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Preparation, characterization, and adsorption evaluation of chitosan-functionalized mesoporous composites

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ABSTRACT

Polymer-modified mesoporous silica materials are of practical interest due to their great potential for adsorption-related applications. In the present work, composites of natural polymer chitosan (CTS) and siliceous mesoporous SBA-15, i.e. SBA-15/CTS(5%), SBA-15/CTS(10%), and SBA-15/CTS(20%), were facilely prepared by prehydrolysis of tetraethyl orthosilicate in the presence of pore-directing agent and subsequent cocondensation with an appropriate amount of CTS-based organosilane. The texture and composition of pure SBA-15 and CTS-functionalized mesoporous products were characterized using various techniques such as TEM, XRD, N_2 adsorption/desorption, ^{29}Si MAS NMR, FT-IR, and TGA measurements. To disclose the adsorption properties of the composites, anionic compound acid red 18 (AR18) was selected as model adsorbate. The effects of pH, ionic strength, contact time, adsorption temperature, and initial concentration of AR18 on adsorption efficiency were investigated. It was found that pure SBA-15 had a negligible adsorption capacity while the CTS-functionalized composites showed large adsorption capacities (up to 232.6 mg g^{-1}) with rapid adsorption kinetics (less than 120 min). It was also observed that the adsorption capacity increased with increase in CTS content of the composite. Results of comparative analysis indicated that SBA-15/CTS(20%) had better adsorption capacity than most of common adsorbents. Experimental kinetic and isotherm data were analyzed by theoretical models including pseudo-first-order and pseudo-second-order kinetics, Weber–Morris diffusion, Freundlich and Langmuir models. Moreover, adsorption thermodynamics has also been evaluated. The study suggests that the CTS-functionalized mesoporous composites are prospective adsorbents for adsorption of anionic compounds, and somewhat exemplifies their adsorbent function for adsorbing some other adsorbates.

1. Introduction

Adsorption is one of the most fundamental processes in a wide range of industrial physicochemical operations such as separation and heterogeneous catalysis [1]. For an adsorption system, adsorbent with high adsorption capacity and rapid adsorption kinetics is very critical. In the last fifteen years, many organic-modified mesoporous SBA-15 materials have been found to possess great potential as highly efficient adsorbents because of their large mesopores, high surface area, and functionalized pore wall [2]. The large pore diameter allows fast mass transfer during adsorption, and the high surface area with numerous surface active sites allows the binding of a large number of adsorbates [2,3].

In general, two methods can be used for organic-modification of SBA-15, namely grafting organic groups onto the pore wall of mesoporous SBA-15 (called as "postsynthesis grafting" method) and direct incorporation of organic moieties into the silica framework (called as "cocondensation" method) [4]. The postsynthesis grafting can avoid damaging the silica frameworks, but it has two major shortcomings: (i) it is difficult to control the loading of the functional groups; (ii) the functional groups easily form local clusters and narrow the pore outlets [5]. The cocondensation is an alternate route for the preparation of such materials, in which the organic component can be incorporated into the silica framework by cocondensation of siloxane and organosilane precursors in the presence of pore-directing agent. Unlike the postsynthesis grafting, the cocondensation allows functionalized SBA-15 to have an uniform organic group distribution on the pore wall, and to avoid the necking of the pore channels [6]. However, the organosilane usually disrupts the cocondensation assembly system, which affects even destroys the ordered meso-structure of SBA-15 [7]. To

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overcome this shortcoming, an improvement over this cocondensation procedure has been recently proposed. That is, siloxane is prehydrolyzed and then cocondensated with organosilane [8]. Nevertheless, the incorporation amount of organic moieties is still limited [9]. Moreover, one organosilane incorporated generally yields only one adsorptive group [10]. Therefore, further investigations are still needed regarding the different possibilities of SBA-15 functionalization.

Incorporating organic polymer within SBA-15 hosts is a good strategy to make organic-modified SBA-15 composites due to the vast functionalization possibilities of organic polymer chemistry. To date, many SBA-15/polymer composites have been prepared mainly by blending or surface polymerization methods [11]. In these systems, however, polymers tended to ultimately clog the mesopores of SBA-15, which greatly lowered their adsorption ability. Madhugiri et al., for the first time, reported that SBA-15/polymer could be prepared via an electrospinning process [12]. In this approach, the organic polymers were incorporated into the silica framework, which could result in unfilled mesopores. But the inorganic matrix and organic species were physically bonded, implying that the composite should be not mechanically strong. In spite of this, it would be interesting to move ahead with this concept by introducing chemical cross-linkages between the reactive groups of organic polymer and the siliceous skeleton. If so, a more effective bonding between the organic and inorganic phases will be achieved, improving the mechanical and chemical stabilities.

Chitosan (CTS), typically obtained by deacetylation of chitin, is one of the most abundant natural polymers, being second only to cellulose on the earth [13]. Amine groups of CTS, especially, are attractive for several adsorption-related applications in base catalysis, CO_2 capture, removal of dyes or heavy metal ions or as binding sites for bioactive molecules and controlled drug release [14]. Because of its solubility in acidic conditions and unsatisfied mechanical property, it is generally required to immobilize CTS onto solid particle surface or enable CTS to react with inorganic precursor to form hybrid composite [14,15]. Recently, Silva et al. demonstrated that the CTS could covalently bond with the organosilane 3-isocyanatopropyltriethoxysilane (ICPTES), and the resultant CTS–ICPTES could further form CTS–silica hybrids by hydrolysis and subsequent condensation processes [16]. Silva's finding is of interest, and more importantly, it might provide an idea to fabricate a new SBA-15/polymer, i.e. CTS-modified SBA-15 (SBA-15/CTS), via cocondensation route using siloxane and CTS–ICPTES as precursors. If this objective is achieved, the resultant SBA-15/CTS would be endowed with some attractive properties such as mechanical and chemical stabilities, unique surface chemistry, and unobstructed mesopore channels.

Thus, the aim of this work is to fabricate the expected SBA-15/CTS composites, and explain their adsorption behavior to see if desired adsorption properties such as high adsorption capacity and rapid adsorption kinetics, have been satisfied. As shown in Fig. 1, the SBA-15/CTS composites were prepared by prehydrolysis of tetraethyl orthosilicate (TEOS) with the addition of pore-directing agent (triblock copolymer P123) and subsequent cocondensation with an appropriate amount of CTS–ICPTES, where CTS–ICPTES was formed via the reaction between CTS and ICPTES according to the method of Silva. This is the first study, to our knowledge, to suggest it may be possible to prepare mesoporous silica/polymer composite by cocondensation method. One of the most fascinating features of the composites is the complexion characteristic of CTS and SBA-15, encouraging us to explore the utility of these composites in adsorption. To evaluate the adsorption properties of the composites, acid red 18 (AR18) was chosen as the model adsorbate because of its well-known adsorption characteristics [17–22], and batch adsorption experiments as well as the theoretical investigation including adsorption kinetics, equilibrium, and adsorption thermodynamics, were carried out. The adsorption study of AR18 on SBA-15/CTS composites should be useful as the basis for a further extension of such composites to effectively perform their adsorbent function for adsorbing some other adsorbates.

2. Experimental section

2.1. Chemicals and reagents

Chitosan (CTS, $M_w \cong 1000$, deacetylation degree >90%) was purchased from Yuhuan Shell Biological Agents Factories (Zhejiang, China). 3-Isocyanatopropyltriethoxysilane (ICPTES) was obtained from Wuhan University Chemical Factory, (Wuhan, China). Pore-directing agent Pluronic P123 triblock copolymer ($EO_{20}PO_{70}EO_{20}$, $M_{av} = 5800$) was purchased from Sigma–Aldrich. Tetraethyl orthosilicate (TEOS), acid red 18 (AR18), and dimethyl formamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). As shown in Fig. 1, AR18 has a dimensions of 1.42 nm (length) × 0.765 nm (width), and the area of AR18

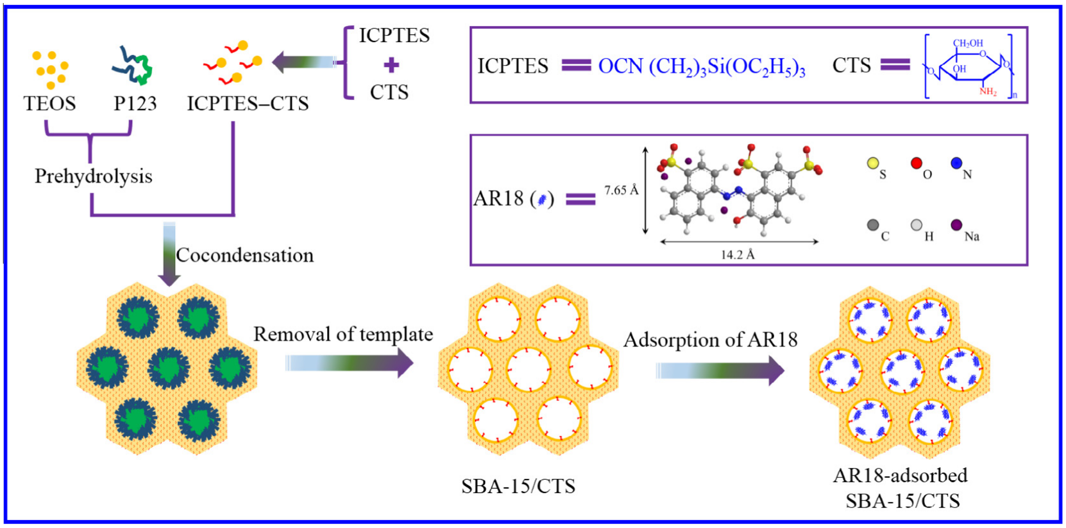

Fig. 1. Preparation scheme of SBA-15/CTS and its application for adsorbing AR18.