



A novel polar-modified post-cross-linked resin and its enhanced adsorption to salicylic acid: Equilibrium, kinetics and breakthrough studies



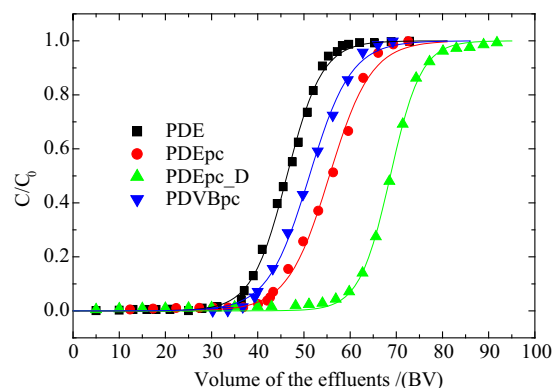
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GRAPHICAL ABSTRACT

PDEpc_D was proven a potential candidate for adsorptive removal of salicylic acid from aqueous solution.



ARTICLE INFO

Article history:

Received 16 January 2016

Revised 2 February 2016

Accepted 18 February 2016

Available online 19 February 2016

Keywords:

Post-cross-linked resin

Polarity

Adsorption

Salicylic acid

ABSTRACT

Improving the surface polarity is of significance for the post-cross-linked resins to enhance their adsorption to polar aromatic compounds. In the present study, we prepared a novel polar-modified post-cross-linked PDEpc_D by the Friedel–Crafts alkylation reaction and the amination reaction, the Brunauer–Emmett–Teller (BET) surface area and pore volume increased significantly after the Friedel–Crafts alkylation reaction and the surface polarity improved greatly after the amination reaction. Batch adsorption showed that PDEpc_D possessed a much enhanced adsorption to salicylic acid as compared the precursors PDE and PDEpc as well as the non-polar post-cross-linked PDVBpc. The equilibrium data was characterized by the Freundlich model, π – π stacking, hydrogen bonding and static interaction were the possible driving forces. The adsorption was a fast process and the kinetic data obeyed the micropore diffusion model. Column adsorption–desorption experiments suggested that PDEpc_D was a potential candidate for adsorptive removal of salicylic acid from aqueous solution.

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1. Introduction

Polymeric adsorbents with high Brunauer–Emmett–Teller (BET) surface area and superior porosity are extensively used in various fields including energy [1], adsorption [2–4], separation [5], medicine [6] and catalysis [7]. They are also employed as the column packing materials in high-performance liquid chromatography (HPLC), ion size-exclusion chromatography and solid-phase extraction, and hence have attracted increasing attention in recent years [8,9].

Particularly, the hyper-cross-linked resins, developed by Davankov and Tsyurupa [10], are proven one of the most promising polymeric adsorbents for industrial application. They are frequently prepared by the typical Friedel–Crafts alkylation reaction from linear polystyrene or low cross-linked poly (styrene-co-divinylbenzene). In this process, external cross-linking reagents such as chloromethyl methylether (CMME) are requested, and a large number of methylene cross-linking bridges connect the neighboring benzene rings of the polymeric chains [11–13]. As a result, a high BET surface area and predominant micro/mesopores are characteristic. However, CMME is recognized as the strong carcinogen, and producing the hyper-cross-linked resins has confronted with the most serious problem. More and more researchers have been exploiting new methods for design and synthesis of novel hyper-cross-linked resins without using CMME. Among which, Ando et al. [14] proposed a method for a further cross-linking of high cross-linked polystyrene (cross-linking degree >80%) without adding external cross-linking reagents. In this procedure, the self pendant vinyl groups are consumed under the help of the Friedel–Crafts alkylation catalysts, and they are further cross-linked with the neighboring benzene rings of the polymeric chains [15,16], resulting in an increased BET surface area and preferable pore structure [15–17].

Nevertheless, the as-prepared post-cross-linked resins are non-polar, their extreme hydrophobic surface is disadvantageous for extraction of polar aromatic compounds like salicylic acid from aqueous solution, and improving the surface polarity is of significance for the post-cross-linked resins to enhance their adsorption to polar aromatic compounds. Zeng et al. [18–20] synthesized a series of ester groups modified post-cross-linked resins by introducing polar monomers such as methyl acrylate (MA), methyl methacrylate (MMA) and N-vinylpyrrolidone (NVP) in the copolymerization. Due to the increased surface polarity, they possessed an enhanced adsorption. More recently, we further increased the surface polarity by introduction of specific amino/amide groups on the post-cross-linked resins [21–23], and there appeared an obvious improvement of the adsorption performance.

Amino and amide groups are regarded as the most efficient functional groups to improve the surface polarity of the polymeric adsorbents [24,25]. If some specific amino and amide groups can upload on the post-cross-linked resins by some typical chemical reactions, the surface polarity would increase greatly for the as-prepared post-cross-linked resins. In particular, the introduced amino groups can interact with the carboxyl groups of salicylic acid via static interaction [26], and the amide groups will affect the hydroxyl groups by hydrogen bonding [11,27], inducing a much enhanced adsorption. For this purpose, in this study, we focused on improving the surface polarity of the post-cross-linked resin, and used the polar-modified post-cross-linked resin for adsorption. Ethyleneglycol dimethacrylate (EGDMA) was adopted as the polar monomer to copolymerize with divinylbenzene (DVB) in the suspension polymerization, and the starting copolymer, poly (divinylbenzene-co-ethyleneglycoldimethacrylate) (PDE), was prepared by a typical suspension polymerization. The Friedel–Crafts alkylation reaction was then carried out for PDE, the residual pendent vinyl groups were further cross-linked,

and the post-cross-linked PDEpc was synthesized. After that, an amination reaction was executed for PDEpc, and a polar-modified post-cross-linked PDEpc_D, which possessed high BET surface area and considerable polar functional groups, was prepared accordingly. Salicylic acid was selected as the adsorbate to evaluate the adsorption of PDEpc_D, and the equilibrium, kinetics and breakthrough studies were comparatively investigated in detail.

2. Experimental

2.1. Materials

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

2.2. Preparation of the starting copolymers

The preparation method for the non-polar PDVB was performed according to the method in Refs. [15,28]. The polar-modified PDE was prepared by a typical suspension polymerization in Scheme 1. Briefly, the organic phase composed of EGDMA (1 g, or 2 g, or 3 g), DVB (19 g, or 18 g, or 17 g), BPO (0.2 g), toluene and *n*-heptane was added to the aqueous phase (200 mL) containing polyvinyl alcohol (PVA, 1 wt% in relation to water). EGDMA was the polar monomer, DVB was the cross-linking reagent and the cross-linking degree of the starting copolymer was 95%, 90% and 85% (w/w), respectively. Toluene and *n*-heptane were the porogens, the total mass of them was 40 g and the mass ratio between toluene and *n*-heptane was defined as 4:1 (w/w). The reaction mixture was copolymerized at 358 K for 12 h and the starting copolymer labeled as PDE (or PDE_10%, or PDE_15%) was collected, washed and extracted by petroleum ether in Soxhlet apparatus for 12 h and then dried under vacuum at 333 K for 8 h.

2.3. Friedel–Crafts alkylation reaction of the starting copolymers and amination of the post-cross-linked resin

20 g the starting copolymers were swollen by 120 mL DCE overnight and 3 g anhydrous ferric (III) chloride was added into the reaction mixture at 318 K. After the added ferric (III) chloride was dissolved completely, the temperature of the reaction mixture rose to 363 K and the reaction mixture was refluxed at this temperature for 10 h, the obtained post-cross-linked PDVBpc and PDEpc were washed by ethanol and 0.1 mol/L hydrochloric acid aqueous solution, and then extracted by ethanol for 12 h. Afterwards, PDEpc was chemically transformed to the polar-modified post-cross-linked PDEpc_D (or PDEpc_D_10%, or PDEpc_D_15%) by an amination reaction with superfluous DETA at 393 K for 12 h [29,30].

2.4. Characterization

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

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