



Short Communication

Efficient removal of BTEX from aqueous solution by β -cyclodextrin modified poly(butyl methacrylate) resinZujin Yang^{a,b}, Jinping Liu^{a,b}, Xingdong Yao^c, Zebao Rui^{a,b}, Hongbing Ji^{a,b,*}^a School of Chemistry and Chemical Engineering, The Key Laboratory of Low-carbon Chemistry & Energy Conservation of Guangdong Province, Sun Yat-sen University, Guangzhou 510275, China^b Huizhou Research Institute of Sun Yat-sen University, Huizhou 516216, China^c School of Chemistry & Chemical Engineering, Guangxi University for Nationalities, Nanning 530006, China

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ABSTRACT

Efficient removal of benzene, toluene, ethylbenzene and xylene (BTEX) from aqueous solution has been studied with a β -cyclodextrin (β -CD) modified poly(butyl methacrylate) resin (poly(BMA-Co-CD)). The effects of the amount of β -CD in poly(BMA-Co-CD), pH, ionic strength, contact time, and temperature of the solution on the adsorption of BTEX were investigated in details. Adsorption data were fitted very well to Freundlich model. The results showed that the β -CD groups on the resin played a significant role for adsorption of BTEX, and quantum chemical calculation confirmed the experimental results. The resin exhibits good performance e.g. high adsorption capacity, high separation efficiency, and easy regeneration.

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1. Introduction

BTEX (benzene, toluene, ethylbenzene, and xylene) are volatile and flammable aromatic hydrocarbons that have been widely used as industrial solvents and exist in fuels such as petroleum and gasoline [1]. They are considered as the most typical water pollutants that appear very often in chemical and petrochemical wastewaters due to gasoline leakage from storage tank, transportation, pipelines and road accidents [2]. These hazardous organic compounds can cause adverse side health effects to humans at very low concentrations due to their toxic properties [3]. The World Health Organization (WHO) guidelines also recommend that the maximum allowable concentrations of benzene, toluene, ethylbenzene, and xylene in drinking water are 0.01, 0.7, 0.3, and 0.5 mg/L, respectively [4,5]. Therefore, it is necessary to develop some effective methods for removal of these compounds. A number of methods such as chemical oxidation, biological treatment, condensation, membrane separation, air stripping and adsorption have been used to remove BTEX from water and wastewater [6].

Adsorption is one of the most efficient methods to remove pollutants from wastewater because it is relatively simple with satisfactory removal efficiencies [7]. Activated carbon is most

commonly used adsorbent for the purpose. High adsorption capacities for BTEX were observed due to its porous microstructures and resultant large surface areas [8]. However, regeneration of the adsorbent has been a difficult task. Other tested adsorbents, such as carbon nanotube [9], surfactant modified zeolites [10], and organo-clays [11] cannot be repeatedly used. Polymeric resin is one of the most promising adsorbents and has been widely applied for the removal of various pollutants from water and wastewater due to its low cost and reliable performance [5,12–14]. The adsorption mainly relies on chemical constituents and physical structures (particle size, specific surface area and pore diameter) [15]. A large surface area is generally contributed to increase the adsorption capacity for adsorbents. However, the functional groups of the adsorbents greatly affect their adsorption properties.

Cyclodextrins (CDs) are cyclic oligosaccharides with 6–8 D-glucopyranose units linked by α -(1–4) glycosidic bonds and named as α -, β - and γ -CD, respectively [16,17]. They have a torus structure with a hydrophobic internal cavity and a hydrophilic exterior, which can form host–guest complexes with many organic compounds, especially aromatics [18]. Among three major types of CDs, β -CD is the most widely used one due to its appropriate cavity, accessibility, and low cost. In this study, we have the first introduced β -CD molecule into the network of poly(butyl methacrylate) resin to provide the desired pores for aromatic components based on the hydrophobic skeleton of BTEX. The hydrophobic cavity inside β -CD is also helpful for BTEX adsorption. The adsorbent with

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a low surface area showed much higher adsorption capacity for BTEX in water than that of the as-prepared high surface-area poly(butyl methacrylate) resin (poly(BMA)). The adsorption performance and adsorption mechanism of the nonporous poly(BMA-Co-CD) was investigated in detail. The effects of surface group of the polymeric adsorbents on their adsorptive properties have been evaluated. It will be useful for removal of different aromatic compounds from water and wastewater.

2. Materials and methods

2.1. Chemicals

Benzene, toluene, xylene, butyl methacrylate (BMA), polyvinyl alcohol (PVA), benzoyl peroxide, N,N-dimethylformamide (DMF), N,N-methylene bisacrylamide (MBA), and triethylamine (TEA) were purchased from Tianjin Damao Chemical Reagent Corp. Ethylbenzene and phenol were supplied by Chengdu Kelong Chemical Reagent Corp. Acryloyl chloride was purchased from Jiaxing Assent Chemical Co., Ltd. β -CD was obtained from Shanghai Boao Biotechnology Co., Ltd. Water was freshly deionized before use. All other reagents and solvents were reagent grade and used without further purification.

2.2. Quantitative analysis

BTEX concentration was determined by a gas chromatography (Agilent GC, 7890A). N₂ (flow rate 25 mL/min) and H₂ (flow rate 30 mL/min) were used as carrier gas and fuel gas, respectively. 5 μ L sample was injected in split mode (1:10) and separated on HP-5 column (30 m \times 250 mm \times 0.25 mm). The oven temperature was increased from 35 $^{\circ}$ C (holding time 5 min) to 150 $^{\circ}$ C at 10 $^{\circ}$ C/min, then to 280 $^{\circ}$ C at 20 $^{\circ}$ C/min (total run time: 21.7 min). The detector temperature was set at 300 $^{\circ}$ C.

2.3. Adsorption experiment

A 250 mL conical flask was employed for the adsorption experiments. 0.5 g poly(BMA-Co-CD) was mixed with 70 mL BTEX solution at 20, 30, and 40 $^{\circ}$ C. The initial concentration of BTEX was 60 mg/100 mL (15 mg/100 mL benzene + 15 mg/100 mL toluene + 15 mg/100 mL ethylbenzene + 15 mg/100 mL xylene) and the initial pH of solution was about 7. The reproducibility for the data was within 5%. The mixture was shaken at 200 rpm for 24 h. After agitation, the mixture was extracted with ethyl acetate, and then centrifuged. The clear supernatant was analyzed for BTEX by GC with naphthalene as internal standard.

The adsorption capacity of poly(BMA-Co-CD) for BTEX was measured as:

$$q_e = \frac{(C_o - C_e)V_o}{W} \quad (1)$$

where q_e is the adsorption capacity of adsorbent (mg/g resin); C_o is the initial concentration of BTEX (mg/L), C_e is the equilibrium concentration of BTEX in solution (mg/L), V_o is the volume of the initial solution (mL); and W is the weight of the dry resin (g).

3. Materials and methods

3.1. Preparation of poly(BMA-Co-CD)

Poly(BMA-Co-CD) were prepared via suspension polymerization in aqueous phase, as depicted in Scheme 1. Firstly, some hydroxyl groups of β -CD (β -CD-6-A) were substituted by reacting with reactive vinyl groups. Then, β -CD-6-A was copolymerized

with butyl methacrylate (BMA) with N,N-methylene bisacrylamide (MBA) as a crosslinking agent and benzoyl peroxide (BP) as the free radical initiator to obtain poly(BMA-Co-CD) (supplementary material).

3.2. Characterization of poly(BMA-Co-CD)

FTIR spectra indicated that β -CD was cross-linked to the polymer network of poly(BMA) successfully (Fig. s1, supplementary material). TGA results showed that the adsorbent are thermal stable up to 150 $^{\circ}$ C (Fig. s2, supplementary material). BET results indicated poly(BMA) has high BET surface areas (469.2 ± 5.0 m²/g) and large pore volumes (0.39 ± 0.02 cm³/g). However, poly(BMA-Co-CD) exhibited low BET surface area (3.4 ± 0.02 m²/g) and an effectively nonporous structure (pore volume 0.016 ± 0.005 cm³/g). The results showed that modification of poly(BMA) by β -CD has caused structural change. Therefore, introduction of β -CD into the polymer networks reduced its BET surface area and pore volume (Fig. s3, supplementary material).

3.3. Effects of the amount of β -CD on the adsorption capacity

Effects of the amount of β -CD in poly(BMA-Co-CD) on the adsorption of BTEX were investigated for its amount from 0 to 76.12 μ mol/g, as shown in Fig. 1.

As shown in Fig. 1, the adsorption capacity (q_e) was significantly increased with increasing amounts of β -CD in poly(BMA-Co-CD) up to 30.95 μ mol/g. However, the adsorption capacity was then decreased with the increase in β -CD amounts from 30.95 μ mol/g to 76.12 μ mol/g. It could be attribute to that the higher β -CD loading amounts over 30.95 μ mol/g may lead to complete occupancy of the interior pores of poly(BMA-Co-CD) that causes penetration of BTEX to these regions to be reduced. Therefore, poly(BMA-Co-CD) with 30.95 μ mol/g for all adsorbents was chosen for the subsequent experiments in this study.

3.4. Effects of ionic strength of solution on the adsorption capacity

Effects of ionic strength (NaCl) of solution on the adsorption of BTEX were studied by varying NaCl concentration from 0 to 0.2 mol/L, as shown in Fig. 2.

As shown in Fig. 2, the change of ionic strength didn't demonstrate significant effects on BTEX adsorption. The results indicated that poly(BMA-Co-CD) as BTEX adsorbents has high stability within a wide range of ionic strength. q_e of BTEX slightly increased from 16.46, 17.34, 18.54, and 20.24 mg/g to 16.73, 17.54, 18.80, and 20.68 mg/g with increasing NaCl concentration from 0 to 0.2 mol/L. The increase of BTEX adsorption with higher ionic strength could be attributed to rise in activity coefficient of BTEX, resulting in decrease of the solubility of BTEX and increasing their adsorption capacity. The adsorption of BTEX became very low as the NaCl concentration exceeded 0.2 mol/L. Thus, 0.2 mol/L NaCl solution was chosen in this study.

3.5. Effects of pH on the adsorption capacity

Effects of pH on the adsorption of BTEX by poly(BMA-Co-CD) were investigated at a pH ranging from 3 to 12. As shown in Fig. 3, pH did not demonstrate significant influences on the adsorption capacity of BTEX. The results indicated that the adsorbent has high stability over a wide range of pH [1].

3.6. Effects of the contact time on the adsorption capacity

The adsorption of BTEX by poly(BMA-Co-CD) against contact time was shown in Fig. 4.

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