



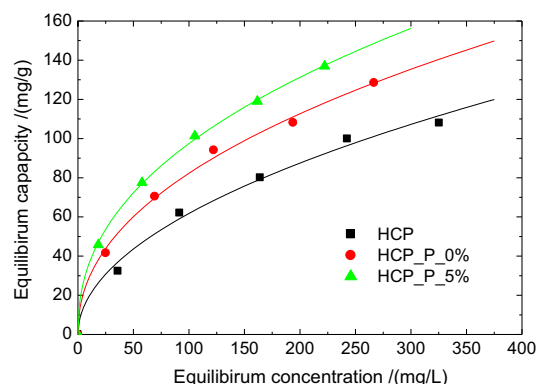
Regular Article

Phenol-modified hyper-cross-linked resins with almost all micro/mesopores and their adsorption to aniline

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GRAPHICAL ABSTRACT

Phenol-modified hyper-cross-linked resins with almost all micro/mesopores possessed an enhanced adsorption to aniline.



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ABSTRACT

Synthesis of hyper-cross-linked resins with almost all micro/mesopores as well as controllable functional groups is still challenging. Herein we developed a kind of phenol-modified hyper-cross-linked resins with almost all micro/mesopores, and controlled the uploading amount of phenol on the surface. The results indicated that, due to producing rigid methylene cross-linking bridges, these resins were typical micro/mesoporous materials, and the micropore surface area and micropore volume were up to 70% of the total Brunauer-Emmett-Teller (BET) surface area and pore volume. Moreover, the functionalized polarity of these resins could be accurately controlled by adding different amount of phenol in the reaction. These as-prepared resins were employed as the adsorbents for adsorption using aniline as the adsorbate, and the adsorption experiments showed that these resins were efficient for adsorption of aniline, and the resin adding 5% (w/w) phenol in the reaction possessed the largest equilibrium capacity ($q_{max} = 169.2$ mg/g). The adsorption was very fast, 40 min was enough for the equilibrium, and the micropore diffusion model described the kinetic data very well.

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1. Introduction

Volatile organic compounds (VOCs) such as benzene, phenol and aniline are often emitted from various industries [1,2]. In

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particular, aniline is a basic raw material extensively applied in pharmaceutical, dyestuff, pesticide; petrochemicals and agrochemical industries, and hence it will be frequently exposed from these industries. In addition to posing disadvantageous effect on human health, aniline will also generate many serious environmental problems due to its high toxicity and environmental accumulation, and hence efficient removal of aniline has attracted increasing attention in recent years [3–5].

Because of the high Brunauer-Emmett-Teller (BET) surface area, favorable pore structure and diverse surface chemistry, hyper-cross-linked resins are proven the efficient polymeric adsorbents for adsorption of aromatic compounds [6,7]. In recent years, the hyper-cross-linking technology has opened up a series of novel three-dimensional (3D) porous polymers, and they have found new perspectives in gas storage [8,9], heterogeneous catalysis [10] and energy conversion [11]. The hyper-cross-linked resins can be prepared from linear polystyrene or low cross-linked polystyrene [12], and the typical Friedel-Crafts reaction is performed by introducing external rigid cross-linkers. The macromolecular assemblies will produce plentiful micro/mesopores in the internal structure, leading to a high BET surface area. The adsorption experiments indicate that they have large equilibrium capacities to non-polar and weakly polar aromatic compounds, and the main driving force is based on hydrophobic interaction and π - π stacking [13,14]. However, they possess a relatively small capacity to polar aromatic compounds such as aniline, phenol and salicylic acid. Hence, chemical modification is often considered to meet this demand [15], and the increased polar matching via specific electrostatic interaction or hydrogen bonding is shown the main driving forces [16,17].

Macroporous chloromethylated polystyrene (MP-CMPS) is a frequently-used raw material for the hyper-cross-linked resins [13–17]. However, due to the special reaction mechanism, in addition to plentiful micro/mesopores [18], the hyper-cross-linked resins also contain quite a few macropores, even ultramacropores, and hence they exhibit a bimodal pore size distribution. We considered that if non-porous gel-type chloromethylated polystyrene (NP-GCMPS) is employed as the raw material, the produced pores by swelling in the solvent are very small. The Friedel-Crafts reaction will be highly limited in the small pores, and hence the produced rigid methylene cross-linking bridges will

reinvest the obtained resins with almost all micro/mesopores, and hence the synthesized resins will have a very narrow pore size distribution. In addition, if phenol is added in the reaction, phenol will be uploaded on the surface, which will interact with aniline via electrostatic interaction or hydrogen bonding in the limited micro/mesoporous domains [3,19], and hence a much enhanced adsorption will be realized [20,21]. As a result, herein we used NP-GCMPS as the raw material, and synthesized a kind of micro/mesoporous resins. Moreover, different quantity of phenol (0%, 5%, 10% or 15% relative to NP-GCMPS, w/w) was added in the Friedel-Crafts reaction, and the as-prepared resins contain considerable phenolic hydroxyl groups on their surface, leading to an efficient adsorption to aniline.

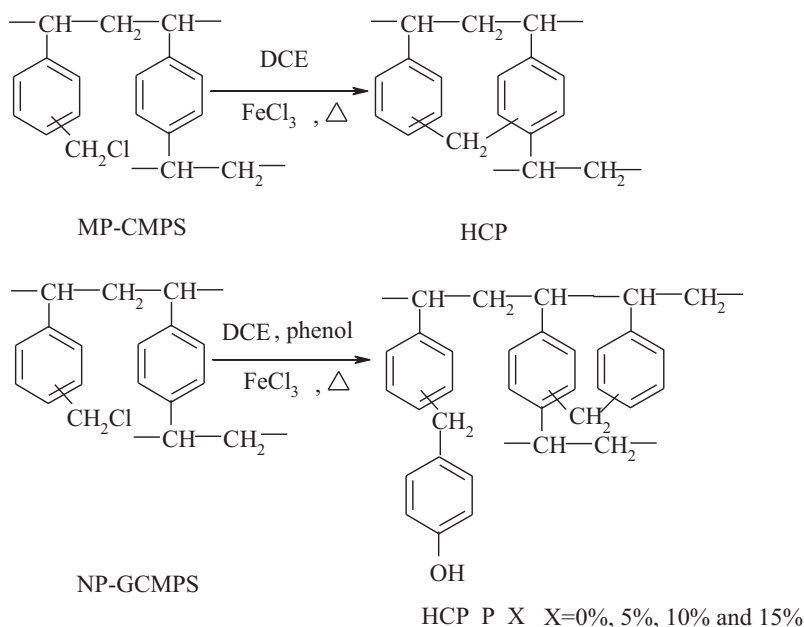
2. Experimental method

2.1. Materials

NP-GCMPS and MP-CMPS were purchased from Nankai University Chemical Plant (Tianjin, China). The cross-linking degree and the chlorine content of NP-GCMPS were 1% and 16.7%, while those of MP-CMPS were 6% and 17.3%, respectively. Aniline applied as the adsorbate in this study was an analytical reagent and used after vacuum distillation. 1,2-Dichloroethane (DCE), anhydrous ferric (III) trichloride and phenol were all analytical reagents and used without further purification.

2.2. Synthesis of phenol-modified hyper-cross-linked resins

As described in Scheme 1, 40 g NP-GCMPS was fully swollen by 120 mL DCE at room temperature for 24 h. A small quantity of phenol (0%, 5%, 10% or 15% relative to NP-GCMPS, w/w) was dissolved by DCE, and added into the reaction mixture. Subsequently, 2.0 g anhydrous ferric (III) trichloride was added at 323 K, and the reaction mixture was heated to 358 K, and retained at this temperature for 8 h [22,23]. The resulting solid particles, named HCP_P_X (X presented the mass percentage of phenol added in the reaction), were filtrated, rinsed by 1% hydrochloric acid (v/v) and anhydrous ethanol. Finally, they were extracted by anhydrous ethanol for 8 h. The hyper-cross-linked resin prepared from



Scheme 1. Synthetic procedure of the phenol-modified hyper-cross-linked resins.

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