Facile Preparation of Hierarchically Porous Aromatic-cyclodextrin Polymers and Their Application for the Selective Adsorption of Cationic Dyes

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Abstract

Porous β -cyclodextrin-containing materials have significant potential as adsorbents for the removal of pollutants from water. However, preparing these porous polymers in the aqueous phase is challenging. In this study, a kind of novel porous aromatic-cyclodextrin polymers (P-aro-CDPs) was designed and synthesized in aqueous solution under mild conditions by exploiting covalence-crosslinking reaction. P-aro-CDPs were characterized using a variety of methods, which revealed that P-aro-CDPs have a hierarchical porous structure, a highly negatively charged surface, and rich in hydroxyl groups. The prepared P-aro-CDPs showed excellent removal efficiency for methylene blue, with a maximum adsorption capacity of 194.17 mg g^{-1} . The adsorption data are well fitted to the pseudo-second-order kinetic model and the Langmuir isotherm. The as-synthesized P-aro-CDPs material exhibited superior adsorption selection toward cationic dyes than anionic dyes whether in single or multicomponent systems. Further, the P-aro-CDPs adsorbent are reusable, and good performance over six adsorption-desorption cycles was demonstrated. Due to its off-the-beaten-path synthesis, low cost, excellent removal efficiency, and recyclability, P-aro-CDPs have great potential for use as an adsorbent in water-treatment applications.

1. Introduction

Globally, increasing industrialization has resulted in increased environmental pollution, and this poses a serious risk to human health [1]. In particular, water pollution exacerbates water shortages, places constraints on economic development, and limits social progress [2; 3]. Therefore, it is crucial to remove the pollutants from contaminated water for alleviating pressure on the planet's limited water resources [4]. Water pollutants include dyes, other organic pollutants, and heavy metals [5]. When discharged as effluents, dyes pose a threat to public health, environment, and ecosystems due to their high toxicities, environmental persistence, and potential for bioaccumulation [6]. Existing wastewater treatment methods include adsorption [7, 8], membrane separation [9, 10], chemical oxidation [11], photocatalysis [12; 13], and Fenton degradation [14, 15]. Among these methods, adsorption is regarded to be the most effective and reliable method due to its accessibility and low cost [16-18]. Porous materials are particularly suitable sorbents for the removal of dyes on account of their high specific surface areas (that is, large numbers of active sites for the adsorption of dye molecules) and their surface functional groups and internal structures [19-23].

β -Cyclodextrin (β -CD) is a naturally occurring compound; it is also inexpensive, nontoxic, biocompatible, and biodegradable. β -CD has a hydrophobic central cavity and a hydrophilic external surface, and can form host-guest complexes with a variety of organic compounds [24, 25]. These unique characteristics have resulted in the use of β -CD in a number of applications, including drug delivery [26] and chiral recognition [27-29], and as structural building blocks [30-32]. In particular, β -CD has been employed as a "green" building block for the construction of a variety of materials [33-35]. β -CD-based polymers are lightweight, chemically diverse, and easily processable [17, 36-38], and have been prepared using crosslinking agents based on flexible structures, such as epichlorohydrin [39], and rigid structures, such

as tetrafluoroterephthalonitrile [40-44]. The use of rigid crosslinking agents results in the formation of polymers with rapid adsorption rates when used as sorbents [45] because the rigid crosslinkers increase pore formation and, as a consequence, the specific surface area of the sorbent [46, 47]. Thus, CD-based polymers have attracted significant attention for use in separation processes and water-treatment applications owing to their porous structure, dispersibility, adsorption capacity, and selectivity [30, 45, 48-52]. However, porous CD-based polymers have previously been prepared in organic phases, and the synthesis of these polymers in the aqueous phase is challenging.

In this study, a CD polymer with a porous structure was synthesized directly in the aqueous phase using an one-pot fabrication technique. The prepared P-aro-CDPs were characterized using various spectroscopic and analytical techniques, and the adsorption performance of P-aro-CDPs for organic dyes was evaluated using methylene blue (MB) as a model dye. Finally, the adsorption performance of P-aro-CDPs toward a wide range of organic dyes was also investigated.

2. Material And Methods

2.1 Chemicals and materials

Benzidine (BZD) was obtained from the Shanghai Aladdin Biochemical Technology Co., Ltd., and β -CD was purchased from the Tianjin Kemiou Chemical Reagent Co., Ltd. All dyes (Table S1) used in our experiments were of analytical grade.

2.2 Material synthesis

BZD (1.5 mmol) was placed in a 250-mL round-bottom flask submerged in an ice bath. After iced water of 100 mL and iced concentrated hydrochloric acid of 0.7 mL were added to the flask, the solution was stirred for 15 min using a magnetic stirrer. Subsequently, 0.1 M NaNO_2 of 30 mL was added dropwise to the solution, and the contents were stirred for a further 25 min to allow the full conversion of the amine to the corresponding diazonium salt. An aqueous Na_2CO_3 solution was then added dropwise until the mixture was slightly alkaline to ensure the removal of excess hydrochloric acid from the solution. A solution of β -CD (0.03 M) and Na_2CO_3 (0.1 M) of 30 mL was added to the diazonium salt solution and allowed to react for another 12 h with stirring. It was observed that bubbles were discharged and aggregation happened during the reaction process. The resulting mixture was centrifuged and the sediment was successively washed with water, methanol, tetrahydrofuran (THF), methanol, and water. The product was then centrifuged and the final product was vacuum freeze-dried for 12 h to obtain the P-aro-CDPs product as a water-insoluble brown powder.

2.3 Batch adsorption experiments

For a single dye adsorption test, the P-aro-CDPs (adsorbent) of 5 mg and the dye solution (200 mg L^{-1}) in 20 mM phosphate buffer with different pH adjusted with NaOH or HCl of 5 mL were added to a 10-mL centrifuge tube, and the tube contents were shaken at 200 rpm in an incubator shaker at 25°C . After

adsorption was complete, the mixture was centrifuged, and the dye concentrations in initial solution and supernatant were monitored using UV-visible spectroscopy with an Evolution 220 spectrometer (Thermo Fisher Scientific Inc., USA) at the maximum absorption wavelength of the dyes (Table S1). The equilibrium adsorption capacity (q_e , mg g⁻¹) was calculated using the following formula:

$$q_e = \frac{(C_o - C_e) \times V}{m} \quad (1)$$

Here, C_o and C_e are the initial and equilibrium dye concentrations (mg L⁻¹), respectively, V is the solution volume (L), and m is the adsorbent mass (g).

For binary dye adsorption studies, two dyes (each 200 mg L⁻¹) were mixed together. The mixed dye solution of 5 mL was added to the adsorbent of 10 mg, and the mixture was shaken in an incubator shaker for different time and then centrifuged. The UV-vis spectra of the supernatant were measured.

2.4 Adsorbent recyclability

After MB had been adsorbed onto P-aro-CDPs, it was desorbed using ethanol. The adsorbent was washed with water and dried for 2 h in a freeze dryer before next use. This adsorption–desorption process was cycled for six times.

3. Results And Discussion

3.1 Synthesis of P-aro-CDPs

The P-aro-CDPs were synthesized through a covalent cross-linking process under mild conditions using water as the solvent (Fig. 1). Firstly, a diazonium salts was synthesized from BZD as the monomer by diazotization under mild reaction conditions. Subsequently, a kind of hierarchically porous aro-cyclodextrin polymers (P-aro-CDPs) was formed through crosslinking reaction. According to the fact of large nitrogen releasing during synthesis process and referring to literature [53], it is suggested that the polymerization reaction could be depicted as Fig. 1, and the polymers should contain main product (1) and by-product (2).

3.2 Material characterization

The synthesized P-aro-CDPs was subjected to FTIR, XPS, and solid-state NMR spectroscopies to investigate the chemical bonds and functional groups on its surface.

Compared the FTIR spectrum of P-aro-CDPs with that of BZD (Fig. 2A), the amine band at 3200–3400 cm⁻¹ is absent, whereas the skeletal vibration peak of the benzene ring at 1615 cm⁻¹ is still present. Comparison the FTIR spectrum of P-aro-CDPs with that of β-CD reveals that the -OH stretching band at 3420 cm⁻¹ and the skeletal vibration peak of β-CD at 534 cm⁻¹ are still present. Aromatic carbon signals

of BZD and aliphatic carbons of β -CD are observed at 120–160 ppm and 72 ppm in the ^{13}C -NMR spectrum of P-aro-CDPs (Fig. S1). These indicate that BZD and β -CD participated in the formation of the compound during the reaction and presented in the final structure of the synthesized polymers.

Two new peaks in FTIR spectrum of as-prepared materials corresponding to -N=N- and C-O-N stretching bands are observed at 1400 and 1000–1200 cm^{-1} . The results of XPS (Fig. 2B) and elemental analyses (Table S2) show that P-aro-CDPs contains C, H, O, and N, and that the two monomers had reacted on the surface. Further, the XPS spectrum of N1s (Fig. S2) could be decomposed into three single peaks that attributed to C-N (399.4 eV), N=N+ (401.7 eV), and N-O (405.4 eV) functional groups [54]. These results show that by-products (2) during polymerization were existed.

The N_2 adsorption–desorption isotherm of P-aro-CDPs (Fig. 2C) of type-IV reveals the presence of micro- and mesopores, as evident from the pore-size distribution curve. The BET surface area and the pore volume of P-aro-CDPs were calculated to be 67.6 $\text{m}^2 \text{g}^{-1}$ and 0.2767 $\text{cm}^3 \text{g}^{-1}$, respectively. From the pore-size distribution curve, pores with diameters < 2 nm are mainly concentrated at 0.8 nm, which indicates the presence of the β -CD monomer. Thus, P-aro-CDPs have hierarchical porous structure and high specific surface area, and may be a promising adsorbent for aqueous pollutants.

The TGA results (Fig. 2D) show that P-aro-CDPs are relatively stable at temperatures below 250 $^{\circ}\text{C}$, and that its thermal behavior can be divided into three stages. A weight loss of approximately 5% was observed in the first stage (0–200 $^{\circ}\text{C}$), corresponding to the loss of water adsorbed on the outer surface layer. A second weight loss of approximately 10% was observed at 200–250 $^{\circ}\text{C}$, attributing to internal polymer dehydration. Finally, the third weight loss of 10–30% occurred at 250–600 $^{\circ}\text{C}$, ascribing to the degradation and carbonization of the polymer backbone.

Zeta potential analysis (Fig. 3A) revealed that P-aro-CDPs had an isoelectric point of approximately 4.0; hence, the surface of P-aro-CDPs is highly negatively charged when the pH is greater than 4.0, which indicates that the as-synthesized material may be used to selectively adsorb cationic compounds.

The XRD pattern of P-aro-CDPs (Fig. 3B) exhibits a broad peak at $2\theta = 15\text{--}30^{\circ}$, which is a characteristic amorphous peak. Therefore, we deduce that the polymer network of P-aro-CDPs has an amorphous structure.

The SEM image of P-aro-CDPs (Fig. 3C) clearly shows that the synthesized polymer nanoparticles are irregularly shaped, with rough and uneven surfaces on the micrometer scale. The TEM image (Fig. 3D) reveals the presence of mesopores and micropores with a variety of diameters within the polymer as well.

3.3 Dye adsorption performance

3.3.1 Effect of pH

The pH effect on the dye-adsorption performance of P-aro-CDPs was investigated ranging pH 2–12, and the results are shown in Fig. 4A. MB adsorption was observed to increase gradually with increasing pH

(2.0–12.0). Less MB is adsorbed under acidic conditions due to the competition between protonated MB and H_3O^+ for adsorption sites. In contrast, the increased negative charge on the adsorbent surface under alkaline conditions facilitates the adsorption of cationic MB, which is consistent with the earlier zeta potential results; that is, the surface of P-aro-CDPs is positively charged at the pH lower than the isoelectric point of P-aro-CDPs (4.0), and it is negatively charged at $\text{pH} > 4.0$. The P-aro-CDPs surface also becomes gradually more negatively charged as the pH is further increased, resulting in increased adsorption of MB on P-aro-CDPs.

3.3.2 Effect of time

The time-dependent adsorption rates of MB at various concentrations on P-aro-CDPs were analyzed (Fig. 4B). The adsorption rate was high and approximately 80% of the total amount of dye was adsorbed in the first 20 min. However, the adsorbed amount still increased with time between 20–100 min, but at a slower rate. Finally, the adsorbed amount was almost constant at time greater than 150 min.

3.3.3 Adsorption kinetics

The adsorption kinetics of various concentrations of MB on P-aro-CDPs were analyzed by fitting the adsorption data to pseudo-first-order, pseudo-second-order, and Elovich kinetic models (Supporting Information) (Fig. 4C, S3, and S4 and Table S3). The experimental data fit pseudo-second-order kinetic model better than pseudo-first-order model, indicating that chemisorption is the rate-limiting step of adsorption process. Rate constant was observed to gradually decrease with increasing initial dye concentration, stating the fact that the adsorption rate is controlled by the rate of dye molecules binding to adsorption sites. As the number of adsorption sites on P-aro-CDPs is limited, higher dye concentration increases the ratio of adsorbates to adsorption sites, which leads to more competition for adsorption sites between dye molecules. Consequently, binding resistance increases and the binding rate descends, resulting in the overall adsorption rate reducing. Furthermore, the experimental data fit the Elovich kinetic model as well, indicating the rate-limiting step of chemisorption, which is likely due electron sharing between the hydrophilic groups on the adsorbent surface and the MB molecules.

To understand the diffusion process, in particular the rate-limiting step that determines MB adsorption onto P-aro-CDPs, the adsorption kinetics were further analyzed using the Weber–Morris intraparticle diffusion and Boyd models (Supporting Information). The process by which the dye is adsorbed onto P-aro-CDPs can be divided into three stages (Fig. S5 and S6). In stage 1, instantaneous or external surface adsorption occurs during the first 20 min of the adsorption process. Because the adsorption process had just started at this stage, there was an abundance of adsorption sites and $-\text{OH}$ groups on the P-aro-CDPs surface, which facilitated the rapid adsorption of MB molecules onto P-aro-CDPs through electrostatic interactions between MB^+ and $-\text{OH}^-$. A change in the adsorption driving force, from electrostatic interactions to a concentration gradient, was observed in stage 2, which occurred between 20 and 150 min after the start of adsorption. Because this stage involves intraparticle diffusion,

it forms part of the rate-limiting step of the entire adsorption process. In stage 3, which occurred after 150 min, a constant rate of adsorption was observed as adsorption equilibrium was reached.

The Weber–Morris model shows that the intraparticle diffusion rate (k_p) increases with increasing initial dye concentration, which shows that a high initial dye concentration results in a greater diffusion driving force, thereby enhancing the dye diffusion rate. Similarly, the boundary layer thickness (C) also increases with increasing initial dye concentration. A higher C value indicates a higher contribution of surface adsorption to chemisorption, which demonstrates that a high initial dye concentration can lead to an enlargement in thickness of diffusion boundary layer. Although the Weber–Morris plot of q_t (adsorption capacity at time t) versus $t^{0.5}$ (square root of time t) shows a linear relationship, the lines of best fit do not pass through origin, which is indicative of intraparticle diffusion. However, this is not sole rate-limiting factor. Likewise, in the Boyd plot of B_t (the Boyd function) versus time t , the lines of best fit do not pass through origin. Therefore, membrane diffusion is rate-limiting step during diffusion process.

3.3.4 Adsorption isotherms

The equilibrium data were analyzed using three isotherm models (Supporting Information) to investigate the saturated adsorption behavior and capacity of P-aro-CDPs for MB. The analyzed results show that the adsorption equilibrium data fit Langmuir model better than Freundlich and Temkin models (Fig 4D, S7, and S8 and Table S4), suggesting that the adsorption of MB onto P-aro-CDPs is limited to a monolayer over uniform adsorption sites. The maximum adsorption capacity of P-aro-CDPs toward MB was 194.17 mg g⁻¹ calculated using Langmuir equation.

3.3.5 Adsorption thermodynamics

In order to investigate the adsorption mechanism for a single dye system, the thermodynamic parameters were determined. For the adsorption of MB onto P-aro-CDPs, enthalpy (ΔH) and entropy changes (ΔS) calculated using the van't Hoff equation (Supporting Information) were 11.17 KJ mol⁻¹ and 35.44 J mol⁻¹ K⁻¹, respectively, which shows that the adsorption process is endothermic with an associated increase in the degree of disorder. Therefore, temperature rising would increase the driving force for adsorption of MB at active adsorption sites, thereby increasing the ability of P-aro-CDPs to capture MB molecules. The Gibbs free energy change (ΔG) went from positive to negative (606.7, 252.34, -102.02, -456.37, and -810.73 J mol⁻¹) as the adsorption temperature raised from 298, 308, 318, 328, to 338 K, indicating that temperature rising within a certain range promotes the spontaneous adsorption of MB onto P-aro-CDPs.

3.4 Repeatability

P-aro-CDPs are easily regenerated after washing several times with ethanol. It can be seen from Fig. 5A that the adsorption rate slightly decreases with increasing number of re-use cycles; however, the adsorption efficiency was maintained at above 80% after six adsorption–desorption cycles. Thus, P-aro-CDPs are recyclable, and this material is a promising industrially applicable adsorbent.

3.4 Adsorption selectivity

The adsorption selectivity of P-aro-CDPs was investigated using 15 dyes, including positively charged MB, rhodamine B (RB), brilliant cresyl blue (BCB), astrazon orange R (AOR), basic red 9 (BR9), auramine O (AO), and basic orange 21 (BO22), as well as negatively charged tartrazine (T23), acid red 73 (AR73), eosin (ES), alizarin red S (ARS), alizarin green (AG), methyl orange (MO), Congo red (CR), and sunset yellow FCF (SY) (seven cationic and eight anionic dyes). The results in Fig. 5B show that the adsorbed amount of dye onto P-aro-CDPs exceeded 70 mg g^{-1} for all cationic dyes but was less than 10 mg g^{-1} for any anionic dyes. Therefore, the adsorption properties of P-aro-CDPs are considerably better for cationic dyes than anionic dyes, indicating that P-aro-CDPs are more selective toward cationic dyes.

The adsorption behavior of P-aro-CDPs for binary dye solutions (MB/T23 and AO/TS) was investigated to further validate the adsorption selectivity of P-aro-CDPs toward cationic dyes (Fig. 5C and 5D). The cationic dye concentration in each mixed dye solution was lower after the addition of P-aro-CDPs, whereas the anionic dye concentration remained essentially unchanged, which confirms that P-aro-CDPs selectively adsorb cationic dyes from dye solutions that contain mixtures of cationic and anionic dyes.

4. Conclusion

In this study, P-aro-CDPs, a porous aro-CD polymer, were synthesized from BZD and β -CD monomers through covalent cross-linking and self-assembly in aqueous solution. Notably, this green and facile preparation approach does not involve cumbersome steps or toxic organic solvents. Characterization data reveal that the as-synthesized material, which is a very stable amorphous polymer with a relatively high specific surface area, has an abundance of hydroxyl groups on its surface. The investigation of adsorption behavior of P-aro-CDPs toward MB showed that the adsorption process follows pseudo-second-order kinetic and Langmuir isotherm. Because the surface of P-aro-CDPs is negatively charged, the adsorbent selectively adsorbs cationic dyes through electrostatic interactions. Furthermore, the adsorbent is easily collected and regenerated. This simple, low-cost, and sustainable synthetic route can be used to develop further porous CD-based materials, with synthesized materials potentially useful for the adsorption, separation, and purification of cationic molecules.

Declarations

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Conflict of interest

The authors declare no competing financial interests.

Author Contributions: Hui-Ling Duan: Conceptualization, Data curation, Methodology, Validation, Project administratin, Writing-Original Draft, Writing-Review and Editing, Funding acquisition. Yu Wang: Formal analysis and Visualization. Kai-Qi Cheng: Investigation. Li-Juan Zhang: Investigation. Ji-Chao Qi: Investigation. Xiang-Ai Ma: Conceptualization, Writing-Review and Editing, Supervision. All authors have read and agreed to the published version of the manuscript.

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Figures

Figure 1

Schematic depicting the synthesis of P-aro-CDPs.

Figure 2

FTIR spectra (A), XPS spectrum (B), N₂ adsorption–desorption isotherm (C), and TGA curve (D) of P-aro-CDPs.

Figure 3

Zeta potential curve (A), XRD pattern (B), and SEM (C) and TEM (D) images of P-aro-CDPs.

Figure 4

Influence of pH (A) and adsorption time (B) on the adsorption of MB on P-aro-CDPs. Data fitting to the pseudo-second-order equation (C) and the Langmuir adsorption isotherm (D).

Figure 5

(A) Adsorption cycling tests. (B) Adsorption selectivity toward various dyes. (C, D) UV-vis spectra of mixed dye solutions before and after the adsorption on P-aro-CDPs.

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