



Review

Cyclodextrin Polymers and Cyclodextrin-Containing Polysaccharides for Water Remediation

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Abstract: Chemical pollution of water has raised great concerns among citizens, lawmakers, and nearly all manufacturing industries. As the legislation addressing liquid effluents becomes more stringent, water companies are increasingly scrutinized for their environmental performance. In this context, emergent contaminants represent a major challenge, and the remediation of water bodies and wastewater demands alternative sorbent materials. One of the most promising adsorbing materials for micropolluted water environments involves cyclodextrin (CD) polymers and cyclodextrin-containing polysaccharides. Although cyclodextrins are water-soluble and, thus, unusable as adsorbents in aqueous media, they can be feasibly polymerized by using different crosslinkers such as epichlorohydrin, polycarboxylic acids, and glutaraldehyde. Likewise, with those coupling agents or after substituting hydroxyl groups with more reactive moieties, cyclodextrin units can be covalently attached to a pre-existing polysaccharide. In this direction, the functionalization of chitosan, cellulose, carboxymethyl cellulose, and other carbohydrate polymers with CDs is vastly found in the literature. For the system containing CDs to be used for remediation purposes, there are benefits from a synergy that arises from (i) the ability of CD units to interact selectively with a broad spectrum of molecules, forming inclusion complexes and higher-order supramolecular assemblies, (ii) the functional groups of the crosslinker comonomers, (iii) the three-dimensional structure of the crosslinked network, and/or (iv) the intrinsic characteristics of the polysaccharide backbone. In view of the most recent contributions regarding CD-based copolymers and CD-containing polysaccharides, this review discusses their performance as adsorbents in micropolluted water environments, as well as their interaction patterns, addressing the influence of their structural and physicochemical properties and their functionalization.

Keywords: cyclodextrins; polysaccharides; pollutants; adsorption; water remediation



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1. Introduction

The exponential degradation of water quality is a major challenge facing both developing and developed countries, recently addressed in The Zero Pollution Ambition plan launched by the European Commission. This plan is a key pillar of the European Green Deal, which is committed to promoting initiatives in strategic fields of energy, industry, mobility, agriculture, biodiversity, and climate towards a zero-pollution strategy by better preventing, remedying, monitoring, and reporting on pollution [1]. These actions have been strongly reiterated by experts in environmental agencies: “Something has really changed in the past year. Everyone is talking about water quality. Local interest groups are attracting not just local media interest but national media interest. Rivers and beaches are all our shop windows. People notice and people care.” [2].

Currently, researchers working in different areas of chemistry, materials science, and engineering are focusing on developing greener, safer, and more cost-effective materials for water remediation. Moreover, an assessment of energy efficiency and the respective environmental benefits and risks are being considered.

Extensive research has been performed to develop new nanotechnologies for remediating water pollution by inorganic and organic contaminants [3]. These include advanced materials, such as those of a polymeric nature, which have been explored with great success for remediation purposes at different functional scales [4–10]. The most recent contributions have emphasized the use of nanobiomaterials to improve the detection, capture, and degradation of emergent and persistent contaminants [11–13].

Specifically, the adsorption of toxic compounds by modified polysaccharides and cyclodextrins (CDs) has evidenced an increasing interest in the synthesis of new low-cost adsorbents for removing contaminants from natural water and wastewater [8,14]. Lately, the number of contributions addressing CD-based polymers and CD-containing polysaccharides, in particular, and CD-grafted and/or CD-coated materials to deal with the remediation of micropolluted water environments has grown exponentially. However, the formulation and understanding of a complete, integrated picture of the major targeted environmental needs and research objectives and the spotting of cutting-edge synthetic routes, analytical techniques, and scaling-up trends in the design of multifunctional CD materials are still critical tasks [4,15–20].

By assessing the multiple facets of CDs and CD-based polymers in environmental remediation, considering specific target contaminants (e.g., dyes, pesticides, pharmaceutical compounds, heavy metals) and target matrices (e.g., water and wastewater), it is possible to identify the most relevant types of pollutants, the removal of which has benefited from the application of CD-based adsorbents. This is particularly important to (i) understanding the dynamics of persistent and emerging contaminants, (ii) developing effective remediation strategies based on CD polymers and CD-containing polysaccharides, and (iii) giving rise to promising research directions. Some reviews have already been published on this matter, targeting a specific kind of CD polymer, such as those crosslinked with epichlorohydrin [4]. However, the present review seeks to provide a comprehensive view, addressing the potential and limitations of CDs, both as backbone constituents and as pendant groups, and the role of different crosslinkers, anchoring groups, and polysaccharides attached to these cyclic oligosaccharides.

2. Cyclodextrin-Based Polymers in Pollutant Removal

Bibliometric indicators have shown an increasing interest in polymers of natural origin as an alternative to conventional adsorbents such as activated carbon, silica gels, and zeolites [14,19,21]. More specifically, oligo- and polysaccharides have been effectively used for pollution remediation on the basis of their high availability, biodegradability, biocompatibility, nontoxicity, and high chemical functionality, allowing researchers to synthesize sustainable, green, and, if desired, selective adsorbents [14,19,21].

In general, polysaccharides are highly hydrophilic polymers whose structure (fundamentally containing hydroxyl groups and, in some cases, acetamido and primary amino groups) confers not only preferential adsorption sites but also reactive sites for the development of new materials. On the other hand, certain oligosaccharides, in particular cyclodextrins, offer more sites for pollutant molecule adsorption. Due to the hydrophobic cavity of cyclodextrins, host–guest assemblies, mainly based on hydrophobic interactions, may occur [14,21–23]. It should, however, be stressed that not only amphiphilic or hydrophobic compounds interact with cyclodextrins. As will be discussed below, metal ions also interact with the protonated or deprotonated hydroxyl groups of CDs, located at both rims of the CD structure, thus allowing their removal from the environment. Therefore, the synergy obtained by the use of CD-containing polysaccharides enlarges their effectiveness in water remediation. It should be expected that the sorption of pollutants on CD-based materials benefits from the formation of the CD–pollutant complex and from other interactions external to the cavity, which are influenced by the contact time, the type of sorbent, and the chemical structure of the pollutant.

Another strategy that takes advantage of the versatile properties of CDs is based on the polymerization or copolymerization of the CDs by using crosslinkers and other grafting

agents [9,24–35]. Furthermore, the alkylation, hydroxyalkylation, and carboxymethylation of natural CDs help broaden the spectrum of guest molecules that can be effectively bound and, thus, the variety of pollutants to be removed [36,37].

Recently, Valente and coworkers [14] provided a summary of the key progress in developing CD-based materials, which include polymers, hydrogels, and nanocomposites, used as sorbents for removing toxic compounds from wastewater. CDs have been modified in different ways to produce derivatives with high affinity towards targeted contaminants in aqueous solutions. Modification relies, e.g., on the direct linkage of β -CD by crosslinking with a coupling agent or on the covalent binding of β -CD molecules to a pre-existing insoluble matrix, including polysaccharides such as chitosan and alginates, nanofibers, textiles, silica beads, and zeolites [14].

One of the most popular crosslinkers is epichlorohydrin (EPI). The existence of two reactive groups in EPI allows its bivalent binding to cyclodextrins, generating hydrophilic polymeric networks (hydrogels) with multiple CD molecules linked by repeating glyceryl moieties [24,25,28,35,38–45]. These materials display high adsorption capability, are efficient in the removal of water contaminants present at trace levels, and show relatively fast kinetics [9,25,26,29,30,33,46–52].

2.1. Synthesis and Properties of CD-Based Materials

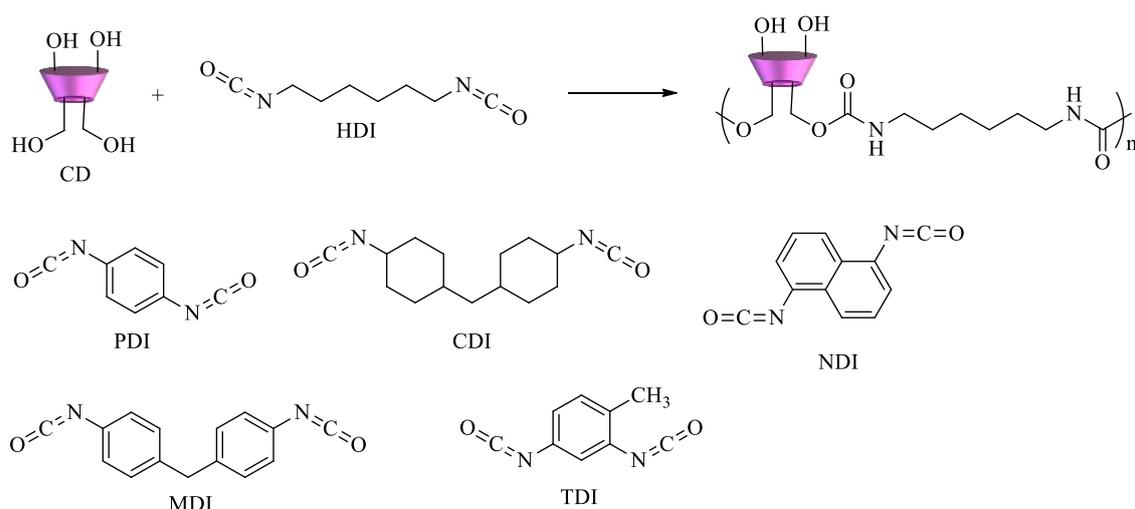
CDs can be considered polyfunctional monomers since they possess several reactive hydroxyl groups at the 2, 3, and 6 positions of each anhydroglucose unit, susceptible to substitution and elimination. The primary hydroxyl groups at the C6 position are usually more reactive than the secondary ones (C2 and C3 positions), although this reactivity order can be reversed by manipulating reaction conditions such as temperature and alkalinity [53]. Due to these intrinsic characteristics, CDs can be directly copolymerized with other monomers or attached to a myriad of materials. Different types of architecture can thus be obtained, including linear, branched, and crosslinked networks. Moreover, CDs can be modified in order to obtain derivatives with other functionalities, from amino to carboxyl groups.

Two main types of CD-based polymers can be prepared: the first involves the use of CDs or CD derivatives such as monomers and their reaction with a coupling agent in order to obtain linear polymers or crosslinked structures; in the second type, CDs are attached to a matrix (organic or inorganic) via chemical or physical interaction [54,55]. It should be noted that in this work, only polysaccharides are surveyed. Consequently, in this work, CD-based materials will be divided into two main groups, depending on whether CDs constitute or coconstitute the backbone of the polymer (polycyclodextrins) or are bound to polymeric matrices.

2.1.1. Polycyclodextrins

As it was discussed before, the reactivity of CDs is mainly based on their hydroxyl groups. They can behave as nucleophiles or electrophiles and react with a variety of other functional groups, resulting in, e.g., ethers, esters, and halides. CD hydroxyl groups can be deprotonated using strong bases, thus originating alkoxide ions, strong nucleophiles that can readily undergo S_N2 reaction. On the other hand, CD ethers can be prepared by protonation of the hydroxyl groups using acids, converting the poor leaving group OH^- to H_2O , a better leaving group, and thus acting as electrophiles in the reaction with other alcohols.

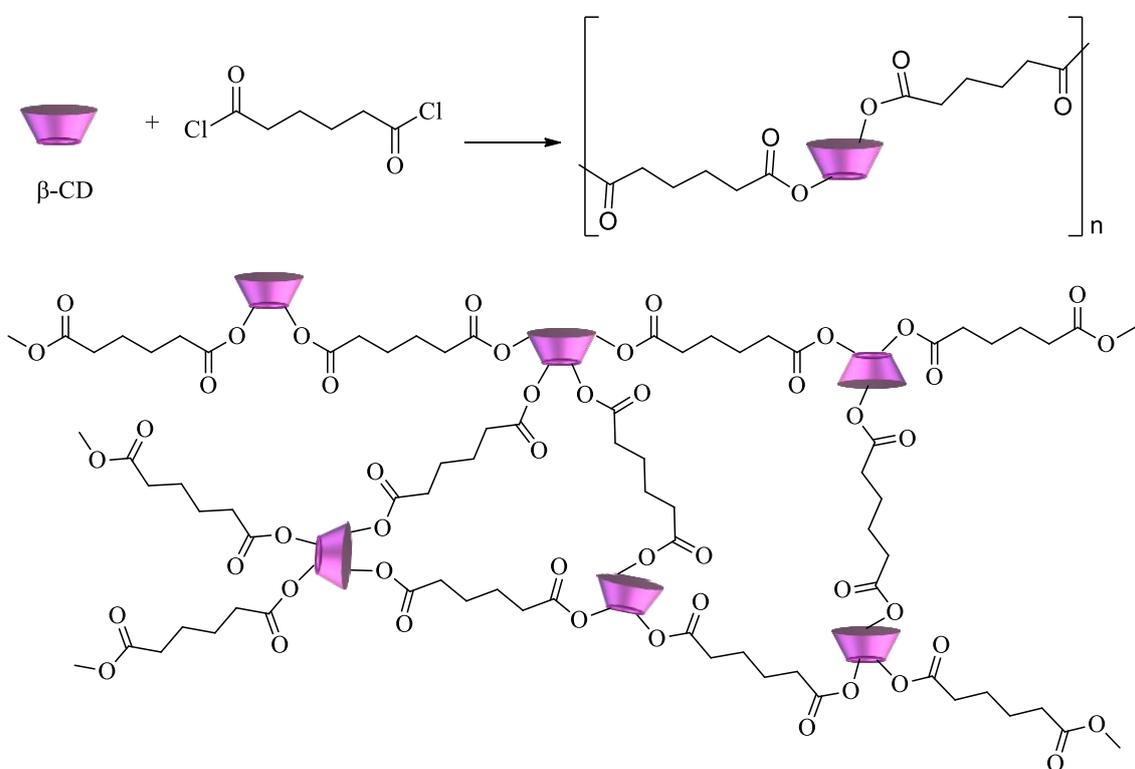
CD crosslinked polymers are particularly important in the context of water remediation due to the cooperative effect between the CD cavity and the polymeric network. Depending on the type of CD, the crosslinking agent, and the reaction conditions, materials with different characteristics can be prepared [15]. Among the diverse choices of crosslinker, epichlorohydrin (EPI) clearly stands out. In fact, CD–EPI polymers were one of the first to be used for pollutant removal [56–58]. These polymers are easily prepared by reacting CDs with EPI under heating, catalyzed by NaOH in a one-pot reaction (Scheme 1).



Scheme 2. Diisocyanates for the synthesis of CD-polyurethane copolymers.

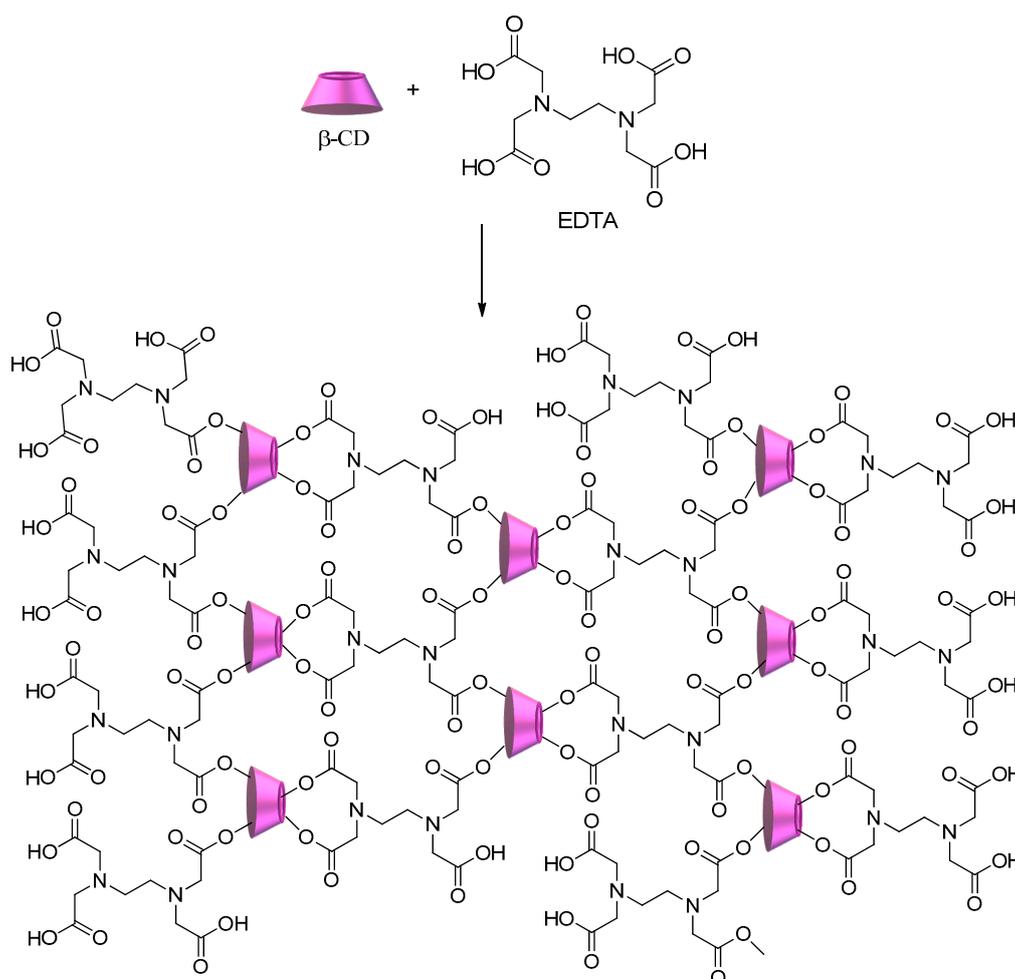
If an excess of diisocyanate is used, highly crosslinked polymers can be obtained. Nanosponge CD polyurethanes have proven to be effective in the removal of several pollutants. Dyes and aromatic amines [71,72], organic matter, *p*-nitrophenol, pentachlorophenol and 2-methylisoborneol [73,74], perfluorinated compounds (PFCs) and pesticides [75,76] are among the pollutants tested.

Cyclodextrin polyesters constitute another important class of CD polymers. They can be obtained by reaction of the oligosaccharides with diacids, diacid chlorides, or dianhydrides. Some of the first examples of these polymers were developed by reacting CDs with succinyl chloride, glutaryl chloride, and adipoyl chloride (Scheme 3) [77,78].



Scheme 3. β -CD polyester using adipoyl chloride as a crosslinking agent.

Another approach for the synthesis of cyclodextrin copolymers consists of using polycarboxylic acids (e.g., citric acid, succinic acid, 1,2,3,4-butanetetracarboxylic acid, and poly(acrylic acid)) as crosslinking agents [79–81]. Scheme 4 shows the synthesis of CD–polycarboxylic polymers using ethylenediamine tetraacetic acid (EDTA) [46,82]. The obtained polymer shows a significant number of sites available to interact with a multitude of pollutants, from metal ions to dyes and herbicides, regardless of their hydrophilic/hydrophobic character.



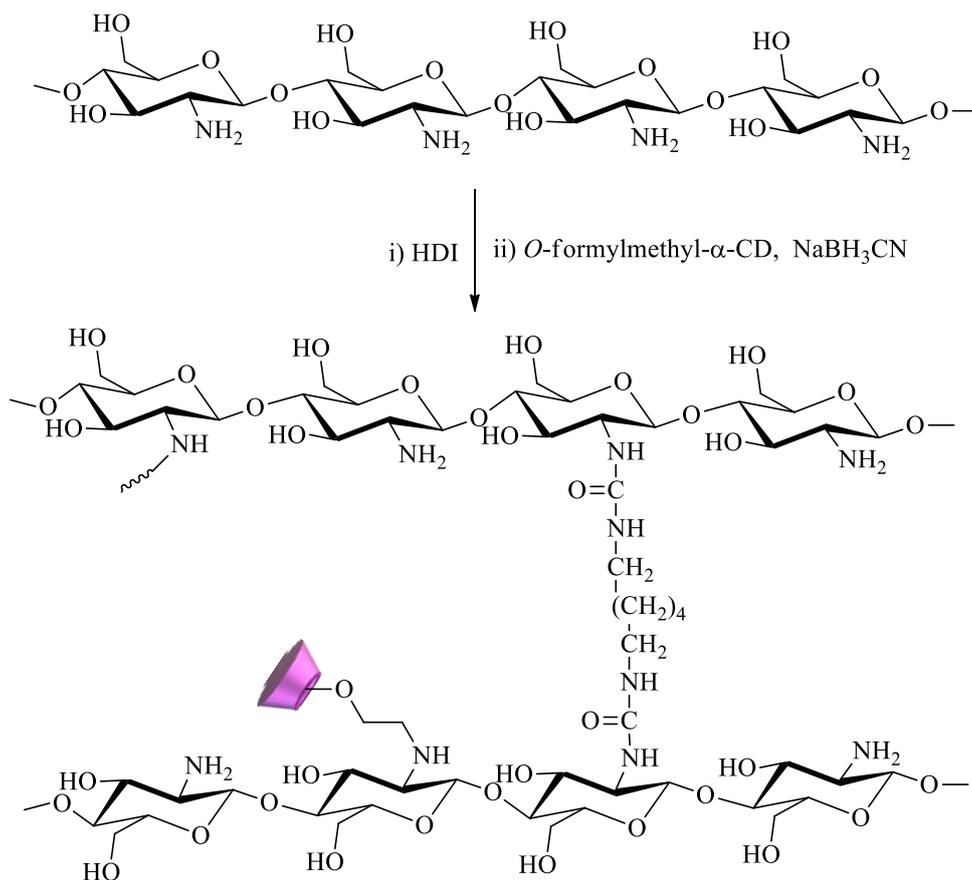
Scheme 4. CD–polycarboxylic polymer using ethylenediamine tetraacetic acid (EDTA) as a crosslinker.

Due to the success of this strategy for the synthesis of amphiphilic polymers, other crosslinkers like 4,4-difluorodiphenylsulfone, tetrafluoroterephthalonitrile, 4,4'-bipyridine, decafluorobiphenyl, bis(4-hydroxyphenyl)sulfone, and 4,4'-bis(chloromethyl)biphenyl have been tested [49,83,84].

2.1.2. Polysaccharides Having CDs as Pendant Groups

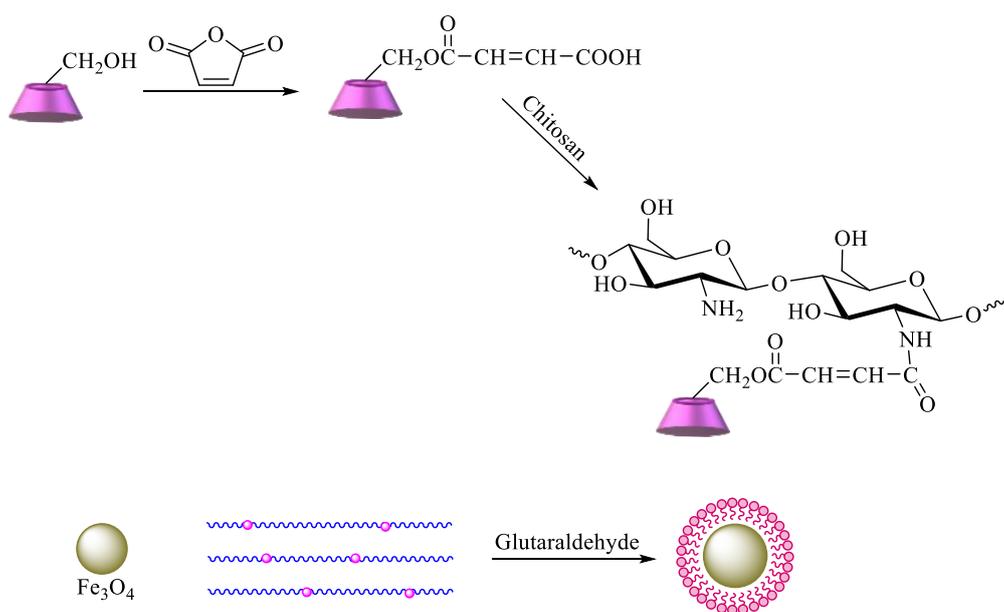
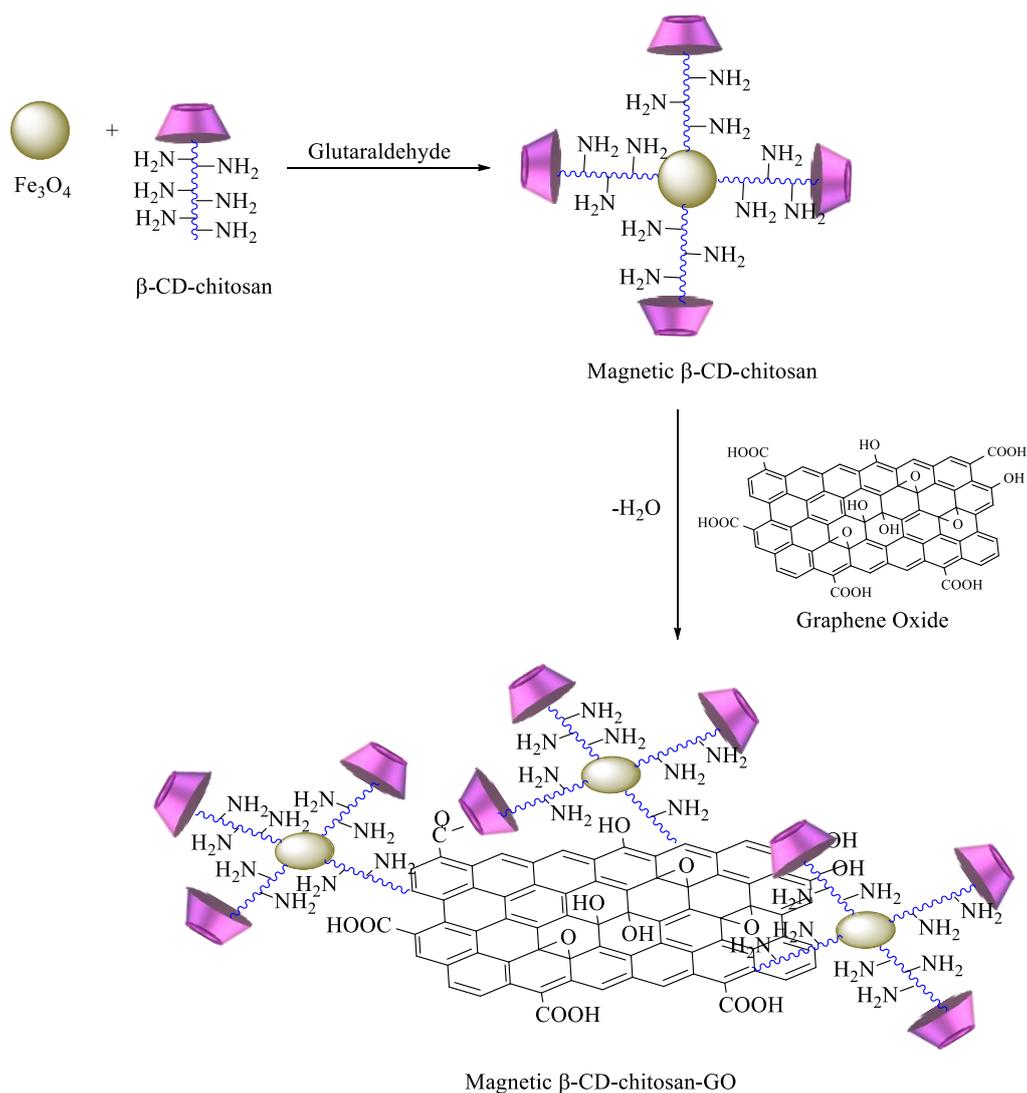
The immobilization of CDs onto natural polymers has been equally described for remediation purposes. Usually, low-cost natural polymers like cellulose, starch, or chitosan are chosen. Several synthetic procedures can be used with this objective, including the previous functionalization of CDs with appropriate reactive groups and the use of linkers. The former is achieved by substituting at least one hydroxyl group of CD with groups such as amino, tosyl, carboxyl, and carbonyl. The latter involves using coupling agents like the ones described above for CD–CD binding, including polyacids, diisocyanates, and, once again, epichlorohydrin [85].

Chitosan, a cationic biopolymer, can be easily obtained through the deacetylation of chitin, a natural polymer found in crustaceans. The presence in this compound of primary amine groups, which exhibit extensive reactivity, is a determining factor for its wide range of applications, including remediation. Owing to this, chitosan is probably the polysaccharide most commonly functionalized with CDs for water remediation. For example, Tojima et al. prepared water-insoluble chitosan beads using 1,6-hexamethylene diisocyanate as a crosslinker (Scheme 5). To this polymer, α -CD was anchored through reaction with 2-*O*-formylmethyl- α -CD in the presence of sodium cyanoborohydride [86,87].



Scheme 5. Chitosan crosslinked with 1,6-hexamethylene diisocyanate (HDI) and modified with α -CD.

A more complex strategy involves the use of magnetic nanoparticles to improve the reuse of adsorbent materials and the recycling of pollutants. Based on these advantages, chitosan functionalized with β -CD can be prepared by reaction of maleoyl- β -CD with chitosan via activation with 3-(ethyliminomethyleneamino)- N,N' -dimethylpropan-1-amine (EDC) and 4-dimethylaminopyridine. Then, β -CD-chitosan is linked to magnetic nanoparticles, namely, Fe_3O_4 , using glutaraldehyde (Scheme 6). The obtained polymer provides an enhanced surface area, leading to higher removal efficiency of pollutants [88]. Graphene oxide (GO) has also been commonly used for the synthesis of new materials, taking advantage of its properties, which include high surface area, a negatively charged surface, and water solubility [89]. Having that in mind, based on the previous description, new GO adsorbents containing CD-chitosan have also been synthesized using the route described in Scheme 7. In brief, maleoyl- β -CD reacts initially with chitosan and subsequently with magnetic particles (pH 8.0–9.0, 55 °C, 1.5 h) in the presence of glutaraldehyde. The carboxylic groups of GO are then reacted with EDC/*N*-hydroxysuccinimide, and the generated amide groups are crosslinked once again by using glutaraldehyde with β -CD-chitosan- Fe_3O_4 [90].

Scheme 6. Synthesis of β -CD-chitosan- Fe_3O_4 .Scheme 7. Synthesis of magnetic β -CD-chitosan-graphene oxide (GO).

Other strategies have been used for similar objectives. For instance, β -CD can be functionalized with monochlorotriazinyl groups and then reacted with chitosan via a substitution reaction [91]. In another study, Aoki et al. prepared crosslinked chitosan modified with β -CD by amidation of the former with succinic anhydride, followed by reaction with mono-6-amino-mono-6-deoxy- β -CD and a carbodiimide [92].

The availability of cellulose is much higher than that of chitin, but the lack of functional groups other than hydroxyl limits its usefulness. Crosslinked networks of carboxymethyl cellulose (CMC), one of the most common and easily synthesized cellulose derivatives, have been widely used as an absorbent in remediation. The grafting of CDs on CMC, achieved with epichlorohydrin in a basic medium, offers even greater versatility, reaching adsorption capacities of 8.55 mg g^{-1} for copper(II) ions [93].

Although chitosan and CMC are among the most cited polysaccharides, reference is also made in the literature to the use of other natural materials such as starch, wood flour, sawdust, and cotton for the removal of various pollutants [94]. Recently, we published a review on the ways to combine CDs and cellulose, with emphasis on pharmaceutical technology, textiles, and sensors, and, consequently, this topic will not be mentioned here [14,19,21].

3. Removal of Pollutants from Water and Wastewaters

In this section, we summarize the most important information related to the application of CD polymers (or copolymers) and CD-containing polysaccharides to the removal of four classes of water and wastewater pollutants: metal ions, dyes, pharmaceutical compounds, and pesticides. The appearance or persistence of such contaminants in natural water and wastewater, along with the respective adverse environmental effects, has boosted the number of studies focused on the adsorption of water pollutants by modified CDs [14].

Water and wastewater comprise a plethora of chemical species and organisms, including emergent and priority pollutants, antibiotic-resistance genes, and emerging pathogens. These entities are, in general, rarely monitored and controlled, toxic or carcinogenic, and nonbiodegradable [14].

The major classical concern about the effect of contaminants on the environment and human health has been associated with heavy metal ions, active ingredients in pesticides, and other persistent organic pollutants. Those detected in water and wastewater comprise (i) inorganic pollutants, including metal and arsenic ions [95], and (ii) organic pollutants composed of polycyclic aromatic compounds, benzene and dibenzofuran derivatives, phenol derivatives (encompassing naphthol derivatives), polychlorobiphenyls, surfactants, pharmaceutical residues, endocrine disruptors, and household and industrial chemicals [40]. Within the latter, organic dyes have been discharged into the environment by paper, textile, and cosmetics manufacturers.

3.1. Metal Ions

Heavy metal pollution is a concerning issue that humanity has struggled to deal with. The term “heavy metal” is defined rather vaguely: elements with specific gravity greater than four, regardless if they are considered metals or, as in the case of arsenic, metalloids [95]. Though naturally occurring, with some being biologically essential (e.g., copper and chromium are micronutrients [96]), industrial and domestic emissions have raised the concentration of these elements in natural environments to dangerous levels [97,98]. Recently, comprehensive reviews on the remediation of heavy-metal-containing residues have highlighted the priority of this topic in terms of the sources of pollution and different available technologies for their treatment [99–101].

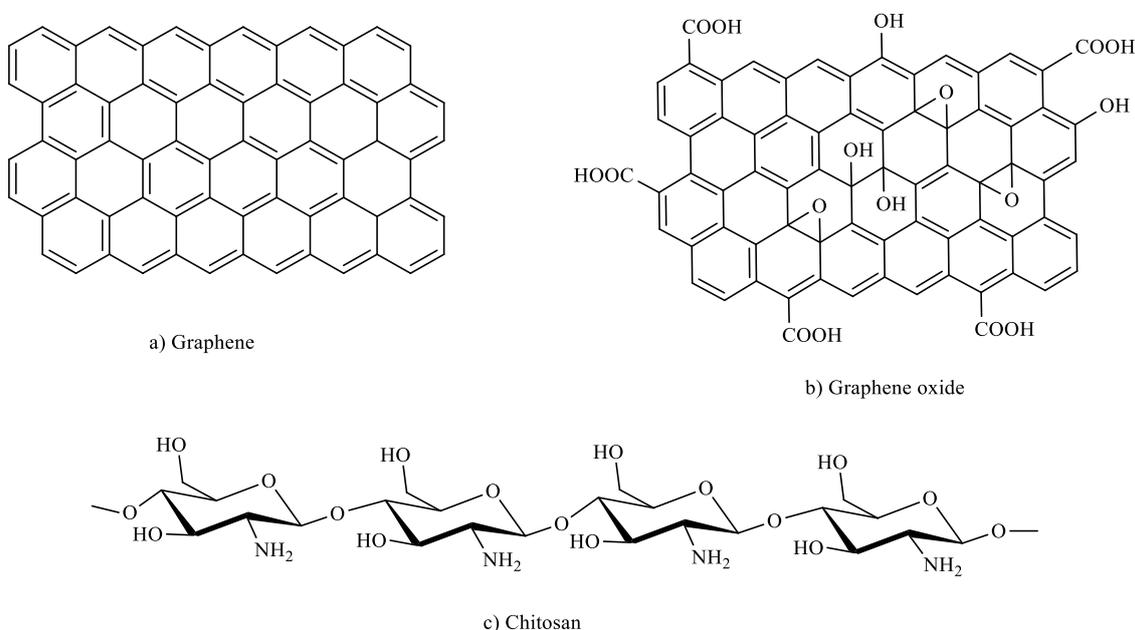
Due to its relevance, the application of CDs to heavy metal treatment has challenged many researchers. However, as we will note later, the effect of CDs on the retention and treatment of heavy metals is not remarkable. This is due to the molecular structure of CDs, i.e., the hydroxyl groups found at both rims of CDs, which have a low ability to coordinate with predominant cations [102–104]. This process depends on the pH; for

example, the interaction between Pb(II) and β -CD is characterized by a high association constant ($\log K_a = 15.5$) at a pH around 10.5 [105]. Against all setbacks, CD-based materials have been developed and assessed for metal ion removal from aqueous media [14].

The use of a polycarboxylic acid to polymerize CDs has been referred to as a promising strategy for the treatment of not only organic but also inorganic pollutants. One common choice of polyacid to perform this crosslinking is citric acid [106]. Poly(β -cyclodextrin-co-citric acid) was evaluated in terms of its removal capabilities towards Cu(II), showing a maximum removal efficiency (*RE*) of 58.6% at pH 6.1 and a maximum adsorption capacity, q_{\max} , of 31.4 mg g^{-1} [46]. However, by testing the effect of different aromatic compounds (bisphenol A and methylene blue (MB)) on simultaneous removal with Cu(II), while the maximum adsorption capacity of Cu(II) remained similar in the presence of bisphenol A, it decreased to 24.8 mg g^{-1} in the presence of MB. This is justified by a competitive interaction between MB and Cu(II) for the carboxylic groups of citric acid, highlighting the weak role of CD cavities in the removal process of the metal ion.

These CD polymers show some drawbacks in the adsorption process as a consequence of their low surface area and high swelling degree. A quick method to overcome that is the preparation of magnetic materials. Taking that into consideration, Badruddoza et al. [107] grafted a copolymer of carboxymethyl- β -CD and epichlorohydrin to the surface of Fe_3O_4 nanoparticles. The adsorption of metal ions (Pb(II), Cd(II), and Ni(II)) onto those nanocomposites led to the following q_{\max} : 64.5, 27.7, and 13.2 mg g^{-1} , respectively, at pH 5.5. These examples clearly suggest that the metal ion adsorption mechanism of CD-based materials is not based on host-guest interactions.

Another approach is the functionalization of polymers with CDs, chitosan being the most common candidate among polysaccharides. This is a consequence of the presence of amino and hydroxyl groups in its structure (Scheme 8), which can readily bind to some pollutants or, alternatively, be modified in order to improve its versatility [108,109]. Heavy metals are among the pollutants well adsorbed by chitosan or chitosan blends/composites [110,111].



Scheme 8. Structures of (a) graphene, (b) graphene oxide, and (c) chitosan.

Magnetic β -CD-chitosan nanoparticles were synthesized by Fan et al. [112]. Initially, by using maleic acid in the presence of 4-dimethylaminopyridine, β -CD is functionalized to form maleoyl- β -CD [113]. The latter compound is then grafted to the chitosan backbone. Following that, Fe_3O_4 nanoparticles are coated by β -CD-chitosan. A peculiar contribution was provided by Elanchezhian and Meenakshi [114], who synthesized chitosan- β -CD

using glutaraldehyde as a crosslinker in the presence of lanthanum, zirconium, or cerium ions. These metal ions were integrated into the adsorbent.

The use of chitosan also shows some drawbacks, including a low compressive strength and the difficulty of producing monoliths. Such limitations can be overcome by the incorporation of graphene oxide onto the polymer structure [115,116]. This hydrophilic derivative of graphene (Scheme 8b,c) has a lower content of carbon in favor of a higher amount of oxygen in the form of hydroxyl, carboxyl, and epoxy groups. This modification of the graphene structure makes GO easily dispersible in aqueous media. Furthermore, GO retains much of the properties of the highly valued pristine graphene, being easier to prepare and process, cheaper [117], and a good candidate for an adsorbent of different types of pollutants [115,118]. It should be stressed that the grafting of CD to GO sheets can also result in a satisfactory adsorbent for metal ions [119,120].

In order to improve the stability of chitosan, as described above, β -CD–chitosan/GO materials have been prepared by Li et al. [121]. The procedure consists of reacting the amine group of chitosan with GO's carboxyl group, forming an amide. The obtained material shows good sorption ability towards Cr(VI). Clearly, the sorption process of this metal ion is slightly different from others, given that Cr(VI) is present in the solution as oxyanions, i.e., CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, or HCrO_4^- [122]. The maximum adsorption capacity for Cr(VI), taking into account all the three anionic species, is 67.66 mg g^{-1} . The mechanism of adsorption is not straightforward since it initially involves electrostatic interactions between the protonated amine groups of chitosan and the chromium-containing anions, followed by the reduction of Cr(VI) to Cr(III) and the consequent interaction with either the carboxylic groups of GO or the β -CD [123].

Cellulose–CD materials have also been studied for the absorption of metal ions. Li et al. [124] modified filter paper with β -CD, using citric acid as a crosslinker. This way, the hydroxyl groups of cellulose and those of β -CD underwent simultaneous esterification with the polyacid. The functionalized filter paper showed a significant adsorption capacity for Cu(II) (39.1 mg g^{-1}) when compared to unmodified filter paper (0.62 mg g^{-1}). As was previously discussed, citric acid, and not the CD cavity, had the main role in the sorption process [124].

3.2. Dyes

More than 100 tons of organic dyes are produced annually [125,126]. This demand is due to the need for colorants for a broad number of industries, including textile [127], leather [128], food [129], and solar cells [130], with a significant part being wasted in the dyeing process [131]. Organic dyes are, in general, nonbiodegradable, toxic, and carcinogenic contaminants present in water, leading to a significant impact on biotic systems and ecosystems [132,133].

Due to its relevance in wastewater, there are several methods that may be used for the removal of dyes from industrial wastewater. They include advanced oxidation [134,135], electrochemical processes [136], and adsorption [137]. The latter method has been extensively used for the discoloration and removal of dyes from wastewater due to its low price, easy availability, and efficiency [138].

Cyclodextrins are among the most used compounds for the removal of dyes and other contaminants from different waste sources [139,140].

3.2.1. CD Polymers

One material successfully proven to act as a sorbent of some dyes is the polymerized β -CD derivative 2,3-di-*O*-methacrylated-6-*tert*-butyldimethylsilyl)- β -CD, using 1-vinylimidazole as a crosslinker [52]. This polymer presents high adsorption removal efficiencies for congo red (CR) and rhodamine B (RB), above 80%, with q_{max} equal to 712 and 175 mg g^{-1} , respectively. Here, in contrast to the metal ion adsorption mechanism, the dyes interact with the CD cavities by forming stable host–guest supramolecular complexes, characterized by stability constants of 1667 and 4266 M^{-1} [141,142], respectively.

However, whilst hydrophobic and π - π interactions are the predominant mechanism for RB adsorption, for CR, electrostatic interactions between the sulfonate groups of the dye also occur [52].

Based on the high ability of CDs to interact with dyes via hydrophobic interactions, the polymerization of CDs is a logical way to synthesize highly efficient adsorbents. Among the different possibilities, the use of epichlorohydrin (EPI) or 4,4'-bis(chloromethyl)biphenyl as a crosslinker is the most common route [9,18].

Recently, β -CD and hydroxypropyl- β -CD (HP- β -CD) were polymerized with EPI. The adsorption of Direct Red 83:1 and Direct Blue 78 onto those polymers was analyzed [16,17]. For an initial concentration of dye equal to 300 ppm, the maximum adsorption capacity for β - and HP- β -CD polymers were, respectively, 13.4 and 3.3 mg g⁻¹. The mechanism of interaction between the dye and different CDs is still unclear. However, a similar trend of adsorption capacity was found for the adsorption of the same dye onto polymeric adsorbents based on α -CD and HP- α -CD [68]. The adsorption of Direct Blue 78 onto a poly(β -cyclodextrin-co-EPI) copolymer also showed high efficiency, with a q_{\max} of 23.47 mg g⁻¹. However, the study was complemented by the use of advanced oxidation processes (AOPs) to remove the remaining dyes. By using the techniques in a sequential way, the removal efficiency of Direct Blue 78 was higher than 99%.

The development of adsorbents for the simultaneous adsorption of dyes (or other pollutants) is always challenging since it depends, in general, on different types of interactions. Following that, the development of poly(β -CD) with the ability of simultaneous sorption of dyes with an opposite charge was carried out by Zhou et al. [143]. The adsorbent was synthesized in a two-step sequence: initially, the β -CD is polymerized via esterification with citric acid; in a second step, the grafting of 2-dimethylamino ethyl methacrylate takes place. The obtained material contains, besides the hydrophobic cavity of the CD, carboxylic groups and tertiary amino groups, providing, in this way, a multitude of sites for the interaction of both cationic and anionic dyes, respectively. The adsorption studies of methylene blue (MB, a cationic dye) and methyl orange (MO, an anionic dye) onto the PCD grafted with 2-dimethylamino ethyl methacrylate showed high q_m values: 335.5 and 165.8 mg g⁻¹, respectively. However, these values were obtained at different pH conditions: 11, 4, and 6.5, respectively. This dependence on environmental conditions hinders the broad use of this pH-responsive material.

3.2.2. Chitosan-Based Sorbents

In a similar way to what was observed for the adsorption of metal ions, chitosan was tested as a polymeric matrix for the adsorption of a large number of different dyes. Zhao et al. measured the removal efficiency of blends of chitosan with poly(β -CD-co-citric acid) for the following set of dyes: C.I. Reactive Blue 49, Reactive Yellow 176, Reactive Blue 14, Reactive Black 5, and Reactive Red 141 [144]. It was found that this blend is highly effective for dye removal, with an *RE* higher than 90%, besides attaining higher q_{\max} values (e.g., for Reactive Blue 49, $q_{\max} = 498$ mg g⁻¹). Such performance is due to the occurrence of electrostatic interactions between the sulfonate groups of all dyes and the protonated ammonium groups of chitosan (pK_a ca. 6.5) [145], along with hydrogen bonding between the amine groups of dyes and the hydroxyl groups of chitosan.

Another blend composed of chitosan and poly(β -CD)/vinyltriethoxysilane copolymer was prepared as a membrane. This membrane was shown to possess high porosity as a consequence of electrostatic repulsion (or steric hindrance) between the CD units and chitosan [146]. Maximum adsorption capacity (13.4 mg g⁻¹) was reached for Acid Red 299. That lower value, associated with an endothermic adsorption process, which might be related to the need to overtake a polymer interface to reach the binding sites, makes the use of membranes rather limited.

The use of γ -CD is not very common because it is expensive and the size of the inner cavity is too large, leading to weak host-guest interactions [147]. Even so, some works report combinations of the largest natural CD with polysaccharides. For example, γ -CD can

be grafted onto starch (from corn) by using epichlorohydrin as an anchor. The adsorption capacity of the material was tested towards Methylene Blue (MB), Methyl Purple, and Congo Red (CR); the former two dyes are cationic and the latter (CR) is anionic. Despite the association constants for the formation of complexes between γ -CD and CR and MB being 3800 M^{-1} [148] and $2.95 \times 10^7 \text{ M}^{-2}$ [149], respectively, REs for all three dyes were around 60% [150].

A different method was followed to prepare a graphene-oxide-containing chitosan/ β -CD hydrogel [151] that consists of mixing β -CD, chitosan, and GO in the presence of genipin and sodium ascorbate as reducing agents [50]. Genipin is a well-known crosslinking agent, widely used for the crosslinking of chitosan; it exhibits reduced toxicity when compared to, for example, glutaraldehyde. Therefore, genipin can promote the linkage between the hydroxyl groups of GO and CD and the amino groups of chitosan. By using MB as a dye model, it has been found that with an initial MB concentration equal to 50 ppm, the adsorption capacity of the CD-containing gel is ca. 225 mg g^{-1} , 50% higher than the hydrogel without CD [151]. However, the maximum adsorption capacity found for chitosan is ca. 5 times higher (1134 mg g^{-1}). This significant adsorption capacity is due to the occurrence of a mesoporous structure associated with the electrostatic interactions between the dye and the adsorbent. In fact, a relevant dependence of the adsorption capacity of MB on pH and ionic strength has been found. This may indicate the occurrence of a screening effect on electrostatic interactions [152].

3.2.3. Cellulose-Based Sorbents

Cellulose chains, although insoluble in water [153], have many active hydroxyl groups. Hence, this linear homopolymer can be chemically modified so as to be capable of forming supramolecular interactions with organic dyes [154].

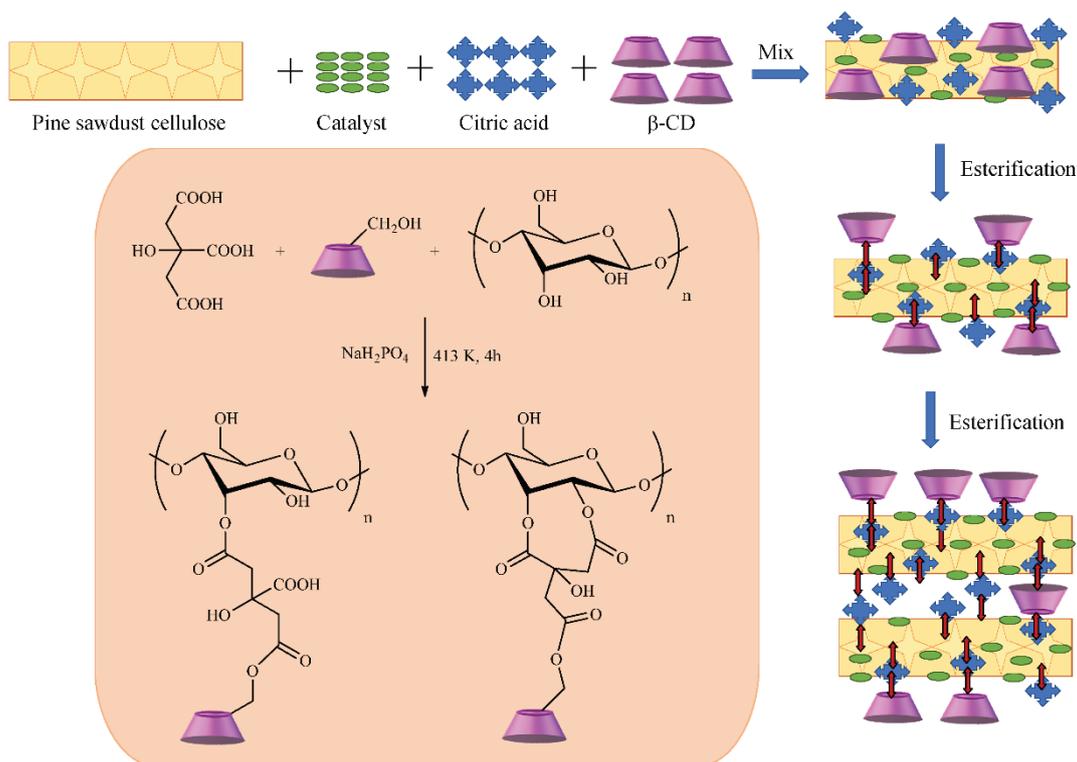
In the previous section, the use of modified filter paper for adsorption of Cu(II) was described [124]. The success of that type of material is of utmost importance, given that the paper companies are incessantly looking for new innovative products and markets. Additional to Cu(II), the adsorption of MB, Brilliant Green, and Rhodamine-B onto modified filter paper has also been evaluated [154]. The modified filter paper was able to adsorb 124.5, 130.4, and 99.7 mg g^{-1} of MB, RB, and BG, respectively. These values drastically decreased to 41.4 and 29.6 mg g^{-1} (for MB and RB, respectively) when the adsorbent material contained 70% of pristine (nonmodified) filter paper, clearly indicating the importance of CD in the adsorption process.

Cotton fiber, a natural fiber consisting almost entirely of cellulose, is a renewable, degradable, cheap, and nonpolluting material. Furthermore, cotton fiber presents a large specific surface area and a hollow, flat-banded structure, which is beneficial for adsorption. Based on that, Yue et al. [155] grafted an amino-terminated hyperbranched polymer, obtained by melt polycondensation of methyl acrylate, diethylene triamine [156], and β -CD onto cotton.

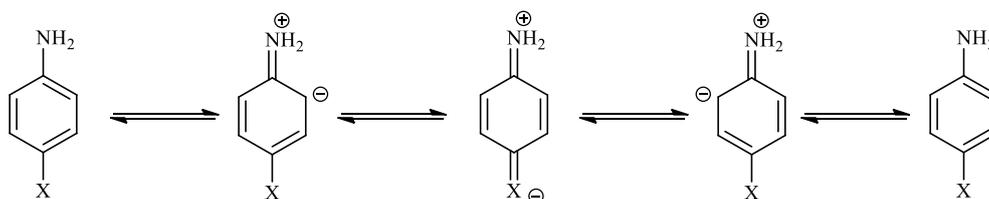
In summary, the chemical modification of cotton occurs after initial oxidation with sodium metaperiodate to obtain dialdehyde-cotton. Subsequently, the modified cotton reacts with β -CD in the presence of EPI. At the end of the process, the hyper-branched polymer is added, and the reaction with the modified cotton occurs between amino groups of the former and the aldehyde groups of cotton. The resulting polymer shows high RE and high q_{max} for Congo Red (94% and 300.8 mg g^{-1} , respectively); however, for MB, the performance is more modest, leading to 42% and 98.7 mg g^{-1} , respectively. Such behavior is explained by the possibility of MB aggregation [155], which hampers adsorption.

As described before, citric acid is commonly used as a crosslinker for the binding of CDs to cellulose-based materials by forming an ester linkage. Zhou et al. [106] have studied the functionalization of pine sawdust (PS) with β -CD by esterification with citric acid (CA) for aniline remediation (Scheme 9). Aniline and derivatives (Scheme 10) are frequently used as organic intermediates in the process of producing dyes, rubber, medicine, and paint. Due to its toxicity and recalcitrant properties, it is highly necessary to develop strategies

for removing aniline from aquatic media [157]. The q_{max} of PS–citric acid–CD towards aniline is 12.3 mg g^{-1} , more than twice the adsorption capacity of PS functionalized with citric acid (5.8 mg g^{-1}). Such improvement is due to the structure of the sawdust; i.e., cell walls of sawdust mainly consist of cellulose and lignin, and many hydroxyl groups are present in tannins or other phenolic compounds. Moreover, the presence of CD improves the sorption capacity through host–guest hydrophobic interactions and hydrogen-bonding via carboxylic groups, whereas PS–citric acid only contains carboxyl groups. In addition, aniline can be protonated, and its pK_a strongly depends on the substituents [158], promoting a further sorption process: the ion-exchange mechanism.



Scheme 9. Pine sawdust modified with β -CD. Adapted with permission from [106]. Copyright (2020) American Chemical Society.



Scheme 10. Resonance structures for aniline derivatives.

A possible approach was reported by Ghemati and Aliouche [159]. The authors modified β -CD through its reaction with *N*-methylol acrylamide to form acrylamidomethyl- β -CD. After that, the modified CD was grafted onto cellulose. The obtained polymer presents a q_{max} for MO and MB ca. 11 and 14 mg g^{-1} at pH 3 and 11, respectively.

3.3. Pesticides

Pesticides are the main organic pollutants used worldwide; they are applied to prevent plant diseases and to improve food quality. Although their initial impact is on soil pollution, by leaching and desorption mechanisms, they end up contaminating water bodies. In general, pesticides are not soluble in water, which limits the choice of remediation. For this

reason, removal strategies based on cyclodextrins have a great advantage in solubilizing and removing such contaminants [7,160]. However, few studies have involved the design and application of CD-based adsorbents for pesticides.

In an attempt to develop highly efficient CD polymers for the separation and removal of ten different pesticides, polycyclodextrins involving only one type of CD or equimolar mixtures of two cyclodextrins, using EPI as a crosslinker, were synthesized as spherical porous particles [44]. The adsorption kinetics and isotherms of the pesticides on the polycyclodextrins showed that adsorbents with a homogeneous open network structure were able to absorb pesticides through multiple adsorption interactions, including inclusion in the CDs, loading into swelling water, and even physical adsorption on the network. Furthermore, the removal efficiency is dependent on the CD content, swelling degree, and surface area. Butenefipronil and fipronil, pesticides with a high octanol–water partition coefficient, showed higher REs, proving that hydrophobic interactions with the CD are of paramount importance in the adsorption mechanism.

Another valuable contribution involves the use of poly(β -CD-co-EPI) for packing a bed for the removal (“trapping”) of pesticides [62]. Using 2-naphthol as a pesticide model, the authors found that the trapping efficiency was around 70%. This removal efficiency is dependent on the acid-base equilibria occurring in natural waters. It was also found that the best trapping efficiencies were obtained for beads with polymers containing a high percentage of EPI, i.e., polymers with a nominal CD/epichlorohydrin ratio of 1:29.

CDs inside nanoporous carbon have also displayed great efficiency for removing the *p,p'*-substituted diphenyl class of pesticides (e.g., DDT, DDD, and DDE). These pesticides showed significant adsorption due to their suitable geometric fit within the cavity of the CD, leading to the formation of stable inclusion complexes (Zolfaghari 2016).

The sorption of two halogenated monophenolic pesticides, 4-chlorophenoxyacetic acid and 2,3,4,6-tetrachlorophenol, by CD polymers in the form of nanosponges has also been assessed and its performance compared with other materials, namely, granulated activated carbon [12]. These designed nanosponges have displayed favorable sorption capacities for chlorinated aromatic guests. The sorption capacity and binding affinity of the sorbents were greater for nanosponges, despite granulated activated carbon possessing a greater surface area. It was suggested that nanosponges possess additional properties, such as serving as stabilization enhancers of nanoparticles.

Among the various methods employed to remove paraquat (a toxic herbicide commonly used for weed and grass control) from aqueous systems, adsorption has demonstrated higher efficiency, straightforward operation, and low cost. Junthip et al. [161] have proposed and tested the adsorption of paraquat in aqueous solutions using a textile coated with anionic polycyclodextrin, with citric acid as an anchor agent. The removal performance was assessed considering different conditions, including an initial concentration of pesticide, pH of the solution, and adsorption temperature. It was found that neutral pH and lower temperatures favored the adsorption of the pesticide on the functionalized textile. The reusability of the material was also relevant, reaching 78.6% of the maximum adsorption capacity after 6 regeneration cycles [161].

3.4. Pharmaceutical Compounds

Pharmaceuticals, including analgesics, anti-inflammatory drugs, and antibiotics, have been introduced into the environment via several routes, including farming, households, medical facilities, hospitals, and pharmaceutical industries. Specifically, these include those compounds that are frequently used and found in wastewater, including ibuprofen, acetaminophen, amoxicillin (β -lactams), streptomycin (amino-glycosides), ciprofloxacin (fluoroquinolones), azithromycin and clarithromycin (macrolides), penicillin, penicillin/streptomycin combinations, and tetracyclines, just to name a few examples [14].

Among the most consumed pharmaceuticals worldwide, ibuprofen is a nonsteroidal anti-inflammatory drug, largely distributed without prescription. Its occurrence in environmental matrices has been markedly observed in industrial and agricultural waste streams,

municipal/hospital wastewater, and surface water. In another context, high concentrations of veterinary drugs, such as ionophore antibiotics, have been detected in sediments and in water (in lower concentrations). Ibuprofen, diclofenac, and gemfibrozil have also been identified in sewage sludge.

Insoluble CD polymers have been employed as cost-effective adsorbents in these scenarios due to their attractive removal performances and the higher number of cycles when compared to conventional strategies [9].

Shahgaldian's group [162] prepared three water-insoluble CD-based polymers aimed at removing three selected pharmaceutically active ingredients—levofloxacin, aspirin, and acetaminophen—in aqueous solutions. The highest sorption capacity was obtained with β -CD polymer, which displayed a higher affinity for aspirin. In general, the interaction kinetics were proved to be fast, reaching 70% of equilibrium sorption capacity within only 10 min.

Moulaheene et al. [163] have proposed insoluble CD-based polymers with high adsorption capacities, containing different types of CD molecules crosslinked with citric acid, towards the removal of ibuprofen in aqueous solutions. Ibuprofen retention in the CD polymers decreased in the following order: α - γ -CD > α -CD > γ -CD > β -CD > α - γ - β -CD. The effect of various operating variables, such as pH, ionic strength, contact time, drug concentration, and mass of adsorbent was evaluated. Maximum adsorption capacity was achieved in acidic pH, in which ibuprofen was in its molecular form, favoring electrostatic interaction and the formation of an inclusion complex. Ionic strength also contributed to increasing the removal performance of the CD polymers. In a similar study [164], the progesterone removal capacity in aqueous solutions of various polycyclodextrins crosslinked with citric acid was investigated. Adsorption capacities up to 20 mg g⁻¹ and removal efficiencies over 80% were obtained. The authors concluded that (i) poly(β -cyclodextrin) showed the best adsorption capacities, a larger number of reuse cycles than activated carbon, and fast adsorption kinetics; (ii) no significant effect of initial pH, initial concentration, and adsorbent amount on the adsorption capacity was observed; (iii) adsorption increased with ionic strength and temperature.

The detection and quantification of diclofenac, a highly efficient and widely consumed anti-inflammatory drug, in water and wastewater samples (in the range 0.3–15.9 mg L⁻¹) have also been developed [165] by resorting to a polycyclodextrin containing a fluorescent dye. The optimal concentration of the sorbent was found to be 50 g mL⁻¹, and the limit of quantification of diclofenac was 0.3 mg L⁻¹.

The nucleophilic substitution of β -CD with tetrafluoroterephthalonitrile (TFP) has been conducted by Zhou et al. [166], aiming at preparing a poly(β -CD) for removing bisphenol A (BPA), chloroxylenol (PCMX), and carbamazepine (CBZ). The maximum adsorption capacities of that poly(β -CD) were shown to be 164.4, 144.1, and 136.4 mg g⁻¹ for BPA, PCMX, and CBZ, respectively. The polymer was able to be regenerated for 5 cycles by methanol soaking, and the removal efficiency of BPA, PCMX, and CBZ was 98.1%, 90.8%, and 65.0%, respectively. The authors found no significant effect of pH, fulvic acid concentration, or ionic strength on the adsorption of the drugs onto the CD polymer.

4. Conclusions

Several strategies have been explored to remediate water pollution by different contaminants, taking advantage of the versatile properties of CD polymers and CD-containing polysaccharides. The most promising combination of CD materials for water remediation must be scaled-up and tested in the field. The selection of the best CD adsorbing materials should be based on the specificity of the target environmental matrix, the nature and concentration of the contaminants, the applicability in situ, removal efficiency, and economic feasibility.

Contaminant removal with CD-based materials should be prioritized over ongoing studies on a lab-scale by considering systematic procedures for assessing the performance of

CD polymers, CD-containing polysaccharides, and other conventional materials, allowing the achievement of effective environmental applications.

Theoretical and/or computational models of the involved interaction patterns/mechanisms are still very scarce; however, they could provide comprehensive rationales for improving the knowledge on the underlying mechanisms that govern the structural modification, performance, and recycling of CD adsorbing materials and on the solubilization and recognition of contaminants.

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Abbreviations

BPA	bisphenol A
CBZ	carbamazepine
CD	cyclodextrin
CMC	carboxymethylcellulose
EDTA	ethylenediamine tetraacetic acid
EPI	epichlorohydrin
GO	graphene oxide
HDI	1,6-hexamethylene diisocyanate
HP- β -CD	hydroxypropyl- β -cyclodextrin
MB	methylene blue
MDI	4,4'-diphenylmethane diisocyanate
NDI	1,5-naphthalene diisocyanate
PCMX	chloroxyleneol
PDI	1,4-phenylene diisocyanate
PS	pine sawdust
TDI	2,4-toluene diisocyanate

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