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Polar-modified post-cross-linked polystyrene and its adsorption towards salicylic acid from aqueous solution

Xiao Ling [a], Hebing Li [b], Hongwei Zha [b], Chunlian He [a,*], Jianhan Huang [b,*]

[a] College of Medicine, Hunan Normal University, Changsha, Hunan 410081, China
[b] College of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410083, China

HIGHLIGHTS

- An effective approach for improving the polarity of post-cross-linked polystyrene was developed.
- A novel polar-modified post-cross-linked polystyrene PGDpc_D was prepared.
- PGDpc_D possessed a much enhanced adsorption in comparison with its precursors and PDVBpc.
- The adsorption was a fast process and the micropore diffusion model fitted the kinetic data.
- PGDpc_D was a potential candidate for treatment of salicylic acid from aqueous solution.

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ABSTRACT

A novel polar-modified post-cross-linked polystyrene PGDpc_D was prepared by the Friedel–Crafts alkylation reaction of the pendent vinyl groups and amination reaction with diethylenetriamine (DETA). The Brunauer–Emmett–Teller (BET) surface area and pore volume of the starting copolymer PGD increased significantly after the post-cross-linking, and the surface polarity of the post-cross-linked polystyrene PGDpc improved greatly after the amination reaction. Batch adsorption runs of salicylic acid on PGDpc_D were studied using its precursors (PGD and PGDpc) and the non-polar post-cross-linked polystyrene PDVBpc as the references. Experimental results indicated that PGDpc_D possessed a much enhanced adsorption towards salicylic acid in comparison with PGD, PGDpc and PDVBpc, and the equilibrium data could be characterized by both of the Langmuir and Freundlich models. The adsorption was a fast process and the kinetic data obeyed the micropore diffusion model. Column adsorption–desorption experiments suggested that PGDpc_D was a potential candidate for treatment of salicylic acid from aqueous solution.

1. Introduction

In 1970s, Davankov et al. [1] synthesized a kind of novel polymeric adsorbent from linear polystyrene by the Friedel–Crafts alkylation reaction, and this novel polymeric adsorbent is generally called "hyper-cross-linked polystyrene". Hyper-cross-linked polystyrene possesses high Brunauer–Emmett–Teller (BET) surface area, adjustable pore structure and excellent recycling property [2,3], and hence is extensively applied as the column packing materials in high-performance liquid chromatography (HPLC), ion size-exclusion chromatography and solid-phase extraction for gases, organic contaminants and organic vapors [4–9]. However, the synthetic procedure for the hyper-cross-linked polystyrene is frequently confronted with some thorny problems, and the most serious one is using chloromethyl methylether (CMME) as the post-cross-linking reagent in the Friedel–Crafts alkylation reaction because CMME is recognized as the strong carcinogen. Hence, many researchers are exploiting new methods for synthesis of hyper-cross-linked polystyrene without using CMME. Macintyre et al. [10] and Bratkowska et al. [11] used vinylbenzyl chloride (VBC) as the polymer monomer containing benzyl chloride and the obtained hyper-cross-linked polystyrene also exhibits high BET surface area and excellent adsorption properties. However, much difference is existent for the monomer reactivity ratio between styrene and VBC, and the production cost of VBC is also rather high. In 1988, Ando et al. [12] developed post-cross-linked polystyrene by consuming the self residual pendent vinyl groups of high cross-linking polystyrene without adding external

* Corresponding authors.
E-mail addresses: chunlianhe69@163.com (C. He), jianhanhuang@csu.edu.cn (J. Huang).

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cross-linking reagent. A considerable number of pendent vinyl groups are proven to be located in the dense cores for the high cross-linking polystyrene [13], and they can also be further cross-linked with the benzene rings of the neighboring polymeric chains by the Friedel–Crafts alkylation reaction, resulting in an increased BET surface area and preferable pore structure [14–17]. As a result, the post-cross-linked polystyrene has attracted many attentions in recent years [18–23].

Due to its extremely hydrophobic surface, the post-cross-linked polystyrene had a relatively low adsorption to polar aromatic compounds [18,19]. To improve the surface polarity of the post-cross-linked polystyrene and increase the equilibrium capacity, Zeng et al. [20–22] synthesized a series of polar-modified post-cross-linked polystyrene by introducing polar monomers such as methyl acrylate (MA), vinyl pyridine (VP) and ethylene glycol dimethacrylate (EGDMA) in the polymerization, the prepared polar-modified post-cross-linked polystyrene possessed an enhanced adsorption due to the increased polarity. Ma et al. [23] prepared another polar-modified post-cross-linked polystyrene using methyl methacrylate (MMA) as the polar monomer, and a synergistic effect is shown for adsorption of tetracycline and Cu^{2+}. Nevertheless, the existing studies indicate that the polarity increasing of the polar-modified post-cross-linked polystyrene is limited, and the enhanced adsorption of the considered resins is not obvious.

Amino and amide groups are proven the most efficient polar groups for greatly improving the surface polarity of the resins [24–26], and the increased polarity will induce a much enhanced adsorption via electrostatic interaction or hydrogen bonding [25–29]. We proposed that if some specific amino, amide and hydroxyl groups were uploaded on the surface of the post-cross-linked polystyrene by a specific chemical reaction, the polarity increasing of the considered resin will be obvious, leading to a much enhanced adsorption. In particular, we focused on improving the surface polarity of the post-cross-linked polystyrene, and used the obtained polar-modified post-cross-linked polystyrene for adsorption of salicylic acid from aqueous solution. For this purpose, glycidyl methacrylate (GMA) was adopted as the polar monomer and poly(glycidylmethacrylate-co-divinylbenzene) (PGD) was prepared by a typical suspension polymerization. GMA, as an efficient polymer monomer in the polymerization, contains both vinyl and epoxy groups. The vinyl groups of GMA allow it copolymerization functionality with some other polymer monomers like DVB, and the epoxy groups permit its structural modification of the polymer backbone that can result in differentiated properties and higher performance. The Friedel–Crafts alkylation reaction was then carried out for the starting copolymer PGD, the residual pendent vinyl groups of PGD were further cross-linked and the post-cross-linked polystyrene PGDpc was synthesized. After that, an amination reaction was executed for PGDpc and hence the polar-modified post-cross-linked polystyrene PGDpc_D was prepared. Salicylic acid was selected as the adsorbate to evaluate the adsorption of PGDpc_D using its precursors (PGD and PGDpc) and the non-polar post-cross-linked polystyrene PDVBpc as the references.

2. Experimental

2.1. Materials

GMA and divinylbenzene (DVB, purity: 80%) were purchased from Gray West Chengdu Chemical Co. Ltd., they were washed by 5% of NaOH (w/v) and followed by de-ionized water, and then dried by anhydrous magnesium sulfate before use. Benzoyl peroxide (BPO) employed as the initiator was recrystallized by methanol. Toluene, *n*-heptane, 1,2-dichloroethane (DCE), anhydrous ferric (III) chloride, and diethylenetriamine (DETA) were obtained from Yongda Chemical Co., and they were all analytical reagents. Salicylic acid employed as the adsorbate was used without further purification.

2.2. Preparation of the polar-modified post-cross-linked polystyrene

The preparation of the spherical non-polar post-cross-linked polystyrene PDVBpc was performed according to the method in Refs. [18,30]. The polar-modified post-cross-linked polystyrene PGDpc_D was prepared by the given procedure in Scheme 1. The starting copolymer PGD was synthesized by the usual suspension polymerization using GMA as the polar monomer and it was 5% or 10% relative to the monomers (w/w), and DVB was the cross-linking reagent. Toluene and *n*-heptane were used as the porogens, they were 200% relative to the monomers (w/w), and the mass ratio between toluene and *n*-heptane was defined as 4:1. The reaction mixture was polymerized at 358 K for 12 h and the prepared spherical PGD beads were collected, washed and extracted by petroleum ether in Soxhlet apparatus for 12 h. The Friedel–Crafts alkylation reaction was then carried out using DCE as the solvent and anhydrous ferric (III) chloride as the Friedel–Crafts catalyst [30]. The reaction temperature was kept at 358 K and the reaction time was 10 h. The obtained post-cross-linked polystyrene PGDpc was extracted by ethanol for 12 h, and it was chemically transformed to the polar-modified post-cross-linked polystyrene PGDpc_D (or PGDpc_D_10% as GMA was 10% relative to the total mass of the monomers) by an amination reaction with superfluous DETA at 393 K for 12 h [31].

2.3. Characterization of the polar-modified post-cross-linked polystyrene

Fourier transform infrared spectra (FT-IR) of the resins were recorded on a Nicolet 510P Fourier transform infrared instrument in 500–4000 cm^{-1} with a resolution of 1.0 cm^{-1}. The pore structure of the resins was 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 of the resins was measured according to the back titration method described in Ref. [32]. The hydroxyl groups of the resins were determined by the acylation method in Ref. [33]. The concentration of salicylic acid in aqueous solution was analyzed via a 2450 UV spectrophotometer at the maximum wavelength of 296.5 nm.

2.4. Equilibrium and kinetic adsorption

For the equilibrium adsorption, about 0.1 g of the resins were mixed with 50 mL of a series of salicylic acid aqueous solutions. The initial concentrations of salicylic acid were set to be about 200, 400, 600, 800 and 1000 mg/L, respectively. The series of solutions were shaken in a thermostatic oscillator at three different temperatures (293, 303 and 313 K, respectively) until the equilibrium was reached. The equilibrium concentration of salicylic acid C_e (mg/L) was determined and the equilibrium 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 was the initial concentration of salicylic acid (mg/L), V was the volume of the solution (L) and W was the mass of the resins (g).

The kinetic adsorption of the resins was similar to the equilibrium adsorption except that the adsorption capacity was determined in real time until equilibrium. During this process, 0.5 mL of the solution was sampled at different time intervals, and the concentration of the residual salicylic acid solution was measured until the equilibrium was reached.