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Review

Achievements in Preparation of Cyclodextrin–Based Porous Materials for Removal of Pollutants

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Abstract: Cyclodextrin–based porous materials have been widely applied in removing various organic pollutants from water environments, due to their unique physical and chemical properties, like the size–matching effect and hydrophobic interaction. Large numbers of hydroxyl groups in its external structure give cyclodextrin a high solubility in water, but the existence of these hydroxyl groups also endows cyclodextrin with the ability to be chemically modified with various functional groups to reduce its solubility in water and, meanwhile, to develop some novel functionalized cyclodextrin–based porous materials for selective removal of the target organic pollutants. This review focuses on the recent development in the synthesis of cyclodextrin–based porous materials (crosslinked cyclodextrin polymers and immobilized cyclodextrins), as well as highlighting their applications and mechanisms in the removal of dyes, endocrine disruptors, and mixed pollutants from water. Finally, the challenges and future perspectives in related research fields are discussed.

Keywords: β–cyclodextrin; adsorption; pollutants; porous materials

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1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides constructed by multiple D–glucose units connecting end–to–end via α–1 and 4–glucoside bonds, occurring naturally from starch through degradation with the enzyme cyclodextrin glucanosyltransferase [1,2]. Based on structural characteristics, cyclodextrins are divided into three types, namely α–cyclodextrin (α–CD), β–cyclodextrin (β–CD), and γ–cyclodextrin (γ–CD), and the number of glucopyranose units contained in the molecular structure of these three cyclodextrins is 6, 7, and 8, respectively [3,4]. Some important physicochemical parameters of the three CDs are listed in Table 1. Throughout the entire research and application history of cyclodextrins, the development of efficient and scalable methods for the preparation of cyclodextrins and their homologues has always been a popular topic of researchers worldwide. Recently, to solve the problem of the availability of cyclodextrins with smaller or larger cavity sizes, chemists have developed some novel chemical or enzymatic synthetic strategies for efficient preparation of multiple cyclodextrin homologues [5,6]. However, all known cyclodextrins were previously only composed of D–glucose. This situation changed when Prof. J. Fraser Stoddart of Northwestern University and Prof. Daniel W. Armstrong of the University of Texas at Arlington collaborated to report the synthesis of three mirror–like cyclodextrins for the first time [7]. In that work, two simple and easily available monosaccharide donors and acceptors were designed and synthesized from commercially available L–glucose. The diastereoselective construction of multiple consecutive 1,2–*cis* L–glycosidic bonds, one–pot rapid assembly of linear glycans, and efficient cyclization were achieved. More importantly, the half–gram preparation of α–, β–, and γ–L–CDs was completed. These advances made

in the preparation of cyclodextrins and their homologues greatly promotes the industrial application of cyclodextrins and cyclodextrins–based functional materials.

Table 1. Physicochemical parameters of three naturally formed CDs [8].

	α–CD	**β–CD**	**γ–CD**
Number of glucose units	6	7	8
Molecular weight (g/mol)	972.0	1135.0	1297.0
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
Cavity volume ($Å^3$)	174.0	262.0	427.0

Seen from a top view in three–dimensional space, cyclodextrin exhibits a conical cylinder structure with a cavity of 4.7~8.3 Å built by the glucose units. All the hydroxyl groups connected to these glucose units are distributed on the outer side of the cylinder, and thus a hydrophobic region is formed in the inner cavity due to the shielding effect of C–H bonds, which gives the cyclodextrin molecule the characteristics of "outer hydrophilic and inner hydrophobic" [9]. It is precisely because of this structural property that some hydrophobic guest molecules can be identified by cyclodextrins to form the inclusion compounds via the size–matching effect and hydrophobic interactions, and to selectively separate the guest molecules from aqueous solutions [10]. Until now, cyclodextrin–based porous materials have been widely used in removing dyes [11–13], heavy metal ions [14–16], endocrine disruptors (EDCs) [17,18], and other organic pollutants from aqueous solutions due to their wide availability of raw material, low cost, environmental friendliness, and ease of degradation [19]. Among the three cyclodextrins, β–CD, as shown in Figure 1, has attracted the most extensive attention due to its greater advantages of low cost, easy availability, and moderate cavity size compared with other two cyclodextrin molecules.

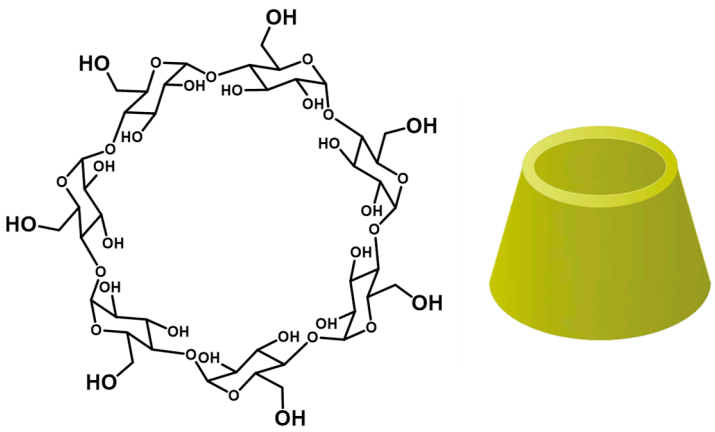

Figure 1. Molecular structure of β–CD (**left**) and its model diagram (**right**).

However, the high solubility of β–CD in aqueous solutions resulting from its hydrophilic nature also limits its application in the removal of contaminants from aqueous solutions [20,21]. At present, two main methods have been used to reduce the solubility of cyclodextrin in aqueous solutions while improving the adsorption performance of cyclodextrin–functionalized materials for guest pollutants. One is to directly use cyclodextrin molecules as monomers to polymerize with the addition of crosslinking agents to obtain crosslinked cyclodextrin polymers [22,23]. The other is to load cyclodextrin onto the different supports by crosslinking agents to prepare cyclodextrin–based porous materials. In addition, researchers have also developed some other new methods, such as molecular imprinting (MIP) [24–26] and ionic imprinting (IIP) [27,28] to synthesize some cyclodextrin–functionalized adsorbents for special applications.

In contrast to other outstanding reviews that have been reported, the latest progress of cyclodextrin–based materials (cyclodextrin polymers, immobilized cyclodextrins, and imprinted cyclodextrins) for removal of pollutants (including inorganic and organic pollutants) from aqueous solutions is presented in detail from a broad perspective. This review minutely summarizes the reported synthetic methods for the preparation and modification of *β*–CD–based porous materials including crosslinked *β*–CD polymers and immobilized *β*–CD composite materials. Additionally, the adsorption properties of *β*–CD porous materials for some specific pollutants such as dyes, EDCs, and mixed pollutants are also summarized, and the adsorption mechanisms of these materials for specific pollutants are discussed. Furthermore, the challenges and future research directions for *β*–CD–based porous materials are also discussed.

2. Crosslinked *β*–CD Polymers

Crosslinked *β*–CD polymers with a large crosslinking network and intrinsic mesoporous structure can be prepared through the crosslinking reaction between *β*–CD molecules and crosslinking agents. These crosslinked *β*–CD polymers have unoccupied cavities and can form inclusion compounds with pollutant molecules through host–guest interactions [29]. In addition, some chemical groups, such as –OH, –COOH, and –NH_2–, contained in these crosslinkers can serve as active sites for adsorption pollutants through electrostatic or hydrogen bonding interactions [30].

To date, the main crosslinking agents that have been reported for crosslinking polymerization of *β*–CD include epichlorohydrin (EPI) [31–33], diisocyanate [34–36], anhydride [37,38], citric acid (CA) [39–41], ethylene diamine tetraacetic acid (EDTA) [42,43], and tetrafluorophenonitrile (TFN) [44–46]. The molecular structures of these crosslinking agents are shown in Figure 2.

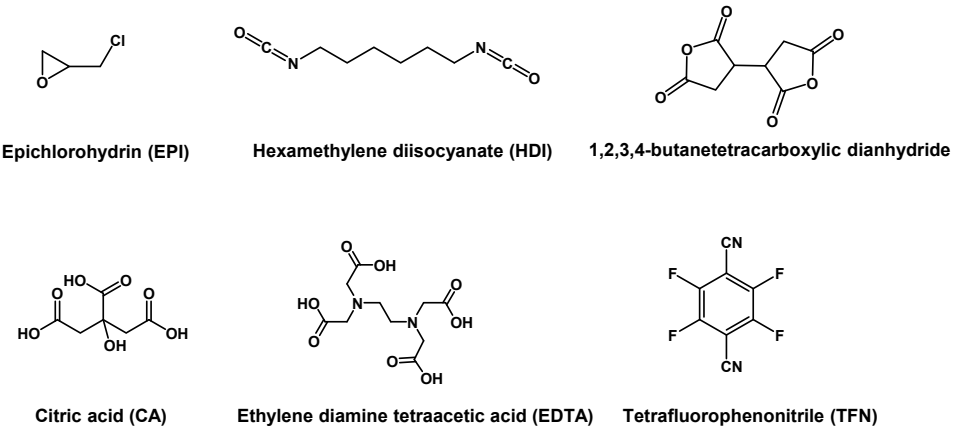

Figure 2. The structure of some crosslinking agents.

EPI is an inexpensive crosslinking agent and has been widely used to prepare the polymer materials for over past 50 years due to its much more easily achievable crosslinking reactions compared with other crosslinking agents [47]. Under alkaline conditions, EPI can crosslink *β*–CD molecules by the condensation reaction between the chemical groups of EPI and hydroxyl groups present in *β*–CD, forming a network structural polymer containing *β*–CD units (Figure 3) [48]. The *β*–CD polymers crosslinked by EPI are among the most widely studied *β*–CD materials so far; they are not only simple to synthesize, but also have excellent adsorption performance for organic pollutants (Table 2) [47,49].

In 2003, Crini et al. [50] synthesized three insoluble *β*–CD polymers, polymer 1 (150 mg of *β*–CD per gram of polymer), polymer 2 (200 mg of *β*–CD per gram of polymer), and polymer 3 (240 mg of *β*–CD per gram of polymer), using EPI as the crosslinking agent. The adsorption capacities of these materials towards some typical dyes (Figure 4a) were investigated. Compared with that of starch, the adsorption capacity of polymer 3 for C.I. Acid Blue 25 (AB 25), C.I. Reactive Blue 19 (RB 19), C.I. Disperse Blue 3 (DB 3), and C.I. Direct

Red 81 (DR 81) was much higher (Figure 4b), which was mainly attributed to the strong host–guest interaction of β–CD. However, the adsorption capacity of polymer 3 to C.I. Basic Blue 3 (BB 3) was very low, which was possibly because BB 3 is a cation dye (Figure 4b), and its dye–polymer interaction was thus weakened by the electrostatic repulsion effect. Meanwhile, with an increase in β–CD content in polymers from 1 to 3, the adsorption capacities of the material for five dyes gradually increased (Figure 4c), demonstrating that β–CD played a key role in the adsorption of dyes from aqueous solutions.

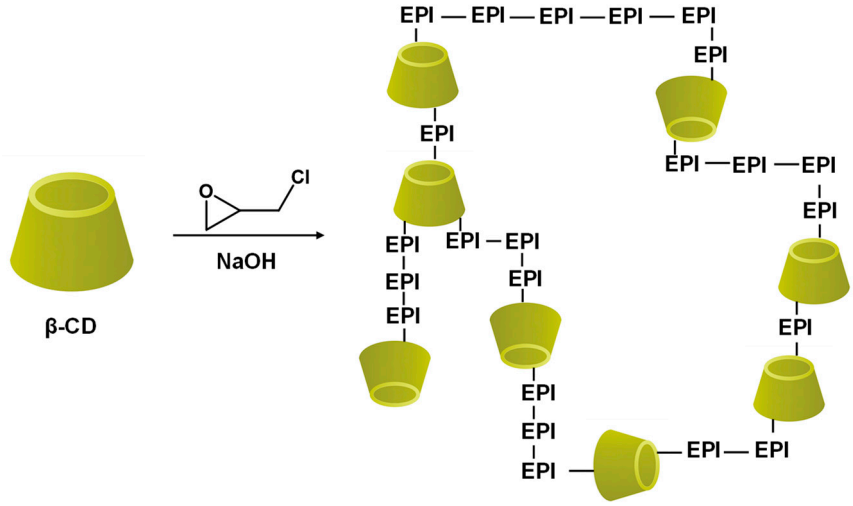

Figure 3. Crosslinking reaction of β–CD with epichlorohydrin [51].

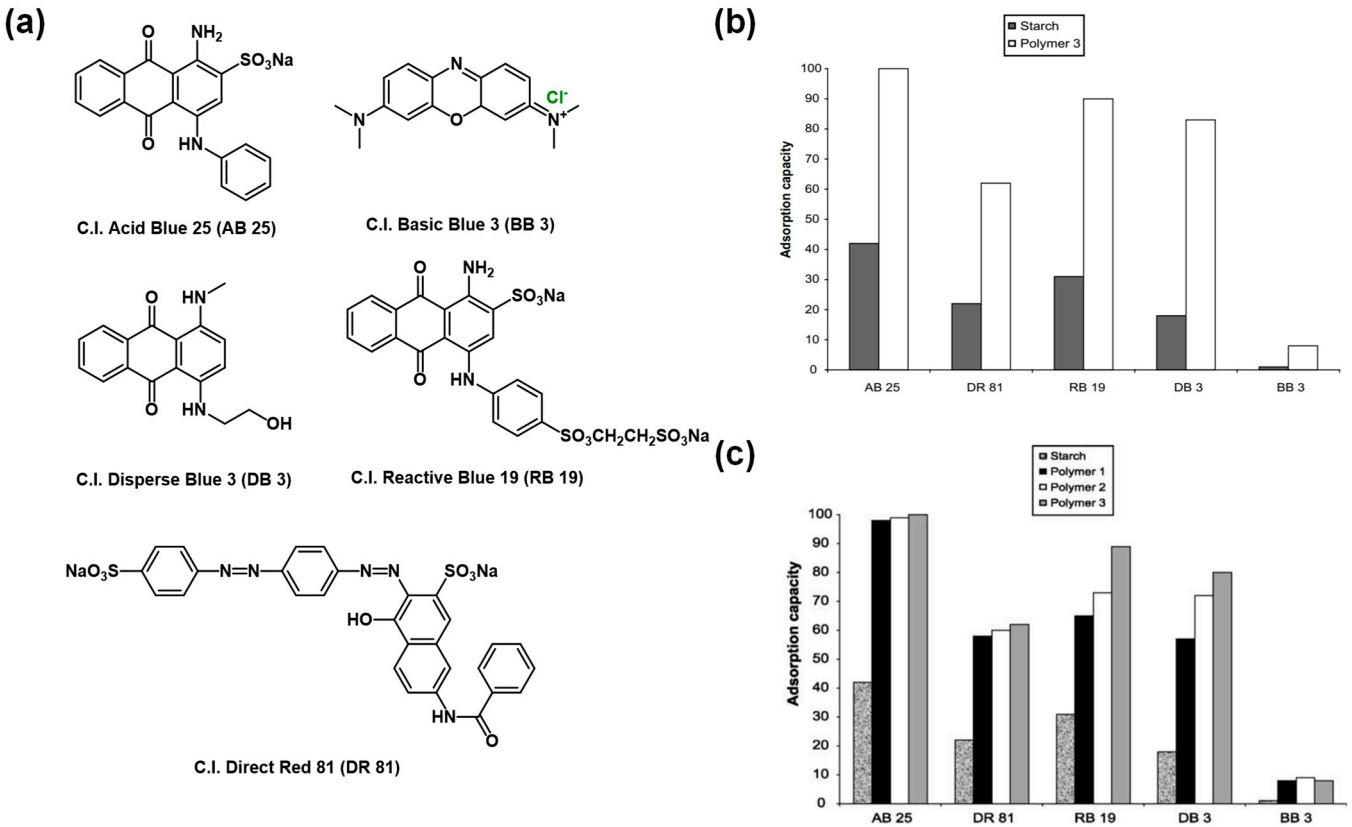

Figure 4. (**a**) The structure of five dyes; (**b**) the adsorption capacity (R in %) of the five dyes on polymer 3 and starch; (**c**) effect of β–CD content on adsorption capacity (R in %) of five dyes [50].

Table 2. The specific surface area and adsorption capacities of crosslinked *β*–CD polymers on pollutants.

Adsorbents	Crosslinking Agents	Specific Surface Area (m^2/g)	Pollutants	Adsorption Capacities (mg/g)	Ref.
β–CD nanospheres	epichlorohydrin	1.5	*p*–nitrophenol	17.2	[33]
PhAEs–*β*–CD	phthalic anhydride	332.1	basic green 4	3288.8	[38]
			crystal violet	2407.9	
			astrazon pink FG	2264.4	
CA–*β*–CD	citric acid	0.8	bisphenol A	83.0	[40]
			methylene blue	295.2	
			Cu^{2+}	585.6	
polyCTR–*β*–CD	citric acid	0.6	paraquat	20.8	[41]
β–CD polymer	tetrafluorophenonitrile	270.8	Pb^{2+}	196.4	[45]
			Cu^{2+}	164.4	
			Cd^{2+}	136.4	
CDP	epichlorohydrin	2.4	C.I. Basic Blue 3	42.4	[51]
			C.I. Basic Violet 3	35.8	
			C.I. Basic Violet 10	53.2	
β–CD–TDI	2,4–toluene diisocyanate	2.5	2,4–dinitrophenol	3.9	[52]
β–CD–HDI	hexamethylene diisocyanate	14.0	2,4–dinitrophenol	3.4	[52]
CDPU–HCP	4,4′–diphenylmethane diisocyanate	1133.1	bisphenol A	371.8	[53]
BnCD–HCPP	formaldehyde dimethyl acetal	1225.0	4–chlorophenol	141.4	[54]
BnCD–DCX	dichloroxylene	1209.0	bisphenol A	278.0	[55]

To overcome the drawback of the low adsorption capacity of *β*–CD polymers for cationic dyes, Crini et al. [51] improved the synthetic method of *β*–CD polymers. In the presence of carboxymethyl cellulose (CMC), one *β*–CD polymer (CMC–*β*–CDP) adsorbent modified with carboxylic groups was prepared in one step when using EPI as the crosslinking agent (Figure 5). The results showed that CMC–*β*–CDP had strong adsorption ability for some cationic dyes like BB 3, C.I. Basic Violet 3 (BV 3), and C.I. Basic Violet 10 (BV 10), indicating that the introduction of carboxyl groups was favorable for adsorption of cationic dyes. This was mainly because, in alkaline media, the hydroxyl and carboxyl groups in the material structure are deprotonated, and thus can be strongly bonded to the positively charged cationic dyes through electrostatic interaction.

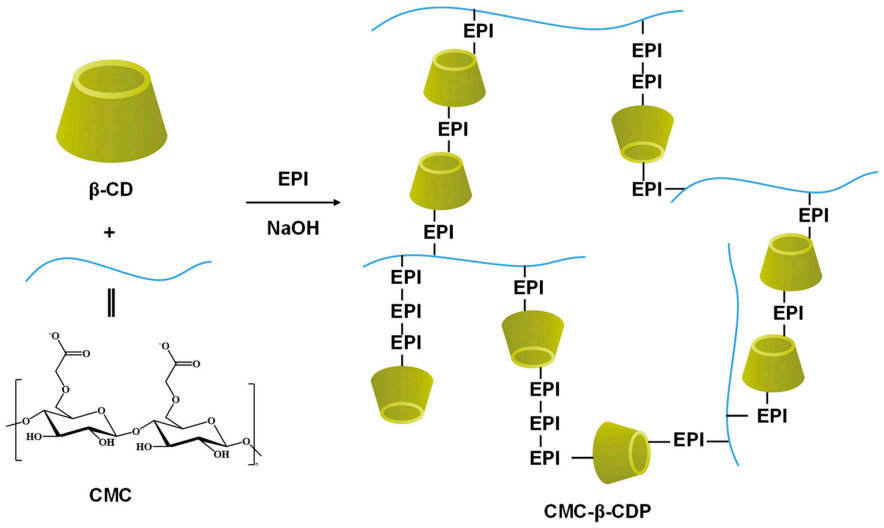

Figure 5. Synthesis route of CMC–*β*–CD polymer [51].

Anne et al. [52] prepared two kinds of β–CD polymers (β–CD–HDI and β–CD–TDI) using hexamethylene diisocyanate (HDI) and toluene–2,4–diisocyanate (TDI) as crosslinking agents, respectively, and studied the adsorption of 2,4–dinitrophenol (2,4–DNP) by these two polymers. It was found that both β–CD–HDI and β–CD–TDI had strong adsorption ability for 2,4–DNP. Compared with β–CD–HDI, β–CD–TDI showed a higher removal rate for 2,4–DNP. However, the surface areas of β–CD–HDI (14.0 m^2/g) and β–CD–TDI (2.5 m^2/g) were relatively low, which significantly reduced their adsorption capacities for organic pollutants. Zhou et al. [53] crosslinked β–CD with 4,4′–diphenylmethane diisocyanate (MDI), and then further used a diplomatic coupling reaction to synthesize hyper–crosslinked β–CD polyurethane (CDPU–HCP, Figure 6a), which had a very high specific surface area (1133.1 m^2/g). The results showed that CDPU–HCP had a high adsorption capacity for bisphenol A (BPA) (371.8 mg/g). After six adsorption–desorption cycles, CDPU–HCP still maintained a high removal efficiency for BPA (>90%). In combination with the results of the DFT calculation, it was found that the formation of the inner inclusion compounds through the hydrophobic interaction of the β–CD cavity with the lowest binding energy (94.4 kJ/mol, Figure 6b) was the main reason for the adsorption of BPA. In addition, the π–π interaction of aromatic rings and the bonding ability of carbamates were also beneficial to the removal of BPA (Figure 6c,d).

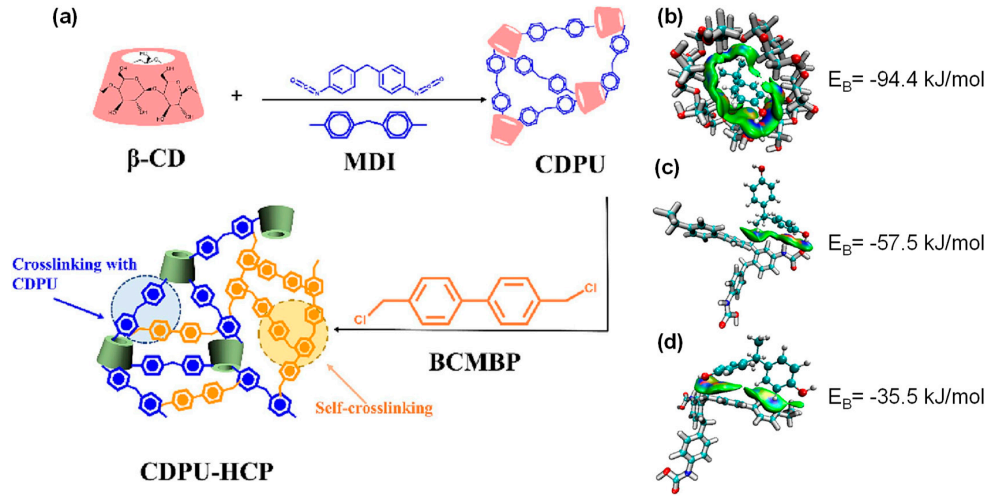

Figure 6. (**a**) Synthesis route of CDPU–HCP; optimized configurations of BPA adsorbed on three active adsorption sites of CDPU–HCP: BPA on (**b**) β–CD cavity, (**c**) urethane bond, and (**d**) aromatic ring of CDPU–HCP and their corresponding binding energies. Illustration of the dispersed IGM isosurface domains (0.003 a.u.) for these configurations [53].

Later, Kono et al. [37] developed water–insoluble β–CD polymers (β–CDPs) using 1,2,3,4–butanetetracarboxylic dianhydride (BTCA) as the crosslinking agent and pyridine as the solvent. The results showed that the water solubility of the obtained β–CDPs depended on the molar feed ratio of β–CD and BTCA, as well as the reaction temperature. When the molar feed ratio of β–CD and BTCA was low and the reaction temperature was high, the water-insoluble β–CDPs could be obtained. At the same time, adsorption experiments showed that water-insoluble β–CDPs showed high adsorption capacity for BPA, especially when the molar feed ratio of β–CD and BTCA was 1:3.5.

However, these crosslinking agents, like epichlorohydrin, diisocyanate, and anhydride, are more toxic than EPI, and can cause serious harm to the human body and environment, thus limiting their further practical application. To overcome this disadvantage, numerous environmentally friendly crosslinking agents, such as CA and EDTA, have attracted more attention.

Preparation of the β–CD polymer using CA and EDTA as crosslinking agents is not only environmentally friendly during the synthesis process, but also can introduce negative

carboxyl groups, so that the obtained polymer can also adsorb some cationic dyes and heavy metal ions through electrostatic interaction, in addition to removing organic pollutants through the host–guest interaction of *β*–CD. It provides one method for the development of multifunctional adsorbents based on *β*−CD for the simultaneous removal of organic and inorganic metal ions pollutants from aqueous solution.

For example, Huang et al. [40] synthesized a *β*–CD based polymer (CA–*β*–CD) at 140 °C using CA as the crosslinking agent and potassium dihydrogen phosphate as the catalyst, which can simultaneously remove BPA, methylene blue (MB), and Cu^{2+} from aqueous solutions (Figure 7a). In a mono–component system, the maximum adsorption capacity for BPA by CA–*β*–CD was 83.0 mg/g, and the maximum adsorption capacity for MB and Cu^{2+} was 295.2 mg/g and 58.6 mg/g, respectively. Multi–component experiments (Figure 7b–d) exhibited that the adsorption of BPA and MB onto CA–*β*–CD was independent from each other, while the adsorption of MB and Cu^{2+} belonged to a competitive adsorption mechanism. Therefore, it can be concluded that the adsorption mechanism of CA–*β*–CD towards BPA was through the host–guest interaction occurring in the hydrophobic cavity of *β*−CD, while adsorption of positively charged MB and Cu^{2+} was through the electrostatic interactions and the bonding interaction between carboxyl oxygen atoms and metal ions. Furthermore, the loaded–*β*–CD could be easily regenerated and reused many times without significant loss of efficiency.

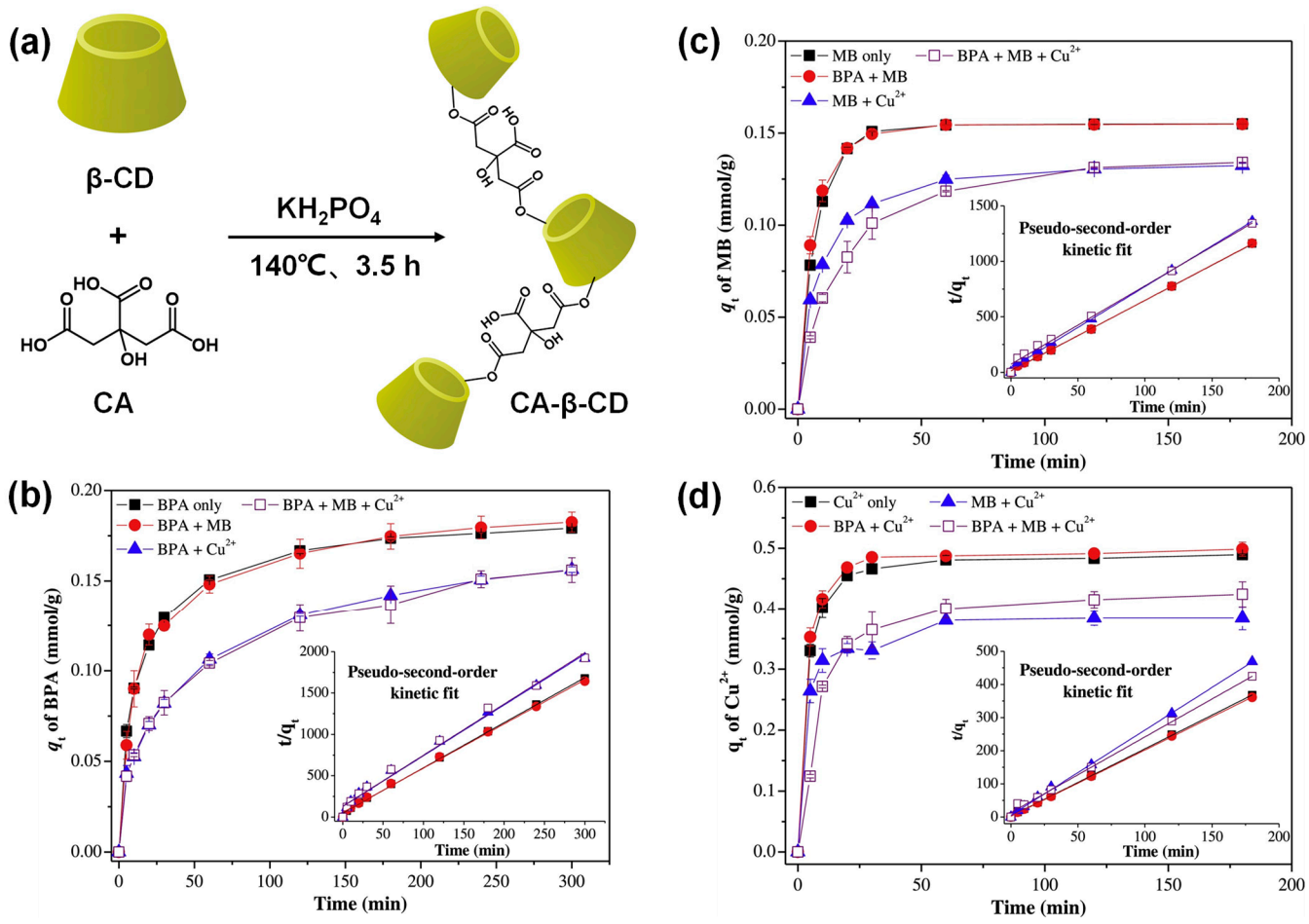

Figure 7. (**a**) Synthesis route of CA–*β*–CD, influence of contact time on the adsorption of (**b**) BPA, (**c**) MB, and (**d**) Cu^{2+} by CA–*β*–CD in single–component or multi–component systems from aqueous solutions [40].

Unfortunately, it was found that the CA–crosslinked *β*–CD (CA–*β*–CD) cannot effectively adsorb anionic dye. To achieve the adsorption of anionic dye, 2–dimethylamino

ethyl methacrylate (DMAEMA) containing tertiary amine groups was used to functionalize the β–CD–based polymers, which can be converted into quaternary amines and create the cationic centers [56]. Zhou et al. [57] utilized CA as a crosslinking agent to firstly prepare one CA–crosslinked β–CD polymer (β–CD/CA) by esterification reaction. Then, the resulting polymer β–CD/CA was grafted onto the DMAEMA using potassium persulfate ($K_2S_2O_8$) as the initiator to obtain a novel amphoteric adsorbent β–CD/CA–PDMAEMA (Figure 8). The results showed that the maximum adsorption capacities of BPA, methyl orange (MO), and MB by β–CD/CA–PDMAEMA were up to 79.0 mg/g, 165.8 mg/g, and 335.5 mg/g, respectively. Furthermore, the multi–component adsorption experiments proved that β–CD/CA–PDMAEMA could effectively remove the BPA from aqueous solutions at pH = 2.0~10.0, and it could also selectively remove the anionic dyes under acidic conditions or cationic dyes under alkaline conditions. In addition, the material had good stability and reusability. The above results suggest that β–CD/CA–PDMAEMA is a very promising candidate for the treatment of dye in wastewater containing multiple contaminants.

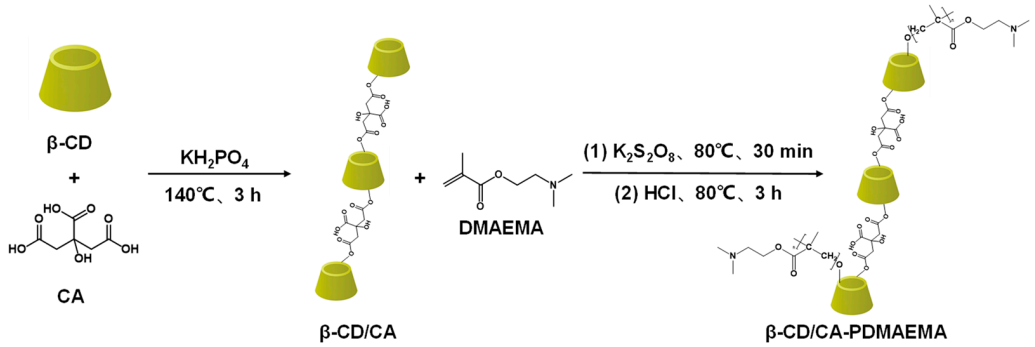

Figure 8. Synthesis route of the amphoteric β–CD/CA–PDMAEMA [57].

Zhao et al. [42] used EDTA as a crosslinking agent with sodium dihydrogen phosphate as a catalyst to prepare an EDTA-functionalized β–CD polymer (EDTA–β–CD) through a polycondensation reaction (Figure 9a), which was also studied for its ability to simultaneously adsorb heavy metal ions and dye molecules. Compared with EPI–β–CD, EDTA–β–CD had a higher removal rate for cationic dyes and metal ions, indicating that the carboxyl groups contained in EDTA provided extra adsorption sites for cationic dyes and metal ions (Figure 9b), but the thermal stability of EDTA–β–CD was reduced due to the presence of EDTA groups. In a single-component system, the adsorption capacities of EDTA–β–CD for Cu^{2+} and Cd^{2+} were 78.8 and 124.8 mg/g, respectively. The adsorption capacities of MB, Safranin O (SO), and Crystal Violet (CV) were 83.8, 59.3, and 114.2 mg/g, respectively. After four sorption–desorption cycles, the regeneration efficiency of EDTA–β–CD still reached almost 95%.

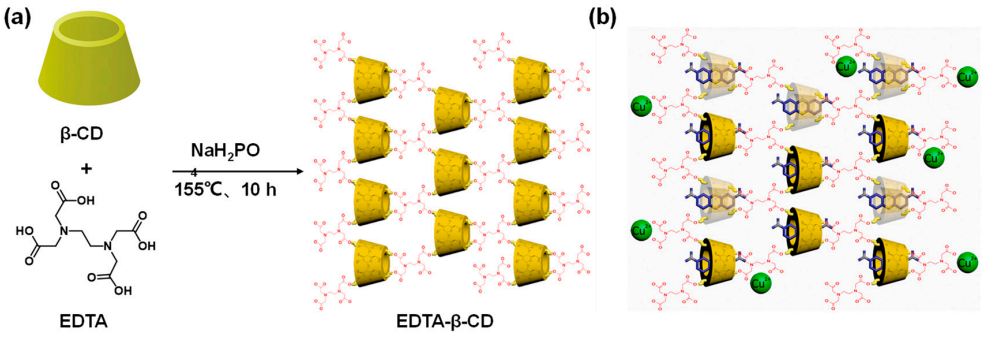

Figure 9. (**a**) Synthesis route of EDTA–β–CD; (**b**) adsorption mechanism of Cu^{2+} and dyes by EDTA–β–CD [42].

As previously reported, most of the β–CD polymers adsorbents prepared using EPI, diisocyanate, CA, or EDTA as crosslinking agents have the drawback of a low specific surface area. To increase the specific surface area of β–CD porous materials, some compounds with rigid aromatic rings have been selected as crosslinking agents since these rigid aromatic compounds can provide a larger specific surface area and more pore structures for adsorption pollutants.

For this purpose, Alsbaiee et al. [44] used TFN as the crosslinking agent to prepare one mesoporous β–CD polymer (P–CDP) in K_2CO_3/tetrahydrofuran (THF) suspension (Figure 10a) and found that P–CDP had a high specific surface area and permanent porosity. The specific surface area of the obtained adsorbent P–CDP was up to 263.0 m^2/g (Figure 10b,c), but with a low yield of 20%. Fortunately, when using a mixed solution of THF and DMF (dimethylformamide) with a volume ratio of 9:1 as the reaction solvent, the yield of P–CDP could be further increased to 45%. The batch adsorption experiments showed that P–CDP could quickly remove 95% of BPA (0.1×10^{-3} mol/L) from aqueous solution with an extremely fast adsorption rate (equilibrium time < 10 s). Compared with activated carbon or non-porous β–CD adsorbents, P–CDP had the faster adsorption rate constant of 1.5 mg/(g·min), which was 15 to 200 times larger than that of activated carbon and non-porous β–CD type adsorbents.

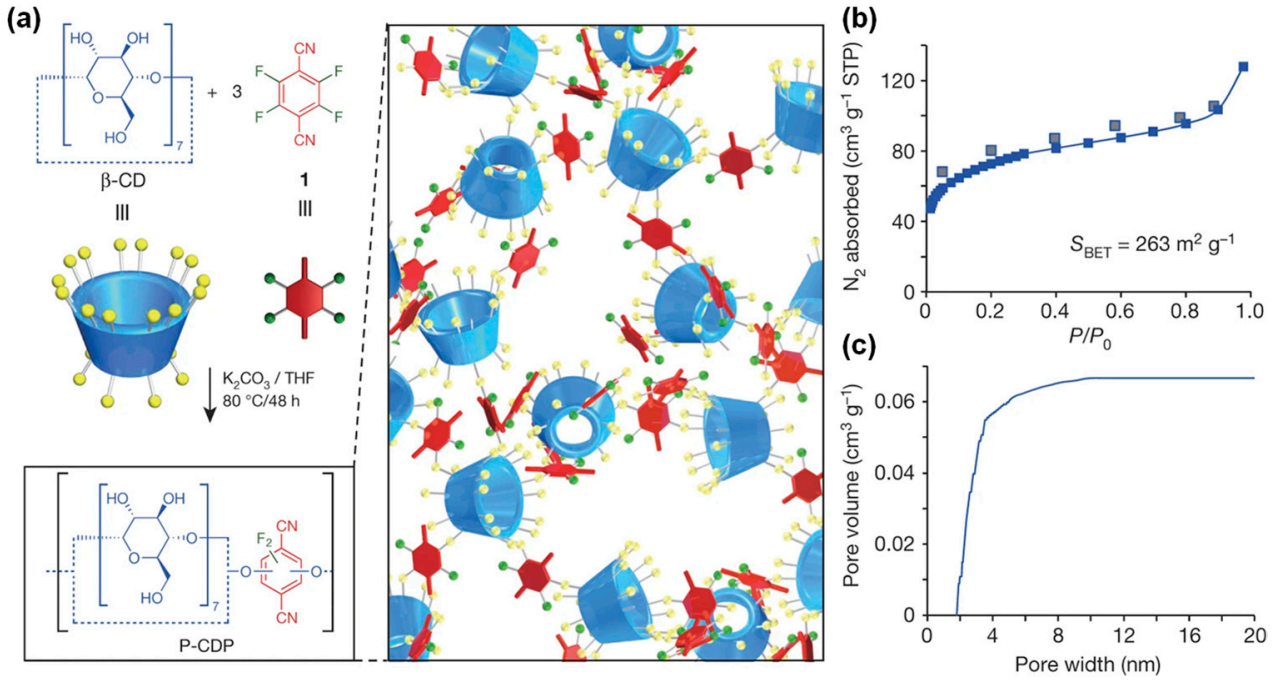

Figure 10. (**a**) Synthesis route of P–CDP; (**b**) N_2 adsorption (blue box) and desorption (gray box) isotherms of P–CDP; (**c**) cumulative pore volume of P–CDP obtained by NLDFT analysis [44].

In addition to choosing TFN as a crosslinking agent, recently, the Friedel–Crafts alkylation reaction [54] has also been reported for the synthesis of hyper–crosslinked β–CD polymers. Li et al. [55] crosslinked benzylated β–CD (BnCD) with di–chloroxylene (DCX) through the Friedel–Crafts alkylation reaction to synthesize a new type of hyper-crosslinked β–CD porous polymer BnCD–DCX (Figure 11a). This polymer had a very high specific surface area (Figure 11b) and strong thermal stability, and could effectively remove BPA from aqueous solution with an adsorption capacity comparable with that of other β–CD–based adsorbents. Notably, it was found that the presence of inorganic metal ions did not interfere with the adsorption of BPA by BnCD–DCX. Based on these results, the authors pointed out that the host–guest and π–π interactions between BPA and BnCD–DCX contributed to the excellent adsorption performances of BnCD–DCX towards BPA. In addition, the NLDFT calculation revealed that the mean pore size of BnCD–DCX

was 1.3 nm (Figure 11c), which was consistent with the size of BPA and favorable for adsorption. This synthesis strategy provided a new approach for the design of highly efficient hyper–crosslinked *β*–CD–based adsorbents for removal of organic pollutants from aqueous solutions.

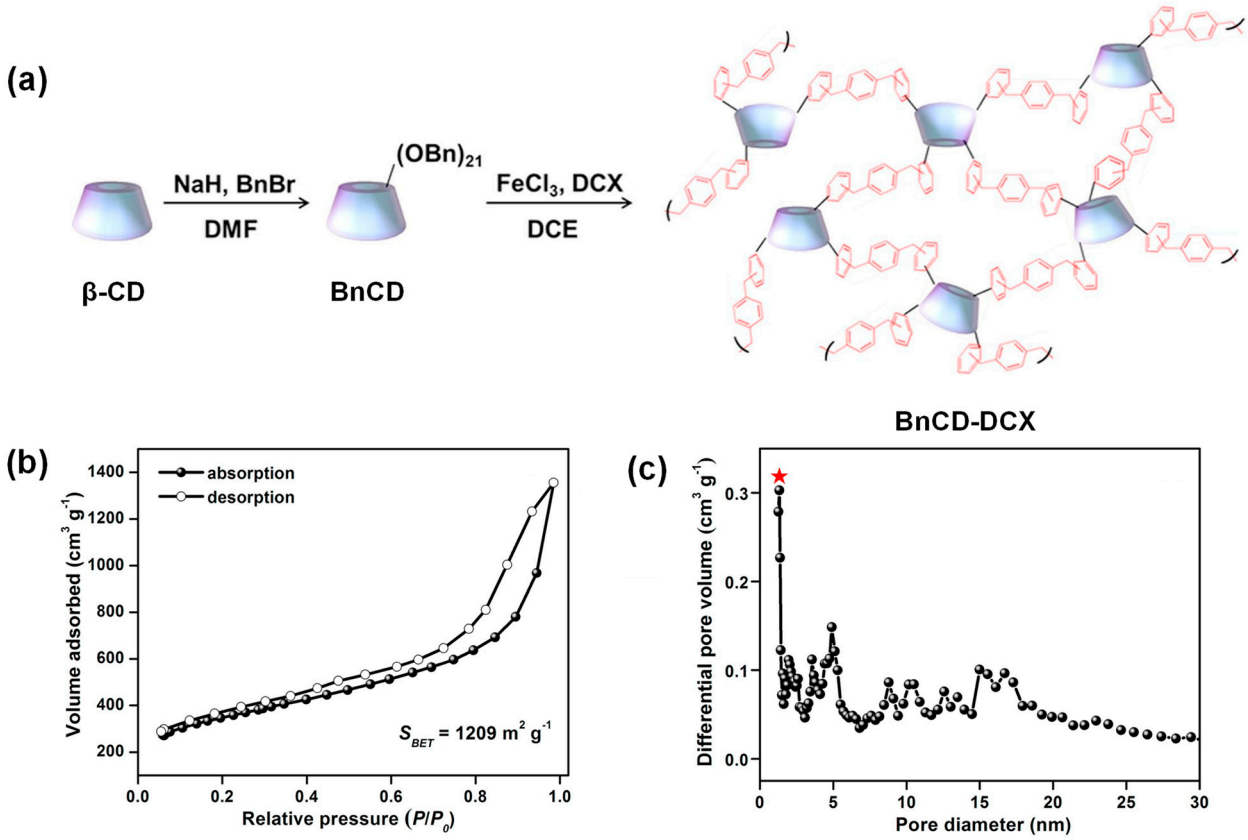

Figure 11. (**a**) Synthesis route of a novel hyper–crosslinked *β*–CD porous polymer BnCD–DCX; (**b**) N_2 adsorption–desorption isotherm of BnCD–DCX measured at 77K; (**c**) the aperture fraction of BnCD–DCX calculated by NDLFT [55].

Covalent organic frameworks (COFs) are a new type of crystalline porous polymer with high porosity, ordered mesoporous structure, large surface area, and excellent thermal stability [58–60]. The integration of supramolecular *β*–CD units into the ordered framework skeleton structure of COFs gives the *β*–CD–based materials the advantages of a regular, highly adjustable porous structure and strong thermal stability. More recently, Wang et al. [61] synthesized a *β*–CD based COF material (*β*–CD@COF) through polycondensation between heptakis(6–amino–6–deoxy)–*β*–CD (Am7CD) and terephthalaldehyde (TPA) catalyzed by acetic acid and ammonia in a mixture of water and ethanol, respectively (Figure 12). The characterization results proved that *β*–CD@COF had a large specific surface area (79.2 m^2/g), uniform pore size, and high thermal stability. Compared with *β*–CD amorphous polymer (*β*–CD@NCP), *β*–CD@COF had a specific molecular recognition effect for (S)–naproxen, 4–nonylphenol, BPA, and Rhodamine B, which resulted from the formation of clathrates between the *β*–CD cavity and the carboxyl or hydroxyl groups, as well as free phenyl or naphthyl parts contained in these adsorbate molecules.

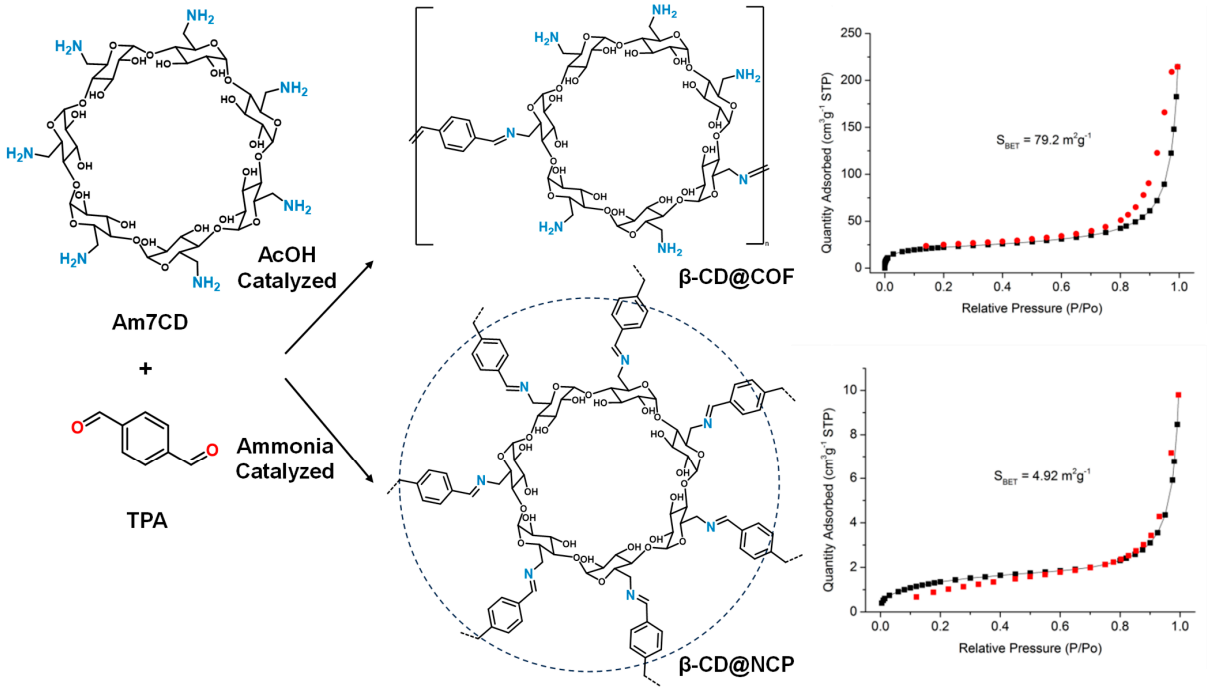

Figure 12. *β*–CD@COF and *β*–CD@NCP prepared under different catalytic conditions and their respective N_2 adsorption (black squares) and desorption (red squares) isotherms measured at 77 K [61].

3. Immobilized *β*–CD

In addition to reducing the solubility of *β*–CD in aqueous solutions using the crosslinking method discussed above, another widely studied method is to load *β*–CD onto a support (the so–called immobilized *β*–CD composite materials). The supports that have been reported for the preparation of *β*–CD composite materials are mainly divided into inorganic supports, and organic synthetic polymer and natural polymer supports. These inorganic or organic support-immobilized *β*–CD composites have the advantages of good mechanical strength, high specific surface area, and high porosity, and thus have been widely studied in the removal of organic pollutants from water environments [2]. Table 3 shows the adsorption properties of some examples of immobilized *β*–CD on different pollutants.

Table 3. Comparison of examples of reported immobilized *β*–CD in the adsorption of pollutants.

Adsorbent	Supports	Pollutants	Equilibrium Time	Adsorption Capacities (mg/g)	Ref.
SiO_2–*β*–CD–NH_2	SiO_2	bisphenol A	180 min	107.7	[62]
SiO_2–*β*–CD–OH	SiO_2	bisphenol A	180 min	112.7	[62]
β–CD/rGO–MWCNTs	graphene oxide multiwall carbon nanotubes	naproxen	24 h	132.1	[63]
MCG	Fe_3O_4 graphene oxide	*p*–phenylenediamines	120 min	892.9	[64]
CDP–MNPs	Fe_3O_4 magnetic nanoparticles	bisphenol A	250 min	74.6	[65]
β–CD@Si	silica gel	resorcin	175 min	114.9	[66]
		p–nitrophenol	5 s	41.5	
G–Fe_3O_4–*β*–CD		bisphenol A	240 min	59.6	[67]
Fe_3O_4–PEI/*β*–CD	Fe_3O_4 magnetic nanoparticles	methyl orange	100 min	192.2	[68]
β–CD@AC	activated carbon	Pb^{2+}	200 min	73.1	[69]
		naphthalene	10 s	178.7	

Table 3. *Cont.*

Adsorbent	Supports	Pollutants	Equilibrium Time	Adsorption Capacities (mg/g)	Ref.
β–CDP	polyvinyl alcohol	methylene blue	30 min	105.0	[70]
		phenol	200 min	13.8	
PVA–SS–β–CD	polyvinyl alcohol	methylene blue	240 min	261.1	[71]
CD@TCT@PEI	polyethyleneimine	hydroquinone	180 min	364.9	[72]
		Pb^{2+}	360 min	113.5	
b–PEI–PEG–β–CD	polyethylenimine	bisphenol A	1140 min	60.1	[73]
		Cu^{2+}	1140 min	50.1	
CDCS–EDTA	chitosan	acid red 73	10 min	754.6	[74]
		Pb^{2+}	20 min	114.8	
CRCSCD	chitosan	methyl orange	180 min	392.0	[75]
NTA–β–CD–CS	chitosan	methyl orange	90 min	132.5	[76]
		Hg^{2+}	90 min	178.3	
β–CD grafted cellulose	cellulose beads	bisphenol A	360 min	30.8	[77]

3.1. Inorganic Support-Immobilized β–CD

At present, the inorganic materials that have been reported for immobilization of β–CD are silica gel [62,78,79], graphene oxide [63,64,80], and magnetic Fe_3O_4 particles [65,81]. These inorganic materials have the merits of being low cost and widely available, and having a relatively high specific surface area. This kind of carrier can enhance the dispersion effect of β–CD in the aqueous phase, thereby improving its adsorption performance.

As a mesoporous material, silica gel is mainly composed of SiO_2, which has high porosity, low toxicity and cost, and a large specific surface area. Furthermore, the surface of silica gel presents high chemical reactivity due to the existence of silanol groups (Si–OH) and large pore channels, which allow selective adsorption for specific pollutants [82]. Loading β–CD onto the surface of silica gel is beneficial to the entry of pollutants into the adsorption site [83].

Shen et al. [66] used (3–chloropropyl) trimethoxy–silane and ethylenediamine as crosslinking agents to load β–CD onto the surface of silica gel and prepared a silica–based β–CD@Si material for the removal of *p*–nitrophenol from aqueous solution (Figure 13a). The results showed that β–CD@Si had a very fast adsorption rate for *p*–nitrophenol and, at pH $\geq$ 8.5, the adsorption of *p*–nitrophenol reached equilibrium within 5 s, which was faster than most other adsorbents. The main reason for this rapid adsorption was that only one hydroxyl group of the β–CD molecule was connected to ethylenediamine during the preparation of β–CD@Si, which was conducive to maintaining the hydrophobic inner cavity of β–CD and thus reducing the diffusion resistance. Furthermore, the adsorption capacity of β–CD@Si towards *p*–nitrophenol was only 41.5 mg/g at equilibrium, which should be further improved for practical application. Additionally, ^{1}H ROESY NMR studies showed that the strong interaction occurred between the protons located in the phenyl ring of *p*–nitrophenol and the H–3, H–5 in the cavity of β–CD (Figure 13b), which was strong evidence for the formation of inclusion complexes. The comparison of infrared spectra before and after adsorption (Figure 13c) showed that the hydroxyl group of cyclodextrin and the hydrogen on the secondary amino group had a hydrogen bonding interaction with *p*–nitrophenol in aqueous solution.

Graphene oxide (GO) is the oxide of graphene. After oxidation treatment, graphite oxide still maintains the layered structure of graphite, but many oxygen–containing functional groups (carboxyl, hydroxyl, epoxide, etc.) are introduced onto the graphene sheet of each layer. These oxygen–containing functional groups are mainly distributed on the edges of each layer of graphene sheets [84]. Graphene oxide is usually applied as an adsorbent [64] due to its relatively high specific surface area and multiple oxygen–containing functional groups [85]. The introduction of magnetic nanoparticles (Fe_3O_4) can promote the separation of adsorbent materials from aqueous solution by a magnetic field [86].

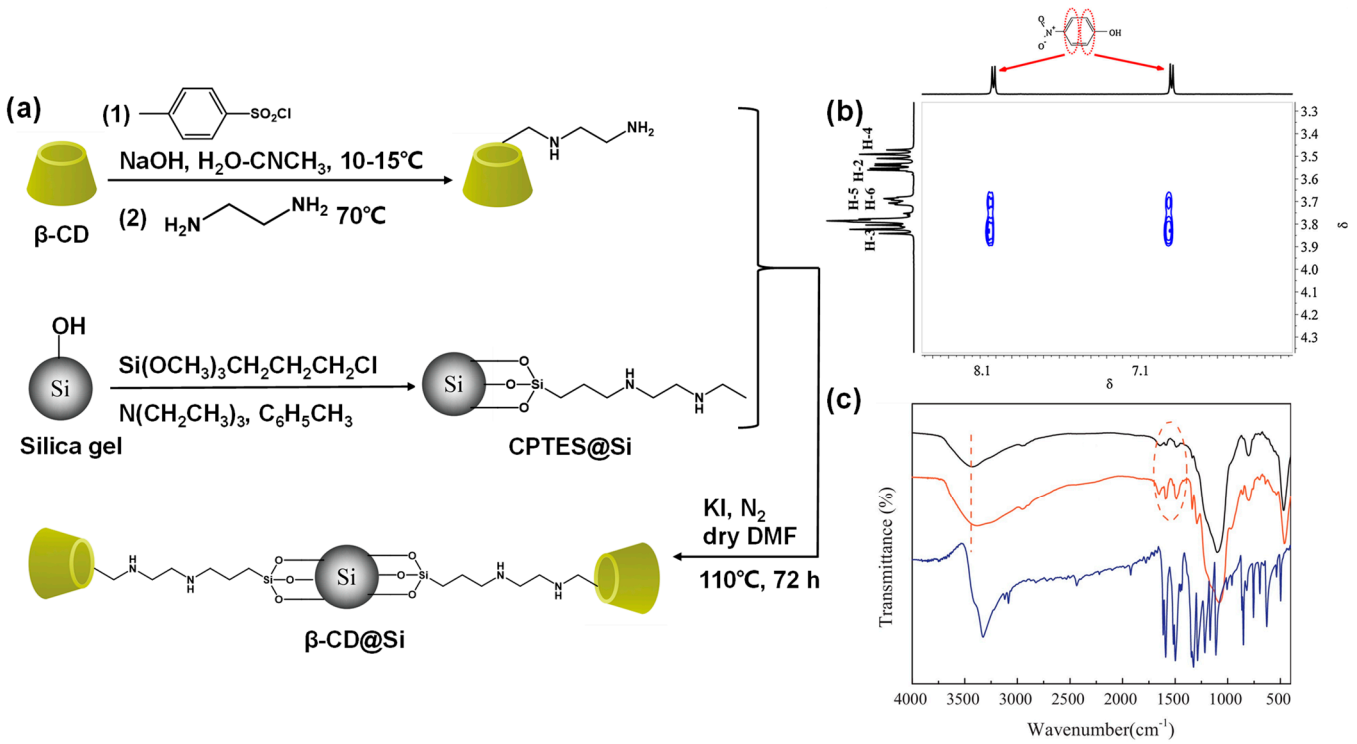

Figure 13. (**a**) Synthesis route of *β*–CD@Si; (**b**) partial ^{1}H ROESY NMR spectra for the formation of inclusion complex between parent *β*–CD and p-nitrophenol; (**c**) FT−IR spectra of *β*–CD@Si (black, before adsorption), *β*–CD@Si (red, after adsorption), and *p*–nitrophenol (blue) [66].

Based on these considerations, Ragavan et al. [67] loaded *β*–CD onto the surface of GO–Fe_3O_4 nanocomposites using ethylenediamine as the crosslinking agent to obtain a *β*–CD–based magnetic nanocomposite (G–Fe_3O_4–*β*–CD) for removal of BPA from aqueous solution (Figure 14a). The results (Figure 14c) showed that G–Fe_3O_4–*β*–CD had better adsorption selectivity for BPA than for bisphenol (BP), bisphenol F (BPF), and bisphenol S (BPS). Compared with BP (Figure 14b), the slightly curved geometry of the BPA molecule and the presence of *π*–*π* interactions between BPA's phenol rings and *β*–CD's glucose monomers favored adsorption to some extent. BPF and BPS have a bent geometry like BPA, but their adsorption capacity is very low; the possible reason for this low adsorption efficiency is the atomic hindrance of these molecules, which prevents the formation of an inclusion complex with *β*–CD. The adsorption capacity of BPA by G–Fe_3O_4–*β*–CD was 59.6 mg/g, and the adsorption process followed the Langmuir model. Furthermore, it was found that the magnetic nanocomposite has superparamagnetic properties at room temperature and can be effectively separated from aqueous solution by an external magnetic field.

Chen et al. [68] successfully constructed a *β*–CD and polyethyleneimine (PEI) bifunctional magnetic nano-adsorbent (Fe_3O_4–PEI/*β*–CD) with spatial separation and adsorption sites through combination of the merits of PEI, *β*–CD, and Fe_3O_4 magnetic nanoparticles for simultaneous capture of MO and Pb^{2+} in wastewater (Figure 15a). It was found that the adsorption capacities of Fe_3O_4–PEI/*β*–CD for MO and Pb^{2+} were 192.2 mg/g and 73.1 mg/g, respectively. Interestingly, the presence of MO in the Pb^{2+}–MO binary system significantly promoted the uptake of Pb^{2+} (Figure 15b). However, the coexistence of Pb^{2+} had almost no effect on MO uptake (Figure 15c). Based on the results of adsorption experiments, diverse mechanisms (such as electrostatic attraction, host–guest inclusion, and chelating) were involved in the adsorption process (Figure 15d). The cavity match effect of *β*–CD and positively charged N-containing groups of PEI were mainly responsible for the effective removal of MO via host–guest inclusion and electrostatic attraction, respectively, and oxygen−bearing groups on the edge of *β*–CD, as well as the free amino moieties in PEI, acted as the active sites for Pb^{2+} uptake.

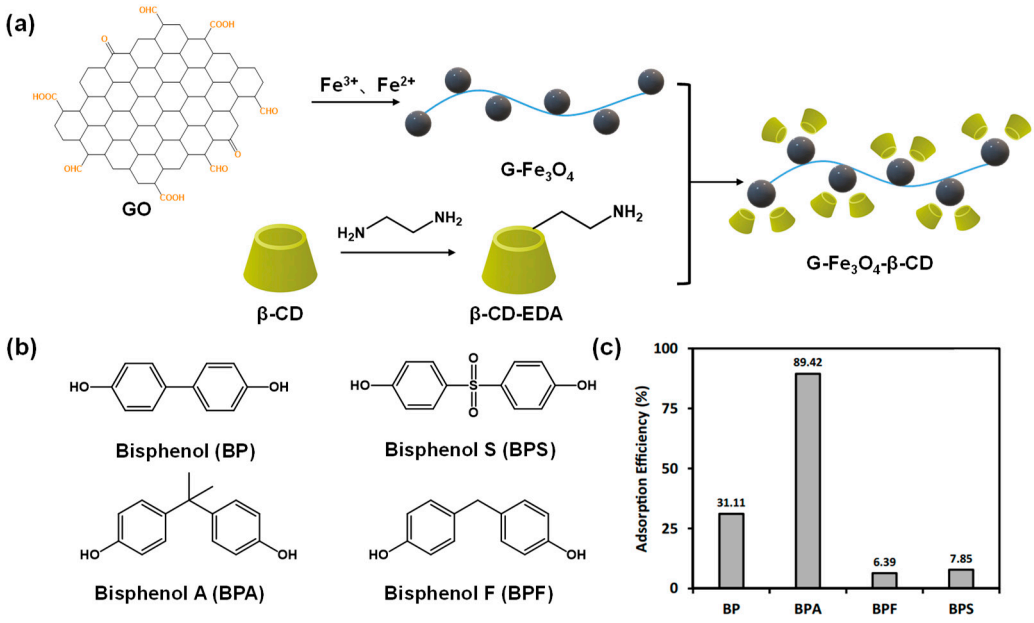

Figure 14. (**a**) Synthesis route of magnetic nanocomposite G–Fe_3O_4–*β*–CD; (**b**) structure of bisphenol analogues; (**c**) the adsorption selectivity of nanocomposites to BPA [67].

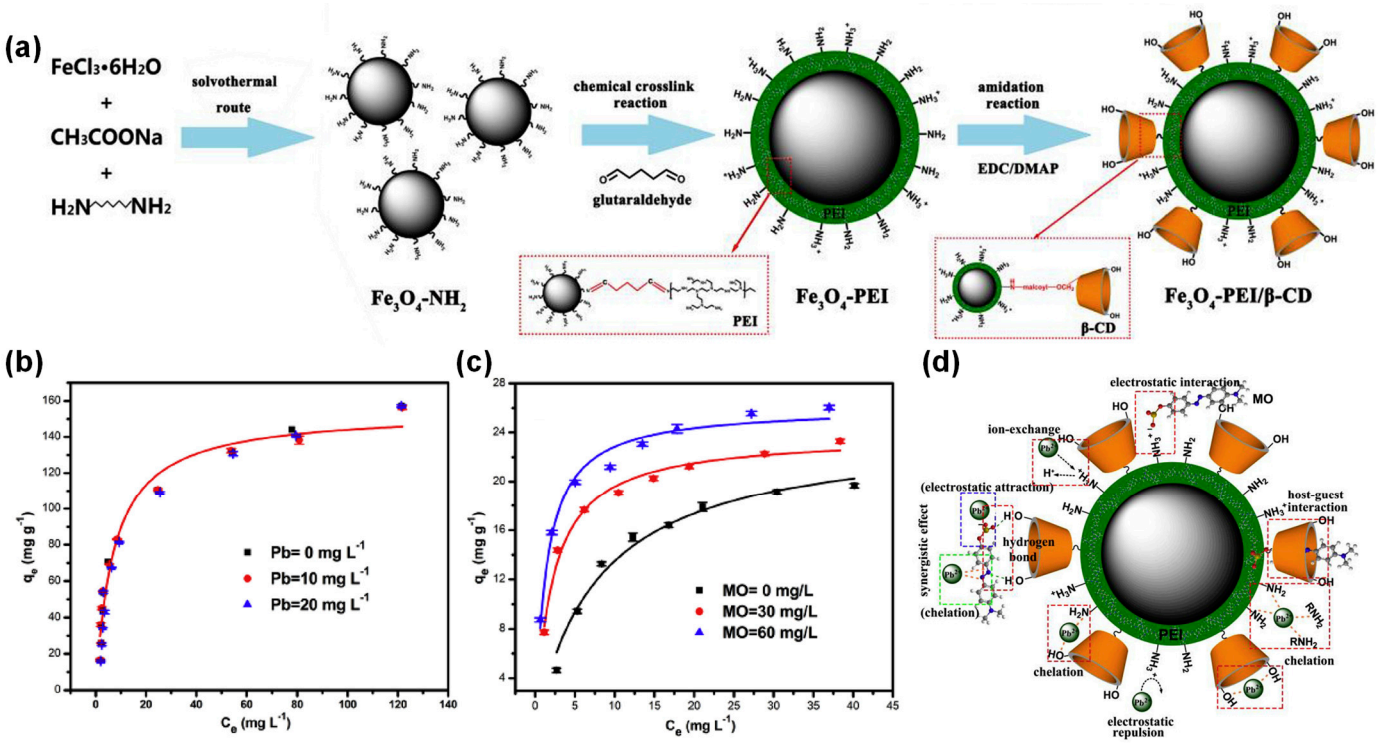

Figure 15. (**a**) Synthesis route of Fe_3O_4–PEI/*β*–CD composite; adsorption isotherms of MO (**b**) and Pb^{2+} (**c**) by Fe_3O_4–PEI/*β*–CD in the presence of different concentrations of Pb^{2+} or MO; (**d**) proposed mechanisms for the simultaneous capture of MO and Pb^{2+} by Fe_3O_4–PEI/*β*–CD [68].

Activated carbon (AC) is also one of the most widely studied materials for adsorption due to its large specific surface area and rich porous structure [87]. However, some inherent drawbacks, such as slow uptake rates for pollutants [88], lower polar organic compound adsorption [89], and high regeneration costs [90], still limit its practical application. He et al. [69] used HDI as the crosslinking agent and loaded *β*–CD onto the surface of oxidized AC using N, N–dimethylformamide as the solvent to prepare a novel hybrid

material β–CD@AC for rapid absorption of naphthalene (Figure 16). The batch adsorption experiments showed that when the grafting ratio of AC/β–CD was 1:1, the adsorption of β–CD@AC towards naphthalene could reach equilibrium within 10 s. The adsorption capacity of naphthalene was around 178.7 mg/g, which was significantly higher than that of AC. To maintain the completeness of the hydrophobic cavity of β–CD, only one hydroxyl group in the β–CD molecule was employed to prepare the β–CD@AC. Furthermore, the adsorption capacity of naphthalene by β–CD@AC reached 87.8% of the initial adsorption capacity after four cycles, which proved that β–CD@AC has good recyclability.

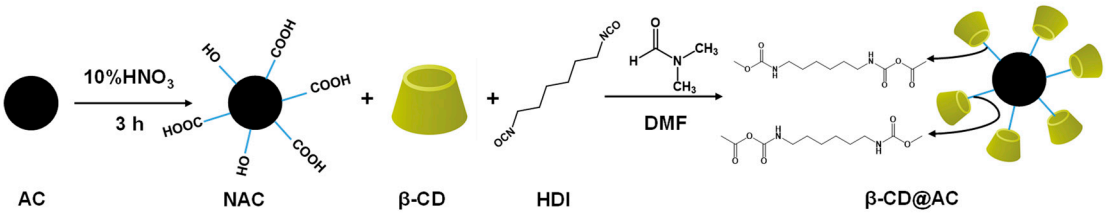

Figure 16. Synthesis route of the novel hybrid material β–CD@AC [69].

3.2. Organic Synthetic Support-Immobilized β–CD

The organic synthetic polymer materials used for loading β–CD mainly include polyvinyl alcohol (PVA) [70,71,91], PEI [72], and polydopamine [92]. Zhao et al. [70] synthesized a water-insoluble β–CD polymer (β–CDP) by loading β–CD onto PVA 1799 using citric acid as the crosslinking agent and sodium dihydrogen phosphate as the catalyst (Figure 17). The adsorption experiments demonstrated that β–CDP had certain adsorption ability for phenol and MB, with the maximum adsorption capacities of 13.8 mg/g and 105.0 mg/g, respectively. The much larger adsorption capacity of β–CDP for MB than that of phenol most likely resulted from the more suitable molecular size of MB for the formation of host–guest β–CD inclusion complexes with β–CD than that of phenol. Furthermore, the electrostatic attraction interaction between alkaline MB and acidic carboxyl in β–CDP also favored the stronger adsorption of MB than phenol. Satisfyingly, the synthesis route of this material did not use any organic solvents or harmful chemicals, which makes β–CDP a very environmentally friendly adsorbent.

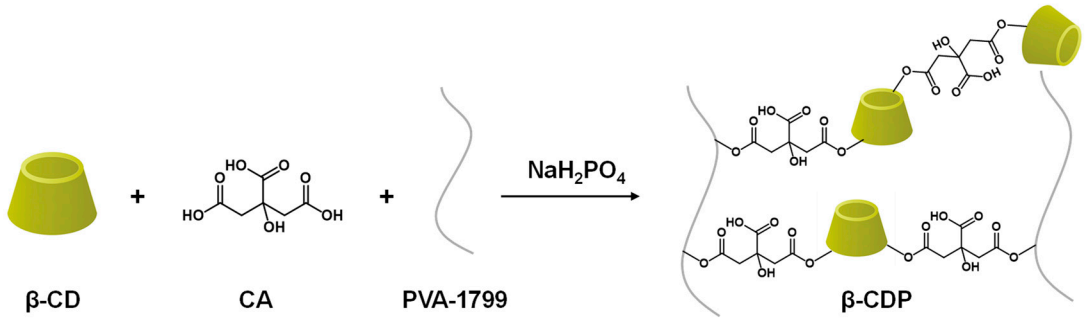

Figure 17. Synthesis route of β–CDP [70].

Zhao et al. [71] developed a new type of water–insoluble sericin/β–CD/polyvinyl alcohol composite nanofiber adsorbent (PVA–SS–β–CD) using electrospinning technology and a thermal crosslinking method (Figure 18). It was found that PVA–SS–β–CD fiber had good adsorption capacity for MB, and the maximum adsorption capacity was 188.0 mg/g, 229.9 mg/g, and 261.1 mg/g at 293 K, 313 K, and 333 K, respectively. Similar to the other β–CD–based composites discussed above, the electrostatic interaction and host–guest interaction also played a key role in the adsorption of organic pollutants by PVA–SS–β–CD. Positively charged MB can be adsorbed onto the negatively charged PVA–SS–β–CD fibers via electrostatic interactions originating from the carboxyl groups of sericin or citric acid. Furthermore, β–CD in PVA–SS–β–CD fiber and MB can capture methylene blue molecules

by forming a host–guest inclusion complex. In addition, the PVA–SS–*β*–CD fiber can be easily separated from the dye solution and has good recyclability. After 5 cycles, the removal rate remained at 93%.

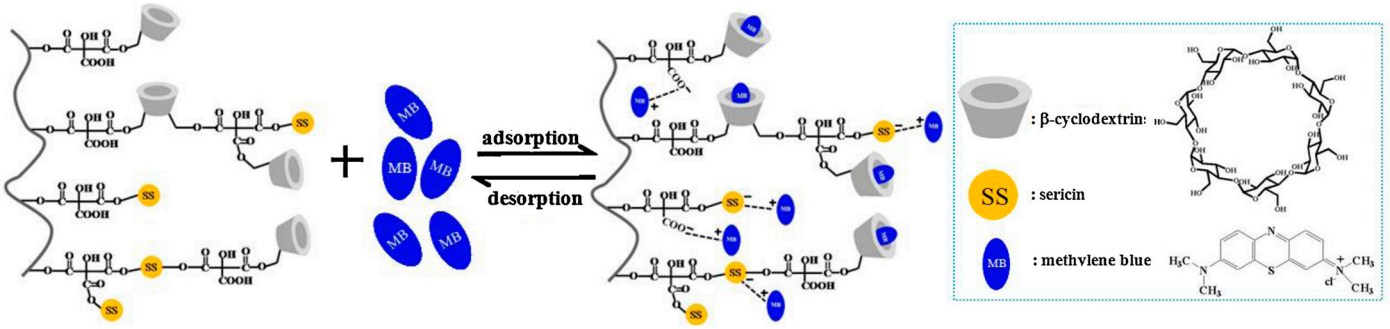

Figure 18. The structures of crosslinked PVA–SS–*β*–CD and their adsorption mechanism towards MB [71].

Heavy metals (HMs) and EDCs are often present as multiplex pollutants in aquatic environments because of their widespread industrial application. In recent years, the coexistence of BPA and Cu^{2+} has been frequently detected in soils, surface waters, and groundwater environments [93]. The molecular chain of PEI has many free amino groups [94], which can easily chelate with metal ions [95]. Therefore, the use of PEI as a carrier to prepare the composite materials can improve the removal efficiency of metal ions.

To removal the multiplex pollutants of BPA and Cu^{2+} from water environments, Lee et al. [73] used polyethylene glycol diglycidyl ether (PEGDE) as the crosslinking agent to load *β*–CD onto a PEI support and prepared a PEI–PEG–*β*–CD polymer adsorbent (Figure 19) named X–CD. The results showed that X–CD held strong affinity for both BPA and Cu^{2+}, with the adsorption capacity of 60.1 mg/g and 50.1 mg/g, respectively. The multi–component adsorption experiments showed that the presence of pluronic F127 and cetyl trimethyl ammonium bromide did not cause an adverse effect on adsorption of BPA by X–CD, but the presence of BPA inhibited the adsorption of Cu^{2+}. These results indicated that the nature of the adsorption of BPA and Cu^{2+} by X–CD was competitive adsorption and the strong affinity of BPA with amine groups via a hydrogen bonding interaction resulted in a decrease in the adsorption of Cu^{2+}. Furthermore, the adsorption rates for BPA and Cu^{2+} by X–CD were slow (adsorption equilibrium time = 1140 min), and should be further improved for practical use.

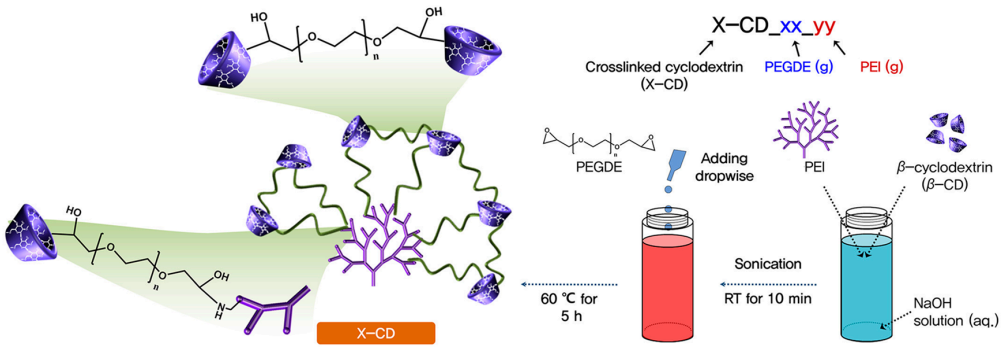

Figure 19. Synthesis route of PEI–PEG–*β*–CD (X–CD) [73].

3.3. Natural Polymer Support-Immobilized β–CD

Natural polymer materials, as carriers for preparing *β*–CD–based adsorbents, can be directly biodegraded, and thus cause minimum harm to the environment. Therefore, these natural polymer *β*–CD–based materials have attracted increasing attention in the removal of pollutants from wastewater. Some common natural polymer carriers that have been studied include chitosan [74,96], cellulose [97,98], and starch [99].

Chitosan is the product of chitin after removing the acetyl group [100] and has good biocompatibility. Its structure contains the active adsorption sites of amino and hydroxyl groups, which are suitable for the adsorption of the organic pollutants from wastewater [101]. Jiang et al. [75] developed a chitosan–supported *β*–CD composite material (CRCSCD) using maleic anhydride as a bridge and the glutaraldehyde crosslinking agent through a two-step reaction (Figure 20a). Under the optimal conditions, the adsorption capacity for MO by CRCSCD reached 392.0 mg/g. This strong adsorption for MO by CRCSCD partly resulted from the electrostatic interaction between $–SO_3^-$ contained in MO and the positively charged $–NH^{3+}$ in CRCSCD (Figure 20b,c). The formation of the clathrate compound by trapping the MO molecule in the hydrophobic cavity of *β*–CD through the host–guest interaction also strengthened the adsorption of MO. Moreover, CRCSCD exhibited much higher selectivity towards MO over MB and Rhodamine B, verifying the above proposed adsorption mechanism.

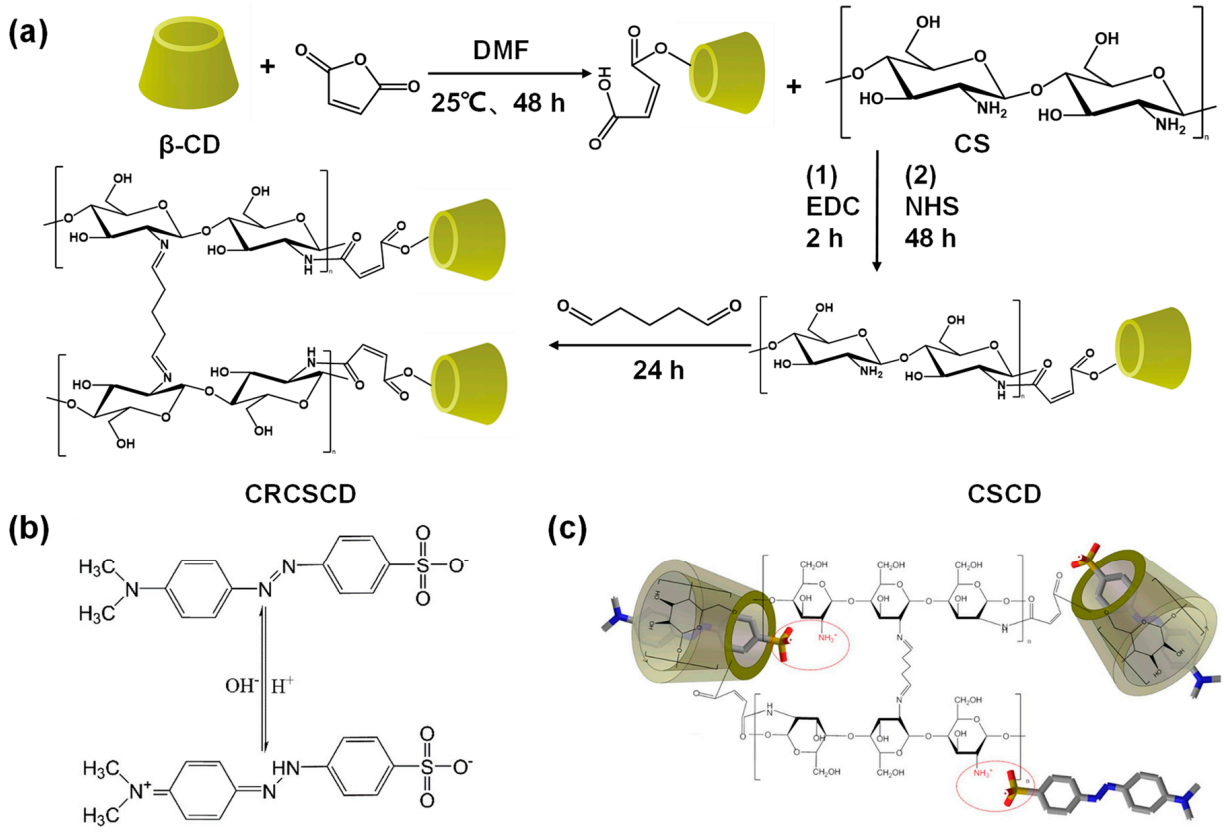

Figure 20. (**a**) Synthesis of CRCSCD; (**b**) the structure of the MO molecule; (**c**) adsorption mechanism of MO adsorbed by CRCSCD [75].

Later, Usman et al. [76] prepared a new adsorbent nitrilotriacetic acid *β*–CD–chitosan (NTA–*β*–CD–CS) for simultaneous removal of dye and metal ions from aqueous solutions. Firstly, NTA–*β*–CD was synthesized using nitrilotriacetic acid as the crosslinking agent and potassium dihydrogen phosphate as the catalyst. Then, NTA–*β*–CD was loaded onto chitosan using glutaraldehyde as another crosslinking agent (Figure 21a). At lower pH values, the surface of the adsorbent was positively charged due to the protonation of the amino group, and NTA–*β*–CD–CS exhibited high adsorption for negatively charged MO through the electrostatic attraction. As pH increased, the surface of the adsorbent became negatively charged due to deprotonation of $–NH_2$, –COOH, and –OH groups, contributing to the adsorption of Hg^{2+}. In the single-component system, the material showed high adsorption efficiency and rapid adsorption rates for Hg^{2+} and MB, with the maximum adsorption capacities of 178.3 and 132.5 mg/g, respectively. Notably, the NTA–*β*–CD–CS

adsorbent was very effective for simultaneously adsorbing both metals and cationic dyes at pH = 6.0, which was consistent with the result of the single–component adsorption system (Figure 21b,c).

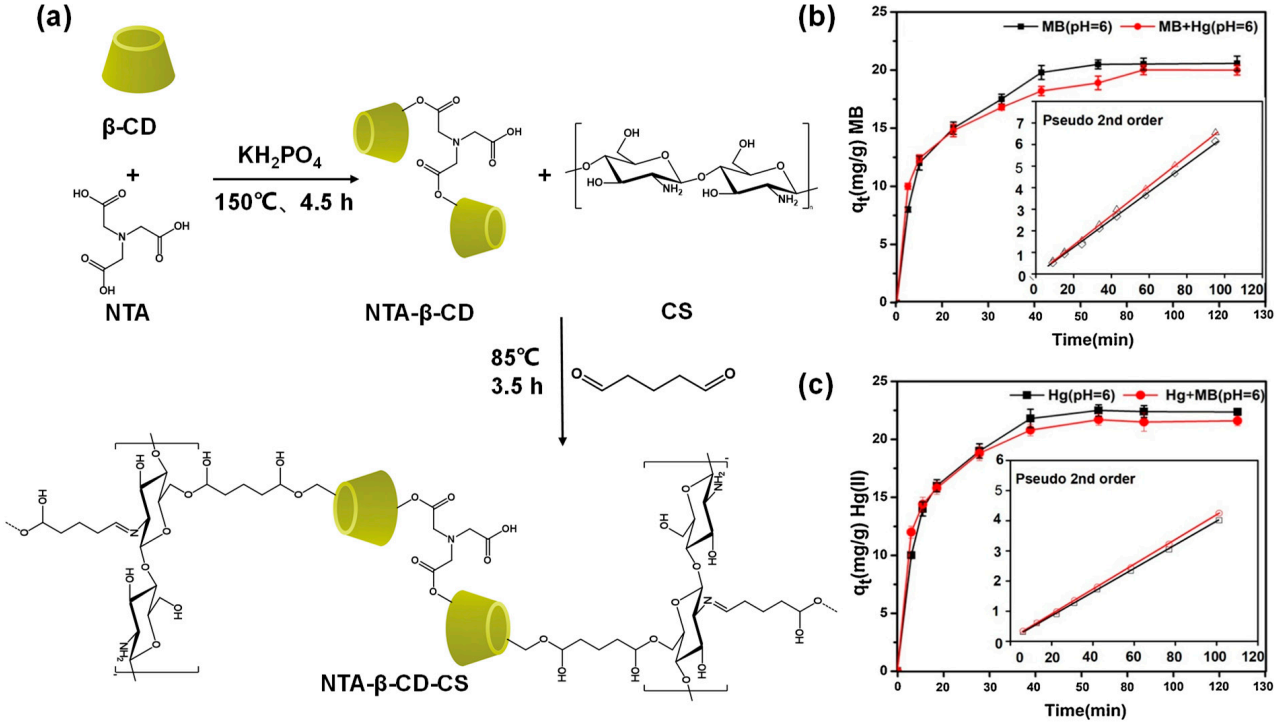

Figure 21. (**a**) Synthesis of NTA–*β*–CD–CS; the effect of contact time on the adsorption of (**b**) Hg^{2+} and (**c**) MB by NTA–*β*–CD–CS in mono and binary systems [76].

The active hydroxyl groups on the cellulose chain can be easily chemically modified [102]. To date, *β*–CD cellulosic fiber and *β*–CD cellulose nanocrystal have been reported for the removal of various organic pollutants. Yue et al. [103] grafted amino–terminated hyperbranched polymer (NH_2–HBP) and *β*–CD on cotton fibers and studied their adsorption capacity for Congo red and MB. Dichtel et al. [97] demonstrated a facile approach to removing micropollutants from water in a continuous manner by polymerizing cyclodextrin polymer networks onto cellulose microcrystals, and thus preparing a core/shell structural adsorbent. Cellulose beads facilitate the separation operation in batch adsorption experiments. Lin et al. [77] has used EPI as a crosslinking agent and loaded *β*–CD onto the prepared fibrin beads, synthesized a *β*–CD–grafted cellulose–type adsorbent, and used it to remove BPA (Figure 22). SEM and BET analysis showed that *β*–CD–grafted cellulose maintains the highly porous morphology of the cellulose beads while increasing the specific surface area of the adsorbent. The maximum adsorption capacity for BPA by the grafted cellulose bead was 30.8 mg/g. With the pH value increasing from 2.0 to 7.0, the adsorption capacity of BPA by *β*–CD–grafted cellulose increased sharply. However, under alkaline conditions, the adsorption capacity of BPA decreased greatly. This suggested that the protonation of the material at a low pH value and the deprotonation of BPA under alkaline conditions may influence the formation of clathrates between the material and BPA. Based on the good adsorption capacity, simple synthetic process, and ease of recycling, *β*–CD–grafted cellulose has great potential for the efficient removal of BPA during water treatment.

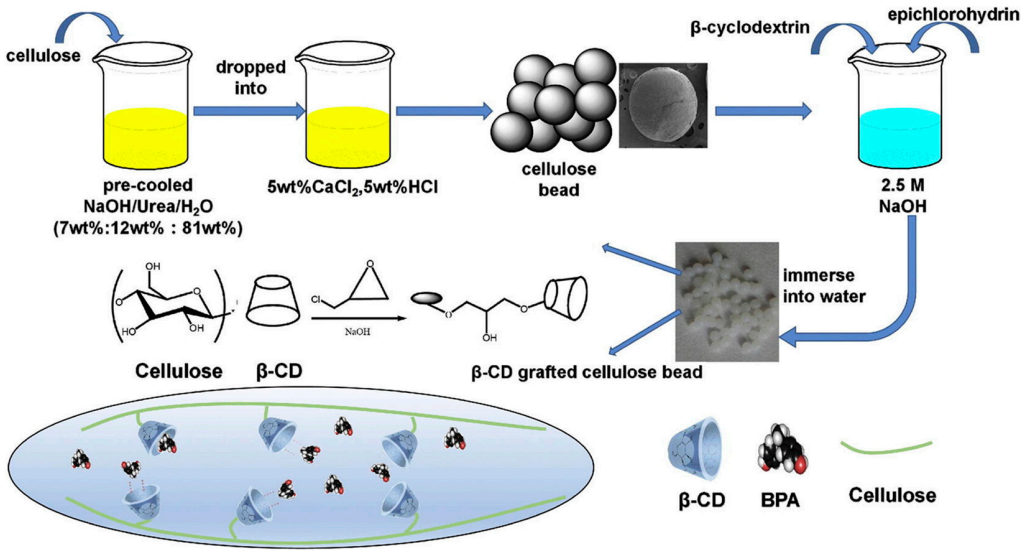

Figure 22. Preparation of *β*–CD-grafted cellulose beads for the removal of BPA via host–guest interactions [77].

4. Conclusion and Perspectives

β–CD is a product of starch after the action of microbial enzymes, has a wide range of sources, and is environmentally friendly. Because of its characteristics of "outer hydrophilic, inner hydrophobic", it has a specific recognition effect on some guest molecules, and is thus widely used in the adsorption field for wastewater treatment. However, its "outer hydrophilic" properties lead to its high solubility in water, which also limits its application in the adsorption of pollutants from water environments. To reduce its solubility in water, it is necessary to make some chemical modifications to prepare water-insoluble *β*–CD–based porous materials.

From the above discussions regarding the removal of organic pollutants by *β*–CD–based porous materials in recent years, some main conclusions were obtained. From the perspective of material synthesis, there is an increasing tendency to use green crosslinking agents and more environmentally friendly bio–based materials to achieve the purpose of designing removal pollutants while avoiding secondary pollution. In addition, materials synthesized using *β*–CD–COF with *β*–CD as the building block will have a regular and highly adjustable porous structure, which further expands the types and scope of *β*–CD–based porous materials. From the perspective of application, the research direction for *β*–CD–based materials has begun to shift from single–function materials to multifunctional materials. Because there is usually a variety of pollutants in real water samples, the development of multifunctional materials can help to simultaneously remove these multiple pollutants. Furthermore, the mechanisms of adsorption of organic and inorganic heavy metal pollutants by these *β*–CD–based materials mainly include host–guest interaction, electrostatic interaction, and ligand–metal coordination bonding. Among these, host–guest interaction is mainly achieved by the cavity of *β*–CD, and the other interactions occur through the functional groups (such as carboxyl and amino groups) by selecting specific crosslinking agents and carriers to bind with cationic or anionic dyes, as well as heavy metal ions. The process of adsorption of pollutants by *β*–CD–based porous materials usually involves the synergistic effects of host–guest interaction and other interactions.

At present, although many advances have made in the modification of *β*–CD–based materials, some challenges still exist. Firstly, the high toxicity of crosslinkers used has greatly restricted the industrial application of *β*–CD-based adsorbents for wastewater treatment. At present, most of the crosslinking agents used in the process of synthesis of *β*–CD-based porous materials are toxic. In the future, low toxicity and green reagents should be selected. Secondly, the synthetic cost of *β*–CD-based porous materials has rarely

been analyzed. The development of low-cost, high-performance, and environmentally friendly adsorbents has always been a key research topic. Finally, to date, few natural polymer materials have been used for the preparation of *β*–CD–based porous materials. Compared with traditional materials based on inorganic or organic polymer supports, natural polymer materials have the advantages of low cost, environmental friendliness, and low toxicity. Therefore, the development of highly efficient natural polymer-based *β*–CD–type materials should be paid more attention in future. We hope that this review can provide some strategies for the design and development of some new *β*–CD-based porous materials for the highly efficient removal of pollutants from wastewater.

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