Fluid Phase Equilibria 438 (2017) 1–9

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Polar hyper-cross-linked resin with abundant micropores/mesopores and its enhanced adsorption toward salicylic acid: Equilibrium, kinetics, and dynamic operation

Zhenyu Fu, Jianhan Huang*

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

A R T I C L E I N F O

Article history:
Received 14 December 2016
Received in revised form
25 January 2017
Accepted 26 January 2017
Available online 30 January 2017

Keywords:
Hyper-cross-linked resin
Polarity
Micropores/mesopores
Adsorption
Salicylic acid

A B S T R A C T

Here, a ternary copolymerization method was performed for *p*-vinylbenzyl chloride (VBC), divinylbenzene (DVB), and methylacrylate (MA), and the precursor resin poly (VBC-*co*-DVB-*co*-MA) (PVDM) was synthesized. After that, the Friedel-Crafts alkylation reaction and the amidation reaction were carried out for the VBC moieties and the acrylate moieties, and hence a polar hyper-cross-linked resin (abbreviated as PVDM-P-A) was prepared. This resin possessed high BET surface area (1010 m^2/g), abundant micro/mesopores, 0.58 mmol/g of amide, and 1.60 mmol/g of amino groups. The adsorption experiments indicated that it had a large equilibrium (457.9 mg/g) and dynamic capacity (394.1 and 453.5 mg/g wet resins for the breakthrough and saturated capacity) toward salicylic acid, and it was superior to its precursor resins and some other adsorbents reported in literature. Particularly, the adsorption was very fast, 40 min was sufficient to reach equilibrium, suggesting that it was a potential candidate for adsorptive removal of salicylic acid from aqueous solution.

1. Introduction

Due to their high Brunauer-Emmett-Teller (BET) surface area and preferred pore structure, nanoporous organic polymers (NOPs) have been attracting increasing attention in recent years [1–8], and they are extensively used as the promising materials in gas storage, heterogeneous catalysis, and energy conversion [9,10]. As the typical NOPs, hyper-cross-linked resins possess predominant micropores/mesopores and different surface chemistry [11–13], and are proven the efficient polymeric adsorbents for adsorptive removal of aromatic compounds from aqueous solution [14–17].

Synthesis of the hyper-cross-linked resins with high BET surface area and polar surface is still challenging [18,19]. The traditional hyper-cross-linked resins do not possess polar functional groups, and introduction of polar functional groups on their surface will make them more attractive [20]. So far, three frequently used methods are employed to increase their surface polarity [21,22]. Specifically, Zeng et al. [23–25] and Li et al. [26] used the polar monomers, such as methacrylate (MA), methyl methacrylate (MMA) and N-vinylpyrrolidone (NVP), to increase the surface polarity. Our group added β-naphthol, hydroquinone, and acetanilide as the polar aromatic compounds in the Friedel-Crafts reaction to synthesize polar hyper-cross-linked resins [16]. Amino, amide, hydroxyl, and carboxyl groups are frequently upoloaded on the surface [27–30]. The polar hyper-cross-linked resins have a relatively larger equilibrium capacity toward the polar aromatic compounds, and the polarity matching *via* electrostatic interaction or hydrogen bonding is deemed as the main driving force [31–34].

As macroporous low cross-linked chloromethylated polystyrene is used as the raw material for the synthesis of the hyper-cross-linked resins [16], due to the special reaction mechanism, the obtained hyper-cross-linked resins contain quite a few macropores except for the predominant micro/mesopores [35], and hence they exhibit a bimodal pore size distribution [36,37]. Liu et al. [38] used vinylbenzyl chloride (VBC), divinylbenzene (DVB) and styrene (St) to perform a ternary copolymerization, and then the Friedel-Crafts reaction was carried out for the precursor resins, and they synthesized the hyper-cross-linked resins with nano-pore structure. However, this kind of resin was non-polar. Herein, we developed a novel polar hyper-cross-linked resin with abundant micropores/mesopores. Moreover, this resin had high BET surface area with polar functional groups on its surface. For this purpose, we firstly performed a ternary copolymerization for VBC, DVB, and

---

* Corresponding author.
E-mail address: jianhanhuang@csu.edu.cn (J. Huang).

http://dx.doi.org/10.1016/j.fluid.2017.01.025
0378-3812/

methylacrylate (MA), and synthesized the precursor resin (PVDM). Then the Friedel-Crafts alkylation reaction and the amidation reaction were carried out, and hence we prepared the polar hyper-cross-linked resin (abbreviated as PVDM-P-A). The adsorption, including the equilibrium, kinetics, and dynamis, was evaluated using salicylic acid as the polar adsorbate.

2. Materials and method

2.1. Materials

VBC, MA, and DVB were purchased from Gray West Chengdu Chemical Co. Ltd. (Sichuan Province, China), they were analytical agents. Before use, they were washed by 5 wt% NaOH to remove the inhibitors, and then dried by anhydrous magnesium sulfate. 2,2-azobisisobutyronitrile (AIBN) was also an analytical agent and it was provided by Yongda Chemical Company (Shandong province, China), and it was purified by recrystallization using methanol as the solvent before use. 1,2-dichloroethane (DCE), anhydrous ferric (III) chloride, diethylenetriamine (DETA), and salicylic acid were all analytical agents and used without further purification.

2.2. Preparation of the polar hyper-cross-linked resin

As shown in Scheme 1, three reactions were employed for synthesis of the polar hyper-cross-linked resin (abbreviated as PVDM-P-A), which included suspension polymerization, Friedel-Crafts alkylation reaction, and amidation reaction. The precursor resin poly(VBC-*co*-DVB-*co*-MA) (denoted as PVDM) was first synthesized by a ternary copolymerization. 1.0 g of DVB, 1.0 g of MA, 18.0 g of VBC, 0.2 g of AIBN, and 40 g of toluene were the oil phase, and they were mixed and poured into 200 mL of 0.05 wt% poly(vinyl alcohol) (PVA) aqueous solution at 318 K. In this reaction, VBC was the monomer, MA was the polar monomer, DVB was the cross-linking agent, and toluene was the porogen. Polymerization reaction was carried out at 348 K for 2 h, 358 K for 2 h, and 368 K for 4 h. The precursor resin PVDM was collected, washed, and extracted by petroleum ether in Soxhlet apparatus for 12 h, and then dried under vacuum at 333 K for 24 h. Then, the Friedel-Crafts alkylation reaction was performed for PVDM according to the method in the literature [12,15]. In this reaction, the benzyl chloride of VBC was performed the electrophilic addition with the neighboring DVB moieties as well as the VBC moieties, and the hyper-cross-linked resin (named as PVDM-P) was obtained. Thereafter, PVDM-P was reacted with DETA at 393 K for 12 h. In this reaction, the MA moieties were performed the nucleophilic substitution with DETA, and the amide as well as the amino groups were uploaded on the surface of the resins, and hence the polar hyper-cross-linked resin PVDM-P-A was prepared. Additionally, the resin without adding the polar monomer MA was labeled as PVD, and the corresponding hyper-cross-linked resin was denoted as PVD-P after the Friedel-Crafts alkylation reaction.

2.3. Characterization

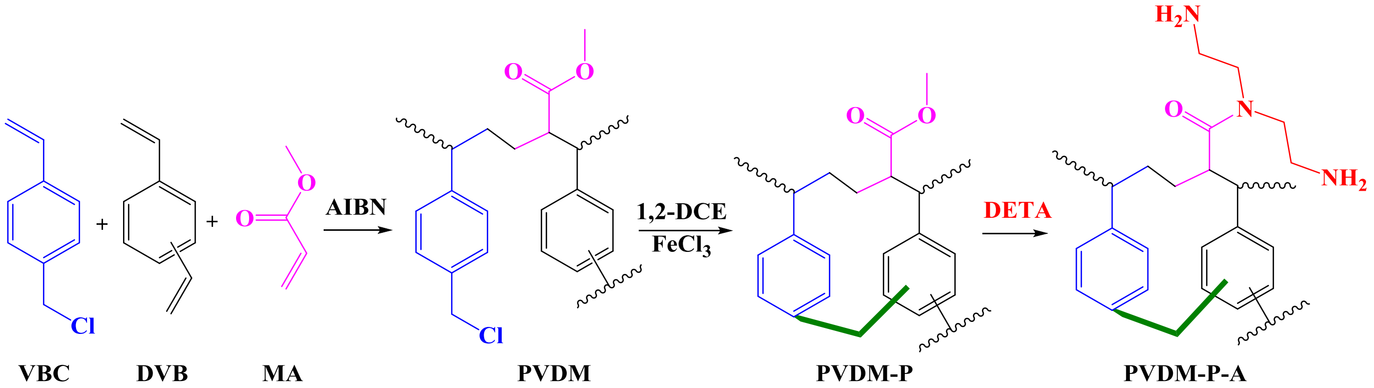
Fourier transform infrared (FT-IR) spectra of the resins were recorded on a Nicolet 510P FT-IR spectrometer (KBr pellets) with the wavenumber ranged from 500 to 4000 cm^{-1}. The pore structure of the resins was determined by N_2 adsorption-desorption isotherms at 77 K via a Micromeritics ASAP 2020 surface area and porosity analyzer. Before the N_2 adsorption-desorption isotherms, degassing under nitrogen flushing was pre-treated for the resins. The degassing temperature was 363 K and the duration time was 3 h. The BET surface area and pore volume were calculated according to the BET model, while the pore size distribution was determined by the Nonlocal density functional theory (NL-DFT) method. The chlorine content of the resins was measured by the Volhard method [39], and the weak basic exchange capacity of the resins was measured according to the back titration method according to a method [40]. The morphology of the resins was detected using the scanning electron microscopy (SEM, PW-100-011, Netherlands), and 800, 3000, and 10,000 magnification were performed for the samples. The concentration of salicylic acid in aqueous solution was measured via a UV-2450 spectrophotometer at a wavelength of 296.5 nm.

2.4. Equilibrium isotherms and kinetics

About 0.05 g of the resins was mixed with 50 mL of a series of salicylic acid aqueous solution. The initial concentration of salicylic acid aqueous solution was preset to be 200.3, 400.6, 600.9, 801.2, and 1001.5 mg/L. The mixed aqueous solutions were shaken in a thermostatic oscillator at a desired temperature (298, 308, or 318 K) until the equilibrium was attained (4 h). The residual concentration of salicylic acid, C_e (mg/L), was determined, and the equilibrium capacity, q_e (mg/g), was calculated as:

$$q_e = (C_0 - C_e) \cdot V/W \quad (1)$$

where C_0 is the initial concentration (mg/L), V is the volume of the solution (L) and W is the mass of the resins (g). The kinetic process was similar to the equilibrium adsorption, and capacity was determined at a real-time until the equilibrium was attained. In this process, 0.5 mL of the solution was withdrawn at a 2-min interval in the beginning ten minutes, a 5-min interval in the following half an



Scheme 1. Synthetic procedure of the polar hyper-cross-linked resin PVDM-P-A.