



Hierarchical porous hyper-cross-linked polymers modified with phenolic hydroxyl groups and their efficient adsorption of aniline from aqueous solution

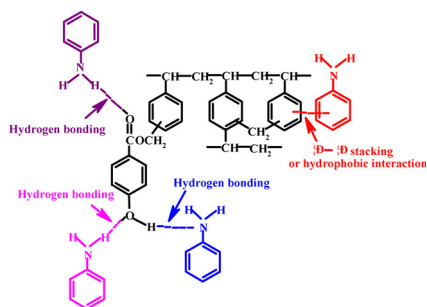
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GRAPHICAL ABSTRACT



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ABSTRACT

Herein two hierarchical porous hyper-cross-linked polymers modified with phenolic hydroxyl (–OH) groups were synthesized and their adsorption was comparatively evaluated using aniline as the adsorbate. The results reveal that the phenolic –OH groups are helpful for the equilibrium adsorption due to the increased polar matching by formation of acid-base complex and hydrogen bonding, and the hierarchical porosity is favorable for the kinetic adsorption because the three dimensional continuous mesopores facilitate the rapid diffusion of aniline. The original aniline solution is optimum for the adsorption and the molecular state of aniline is preferable. The maximum equilibrium capacity is predicted to be 184.8 mg/g by the Langmuir model, and the enthalpy change, Gibbs free energy change, and entropy change are calculated to be negative. The adsorption can reach equilibrium within 60 min, the kinetic data obey the pseudo-second-order rate equation and the first step of the adsorption is mainly controlled by the intra-particle diffusion model.

1. Introduction

In 1969, Davankov and coworkers developed a hyper-cross-linking technique for the synthesis of hyper-cross-linked polymers (HCLP) [1], and this unique technique has produced various novel three dimensional microporous organic polymers (MOPs) in recent

years [2–7]. The HCLP are originally constructed by means of a further cross-linking of polystyrene (PST) according to the Friedel-Crafts reaction [8], and external cross-linking agents are frequently employed to link the polymer chains. In this process, the external cross-linking agents are the electrophilic agents, which carry out the electrophilic substitution reaction with the adjacent phenyl groups of

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the polymers. As a consequence, the newly formed methylene groups will connect the neighboring phenyl groups [9]. After the solvents are extracted, these rigid methylene groups will bring forth abundant new micropores, and hence the resulting HCLP are impressively recognized by the great increase of the specific surface area and predominant micropores [10,11]. The outstanding structure endows them with efficient removal of organic vapors, aromatic compounds, and toxic metals [4,12–15]. More recently, the HCLP have opened up new application prospect in gas storage [5,6,16–18], heterogeneous catalysis [19], and energy conversion [20].

On the other side, the skeletons of HCLP are built up with extremely hydrophobic monomers such as styrene (St) and divinylbenzene (DVB), the resulting HCLP certainly have large equilibrium capacities to non-polar and weakly polar aromatic compounds [21], and hydrophobic interaction and π - π stacking are the main driving forces. However, the extremely hydrophobic surface is unbeneficial for adsorption of polar aromatic compounds. In addition, their hydrophobic surface is disadvantageous in industrial application because a time-consuming process is necessary for making the polymers suitable for use in aqueous solution. As a result, the synthesis of the HCLP with specific functional groups is often considered, and some polar polymer monomers containing specific functional groups or post-functionalization are often designed [22,23]. Phenolic hydroxyl ($-OH$) groups are acidic functional groups, which can interact basic adsorbates like aniline by formation of acid-base complex and hydrogen bonding. For example, Deng et al [3] reported that the hierarchical porous phenolic resin (PFN-P) has a high catalytic performance, and the abundant $-OH$ and tri-phenylphosphine groups in the networks make enormous contributions. Huang et al [24] fabricated a kind of MOPs with plentiful free phenolic $-OH$ groups, and it owns large adsorption capacity (1153 mg/g) to methylene due to the strong acid-base interaction and electrostatic interaction. Huang et al [25,26] prepared the phenolic $-OH$ groups modified hyper-cross-linked resins via post-functionalization, and the uploaded phenolic $-OH$ groups are advantageous for the adsorption *p*-nitroaniline.

Macroporous low cross-linked chloromethylated polystyrene (CMPS) is frequently used for the synthesis of HCLP. For example, Ahn et al [27] prepared the HCLP using gel-type *p*-vinylbenzyl chloride-divinylbenzene (VBC-DVB) copolymers, and it possesses the highest Brunauer-Emmett-Teller (BET) surface area of 2080 m²/g. More recently, Kim et al [28] demonstrated that the VBC content is responsible for the microporosity, while the DVB content has a strong influence on the mesoporosity. As a result, as macroporous CMPS is used as the raw material, the prepared HCLP should contain a few broad mesopores in addition to plentiful micropores and narrow mesopores, and hence the hierarchical pores are presented for these polymers. We considered that the hierarchical porous polymers with micropores and mesopores are indeed extremely useful for the adsorption [3,29]. The micropores are advantageous for the equilibrium adsorption because they can efficiently capture the adsorbates by micropore-filling mechanism [30–32], while the mesopores are beneficial for the kinetic adsorption due to the rapid diffusion of the adsorbates in the pores [33], and hence the active sites of the polymers can be quickly and fully accessible. As a result, the polymers with hierarchical porosity may be preferable for the adsorption.

For this purpose, in the present report, CMPS was used as the raw material and the Friedel-Crafts reaction was firstly performed using anhydrous FeCl₃ as the catalysts. Afterwards, the as-prepared HCLP were esterified with salicylate and *p*-hydroxybenzoate via post-functionalization, and hence considerable phenolic $-OH$ groups were uploaded and hence the phenolic $-OH$ groups modified HCLP were prepared. Their surface chemistry and porosity were characterized and their adsorption was comparatively evaluated using aniline the adsorbate.

Table 1
Textural Properties of the Polymers.

Functional groups	CMPS -CH ₂ Cl	HCLP -CH ₂ Cl	SA-HCLP Phenolic hydroxyl, ester	PHBA-HCLP Phenolic hydroxyl, ester
S_{BET} /(m ² /g) ^a	14.1	1027	831	818
S_{micro} /(m ² /g) ^b	–	554	429	457
V_{total} /(cm ³ /g) ^c	0.024	0.86	0.51	0.49
V_{micro} /(cm ³ /g) ^b	–	0.42	0.25	0.30
Average pore size /(nm)	6.87	2.3	2.7	2.5
Chlorine content /(mmol/g) ^d	4.88	1.27	0.32	0.29
Weak acidic exchange capacity (mmol/g) ^e	–	0.05	0.88	0.93
Swelling ratio in water ^f	1.02	1.22	1.36	1.47
Water uptake (g/g) ^g	0.03	0.9	1.1	1.3
Particle size /(mm)	0.3–0.6	0.3–0.6	0.3–0.6	0.3–0.6

^a Computed from the N₂ adsorption isotherms and BET analysis.

^b Calculated using NLDFT model.

^c Calculated at $P/P_0 = 0.99$.

^d Determined by the Volhard method.

^e Determined by titration method.

^f Determined by volumetric analysis.

^g Measured by gravimetric method.

2. Materials and methods

2.1. Materials

CMPS were purchased from Tianjin Nankai HECHENG S&T Co., Ltd (Tianjin, China), its cross-linking degree was 6% and its textural parameters were listed in Table 1. Amberlite XAD-4 was purchased from Rohm & Haas Company (USA). 1,2-Dichloroethane (DCE), anhydrous FeCl₃, *N,N*-dimethyl formamide (DMF), sodium bicarbonate (NaHCO₃), salicylic acid (SA), and *p*-hydroxybenzoic acid (PHBA) were obtained from Shandong Xiya reagent chemical industry Co. Ltd (Shandong, China), these reagents are all analytical agents and used without further purification. Aniline was bought from Aladdin, it was applied as the adsorbate in this study and used after vacuum distillation.

2.2. Preparation of the hyper-cross-linked polymers

As shown in Scheme 1, the phenolic $-OH$ groups modified hyper-cross-linked polymers namely SA-HCLP and PHBA-HCLP were prepared by two continuously steps. The first Friedel-Crafts reaction was performed using 40 g CMPS as the raw material and 120 mL DCE as the solvent [23]. 4 g anhydrous FeCl₃ was employed as the catalysts and the reaction was retained at 368 K for 5 h, and hence the hyper-cross-linked polymers abbreviated HCLP were achieved. Afterwards, 10 g SA or PHBA was dissolved with 80 mL DMF and the mixture was employed as the solvent to swell 20 g HCLP at room temperature for 12 h [25]. 6 g NaHCO₃ was then added and followed by increasing the temperature to 368 K. After the esterification reaction was completed at 368 K for 10 h, the reaction mixture was filtered and the solid particles denoted SA-HCLP or PHBA-HCLP were rinsed with 1% HCl and deionized water until neutral pH, and finally the products were purified further by Soxhlet extraction with ethanol for 24 h and dried in a vacuum at 333 K for 12 h to give solvent-free polymers.

2.3. Equilibrium adsorption

Equilibrium adsorption of aniline on the polymers was performed at three temperatures of 298, 308, and 318 K, respectively. About 0.1 g the polymers was accurately weighed and mixed with 50 mL aniline aqueous solution with different initial concentration C_0 (mg/L). The initial concentration of aniline was 121.3, 242.6, 363.9, 485.2, and 606.5 mg/L

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