



An ethylenediamine-modified hypercrosslinked polystyrene resin: Synthesis, adsorption and separation properties

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HIGHLIGHTS

- The ethylenediamine-modified hypercrosslinked resin was synthesized.
- The ethylenediamine-modified hypercrosslinked resins had different pore structure.
- The ethylenediamine-modified hypercrosslinked resins owned different polarity.
- The equilibrium and column breakthrough performance of the resin were determined.
- The separation performance of the resin from the mixed solution was measured.

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ABSTRACT

We developed an effective approach for increasing phenol uptakes on a hypercrosslinked polystyrene resin and separating phenol from methyl orange or Congo red from the mixed solution. The ethylenediamine-modified hypercrosslinked polystyrene resins were synthesized, the equilibrium and breakthrough performance of the resins were determined on a selected resin named HJ-D33. The phenol uptakes on HJ-D33 were remarkably larger than that on its precursor and the commercial adsorbents like XAD-4, D301. The breakthrough capacity of phenol on HJ-D33 was 50.37 mg/ml wet resin at an initial concentration of 800.8 mg/L and a flow rate of 8.0 BV/h and the used HJ-D33 could be completely regenerated by a mixed solvent containing 0.01 mol/L of sodium hydroxide and 50% of ethanol. Methyl orange (or Congo red) and phenol could be dynamically separated by HJ-D33 resin column as the effluent was in the range of 0–60 BV.

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1. Introduction

In 1969, Davankov and Tsyurupa proposed a fundamentally novel approach to obtain a kind of uniformly crosslinked polystyrene [1], and which leads to a creation of a so called “hypercrosslinked polystyrene” resin which had unique structure and extraordinary properties [2,3]. The hypercrosslinked polystyrene was proven an efficient polymeric adsorbent for adsorptive removal of aromatic compounds such as benzene, toluene and phenol from aqueous solutions. It was also widely applied as column packing materials in high-performance liquid chromatography (HPLC), ion size-exclusion chromatography materials and solid-phase extraction materials for gases, organic contaminants and organic vapors [4–6].

Hypercrosslinked polystyrene was generally prepared from a linear polystyrene or a low crosslinked polystyrene by adding typical bis-chloromethyl derivatives of aromatic hydrocarbons such as 1, 4-bis-(chloromethyl)-diphenyl, *p*-xylylenedichloride, 1, 4-bis-(*p*-chloromethylphenyl)-butane or 1, 3, 5-tris-(chloromethyl) mesitylene by a Friedel–Crafts reaction under the help of catalysts including anhydrous zinc chloride, iron (III) chloride or stannic (IV) chloride [7,8]. After the corresponding reaction, intensive networks with long-chain bridges between the initial polystyrene chains and the conformationally rigid links were formed accordingly, and which results in a major shift of the pore width distribution from predominately mesomacropores to meso/micropores distribution as well as a sharp increase of the Brunauer–Emmet–Teller (BET) surface area and pore volume [9,10].

Hypercrosslinked polystyrene can also be prepared from low crosslinked polystyrene using monochlorodimethyl ether as the crosslinking reagent according to two continuous steps. The first

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step contains a chloromethylation of the polystyrene under mild conditions and hence the chloromethylated polystyrene with quantitative chloromethyl groups will be achieved, the introduced chloromethyl groups can further react with another phenyl ring of the polystyrene by formation of an equivalent number of diphenylmethane-type rigid bridges through a typical Friedel–Crafts reaction, resulting in the post-crosslinking of the polystyrene and formation of hypercrosslinked polystyrene [11,12]. It was deemed that the residual chlorine content of the chloromethylated polystyrene reduced sharply after the Friedel–Crafts reaction [13]. In particular, it declined rapidly at the beginning and subsequently decreased slowly as the reaction proceeded, and hence the hypercrosslinked polystyrene with different residual chlorine content can be synthesized by regulating the Friedel–Crafts reaction time [13,14]. The residual chlorine content of the obtained hypercrosslinked polystyrene determines the pore structure and polarity of the products, and it is feasible to adjust the pore structure and polarity of the hypercrosslinked polystyrene by simply controlling the Friedel–Crafts reaction time. To the best of our knowledge, this approach for optimizing the hypercrosslinked polystyrene is little reported in the literature yet.

In this study, four hypercrosslinked polystyrene resins were synthesized from macroporous crosslinked chloromethylated polystyrene through the Friedel–Crafts reaction by regulating the Friedel–Crafts reaction time (0.5, 1.0, 3.0 and 5.0 h, respectively). These hypercrosslinked polystyrene resin were then chemically modified by an amination reaction with ethylenediamine to produce the ethylenediamine-modified hypercrosslinked polystyrene. Thereafter, the adsorption selectivity of the resins towards phenol was confirmed by the batch adsorption, and the most promising resin HJ–D33 was selected for detailed experimental studies for adsorptive removal of phenol from aqueous solutions and separation of phenol from other molecules with larger molecular size such as methyl orange and Congo red.

2. Experimental

2.1. Materials

Macroporous crosslinked chloromethylated polystyrene was purchased from Langfang Chemical Co., Ltd., China, its crosslinking degree was 6%, chlorine content was measured to be 17.3%, its Brunauer–Emmett–Teller (BET) surface area was 28 m²/g with an average pore width of 25.2 nm. Anhydrous iron (III) chloride, 1, 2-dichloroethane, ethylenediamine and ethanol was analytical reagents. Phenol (C₆H₅OH, Molecular weight (MW): 94.1), methyl orange (C₁₄H₁₄N₃NaO₃S, MW: 327.3) and Congo red (C₃₂H₂₂N₆Na₂O₆S₂, MW: 696.7) applied as the adsorbates were analytical reagents and used without further purification.

2.2. Synthesis of ethylenediamine-modified hypercrosslinked polystyrene resins

Ethylenediamine-modified hypercrosslinked polystyrene resin was synthesized by two continuous steps (Scheme S1). One is Friedel–Crafts reaction of macroporous crosslinked chloromethylated polystyrene, which performed by a similar procedure in Refs. [13,15], the hypercrosslinked polystyrene resin was obtained in this step, and the other is amination reaction of the hypercrosslinked polystyrene resin. Typically, 1, 2-dichloroethane was applied as the solvent to swell macroporous crosslinked chloromethylated polystyrene at room temperature for 24 h. Catalytic amounts of anhydrous iron (III) chloride was used as the catalysts. After refluxing reaction mixture for 0.5 h, 1 h, 3 h and 5 h, respectively, the hypercrosslinked polystyrene resins named HJ–

05, HJ–11, HJ–33 and HJ–55 was obtained. After rinsing, the hypercrosslinked polystyrene resins were mixed with superfluous ethylenediamine and the reaction mixture was kept at 393 K for 20 h, and hence the ethylenediamine-modified hypercrosslinked polystyrene resins were prepared (labeled as HJ–D05, HJ–D11, HJ–D33 and HJ–D55).

2.3. Characterization of the resins and analysis of the adsorbates

The pore structure of the resins in the dry state such as the BET surface area, Langmuir surface area, t-plot micropore surface area, pore volume, t-plot micropore volume, average pore width and pore width distribution of the resins were determined by the N₂ adsorption and desorption isotherms at 77 K using a Micromeritics Tristar 3000 surface area and porosity analyzer. The total surface area and pore volume of the resins were calculated according to BET model while the t-plot micropore surface area and t-plot micropore volume were calculated by the Barrett, Joyner and Halenda (BJH) method, the pore width distribution of the meso/macroporus region of the resins was determined by applying BJH method to the N₂ desorption data, while the pore width distribution of the microporous region of the resin was determined by density functional theory (DFT) (Model: Carbon, Slit pores; Method: Non-negative regularization; No Smoothing, Standard deviation of fit: 3.308 cm³/g) method using a Micromeritics ASAP 2020 Physisorption Analyzer. The Fourier transform infrared spectroscopy (FT-IR) of the resins was collected by KBr disks on a Nicolet 510P Fourier transformed infrared instrument. The chlorine content of the resins was measured by the Volhard method [16] and the weak basic exchange capacity of the resin was determined by another established method [17]. The morphology of the resins was carried out by scanning electron microscopy (SEM) performed on a JSM-6360LV SEM tester. The concentration of phenol, methyl orange and Congo red in aqueous solution was analyzed by UV analysis at the wavelength of 269.5, 463.5 and 498.0 nm, respectively.

2.4. Equilibrium adsorption

About 0.1000 g of the resin was accurately weighed and mixed with 50 ml phenol aqueous solution at an initial concentration of about 100, 200, 300, 400 and 500 mg/L in a conical flask. 1.0 mol/L of hydrochloric acid or 1.0 mol/L of sodium hydroxide was employed to adjust the solution pH. Sodium chloride and cadmium nitrate were used to investigate the salinity and heavy metal ion effect on the adsorption. The flasks were then continuously shaken in a thermostatic oscillator at a desired temperature (300, 305 or 310 K) until the adsorption equilibrium was reached. The equilibrium concentration of phenol C_e (mg/L) was calculated and the equilibrium phenol uptakes on the resin q_e (mg/g) was determined as:

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

where C₀ is the initial concentration (mg/L), V is the volume of the phenol aqueous solution (L) and W the mass of the resin (g).

2.5. Dynamic adsorption, desorption and separation

The resins were immersed in de-ionized water at room temperature for 24 h and then packed in a glass column (inner diameter: 16 mm) densely to assemble a resin column. In the dynamic adsorption experiment, the phenol aqueous solution at an initial concentration of 800.8 mg/L was passed through the resin column at a flow rate of 8.0 BV/h (1BV = 10 ml). In the dynamic separation experiment, a synthetic mixed solution containing a prepared solution containing 500.5 mg/L of phenol and 498.6 mg/L of methyl orange or 504.8 mg/L of phenol and 502.3 mg/L of Congo red was

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