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Hydrophobic-hydrophilic interpenetrating polymer networks (IPNs) composed of hydrophobic polystyrene (PST) and hydrophilic polyacryldiethylenetriamine (PADETA) networks and their high efficient adsorption to salicylic acid

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ABSTRACT

Herein we synthesized a kind of novel hydrophobic-hydrophilic interpenetrating polymer networks (IPNs) composed of hydrophobic polystyrene (PST) and hydrophilic polyacryldiethylenetriamine (PADETA) networks, and the as-prepared PST/PADETA IPNs possessed both hydrophobic-hydrophilic property and medium high Brunauer-Emmett-Teller (BET) surface area, and hence bringing to much greater adsorption to the hydrophobic-hydrophilic adsorbate like salicylic acid. Particularly, PST/PADETA IPNs were much superior to some other adsorbents reported in the literatures.

1. Introduction

Aromatic compounds such as benzene, toluene, phenol, and salicylic acid are typical organic pollutants in wastewater [1–3], and their efficient removal from aqueous solution is of great importance and has received increasing attention in recent years [4,5]. Salicylic acid is a typical bifunctional aromatic compound with both phenolic hydroxyl and carboxyl groups. Moreover, the substituted carboxyl group is neighboring with the phenolic hydroxyl group, resulting in formation of a new hexatomic ring by an intramolecular hydrogen bonding between the adjacent phenolic hydroxyl and carboxyl groups [6]. On the other hand, the benzene ring of salicylic acid is hydrophobic, and the newly formed hexatomic ring is hydrophobic as well, whereas the two functional phenolic hydroxyl and carboxyl groups are hydrophilic. As a result, salicylic acid can be deemed as a well-balanced molecule with both hydrophobic and hydrophilic portions. According to the particular hydrophobic-hydrophilic structure of salicylic acid, if amphiphilic (both hydrophobic and hydrophilic) polymeric adsorbents are utilized as the adsorbents, and salicylic acid is employed as the adsorbate for the adsorption, the hydrophobic networks of the amphiphilic polymeric adsorbents can interact with the hydrophobic portion of salicylic acid by hydrophobic interaction [7], whereas the hydrophilic networks will have a much strong affinity to the hydrophilic portion [8], and hence the polarity matching will make a much improved adsorption. Therefore, successful preparation of the amphiphilic polymeric adsorbents is the first and most important as considered for adsorptive removal of salicylic acid.

Interpenetrating polymer networks (IPNs) are proven the efficient polymeric materials applied in damping materials and functional materials, they are also widely used as the polymeric adsorbents for adsorption of aromatic compounds [9,10]. However, there appear few reports for hydrophobic-hydrophilic IPNs in the literatures [11–13]. Among them, Xiao et al. [5] synthesized the hydrophobic-hydrophilic PDVB/PMAEM IPNs based on the similar hydrophobic PDVB/PMMA IPNs, and they found that the hydrophobic-hydrophilic IPNs possessed a decent adsorption to the hydrophobic-hydrophilic adsorbates like 5-sulfosalicylic acid. More recently, our group synthesized a series of novel hydrophobic-hydrophilic (or hydrophilic-hydrophobic) IPNs by a sequential technique [7,13], and they showed an excellent adsorption to *o*-aminobenzoic acid and salicylic acid. However, the present reported IPNs possess a low Brunauer-Emmett-Teller (BET) surface area, resulting in an ineffective adsorption. Our group applied the post-cross-linking technology for the first time, and prepared some

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novel IPNs with medium high BET surface area [2,14,15], and the post-cross-linking technology is proven an effective method for improving the BET surface area of the IPNs.

On the other hand, we proposed that the synthesized hydrophobic-hydrophobic IPNs would hold a medium high BET surface if the commercial resins with a high BET surface area were employed as the raw materials. Herein we used the commercial Amberlite XAD-4 (hydrophobic polystyrene) resins (BET surface area: 873.1 m^2/g) as the first networks, and synthesized both hydrophobic polystyrene/polymethylacrylate (PST/PMA) IPNs by suspension polymerization, then the polymethylacrylate (PMA) networks was transformed to the hydrophilic polyacryldiethylenetriamine (PADETA) networks using a specific chemical reaction (amidation reaction), and hence obtained the hydrophobic-hydrophilic PST/PADETA IPNs with a medium high BET surface area. Due to both the hydrophobic-hydrophilic property and medium high BET surface area, PST/PADETA IPNs were efficient for adsorption of the hydrophobic-hydrophilic adsorbate like salicylic acid.

2. Experimental

2.1. Materials and chemicals

The Amberlite XAD-4 resins were purchased from Rohm & Haas Company. Methylacrylate (MA) was eluted by 5% NaOH (w/v) to remove the polymerization inhibitor before use. Triallylisocyanurate (TAIC) was an industrial grade agent and its content was 98% (w/w). 2,2-azobisisobutyronitrile (AIBN) was recrystallized before use. Butyl acetate, *n*-heptane and diethylenetriamine (DETA), phenol and salicylic acid were analytical agents and used directly as purchased.

2.2. Synthesis of PST/PADETA IPNs

40.0 PST were firstly swollen by a mixture of 36 g MA, 4 g TAIC, 80 g butyl acetate, 20 g *n*-heptane and 0.8 g AIBN for 24 h. In this reaction, MA was the polymeric monomer and TAIC was the crosslinking reagent in the polymerization, whereas butyl acetate and *n*-heptane were employed as the porogens. The swollen PST beads were filtered from the mixture, and they were added into a 0.5% polyvinyl alcohol aqueous solution (w/w, 300 parts). Then the temperature of the reaction mixture was risen to 358 K and kept for 12 h. The resultant PST/PMA IPNs were chemically transformed to PST/PADETA IPNs via an amidation reaction by performing PST/PMA IPNs with superfluous DETA with the temperature at 403 K for 15 h.

2.3. Characterization

Fourier transform infrared spectroscopy (FT-IR) was recorded on a Nicolet 510P Fourier transformed infrared instrument in 500–4000 cm^{-1}. The BET surface area and pore volume were determined by N_2 adsorption-desorption isotherms at 77 K using a Micromeritics Tristar 3000 surface area and porosity analyzer. The weak basic exchange capacity was measured according to the method in Ref. [16]. The swelling ratio in different solvents was calculated according to the method in Ref. [5].

2.4. Equilibrium adsorption

Three temperatures (298, 308 and 318 K) were applied for the equilibrium adsorption, and the weighed PST/PADETA IPNs was about 0.1 g. Typically, the PST/PADETA IPNs were mixed with 50 mL of salicylic acid aqueous solution, and the initial concentrations of salicylic acid were pre-set to be 201.6, 403.2, 604.8, 806.4, and 1008 mg/L, respectively. The reaction mixtures were continuously agitated at the desired temperature for 24 h until equilibrium. The equilibrium concentration of salicylic acid was determined and the equilibrium capacity was calculated by conducting a mass balance of salicylic acid on the PST/PADETA IPNs before and after the equilibrium.

2.5. Dynamic adsorption and desorption

PST/PADETA IPNs were fully immersed in de-ionized water for 24 h, and the wetted resins with a column of 10 mL were then packed densely in a glass column to assemble a resin column. The initial concentration of salicylic acid was set 1029 mg/L, and the flow rate of the effluent was defined to 51, 86 or 124 mL/h, respectively. The salicylic acid aqueous solution passed through the resin column at a constant flow rate, and the residual concentration of salicylic acid from the effluent was continuously recorded until it reached the initial concentration. After the dynamic adsorption, 300 mL of the desorption solvent got through the resin column at a flow rate of 40 mL/h and the concentration of salicylic acid from the effluent was determined until it was about zero.

3. Results and discussion

3.1. Characterization of PST/PADETA IPNs

Fig. 1 indicated that PST had three characteristic vibrations at 1601, 1500 and 1452 cm^{-1}, and these vibrations was assigned to the C=C stretching of the benzene ring [17]. PMA held a very strong band at 1739 cm^{-1}, and this band was related to the C=O stretching of the ester carbonyl of MA. Meanwhile, another shoulder band also appeared at 1697 cm^{-1}, and which was involved to the amide carbonyl of TAIC [2,18]. All of the above absorption for PST and PMA were present in the FT-IR spectrum of PST/PMA IPNs, revealing that not any new chemical bond formed between PST and PMA networks, and we have obtained a kind of real IPNs. After the amidation, the ester carbonyl groups at 1739 cm^{-1} was much weakened, while a new moderate vibration appeared at 1654 cm^{-1}, and this vibration is connected to the amide carbonyl groups [19,20], this phenomenon stated that the ester carbonyl of PMA networks transformed to the amide groups. Additionally, another broad $-NH-/-NH_2$ vibration at 3404 cm^{-1} also appeared for PST/PADETA IPNs, and its weak basic exchange capacity was 2.217 mmol/g (Table 1), suggesting we prepared PST/PADETA IPNs successfully.

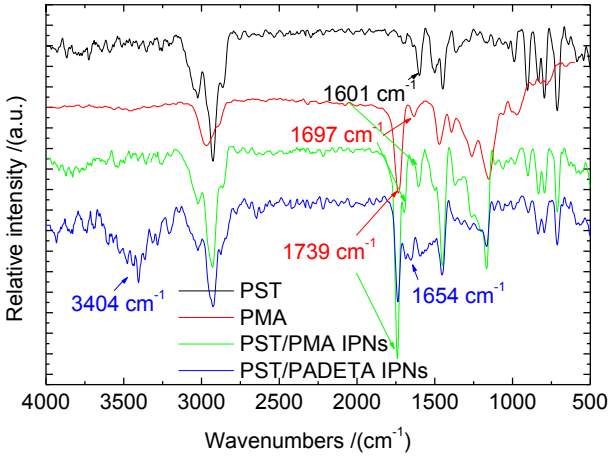

Fig. 1. FT-IR spectra of PST, PMA, PST/PMA IPNs and PST/PADETA IPNs.