B-Cyclodextrin-Based Porous Organic Polymers for the Removal of Environmental Pollutants from Water

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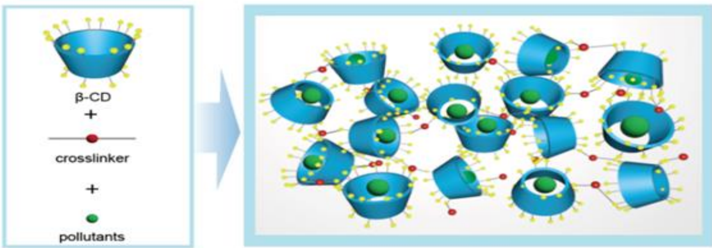
Abstract

As a macrocyclic host, β-cyclodextrin has a deep cavity of fixed size, as well as a unique internal hydrophobic and external hydrophilic cavity, which has excellent performance in host-guest recognition, and has been widely used in molecular recognition detection, drug delivery and other fields. Porous organic polymers have the characteristics of large specific surface area and pores, and have a good application prospect in the field of water pollution treatment.Therefore, the synthesis of β-cyclodextrin-based porous organic polymers not only has excellent host-guest recognition performance, but also has the characteristics of large specific surface area and multiple binding sites, so it has become the main design method at present. In this paper, the research status of β-cyclodextrin-based porous organic polymers in structural design and adsorption of pollutants was reviewed. The relationship between polymer structure design and adsorption performance was discussed, including adsorption of heavy metal ions and organic molecules in water. The application prospect and future development direction of β-cyclodextrin-based porous organic polymers were prospected.

Keywords: Cyclodextrin ; Porous organic polymer ; Adsorption separation

Graphical abstract



In this paper, we reviewed the research status of β-cyclodextrin-based porous organic polymers, discussed the relationship between structure and properties, and prospected the application prospect and future development direction.

1 Introduction

With the continuous development of society and economy, the problem of water pollution is becoming more and more serious, which poses a great threat to human production，life and the environment. Organic micro-pollutants, heavy metal ions and other major pollutants gather in large quantities in water, seriously exceeding the purification capacity of the water environment itself, causing irreversible impact on the water system. Therefore, finding an efficient and low-cost water pollution treatment method has become the main research direction at present[1]. In the current main treatment methods (chemical precipitation[2], membrane separation[3], ion exchange[4], solvent extraction[5], etc.), adsorption method has been widely concerned because of its fastness and efficiency, simple operation, wide range of adaptation, good stability, and no pollution to the environment[6]. The main factors affecting adsorption are adsorption capacity, chemical stability and selectivity of adsorbent materials in water. Therefore, the design and synthesis of adsorbent materials with high adsorption capacity, chemical stability and selectivity have become urgent problems to be solved. In the adsorption materials, porous organic polymer is a kind of porous network material composed of organic building elements connected by covalent bonds. It has the characteristics of designability, easy functionalization, high specific surface area, low density, excellent stability and uniform pore size, etc., which makes it show unique advantages in improving adsorption capacity and selectivity[7-8].

Porous organic polymers are generally synthesized for functional applications by screening for suitable chemical reactions. Therefore, the design and development of new functional building elements has gradually become a key factor to solve the innovative development of porous organic polymer materials[9]. The supramolecular macrocyclic main compound provides a new idea and method for the design and synthesis of porous organic polymers with its unique host-guest chemical properties, easy functionalization and adjustable configuration[10].

Cyclodextrins, as the main body of the second generation of supramolecular molecules, are large cyclic molecules composed of many molecules connected end to end by α-1, 4-glucoside bonds, with a spiral structure in space, and are a very important class of macrocyclic receptors, among which α, β and γ cyclodextrins are the most studied. β-cyclodextrin is the most widely used because of its insoluble in water and moderate cavity size. β-cyclodextrin has a hydrophilic outer margin and hydrophobic inner cavity structure, which enables it to form clathrates with organic molecules and heavy metal ions through van der Waals force, hydrophobic interaction, host-guest interaction and so on[11-12]. This excellent recognition property makes it widely used in the field of adsorption separation. The introduction of β-cyclodextrin into porous organic polymers can not only improve the adsorption capacity of polymer materials for pollutants, but also improve the adsorption selectivity. This method is an effective way to improve the adsorption and separation performance of porous organic polymers.

This paper discusses the adsorption of different types of pollutants by β-cyclodextrin-based porous organic polymers, summarizes the relationship between structural design and adsorption properties, and puts forward some challenges and future development directions of β-cyclodextrin-based polymers in the field of pollutant treatment.

β-cyclodextrins contain rich hydroxyl groups and internal hydrophobic cavities, which can bind chemical compounds and metal ions[13-15]. They are able to combine with organic molecules to construct porous organic polymer materials with unique functions; At the same time, because of its large specific surface area and abundant active sites, β-cyclodextrin-based organic polymer framework materials have become a design direction. In this paper, we mainly introduce the relationship between the structural design and adsorption properties of β-cyclodextrin-based porous organic polymers and their framework materials.

2.Adsorption of heavy metal ions by β-cyclodextrin-based porous organic polymers

The adsorption of metal ions by β-cyclodextrin-based porous organic polymers depends on the adsorption of metal ions by β-cyclodextrin monomers. Since β-cyclodextrins have only hydroxyl groups, they can only bind to metal ions under alkaline conditions. Matsui reported that β-cyclodextrins interact with metal ions in compounds where, under alkaline conditions, unprotonated 2- and 3-hydroxyl groups coordinate with copper ions (as shown in Figure 1a)[16]. The structure of binuclear hydroxyl bridging was inferred by spectroscopic and potential analysis. Since the interaction between β-cyclodextrin monomer and metal ions mostly belongs to van der Waals force, hydrogen bond, hydrophobic interaction, etc., the obtained compounds are unstable. By chemically combining β-cyclodextrin with other molecules and synthesizing porous polymers, the stability of the polymers can be improved and heavy metal ions can be adsorbated quickly and efficiently.

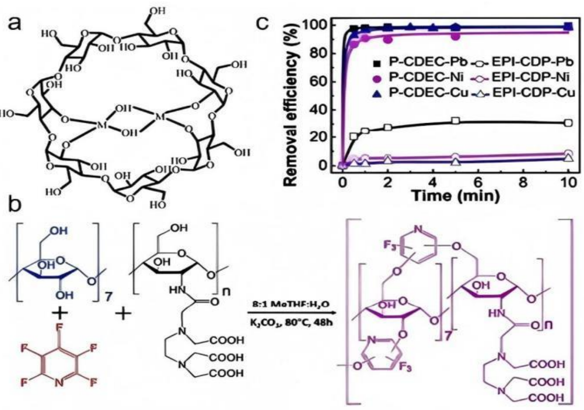


Figure 1. a. Complexes of β-cyclodextrins and metal ions; b. β-cyclodextrin-based porous polymer; c. adsorption property curve of β-cyclodextrin-based porous organic polymer

Tingting Yu et al. prepared β-cyclodextrin-based porous organic polymer, and studied its adsorption of Li^{+}, Cu^{2+} and Ni^{+} in aqueous solution[17]. The results showed that after combining β-cyclodextrin with biomass molecules and synthesizing polymers, the adsorption efficiency was greatly improved (as shown in Figure 1b). In the system where Li^{+}, Cu^{2+} and Ni^{+} coexist, the adsorbents containing β-cyclodextrins have higher adsorption selectivity for Li^{+}. However, when the β-cyclodextrin-containing polymers were prepared by chemical grafting, the grafting rate became one of the factors affecting the adsorption performance of the adsorbent materials[18]. With the increase of grafting rate, the adsorption capacity first increased and then decreased. This is due to the increased interaction between polymer and metal ions as the grafting rate increases; with the further increase of grafting rate, the number of metal ions adsorbed on each chain decreases. The adsorption properties of the adsorbent material prepared by introducing β-cyclodextrin into the polymer by chemical binding and non-chemical binding, the non-chemical binding β-cyclodextrin polymer loses β-cyclodextrin molecules during use, resulting in poor adsorption properties and recyclability. Therefore, chemical binding should be considered when designing and synthesizing β-cyclodextrin-based polymer adsorption materials. At the same time, the adsorption performance of β-cyclodextrin-based polymers can be greatly improved by designing polymers with specific binding.

Monu Verma et al. successfully prepared β-cyclodextrin-based porous polymers by cross-linking β-CD with CS (chitosan) via EDTA (ethylenediamine tetraacetic acid) by amidation reaction (Figure 2)[19].The β-cyclodextrin structure is evenly distributed in the polymer, and the rigid cross-linked chain ensures the stability of the polymer microporous structure. The polymer can efficiently adsorb both Hg^{2+} and Cd^{2+} , which is attributed to the interaction of metal ions and EDTA carboxylic acid groups.

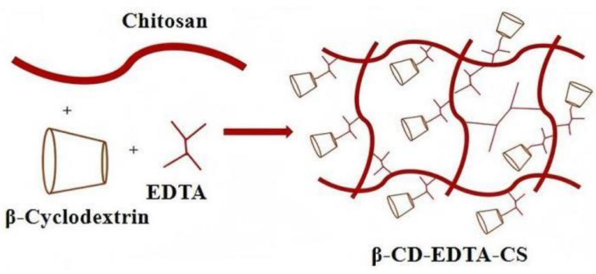


Figure 2. Crosslinked β-cyclodextrin-based porous organic polymer ;

In the above amorphous polymers, the disordered arrangement of polymer chains easily leads to the distortion of β-cyclodextrin structure, which makes the stability of the polymer β-cyclodextrin difficult to guarantee. However, the long-term ordered arrangement of the polymer chains can maintain the stability of the β-cyclodextrin structure, which is conducive to predicting the adsorption selectivity of the polymer. Jie Jia et al. introduced a cross-linked hydrogel network based on acrylic acid (AA) and N,N' -dimethylacrylamide (MBA) monomers into a β-CD-MOF structure to prepare a β-CD-MOF based multi-pore hydrogel (as shown in Figure 3)[20]. The synthetic porous hydrogel, called A/M-CDMOF-gel, not only has greater structural stability, but also has excellent properties for simultaneous adsorption of Au^{3+}, Ag^{+}, and Pb^{2+} .The maximum adsorption capacities of A/M-CDMOF-gel for Au^{3+}, Ag^{+} and Pb^{2+} were 316.4, 60.9 and 414.2mg/g, respectively.

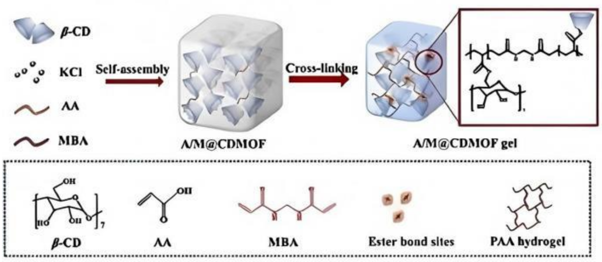


Figure 3. β-cyclodextrin-based MOF structure;

3 Adsorption of organic pollutants by β-cyclodextrin-based porous organic polymers

The oxygen atoms and hydroxyl groups in the structure of β-cyclodextrins provide a wealth of lone electron pairs, which can identify not only metal ions, but also organic molecules through hydrogen bonding, electrostatic interaction, hydrophobic interaction, etc. By introducing β-cyclodextrin into polymer, the β-cyclodextrin-based polyporous organic polymer can be used for adsorption and separation of organic matter in water by using the selectivity of β-cyclodextrin and reasonable structural design.

Guizhou Xu et al. prepared an ultra-porous β-cyclodextrin-based polymer in the aqueous phase for the first time by simultaneously cross-linking β-cyclodextrins with flexible and rigid crosslinkers (as shown in Figure. 4)[21]. Compared with β-cyclodextrins cross-linked with a single flexible or rigid crosslinkers, T-E-CDP (β-cyclodextrin-based polymer) can adapt well to the size of guest molecules and maintain a certain degree of rigidity. T-E-CDP adsorbs bisphenol A, a pollutant in water, and quickly reaches equilibrium within 1min, and the adsorption efficiency is as high as 92.4%. In contrast, the adsorption efficiencies of EPI-CDP, DARCO-AC and XAD-4 within 1min were 22%, 46.7% and less than 5%, respectively. However, the use of rigid crosslinkers will affect the water expansibility of the adsorbent to some extent. The water expansibility of T-E-CDP (2.63 $cm^3\ g^{-1}$) is lower than that of EPI -CDP (3.46 $cm^3 g^{-1}$) , and T-E-CDP (0.31$m^2 g^{-1}$) has a low BET specific surface area like other β-cyclodextrin-based polymers. The bottom-up design can effectively ensure the uniform distribution and high content of β-cyclodextrin structure in the polymer, and the introduction of non-planar construction elements into the polymer can significantly increase the specific surface area of the porous material. Haiying Li et al. designed and synthesized an overcrosslinked porous β-cyclodextrin polymer (BnCD-HCPP) through benzylation of β-cyclodextrin and Friedel-Crafts alkylation (as shown in Figure 5)[22]. BnCD-HCPP has a very high BET surface area, large pore volume and high thermal stability, making it an efficient adsorbent for removing aromatic pollutants from water. The distribution coefficient of adsorption efficiency, defined as the ratio of adsorption capacity to equilibrium adsorbent concentration, ranges from 103 to 106 mL g^{-1} in a concentration of 0-100 ppm, an order of magnitude higher than other β-cyclodextrin-based adsorbents previously reported. The molar ratio of β-cyclodextrin exceeds 300%, indicating that adsorption occurs not only through 1:1 complexation, but also in the nanopore of BnCD-HCPP produced during the overcrosslinking process.

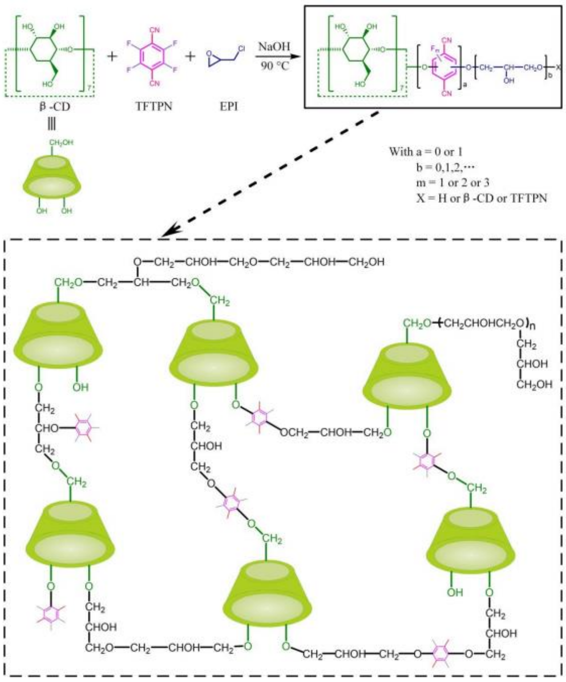


Figure 4. Synthesis method of T-E-CDP;

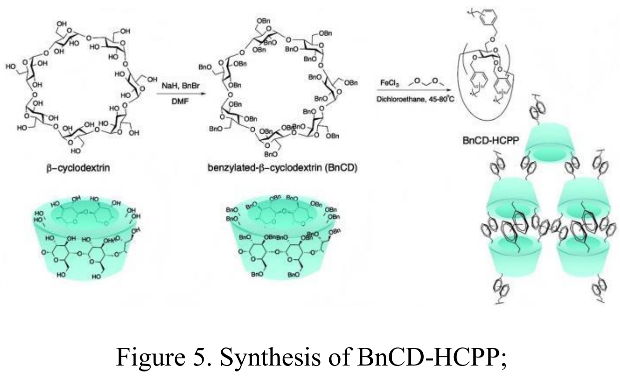


Figure 5. Synthesis of BnCD-HCPP;

In the design and synthesis of porous organic polymers, β-cyclodextrin-based polymers are introduced into two-dimensional microporous organic networks in order to obtain greater absorption capacity and faster absorption rate. Yuan-Yuan Cui et al. synthesized two-dimensional β-cyclodextrin-based polymers using the coupling reaction of 7-I-β-CD and DBP in different solvents (see Figure 6a)[23]. The BET surface areas of CD-MON-PhMe, CDMON-THF, and CD-MON-DMF are 518, 468, and $645 m^2 g^{-1}$, respectively. The total pore volumes of CD-MON-PhMe, CD-MON-THF, and CD-MON-DMF are 0.43, 0.27, and $0.56 cm^3 g^{-1}$, respectively. This is because the reaction solvent can realize the adjustment of BET surface area, pore volume and pore size by controlling the morphology or aggregation degree of CD-MON. The adsorption of BPAF with an initial concentration of 50 mg L^{-1} by CD-MON-THF and CD-MON-PhMe was completed within 5min, while the adsorption of pollutants with the same concentration by CD-MON-DMF was completed within 10s. As the initial concentration of BPAF increased, the time difference became more obvious. This difference indicates that CD-MON-DMF can provide more adsorption sites, and it is easy to disperse and contact with BPAF in aqueous solution, and the adsorption kinetics is super fast and the removal effect is good through the combination of hydrophobic interaction, π-π-interaction and hydrogen bond.

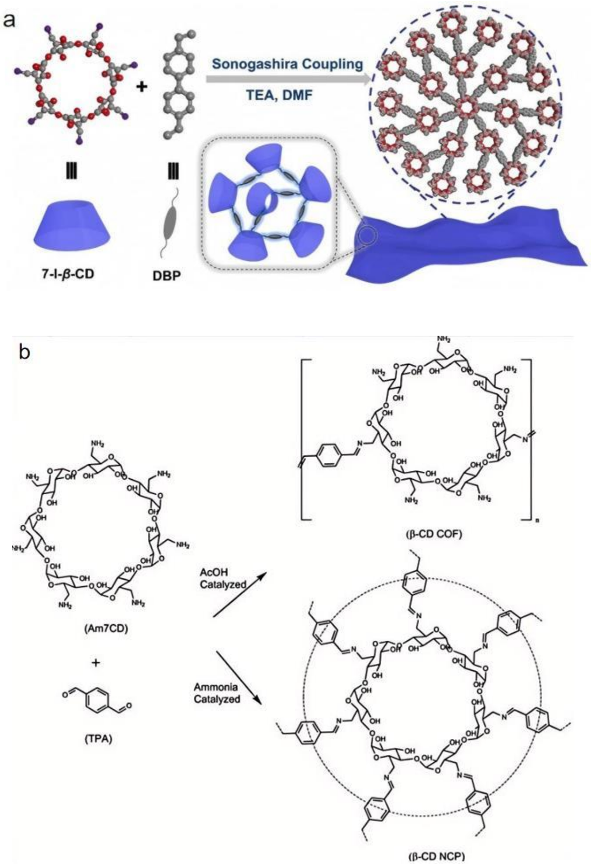


Figure 6. a. Synthesis diagram of CD-MON-DMF; b. Synthesis of β-COF and β-CD-NCP;

Covalent organic frame materials have become the focus of research because of their excellent porous properties and structural stability. With the deepening of research, β-cyclodextrin-based covalent organic framework materials have been developed continuously, and have shown good application prospects in the field of adsorption and separation of organic molecules. Ren-Qi Wang et al. first synthesized β-CD COF using heptaalkyl (6-amino-6-deoxy)-β-CD (Am7CD) and terylene acid (TPA) via acid-catalyzed aldehyde-diamine condensation in water and ethanol (Figure 6b)[24]. Compared with the amorphous β-CD polymer (β-CD-NCP), β-CD COF has a larger surface area, more uniform pore size and higher thermal stability. In neutral water, the removal rates of β-CD COF for ibuprofen and naproxen were 78% and 98%, respectively, within 10 min. This is due to their different molecular structures, β-CD COF has a large number of amino and hydroxyl groups and is a supplying substructure, while naproxen is an electron-absorbing structure. Therefore, electron donor-acceptor interactions play an important role in the adsorption mechanism.

4 Summary and outlook

In summary, β-cyclodextrin-based porous organic polymers, as a novel macrocyclic host polymer, has a broad application prospect in wastewater treatment due to their advantages of excellent selectivity, high specific surface area and good stability. In this article, the structural design and selective adsorption properties of β-cyclodextrin-based porous organic polymers are discussed systematically. The results indicate that the β-cyclodextrin-based porous organic polymer has high selective adsorption performance for metal ions, which is contingent upon the stability of β-cyclodextrin in the polymer system. In this system, β-cyclodextrins can not only improve the specific surface area and porosity of the polymer, but also interact effectively with metal ions and organic pollutants and so on, and have higher selectivity compared to traditional amino, carboxyl, hydroxyl and other functional groups.

From the perspective of application, adsorption method can serve as a promising method to detect pollutants in water environment. Although β-cyclodextrin-based porous organic polymers have achieved some success in wastewater treatment, there are still some challenges. The selective adsorption of metal ions by β-cyclodextrin-based porous organic polymers depends on the structure of β-cyclodextrins. How to more accurately regulate the conformational changes of flexible β-cyclodextrin macrocyclic in polymers is a problem that needs further exploration. Secondly, the selective adsorption of metal ions by β-cyclodextrin-based porous organic polymers is more demanding than that of organic pollutants, and the difference of selective adsorption of organic pollutants by amorphous and crystalline polymers has not been discussed. Thirdly, the adsorption tests of actual water samples of β-cyclodextrin-based porous organic polymers are few, which is also the key data for optimizing their performance in the future. We believe that with more in-depth research, these problems will ultimately be solved.

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Conflictofinterestaatement. None declared

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