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Magnetic polar post-cross-linked resin and its adsorption towards salicylic acid from aqueous solution

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HIGHLIGHTS

- A strategy to synthesize magnetic polar post-cross-linked resin was proposed.
- This resin had a large equilibrium and dynamic capacity to salicylic acid.
- This resin exhibited fast kinetics because of its micropores and its polar groups.
- This resin can be repeatedly used with the excellent regeneration behavior.

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ABSTRACT

A novel magnetic polar post-cross-linked resin M-PMD-P-A was prepared, characterized and evaluated for its adsorption towards salicylic acid from aqueous solution. M-PMD-P-A was prepared using suspension polymerization of methyl acrylate (MA) and divinylbenzene (DVB) with addition of oleic acid-coated Fe_3O_4 nanoparticles, followed by a Friedel–Crafts reaction and an amination reaction. The results indicated that M-PMD-P-A had a large equilibrium capacity towards salicylic acid, and both of the Langmuir and Freundlich models were appropriate for fitting the equilibrium data. The breakthrough capacity at $C/C_0 = 0.05$ and saturated capacity at $C/C_0 = 0.95$ of salicylic acid on M-PMD-P-A were measured to be 45.65 and 62.25 mg/mL wet resin, respectively. A mixture desorption solvent containing 0.01 mol/L of NaOH (w/v) and 20% of ethanol (v/v) could regenerate the resins completely and the resins exhibited good reusability.

1. Introduction

Salicylic acid is widely used as an important pharmaceutical intermediate for production of medicines such as aspirin, lopirin, fenamifuril, diflunisal, salicylamide, and benorylatum [1–3]. However, salicylic acid is a typical pollutant in the industrial wastewater, capable of causing serious environmental problems. Moreover, salicylic acid is toxic to the human being owing to it can induce headache and nausea and even affect the normal functions of liver and kidney. For these reasons, efficient removal and recycling of salicylic acid from aqueous solution is a pressing problem and has attracted numerous attentions in recent years [4,5]. A lot of methods and technologies including catalytic oxidation, biodegradation, membrane separation, molecularly imprinted solid-phase extraction and adsorption have been developed for removal of aromatic compounds [6–13], among which adsorption is proved to be one of the most attractive and effective techniques [14,15].

Synthetic resins possess controllable chemical structure, excellent pore structure and outstanding regeneration performance, hence are proven to be efficient polymeric adsorbents for adsorptive removal of aromatic compounds from aqueous solution [3–5,14,15]. In 1988, Ando et al. synthesized a kind of post-cross-linked resins by consuming these residual pendent vinyl groups of the high crosslinked polystyrene under the help of Friedel–Crafts catalysts [16]. The obtained post-cross-linked resins possess a considerable increase of Brunauer–Emmett–Teller (BET) surface area and remarkable micropores, leading to excellent adsorption towards aromatic compounds [17–19]. Furthermore, Yan et al. [20] and Jerabek et al. [21] investigated the reaction mechanism of the post-cross-linked resins. Li et al. [22,23] prepared some post-cross-linked resins for adsorption of aromatic compounds from aqueous solution. Due to the high hydrophobicity of these post-cross-linked resins, Zeng et al. applied methyl methacrylate (MMA), ethylene glycol dimethacrylate (EGDMA)

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and *N*-vinylpyrrolidone as the polar monomers in the polymerization to increase the polarity of the post-cross-linked resins, and they found that these polar post-cross-linked resins had a relatively larger equilibrium adsorption capacity towards the polar aromatic compounds [24–26]. Our group synthesized a series of diethylenetriamine, *N*-methylacetamido, aniline and ethylenediamine modified post-cross-linked resins [27–29], and it was found that the polar groups on the resins could greatly improve the performance of the adsorption of aromatic compounds from aqueous solution.

In the recent fifteen years, the magnetic ion-exchange resins (MIEX), firstly developed by Watercare [30–34], have been increasingly employed to remove organic pollutants from wastewater. Owing to their convenient separation characteristics, magnetic resins can be easily separated from aqueous solution by the magnetic force, and are extensively used in a mixed contactor process for wastewater treatment [35]. The magnetic resins separation process can significantly increase the amount of wastewater treatment and decrease the operation costs in comparison with the fixed beds, and thus extend the working life of the resins [36]. In recent years, magnetic post-cross-linked resins with functional groups showed high equilibrium adsorption capacity and excellent separation ability, and which were extensively used for adsorptive removal of organic micropollutants from aqueous solution [37–39]. However, to the best of our knowledge, few works were reported to use magnetic resins to adsorb the aromatic compounds by the magnetic polar post-cross-linked resins [40].

The main objective of our work was to develop a novel magnetic polar modified post-cross-linked resin for adsorptive removal of salicylic acid from aqueous solution. The magnetic amide and amino-modified post-cross-linked resin M-PMD-P-A was prepared using copolymerization of methyl acrylate (MA) and divinylbenzene (DVB) with addition of oleic acid-coated Fe_3O_4 nanoparticles followed by a Friedel–Crafts reaction and amination reaction. The physicochemical properties of M-PMD-P-A were characterized by Fourier transform infrared (FT-IR), N_2 adsorption–desorption isotherms, vibrating sample magnetometer (VSM) and transmission electron microscopy (TEM). And the adsorption equilibrium, column breakthrough and regeneration of M-PMD-P-A were determined and analyzed in detail.

2. Materials and methods

2.1. Materials

Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$) oleic acid (OA) and ammonium hydroxide were purchased from Shanghai Chemical Reagents Company, China. Methyl acrylate (MA) and divinylbenzene (DVB) were purchased from Gray West Chengdu Chemical Co. Ltd., and they were washed three times using 5 wt% NaOH to remove the inhibitors, and then dried by anhydrous magnesium sulfate. 2,2-Azobisisobutyronitrile (AIBN) was purified by recrystallization before use. Anhydrous ferric chloride, salicylic acid and diethylenetriamine (DETA) were obtained from Yongda Chemical Reagents Company. 1,2-Dichloroethane (DCE) used as the solvent was anhydrate by mesoporous molecular sieve before use.

2.2. Preparation of magnetic polar modified post-cross-linked resin

As shown in Scheme 1, the magnetic resin M-PMD-P-A was prepared as follows. The OA-coated Fe_3O_4 nanoparticles were firstly prepared according to the co-precipitation method performed in Ref. [41], and they were stored in toluene to form a stable organic ferrofluid (Fe_3O_4 was about 20 wt%). 200 mL 0.05 wt% of polyvinyl alcohol aqueous solution was loaded in 500 mL of flask at 318 K. Under nitrogen protection, MA (4.0 g), DVB (16.0 g), AIBN (0.20 g), toluene (23.2 g), *n*-heptane (6.8 g) and OA-coated Fe_3O_4 ferrofluid (10.0 g) were added into the flask. The temperature of the reaction mixture was gradually risen to 348 K and retained for 4 h, 358 K for 2 h, and 368 K for 4 h. The obtained polymer M-PMD was post-cross-linked according by a Friedel–Crafts reaction performed according to the method in Ref. [26] and hence the magnetic post-cross-linked resin M-PMD-P was obtained. M-PMD-P was mixed with 60 mL of DETA and thereafter the reaction mixture was kept at 393 K for 12 h in an oil bath, and hence the magnetic amide and amino-modified resin M-PMD-P-A was prepared.

2.3. Characterization of the resins

FT-IR spectra of the resins were recorded on a Nicolet 510P Fourier transformed infrared instrument in 500–4000 cm^{-1} with a resolution of 1.0 cm^{-1}. The BET surface area, pore volume, and pore diameter distribution of the resins were determined by N_2 adsorption–desorption isotherms at 77 K using a Micromeritics Tristar 3000 surface area and porosity analyzer. The morphology of the resins was observed using transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan). The crystal structure of the OA-coated Fe_3O_4 was investigated by powder X-ray diffraction (XRD, D/Max 2500, Rigaku Co. Japan). The magnetization curves of the magnetic resins were measured by a vibrating sample magnetometer (VSM, Lakeshore 7307) at 300 K.

2.4. Adsorption isotherms

About 0.1000 g of resins was mixed with 50.00 mL of a series of salicylic acid aqueous solutions with the concentrations of about 200, 400, 600, 800 and 1000 mg/L. The series of solutions were then shaken in a thermostatic oscillator at a desired temperature (298, 308 or 318 K) at the agitation speed of 200 rpm until the equilibrium was reached. The equilibrium concentration of salicylic acid C_e (mg/L) was determined and the equilibrium adsorption capacity q_e (mg/g) was calculated based on the following equation:

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

where C_0 is the initial concentration of salicylic acid (mg/L), V is the volume of the solution (L) and W is the mass of the resins (g).

2.5. Adsorption kinetics

For the kinetic experiments, about 1.000 g of M-PMD-P-A was mixed with 250.00 mL of a salicylic acid solution with an initial concentration of 502.0 mg/L. The flasks were then continuously shaken at 298 K until adsorption equilibrium was reached. In this process, 0.50 mL of the solution was withdrawn at a 10-min interval in the first hour and a 20-min interval in the subsequent hours and the concentration of salicylic acid was determined, the adsorption capacity at a contact time t was calculated as:

$$q_t = (C_0 - C_t) \cdot V/W \quad (2)$$

where q_t (mg/g) and C_t represent the adsorption capacity and the concentration at contact time t (mg/L), respectively.

2.6. Column adsorption and desorption breakthrough

2.770 g of the M-PMD-P-A (these wetted resins were measured to be 10.00 mL) was firstly immersed in de-ionized water at 298 K for about 24 h and then densely packed in a glass column with an inner diameter of 16 mm (D = 16 mm). The salicylic acid aqueous