



Macroporous crosslinked polydivinylbenzene/polyacryldiethylenetriamine (PDVB/PADETA) interpenetrating polymer networks (IPNs) and their efficient adsorption to *o*-aminobenzoic acid from aqueous solutions



Xiaomei Wang^{a,*}, Limiao Chen^b, You-Nian Liu^b, Jianhan Huang^b

^a Department of Bioengineering and Environmental Science, Changsha University, Changsha, Hunan 410003, China

^b College of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410083, China

ARTICLE INFO

Article history:

Received 5 February 2014

Accepted 20 April 2014

Available online 2 May 2014

Keywords:

Polydivinylbenzene/
polyacryldiethylenetriamine (PDVB/
PADETA)
Interpenetrating polymer networks (IPNs)
Adsorption
o-Aminobenzoic acid

ABSTRACT

Macroporous crosslinked polydivinylbenzene/polyacryldiethylenetriamine (PDVB/PADETA) interpenetrating polymer networks (IPNs) were prepared in this study and their adsorption performance was investigated using *o*-aminobenzoic acid as the adsorbate. The results indicated that PDVB/PADETA IPNs had a large equilibrium capacity to *o*-aminobenzoic acid, the Freundlich and Sips models were appropriate for fitting the equilibrium data, and the isosteric enthalpy kept constant (about -30 kJ mol^{-1}) with the equilibrium capacity at $5\text{--}125 \text{ mg g}^{-1}$. The pseudo-first-order rate equation characterized the kinetic data better than the pseudo-second-order rate equation. At an initial concentration of 593.1 mg L^{-1} and a flow rate of 84 mL h^{-1} , the breakthrough and saturated capacities were 50.62 and 95.70 mg mL^{-1} wet resin, respectively, and the resin column could be regenerated by 0.1 mol L^{-1} of sodium hydroxide (w/v) and 40% of ethanol (v/v).

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

Interpenetrating polymer networks (IPNs) are the most efficient materials in application of reinforced rubbers, toughened plastics, chemical coatings, and functional materials due to their unique strong forced compatibility [1–3]. In particular, IPNs technology is a proven to be a special strategy for stable integration of two polymer networks with different properties by physical entanglements [4–6]. However, there appears a strong phase-separation behavior between the hydrophobic polymer networks and the hydrophilic polymer networks, and hence the hydrophobic-hydrophilic IPNs cannot be synthesized directly. At present, the hydrophobicity or the hydrophilicity of the two polymer networks composed of the IPNs is similar [7–10], while few researchers report the hydrophobic-hydrophilic IPNs in the literatures [11–14]. We propose that the phase-separation behavior may not be very serious as the second hydrophobic polymer networks of the hydrophobic-hydrophobic IPNs are transformed to hydrophilic polymer networks by a certain chemical reaction, and hence the hydrophobic-hydrophilic IPNs will be synthesized in a simple

way. What is more, this kind of hydrophobic-hydrophilic IPNs should have a special adsorption affinity to the hydrophobic-hydrophilic adsorbate like *o*-aminobenzoic acid.

In comparison with aniline, *o*-aminobenzoic acid has another carboxyl group on the benzene ring, and the carboxyl group is at the *ortho*-position relative to the amino group. Moreover, the carboxyl group forms weak intramolecular hydrogen bonding with the amino group [15–17], which makes *o*-aminobenzoic acid a well-balanced molecule with both hydrophobic portion and hydrophilic portion. If *o*-aminobenzoic acid is applied as the adsorbate, and it is adsorbed on the hydrophilic-hydrophobic IPNs, the hydrophobic portion of *o*-aminobenzoic acid will have a relative strong affinity to the hydrophobic polymer networks of the IPNs, while the hydrophilic portion of *o*-aminobenzoic acid is inclined to approach the hydrophilic polymer networks of the IPNs. As a result, an efficient adsorption of *o*-aminobenzoic acid will be achieved on the hydrophilic-hydrophobic IPNs.

Based on the discussions above, we firstly synthesized a hydrophobic-hydrophilic polydivinylbenzene/polymethylacrylate (PDVB/PMA) IPNs after preparation of hydrophobic macroporous crosslinked polydivinylbenzene (PDVB), and the second hydrophobic polymethylacrylate (PMA) networks were then transformed to the hydrophilic polyacryldiethylenetriamine (PADETA) networks

* Corresponding author.

E-mail address: wxm@ccsu.cn (X. Wang).

by an amidation reaction, hence PDVB/PADETA IPNs were prepared and the obtained PDVB/PADETA IPNs were both hydrophobic and hydrophilic. After characterization of PDVB/PADETA IPNs, the adsorption property of PDVB/PADETA IPNs using *o*-aminobenzoic acid as the adsorbate was studied from aqueous solutions in detail.

2. Materials and methods

2.1. Materials and chemicals

Divinylbenzene (DVB) was purchased from Gray West Chengdu Chemical Co. Ltd. (Sichuan Province, China) and its content was 80% (w/w), it was eluted by 5% of sodium hydroxide (w/v) and de-ionized water, and then dried by anhydrous magnesium sulfate before use. Industrial triallylisocyanurate (TAIC) was purchased from Liuyang Chemical Co. Ltd. (Hunan Province, China) and its content was 98% (w/w). Benzoperoxide (BPO) and 2, 2-azobisisobutyronitrile (AIBN) were purified by recrystallization before use. Methylacrylate (MA), toluene, butyl acetate, diethylenetriamine (DETA) and *n*-heptane were also employed in this study and they were all analytical reagents. Aniline and *o*-aminobenzoic acid applied as the adsorbates were analytical reagents and used without further purification.

2.2. Preparation of PDVB/PADETA IPNs

As shown in Scheme S1, the PDVB/PADETA IPNs were synthesized by interpenetration of PMA in the pores of PDVB, and the obtained PDVB/PMA IPNs were thereafter chemically modified by DETA by an amidation reaction. The synthetic method for macroporous crosslinked PDVB was the same as the method. The obtained PDVB beads were firstly swollen by a mixture solution of MA, TAIC, butyl acetate, *n*-heptane and AIBN for 24 h. Butyl acetate and *n*-heptane (250% relative to the monomers (MA and TAIC) and the ratio was 4:1, w/w) was employed as the porogens, the ratio of MA to TAIC was defined to be 9:1 (w/w) and that of the monomers to PDVB was determined to be 1:1 (w/w). The swollen PDVB beads were then separated from the mixture solution and added into the 0.5% of PVA aqueous solution (w/w, 300 parts). At a moderate stirring speed, the temperature of the reaction mixture was resin to 358 K and the reaction mixture was kept at this temperature for 12 h. The resultant products, PDVB/PMA IPNs, were performed with superfluous DETA solution at 403 K for 15 h, and hence PDVB/PADETA IPNs was synthesized accordingly.

2.3. Characterization of PDVB/PADETA IPNs

Fourier Transform infrared (FT-IR) spectroscopy of the resins was recorded on a Nicolet 510P Fourier transformed infrared instrument in 500–4000 cm^{-1} with a resolution of 1.0 cm^{-1} . The weak basic exchange capacity of the resins was measured according to the method in Ref. [18]. The specific surface area, pore volume and pore diameter distribution were determined by N_2 adsorption–desorption isotherms at 77 K using a Micromeritics Tristar 3000 surface area and porosity analyzer. The total specific surface area and pore volume were calculated according to the Brunauer–Emmett–Teller (BET) model while the pore diameter distribution was calculated by applying the Barrett–Joyner–Halenda (BJH) method to the N_2 desorption data.

2.4. Equilibrium and kinetic adsorption

The accurately weighed PDVB/PADETA IPNs (about 0.1 g) were mixed with 50 mL of *o*-aminobenzoic acid aqueous solution

at different initial concentrations. The initial concentrations of *o*-aminobenzoic acid were pre-set to be 199.5, 399.0, 598.6, 798.1 and 997.6 mg L^{-1} , respectively. The mixtures were continuously shaken at a desired temperature (303, 313 and 323 K, respectively) for 24 h until equilibrium. The equilibrium concentration of *o*-aminobenzoic acid was determined by UV analysis on a UV 2450 spectrophotometer and the equilibrium capacity was calculated by conducting a mass balance of *o*-aminobenzoic acid before and after the equilibrium. The kinetic adsorption of *o*-aminobenzoic acid on PDVB/PADETA IPNs was similar to the equilibrium adsorption except that the adsorption capacity was determined in real time until equilibrium.

2.5. Dynamic adsorption and desorption

10 mL of wet PDVB/PADETA IPNs were packed densely in a glass column (16 mm diameter) and used as the resin column. *o*-Aminobenzoic acid aqueous solution at an initial concentration of 593.1 mg L^{-1} was passed through the resin column at a flow rate of 84 mL h^{-1} and the residual concentration of *o*-aminobenzoic acid from the effluent was dynamically recorded until it reached the initial concentration. After the dynamic adsorption, the resin column was roughly rinsed by 10 mL of de-ionized water and a mixture solvent including 0.1 mol L^{-1} of sodium hydroxide (w/v) and 40% of ethanol (v/v) was used as the desorption solvent for the dynamic desorption process. 200 mL of the desorption solvent got through the resin column at a flow rate of 42 mL h^{-1} and the concentration of *o*-aminobenzoic acid from the effluent was determined until it was about zero.

3. Results and discussion

3.1. Characterization of PDVB/PADETA IPNs

After interpenetrating PMA networks in the pores of PDVB, the obtained PDVB/PMA IPNs has a decreased BET surface area (325.3 $\text{m}^2 \text{g}^{-1}$) and pore volume (0.8244 $\text{cm}^3 \text{g}^{-1}$), respectively (Table 1). Additionally, after the amidation of PDVB/PMA IPNs with DETA, the BET surface area and pore volume of the obtained PDVB/PADETA IPNs are further reduced to 239.9 $\text{m}^2 \text{g}^{-1}$ and 0.5736 $\text{cm}^3 \text{g}^{-1}$, respectively.

The FT-IR spectrum of PDVB/PMA IPNs is shown to be completely superimposed by that of PDVB and PMA (Fig. S1). The strong C=C stretching vibrations of PDVB, with frequencies at 1600, 1500 and 1450 cm^{-1} , are appeared in the FT-IR spectrum of PDVB/PMA IPNs [17,19]. Additionally, the characteristic C=O stretching band of the ester carbonyl of PMA, with frequency at 1739 cm^{-1} , is also emerged in the FT-IR spectrum of PDVB/PMA IPNs [17]. These results reveal that not any new chemical bond is formed between the PDVB and PMA networks, and the obtained PDVB/PMA IPNs are real IPNs. After the amidation of the PDVB/PMA IPNs with DETA, the characteristic C=O stretching band of the ester carbonyl of PMA is sharply weakened, while a new strong band appears at 1687 cm^{-1} in the FT-IR spectrum of PDVB/PADETA IPNs. This strong band can be assigned to the characteristic C=O stretching of the amide carbonyl of PADETA networks [17]. Moreover, another new band with frequency at 3282 cm^{-1} is also observed for PDVB/PADETA IPNs [17,20], and this band may be concerned with the N–H stretching of the –NH– or –NH₂ vibrations. 1.808 mmol g^{-1} of weak exchange capacity is determined for PDVB/PADETA IPNs, while that of PDVB and PDVB/PMA IPNs is zero. The percentage of the nitrogen element increases from 7.520 wt% (PDVB/PMA IPNs) to 11.06 wt% (PDVB/PADETA IPNs) (Table S1). All of these results suggest that the PMA networks of

Download English Version:

<https://daneshyari.com/en/article/607206>

Download Persian Version:

<https://daneshyari.com/article/607206>

[Daneshyari.com](https://daneshyari.com)