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Amino-modified hierarchically macro-mesoporous cross-linked polystyrene: A novel adsorbent for removal of salicylic acid from aqueous solution

Hongqi Zhang[a], Tiantian Zhang[a], Lei Tian[b], Jiayan Qu[a], Pange Liu[a], Xiaomei Wang[a,*], Xu Zhang[a,*]

[a] School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, PR China
[b] State Key Laboratory of Separation Membranes and Membrane Processes/National International Joint Research Center for Separation Membranes, Tianjin Polytechnic University, Tianjin 300387, PR China

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ABSTRACT

A novel amino modified hierarchically macro–mesoporous cross-linked polystyrene adsorbent (HP CLPS-EDA) was fabricated via the combination of colloidal crystal templating method with Friedel–Crafts (F-C) technique, and adsorption performance of salicylic acid (SA) from aqueous solutions on HP CLPS-EDA was investigated. Compared with the amino modified three dimensional ordered macroporous CLPS (3DOM CLPS-EDA), the HP CLPS-EDA showed the largest adsorption capacity towards SA and maximum utilization of amino groups. Furthermore, the adsorption characteristics of HP CLPS-EDA including adsorption isotherms, adsorption kinetic, effect of solution pH on adsorption and the regenerations performance were researched and discussed. It was shown that, the maximum adsorption capacity of HP CLPS-EDA predicted by the Langmuir model was much higher than the most adsorbents reported in literatures. Additionally, the adsorption capacity of HP CLPS-EDA towards SA was well retained in a wide range of solution pH. After fifteen times regenerations, over 95% of the initial adsorption capacity of HP CLPS-EDA was preserved and the morphology was well retained.

1. Introduction

Water pollution by phenolic compounds has received widespread concerns in recent years. Many methods and technical process have been developed to reduce the pollution, such as membrane separation [1], photo catalytic degradation [2], extraction [3], and adsorption [4–6]. Particularly, adsorption is considered to be one of the most efficient methods in wastewater treatment due to the high concentrating ability and reusability of the adsorbents.

The design and synthesis of polymeric adsorbents have attracted wide attentions due to its favorable physicochemical stability, large adsorption capacity and facile functionalization [7–9]. Recently, synthesis and applications of hierarchically structured porous materials have become a rapidly evolving field of current interest [10]. Compared with single-sized porous materials, hierarchically porous (HP) materials exhibit enhanced properties in mass transport and diffusion, which mainly result from the high surface area, large accessible space, and interconnected hierarchical porosity at different length scales. Mesopore or micropore is more likely for the location of active sites [11,12], and sorbents with abundant mesopores have demonstrated higher mass loading capacities irrespective of the surface area due to the improved accessibility of the adsorbate to the internal surfaces [13–15]. Additionally, macropores facilitate mass diffusion toward and away from these active sites and reduce transport limitations [10,11]. For example, Xiao et al. synthesized adsorption resins with macro-micro pore structures by Friedel–Crafts reaction base on the macroporous chloromethylated polystyrene resin [6]. Furthermore, high interconnectivity between different length scale pores is of great significance for mass transport through porous framework [16]. Consequently, to fabricate a novel hierarchically porous polymeric adsorbent with highly interconnected macro–mesoporous structure as well as high surface area seems to be an effective way of maximizing the utilization of active sites imbedded into porous frameworks (or adsorption efficiency) and improving adsorption capacity.

Fabrication of three dimensionally ordered macroporous (3DOM) structure, meanwhile constructing mesopores on the ultrathin pore walls of 3DOM materials offer an efficient way for the construction of hierarchically macro–mesoporous architectures

* Corresponding authors.
E-mail addresses: xmwang@hebut.edu.cn (X. Wang), xuzhang@hebut.edu.cn (X. Zhang).

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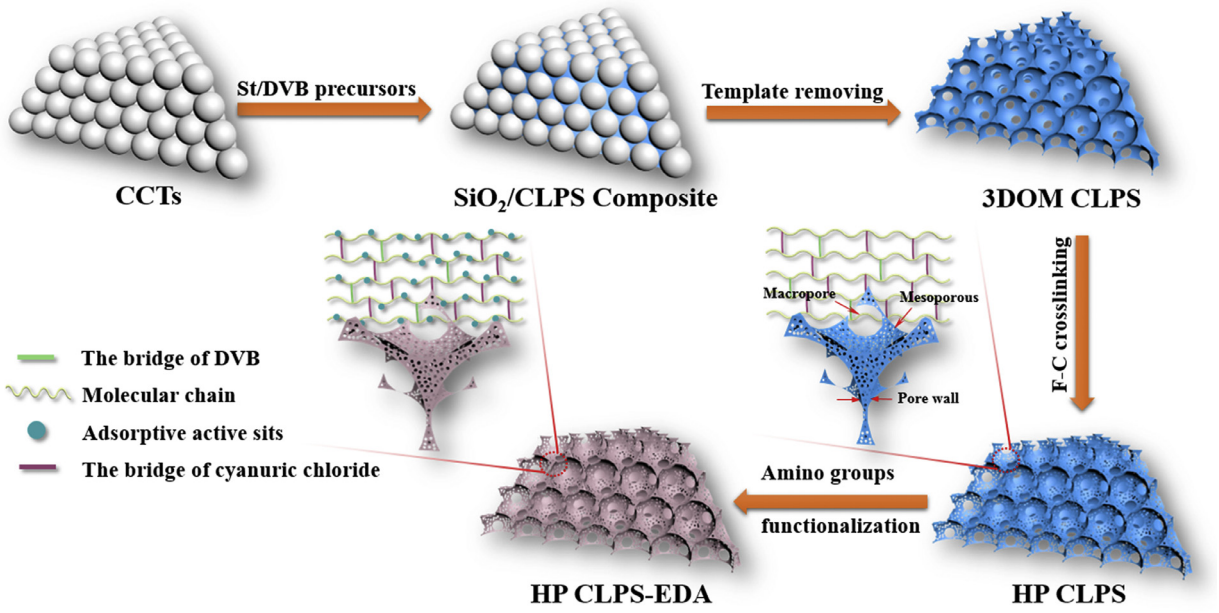

Fig. 1. Schematic synthesis of the HP CLPS-EDA.

with high surface area and interconnectivity [10–12]. It is worth mentioning that, to the best of our knowledge, there are few studies focused on incorporation of mesopores into the ultrathin pore walls of 3DOM resins to obtain polymeric adsorbents with large surface area and high interconnectivity, which maybe induce high adsorption capacity and improved adsorption efficiency. It may be challenging but meaningful to develop an effective functional hierarchically macro-mesoporous polymeric absorbent with high interconnectivity and large surface area.

Herein, we propose a novel fabrication strategy of hierarchically macro–mesoporous cross-linked polystyrene (HP CLPS) through the combination of colloidal crystal templating (CCT) method with Friedel–Crafts (F-C) reaction technique. Cyanuric chloride was employed as the post cross-linking agent for the formation of mesopores [17]. SA was chosen as the model adsorbate due to its high toxicity and accumulation in the environment. Then HP CLPS resins were further functionalized with ethylenediamine (EDA) through a facial reaction, since polar amino groups can interact with SA by polarity matching [5,18]. Thus, a novel amino-modified hierarchically macro–mesoporous cross-linked polystyrene adsorbents (HP CLPS-EDA) was prepared accordingly. The ultrathin pore walls with adsorption sites (amino groups) and hierarchically macro–mesoporous structure will extremely improve the adsorption efficiency of the adsorption sites, accordingly increase the adsorption capacity. The overall fabrication procedure is shown in Fig. 1. The adsorption behaviors including the equilibrium, kinetics, effect of solution pH and reusability were also investigated in detail.

2. Materials and methods

2.1. Chemicals and reagents

Nitrobenzene (Tianjin Dengfeng Chemical Company, 99%) was dehydrated by molecular sieves (4 Å) before use. Styrene (St, 98%), divinylbenzene (DVB, 80% isomer), and 2,2-azobisisobutyronitrile (AIBN) were purchased from Tianjin Guangfujingxi Chemical Company. St and DVB were dried over calcium hydride overnight and distilled under reduced pressure, then stored under argon at −10 °C. AIBN were purified by recrystallization in methanol. Cyanuric chloride (99%), ethylenediamine (EDA, 99%), ferric chloride (99.9%) and salicylic acid (99.5%, SA) were obtained from Aladdin Industrial Corporation and used as received.

2.2. Preparation of 3DOM CLPS

The preparation of 3DOM CLPS with a pore size of 245 nm by CCT method was performed according to our previous work [19]. The difference is that the mass percentage of DVB is 6% (w/w).

2.3. Fabrication of HP CLPS

A representative example of fabricating HP CLPS is described as follows: anhydrous ferric chloride was used as F-C catalyst, cyanuric chloride as cross-linker, and nitrobenzene as solvent. The accurately weighted 0.4 g of 3DOM CLPS was swollen in 20 mL of nitrobenzene overnight at room temperature. Cyanuric chloride (0.7492 g) dissolved by 10 mL of nitrobenzene was then added into above mixture. Then, 2.0 g of anhydrous ferric chloride dissolved in another 10 mL nitrobenzene and was added into the reaction mixture. The reaction mixture was stirred for half an hour at 25 °C. After a short period of heating process, the temperature of the reaction mixture was increased to 100 °C and was stirred with magnetic stirring for 10 h. Subsequently, the resulting solid particles were filtrated from the solution, and then washed with ethanol and 1% of hydrochloric acid and anhydrous ethanol mixture until the effluents were transparent. Finally, the products were extracted by Soxhlet extractor with ethanol for 12 h and freeze-dried with 1,4-dioxane. The products named HP CLPS was obtained accordingly.

2.4. Functionalization of HP CLPS

The chloromethylation reaction of HP CLPS was performed according to the method in Ref. [19], and the products were denoted as HP CLPS-CH_2Cl. A representative amino modification of the HP CLPS is described as follows: the accurately weighted HP CLPS-CH_2Cl (0.5 g) were placed into a 100 mL of two-necked flask with a magnetic bar and vacuumed under ambient temperature for 2 h, then methanol (25 mL) was injected into the flask under vacuum conditions and stirred slowly. Afterwards, the reaction device was

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