not finding a very significant influence of the matrix on the sorption capacity of the materials, except for the CC-BP system. In this case, when the solvent was water, BP did not sorption at all. All materials show a much greater affinity for cationic dyes. The removal rate was high, ranging from 72% for the CG-BG system to 98.9% for the CD-2-BT system. Among the anionic dyes, CTC is the best sorbent for CG (RME = 77.8%). These preliminary results as well as high values of the maximum sorption capacity predicted the use of the cheapest adsorbent, i.e. CG, as a filling of actual filters supporting the process of wastewater treatment containing dyes and other organic compounds.

3.2.7. Regenerative experiments

An integral part of the sorption treatment process is the regeneration step, which is often a significant component of the total cost of the process and waste generation (Alzate-Sánchez et al., 2019, 2018; Menkiti and Aniagor, 2018). Seven sorbents were used for the tests, characterized by a different affinity for the CV, and thus the degree of difficulty in removing it from the surface during regeneration. For this purpose, methanol was used in which the CV is perfectly soluble. Methanol, on the other hand, is a cheap solvent, with a low boiling point and does not form an azeotrope with water, which considerably reduces the cost of a unit operation. As shown in Scheme 2, the most difficult was CC and CT regenerations (Usman et al., 2021). This process was the most efficient in the case of the low-cost CG, but it was less effective for CV removal in subsequent repetitions similar to CC (Lafi et al., 2014; Marincas et al., 2016). The opposite situation was observed for CD-containing materials (Skwierawska et al., 2021). This result was probably due to the materials' ability to remember the shape of the complexed dye after the second repetition (Xia et al., 2020). Spontaneous preorganization will remain intact during subsequent applications (Fig. 9a.).

All sorbents presented in this work were oligomers or polymers of D-glucose, so theoretically they should not have a negative impact on the natural environment during disposal in a manner similar to agricultural

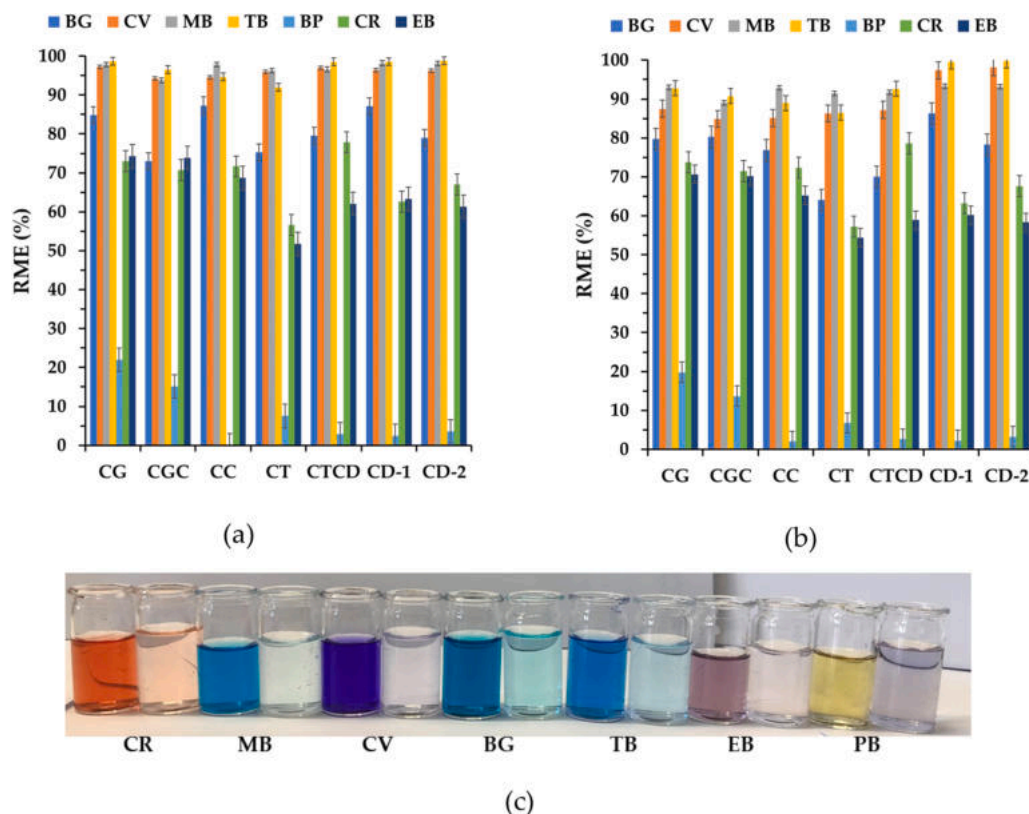
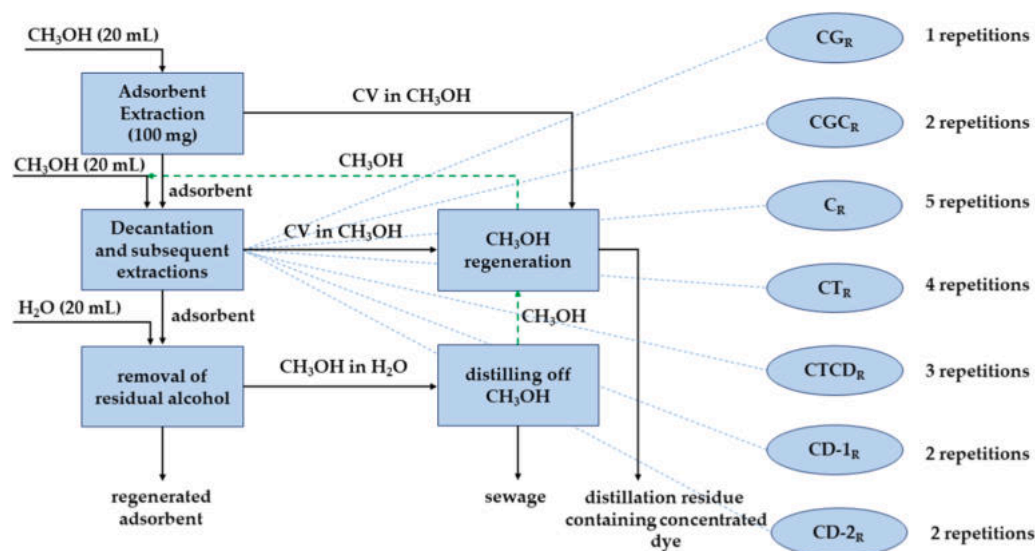


Fig. 8. The average efficiency of dyes ($C_{dye} = 0.025 \text{ mmol L}^{-1}$, $m_{sor} = 10 \text{ mg}$) removal from: (a) synthetic wastewater; (b) effluents; (c) Photo showing dye solutions before and after adsorption on CG.



Scheme 2. A simplified schematic diagram of the adsorbent regeneration process.

waste (Afriliana et al., 2021). For this purpose, another experiment was carried out using mash obtained from baker's yeast and adsorbents after the fifth regeneration cycle (Table S12 and Table S13). The materials and mash were suspended in CV solution in the wastewater. After five days of the experiment, the materials were centrifuged and the COD and pH of the supernatants were determined by comparing them with the blank containing only yeast and sewage. In the case of CG, CD-1, and CD-2, the pH of the supernatants decreased to 2. The COD parameter decreased in each case in the range from 29% (CG) to 40.5% (CC) (Chen

and Jin, 2006). In the first case, the color intensity of the supernatant was increasing with time (Fig. 9d). Appropriate types of yeast are used in the production of coffee, which in itself was an excellent breeding ground for microorganisms (Ruta and Farcasanu, 2021). It is also important that yeast greatly facilitates the removal of dye from the surface of the sorbent. One-time extraction with methanol enabled the quantitative removal of CV from the surface of each sorbent (Fig. 9e.) (Table S5).

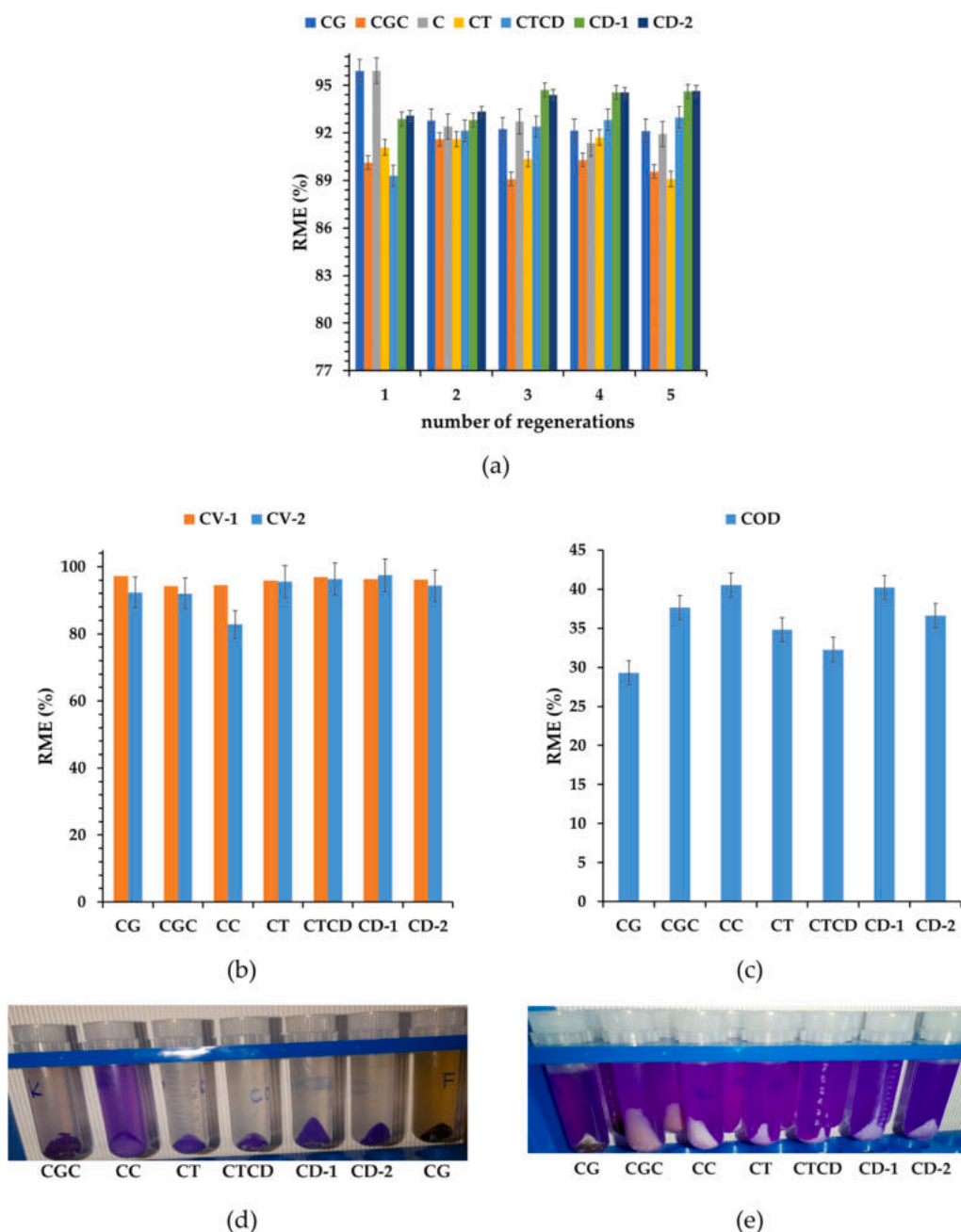


Fig. 9. (a) The average efficiency of CV ($C_{CV} = 10.20 \text{ mg L}^{-1}$, $m_{sor} = 10 \text{ mg}$) removal by sorbents after consecutive regeneration cycles; (b) The effects of CV removal from effluents containing yeasts; (c) The effects of yeasts on COD removal from effluents; (d) C-1, CV solution in tap water ($C_{CV} = 10.20 \text{ mg L}^{-1}$, $m_{sor} = 50 \text{ mg}$), C-2, CV solution in effluents ($C_{CV} = 10.20 \text{ mg L}^{-1}$, $m_{sor} = 50 \text{ mg}$, $C_{yeast} = 1 \text{ g L}^{-1}$).

3.2.8. Adsorption mechanism

The main mechanism of dye sorption was based on the formation of hydrogen bonds and van der Waals interactions. The best example was CC which had a very ordered microcrystalline structure. A significant number of hydroxyl groups form hydrogen bonds. During sorption, they are partially destroyed in favor of new fibers connecting with the dye. The process was endothermic, but the resulting system provided a greater degree of disorder. The obtained energy minimum prevented the destruction of the new structure, hence the greatest difficulties with dye desorption. Cross-linking CC with toluene-2,4-di-isocyanate formed an amphiphilic system. The hydrophobic groups had the capacity to form hydrogen bonds, but the hydrophobic aromatic rings significantly reduced the wettability and thus the amount of water retained. Consequently, less energy must be supplied to the system during the sorption

of the dye, which interacted with the surface not only through hydrogen bonds and van der Waals forces but also through π - π relations. As a result, the amount of retained dye was increased. Nevertheless, the introduction of spatial elements (aromatic rings) and groups competing in the formation of hydrogen bonds (urethane groups) facilitates desorption. The influence of other groups becomes apparent during CV sorption by CG and CGC. Probably, in this case, additional salts were formed by the reaction of the carboxyl and amino groups. CTCD was the system with the greatest potential to interact with dyes, as it is a structure composed of fibers and macrocycles linked together by TDI. Interactions intensifying during sorption were the sum of those described for CT and supramolecular ones. The latter allowed for better matching of the dye molecule to the sorbent structure. Additionally, the process gained selectivity. Forming supramolecular complexes forced

the preorganization of the material, which allowed for a better adjustment of the structure of the guest to the host. The new order facilitated sorption and desorption at the same time. The last two materials were made of cross-linked CD. The use of two different solvents had a significant impact on the physicochemical properties. The CD-1 kept the most CVs among the discussed above. The amount of embedded CD, assuming the formation of a 1: 1 complex, will only complex 179.73 mg g^{-1} , which meant that the residual amount was retained in the remaining structural elements of the network. Likewise, in the case of CD-2, which was obtained by reactions also allowing the condensation of secondary hydroxyl groups. A more random substitution led to a polymer in which a structurally distinct network connecting the CD torus also participates in sorption.

4. Conclusions

The paper presents a holistic approach to the sorption process carried out with the use of natural and semi-natural resources. Attention was drawn to the paradox resulting from the amount of generated wastewater in the case of using renewable raw materials and their lack of organic synthesis. The significant influence of the solvent and the cross-linking agents on the properties of the polymer as well as the significant share of hydroxyl groups in the structure of sorbents was demonstrated. Characterization analysis (TG / DTA, FTIR, EA, SEM) showed that the cellulose-containing materials are partially crystalline and partially amorphous. The degree of substitution of dehydroxyglucose monomers in chemically modified materials was in each case close to one, and the CD content is up to 50%. The materials were mesoporous. The CGC additionally contained macropores. Sorbents retained water to varying degrees, among them the most CGC (3 g g^{-1}). Materials in solutions with different pH achieve a point charge of zero, therefore a cationic dye was selected for the study. The results showed that CG, CGC, and CD-2 are the least sensitive to pH and can work efficiently in the range from 4 to 11. Kinetic and isothermal studies have shown that CV adsorption takes place on a relatively homogeneous surface. The dye adsorption by CG and CGC followed the pseudo-second model, while in the remaining cases it followed the pseudo-first model. The data on the material adsorption equilibria fit well with the two Langmuir and Sips models. The determined values of the maximum adsorption capacity for all materials were very high and exceed the value of 1000 mg g^{-1} .

All materials effectively remove other cationic dyes from wastewater. The materials after the sorption of impurities can be regenerated under mild conditions and used at least five times. Waste sorbents are not toxic to yeasts and can be decomposed during composting assisted with this type of microorganisms. The yeast enables the quantitative desorption of the dye in the first step. From the point of availability of the raw material, the possibility of its final decomposition by composting, ordinary Arabica coffee grounds are the best choice. On the other hand, when assessing the stability during regeneration and even the increase in sorption capacity, as a result of probably remembering the shape of pollutants, materials containing CD win the race.

Environmental implication

Adsorption is one of the basic processes for removing organic pollutants from wastewater. Nevertheless, a serious disadvantage of this method is the issue of managing the used adsorbents. The new idea is to use renewable raw materials in a native or processed form with the assumption of their potential biodegradation. These types of adsorbents can be obtained from plant waste, which significantly reduces the cost of the process. It also gives the opportunity to make better use of native waste. The used sorbents can be composted and thus transformed into organic fertilizer, which solves the issue of storage.

CRediT authorship contribution statement

Anna Skwierawska: Conceptualization, Methodology, Investigation, Formal analysis, Validation, Writing - original draft, Visualization, Writing - review & editing. **Monika Bliźniewska:** Investigation, Writing - review & editing. **Kinga Muza:** Investigation, Writing - review & editing. **Agnieszka Nowak:** Investigation, Writing - review & editing. **Dominika Nowacka:** Validation, Writing - review & editing. **Shan E Zehra Syeda:** Investigation, Writing - review & editing. **Muhammad Shahzeb Khan:** Investigation, Writing - review & editing. **Bogusława Łęska:** Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2022.129588](https://doi.org/10.1016/j.jhazmat.2022.129588).

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Supplementary Material

Cellulose and its derivatives, coffee grounds, and cross-linked
 β -cyclodextrin in the race for the highest sorption capacity of cationic
dyes in accordance with the principles of sustainable development

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Abbreviations¹

¹BG brilliant green

BP bromocresol purple sodium salt

CC cellulose microcrystalline

β -CD (CD) β -cyclodextrin

CD-1 sorbent obtained in reaction of cyclodextrin with toluene-2,4-di-isocyanate conducted in a pyridine medium

CD-2 sorbent obtained in reaction of cyclodextrin with toluene-2,4-di-isocyanate conducted in a dimethylformamide medium

CG coffee grounds

CGC cellulose obtained from coffee grounds

CR Congo red

CT cellulose sorbent obtained in reaction microcrystalline cellulose with toluene-2,4-di-isocyanate in a pyridine medium

CTCD sorbent obtained in reaction of microcrystalline cellulose and cyclodextrin with toluene-2,4-di-isocyanate in a pyridine medium

CV crystal violet

DMF dimethylformamide

EB eriochrome black

HA a mixture of humic acids 50% fulvic acids

MB methylene blue

TB toluidine blue and TDI toluene-2,4-di-isocyanate

S1 Characteristics of the obtained materials.

Determination of acidic and basic groups of CG and CGC identification

The method described by Boehm (Boehm, 1966) was used to determine the surface functional groups of the adsorbent using coffee grounds (CG) and cellulose (CGC). Aqueous solutions of NaHCO_3 (0.10 mol L^{-1}), Na_2CO_3 (0.05 mol L^{-1}), NaOH (0.10 mol L^{-1}) and HCl (0.10 mol L^{-1}) were prepared. The solutions (5 mL) were then added to vials containing 0.1 g of adsorbents. The vials were purged with nitrogen. It was then sealed, shaken (140 rpm) for 24 hours, and the product was filtered. Moreover, five blank solutions (no adsorbent) were also prepared. The number of free basic groups was calculated from the amount of HCl reacted. Various acidic free groups were determined based on the assumption that NaOH neutralizes carboxyl, lactone, and phenol groups. Furthermore, Na_2CO_3 neutralizes carboxyl and lactone groups, whereas NaHCO_3 neutralizes solitary carboxyl groups. The excess of base or acid was determined by back titration with solutions using NaOH (0.10 mol L^{-1}) and HCl (0.10 mol L^{-1}).

Table S1. Content of functional groups in materials determined on the basis of Boehms' method.

material	Group type (mmol g^{-1})				
	Carboxylic	Lactone	Phenolic	Σ acid groups	Basic
CG	1.003	0.013	0.148	1.164	0.911
CGC	0.965	0.013	0.06	1.038	0.875

Table S2. Infrared crystallinity ratio and hydrogen bond intensity (HBI) of the materials.

Material	$\frac{1372 \text{ cm}^{-1}}{2900 \text{ cm}^{-1}}$ (TCI)	$\frac{1429 \text{ cm}^{-1}}{897 \text{ cm}^{-1}}$ (LOI)	$\frac{3400 \text{ cm}^{-1}}{1320 \text{ cm}^{-1}}$ (HBI)
CG	1.048	0.870	0.629
CGC	1.036	0.880	0.694
CC	1.016	0.919	0.730
CT	1.289	0.887	0.393
CTCD	1.006	0.821	0.758

Table S3. Energy of hydrogen bonds and distance of hydrogen bonds in materials determined on the basis of (Pimentel and Sederholm, 1956; Poletto et al., 2014; Struszczyk, 1986).

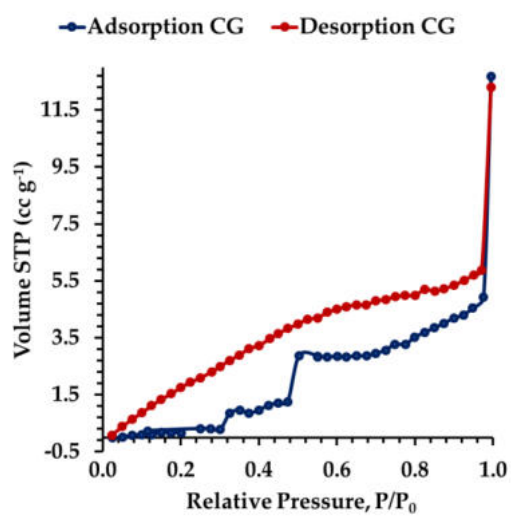
Material	3567 (cm ⁻¹)		3423 (cm ⁻¹)		3342 (cm ⁻¹)		3278 (cm ⁻¹)		3221 (cm ⁻¹)	
	E _H (kJ)	R (Å)	E _H (kJ)	R (Å)	E _H (kJ)	R (Å)	E _H (kJ)	R (Å)	E _H (kJ)	R (Å)
CG	64.516	2.837	125.531	2.836	107.647	2.836	8.2548	2.837	57.443	2.838
CGC	41.854	2.838	76.582	2.837	64.463	2.837	4.653	2.838	28.878	2.839
CC	48.498	2.838	89.007	2.836	78.540	2.837	6.244	2.837	42.273	2.838
CT	76.967	2.837	155.203	2.837	114.406	2.838	7.276	2.838	31.045	2.839
CTCD	43.735	2.838	98.777	2.836	98.985	2.836	8.453	2.836	62.477	2.837

Table S4. The degree of substitution of hydroxy groups and CD content.

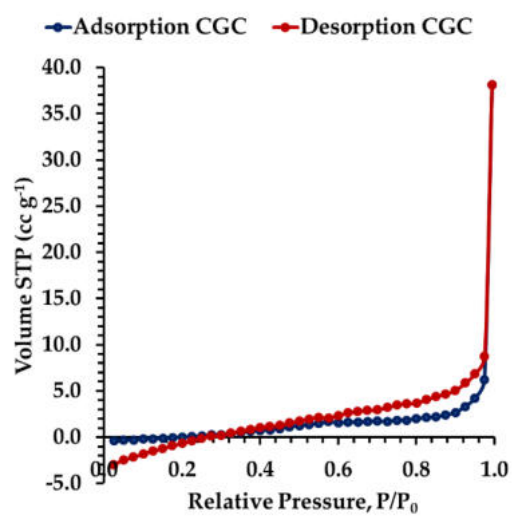
method	DS	CT	CTCD	CD-1	CD-2
Elemetar analysis	(C%)	0.9333	0.9333	0.9333	0.9333
Elemetar analysis	(N%)	0.954	0.950	0.948	0.950
FTIR	DS	0.996	0.994	0.929	0.948
phenolphthalein	CD (%)	-	50.99	49.95	49.55

EA: (Qin et al., 2017)(Zhang et al., 2019) (Zhong, 2020); FTIR spectroscopy (Li et al., 2019) and additionally for systems containing β -CD phenolphthalein complexation (Cadena et al., 2009) (Mohamed et al., 2012)(Cadena et al., 2009; Goel and Nene, 1995; Mohamed et al., 2012).

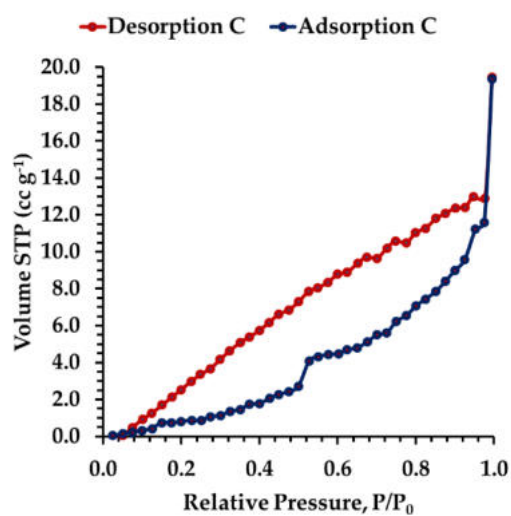
BET isotherms obtained during N₂ adsorption and desorption by materials at 77.35 K.



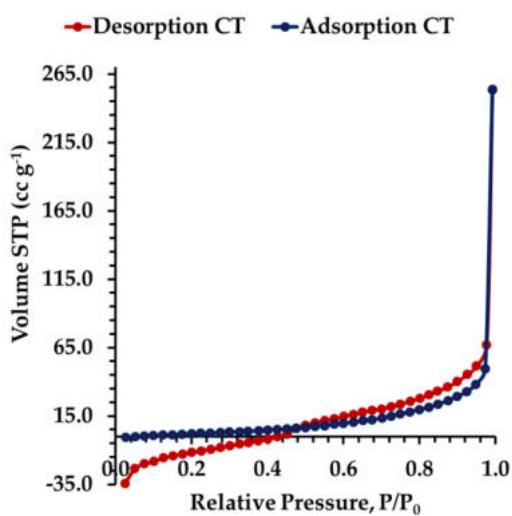
(a)



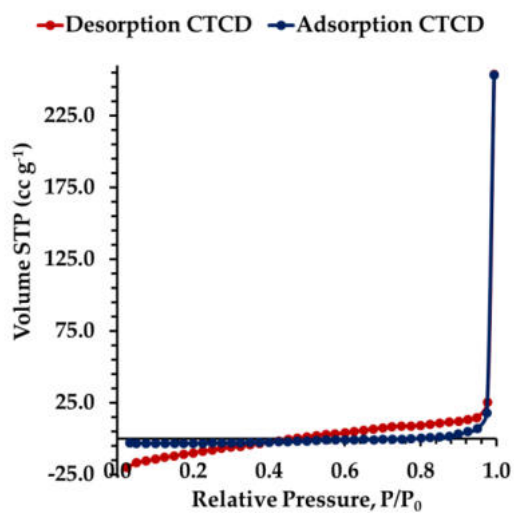
(b)



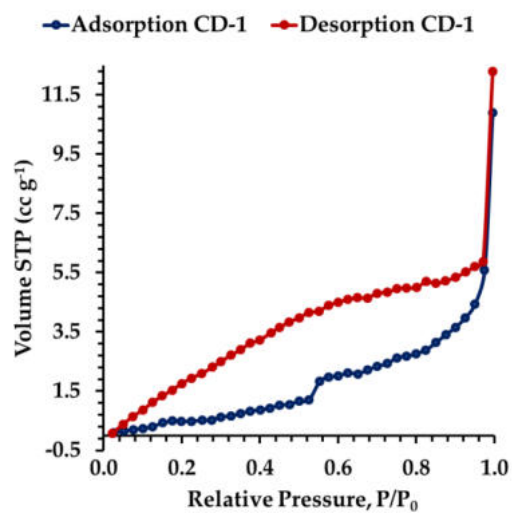
(c)



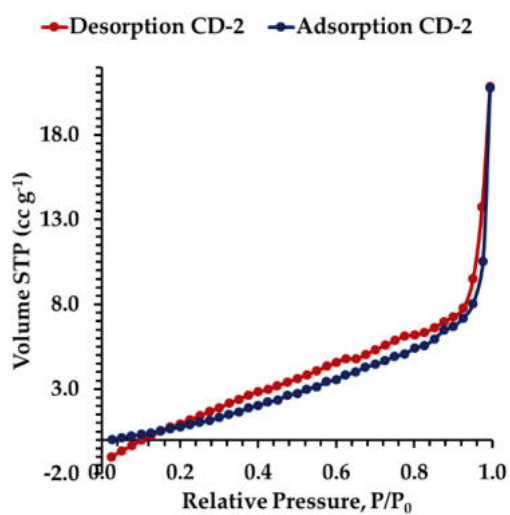
(d)



(e)



(f)



(g)

Fig. S1. N_2 adsorption–desorption isotherms recorded at 77 K: CG for (a); CGC (b); C (c); CT (d); CTCD (e); CD-1 (f) and CD-2 (g); the water holding capacity of material.

Table S5. Description of linear equations of BET isotherms and parameters determined on the basis of BET and BJH isotherms.

isotherm	CG	CGC	CC	CT	CTCD	CD-1	CD-2
MBET							
slope	448.286	16254.924	286.971	-48.103	-413.407	1229.721	-50.751
intercept	944.1	-1387	207.7	113.8	19.14	193.9	270.7
Correlation coefficient (r)	0.2107	0.2430	0.5304	0.6070	0.9938	0.9004	0.6668
C constant	1.475	-10.723	2.382	0.577	-20.601	7.341	0.812
Surface area (m ² g ⁻¹)	3	< 1	7	53	<< 1	3	16
BJH adsorption							
Surface area (m ² g ⁻¹)	6.13	8.02	14.45	80.46	37.69	5.72	9.10
Pore volume (cc g ⁻¹)	0.02	0.06	0.03	0.44	0.42	0.02	0.03
Pore diameter Dv(d) (nm)	3.95	3.72	4.19	4.18	4.18	4.46	2.97
Total pore volume (cc g ⁻¹)	< 400.61	< 326.24	< 352.23	< 257.22	< 309.25	< 381.72	< 306.87
Average pore D (nm)	31.47	101.0	17.06	29.63	-	27.62	8.14

[a] BET surface area obtained from N₂ adsorption-desorption isotherms.

[b] BJH adsorption cumulative pore volume with a diameter below that indicated for each material individually and expressed in nanometers (nm).

[c] BJH adsorption average pore diameter.

The water holding capacity and elemental (WHC) analysis of materials

The water holding capacity (WHC) was determined by mixing a 100 mg sample with 5 ml of distilled water. The mixtures were vortexed for 1 min, centrifuged at 2330 g for 30 min and the volume of the supernatant was determined. WHC is expressed as grams of water retained per gram of sample.

Table S6. Summary of the results of elemental and water holding capacity.

material	CG	CGC	CC	CT	CTCD	CD-1	CD-2
WHC (g g ⁻¹)	1.28	2.96	1.21	0.79	0.91	0.41	0.38
Elemental analysis							
H (%)	6.45	6.74	6.24	6.25	4.90	4.70	4.90
N (%)	2.33	0.42	-	6.70	8.00	9.02	8.12
O (%)	undefined	undefined	49.34	37.20	33.85	31.56	33.88

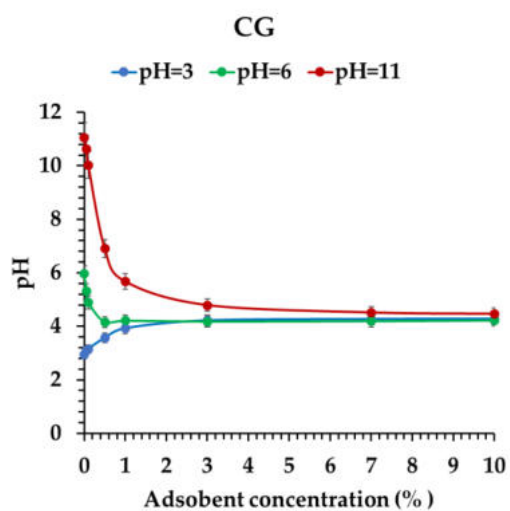
The surface charge and pH_{PZC} of the adsorbents

Reverse mass titration.

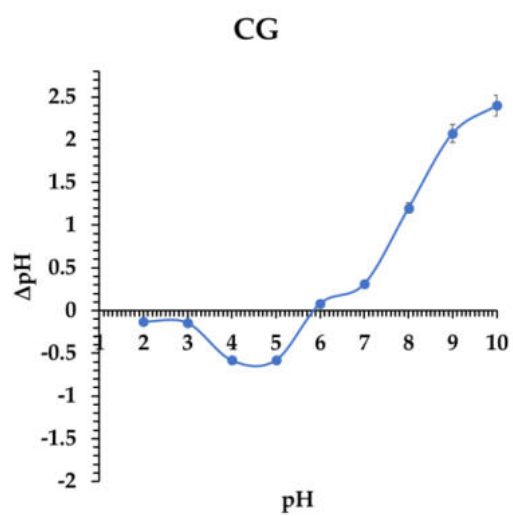
Three aqueous solutions with pH 3, 6, and 11 were prepared. Next, materials were added to vials containing 5 mL of each solution to prepare 0.05%, 0.1%, 0.5%, 1.0%, 3.0%, 7.0% and 10.0% suspensions which were purged with N₂ to eliminate CO₂ and sealed. The samples were left to equilibrate for 24 h under agitation (140 rpm) at 25 °C. Then, the pH of each solution was measured. Moreover, pH_{PZC} was obtained from the plot of pH vs. adsorbent concentration.

Salt addition technique

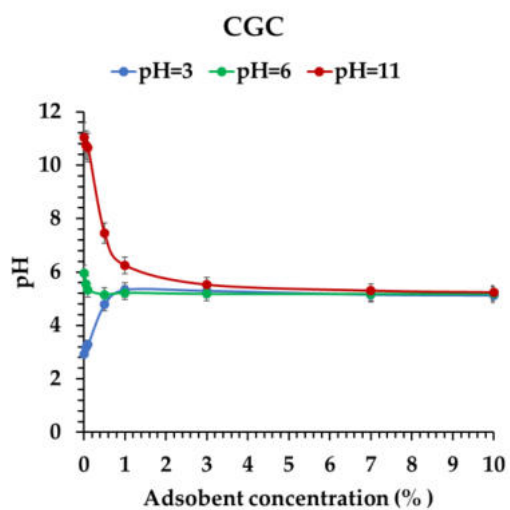
In a series of vials containing 5 ml of NaCl solution (0.1M) each, a mass of 10 mg of adsorbent was added. The pH (2 – 11) was adjusted with the solutions of HCl (0.1 M) and NaOH (0.1 M). The samples were left to equilibrate for 24 h under agitation (140 rpm) in an inert atmosphere at 25 °C. The pH values were measured after 24 hours. pH_{PZC} was obtained from the plot of ΔpH vs. pH at ΔpH = 0.



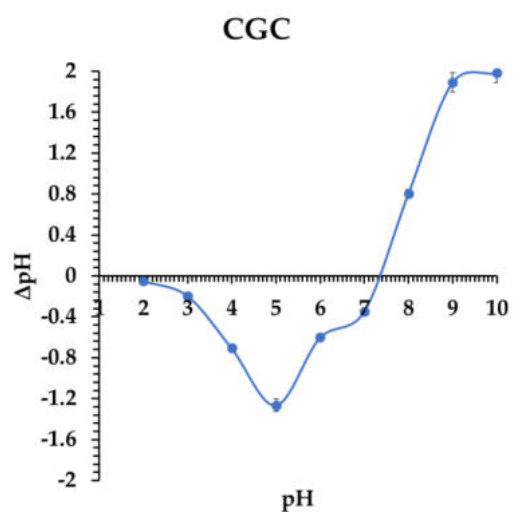
a)



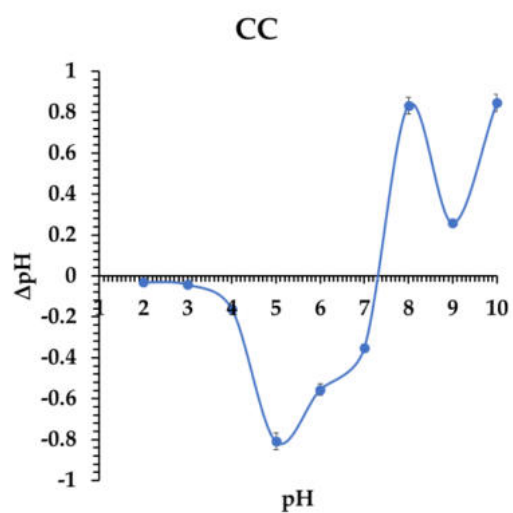
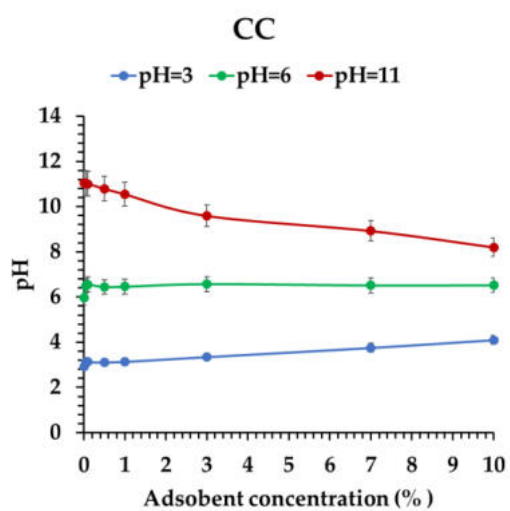
b)

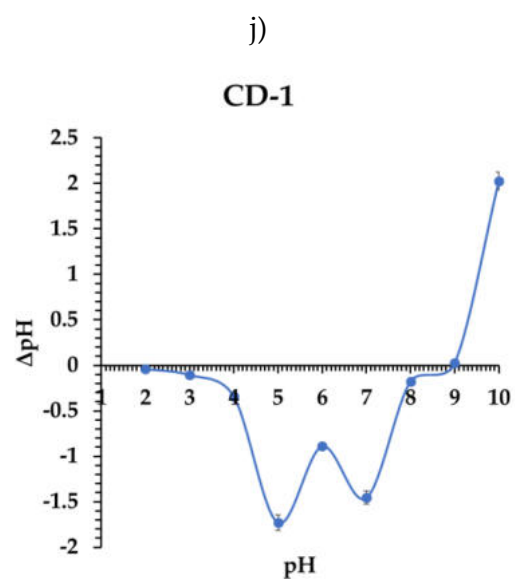
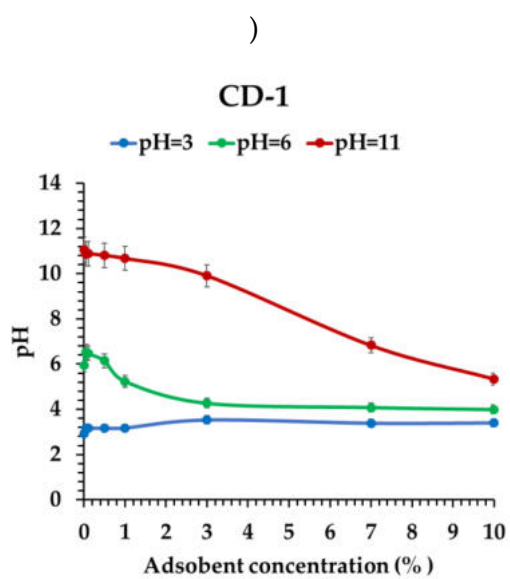
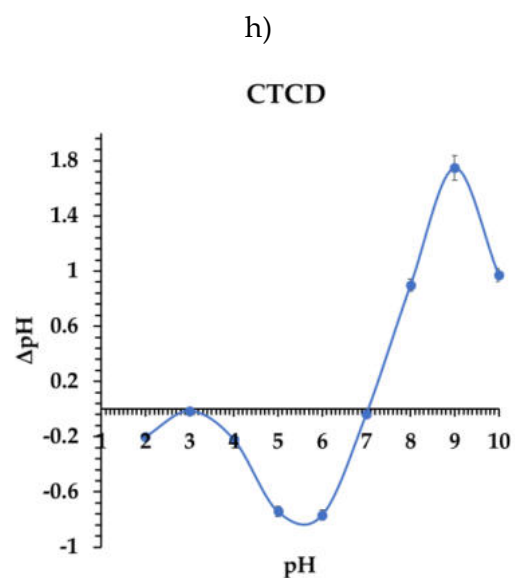
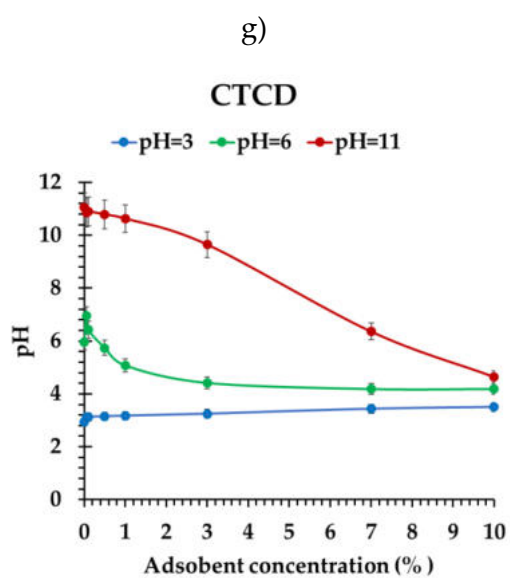
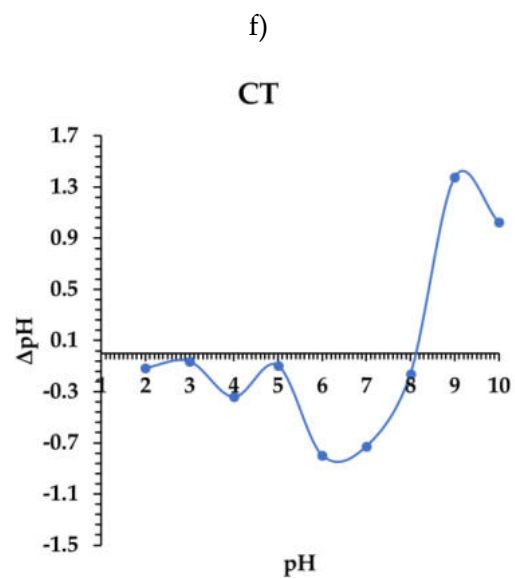
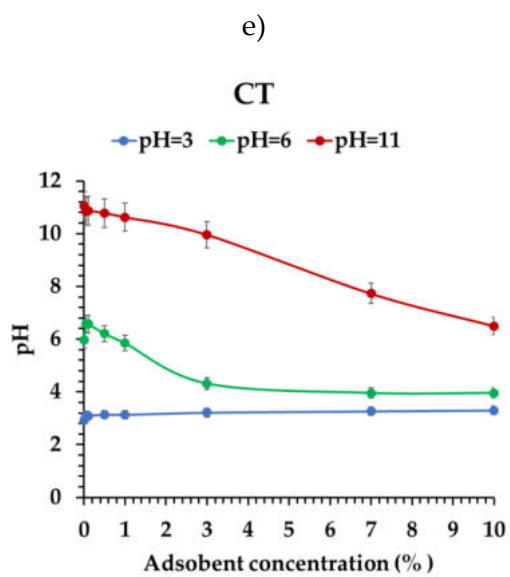


c)



d)





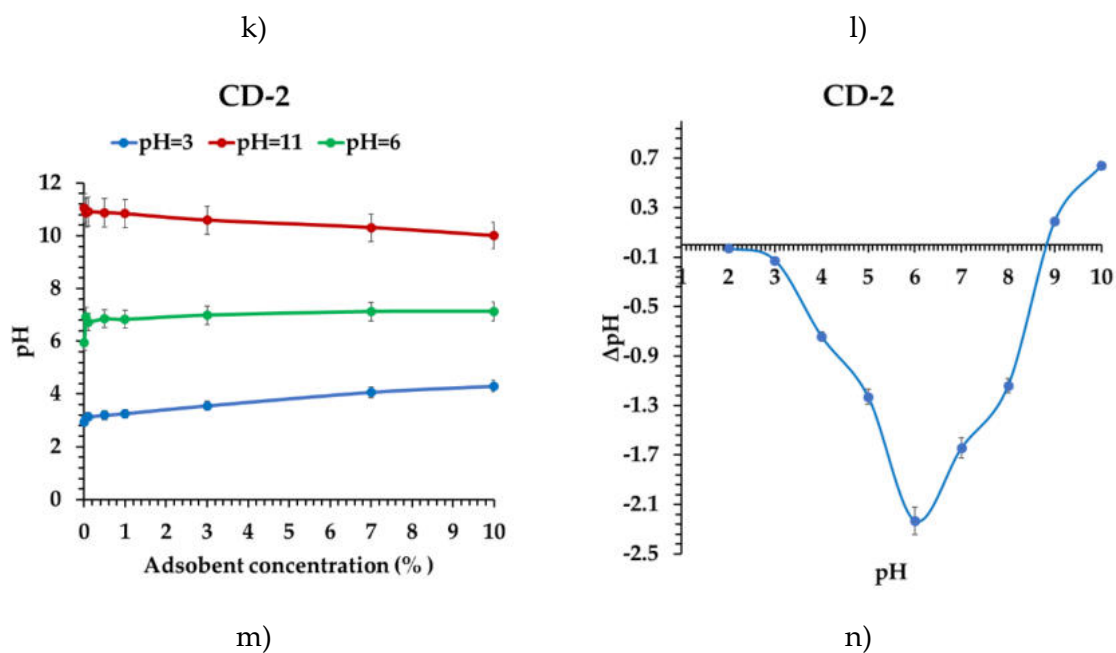


Fig. S2. The curves obtained during the determination of the zero point of the charge using reverse mass titration (a, c, e, g, I, k, and m) and salt addition technique (b, d, f, h, j, l, n).

Table S7. Summary of the determined PZC values.

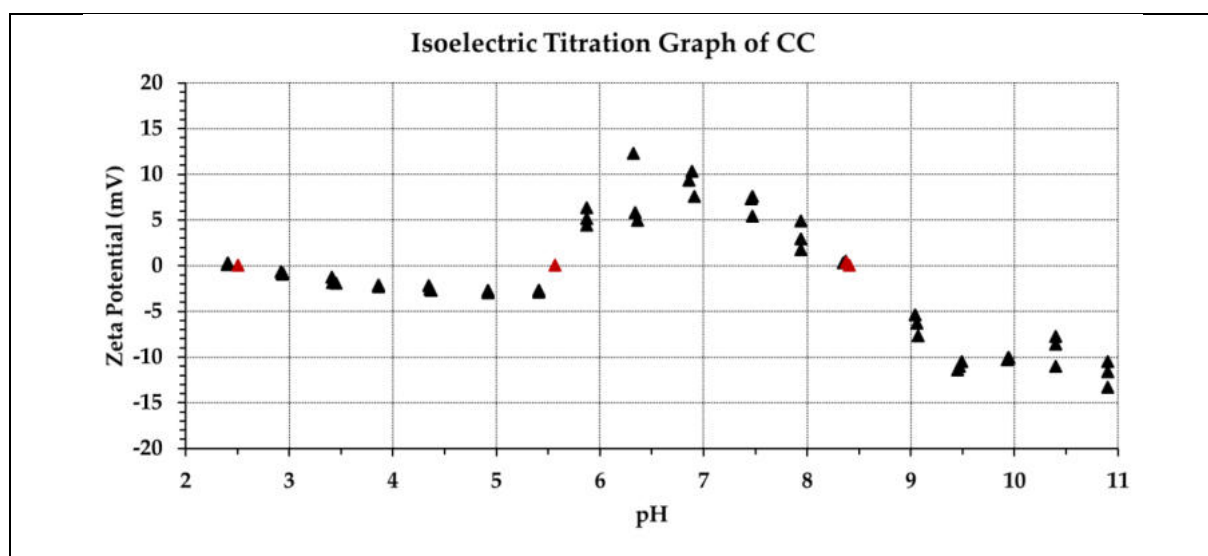
material	CG	CGC	CC	CT	CTCD	CD-1	CD-2
PZC ^a	5.30	4.18	6.52	3.96	7.12	4.02	4.38
PZC ^b	5.93	7.35	7.30	8.15	7.05	8.94	8.81

[a] Reverse mass titration;

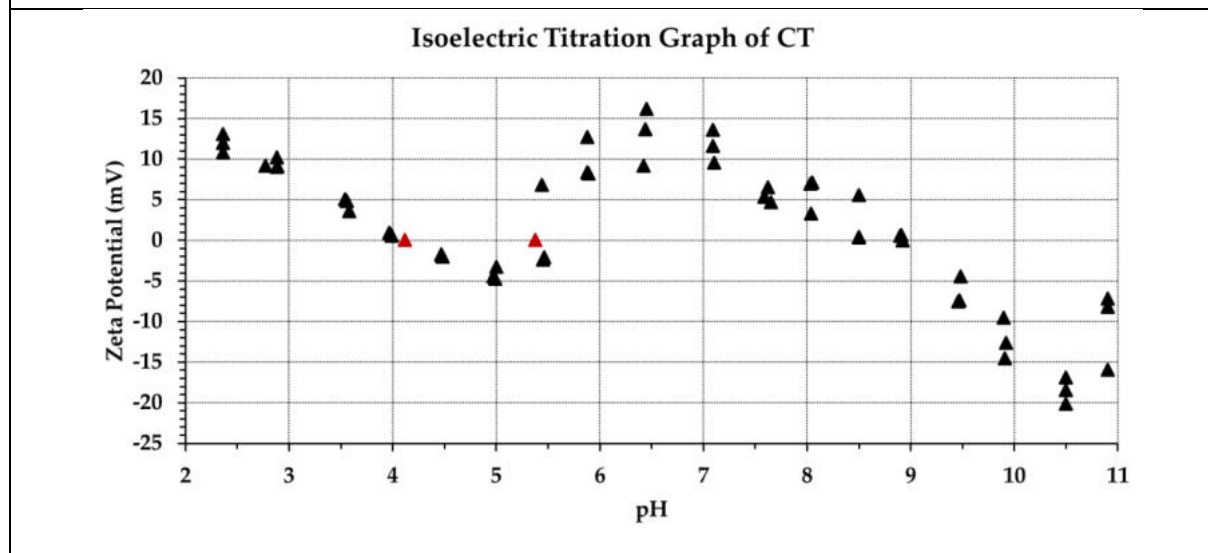
[b] Salt addition technique

Zeta potential measurement

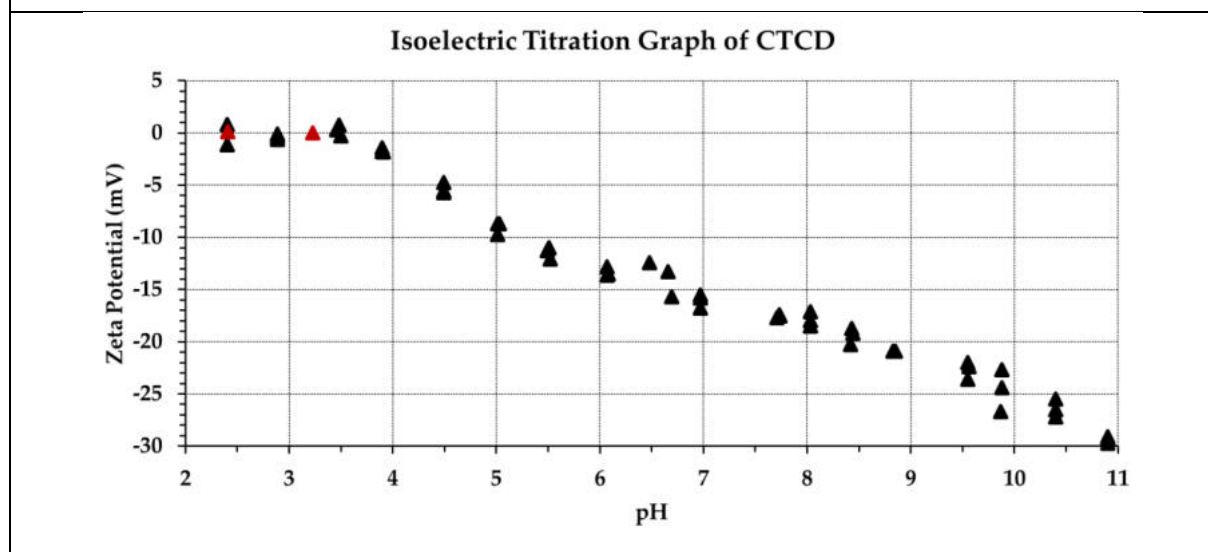
Zeta potential measurements were carried out by a zeta potential meter (Malvern ZS90) at 298 K. For measurement, the sample was dispersed in the deionized water with the concentration of 1 mg mL^{-1} and the pH value was adjusted in the range of 2 - 11 by adding HCl (1 mol L^{-1}) or KOH (0.5 mol L^{-1}) in case of titration for CC, CT, and CTCD. In the experiment with CD-1 lower concentration of acid was used (0.3 mol L^{-1}). The physicochemical properties of CG, CGC, and CD-2 materials made it impossible to conduct the research.



a) isoelectric points: pH = 2.51; 5.57 and 8.41



b) isoelectric points: pH = 4.12 and 5.38



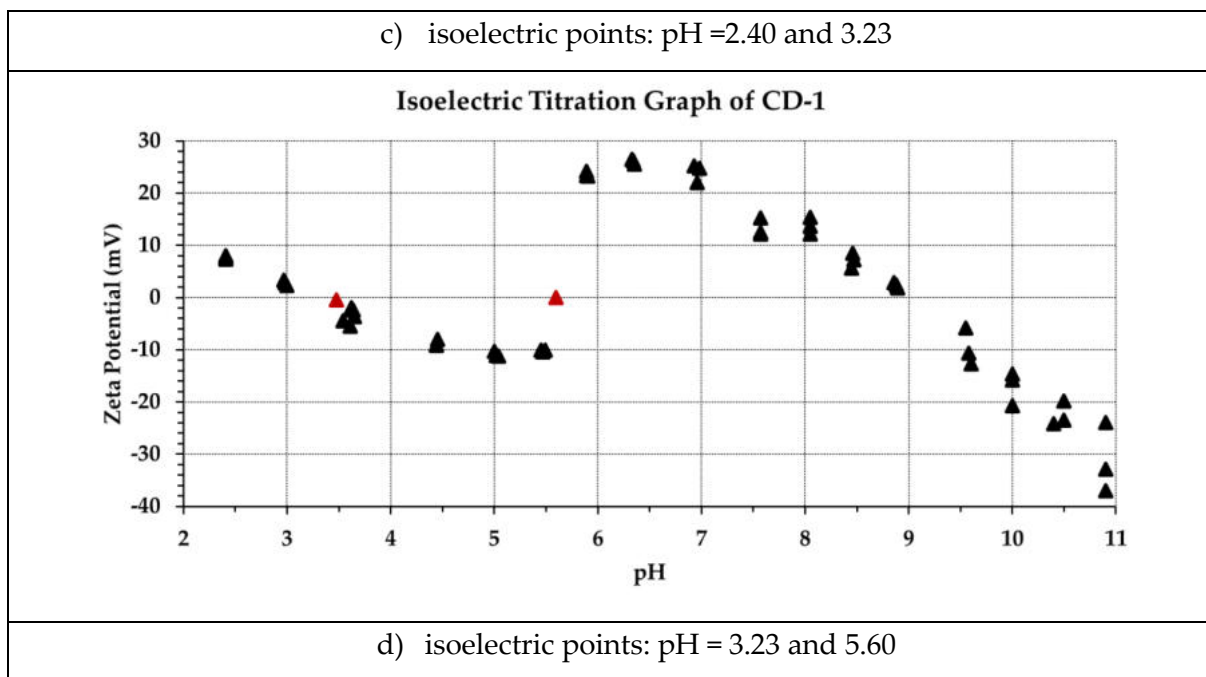
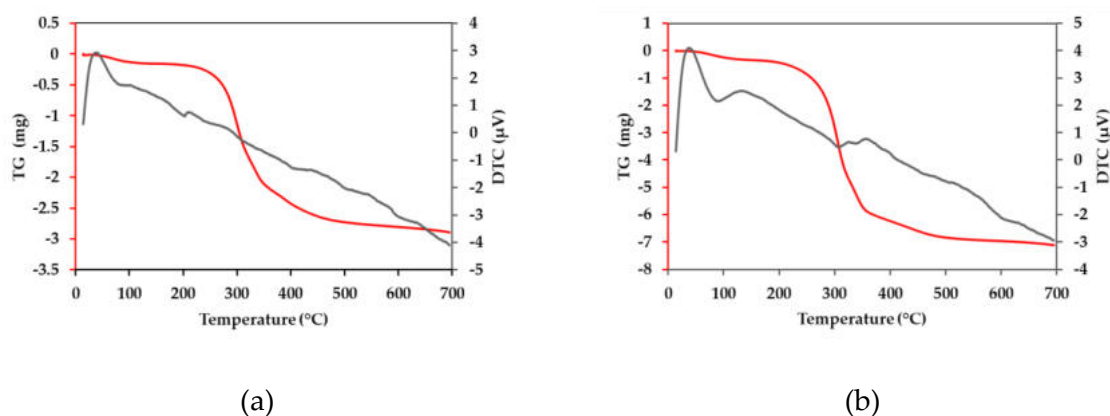
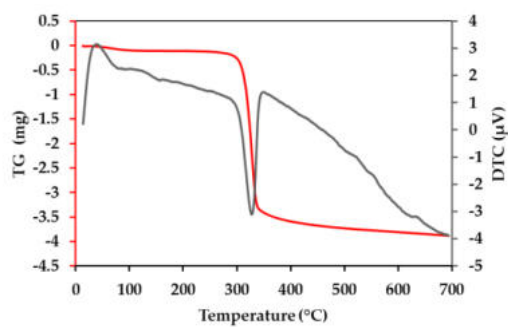


Fig. S3. The curves obtained during the isoelectric titration of: a) CC; b) CT; c) CTCD; d) CD-1 suspensions in water with HCl and KOH solutions.

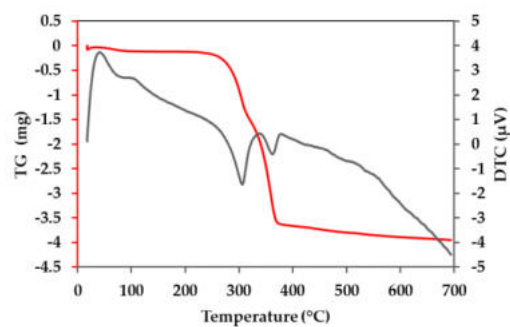
Thermal analyzes TG and DTA

The simultaneous TG–DTA curves were obtained at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ keeping temperature between $30\text{--}700\text{ }^{\circ}\text{C}$, by using alumina crucibles, and the samples mass range was from 3.7 to 9.6 mg. The experiments were carried out under nitrogen atmosphere at a flow rate of 50 ml min^{-1} , in a SETSYS - 1200 (TG-DTA 1600°C) system. The instrument was preliminarily calibrated with standard mass and with standard calcium oxalate monohydrate.

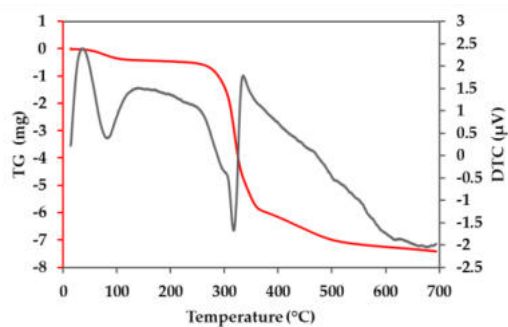




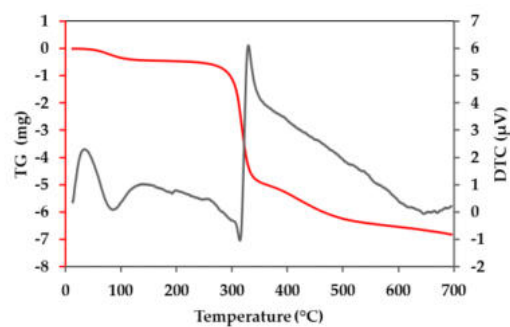
(c)



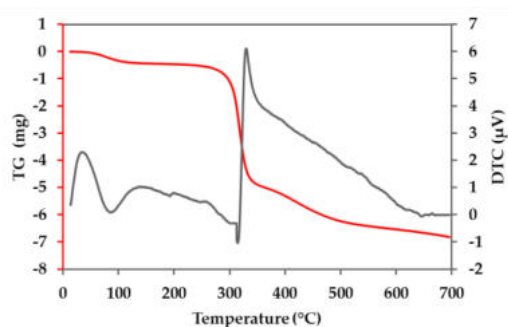
(d)



(e)



(f)



(g)

Fig. S4. TG and DTA curves recorded during thermal decomposition of materials carried out at temperatures up to 700 °C, under nitrogen atmosphere: CG (a); CGC (b); CC (c); CT (d); CTCD (e); CD-1 (f); CD-2 (g).

Water content in tested materials.

Table S8. The water content was determined on the basis of the weight loss between the ambient temperature and 150 °C based on the results of the TG analysis.

material	CG	CGC	CC	CT	CTCD	CD-1	CD-2
Water (%)	5.16	5.04	2.5	2.67	4.82	4.76	4.75

Table S9. Thermogravimetry/differential thermal analysis steps under nitrogen atmosphere. Distinct experimental condition levels.

sample	ΔT (°C)	Δm (%)	ΔT (°C)	Δm (%)	T_p (°C)	T_p (°C)
CG	14 – 113	3.84	234 – 359	52.22	84 (endo)	505 (endo)
	113 – 234	2.65	259 – 650	18.11	204 (endo)	601 (endo)
					405 (endo)	
CGC	14 – 121	3.65	358 – 502	11.18	90 (endo)	341 (endo)
	121 – 218	2.59	502 – 694	3.18	307 (endo)	606 (endo)
	218 – 358	63.06				
CC	14 – 86	3.18	272 – 355	74.77	81 (endo)	328 (endo)
	86 – 272	15.91	355 – 651	9.32	159 (endo)	
CT	14 – 88	2.17	316 – 376	47.83	85 (endo)	
	88 – 226	2.83	376 – 693	7.17	306 (endo)	364 (endo)
	226 – 316	28.04				

CTCD	14 – 107	3.96				
			375 – 506	10.94	83 (endo)	337 (exo)
	107 – 241	1.46				
			506 – 693	4.06	317 (endo)	676 (endo)
	241 – 375	56.77				
CD-1	13 – 112	4.06				
			348 – 503	14.38	86 (endo)	331 (exo)
	112 – 248	1.46				
			503 – 696	5.94	314 (endo)	645 (endo)
	248 – 348	45.21				
CD-2	13 – 120	4.56				
			346 – 497	15.11	87 (endo)	331 (exo)
	120 – 231	1.00				
			497 – 695	6.56	314 (endo)	646 (endo)
	231 – 346	48.44				

Δm - mass difference; ΔT - temperature difference; T_p - peak temperature

Hydrophilic and hydrophobic properties materials.

The hydrophobic and hydrophilic properties of sorbents were determined on the basis of two experiments. At first, the materials were measured (300 mg in a 10 mL open glass vial) in two tightly closed chambers containing 200 ml of water or toluene for 24 hours at 25 ° C. The experiment was repeated three times. The capacities of the solvents were determined on the basis of the weight gained. Moreover, the ratio of toluene capacity to water capacity allowed for the estimation of the HI_{static} value.

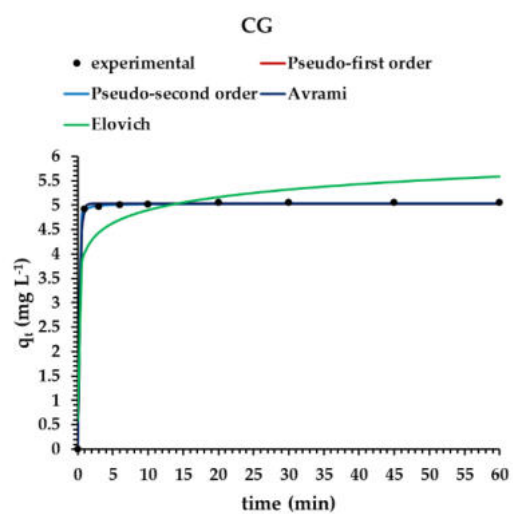
In the second experiment, a two-component system consisting of toluene and water was used. Equal volumes of solvents (10 mL) were measured into the beakers placed on magnetic stirrers and the sorbent (30 mg) was added in one portion, the falling time was also measured. After 2 minutes, the contents of the beakers were vigorously mixed for 15 minutes and the phases were allowed to separate. The course of the experiment was documented by means of pictures.

Table S10 Water and toluene adsorption capacities and HI_{static} index of studied materials.

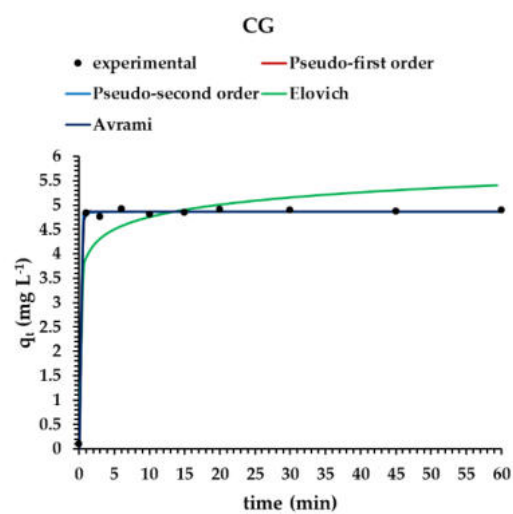
Samples	Water adsorption capacity (mg g ⁻¹)	Toluene adsorption capacity (mg g ⁻¹)	HI_{static}^b	P _i	P _f
CG	84.10	46.23	0.55	interface	water
CGC	96.71	35.49	0.37	interface	water
CC	62.59	3.07	0.05	water	water
CT	63.33	85.12	1.34	interface	toluene
CTCD	56.90	69.69	1.22	interface	Interface/water
CD-1	60.12	20.15	0.34	interface	water
CD-2	68.98	17.49	0.25	interface	water

P_i and P_f particles position before and after mixing, respectively

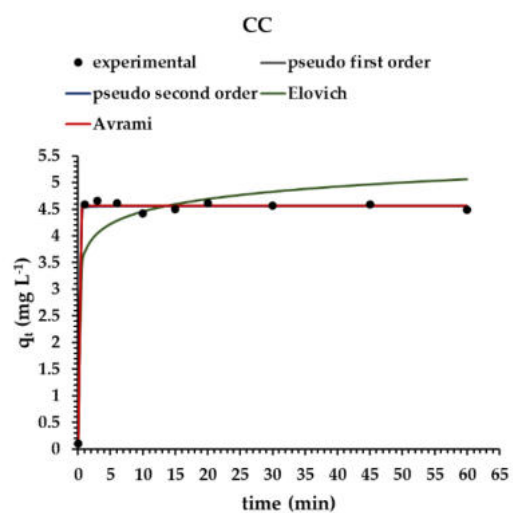
Kinetics model fitting



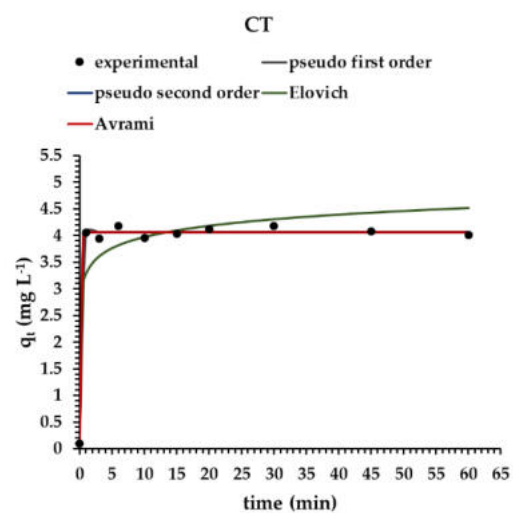
a)



b)



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d)

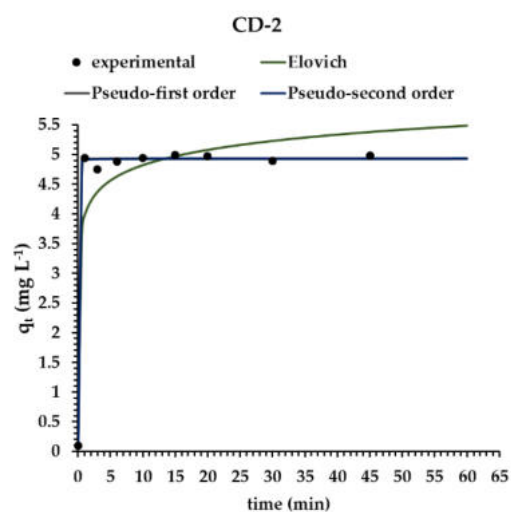
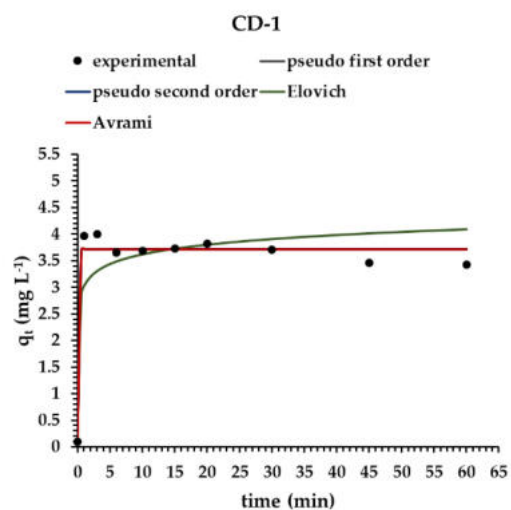
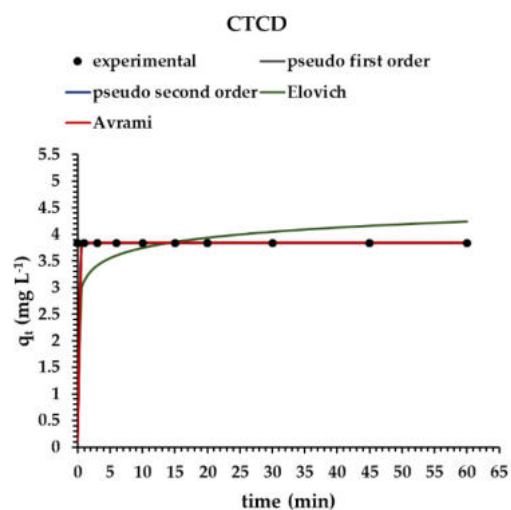
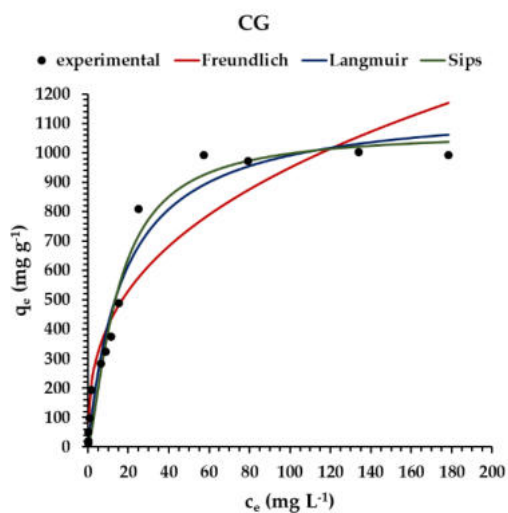


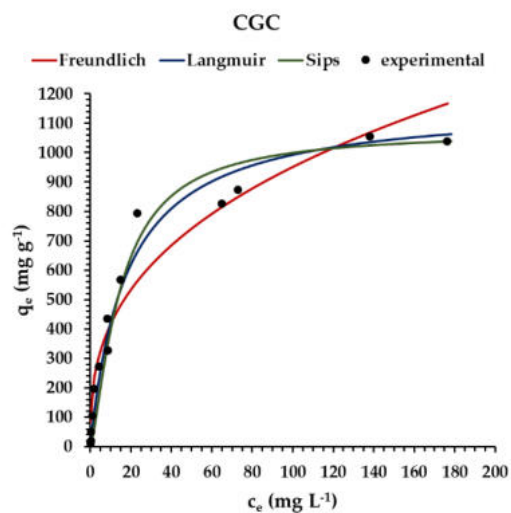
Fig S5. The curves obtained when fitting the nonlinear kinetics models to the experimental points obtained for:

a) CG; b) CGC; c) CC; d) CT; e) CTCD; f) CD-1 and g) CD-2.

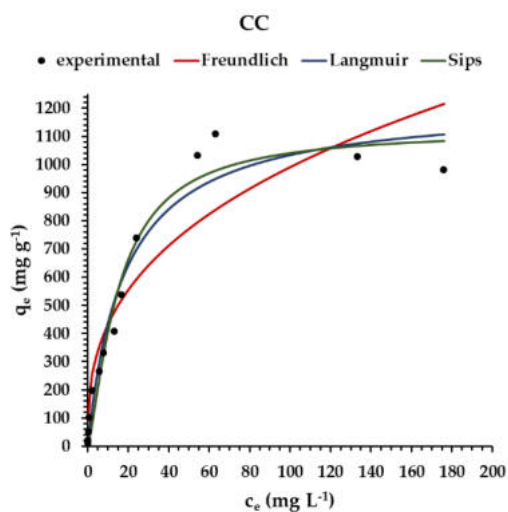
Isotherms



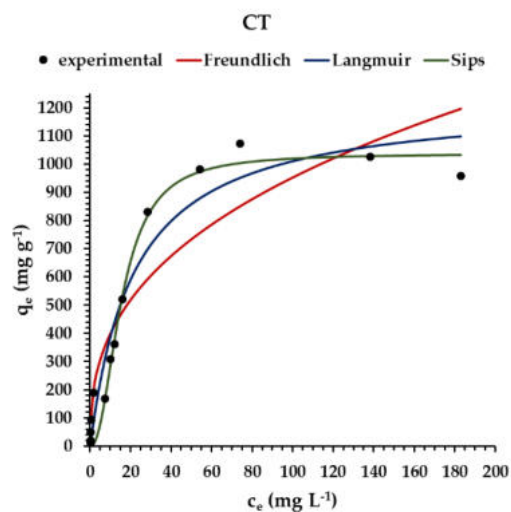
a)



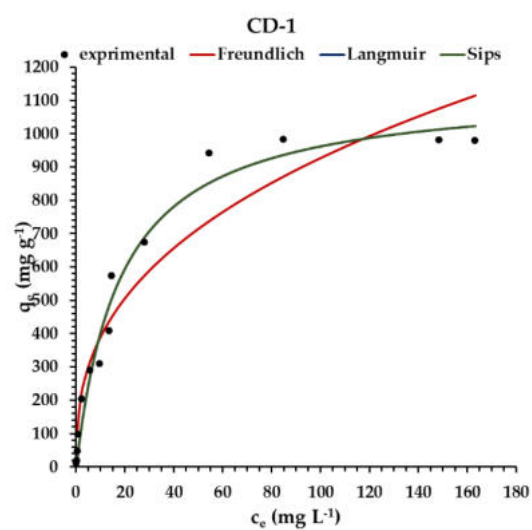
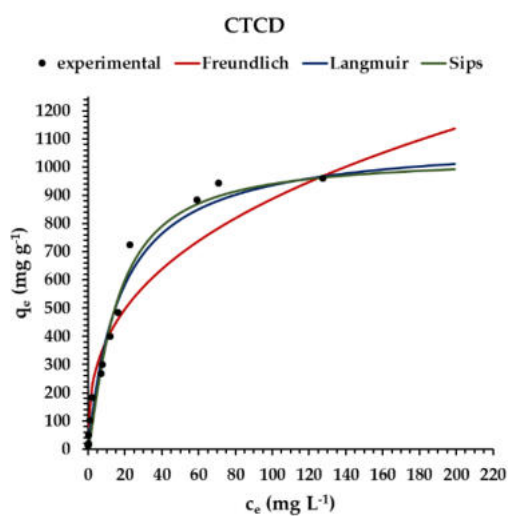
b)



c)



d)



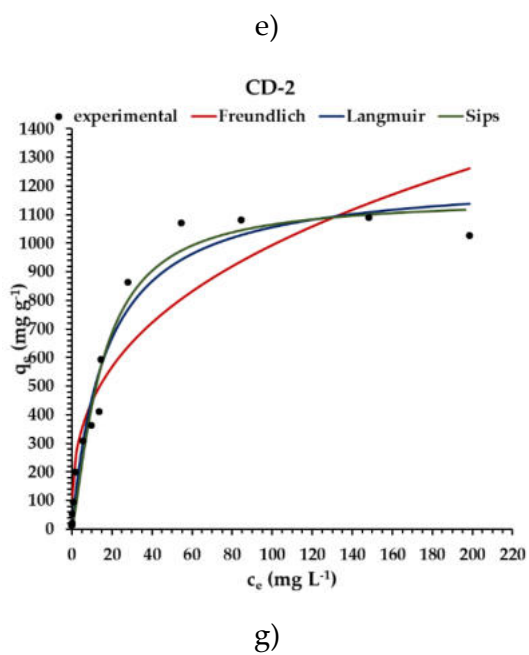


Fig S6 The curves obtained when fitting the nonlinear isotherm models to the experimental points obtained for:
a) CG; b) CGC; c) CC; d) CT; e) CTCD; f) CD-1 and g) CD-2.

Effluents discription

Table S11 List of dyes and characterization of effluents from municipal sewage treatment plant.

pollutant	Effluents without dye	
	parameter	value
anionic dyes		
Congo red	BOD ₅	29 mg L ⁻¹ O ₂
eriochrome black	COD	110 mg L ⁻¹ O ₂
bromocresol purple	TOC	2.2 mg L ⁻¹ C
cationic dyes	Total suspended solids	42 mg L ⁻¹
toluidine blue	Total nitrogen	10 mg L ⁻¹
Crystal violet	total phosphorus	0.5 mg L ⁻¹
brilliant green	Conductivity	1120 μ S cm ⁻¹
methylene blue	pH	7.2

Degradation

Biological degradation of adsorbents under the influence of yeast from baker.

In a 2 L vessel, 2 g of yeast (Table 4) was ground with 2 g of sugar and left for an hour at room temperature. Then, a liter of warm tap water was added. The suspension was stirred (150 rpm) at room temperature in an open vessel for another eight hours. Furthermore, 50 mg of the adsorbent was weighed into the falcon tubes and 7.5 ml of sewage containing CV with a concentration of 10.20 mg L⁻¹. The vials were sealed and the mixtures were shaken on a digital vortex mixer at 700 rpm for 20 min at 25 °C. After that, 0.5 ml of yeast suspension was added to each vial. Also, the blanks were prepared in the same way without the addition of an adsorbent and CV. The falcon tubes were sealed with gas-permeable cotton plugs and placed on a shaker (150 rpm) for five days. Later, the swabs were replaced by plastic stoppers, and the falcon tubes were centrifuged at 2000 g for 30 min. The supernatant was drained and analyzed for COD. These experiments were performed in triplicates.

Table S12. Microbiological characteristics of baker's yeast.

parameter	value
the number of aerobic mesophilic bacteria	not greater than 1×10^5 cfu g ⁻¹
spore-forming anaerobic bacteria	0.1 g: absent
number of forms	max. 10 cfu g ⁻¹
Listeria monocytogenes	max. 10 cfu g ⁻¹
Salmonella bacteria	absent in 25 g
Escherichia coli	10 cfu g ⁻¹
durability determined by the thermostat test	no changes
method in accordance with PN-A-79005-6	

Table S13. The results of biological degradation of the mixture of CV, and sewage by baker's yeast.

Adsorbent	Amount of CV in supernatant	Amount of desorbed	COD
	(mg L ⁻¹)	CV (mg L ⁻¹)	(O ₂ mg L ⁻¹)
CG	0.729	9.015	24475
CGC	0.760	7.137	21600
CC	1.639	6.607	20600
CT	0.422	8.719	22570
CTCD	0.353	9.370	23450
CD-1	0.242	9.068	20700
CD-2	0.539	9.380	21950
blank with yeast	-	-	34625

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Publication 4

Structural Adaptive, Self-Separating Material for Removing Ibuprofen from Waters and Sewage –
Materials, 2021

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Article

Structural Adaptive, Self-Separating Material for Removing Ibuprofen from Waters and Sewage

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Abstract: β -cyclodextrin nanosponge (β -CD-M) was used for the adsorption of ibuprofen (IBU) from water and sewage. The obtained material was characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), Brunauer–Emmett–Teller (BET), Barrett–Joyner–Halenda (BJH), Harkins and Jura t-Plot, zeta potential, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and elementary analysis (EA). Batch adsorption experiments were employed to investigate the effects of the adsorbent dose, initial IBU concentration, contact time, electrolyte ions and humic acids, and sewage over adsorption efficiency. The experimental isotherms were shown using Langmuir, Freundlich, Hill, Halsey and Sips isotherm models and thermodynamic analysis. The fits of the results were estimated according to the Sips isotherm, with a maximum adsorption capacity of 86.21 mg g^{−1}. The experimental kinetics were studied by pseudo-first-order, pseudo-second-order, Elovich, modified Freundlich, Weber Morris, Bangham's pore diffusion, and liquid film diffusion models. The performed experiments revealed that the adsorption process fits perfectly to the pseudo-second-order model. The Elovich and Freundlich models indicate chemisorption, and the kinetic adsorption model itself is complex. The data obtained throughout the study prove that this nanosponge (NS) is extremely stable, self-separating, and adjusting to the guest structure. It also represents a potential biodegradable adsorbent for the removal IBU from wastewaters.

Keywords: adsorption; pharmaceutical pollutants; β -cyclodextrin; sewage



Citation: Skwierawska, A.M.; Nowacka, D.; Nowicka, P.; Rosa, S.; Kozłowska-Tylingo, K. Structural Adaptive, Self-Separating Material for Removing Ibuprofen from Waters and Sewage. *Materials* **2021**, *14*, 7697. <https://doi.org/10.3390/ma14247697>

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1. Introduction

Currently, worldwide concern about the presence of ibuprofen (IBU) and other pharmaceuticals in the environment is growing [1–5]. Drugs are released to the environment from various sources as parent compounds and metabolites. They are continuously introduced into the sewage from households, hospitals, production sites and others [6–11]. Their presence in surface waters and in drinking water has a negative impact on the environment and human health [3,12–16]. This is due to the fact that in wastewater treatment plants, active pharmaceutical ingredients (API) undergo only partial degradation [12,17–19] (Table S1 in the Supplementary Materials provides data on the content of the title drug in different waters).

Fortunately, there are methods to remove drugs from waters, which include adsorption, electrochemical techniques, photocatalytic degradation, ultrasonic processes, oxidation and membrane technologies [17,19–23]. Among these, adsorption is the most common [24–29]. Adsorption processes ensure the removal of both organic and inorganic pollutants. The most popular adsorbents are: graphene and its derivatives, zeolites, polymers [21,24,25,30–32] and activated carbons (AC) [27,33–35]. The last one has a very

developed specific surface area and may allow even 100% efficiency of removing drugs from wastewater [36]. Nevertheless, this material has disadvantages, such as production under high-temperature conditions and unprofitable regeneration in the case of API [36,37].

A novel class of adsorbents is cyclodextrin nanosponges (NS). They consist of cyclodextrin (CD) and a cross-linking agent. CD are cyclic oligosaccharides with a truncated cone shape [38,39]. The arrangement of the hydroxyl groups makes the exterior of the torus hydrophilic and the interior hydrophobic [40]. In aqueous solutions, cyclodextrins include organic compounds containing hydrophobic structural elements forming supramolecular complexes [41–44]. The resulting structures are based mainly on weak van der Waals interactions and hydrogen bonds. In terms of the stoichiometry, the most common types of complexes are considered in CDs: guest molecules with a 1:1, 1:2, 2:1 and 2:2 ratio [45]. Good solubility of CD in water excludes their direct use in water treatment [46]; however, an appropriate modification consisting of obtaining a cross-linked structure makes this possible [47,48]. Depending on the volume of the CD cavities (α -CD 17.4; β -CD 26.2 and γ -CD 25.6 nm³) [49], various organic compounds can be captured from the aqueous solutions and released in a subsequent step by using a suitable solvent [50–52]. The advantages of such sponges are high adsorption efficiency compared to a small surface area, no toxicity, the possibility of multiple regeneration and reuse, modeling of specific interactions, and low cost of production and use [47,51,53–55]. Their positive features make them a promising material in removing pollutants from water. There are reports in the literature on the adsorption of dyes [41,56–59], pesticides [41,60–62], fluorocarbons [63,64], organic and inorganic compounds [56,65,66] from waters. The synthesis of NS is cost-effective, easy to control and safe for the environment [41,67]. A favorable aspect of using CD-materials is their easy biodegradation by fungi [68]. For example, native β -CD and its derivatives are widely used in the production of more stable and more soluble forms of nonsteroidal anti-inflammatory drugs (NSAIDs) such as IBU, diclofenac and ketoprofen. [69–74]. Nevertheless, the literature on the use of NS to remove the abovementioned drugs from aqueous solutions is sporadic [75–79]. The presented work fills this gap for IBU. For the first time, we present a material in the form of native cross-linked β -cyclodextrin (β -CD-M) for removal of IBU from aqueous solutions and sewage.

2. Materials and Methods

2.1. Reagents and Techniques

Hexamethylene diisocyanate (1,6-HMDI $\geq 99\%$), β -cyclodextrin (β -CD $\geq 97\%$), ibuprofen (drug meet USP testing specifications), and pyridine (anhydrous ≥ 99.8) were purchased from Sigma Aldrich (Poznan, Poland). Acetonitrile (HPLC grade) was supplied by Chempur (Poznan, Poland). Methanol (CH₃OH $\geq 99.8\%$), sodium and calcium chlorides, as well commercial humic acids containing 50% of humic acids and 50% fulvic acids (HA, 90% dry matter) were purchased from POCH (Gliwice, Poland) and Agraplant (Kalisz, Poland), respectively. Potassium bromide (KBr spectroscopy grade) was delivered by Fisher Scientific (Warszaw, Poland) and dried before use. All chemicals were used without further purification. Hach cuvette tests (Poznan, Poland) were used to determine BOD₅, COD, total nitrogen and phosphorus. Water purified by a Hydrolab-system was used to prepare the stock solutions (HLP-SPRING, Straszyn, Poland, temp. 22 °C, $\kappa = 2.70$ μ S). The treated sewage was collected from a home sewage treatment plant operating in a system consisting of two settling tanks, a reed plot (first stage of treatment) and a plot planted with energy willow (second stage of treatment).

The final form of the adsorbent was obtained after drying material in a moisture analyzer (MA50/1.R, Radwag, Radom, Poland) and grinding in a ball mill (Pulverisette 7 classic line, Fritsch, Poznan, Poland). Fourier transform infrared (FT-IR) spectra were performed on a Thermo Nicolet iS10 (Warsaw, Poland) using the KBr pellet method. The spectral resolution was 4 cm^{−1} and the scanning range was from 400 to 4000 cm^{−1}. In order to determine the adsorption mechanism, the interactions between β -CD and IBU were analyzed by means of one- and two-dimensional proton magnetic resonance. ¹H NMR

spectra were recorded in D₂O on a Bruker Advance III HD 400 MHz spectrometer at 25 °C. The specific surface area was measured by the Brunauer–Emmett–Teller (BET) method [80], and pore size distribution (PSD) was measured using the classical Barrett–Joyner–Halenda (BJH) model [81] and the Harkins and Jura t-Plot method. The surface charge properties of the adsorbents were investigated by Zeta potential measurements, which were conducted at a different equilibrium pH using a Nano-ZS Zetasizer (Malvern Instruments Inc., Poznan, Poland). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on β -CD-M using a Mettler-Toledo TGA/DSC thermogravimetric analyzer. Samples were heated from 0 to 1000 °C at the rate of 10 °C/min under nitrogen or the air atmosphere (flow rate: 10 mL/min). The surface morphology β -CD-M was studied using scanning electron microscopy (SEM) on a Quanta FEG 250 scanning electron microscope (Poznan, Poland) operating at 10 kV. The elemental FLASH 2000 analyzer (Poznan, Poland) operating in the dynamic separation technique was used to measure the content of carbon, hydrogen and nitrogen. The oxygen content analysis was performed by the device in the pyrolysis mode.

2.2. Synthesis of β -CD-M

β -CD-M was synthesized following the procedure previously reported [82] with major modifications. To a flask containing 150 mL of dry pyridine, heated to 80 °C, 10 g of CD and 5.93 g of 1,6-HMDI were added simultaneously over two hours with vigorous stirring, which was continued for an extra 8 h. After cooling to room temperature, 300 mL of acetone was poured into the reaction mixture to precipitate the product. The precipitate was filtered after 24 h and air dried. To remove unreacted cyclodextrin, the precipitate was quantitatively transferred to a beaker with 200 mL of water and was stirred for 0.5 h. Next, the precipitate was again filtered and transferred to a beaker with stirring 200 mL of 0.1 M hydrochloric acid. The gradual release of pyridine was accompanied by an increase in pH, which has been corrected by adding a few drops of concentrated hydrochloric acid. After stabilizing the pH at 2, the precipitate was filtered off, rinsed with distilled water until the filtrate had a neutral pH, then the precipitate was allowed to dry at room temperature. The product was placed in a moisture analyzer and dried at 120 °C until constant weight. The thus dried product was ball milled, sieved and stored in a desiccator. The final reaction yield was 11.15 g. Detailed information on material analysis is presented in the Supplementary Material (Chapter S1).

2.3. Determination of Grafted β -CD Able to Form Complex

The content of β -CD in the synthesized material was determined by the classical method based on phenolphthalein complexation [83–86]. The amount of that β -CD in the material (involved in complexation) was calculated using the following formula:

$$\beta - \text{CD grafted (\%)} = \frac{W_{\beta\text{-CD}}}{W_{\beta\text{-CD-M}}} \times 100, \quad (1)$$

where: $W_{\beta\text{-CD}}$ is the weight of the bound β -CD (mg) and $W_{\beta\text{-CD-M}}$ is the weight of material (mg). Detailed information is presented in Supplementary Data (Chapter 1, Table S4).

2.4. Water Regain Analysis

Water regain (WR) is one of the important properties of materials for water treatment. It can be used to investigate the hydrophilicity of the adsorbent [48,87,88]. A total of 100 mg of β -CD-M was dispersed in deionized water for 24 h to reach the swelling equilibrium state. Then the wet polymer was drained through filter paper. The collected material was additionally blotted using dry filter paper and then weighed. These experiments were carried out with five replicates. Next, the water regain was calculated by Equation (2).

$$\text{Water regain (\%)} = \frac{W_w - W_d}{W_d} \times 100, \quad (2)$$

where W_d (mg) and W_w (mg) represent the mass of material in dry and wet form, respectively.

2.5. Adsorption Procedure

2.5.1. Analytical Method of Pollutant Concentration Determination

The concentrations of IBU in samples were determined by high pressure liquid chromatography (HPLC Agilent Technologies 1200 Series, Warsaw, Poland) using an ultraviolet detector. The analytical IBU detection method was obtained from the reported literature [89–91]. The samples were injected at a volume of 1 μ L, and the flow rate of the mobile phase (using acetonitrile: acetate buffer pH 3.2, ratio 60:40) through the C-18 column (Zorbax Eclipse PAH, 4.6×100 mm², 3.5 μ m, Agilent Technologies, Warsaw, Poland) was set at 1.0 mL min^{−1}. The concentration of IBU was measured by the UV detector at the wavelength of 220.8 (ref. 360 ± 100) nm.

IBU removal efficiency (RME) was determined by Equation (3),

$$RME (\%) = \frac{C_0 - C_t}{C_0} \times 100, \quad (3)$$

where the RME (%) was the efficiency of API removal, and C_0 (mg L^{−1}) and C_t (mg L^{−1}) were the initial concentration and concentration at time t of the drug in the sample. In each case, at least three series of samples were prepared. Based on the obtained results, the means and standard deviations were calculated.

2.5.2. Adsorption Kinetics in Batch Experiments

A total of 100 mg of β -CD-M was introduced into plastic vials containing 50 mL of an IBU solution (initial concentration of 20 mg L^{−1}), respectively. The vials were shaken on a digital vortex mixer at 700 rpm at 25 °C. The supernatant liquids were sampled at different times (0, 1, 3, 6, 10, 20, 30, 40, 60 min) and filtered (Whatman Grade 540 filter paper). The amount of API bound to the adsorbent was determined by Equation (4),

$$q_t = \frac{(C_0 - C_t)V}{m}, \quad (4)$$

where m (mg) is the adsorbent dosage and V (mL) is the solution volume used in the study. Because each model of adsorption kinetics analyzes different interactions between the solid phase and the components of the solution, seven models were selected for consideration. The linear models presented in Table 1 were used in further calculations, and linear regression analysis was used to evaluate the fit of the theoretical model.

2.5.3. Adsorption Isotherms

The adsorption isotherm study was conducted to evaluate the adsorption capacity of the adsorbent. A total of 1 mg of the β -CD-M was added to 5 mL of IBU solutions (with initial concentration ranging from 10 to 100 mg L^{−1}) and shaken on a digital vortex mixer at 700 rpm at 25 °C for 1 h. Then the supernatant liquid was sampled and filtered. The adsorption equilibrium concentration of each sample was measured by the HPLC. To gain satisfactory data on IBU adsorption as well as to obtain an optimal fit of the theoretical model, these experimental data were analyzed using two and three parameter isothermal equations (i.e., Langmuir, Freundlich, Halsey, Hill and Sips), and linear regression analysis was used to evaluate the fit of the theoretical model (Table 2).

Table 1. Description of the models used in the calculation of kinetic constants and parameters.

Kinetic Model	Linear Form	Plot	Ref.
Pseudo-first-order	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$\ln(q_e - q_t)$ vs. t	[92]
Pseudo-second-order	$\frac{t}{q_t} = \frac{1}{K_2} q_e^2 + \frac{t}{q_e}$	$\frac{t}{q_t}$ vs. t	[20]
Weber and Morris	$q_t = K_{id} t^{1/2} + C$	q_t vs. $t^{1/2}$	[93]
Liquid film diffusion	$\ln\left(1 - \frac{q_t}{q_e}\right) = -K_{lf} t$	$\ln\left(1 - \frac{q_t}{q_e}\right)$ vs. t	[94,95]
Bangham's diffusion	$\log \log \left\{ \frac{c_0}{c_0 - m q_t} \right\} = \log \left\{ \frac{m K_B}{2.303 V} \right\} + \delta \log t$	$\log \log \left\{ \frac{c_0}{c_0 - m q_t} \right\}$ vs. $\log t$	[96]
Elovich	$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln(t)$	q_t vs. $\ln(t)$	[97]
Modified Freundlich	$\ln q_t = \ln(k_f c_0) + \frac{1}{m} \ln t$	$\ln q_t$ vs. $\ln t$	[98]

Table 2. Models of adsorption isotherms and applied plots in the research.

Model *		Model in Linear Form *	Plot	Ref.
Langmuir	$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$	$\frac{C_e}{q_e}$ vs. C_e	[99]
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	$\log q_e = \ln K_F + \frac{1}{n} \log C_e$	$\log q_e$ vs. $\log C_e$	[100]
Halsey	$q_e = \exp\left(\frac{\ln K_H - \ln C_e}{n_H}\right)$	$\ln q_e = \frac{1}{n_H} \ln K_H - \frac{1}{n_H} \ln \frac{1}{C_e}$	$\ln q_e$ vs. $\ln \frac{1}{C_e}$	[101]
Hill	$q_e = \frac{q_{sH} C_e^{n_H}}{K_D + C_e^{n_H}}$	$\log\left(\frac{q_e}{q_H - q_e}\right) = n_H \log(C_e) - \log(K_D)$	$\log\left(\frac{q_e}{q_H - q_e}\right)$ vs. $\log(C_e)$	[102]
Sips	$q_e = \frac{q_{max} K_S C_e^{\frac{1}{n}}}{1 + K_S C_e^{\frac{1}{n}}}$	$\frac{1}{q_e} = \frac{1}{q_{max} K_S} \left(\frac{1}{C_e}\right)^{\frac{1}{n}} + \frac{1}{q_{max}}$	$\frac{1}{q_e}$ vs. $\left(\frac{1}{C_e}\right)^{\frac{1}{n}}$	[103]

* q_{max} —maximum adsorption capacity (mg g^{-1}); K_L —adsorption equilibrium constant (L mg^{-1}); K_F —adsorption capacity constant (L g^{-1}); K_H and n_H —Halsey constants; n_H —Hill coefficient, K_D —Hill dissociation constant; K_S —Sips equilibrium constant (L g^{-1}), n —heterogeneity factor.

2.5.4. Thermodynamic Analysis

The key thermodynamic parameters of adsorption were determined on the basis of the following equations.

$$\ln(K_e^0) = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R}, \quad (5)$$

$$\Delta G^0 = -RT \ln(K_e^0), \quad (6)$$

$$K_e^0 = \frac{K M_a C_a^0}{\gamma}, \quad (7)$$

where ΔH^0 , ΔS^0 , ΔG^0 are standard enthalpy, entropy and free energy and K_e^0 is a dimensionless thermodynamic equilibrium constant, which is calculated from the best isotherm fitted K (L g^{-1}) estimated at temp. 20–60 °C, M_a and C_a^0 are molecular weight and standard concentration of the adsorbate (1 M), and γ is the coefficient of activity, respectively [104].

2.5.5. Effects of the Dosage of the Adsorbent, pH, Humic Acid and Ionic Strength

The effect of the adsorbent dosage was conducted by addition of the β -CD-M (1–100 mg) to the plastic vials (8 mL) containing an IBU solution (5 mL, 20 mg L^{-1}) and shaken on a digital vortex mixer at 700 rpm at 25 °C for 1 h. Then the supernatant liquid was sampled and filtered. The adsorption equilibrium concentration of each sample was measured by HPLC. The influence of ionic strength was investigated analogously, using drug solutions enriched with appropriate salts, humic and fulvic acids, and the pH was adjusted to the appropriate value in the range from 2 to 11 with 0.1 N HCl and 0.1 N NaOH.

2.5.6. Sewage Treatment

The wastewater (Table 3) was used to make solutions containing a drug. Relatively high concentrations of IBU, compared to those determined in the natural environment, were used deliberately as a simulation of a situation where the compound is discharged

directly into the sewage system. The adsorption procedure was the same as for model water samples with one difference, and the filtered wastewater obtained during the second biological treatment was used to prepare the solutions instead of pure water. The 5 mL of IBU (0.021, 0.206 and 2.06 mg L⁻¹) solutions were added to plastic vials containing 10 mg of β -CD-M, individually. The vials were sealed, and the mixtures were shaken on a digital vortex mixer at 700 rpm for 1 h at 25 °C. Then the supernatant liquid was sampled and filtered. The adsorption equilibrium concentration of each was measured by the HPLC.

Table 3. Characteristics of the sewage used in tests obtained from a home plant sewage treatment unit.

Parameter	Second Stage
BOD ₅ (mg L ⁻¹ O ₂)	30
COD (mg L ⁻¹ O ₂)	114
TOC (mg L ⁻¹ C)	2.2
Total suspended solids (mg L ⁻¹)	40
Total nitrogen (mg L ⁻¹)	10
total phosphorus (mg L ⁻¹)	0.5
Conductivity (μS cm ⁻¹)	1120
pH	6.2

2.5.7. Material Regeneration

A total of 100 mg of β -CD-M was added to 50 mL of a solution containing IBU (20 mg L⁻¹). The mixture was shaken in a digital vortex mixer at 700 rpm (25 °C, 1 h). After five minutes, the solution was decanted from the surface of the precipitate and, in its place, 20 mL of methanol was added, soaking for 10 min. The procedure was repeated using distilled water. The adsorption-desorption experiment was performed five times.

3. Results and Discussion

3.1. Adsorbents Properties

The method of β -CD crosslinking was selected based on a literature report [82]. In the characteristics of the new material, the authors indicated a quite large specific surface area of 78.06 m² g⁻¹ in the case of using a fourfold excess of HMDI and an extraordinary selectivity of the substitution of the primary hydroxyl groups. We were concerned about the limited solubility of β -CD in dry pyridine, used as a solvent so, the procedure has been modified by introducing both reagents gradually. This change resulted in a completely different material. The elemental analysis of the material showed a higher than the assumed degree of the CD cross-linking (Chapter S1 in Supplementary Data). On average, five/six hydroxyl groups of the β -CD molecule were substituted. It can be expected that the structural element (basic unit) of the material is composed of three β -CD molecules. Assuming the preferred mechanism of primary alcohol substitution, a total of 21 groups are available in a single β -CD, 16 are substituted, of which 14 are involved in urethane bonds and the other two in allophanate structures. The presence of both types of groups was confirmed by FTIR analysis, as was the disappearance of acute overtone 1078.86 cm⁻¹, belonging to OH stretching primary alcohol (Figure 1c and Table S2). Taking the described system as the basic structural element of the adsorbent, it should be expected that the average β -CD content in the material is about 54%. This could easily be confirmed by colorimetric measurements using phenolphthalein as a model (Figure S1 and Table S4). The obtained average result was 55.1% for 10 mg of β -CD-M. It should be kept in mind that this method has significant limitations resulting from the range of β -CD concentrations used [83,105]. Nevertheless, the convergence of the results is quite substantial, and it suggests that most macrocycles are available and will be able to take part in the removal of drugs from aqueous solutions. The surface analysis of the obtained material showed that it is a completely different material from the one described earlier by Ding [82]. The BET surface area of the material is 7.31 m² g⁻¹, which is quite typical [106] (Figure S2 and Table S5), whereas the average pore size is 16.8 nm and the total pore volume is 3.08 mL g⁻¹.

(Figures S3–S5 and Tables S5–S8). The mean particle size of β -CD-M is between 270 and 600 μm , estimated by SEM. The particles have a distinct porous structure, resembling a pumice stone (Figure 1e,f). As estimated by TGA analysis, the material is thermally stable below 250 $^{\circ}\text{C}$, followed by its decomposition. The ultimate weight loss is observed at 333.13 $^{\circ}\text{C}$ (61.82%) in an air and 346.67 $^{\circ}\text{C}$ (55.46%) in a nitrogen atmosphere, respectively (Figures S6 and S7). The material is intended for the treatment of wastewater, the temperature of which, even in industrial conditions, is not higher than 40 $^{\circ}\text{C}$; therefore, it should be considered as completely durable. The tested Zeta potential (ξ) of β -CD-M in the pH range from 2 to 11 is 0 for pH = 2.53, and above this value it is constantly negative, assuming the value of -15 mV for a neutral pH. The system oscillates at the border of the agglomeration threshold up to a pH of 9, achieving then moderate stability with slight dispersion ($\xi = -21$ to -28 mV) (Figure 2). The high degree of cross-linking increases the hydrophobicity of the material and the tendency to accumulate, making it extremely easy to separate and regenerate. Due to the large particle size, the adsorbent settles completely within five minutes after stopping mixing. This property is a great advantage of β -CD-M when treating post-production wastewater before it is sent to a biological treatment plant, as it enables simple separation techniques such as decantation to be used. During mixing, the material slightly crumbles. The resulting particles form agglomerates very quickly, which prevents material loss during sedimentation or filtration. The material does not permanently retain water. The conducted tests showed an increase in the mass of the adsorbent samples up to 20%. After 24 h at room temperature, the samples returned to their original weight (Figure 3). The material used for wastewater treatment in dry and wet form shows the same sorption capacity in relation to the tested IBU. The adsorbent has no tendency to swell, which additionally confirms the high degree of cross-linking of the material [67].

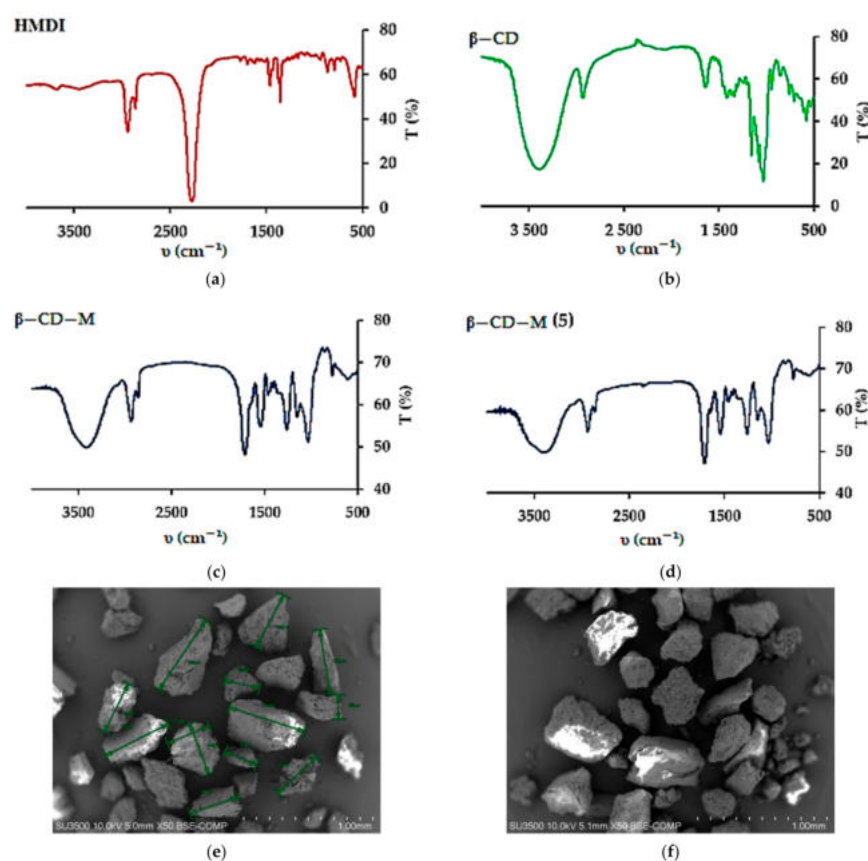


Figure 1. FTIR spectra (ν , KBr): (a) HMDI; (b) β -CD; (c) β -CD-M; (d) five times regenerated β -CD-M; (e,f) SEM images of β -CD-M.

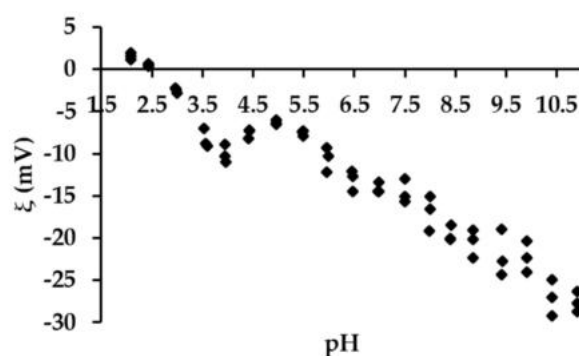


Figure 2. Zeta potential changes during titration of the range of pH 2–11.

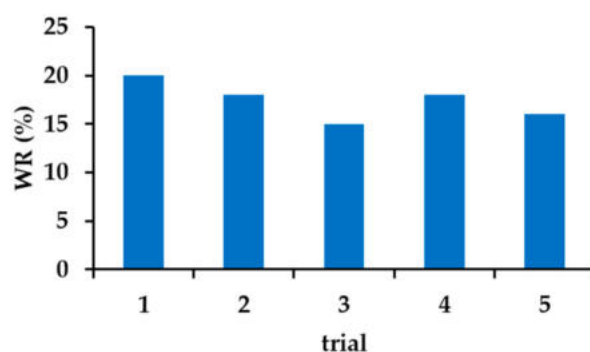


Figure 3. The amount of water retained in the β -CD-M.

3.2. Adsorption Experiments

3.2.1. Effect of Adsorbent Mass on the Removal Efficiency

This is quite typical of a gradual increase in sorption due to the increased weight of the adsorbent. This is usually the result of incomplete filling of the adsorbent surface, as stabilization occurs only after the material is saturated. Hence, the IBU adsorption mechanism must be different. In the range of adsorbent concentrations (2 g L^{-1}), the RME parameter decreases in relation to the initial value (0.2 g L^{-1}) and then increases finally reaching 90% (Figure 4a). The adsorption capacity of the material reaches its highest value when the minimum amount of the adsorbent is used (Figure 4b). A quite characteristic feature of cyclodextrin NS is the ability to quantitatively capture organic substances present in very low concentrations, which cannot be said about other adsorbents [107]. The initial pH of the API solutions (20 mg L^{-1}) was not corrected.

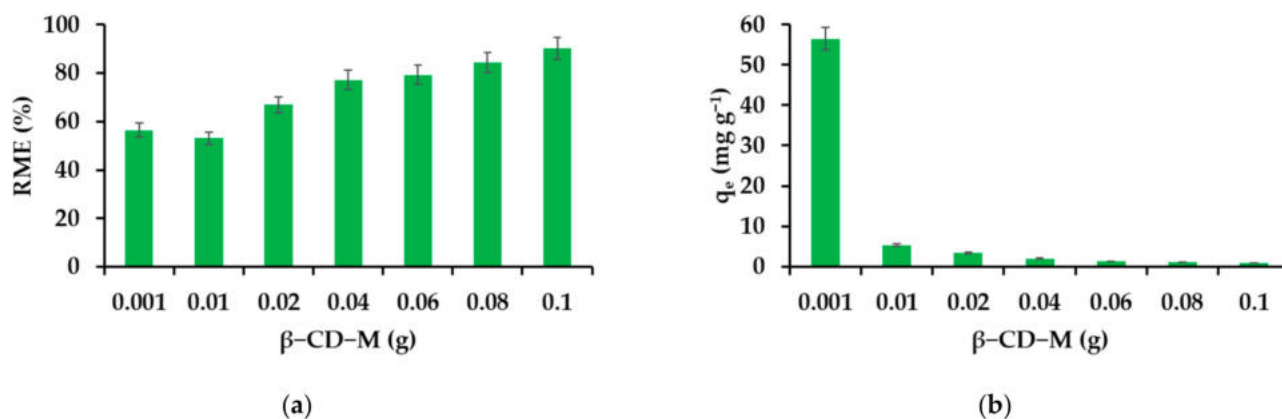


Figure 4. Effect of the adsorbent mass on the removal efficiency (a) and adsorption capacity (b).

3.2.2. Effect of IBU Initial Concentration on the Removal Efficiency

Figure 5a shows the effect of an initial API concentration in the range of 1–100 mg L^{−1} for drug removal. The initial concentration is the driving force needed to overcome the resistance to mass transfer between the aqueous and solid phases. At the first moment of contact, the solid phase has the greatest number of centers capable of interacting with the components of the aqueous phase, so IBU is removed quantitatively from the most diluted solution (1 mg L^{−1}). At higher concentrations, an additional barrier to overcome is in the form of API particles protruding from toruses causing steric hindrance or simply accumulating on the outer surface of β -CD-M. Therefore, the participation of deeper structures in the process is limited and, consequently, a reduction in IBU removal is observed. However, when considering the degree of material filling depending on the value of the initial concentration of IBU, an upward trend can be noticed with the maximum saturation falling for the concentration of 80 mg L^{−1} (Figure 5b). The concentration of 20 mg L^{−1} was selected for further research.

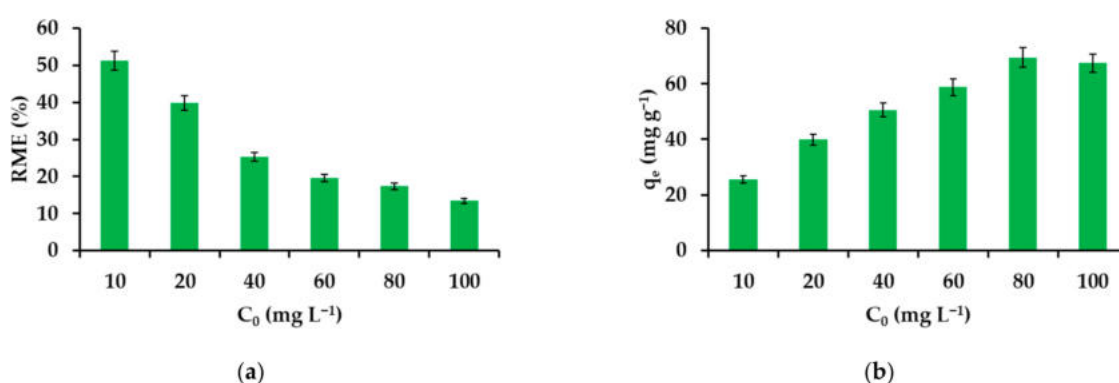


Figure 5. Effect of the initial IBU concentration on the removal efficiency (a) and adsorption capacity (b).

3.2.3. Effect of Contact Time in the Adsorption Experiments

Time is a determining parameter describing adsorption. The time taken to reach the maximum degree of removal depends on the reaction rate required to establish equilibrium. The optimal time for IBU seems to be 60 min (Figure 6a,b). The noted value of the RME parameter is 48.7% and the equilibrium capacity is 4.82 mg g^{−1}, respectively. The greatest changes in the amount of IBU retained in the solid phase are visible in the first 10 min of the process, during which 4.26 mg is adsorbed per gram of adsorbent, and in the next 50 min—another 0.56 mg. In the case of less concentrated solutions, the equilibrium is established within the first two minutes. The high dynamics of the process will potentially enable the material to be used in environmental and industrial conditions, where time is of particular importance.

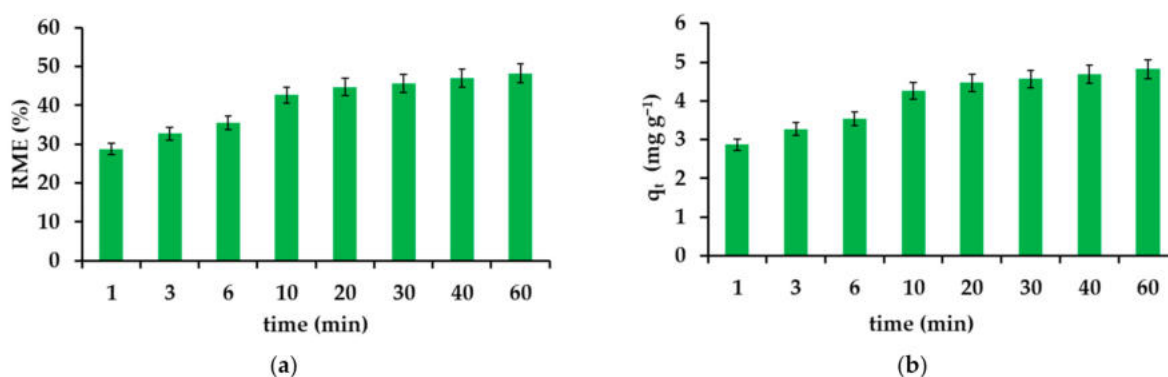


Figure 6. Effect of time on the removal efficiency (a) and adsorption capacity (b).

3.2.4. Effect of the pH on the Removal Efficiency

IBU is moderately pH-sensitive (Figure 7). The electrokinetic potential of the various scattered phases depends largely on the concentration of hydrogen ions. In the case of the tested material, the electrokinetic potential is zero at $\text{pH} = 2.53$. The highest degree of IBU removal is placed exactly in the range of $\text{pH} 2\text{--}3$. This is the area close to the complete disappearance of anticoagulant electrostatic repulsion. However, in order to restore normal adsorption conditions, the pH of the IBU solutions used in further tests was not corrected and amounted to 4.54.

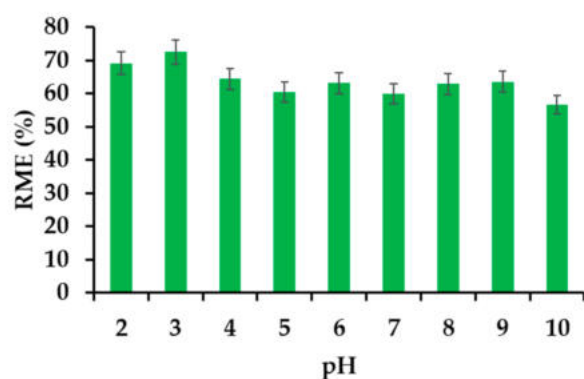


Figure 7. Effect of pH on the removal efficiency of IBU.

3.2.5. Effect of Salts, Humic and Fulvic Acids on the Removal Efficiency

The presence of salt affects the effective removal of all tested drugs. In the case of IBU, both sodium and calcium chloride increase the effectiveness of drug removal by several percent. The addition of humic and fulvic acid also increases the removal of IBU. Acids have the greatest positive effect on adsorption when used in a concentration of 10 mg L^{-1} . In this case, the value of the RME parameter increases by 66%. The obtained preliminary results indicate that the tested material should work properly in the case of real samples (Figure 8).

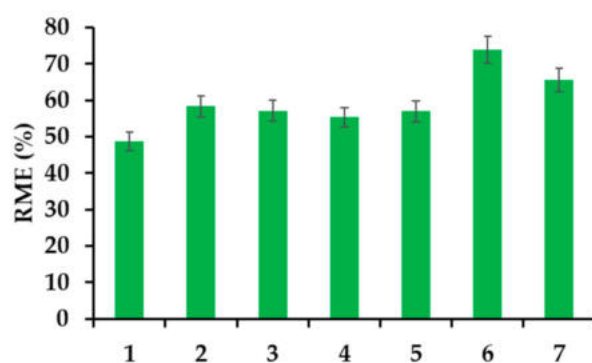


Figure 8. Effect of electrolytes and humic acids on the removal efficiency of IBU (20 mg L^{-1}); (1) IBU in deionized water; (2) IBU in solution of NaCl (30 mg L^{-1}) (3) IBU in solution of NaCl (300 mg L^{-1}); (4) IBU in solution of CaCl_2 (30 mg L^{-1}) (5) IBU in solution of CaCl_2 (300 mg L^{-1}); (6) IBU in solution of humic acids (10 mg L^{-1}) (7) IBU in solution of humic acids (30 mg L^{-1}).

3.2.6. β -CD-M Regeneration

The presented material contains elements of various flexibility, enabling a better adaptation to the structure of the adsorbed drugs. β -CD-M has a structure shaped during synthesis and contact with the pyridine template. During adsorption, the material is reorganized and arranged according to the structure of IBU. The drug molecules are very efficiently and quickly desorbed with methanol. The low boiling point of alcohol and the lack of azeotropes with water makes the regeneration stage relatively cheap and

waste-free. The described adsorbent probably remembers the shape of the API and does not return to its initial state, which explains the initial increase in IBU adsorption and further stability in the degree of drug removal in subsequent trials using regenerated material (Figures 1d and 9; Table S3).

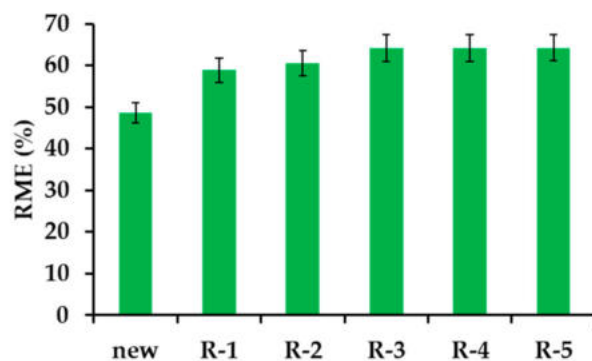


Figure 9. Comparison of the removal efficiency of IBU using a new and sequentially regenerated adsorbent.

3.2.7. Adsorption of Pharmaceuticals Present in Biologically Treated Sewage of Municipal Type

Wastewater (W) from a household sewage treatment plant after the second stage of treatment was used for the research. The mixtures were subjected to initial filtration, and the obtained solutions were used to determine the basic parameters, which are summarized in Table 3. For obvious reasons, the actual sewage differed significantly in the content of carbon, nitrogen and phosphorus from artificial ones, which could significantly affect the IBU adsorption process. Preliminary studies have shown that IBU can be removed from the actual wastewater with very high efficiency from 84% to 100% for concentrations ranging from 2.06 to 0.021 mg L⁻¹, respectively (Figure 10). The highest concentration of IBU in raw sewage, which was recorded in Scotland, was 0.028 mg L⁻¹ (Table S1) [108].

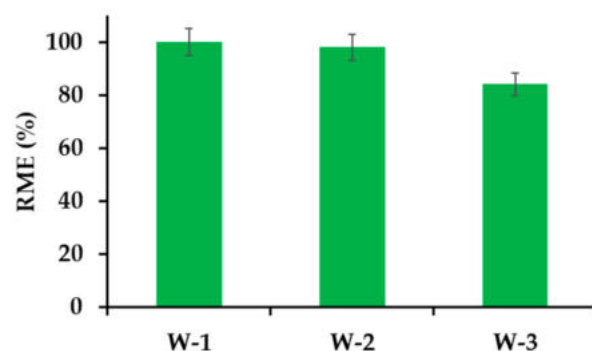


Figure 10. Effect of sewage containing different amounts of API (W-1, IBU 0.021 mg L⁻¹), (W-2, IBU 0.206 mg L⁻¹), and (W-3, IBU 2.06 mg L⁻¹) on the removal efficiency.

3.2.8. Adsorption Isotherms

A nearly straight line usually represents the equilibrium between the adsorbed amount and the residue in the solution. This Giles adsorption isotherm belongs to class C, describing a constant division of the adsorbed substance between the surface layer and the solution [109]. The obtained isotherm (Figure 11) is difficult to unambiguously assign to a given class.

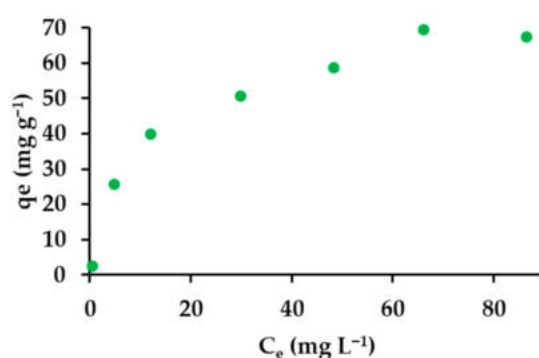


Figure 11. Equilibrium adsorption isotherm of IBU.

Adsorption isotherms are in the form of mathematical equations, describing the relationship between the number of adsorbed molecules and those remaining in the solution. They are pressure, temperature and pH-dependent. Adsorption isotherms exhibit the path of a substance from an aqueous medium to a solid phase in a state of equilibrium. Five models of equilibrium isotherms were used in the work (Tables 2 and 4).

Table 4. Parameters of the equilibrium sorption models and of linear (R^2) regression coefficients.

Isotherm Model	Parameters	IBU
Langmuir	K_L (L mg ⁻¹)	0.082
	q_{max} (mg g ⁻¹)	77.52
	R^2	0.990
$R_L = \frac{1}{1+K_L C_0}$	R_L	0.11–0.55
Freundlich	K_F (L g ⁻¹)	15.823
	n	2.937
	R^2	0.9763
Halsey	K_H (L g ⁻¹)	1.001
	n_H	0.0003
	R^2	0.9763
Hill	K_D (L g ⁻¹)	−0.994
	n_H	0.0014
	R^2	0.9818
Sips	K_S (L mg ⁻¹)	0.129
	n	1.33
	q_{max} (mg g ⁻¹)	86.21
	R^2	0.9934

The Langmuir model assumes that monolayer adsorption of molecules can take place only in specific, determined places at homogeneous adsorption energies on the surface without migration of the adsorbate in the surface plane. The empirical model describes quite imaginary conditions, i.e., homogeneous adsorption, and excludes interactions and steric hindrance between adsorbed molecules.

The essential characteristic of the Langmuir isotherm is complemented by the dimensionless separation coefficient R_L parameter, the values of which indicate the type of the isotherm. Thus, an irreversible isotherm is described by a coefficient value of zero, favorable ($0 < R_L < 1$), linear ($R_L = 1$), and unfavorable ($R_L > 1$). The calculated values of the parameter clearly indicate the privileged course of the process (Table 4).

The Freundlich isotherm is used to describe multilayer adsorption and inhomogeneous surfaces with non-uniform heat distribution of adsorption. The Freundlich equation and its linear form are presented in Table 2. The value of the parameter n determines the quality of the adsorption process; when it is between 1 and 10, the process is favorable, and

when it is less from 1, it is poor. The correlation coefficients for IBU are worse compared to the Langmuir and Sips models. Nevertheless, the determined values of the parameter n indicate a favorable adsorption process in the studied concentration range of IBU (Table 4).

The Halsey isotherm can be used in determining the multilayer adsorption of heterosporous materials. High values of the linear regression coefficient indicate a fairly good fit to the discussed model, confirming the existence of different pores.

The Hill model makes it possible to distinguish the type of bonds of various molecules with homogeneous surfaces through the n_H constant, which is a measure of the molecular interactions. The assumption of this model is that adsorption is a cooperative phenomenon with the adsorbate having the ability to bind at one site on the adsorbent, which may affect other binding sites on the same adsorbent. Moreover, in this model, it is assumed that if the coefficient $n_H = 1$, then the binding is non-cooperative, and when $n_H > 1$, the binding has a positive cooperation and a negative one when $n_H < 1$. The last one describes the interaction of the β -CD-M with the IBU [110].

The Sips model works well for localized adsorption without the adsorbate–adsorbate interaction. As C_e approaches a low value, the Sips isotherm effectively reduces to Freundlich, while at high C_e , it predicts the sorption properties of the Langmuir monolayer. The Sips isotherm equation is characterized by a dimensionless heterogeneity coefficient, n , which can also be used to describe the heterogeneity of a system if n is between 0 and 1. When $n = 1$, the Sips equation becomes Langmuir and represents the homogeneity of the adsorption process. In this case, $n = 1.33$ may indicate that the sorption of one (first) IBU molecule increases the sorption of more of the others, which may appear to be apparently contradictory to the information obtained from the Hill model. However, when it is recognized that this is not the result of complex formation with a few ligands, but only adsorbent preorganization followed by proper adsorption, everything becomes coherent.

IBU adsorption fits well to the Sips model ($R^2 = 0.9934$), which was also used to determine the highest value of the maximum adsorption capacity (q_{max}), which was 86.21 mg g^{-1} . By comparing the q_{max} value with the values given in Table 5, it can be seen that this is a promising result considering the low cost of synthesizing the material based on general availability, production on a large-scale raw material, the simplicity of regeneration and no reduction in IBU removal efficiency.

Table 5. Maximum adsorption capacities for previously studied adsorbents for IBU removal from waters.

Adsorbent	Q_{max} (mg g^{-1})	Adsorption Conditions				Specific Surface Area ($\text{m}^2 \text{g}^{-1}$)	Reference
		pH	Temp. ($^{\circ}\text{C}$)	Time (h)	C_0 (mg L^{-1})		
Magnetic core-modified silver nanoparticles	0.29	7	25	0.75	0.2	116.48	[111]
Multiwall carbon nanotubes	1.15	4	25	2	200	151	[112]
Jordanian zeolite	1.23	2	25	1.33	510	41.20	[35,36]
Cocoa Shell biomass	21.43	2	30	10	30	no data	[113]
Acid-modified kola nut husk (KNHA)	28.22	not adjusted	30	3	20	712	[92]
Copper nanoparticles (Cu NPs)	33.9	4.5	25	1	10–40	no data	[114]
Chitosan-modified waste tire crumb rubber	70.00	6	25	24	40	no data	[27]
β -CD-M	86.21	4.54	25	1	1–100	7.31	this work
2-hydroxypropyl- β -cyclodextrin polymers	87.50	5	25	2	50	no data	[75]
Activated Carbon	105.91	4	25	3	50	642	[9]
Zinc oxide sheet	220.00	no data	25	0.83	100	no data	[115]

The thermodynamic parameters, determined using the van't Hoff equation, showed the spontaneity of the adsorption process of IBU. Adsorption is an exothermic process leading to an increase in disorder at the solid–liquid interface. Negative Gibbs free energy values indicate that sorption is sporadic and beneficial. In this case, the low enthalpy value confirms the formation of supramolecular complexes based mainly on van der Waals forces. (Table 6).

Table 6. Thermodynamic parameters for IBU adsorption on β -CD-M.

Temperature (K)	ΔH^0 (kJ mol ^{−1})	ΔS^0 (J K ^{−1} mol ^{−1})	ΔG^0 (kJ mol ^{−1})
293	−11.37	27.13	−19.32
313			−19.83
333			−20.40
linear equation	value	SE	R ²
intercept	3.2628	0.02007	0.9989
slop	1367.1	15.04890	

3.3. Kinetic Models

The adsorption rate is an important parameter used to describe the adsorption process. Many applications, such as wastewater treatment and drug disposal, require a fast adsorption rate and a relatively short contact time. To investigate the removal of IBU from water, seven models were used (Table 1). The constants of all kinetic models were calculated and summarized in Table 7. As can be seen in Table 7, the correlation coefficient (R^2) obtained from the pseudo-second-order was 0.9994 and was greater than for the pseudo-first-order model (0.965). Calculated values of q_e (q_e , cal) on the basis of these two models unequivocally showed that only the pseudo-second-order model gives full agreement with the experimental values of q_e (q_e , exp). Transport of the adsorbate from the solution to the adsorbent surface takes place in at least two stages. The phenomenon can therefore be controlled by film or external diffusion, pore diffusion, surface diffusion and pore surface adsorption, or a combination of more than one process. This theory was confirmed by a non-linear course of the intramolecular diffusion model, which shows that there are two separate stages of the drug sorption on β -CD-M, i.e., external diffusion and intergranular diffusion. The adsorption stage is generally very fast for porous adsorbents versus external or internal diffusion, and it is known that an adsorption equilibrium can be reached within minutes in the absence of internal diffusion [116–119]. However, the complete kinetics of the drugs adsorption process were described by a pseudo-second-order model, and it was not possible to clearly distinguish the rate-limiting stage of the process. That can be the boundary layer (film) or the diffusion inside the solid surface particles (pores) of substances dissolved in the solution. In the case of the obtained results, the long time to achieve the adsorption equilibrium (15 approx. 1 h) indicates that internal diffusion may dominate the general kinetics of adsorption. To confirm unequivocal information about the rate-limiting stage, the assumptions of Weber and Morris were used on the basis of the internal diffusion model [118]. This model describes the equation shown in Table 1, where k_{id} is the intra particle diffusion rate constant and C is the layer thickness. The greater the value of C , the greater the boundary layer influence will be on the adsorption process. If the factor limiting the process rate is diffusion inside the particles, then the dependence of the q_t function of the square root on the time $t^{1/2}$ is a straight line through the origin of the coordinate system, i.e., $C = 0$. The deviation from linearity clearly indicates that the rate-limiting factor may be a boundary layer (film) controlled by the diffusion process. As a result of the linear extrapolation of the first part of the straight line and its intersection with the ordinate, a value was obtained that corresponds to the diffusion boundary layer of adsorption or film thickness, while the second linear part concerns the diffusion inside the pores. The values of k_{id-1} , k_{id-2} as well as C_1 and C_2 were calculated by determining the slope of the lines defined by the experimental points in two-time intervals; the first in the range of 0 to 10 min and the second in the rest range. The values of these parameters are given in

Table 7. The values of constants of k_{id-1} are greater than of k_{id-2} , which may indicate that the adsorption process is initially controlled by the diffusive boundary layer (film). The C parameter value points to a greater boundary layer effect in the IBU adsorption process. Analyzing the data, it can be noticed that there are two separate stages of adsorption of IBU. The sharp linear course of the first part of the process it is associated with a diffusive boundary layer (film), so-called external diffusion, external surface adsorption or internal mass transfer effect. The second stage describes the gradual adsorption, surface diffusion and adsorption on the pore surface. The analysis of the intramolecular diffusion rate model also showed that the process takes place in two stages. During the first ten minutes, the adsorbate diffuses through the solution to the outer surface of the adsorbent. No sorption on the outer surface is observed. The second part that determines the rate (step 2. 10 to 60 min) is the gradual adsorption of drugs. There is still the question of whether the observed phenomena correspond to physical or chemical sorption. For this purpose, the Elovich and modified Freundlich models were applied. Both in the whole range were linear, and the slope describing the modified Freundlich kinetic model well below the value of one confirms the chemisorption of IBU at the concentration of 20 mg L⁻¹. Tests with fewer concentrated solutions only allowed to determine the fit to the pseudo-second-order model, due to the very fast saturation of the adsorbent.

Table 7. Kinetic model constants of single-component mixtures and their error analysis.

Isotherm Model	Intercept and Slope The Time Interval (min)	Parameters	IBU
First-order kinetic model	−0.0513	q_e (mg g ⁻¹)	0.0513
	0.446	k_1 (min ⁻¹)	1.56
	1–60	R ²	0.965
Second-order kinetic model	0.2043	q_e (mg g ⁻¹)	4.89
	0.3105	k_2 (g min ⁻¹ mg ⁻¹)	77.162
	1–60	R ²	0.9994
Bangham's pore diffusion model	0.1647	δ	0.1647
	−3.2093	K_B (mL L ⁻¹ g ⁻¹)	0.712
	1–10	R ²	0.9936
	0.2588	δ	0.0702
	−3.466	K_B (mL L ⁻¹ g ⁻¹)	0.905
	10–60	R ²	0.9891
Weber and Morris	0.6165	C_1	2.269
	2.2692	K_{id-1} (g mg ⁻¹ min ^{-1/2})	0.616
	1–10	R ²	0.9988
	0.109	C_2	3.983
	3.9827	K_{id-2} (g mg ⁻¹ min ^{-1/2})	0.109
	10–60	R ²	0.9901
Liquid film diffusion	−0.1173	K_{lf} (g mg ⁻¹ min ⁻¹)	0.117
	−0.7814		
	1–10		
	−0.0322	R ²	0.9988
	−0.5524	K_{lf} (g mg ⁻¹ min ⁻¹)	0.043
	10–60		
Elovich	0.4936	β (g mg ⁻¹)	2.026
	0.9835	α (g mg ⁻¹ min ⁻¹)	176.080
	1–10	R ²	0.9835
modified Freundlich	0.1364	1/m	0.136
	1.0731	k_F (L g ⁻¹ min ⁻¹)	0.146
	1–10	R ²	0.9767

3.4. Mechanism of Adsorption

β -CD-M can be compared to a honeycomb, the cells of which are β -CD molecules and whose backbone is elastic urethane and allophanate chains. Once placed in the IBU solution, the material is preorganized to allow the host to better suit the requirements of the guest molecules. The β -CD content in the structure of NS is 55.1%, which means that theoretically the maximum adsorption capacity may be as high as 100.15 mg g^{-1} (Figure 12). The actual result is lower and reached 86.21 mg g^{-1} , which may mean that not all tori are involved in supramolecular complexes. It also means that physical sorption outside the β -CD cavities can be ruled out. By examining the interaction of β -CD with IBU in a D_2O solution, it can be concluded that the drug is an example of an excellent β -CD guest (Figure 13a). It contains a flat ring, substituted with linear groups in positions 1 and 4, which facilitates the insertion of the molecule into the CD cavity while involving the functional groups in the stabilization of the system (Figure 13b). All aromatic and even aliphatic protons take part in the complex formation (Figure 13b). The most stable complex is described by the 1:1 stoichiometry (Figure 13c). The strongest interactions occur between the H-5 protons, much weaker with H-3 and additionally H-6 with β -CD. In this case, the inclusion of the guest molecule is possible from both the smaller and the larger periphery. However, the ibuprofen molecule is too large to fit completely into the β -CD cavity; therefore, the protruding part of the linear fragments interacts with the H-6 β -CD protons outside the torus (Figures 12 and 13d). The elements protruding from the cavity may impede other molecules trying to lodge in free cells as evidenced by the negative cooperation found with the Hill model. Nevertheless, it should be noted that the specific surface of the material is efficiently used, for example, compared to active carbon, whose maximum sorption capacity is only 19.7 mg g^{-1} greater, with the surface area almost 88 times greater (Table 4).

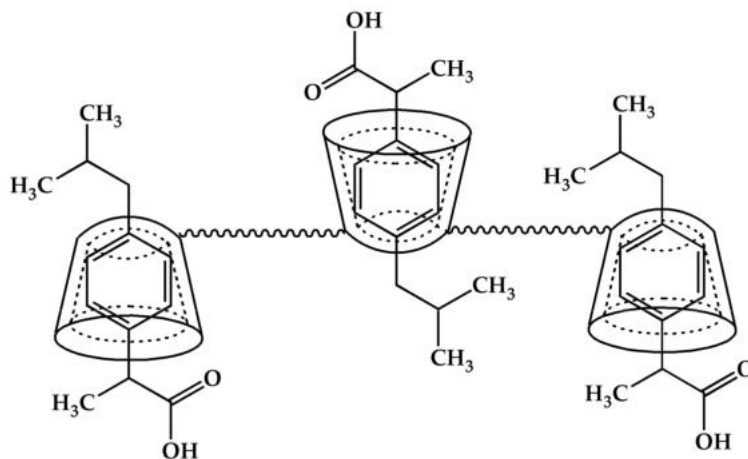


Figure 12. A probable fragment of a nanosponge structure containing absorbed IBU particles.

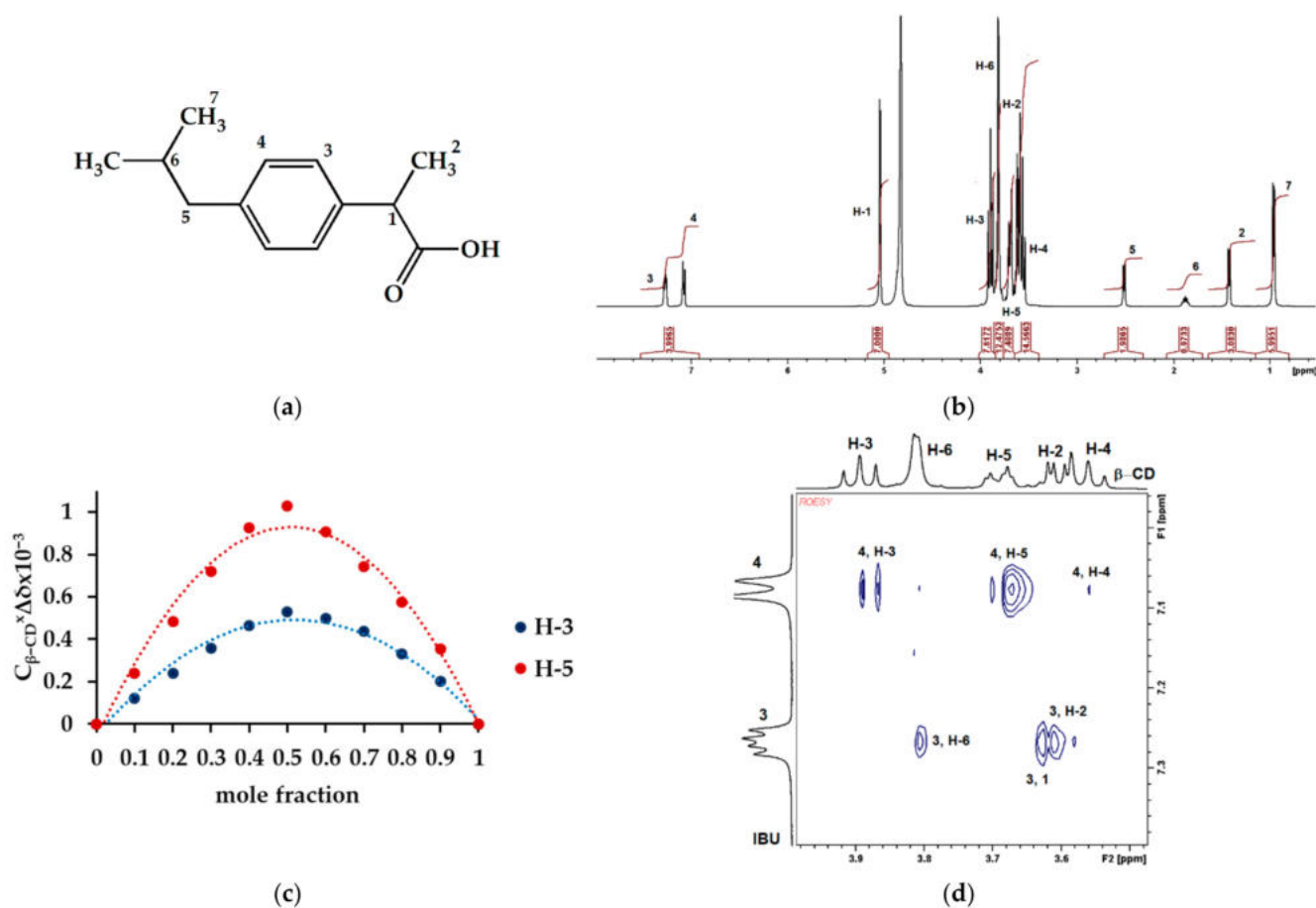


Figure 13. IBU complex with β -CD. (a) Chemical structure of IBU; (b) ^1H NMR (δ , 400 MHz) spectrum of the complex registered in D_2O ; (c) complex stoichiometry determined on the basis of ^1H NMR (δ , 400 MHz) spectra (continuous change method); (d) ROESY spectrum of the complex (1:1) in D_2O .

4. Conclusions

The article presents the synthesis of material obtained in the reaction of native β -CD, much cheaper than hydroxypropyl- β -cyclodextrin, with hexamethylene diisocyanate. The material is highly cross-linked, as evidenced by the lack of swelling and the rapid desorption of water from the surface.

The adsorbent is easy to separate from the mixture as it is decanted in just a few minutes, which is extremely valuable when used as a movable bed. The sorption capacity remains unchanged after the next regeneration cycles.

Despite the small specific surface, the material is able to remove ibuprofen from wastewater even in concentrations much higher than usually found in the environment, which makes it possible to use it in the treatment of municipal and industrial wastewater, even very acidic.

The adsorption process requires about an hour of contact of the material with wastewater containing IBU and is described by a pseudo-second-order kinetic model and a Sips isotherm with a maximum adsorption capacity of 86.21 mg g^{-1} .

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/ma14247697/s1>, Chapter 1 presenting descriptions: elemental analysis and methodology for determining the content of β -CD molecules capable of forming complexes. Figure S1. Spontaneous decrease in absorbance of phenolphthalein solution ($\lambda = 550 \text{ nm}$), Figure S2. N₂ adsorption–desorption isotherms for β -CD–M at 77 K, Figure S3. Barrett–Joyner–Halenda (BJH) pore size distribution from N₂ adsorption isotherm expressed as pore volume for β -CD–M, Figure S4. Harkins and Jura t-Plot for β -CD–M. Blue dots correspond to the estimated isotherm, red represents the non-fitted points,

Figure S5. Horvath–Kawazoe Isotherm Linear Plot of β -CD–M, Figure S6. Thermogravimetric analysis of β -CD–M in the air atmosphere, Figure S7. Thermogravimetric analysis of β -CD–M in nitrogen atmosphere, Table S1. The reported concentrations of ibuprofen in waters, Table S2. Selected FTIR bands recorded during the analysis of raw material and product samples (KBr pellet), Table S3. List of selected FTIR bands recorded during the analysis of regenerated β -CD–M samples (KBr pellet), Table S4. Changes in the value of phenolphthalein absorbance (A) in contact with 10 mg of β -CD–M, Table S5. BET Surface Area Report for β -CD–M, Table S6. Porous property of β -CD–M, Table S7. t-Plot Report for β -CD–M, Table S8. Summary rapport of β -CD–M microporous.

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Structural Adaptive, Self-Separating Material for Removing Ibuprofen from Waters and Sewage

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Table S1. The reported concentrations of IBU (ng L⁻¹) in waters.

Country	River	Concentration	References
France	NA	4.5	[1]
Greece	Aisonas	17	[2]
Mexico	–	1406	[3]
Portugal	Lima River	723	[4]
USA	Mississippi	34	[5]

Country	Concentration in Raw Sewage	Concentration in Treated Sewage	Removal Efficiency [%]	References
Poland (Hajdów Lublin)	649	412	37	[6]
Poland (Gdańsk)	1664	679	59	[6]
Poland (Szczecin)	894	516	42	[6]
USA (Maryland)	9500–14700	10–20	99	[7]
Switzerland	2000–3000	600–800	53–79	[7]
United Kingdom	5700	180	97	[8]
Scotland	28000	3000	98	[9]
Algeria	1607.8	341.4	79	[10]

Country	Concentration	References
France	6	[1]
Algeria	142.1	[10]
Kolumbia	7–58	[11]

S1. Material characterization (β-CD-M)

Elemental Analysis

Preparation of samples for elemental analysis consisted in drying at the temperature of 100 °C in a moisture analyzer until a constant mass was obtained. The powders were immediately transferred into packages, which were sealed and sent to the elemental analysis laboratory.

The basic element of the material most likely contains three β-CD molecules. One has as many as six substituted hydroxyl groups, while the other two only have five. Fourteen hydroxyl groups were involved in the usual polyurethane bonds while two others form the allophanate system, which explains the high nitrogen content.

Anal. Calcd. (β-CD-M): C₂₆₂H₄₃₄N₃₆O₁₄₁: 7.95 (N), 49.60 (C), 6.89 (H), 35.56 (O).

Anal. found. (β-CD-M): 7.93 (N), 49.26 (C), 6.84 (H), 35.05 (O).

Table S2. Selected FTIR bands recorded during the analysis of raw material and product samples (KBr pellet).

Compound	Wavenumber (cm ⁻¹)	Vibration Allocation
β -CD	3385.45 (strong, broad)	OH stretching intermolecular bonded
	2929.23 (medium, broad)	OH stretching intermolecular bonded
	1636.38 (medium, broad)	C=O stretching hemiacetal
	1412.06 (medium, broad)	OH-bending
	1157.02 – 1029.20 (strong, broad)	OH stretching
	1157.02 (sharp overtone)	OH stretching secondary alcohol
	1078.86 (Sharp overtone)	OH stretching primary alcohol
HDI	2939.74 (medium, broad)	C-H stretching methylene group
	2861.62 (medium, sharp)	C-H stretching methylene group
	2274.84 (strong, broad)	N=C=O stretching isocyanate
	1463.47 (sharp)	CH bending methylene group
	1355.46 (sharp)	CH bending methylene group
	863.50 (sharp)	CH ₂ rocking methylene group
	792.88 (sharp)	CH ₂ rocking methylene group
β -CD-M	3420.01 (strong, broad)	OH stretching intermolecular bonded
	2934.19 (medium, broad)	C-H stretching alkane
	2860.08 (medium, sharp)	C-H stretching alkane
	1715.86 (strong, split)	C=O stretching urethane and allophanate
	1653.07, 1646.76 and 1636.22 (strong, split)	C=O stretching urethane and allophanate
	1557.86, 1540.70, 1533.92 (strong, split)	C=O stretching hemiacetal
	1457.28 (split)	C-N-H stretching urethane and allophanate
	1418.01 (split)	CH bending methylene group
	1260.48 (sharp)	CH bending methylene group
	1151.52 – 1033.29 (strong, broad)	OH stretching ester group C-(O)-O-C
	1151.52 (sharp)	OH stretching
	773.93 (sharp)	OH stretching secondary alcohol
		CH ₂ rocking methylene group

Table S3. List of selected FTIR bands recorded during the analysis of regenerated β -CD-M samples (KBr pellet).

Compound	Wavenumber (cm ⁻¹)	Vibration allocation
β -CD-M first regeneration	34219.59 (strong, broad)	OH stretching intermolecular bonded
	2935.06 (medium, broad)	C-H stretching alkane
	2860.51 (medium, sharp)	C-H stretching alkane
	1705.72 (strong, split)	C=O stretching urethane allophanate
	1653.07 and 1646.76	C=O stretching urethane and allophanate
	1636.22	C=O stretching hemiacetal
	(strong, split)	
	1540.74 (strong, split)	C-N-H stretching urethane and allophanate
	1457.53 (split)	CH bending methylene group
	1417.47 (split)	CH bending methylene group
	1261.27 (sharp)	OH stretching ester group C-(O)-O-C
β -CD-M fifth regeneration	1151.68–1031.97 (strong, broad)	OH stretching
	1151.68 (sharp)	OH stretching secondary alcohol
	774.33 (sharp)	CH ₂ rocking methylene group
	3415.26 (strong, broad)	OH stretching intermolecular bonded
	2933.77 (medium, broad)	C-H stretching alkane
	2859.74 (medium, sharp)	C-H stretching alkane
	1709.26 (strong, split)	C=O stretching urethane and allophanate
	1651.57 (strong, split)	C=O stretching urethane and allophanate
	1546.18 (strong, split)	C-N-H stretching urethane and allophanate
	1461.12 (split)	CH bending methylene group
	1412.01 (split)	CH bending methylene group
	1261.20 (sharp)	OH stretching ester group C-(O)-O-C
β -CD-M fifth regeneration	1150.72–1033.37 (strong, broad)	OH stretching
	1150.72 (sharp)	OH stretching secondary alcohol
	773.62 (sharp)	CH ₂ rocking methylene group

Buffer (0.05 M trisaminomethane hydrochloride—Tris HCl; pH = 7) was used to prepare standard β -CD solutions (0.1–0.5 mmol L⁻¹). Phenolphthalein working solution (0.6 mmol L⁻¹) was prepared by dissolving 1.5 ml of phenolphthalein stock solution (4 mmol L⁻¹ in ethanol) in carbonate buffer at pH 10.5 just before the measurements. Test samples were prepared by mixing 1 mL of β -CD solution with 4 mL of phenolphthalein working solution. Separately, the 10 mg (20 mg) of material was suspended in a mixture of 1 ml of Tris HCl buffer and 4 ml of working phenolphthalein solution. All samples were shaken for one hour prior to absorbance measurements. The adsorbent was filtered off through Whatman Grade 540 filter paper. The absorbance of the standard solution and the samples was measured at 550 nm with a UV-VIS spectrophotometer (Hach Lange UV-vis DR 6000). A mixture of 1 ml of Tris HCl buffer and 4 ml of working phenolphthalein solution was used as a control solution. A calibration curve in form of absorbance as a function of β -CD weight was plotted for the standard solutions and an available for complexation β -CD was determined. Measurements were made in triplicate [12–14].

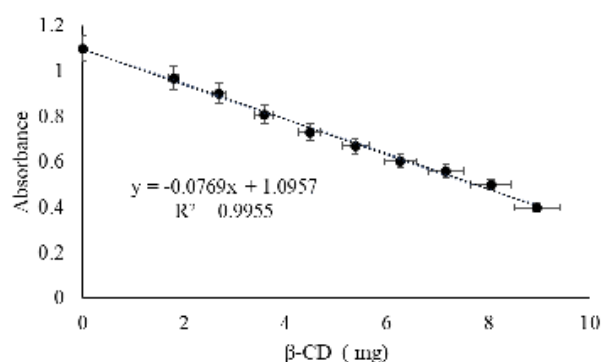


Figure S1. Spontaneous decrease in absorbance of phenolphthalein solution ($\lambda = 550$ nm).

Table S4. Changes in the value of phenolphthalein absorbance (A) in contact with 10 mg of β -CD-M.

β -CD-M (mg)	A ($\lambda = 550$ nm)	A Average
10	0.673	0.672
10	0.668	
10	0.675	

The amount of CD in the samples determined on the basis of the standard curve is 5.51 mg.

Specific Surface Area and Pore Size Distribution of Examined Adsorbent

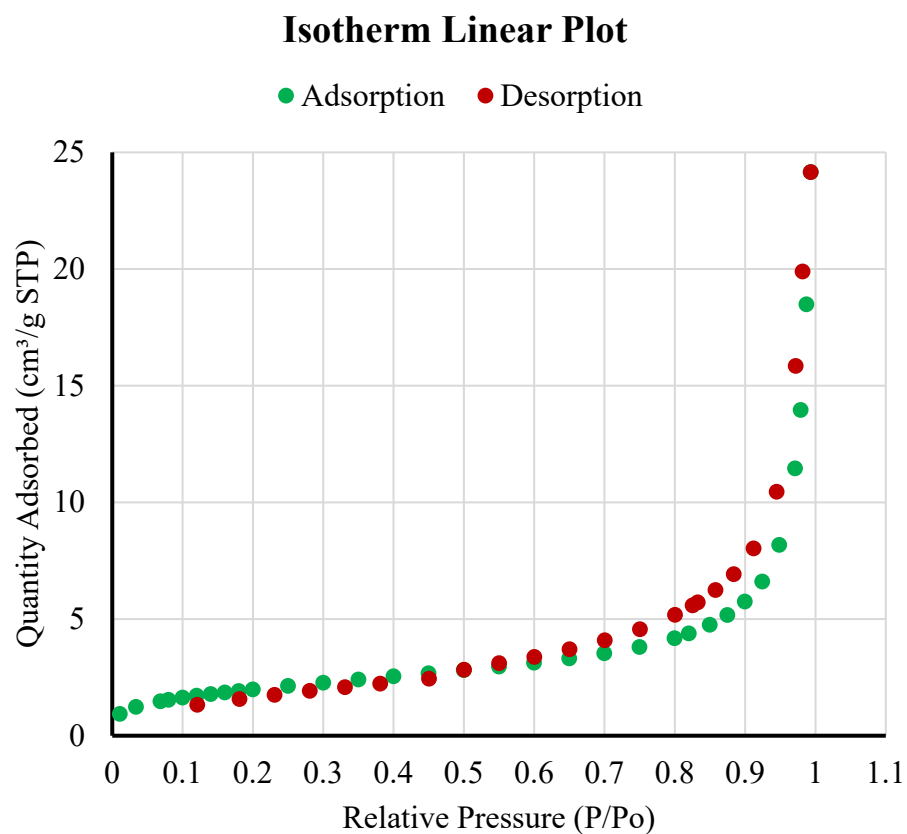


Figure S2. N₂ adsorption–desorption isotherms for β-CD-M at 77 K.

Table S5. BET Surface Area Report for β-CD-M.

Parameter	Value
BET Surface Area	7.3092 ± 0.0251 m ² /g
Slope	0.585891 ± 0.002021 g/cm ³ STP
Y-Intercept	0.009684 ± 0.000313 g/cm ³ STP
C	61.499882
Qm	1.6790 cm ³ /g STP
Correlation Coefficient	0.9999583
Molecular Cross-Sectional Area	0.1620 nm ²

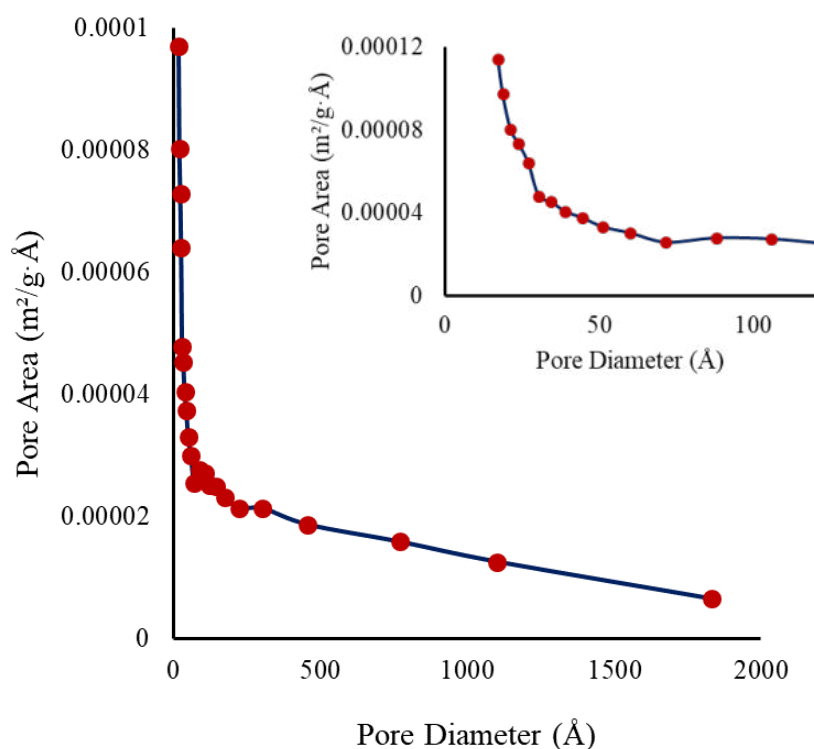


Figure S3. Barrett-Joyner-Halenda (BJH) pore size distribution from N₂ adsorption isotherm expressed as pore volume for β -CD-M.

Table S6. Porous property of β -CD-M.

Pore Diameter Range (Å)	Average Diameter (Å)	Incremental Pore Volume (cm ³ /g)	Cumulative Pore Volume (cm ³ /g)	Incremental Pore Area (m ² /g)	Cumulative Pore Area (m ² /g)
2947.2–1534.1	1830.774	0.009238	0.009238	0.201839	0.201839
1534.1–942.5	1102.189	0.007448	0.016686	0.270286	0.472125
942.5–682.2	770.697	0.004129	0.020815	0.214321	0.686446
682.2–387.8	457.6209	0.0055	0.026315	0.480775	1.167221
387.8–266.4	304.4597	0.002589	0.028905	0.340187	1.507408
266.4–201.4	224.6045	0.001389	0.030294	0.247348	1.754757
201.4–161.8	177.0667	0.000919	0.031213	0.20767	1.962427
161.8–135.0	145.8403	0.000666	0.031879	0.182658	2.145085
135.0–112.5	121.5831	0.000565	0.032444	0.185824	2.330908
112.5–100.9	106.0269	0.000315	0.032759	0.118879	2.449788
100.9–80.2	88.0325	0.000572	0.033331	0.259916	2.709704
80.2–66.2	71.72943	0.000359	0.03369	0.200382	2.910086
66.2–56.0	60.12403	0.000307	0.033997	0.204264	3.11435
56.0–48.1	51.39819	0.000258	0.034255	0.200487	3.314837
48.1–41.9	44.56554	0.000232	0.034487	0.208325	3.523163
41.9–36.9	39.0399	0.000206	0.034692	0.210607	3.733769
36.9–32.6	34.45013	0.000193	0.034885	0.22353	3.9573
32.6–29.0	30.5469	0.000175	0.03506	0.228849	4.186148
29.0–25.8	27.16056	0.000204	0.035264	0.300578	4.486727
25.8–22.9	24.15764	0.000208	0.035472	0.345152	4.831878
22.9–20.3	21.43404	0.00021	0.035682	0.391274	5.223152
20.3–17.9	18.91799	0.000236	0.035918	0.498134	5.721286
17.9–16.9	17.37733	0.000107	0.036025	0.246704	5.96799

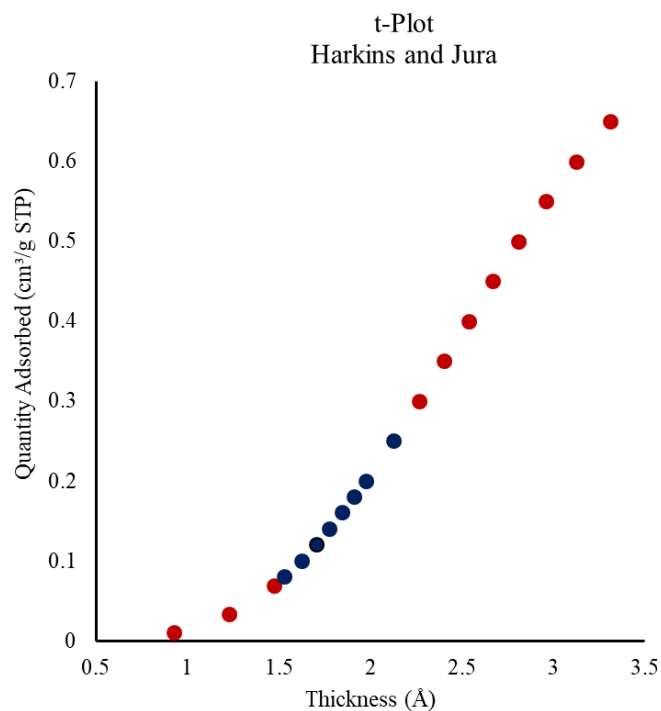


Figure S4. Harkins and Jura t-Plot for β -CD-M. Blue dots correspond to estimated isotherm, red represent not fitted points.

Table S7. t-Plot Report for β -CD-M.

Parameter	Value
Micropore Volume:	-0.000364 cm ³ /g
Micropore Area:	*
External Surface Area:	7.8226 m ² /g
Slope:	0.505726 $\pm$ 0.008214 cm ³ /g·Å STP
Y-Intercept:	-0.235420 $\pm$ 0.033394 cm ³ /g STP
Correlation Coefficient:	0.999210
Surface Area Correction Factor:	1.000
Density Conversion Factor:	0.0015468
Total Surface Area (BET):	7.3092 m ² /g
Thickness Range:	3.5000 Å to 5.0000 Å
Thickness Equation:	Harkins and Jura

*The micropore area is not reported because the micropore volume is negative.

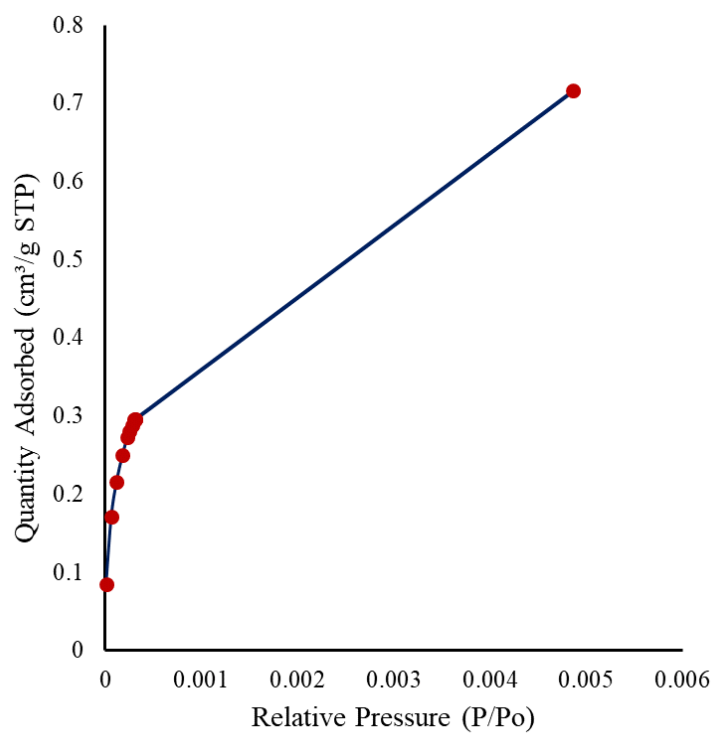


Figure S5. Horvath-Kawazoe Isotherm Linear Plot of β -CD-M.

Table S8. Summary rapport of β -CD-M microporous.

Parameter	Value
Volume in Pores<8.01 Å	0.00018 cm ³ /g
Total Volume in Pores ≤ 19.43 Å	0.00118 cm ³ /g
Area in Pores>19.43 Å	0.000 m ² /g
Total Area in Pores ≥ 8.01 Å	1.490 m ² /g
Maximum pore volume at P/P ₀ = 0.004867606	0.001107 cm ³ /g
Median pore width	8.415 Å

Thermogravimetric Analysis of β -CD-M

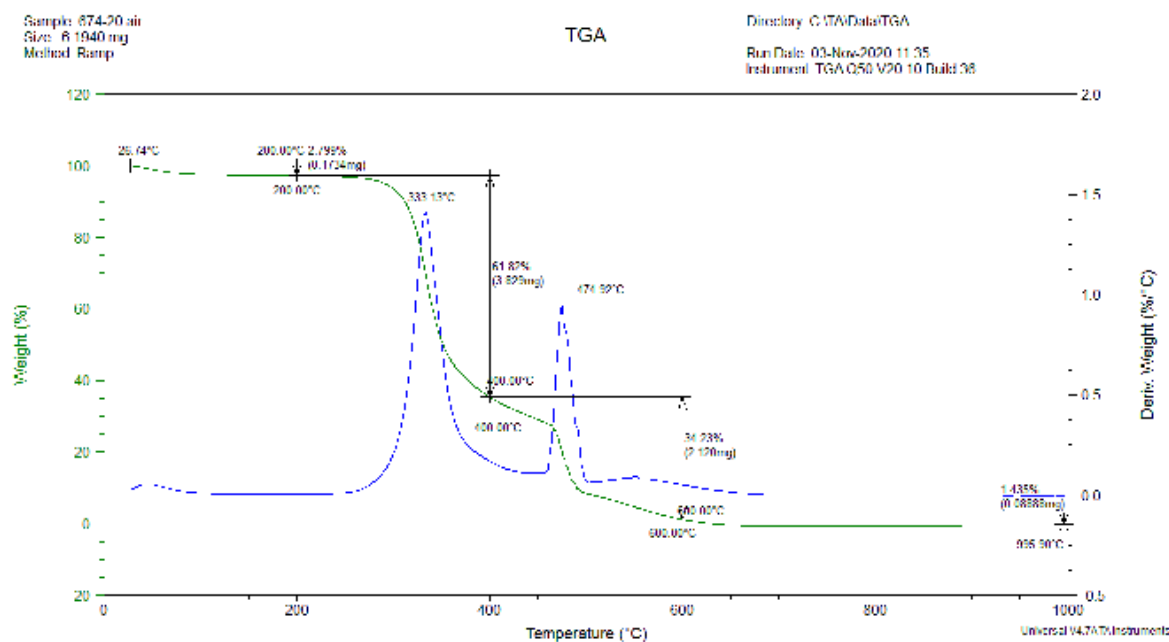


Figure S6. Thermogravimetric analysis of β -CD-M in the air atmosphere.

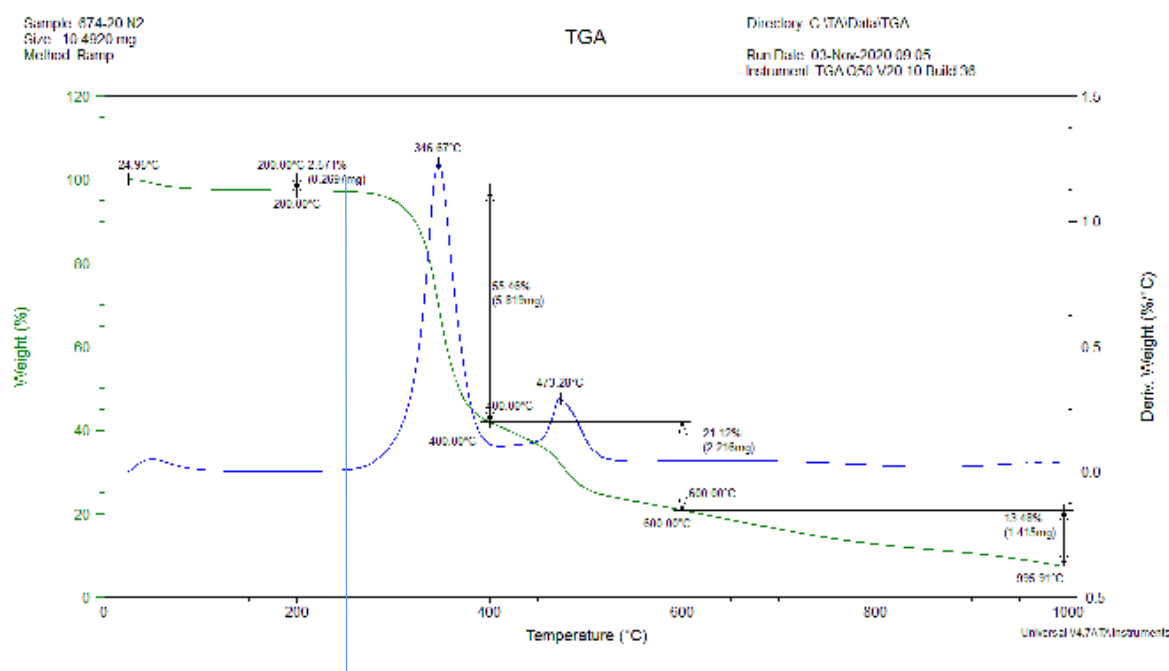


Figure S7. Thermogravimetric analysis of β -CD-M in nitrogen atmosphere.

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Publication 5

Recent Advancements in Cyclodextrin-Based Adsorbents for the Removal of Hazardous Pollutants from Waters – *Polymers*, 2022

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Review

Recent Advancements in Cyclodextrin-Based Adsorbents for the Removal of Hazardous Pollutants from Waters

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Abstract: Water is an essential substance for the survival on Earth of all living organisms. However, population growth has disturbed the natural phenomenon of living, due to industrial growth to meet ever expanding demands, and, hence, an exponential increase in environmental pollution has been reported in the last few decades. Moreover, water pollution has drawn major attention for its adverse effects on human health and the ecosystem. Various techniques have been used to treat wastewater, including biofiltration, activated sludge, membrane filtration, active oxidation process and adsorption. Among the mentioned, the last method is becoming very popular. Moreover, among the sorbents, those based on cyclodextrin have gained worldwide attention due to their excellent properties. This review article overviewed recent contributions related to the synthesis of Cyclodextrin (CD)-based adsorbents to treat wastewater, and their applications, especially for the removal of heavy metals, dyes, and organic pollutants (pharmaceuticals and endocrine disruptor chemicals). Furthermore, new adsorption trends and trials related to CD-based materials are also discussed regarding their regenerative potential. Finally, this review could be an inspiration for new research and could also anticipate future directions and challenges associated with CD-based adsorbents.

Keywords: cyclodextrin-based adsorbents; water pollution; heavy metals; dyes; organic pollutants



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1. Introduction

Water is a vital substance for all living organisms [1], and it plays an essential role in medical, energy and agricultural fields [2]. Through natural and anthropogenic activities, there has been an increase in contaminants and water bodies have deteriorated. Heavy metals, pesticides, dyes, pharmaceutical waste, and other emerging pollutants, have become a burden on the ecological environment [3–5]. These harmful contaminants could be bio-accumulated in the food chain and cause adverse human health impacts [6]. Pharmaceutical residues in water have become life-threatening, and directly affect the ecosystem and human health [7]. They get released in an aqueous environment through treatment plants and industrial effluent. Removal of toxic xenobiotic pollutants has become a growing concern in water treatment. Moreover, the concentration of pharmaceutical contaminants in water resources is directly connected to human consumption patterns, population growth, industrial activities, and wastewater treatment [8]. Recently, low concentrations have been found to possess higher toxicity and their removal from the aqueous environment has become a matter of urgency. To remove such pollutants, some biological, chemical, and physical approaches, including adsorption, filtration, coagulation, flocculation, and precipitation, have been utilized [9–13].

Furthermore, it is reported in many studies that pesticides are toxic substances for the environment and human health [14]. The frequent use of pesticides poses a threat to ecosystems and directly affects wildlife, birds, domestic animals, livestock, fish, and soil [15]. In addition, many pesticides could be stable over time, transported in water and air, and ultimately contaminate areas far from their point of origin [16]. The enormous increase

in the world population from 1900 to 2000 (1.5 billion to 6.9 billion) has also increased pressure on food demand; hence, the usage of pesticides has increased exponentially to meet production and economic profit levels [17]. Therefore, the removal of pesticides is a crucial research domain [18,19], so, various treatment techniques have been used to remove them. Currently, advanced oxidation processes (AOPs) [20], photochemical degradation [21], chlorination [22], and adsorption are favored techniques.

Dyes also pose considerable concerns to the environment and ecosystem due to their high toxic levels, and some of the colorants have products after their reactions. They may cause adverse impacts on aquatic life by disrupting biological processes [23,24]. As a result, heavy metals are more complicated to remove than the dyes, and thus they accumulate in water and soil [25,26]. They could also cause toxicosis in humans by contaminating water and crops [27,28]. Researchers pay special attention to the heavy metals present in ground and surface water [29]. Heavy metals, such as As(III), As(V), Cu(II), Ni(II), Co(II), Cd(II), Pb(II), Cr(III), etc., can be discharged directly and indirectly into water bodies [30–32]. Since they are carcinogenic and non-biodegradable, they can affect the growth of biological tissues in living organisms [33,34].

People have been so focused on industrial development that they stopped paying attention to the environment, and hence pollutants became stronger, more resistant, and progressively deposited in organisms [35,36]. Consequently, researchers have fixated on the research domain related to developing cost-effective removal techniques for heavy metals, organic pollutants, and dyes. Bio-filtration and traditional activated sludge processes are less efficient in removing all types of contaminants [37]. Membrane treatment and Active Oxidation Processes (AOPs) have shown higher efficiency in removing organic pollutants from waters [38–41]. Compared with other treatment processes, adsorption technology has been widely utilized for its efficient and economic characteristics. Over the last few years, various practical and efficient adsorbents have been used for wastewater treatment [42–44]. In recent years, the research society has focused on improving limitations previously associated with the adsorption process, such as selectivity for removing pollutants [45,46].

According to Somma et al. [47], adsorption is an effective technique, and the most frequently used method regarding water quality and purification, as it offers high efficiency in both organic and inorganic pollutant removal, and has the potential to treat larger quantities of water for several purposes. The adsorption capacity is entirely dependent on such factors as contact time, concentration, dosage, kinetics, isotherm models and reaction conditions [48]. The porous structures of adsorbents also help in capturing pollutants from wastewater [49].

Some inexpensive and nontoxic polysaccharides from various sources have been moderately applied for environmental protection in recent years. Cyclodextrins (CDs) are cyclic polysaccharides and have been commonly used in textile, food, medicine, and other fields [50–52]. They were first synthesized by Antoine Villiers in the late 19th century [53], and the structures are shown in Figure 1. They were first used in the food and pharmaceutical industries and in chromatography in the 1980s, and then in other fields. In 1999, it was proved that CDs are non-toxic adsorbents by conducting research with the use of CD-containing materials [54]. Native CDs have primary and secondary hydroxyl groups in their structures. They can guarantee coordination sites that are able to chelate metal ions. In addition, OH groups at basic pH can be deprotonated and form covalent bonds [55]. Modified CD adsorbents provide novel structures for higher adsorption and address CD monomers' limitations. In addition, novel CD adsorbents have been found effective for the simultaneous removal of several pollutants [56], and they were quickly separated while efficiently adsorbing [57].

This review paper aimed to overview various articles related to the adsorption of several pollutants by CD-based adsorbents and features the associated limitations and challenges. This paper summarizes developed synthetic methodologies and processes for the modification and preparation of CD adsorbents in detail. Moreover, CD-based adsorbents' adsorption properties for particular pollutants, including heavy metal ions,

pesticides, pharmaceutical residues, and dyes, are summarized. Furthermore, this paper explicitly addresses prospects, developments and challenges in applications.

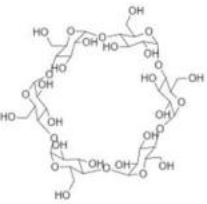
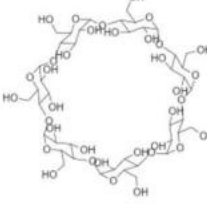
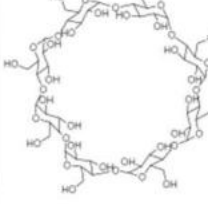
Properties of CDs	α -Cyclodextrin	β -Cyclodextrin	γ -Cyclodextrin
Glucose unit	6	7	8
Molecular weight	972	1135	1297
Inside diameter (Å)	4.7-5.3	6.0-6.5	7.5-8.3
Outside diameter (Å)	14.6 ± 0.4	15.4 ± 0.4	17.5 ± 0.4
Molecular height (Å)	7.9 ± 0.1	7.9 ± 0.1	7.9 ± 0.1
Cavity volume	174	262	427
Molecular structure			

Figure 1. Properties and structures of cyclodextrins.

2. Synthesis of Cyclodextrin-Based Adsorbents

CD is used as an additive for food and medicine application and is approved by the FDA [58,59]. CD is an oligosaccharide fabricate using enzymatic hydrolysis of starch, connected by α -1, 4-glycosidic bonds, which are divided into three types (α -, β -, and γ -CD) [60,61]. After producing enzymatic hydrolysis, experiments revealed that there are many other CD derivatives other than the three common types mentioned above, and their properties are also comparable to the most common CDs [62,63]. In addition, modification methods and synthesis can be split into three main classifications, and they are briefly discussed in the section below. The synthesis scheme is shown in Figure 2.

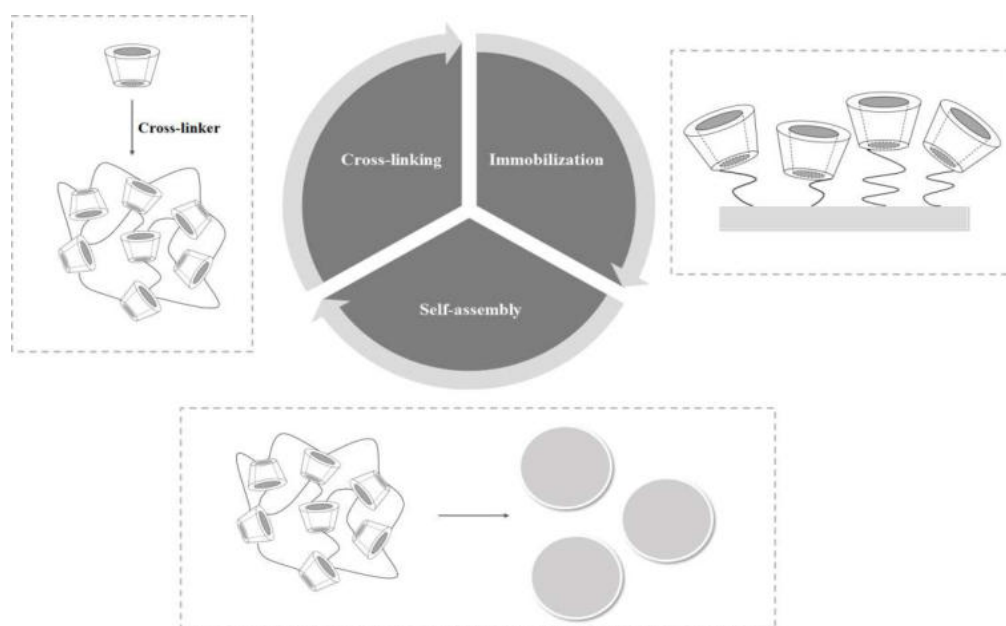


Figure 2. Synthesis scheme for CD-based materials.

2.1. Cross-Linking

Cross-linking concerns reactions to get stable molecular structures where molecules are bonded to each other. The authors mainly discuss the cross-linkers for polymer adsorbents and their properties, along with the adsorption mechanism of several adsorbents.

Cross-linking with epichlorohydrin has been widely used for over 50 years [64]. Another cross-linker, such as polyvinyl alcohol, was also considered for some practical applications, due to their low cost and easy preparation [65]. Chitosan (CS)-gamma CD, an adsorbent, has shown high stability and long life [66], proving to be a practical application. Similarly, CS-grafted beta-CD cross-linked using glutaraldehyde was confirmed to have characteristics and properties of CD and CS [67]. However, glutaraldehyde and EPI cross-linkers cause harm to the ecosystem and humans. They react with aromatic groups (rigid) and make them toxic. Various environmentally-friendly cross-linkers have gained much attention to remove contaminants.

Ethylenediamine tetraacetic acid (EDTA) has been commonly used as a cross-linker. It is cross-linked with the adsorbents, and they have been effective for metal removal because of the chelating reaction between metals and EDTA [68]. Citric Acid (CA) has also become extensively utilized as a cross-linker in recent years. When CA cross-links adsorbents it results in majorly rich groups that are effective and higher in adsorption efficiency [69]. Conclusively, cyclodextrin-based adsorbents obtained using cross-linkers appear to be effective for removing metals, dyes, and other organic pollutants.

2.2. Immobilization

Immobilization involves immobilizing material on the solid supporter by physical or chemical methods. Besides the preparation concept, immobilization also refers to the different types of adsorbents with a macromolecular structure used as a supporter. Immobilization is dependent on the kind of supporter for CDs and is categorized into two separate parts: fiber composites and magnetic materials.

Fiber composites possess a stable property with several functional groups. CDs immobilized by the chemical cross-linking process primarily produce fibers. To prepare polymer fibers, N-isopropyl acrylamide (NIPAM) could settle cyclodextrin molecules to obtain a porous material, and it has been found to be helpful to remove more than a gram of crystal violet dye by a gram of adsorbent [70]. Moreover, electrostatic force has been a widely utilized method for immobilization. An environmentally-friendly composite fibrous adsorbent, synthesized from gelatin and β -CD molecules by the electrospinning method, has been used for Methylene Blue (MB) [71]. Carbon nanofibers have been used as adsorbents in several applications and have been used as carriers for decades. They have also shown a higher adsorption capacity when CD molecules are introduced. Furthermore, Li and co-authors prepared CD-based carbon nanoparticles via electrospinning. They gained a larger specific surface area, more porous structure, and larger pore volume than typical carbon nanofibers [72].

Natural fibers refer to materials derived from natural resources, like straw, cotton, and wood. CD was introduced onto cotton fibers by chemical interaction to enhance the adsorption capacity for Methyl Blue and Congo Red (CR) [73]. For dyes, macromolecules have good properties and have higher adsorption capacities when connected with β -CDs.

However, magnetic adsorbents have more practical applications, compared to fibrous composites. Iron oxide (Fe_3O_4), a standard magnetic material, has been extensively used as an excellent solid supporter [74] in the last decade. CD introduced with Fe_3O_4 has been extensively used to remove heavy metals and dyes. By chemical reaction, β -CD is modified on Fe_3O_4 NPs when reacted with CS (CDCM) [75]. Similarly, CD immobilized EPI cross-linked with Fe_3O_4 could be effective for dyes and heavy metals [76]. Therefore, graphene oxide (GO) has also been utilized as a magnetic support for the adsorbent, and this offered excellent removal of atrazine (ATZ) [77]. By using the magnetic properties of iron oxide, the adsorbent can be rapidly and easily extracted from water through magnetic attraction.

2.3. Self-Assembly

Self-assembly refers to the procedure of a system's transition from an unorganized state to a well-structured state while the components are interacting, which happens in organisms and in nature [78,79]. CD-based molecules, when self-assembled, have been used for wastewater treatment because of the unique structure of the cavity of cyclodextrin. Self-assembled polymers were used to remove manifest pollutants, like imprinted molecules. Moreover, a β -CD-based adsorbent was synthesized into a film by adding bisphenol A (BPA) as a template molecule [80], and it showed excellent removal properties for BPA. In addition, CD molecules were embedded in the pore diameter of nano-porous carbon to acquire a self-assembly mechanism for CD functionalization and nano-porous carbon (ONC). Due to the availability of a specific cavity of CD molecules in the adsorbents, the pollutants were adsorbed quickly. However, it is challenging to use self-assembled adsorbents to treat more significant quantities. They have better efficiency for single pollutants, but are limited regarding multiple pollutant removal.

2.4. Characterization

The materials synthesized as described above were initially characterized by determining the content of the complex cyclodextrin, water absorption, point of zero charge, and decomposition temperature. The degree of cross-linking could be determined from the FTIR spectra. Optimum adsorption conditions were also determined, i.e., initial concentration of impurities and sorbents, contact time, pH, presence of salts and humic acids. Regeneration and characterization of the regenerated material were also carried out. All experimental points were adjusted to appropriate kinetic and adsorption models from which the main parameters, such as rate constants, equilibrium constants and maximum occupancy, were determined. Additionally, material samples could be subjected to other tests necessary for full material characterization, such as SEM, elemental analysis, BET isothermal analysis and thermogravimetric analysis. The final test is the use of real environmental samples.

3. The Mechanism and Function of CDs in Adsorbents

Cyclodextrin adsorbents are systems in which sugar macrocycles are part of the synthesized network. In this system, interactions with the adsorbate are based on several phenomena. The most important, explaining the legitimacy of using CD, is the inclusion of the guest molecule inside the torus [81–83]. Many organic molecules are present in environmental waters. As the interior of the CD is hydrophobic, matrix components that do not contain lipophilic elements are discriminated against. Most dyes and endocrine active molecules are aromatic compounds with at least one benzene ring that slips easily into the torus [84]. The outer part of the torus is hydrophilic and can participate in interactions involving functional groups formed during the reaction with the cross-linking agent [85]. If, for example, polyfunctional derivatives of hydroxy acids, amino acids or polyamines have been used in cross-linking, the adsorbent may additionally retain metals by chelation [86,87]. The selection of the cross-linking agent is crucial at the macromolecule design stage [88].

When the adsorption mechanism is based solely on the formation of supramolecular complexes, the amount of pollutant removed is the result of the number of available tori. Therefore, it is customary to specify the CD content of the material [89,90]. Moreover, the mechanism of cyclodextrin is shown in the Figure 3. It sometimes happens that the degree of capacity is significantly greater, which indicates the synergistic interaction of other elements of the structure [91]. The explanation may also be the formation of complexes with a different stoichiometry than assumed and based on research carried out with the use of native cyclodextrin solutions.

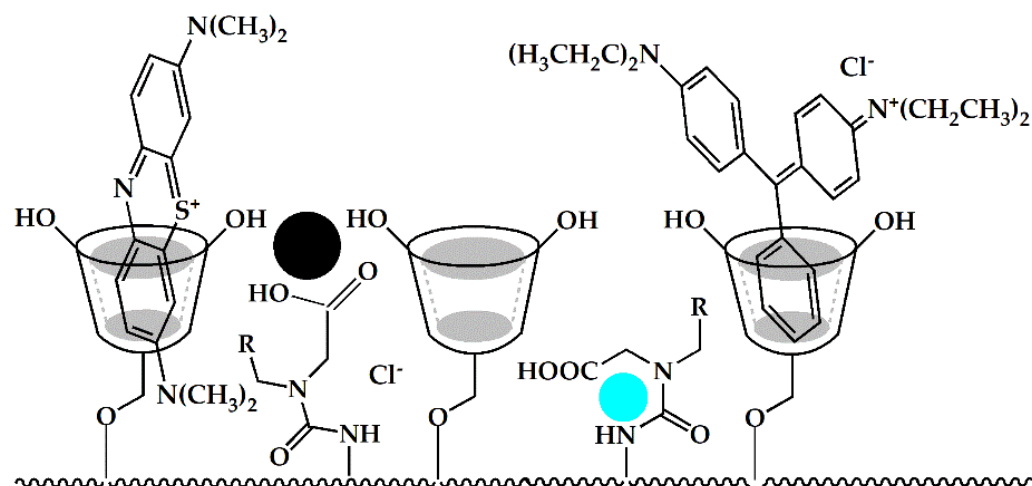


Figure 3. Fragment of the structure of the cyclodextrin adsorbent interacting with dyes and metal cations.

4. Application of Cyclodextrin-Based Adsorbents

4.1. Removal of Dyes

Dyes are being removed with high efficiency by using CD-based adsorbents. Various studies related to dye adsorption. Adsorption efficiency depends upon the interactions of analyte molecules with the adsorbent [92]. Various adsorbents have different abilities to uptake the dye in their matrix. The β -CD surface is rich in oxygen, and $0.1 \text{ m}^2/\text{g}$ surface area adsorbs CR and MB with a maximum capacity of $1.80 - 10^{-2} \text{ mmol/g}$ but a higher affinity for CR, because of the CD and hydrophobic dye interactions. In contrast, MB has weak interaction of forces at the hydrophilic surface of β -CD [93].

Host-guest complexation has become the advanced and economical adsorption technique. In a new study, β -CD and oil orange SS (OOSS) azo dye complexes were formed by the coprecipitation method to check their water purification ability. OOSS dye encapsulation with the β -CD hydrophobic cavity was confirmed by thermal analysis and FTIR. The complexation induced stability in the matrix, due to host-guest complex formation [94]. In another study, β -CD and ϵ -polycaprolactone (PCL) composite fibers were prepared by the electrospinning method through the host-guest complexation mechanism, as shown in Figure 4. The adsorbents were characterized by SEM, XRD, EDXS, and FT-IR. The synthesized fiber exhibited selective response for the 4-aminoazobenzene and MB solutions. The dye elution efficiency was achieved at 24.1 mg/g towards 4-aminoazobenzene. Adsorption stability, sensitivity, and selectivity of the electropunk fibers encourage their potential use at a large scale for dye adsorption [95]. Natural polysaccharides can perform surface modification of GO due to various active functional groups. In a new study, the GO/ β -CD composite was prepared by the cross-linking method to study its performance in MB adsorption. The new material was characterized by SEM, XRD, FT-IR, Raman and TGA analysis. GO/ β -CD exhibited the maximum adsorption capacity of 76.4 mg/g in six consecutive adsorption–desorption cycles [96].

Functionalized polymer composites gained much attention due to their high sensitivity, easy availability, good separation, and various active groups in the polymeric chain. Combining functionalized polymers with nanoparticles induces excellent properties in adsorbent materials. Yadav et al. reported a magnetic polymer nanocomposite by the addition of Fe_3O_4 nanoparticles (NPs) with β -CD/activated charcoal (AC)/sodium alginate (Alg). Figure 5 shows the SEM images and elemental analysis of the synthesized adsorbent. Langmuir isotherm fitted on the adsorption studies and prepared polymer composite exhibited the adsorption capacity of 10.63 mg g^{-1} for MB with an elution rate of 99.53% [97].

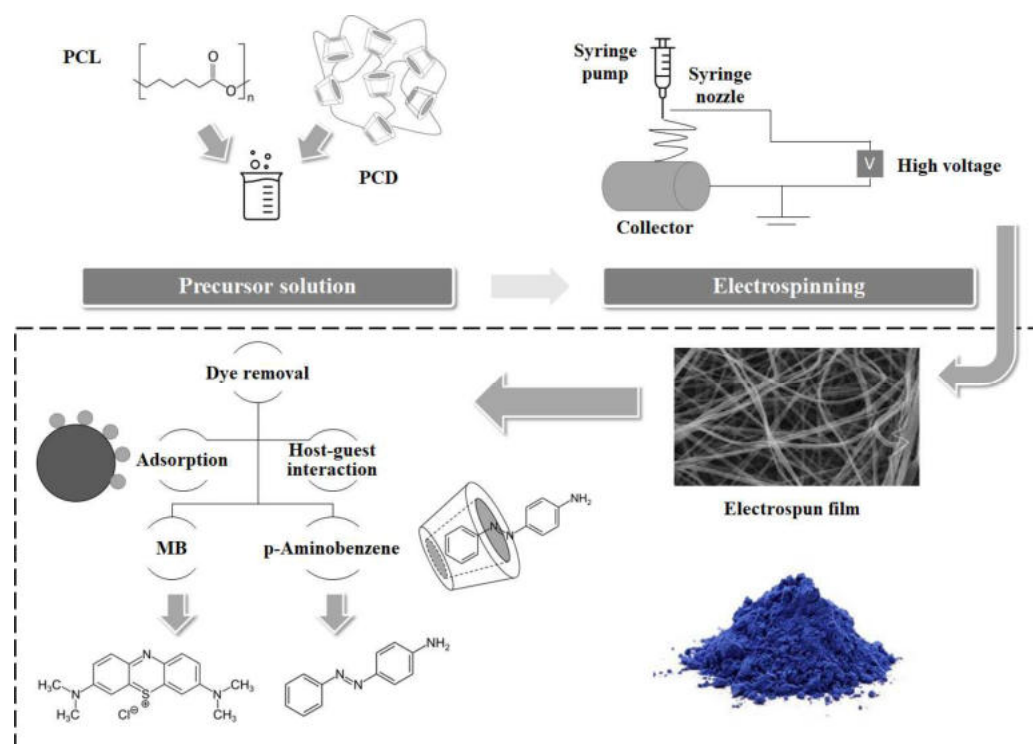


Figure 4. Schematic representation for the synthesis and adsorption mechanism of β -CD/PCL composite fibers for MB [95].

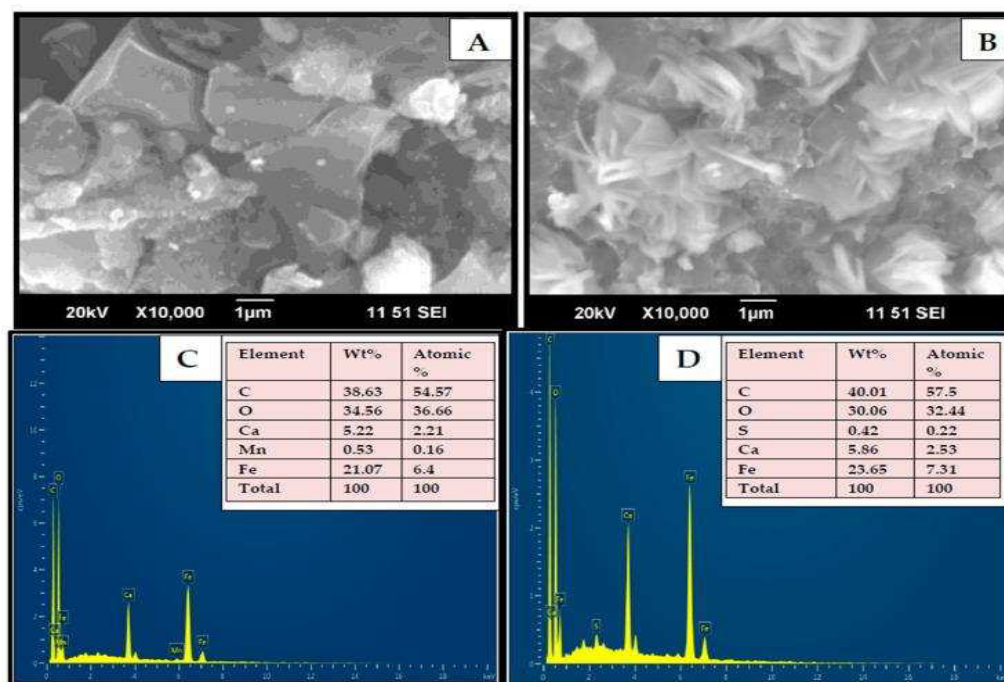


Figure 5. SEM-Energy Dispersive X-ray Spectrometry (EDX) images of $\text{Fe}_3\text{O}_4/\text{AC}/\text{CD}/\text{Alg}$ polymer beads before (A) and after (B) adsorption. $\text{Fe}_3\text{O}_4/\text{AC}/\text{CD}/\text{Alg}$ elemental analysis before (C) and after (D) adsorption [97].

A combination of adsorption and membrane technology enhances the adsorbent performance. Li et al. modified filter paper with CD and citric acid to remove dual molecules, including dyes and Cu ions. Adsorption capacities of 39.1 mg g^{-1} , 99.7 mg/g , 124.6 mg g^{-1} , and 130.4 mg g^{-1} were determined for the Cu(II), Rhodamine-B (RB), Methylene Blue (MB),

and Brilliant Green (BG), respectively. CD-based membranes can reduce the risk of various diseases if implanted in different dyes in affluent places and suggest new paths in the adsorption field, according to [98], which also discussed CD-based adsorbents' interaction, complexation, and membrane mechanism for the removal of dyes. Every process has its positive aspects, and also the adsorption capacity depends upon some other factors like temperature and pH, depending on the adsorbate material composition. Furthermore, Table 1 summarizes the adsorption capacity and removal efficiencies of several CD-based adsorbents for dyes.

Table 1. Adsorption capacities of various CD-based adsorbents for dyes.

Adsorbent	Dye	Adsorption Capacity	Removal Efficiency (%)	pH	References
Fe ₃ O ₄ /AC/CD/Alg	MB	10.63 mg/g	99.53	6.0	[97]
β-CD/GO	MB	76.4 mg/g	90.00	7.0	[96]
β-CD filter paper	MB	124.6 mg/g	92.94	5.5–6	[98]
	BG	130.4 mg/g		5.5–6	
	RB	99.7 mg/g		5.5–6	
Fe ₃ O ₄ /b-CD/GO	MG	990.1	98.00	7.0	[99]
Fe ₃ O ₄ -PEI/b-CD	MO	192.2	83.90	1	[76]
β-CD	CR	12 mg/g	65.00	-	[93]
PA-β-CD	MB	1095	90.00	6–10	[100]
PA-β-CD	BG 4	2005.58		6–10	
	CV	1930.23		6–10	

4.2. Removal of Heavy Metals

Generally, metals can be eliminated through complexation, interaction, or ion exchange mechanisms. The efficiency of the adsorbent depends upon various factors, especially on the preparation technique and optimal pH. The CD polymer has deprotonated hydroxyl groups, which bind the metal strongly under primary conditions. The stability towards environmental conditions is enhanced by polymerizing Poly-CD/metal ion complex with polyacids. Anceschi reported Poly-CD/PVA fibers by the electrospinning of various Poly-CD and PVA solutions for the adsorption of Cu (II) ions. The fiber morphology was investigated by SEM, and physical-chemical properties were examined by FTIR and TGA. The ability of the insoluble CD-based fibers to eliminate heavy metals from wastewater was examined by analyzing the adsorption of Cu²⁺ and Cd²⁺ using ICP-OES. Poly-CD/PVA fibers exhibited an excellent response, especially towards the Cu(II), with a maximum adsorption capacity of 48.15 mg/g [101]. In another study, nano-sponges were fabricated through a complexation mechanism by cross-linking linecaps and CD with citric acid. Another pyromellitate nano-sponge was synthesized by the same reaction with pyromellitic dianhydride to compare the responses. The response was recorded at the 500 pm metal concentration, and pyromellitate exhibited a higher retention capability than the citrate-based nano-sponges. Pyromellitate adsorbent showed an adsorption capacity of 272 mg/g and 81 mg/g for the Pb(II) and Cu(II) [102]. Dual adsorbents are a new addition to adsorption technology. Single class pollutants have been reported, and it is challenging to eliminate organic and inorganic contaminants with the same adsorbents. Recently, Verma et al. reported β-CD-CS-EDTA adsorbent for the extraction of heavy metals (Ni(II), Cu(II), and Pb(II)) and ciprofloxacin (CIP). Figure 6 represents the synthesis mechanism of the adsorbent material. The adsorption mechanism was examined using EDX, FTIR, and elemental mapping methods. Heavy metals adsorption was more rapid than the CIP, with an adsorption capacity of 118.90, 161, and 330.90 mg/g for Ni(II), Cu(II), and Pb(II), respectively, while the CIP adsorption capacity was found to be 25.40 mg/g. It is a direction toward new research related to the elimination of organic and inorganic pollutants from water at the same time by a single adsorbent [103].

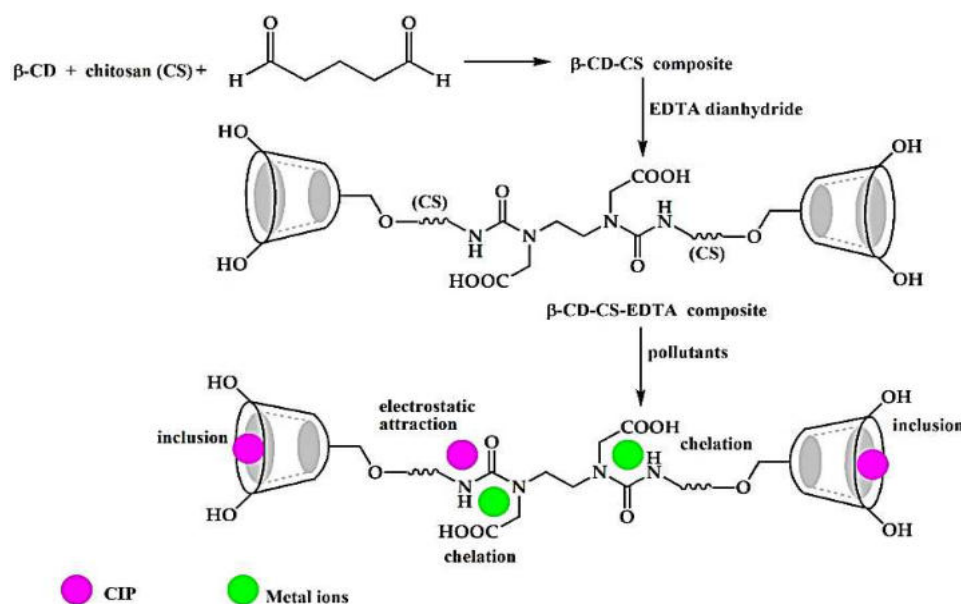


Figure 6. Schematic representation for the preparation of β -CD-Chitosan adsorbent [103].

Magnetic composites are frequently used in adsorption due to their strong hydrophilicity, greater surface area, and various active sites [104,105]. The addition of magnetic composite with poly (vinylidene fluoride) PVDF membranes is due to the characteristics mentioned above. Zhang et al. modified PVDF with β -CD/GO/ Fe_3O_4 to remove Cu(II) metal ions. The morphological and structural properties of the nanocomposite were investigated by TEM, XRD, FTIR, EDX and VSM techniques. The prepared adsorbent exhibited an adsorption capacity of 0.94 mg/g, and pH > 6 enhanced Cu's elimination rate (II). The high-performance membranes, modified with biomaterial/nanoparticles composite, had excellent efficiency in adsorbing heavy metals from water [106]. Nano-porous carbons are getting research attention and are being frequently applied in adsorption applications, due to their various essential characteristics. Metal-organic framework (MOF) is a new class of nanoarchitecture particles with excellent stability and sensitivity [107,108]. Liu et al. prepared a γ -CD-MOF composite by carbonizing the framework with potassium ions and γ -cyclodextrin. Figure 7 represents the SEM, TEM, and elemental mapping of the prepared adsorbent. The γ -CD-MOF-based adsorbent exhibited an adsorption capacity of 140.85 mg/g for Cd(II) ions that the Langmuir model calculated. The adsorption followed the ion exchange mechanism due to oxygen-comprising functional groups [109]. These studies revealed that CD has a remarkable ability to remove metal ions from water under laboratory conditions, making it a solid foundation for industrial research. Furthermore, Table 2 summarizes the adsorption capacity and removal efficiency for several heavy metals on CD-based adsorbents.

Table 2. Adsorption capacities of various CD-based adsorbents for metals.

Adsorbent	Dye	Adsorption Capacity (mg/g)	Removal Efficiency (%)	pH	References
Poly-CD/PVA	Cu(II)	48.15	85.00	8	[101]
β -PMDA	Pb(II)	272	95.00	-	[102]
	Pb(II)	330.90	-	5	
β -CD-CS-EDTA	Cu(II)	161	95.00	5	[103]
	Ni(II)	118.9	95.00	5	
Fe_3O_4 /GO (β -MGO)	Cu(II)	0.94 mg/g	93.14	6–7	[110]
α -CD MOF-NPC	Cd(II)	140.85	90.00	4	[109]

Table 2. Cont.

Adsorbent	Dye	Adsorption Capacity (mg/g)	Removal Efficiency (%)	pH	References
β -CDs polymer	Pb(II)	196.4	83.30	2	[111]
Zr/CM- β -CD	Cd(II)	118.3	-	7.0	[112]
Fe ₃ O ₄ -PEI/ β -CD	Pb(II)	73.1	73.40	6.0	[113]
CD-Fe ₃ S ₄	Pb(II)	256.0	74.47	6.0	[114]
β -CDPP	Pb(II)	576.92	95.00	2	[115]

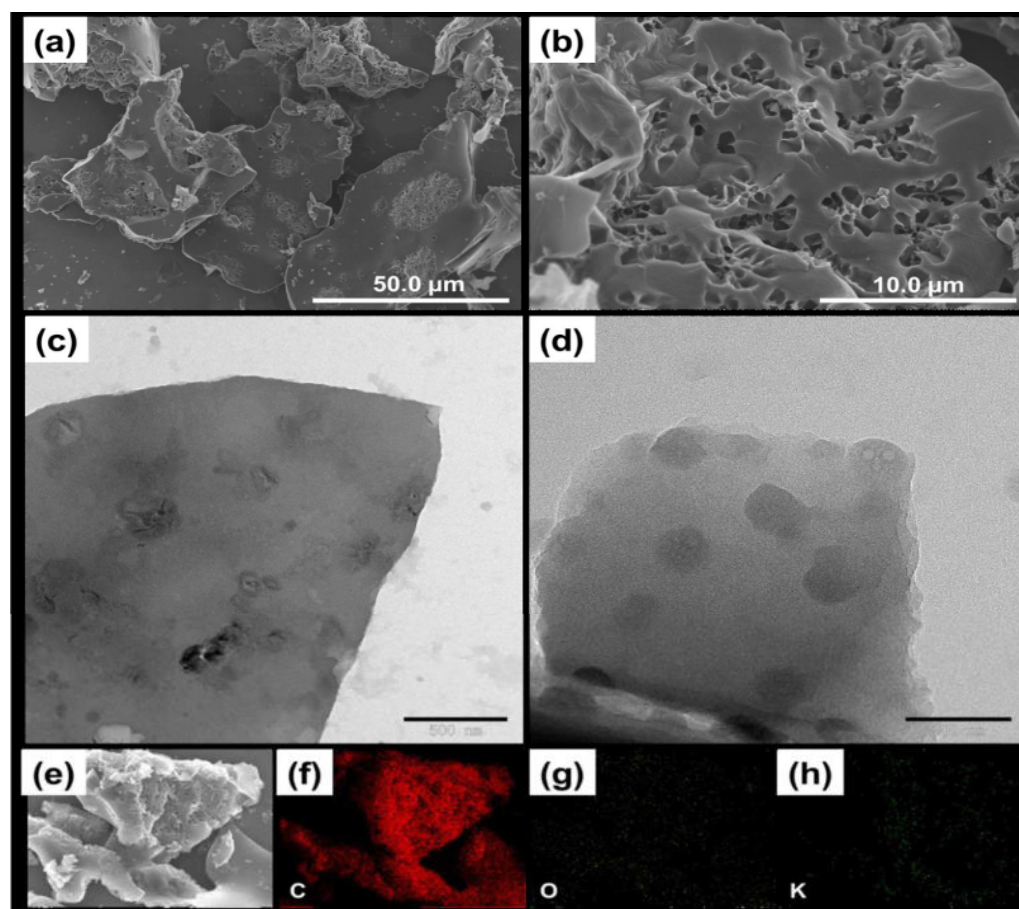


Figure 7. γ -CD MOF-NPC; SEM images (a,b), TEM images (c,d) and the mapping of C, K and O element(e–h) [109].

4.3. Removal of Organic Compounds

Along with the evolution of civilization, the progress of industrial processes is also taking place, due to the growing demands of people for resources, including resources for medicines and food. During the drug production process in pharmaceutical companies, an inseparable part of it is the generation of huge amounts of wastewater. Due to incomplete treatment, residues in sewage will be released into the environment and then into the human body, causing negative consequences over the years [116].

It is similar in the case of the food and packaging industry, which uses harmful endocrine-active compounds (EDCs) in the production of food packaging [117]. Due to increased temperature (e.g., when heating food), they enter the body along with food [118]. In addition, cans or plastic packages containing toxic EDCs often get into the water through inappropriate garbage handling. In the waters of the seas, lakes, and oceans, these toxic EDCs degrade into micro- and then nano-plastic, harming many species of animals, plants,

and others. Therefore, endocrine-active compounds and drugs remain in, and accumulate in, polluted water, which has gradually attracted the attention of people [119]. Most organic pollutants in this section tend to bio-accumulate, persist in the waters for an extended time and are highly toxic to humans and animals [120]. Since cyclodextrins can self-adapt their structure to the structure of the adsorbed pollutant by reorganization, they are an ideal example of a material with great potential to remove organic contaminants from the environment. Adsorption of organic pollutants as a means of removal was tested on cyclodextrin-based materials [121]. Previous work has shown that cyclodextrins help remove endocrine-active compounds, pharmaceuticals, and other organic compounds [122,123]. Furthermore, removing the aforementioned groups of impurities involves model compounds, such as bisphenol A, nonylphenol, estrogen, carbamazepine, ibuprofen, naproxen and ciprofloxacin [124,125]. The maximum adsorption capacities and removal efficiencies of various CD-based adsorbents for selected organic compounds are listed in Tables 3 and 4.

4.3.1. Endocrine Disruptors

Bisphenol A (BPA) is a commercial substance from a group of phenols that have been commonly used since the 1960s. For years, BPA has been used in the chemical industry, particularly in producing polycarbonate plastics and resins [126,127]. Exposure to bisphenol A may affect the occurrence of, among other things, diabetes, obesity, metabolic syndrome, cancer, and fertility disorders [128]. To remove chemicals that disrupt the functioning of the endocrine system, CD-MG, mesoporous magnetic clusters connected with β -cyclodextrin, were synthesized and studied. Adsorption isotherms showed that BPA adsorption was 52.7 mg/g. In addition, the adsorbent showed an admirable quality of 84.5% in reusability test experiments after four cycles. Their quick process kinetics, delightful adsorption capacity, and CD-MG adsorption mechanism result in high potential for removing active endocrine compounds from the environment [120].

Another work presented an ecological and straightforward method of producing porous poly (chloromethyl styrene) resin modified with β -cyclodextrin with a spongy cross-linked material, namely PS@CM-CDP, for the ultrafast and effective removal of organic contamination from aquatic solutions. The obtained PS@CM-CDP, which stood out as having maximum adsorption capacity for BPA, could reach beyond 8.25 mg/g. In addition, the circular identity of the resin rendered native β -CD polymers reusable, even after six usages, without significant performance degradation. The paper also presented the practical application of the obtained material, which illustrated multiple perspectives on the water treatment column [129].

In work from 2021, a cyclodextrin material was designed, produced, and used to eliminate Pb (II) and BPA, which may coexist in the aquatic environment. The characterization outcomes corroborated successful β -CD grafting and Fe_3O_4 loading. Moreover, the resulting material β -CD@MRHC had commendable magnetic properties for efficient regeneration from water, unaffected by pollutant adsorption. The synthesized material showed excellent adsorption efficiency with a maximum bisphenol A uptake of 412.8 mg/g, and it only took 7.5 min to achieve adsorption equilibrium. In addition, the material accomplished synergistic elimination of Pb(II) and BPA by reversing their competing behaviors, thanks to different holding mechanisms. The adsorbent was found to be promising and suitable for practical use in the simultaneous elimination of heavy metals and organic matter from water resources, employing high-efficiency magnetic recovery [130].

Moreover, Bucur S. et al. synthesized silica particles with β -cyclodextrin that showed the ability to remove bisphenol A (BPA) from sewage water. It turned out that this was related to the presence of β -CD groups on the silica surface. The experiments showed that the q_e values were 107 mg/g for SiO_2 - β -CD-OH and 112 mg/g for SiO_2 - β -CD-NH₂, respectively, while adsorption equilibrium was reached after 180 min [116]. The bagasse- β -cyclodextrin polymer, namely SB- β -CD, accounted for 121 mg/g [131], and showed similar values of the maximum BPA adsorption capacity.

Table 3. Maximum adsorption capacities and removal efficiencies of various CD-based adsorbents for selected endocrine disrupting compounds.

Adsorbent	Pollutant	q _{max}	Removal Efficiency [%]	References
β-CDPs	Bisphenol A	460.0	>99.9	[126]
GO-β-CD nanocomposites	Bisphenol A	373.4	95.0	[127]
Hyper-cross-linked β-CD porous polymer	Bisphenol A	278.0	78.8	[128]
Zr/CM-β-CD	Estrogens estradiol	210.5	>97.0	[112]
β-CD-TFP	Bisphenol A	164.4	98.1	[129]
β-CD-DFDS	Bisphenol A	113.0	90.0	[130]
Diatomite cross-linked BCD polymers	Bisphenol A	83.6	91.2	[131]
β-CD polymer-functionalized Fe ₃ O ₄ magnetic nanoparticles	Bisphenol A	74.6	41.0	[132]
β-CD-Functionalized Mesoporous Magnetic Clusters	Bisphenol A	52.7	84.5	[133]
CS-ED-CD	Bisphenol S	44.3	87.0	
β-CD-modified graphene oxide membranes	Bisphenol A	25.5	100	[134]
β-CD-poly(glycidyl methacrylate)-SiO ₂ -nanoparticles	Bisphenol A	22.5	97.2	[135]
β-CD-alginate GPP	Nonylphenol	22.0	46.0	[136]
	Dialkyl phthalates	6.6	72.9	[137]

Synthetic zeolite with NaX structure was modified with β-cyclodextrin (CD) and used for adsorption of, for example, BPA and ibuprofen from model solutions. The best fit to the Langmuir model shown in adsorption experiments indicated monolayer adsorption and the formation of inclusion complexes with hydrogen bonding. The researchers mentioned that the q_{max} parameter was 32.7 mg/g for BPA. The adsorptive behavior of NaX-CD designated that it could be a skillful adsorbent for the eradication of EDC pollutants from contaminated water [132].

A new β-CD modified graphene oxide membrane (CDGO) was synthesized in 2019 to effectively remove bisphenol-A. The CDGO membranes were produced by vacuum filtration and laying CDGO nanosheets onto spongy compounds. Nanosheets were produced by chemically grafting β-CD particles on both sides of graphene oxide nanosheets. The BPA adsorption efficiency by the synthesized material was several times higher than that of the affinity membranes that were earlier used. In addition, this material was readily regenerated by treatment with ethanol. After a few cycles, it was possible to restore the effectiveness of BPA removal to almost 100% [123].

In 2020, a porous membrane made of cellulose nanofibers with modified β-cyclodextrin (CA-P-CDP) was produced and tested. The impurities used were model bisphenol compounds bisphenol A, bisphenol S, and bisphenol F. In addition, temperature, adsorbent dosage, and pH were tested during the adsorption process, and it was shown that they had a significant effect on the adsorption efficiency. Under chosen conditions (25 °C, 7.0 pH, and 0.1 g/L dose of material), the removal of model pollutants reached equilibrium within 15 min, and the q_{max} parameter was 50.37, 48.52, and 47.25 mg/g for bisphenol A, S and bisphenol F, respectively. The work focused on the interaction of hydrophobic effects, hydrogen bond interactions, and π-π stacking interactions. In addition, it was proved that the amount of treated solution by CA-P-CDP was 14.5 times greater than that of a pristine-cellulose membrane. In addition, the authors also indicated the complete removal of pollutants during the treatment of natural water samples, which proved that the tested material could be used in practice [133].

Another example of the application of CD-based adsorbents may be using a new, environmentally friendly adsorbent formed by cross-linking with β-cyclodextrin diatomite

(DA@ β -CD) for the removal of EDCs. The synthesized DA@ β -CD had 1.4 to 2.5 times higher BPA removal capacity than DA. The test material was steady and reusable after washing with an alkaline solution. A removal held after three regeneration cycles, still achieved a stable removal rate of 91.15% [118].

Cyclodextrin-based materials can remove many contaminants other than BPA. For example, in one study, Fe₃O₄@CD MNPs were produced by chemical co-precipitation, and could quickly be isolated from the water phase by a magnet. The efficiency of 1-naphthol removal by the mentioned material was tested according to the batch technique. The $q_{\max}$ parameter of Fe₃O₄@CD MNPs was higher than that of several adsorbing materials tried before. Moreover, the paper showed the cost-effective and advantageous removal of Co(II) and 1-naphthol simultaneously by Fe₃O₄@CD MNPs [134].

In addition, core-shell nanoparticles can also be used to adsorb harmful compounds. An example may be the magnetic and photocatalytic Fe₃O₄@TiO₂ prepared and described by researchers. It is formed when cyclodextrin cavities are anchored in TiO₂ coating. The model pollutant used in the study was butyl phthalate. An undeniable advantage of this type of material was the possibility of separating the functionalized nanoparticles by magnetic action and reusing them. The dispersibility of nanoparticles in water captured organic impurities, due to the presence of cyclodextrin in the composite material. Moreover, the desirable feature of these adsorbents was that they could be removed entirely and reused, while maintaining the current adsorption capacity [135].

Researchers also undertook the removal of estrogens (including estradiol and estrone) from the environment using Zr/CM- β CD, i.e., the Zr(IV)-cross-linked carboxymethyl- β -cyclodextrin, which was constructed by an easy, all-purpose and environmentally friendly method. Namely, this material could be obtained by a chelation reaction between Zr(IV) and the carboxyl group of the cyclodextrin used. Furthermore, the CD cavities encapsulated estrogenic contaminants through inclusion complexes. It was also possible to remove metals simultaneously with this material as it has been suggested that the carboxyl groups should react by chelating metal ions. In the one-component system, the $q_{\max}$ parameter of Zr/CM- β -CD towards estradiol was 210.53 mg/g. The adsorption capacity of the Zr/CM- β -CD remained high after five cycles. Interestingly, the material was very economical at concurrent removal of EDCs and metals [98].

The mechanism of EDC adsorption by CD-based adsorbents is different than that for the removal of heavy metals and dyes described in this paper. The CD cavity does not have the role of enriching the uptake of contaminants but also plays a role as the location of in situ catalytic degradation [136]. On the other hand, selective matching between guest and host can be a limiting step in the adsorption process [137].

4.3.2. Pharmaceutical

Pharmaceutical contaminants have been found in water bodies and pollute the entire ecosystem. For example, carbamazepine, a dibenzoazepine derivative, is used as a psychotropic, anticonvulsant, and mood-stabilizing drug, mainly to treat epilepsy and bipolar disorder. The drug is widely detected in European and North American water [138]. Its presence has also been demonstrated in green algae, crustaceans, stinging beetles, and hydroids [139]. This toxic compound is tough to degrade [140]. For this reason, studies have been conducted that showed that the maximum adsorption capacity ($q_{\max}$) of carbamazepine by cyclodextrin material is 136.4 mg/g [141].

The above-described case of finding pharmaceuticals in water is not an isolated one. Another example is non-steroidal anti-inflammatory drugs (NSAIDs), which include ibuprofen, ketoprofen, and diclofenac. In one of the articles, the authors used CDs combined with nano-filters to eliminate these pollutants from the aquatic environment. The tested nano-filters were of different thicknesses and chemical compositions. In the study, the maximum adsorption capacity was estimated using ibuprofen as a model by measuring the removal of pharmaceutical residues from municipal wastewater. After use, nano-filters can be regenerated using ethanol, and the $q_{\max}$ of chemicals can be improved [142].

A notable example of attempts to remove NSAIDs from water is the use of CD polymer as the third step in treating biomechanical municipal wastewater in a wastewater treatment plant. Fenyvesi and colleagues found a very high level of contamination removal in a relatively short time [143].

In another study, the hydrothermal method was used to obtain a composite of reduced graphene oxide immobilized with β -cyclodextrin (β -CD/rGO) in one step to eliminate naproxen from water. The material with a high porosity structure with numerous hydroxyl groups showed the stable removal of NSAID and an excellent adsorption capacity of 361.85 mg/g at 313 K temperature [144].

In another research, innovative $\text{Fe}_3\text{O}_4/\text{CD}/\text{AC}/\text{SA}$ polymer gel beads, consisting of functionalized iron oxide activated carbon particles, sodium alginate polymer, and β -cyclodextrin, were obtained by a straight, repeatable, and cheap method. The maximum adsorption capacity of this material was 3.125 mg/g for ciprofloxacin, the most potent drug among the fluoroquinolones, with a bactericidal effect, showing its activity by inhibiting bacterial DNA topoisomerase and DNA gyrase [124]. Moreover, $\text{Fe}_3\text{O}_4/\text{CD}/\text{AC}/\text{SA}$ can be regenerated and smoothly separated from solutions without losing removal efficiency. After regeneration, they have the same adsorption capacity for up to four desorption and adsorption cycles [145]. The problem of the presence of drugs in sewage can be reduced by absorbing the substances with derivatives of cyclodextrin polymers. The CD polymer/pulsed light sequential method was tested for contaminant removal to overcome this problem, and the simulations showed that the cyclodextrin 3D network gives the CD polymer amphiphilic features, which help to reduce the concentration of impurities by 77%. Moreover, after using the CD polymer on contaminated water, the authors treated it with pulsating light, by which the presence of contaminants was further reduced by up to 91%. The CD polymer was shown to be reusable at least ten times while eliminating one of the most popular NSAIDs, ibuprofen. For this reason, a CD polymer system, combined with pulsating light, can be an innovative and efficient method of removing NSAIDs from water [146].

Table 4. Maximum adsorption capacities and removal efficiencies of various CD-based adsorbents for selected pharmaceutical compounds.

Adsorbent	Pollutant	q_{max}	Removal Efficiency [%]	References
CNPs	Tetracycline (TC)	543.5	93.8	[72]
β -CD-M	Ibuprofen	86.2	90.0	[147]
	Procaine	48.0	86.0	
CS-ED-CD	Imipramine	47.1	85.0	[148]
	Ciprofloxacin	47.1	83.0	
β -CD/rGO	Naproxen	361.9	79.3	[144]
β -CD COF	Naproxen	-	98.0	[149]
	Ibuprofen	-	78.0	
Ca(II)-doped chitosan/ β -CD composite	Acetaminophen	200.9	99.9	[150]
CD@Clay-PVP	Ibuprofen	3.46	83.9	[151]
β -CD polymer with tetrafluoroterephthalonitrile	Carbamazepine	136.4	65.0	[83]
GD-EDTS	Salbutamol	140.2	71.3	[146]
	Atenolol	236.9	70.4	

Drugs often used to treat chronic diseases, such as Salbutamol (SAL) and Atenolol (ATL), were tested in 2021 for their removal from the environment. Unfortunately, traditional wastewater treatment plants cannot cope with their complete removal. To efficiently remove the above-mentioned compounds, silanized adsorbents of β -cyclodextrin compounds (GD-EDTS) were designed and tested. Due to the introduction of carboxyl groups into this composite, it was possible to sustain satisfactory adsorption efficiency over a

broad pH range. The maximum SAL and ATL adsorption capacities were 140.24 mg/g and 236.92 mg/g. Moreover, the poor rivalries behavior between SAL and ATL resulted in the fact that both impurities could be removed simultaneously with the test adsorbent.

5. Regeneration

Regeneration of an adsorbent plays a vital part in the determination of its efficiency and longer usage. Many adsorbents have been prepared but due to their lacking regeneration properties, they were not popular among researchers. Regeneration is always a key challenge (Figure 8). In most studies, solvent regeneration has been used for pollutants [152]. However, the efficiency of regeneration depends on the pollutant's solubility in the solvent for regeneration [153,154]. In addition, to regenerate the adsorbent's activity, the solvent regeneration process is used in β -CD functionalized adsorbents. However, it has been reported in many studies that the adsorbents lose their capacity to adsorb after each cycle [154,155]. In the adsorption/desorption part of a study by Qiang Lin and co-authors, in 2019, it was revealed that B-CD grafted cellulose beads were regenerated easily in methanol [82]. In another research by Usman and co-authors, in 2021, regeneration revealed that NTA-B-CD-CS acquired remarkable potential to treat and model wastewater several times [87]. Furthermore, it was reported in research that P-CDEC has shown no such decrease in removal efficiency for Ni(II) and BPA when compared to other polymers, and its regeneration was more than 90%, even after the fifth cycle [86].

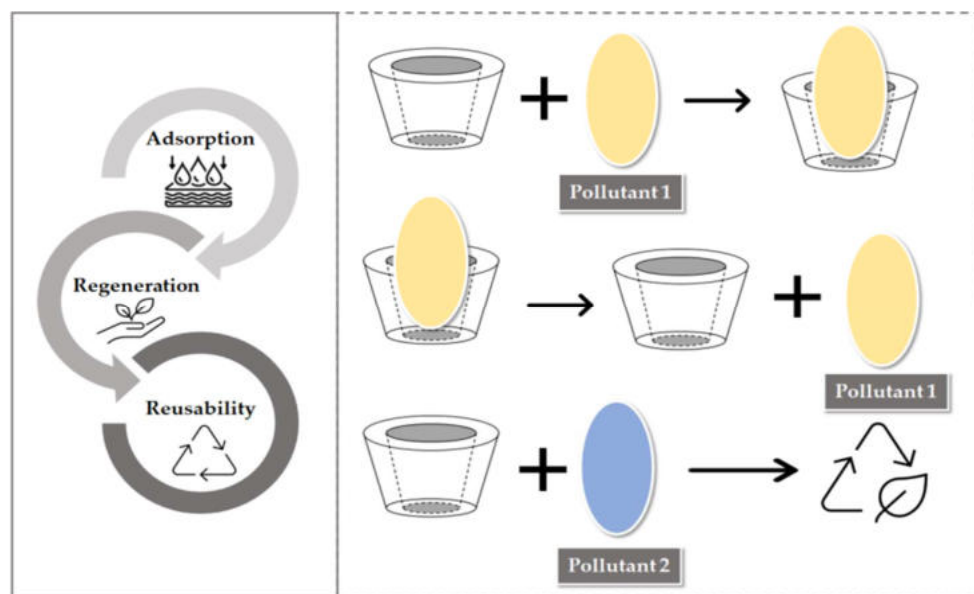


Figure 8. Schematic diagram of adsorption-regeneration-reusability.

6. Conclusions

Environmental pollution induces toxicity and affects human health. Researchers are exploring new routes to resolve issues of environmental pollution to regain the safe environment and ecosystem that existed before the commencement of pollution. Most pollutants, such as heavy metals, organic contaminants, and others, are bio-accumulated in food chains through water sources and ultimately disturb natural water bodies. These pollutants are resistant to degradation and accumulate in the biological system to produce toxicity, side effects, and diseases. Researchers have developed various technologies to reduce contaminants in the environment, and to protect the environment. Moreover, adsorption has gained considerable attention around the globe due to its unique characteristics. Macro-cyclic molecules adsorb pollutants and ease multiple environmental and health concerns. CD is frequently used for adsorption due to its critical feature of water solubility for water remediation. Various CD-based adsorbents have been summarized in this paper, indicating

recent progress in adsorption technology and the identification of research gaps to make the environment safe and healthy. The structural features of three types of cyclodextrins have been described, and finally an overview of the adsorption of heavy metals, dyes, pharmaceuticals and other organic contaminants by CD was provided. In addition, the modification of CD with nanoparticles, membranes, and fibers enhances the adsorption capacity and efficiency of the adsorbent material. CD adsorbents prepared by cross-linking have larger surface area and also a three-dimensional porous structure that is beneficial for the treatment of wastewater. Furthermore, hydrogen bonding, host-guest networks, electrostatic forces, and hydrophobic and acid-base interactions between CD and pollutants make the adsorption mechanism efficient. Many future aspects need to be explored for the commercial use of CD-based adsorbents. Although CD possesses several advantages over many adsorbents, many problems are still associated with CD composites. CD is a natural substance, but the green composites products, and their sustainability, remain a challenge for researchers, and there is a dire need for further studies. Degradation and toxicological studies need to be explored to make CD a versatile and commercial adsorbent. Adsorption on real water samples is also a key challenge because experiments are still performed at the laboratory level, so, there is a lot of work remaining to make CD-based adsorbents at an industrial level. Conclusively, any concerns related to CD-based adsorbents, in terms of low-cost, eco-friendliness, practicality, reproducibility, long-term stability, and reusability should be resolved for application at industrial levels.

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