



Aniline modified hypercrosslinked polystyrene resins and their adsorption equilibria, kinetics and dynamics towards salicylic acid from aqueous solutions

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HIGHLIGHTS

- Novel aniline modified hypercrosslinked polystyrene resins were synthesized.
- These resins possessed different adsorption selectivity towards salicylic acid.
- The adsorption process might be concerned with a chemical reaction.
- The resins have an excellent dynamic adsorption towards salicylic acid.
- The resins exhibited good reusability.

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ABSTRACT

A series of aniline modified hypercrosslinked polystyrene resins named as HJ-Y0, HJ-Y2, HJ-Y4, HJ-Y8 and HJ-Y12 were synthesized from macroporous crosslinked chloromethylated polystyrene by adding different quantity of aniline in the Friedel–Crafts reaction and these resins were evaluated for adsorption of salicylic acid from aqueous solutions. The structure characterization indicated that Brunauer–Emmett–Teller (BET) surface area and pore volume decreased with increment of the added quantity of aniline whereas the nitrogen content increased, which implied these resins possessed different adsorption selectivity towards aromatic compounds. HJ-Y4 possessed the largest uptake towards salicylic acid, the Freundlich model was more suitable for fitting the equilibrium data and the isosteric enthalpies decreased with increasing of the fractional loading due to the surface energy heterogeneity. The pseudo second-order rate equation was more appropriate for characterizing the kinetic data and the adsorption process might be concerned with a chemical reaction. The breakthrough capacity ($C/C_0 = 0.05$) of salicylic acid on HJ-Y4 resin column was measured to be 50.24 mg/mL wet resin and the resin column could be regenerated completely by a mixture desorption reagent containing 0.01 mol/L of NaOH (w/v) and 40% of ethanol (v/v) and the resins exhibited good reusability.

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1. Introduction

Wastewater containing phenols and related aromatic compounds such as phenol, salicylic acid and other volatile organic compounds (VOCs), is dark-colored, high toxic and non-biodegradable. Thus, an efficient removal of the aromatic compounds from these wastewaters has been a significant public concern [1]. A lot

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of physical and chemical technologies including photocatalytic oxidation, membrane separation, electrochemical oxidation, solvent extraction and adsorption are frequently employed for removal of the aromatic compounds from aqueous solutions [2–6], and adsorption based on adsorbents is one of the most popular methods [7,8].

Recently, synthetic polymeric adsorbents are widely used in the fields of adsorption and separation due to their relatively high uptakes, decent selectivity, diverse chemical structure and easy regeneration [9–11]. In particular, the hypercrosslinked polystyrene resins prepared from linear polystyrene or low crosslinked polystyrene are proven to be the most efficient polymeric adsorbents for

removal of the aromatic compounds from aqueous solutions [12–14]. These resins had a very high Brunauer–Emmet–Teller (BET) surface area, pore volume and predominant mesopores/micropores distributions [15], which contribute to their excellent adsorption behaviors. However, due to the high hydrophobicity of their matrix, some polar solvents like methanol have to be applied to pre-wet the resins so that they can be used in aqueous solution, which composes of a tedious pre-treatment process. Moreover, their adsorption capacities towards polar aromatic compounds are relatively low due to the unmatched polarity between the adsorbates and the adsorbent. In order to increase the adsorption capacities towards polar aromatic compounds, these hypercrosslinked polystyrene resins are often chemically modified by introduction of the polar units into the copolymers, use of polar compounds as the cross-linking reagent and addition of polar compounds in the Friedel–Crafts reaction [16–19].

In our previous work, some polar aromatic compounds such as hydroquinone, β -naphthol and bisphenol-A were added in the Friedel–Crafts reaction of macroporous crosslinked chloromethylated polystyrene [20–22]. We found that at least two Friedel–Crafts reactions occur in the reaction system, one is the Friedel–Crafts reaction of the macroporous crosslinked chloromethylated polystyrene itself, the other is that between the chloromethylated polystyrene and the polar aromatic compounds. Moreover, the polarity of these resins was enhanced because of the polar aromatic compounds, which improves their adsorption capability towards polar compounds. Furthermore, the chemical structure as well as the pore structure of the obtained resins is affected by the amount of polar aromatic compounds in the reaction, inducing different adsorption selectivity. Aniline is a weakly basic aromatic compound and it may interact with salicylic acid by acid–basic interaction. Hence, if aniline can be loaded on the hypercrosslinked resins and they are employed to adsorb salicylic acid from aqueous solutions, the adsorption may involve a weak chemical bond formation between salicylic acid and the aniline modified hypercrosslinked resin.

2. Experimental method

2.1. Materials and reagents

Macroporous crosslinked chloromethylated polystyrene beads applied as the synthetic precursor in this study was purchased from Langfang Chemical Co. Ltd. (Hebei, China). Its crosslinking degree was 6% and its chlorine content was measured to be 17.08%. Its BET surface area was determined to be $28 \text{ m}^2/\text{g}$ and the pore volume was $0.0036 \text{ cm}^3/\text{g}$. Salicylic acid (Molecular formula: $\text{C}_6\text{H}_4(\text{o-OH})(\text{COOH})$, Molecular weight: 138.1) applied as the adsorbate was an analytical reagent and used without further purification. The Amberlite XAD-4, XAD-7 resins were purchased from Rohm & Haas Company (Philadelphia, USA).

2.2. Preparation of HJ-Y series hypercrosslinked polystyrene resins

The HJ-Y series hypercrosslinked polystyrene resins were prepared by the Friedel–Crafts alkylation reaction of macroporous crosslinked chloromethylated polystyrene with aniline and the detailed process was given in Scheme S1. 40 g of chloromethylated polystyrene beads were swollen by 200 mL of 1,2-dichloroethane and a small quantity of aniline in a flask overnight at 298 K. The mass percentage of aniline in the reaction was set to be 0%, 2%, 4%, 8% and 12% relative to the chlorine content of the macroporous crosslinked chloromethylated polystyrene (w/w), respectively. Anhydrous iron (III) chloride (4.50 g) applied as the catalysts was added into the reaction flask as quickly as possible and then the reaction mixture was heated so that the reaction mixture can be refluxed. After

keeping the reaction mixture for about 10 h, the HJ-Y series aniline modified hypercrosslinked polystyrene resins named as HJ-Y0, HJ-Y2, HJ-Y4, HJ-Y8 and HJ-Y12 were synthesized accordingly.

2.3. Adsorbent characterization and analytical methods

The chlorine content of the resins was measured according to a Volhard method [23]. The specific surface area and pore volume of the resins were determined by nitrogen adsorption–desorption isotherms at 77 K using a Micromeritics Tristar 3000 surface area and porosity analyzer. The total specific surface area and pore volume were calculated according to BET, Langmuir and Barrett–Joyner–Halenda (BJH) models while the pore size distribution was calculated by applying BJH method to the nitrogen desorption data. Fourier Transform infrared (FT-IR) spectroscopy of the resins was collected on a Nicolet 510P Fourier transformed infrared instrument with the wavenumbers ranged in $400\text{--}4000 \text{ cm}^{-1}$. The elemental analysis of the resins was performed by a VarioEL Elemental Analysis System. The concentration of salicylic acid in aqueous solution was analyzed via a UV-2450 spectrophotometer at a wavelength of 296.5 nm.

2.4. Adsorption experiments

Batch adsorption studies were performed by mixing about 0.1000 g of the resins with 50 mL of salicylic acid aqueous solutions at various concentrations (from about 200 mg/L to 1000 mg/L with 200 mg/L interval) in a 150 mL glass flask. To study the pH effect, 0.1000 g of the resins was dispersed in 50 mL of salicylic acid aqueous solutions (about 500 mg/L) for about 8 h. The initial solution pH was adjusted from 1.02 to 13.4 by using a certain amount of dilute HCl or NaOH solutions. The effect of temperature (298 K, 303 K, 308 K and 313 K, respectively) on the adsorption was investigated by about 0.1000 g of the resins with 50 mL of salicylic acid aqueous solutions at various concentrations. Kinetic studies were conducted using about 1.000 g of the resins and 250 mL of salicylic acid aqueous solutions (about 500 mg/L) with different temperature (298 K, 303 K, 308 K and 313 K, respectively) and the contact time between the resins and the solutions was ranged from 0 h to 6 h. The equilibrium adsorption capacity, q_e (mg/g), was calculated by conducting a mass balance of salicylic acid on the resins before and after the experiment.

Column experiments were carried out in a glass column (16 mm diameter). The resins were firstly immersed by de-ionized water for 24 h and then packed in the glass column densely to assemble into a resin column. The wet resin column was measured to be 1 BV (1 BV = 10 mL). Salicylic acid aqueous solution at a feed concentration of 502.4 mg/L was passed through the wet resin column at a flow rate of 9.0 BV/h and the residual concentration of salicylic acid from the effluent, C (mg/L), was dynamically recorded until it reached the initial concentration. After the adsorption, the resin column was carefully rinsed by 20 mL of de-ionized water and a desorption reagent was applied for the dynamic desorption experiment. In this study, the desorption reagent was a mixture solution containing 0.01 mol/L of NaOH (w/v) and 40% of ethanol (v/v). About 200 mL of the desorption reagents were passed through the resin column at a flow rate of 4.5 BV/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 aniline modified hypercrosslinked polystyrene resins

As listed in Table 1, the residual chlorine content of the HJ-Y series hypercrosslinked polystyrene resins sharply decreased from

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