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A water-insoluble viologen-based β-cyclodextrin polymer for selective adsorption toward anionic dyes

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ABSTRACT

The viologen-based β-cyclodextrin polymer (V-CDP) was successfully prepared *via* a Menshutkin reaction for the first time, and its organic dyes uptake capacities were investigated. The synthesized polymer showed BET surface area of 22 $m^2 g^{-1}$ and exhibited highly charge-selective adsorption of anionic dyes, *i.e.* congo red and methyl orange. Remarkably, the polymer could efficiently absorb anionic dyes from binary cationic-anionic dye mixtures in a 1:1 mass ratio. The adsorption process of the two anionic dyes on the polymer both followed the pseudo-second-order rate equation and the Langmuir adsorption model. According to the Langmuir isotherm, the maximum adsorption capacity of V-CDP for congo red and methyl orange was calculated to be 323 mg g^{-1} and 370 mg g^{-1}, respectively. Additionally, the polymer can be easily regenerated and reused at least 5 times with no loss of adsorption efficiency, demonstrating its potential application in dye removal.

1. Introduction

Water resources are under threat from anthropogenic toxic contaminants [1], especially organic dyes, which not only exacerbate water crises but also harm human beings [2]. Efficient techniques for the removal of organic dyes from polluted water and wastewater have drawn significant interests, such as adsorption, catalytic degradation, membrane separation, photo degradation, and chemical oxidation. Among them, adsorption is regarded as a promising strategy due to its low cost, convenient operation, and high efficiency [3]. Up to now, a variety of materials including β-cyclodextrin (β-CD) [4–10], activated carbon [11,12], graphene [13,14], mesoporous silica [15], metal-organic frameworks (MOFs) [16], and porous organic polymers (POPs) [17] have been investigated for dye removal. Among these adsorbents, β-CD-based materials have received much attention in recent years.

β-cyclodextrin (β-CD), a macrocycle of seven α-linked D-glucopyranose units is inexpensively derived from corn starch and is a unique cyclic oligosaccharide because it can form host-guest complexes with nonpolar suitable sized molecules [18,19], endowing its great potential for pollutants removal from water. Recently, β-CD-based polymers have been widely used to remove dye contaminants from water *via* hydrogen bonding, π–π, and host–guest interactions [6,7]. Introduction of electrostatic interactions into β-CD-based polymers would allow for the enhancement of adsorption performance as well as the selectivity to organic dyes [10]. Research interests of charged β-CD-based polymer are mainly focused on two strategies. (1) Cationic β-CD polymers are usually synthesized by crosslinking β-CD with epichlorohydrin in the presence of cationic groups, *e.g.* polymer/oligomers, choline chloride and glycidyltrimetryl ammonium chloride [20–23]. The resultant cationic polymers are widely used in drug delivery due to their water-soluble property, which limits their application in water treatment. (2) Anionic β-CD polymers are often obtained by polyesterification reaction with di- and poly(carboxylic acid)s [10,24,25]. Carboxylic acid groups participate in the reaction with −OH group of β-CD, which will weaken the electrostatic interactions. Therefore, it is a hot top to design water-insoluble charged β-CD polymers and apply them to the field of water treatment.

Viologens are good candidates for endowing a material with charged properties. Viologens are a class of compounds that contain a dicationic 4,4′-bipyridinium unit and have three distinct redox states dicationic, radical-cationic and neutral [26–28]. Compared with polyesterification reaction, the polymer charged by viologens will not suffer from the disadvantage of weakening the electrostatic interactions. Several methods such as Menshutkin reaction [29–31], Sonogashira-Hagihara coupling reaction [32], and Zincke reaction [31,33] have been utilized for incorporating viologens. For example, Das et al. [29] synthesized a viologen-based covalent organic polymer and the resultant polymer in its dicationic state had remarkable adsorption ability for hydrophilic and anionic dyes. Li et al. [32] prepared a viologen-based two-dimensional (2D) covalent organic framework (COF) and the

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polycationic 2D COF exhibited high uptake capacity toward a low concentration of anionic dyes from water. A literature survey revealed that few studies have been reported about the removal of dyes with viologen-based materials except the above literatures [29,32].

Herein, for the first time, we prepared a viologen-based β-CD polymer and the resultant polymer was applied to remove organic dyes from water. Benzyl chloride groups were introduced into β-CD to improve the water-insoluble property and provide $–CH_2Cl$ groups to react with 4,4′-bipyridine. The formation and structure of the polymer was verified by Fourier-transform infrared spectroscopy, X-ray photoelectron spectrometer, thermogravimetric analysis, N_2 adsorption-desorption measurements, scanning electron microscopy, and transmission electron microscopy. Two cationic dyes and two anionic dyes were utilized as model dyes to evaluate the adsorption performance of the developed absorbent. Furthermore, adsorption kinetics, isotherms, and the recyclability of the adsorption process were discussed in detail.

2. Experimental section

2.1. Materials

β-CD, sodium hydride (NaH, 60% dispersion in mineral oil), and *N*,*N*-dimethylformamide (DMF) were from Aladdin Reagent Company (Shanghai, China). 4,4′-Bipyridinium (98%), dichloroxylene (DCX, 98%), and tetrabutylammonium chloride were obtained from Zhengzhou Alfachem Company (Zhengzhou, China). Methanol (MeOH), methylene chloride (CH_2Cl_2), acetonitrile (MeCN), and *n*-hexane were purchased from Beijing Chemical Works (Beijing, China). Methyl orange (MO), congo red (CR), rhodamine B (RhB), and methylene blue (MB) were supplied by Tianjin Chemical Plant (Tianjin, China). Water was purified on a Milli-Q-SP system (Millipore, Milford, MA, USA).

2.2. Characterization

Fourier-transformed infrared (FT-IR) spectra were measured on a 60 Thermo Nicolet 670 FTIR instrument (Thermo, USA). An X-ray photoelectron spectrometer (XPS, ESCALAB250, Thermo Electron Corporation, USA) was used to obtain XPS data. Scanning electron microscopy (SEM) images were recorded on an S4800 ESEM Hitachi microscope (Hitachi, Japan). Transmission electron microscope (TEM) images were acquired on an H600 electron microscope (Hitachi, Japan) with an accelerating voltage of 100 kV. Thermal gravimetric analysis (TGA) was performed by a Q500 thermal gravimetric analyzer (TA, USA). N_2 adsorption-desorption isotherms were determined at 77 K with a Quantachrome Nova 4200e analyzer (Quantachrome Instruments, USA). Samples were degassed under vacuum at 100 °C for 8 h. The Brunauer-Emmett-Teller (BET) equation was used to calculate the cumulative apparent surfaces areas. Electrochemical properties of the polymer were investigated by an electrochemical analyzer (CHI660A; CH Instruments, China) using a Pt wire working electrode, a Pt foil counter electrode, and a saturated calomel (SCE) reference electrode. Cyclic voltammetry was determined in deaerated DMSO with tetrabutylammonium chloride (0.1 mol L^{-1}) as the supporting electrolyte. The UV–Vis absorption spectra were determined by a Shimadzu UV-1601PC spectrophotometer (Shimadzu, Japan).

2.3. Synthesis of benzyl chlorided β-CD

Benzyl chlorided β-CD (BnClCD) was synthesized as followings. β-CD (500 mg) was dissolved in dry DMF (10 mL). Then the solution was cooled to 0 °C and added NaH (60%, 740 mg) portionwise under nitrogen atmosphere. After stirring for 15 min, DCX (3.24 g) was slowly added and the reaction mixture was warmed to room temperature. After stirring for 5 days, the reaction mixture was quenched by adding methanol (5 mL) and diluted with water (100 mL). The precipitate was filtered, washed with CH_2Cl_2, and dried under vacuum for 24 h.

2.4. Synthesis of water-insoluble viologen-based β-CD polymer

The water-insoluble viologen-based β-CD polymer (V-CDP) was synthesized through a Menshutkin reaction between BnClCD and 4,4′-bipyridine. Typically, BnClCD (0.24 g) and 4,4′-dipyridine (0.1 g) were dissolved in MeCN (30 mL) and the reaction mixture was stirred in a sealed flask at 85 °C for 72 h. After the reaction, the precipitate was filtered, thoroughly washed with MeCN, water, *n*-hexane, and acetone. Finally, the solid was dried under vacuum at 60 °C for 72 h.

2.5. Water regain analysis

V-CDP was immersed in water at room temperature for 96 h and then filtered using filter paper. The polymer was weighed after blotting out the excess of water with additional filter paper. The water regain of V-CDP was determined from the average of three measurements by the following equation [19]:

$$\text{Water regain } (\%) = \frac{W_w - W_d}{W_d} \times 100 \quad (1)$$

where W_w (mg) and W_d (mg) are the weight of the wet and dry polymer, respectively.

2.6. Adsorption and renewable experiments

Two anionic dyes, *i.e.*, CR and MO, and two cationic dyes, *i.e.*, MB and RhB, were chosen as the model targets for the test of adsorption performance. For dye adsorption experiments, 5 mg synthesized adsorbents were added into 10 mL certain concentration of dye solution with continuous shaking. All studies were conducted at 25 °C on a thermostatic oscillator with a stirring rate of 250 rpm. A small amount of solution was taken out by a syringe and filtered immediately by a 0.2 μm inorganic membrane filter. The concentrations of dyes in the filtrates as well as the initial solutions were determined by UV–Vis spectroscopy based on calibration.

For the recycle test, the absorbent was collected by centrifuging after dye adsorption. Subsequently, V-CDP was washed with ethanol and dried overnight under vacuum at 60 °C. The regenerated absorbent was then used for the next cycle of dye removal study. To investigate the recyclability of V-CDP, the above-mentioned adsorption-desorption studies were carried out for 5 cycles.

3. Results and discussion

3.1. Characterization of materials

The viologen-based β-CD polymer was synthesized in two steps as shown in Fig. 1. BnClCD was prepared *via* the reaction between DCX and β-CD in the presence of NaH. The successful synthesis of BnClCD was confirmed by FT-IR and XPS (Fig. 2). Compared with the FT-IR spectrum of β-CD, the spectrum of BnClCD revealed a band at 1265 cm^{-1} (Fig. 2a), indicating the presence of $-CH_2Cl$, which is in accordance with previous reports [34,35]. The presence of O—H stretching band at around 3400 cm^{-1} suggested the partial conversion of —OH in the synthesis of BnClCD. The signals at around 1610 and 1502 cm^{-1} were attributed to skeleton vibrations of the aromatic ring, while the peak at 3100–3000 cm^{-1} belonged to stretching vibrations of C—H in the aromatic ring [31,36,37]. XPS of BnClCD showed peaks of C1s, O1s, and Cl2p (Fig. 2b), further demonstrating the successful synthesis of BnClCD.

V-CDP was synthesized by Menshutkin reaction between BnClCD and 4,4′-bipyridine in MeCN. After purification, the yellow solid was reproducibly collected in a yield of > 40%. The polymer formation was also supported by FT-IR (Fig. 2a) and XPS (Fig. 2b). Compared with FT-IR spectrum of BnClCD, the new band at 1633 cm^{-1} with moderate intensity indicated the presence of C═N stretching vibration originated