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Effect of framework structure, pore size and surface modification on the adsorption performance of methylene blue and Cu^{2+} in mesoporous silica

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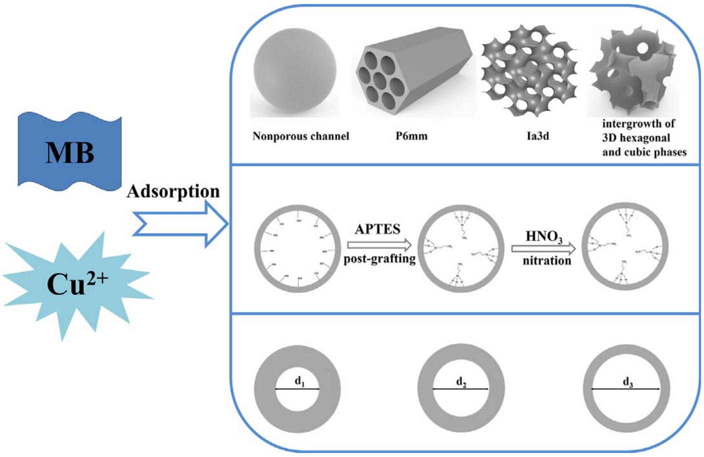
GRAPHICAL ABSTRACT



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ABSTRACT

A series of silica with diverse channel structures or pore diameters were synthesized *via* the hydrothermal method. Corresponding amine/nitro-modified materials were obtained by grafting, nitrating reaction, respectively. Textural and chemical properties were analyzed by Scanning electron micrograph (SEM), Small angle powder X-ray diffraction (SAXRD), Nitrogen adsorption-desorption measurement, Fourier transform infrared spectroscopy (FTIR), Thermogravimetric (TG) analysis and Zeta potential. Batch adsorption results revealed that distinct uptake capacities of Cu^{2+} and methylene blue occurred at the solid-liquid interface of prepared adsorbents. Especially, pure SBA-12-OH displayed the highest removal behavior toward methylene blue, mainly owing to its larger pore diameter. Amine-grafted SBA-12 (SBA-12-NH_2) presented higher affinity to Cu^{2+} than others, originating from the complexation function of amine groups and its superior framework structure. Moreover, their adsorption isotherms and kinetics were further investigated to explore the application in industrial operation system.

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1. Introduction

In last few decades, industrial development, energy consumption as well as tremendous increase of human population have produced a large number of environment pollutants such as carcinogenic heavy metal ions, toxic organic compounds [1–3]. These contaminants will cause a persistently harmful impact on aquatic ecosystems and human health because of their hard biodegradation and high bioaccumulation in the food chain [4–6]. For instance, too many zinc, copper ions or methylene blue (MB) existing in body might bring about vomiting and nausea problems [7,8]. The excessive ingestion of nickel, chromium or Rhodamine B perhaps results in severe lung carcinoma [6,9]. Methyl mercury and cadmium ions in aqueous phase respectively cause the awful Minamata, Itaiitai disease [10]. Thus, decontamination of wastewater prior to its discharge is crucially essential to ecological environment. Up to now, many physical, chemical and biological methods have been adopted to reduce the pollutants in sewerage, containing adsorption, ultrafiltration, ion exchange, electrochemical and microorganism treatment [11,12]. Herein, the adsorption technique is extensively applied in sewage plants, because of its effective removal, flexibility of design, simplicity of operation and low-cost [13,14]. Moreover, it does not bring other poisonous substance into the effluent.

Therefore, as the core of adsorption installation, preparing adsorbents with preferable properties and inexpensive investment is extremely indispensable to perform waste-water purification process excellently. Among numerous novel adsorbents, mesoporous silica furnishes more opportunities for easy surface modification, massive adsorption sites loaded, favorable dispersity and biocompatibility in water, according to the advantages including versatile porous phases, tunable pores size, high surface area as well as rich silanol groups [15–18]. Therefore, it has obtained much attention as an adsorbent. Tesser et al. [19] constituted an MB adsorption system over raw silica pellets from batch to continuous operation, confirming that silica could widely adsorb MB. Zhao et al. [20] synthesized ordered mesoporous silica with various morphologies by a nonpolar solvent-assisted StÖber method and reported excellent adsorption capacities for cationic Rhodamine B molecules. Kao et al. [21] fabricated —COOH groups modified SBA-16 *via* one-pot synthesis route and demonstrated effective removal of methylene blue and phenosafranine. Ge et al. [22] prepared the fibrous amidoxime-functionalized mesoporous SiO_2 microspheres, exhibiting a selective adsorption for Pb^{2+} in a solution of mixed metallic ions.

Meanwhile, lots of works have been done to ascertain the influent factors in present adsorbents. For example, Arencibia [23] and Machida et al. [10] examined the role of surface functionality on silica to remove heavy metal ions. Anbia et al. [24] respectively explored the adsorption capacity of different alkyl-amino functionlized SBA-3 toward acid dyes. However, to the best of our knowledge, no systematic study concerning the influence of channel structure, pore size and surface property in mesoporous silica on adsorption performance has been published yet. In this paper, several mesoporous silica with typically different open-frameworks, pore sizes were synthesized by adopting diverse structure-directing agents or preparation processes, and modified with amino/nitro groups, respectively. All samples were used to adsorb heavy metal ion (Cu^{2+}) and organic dye (MB) to investigate the function of structure and modification in detail. This work would provide an important foundation for the fabrication of efficient adsorbents and facilitating their industry applications in purification operation.

2. Experimental

2.1. Preparation of silica with diverse channel structure

2.1.1. Synthesis of nonporous silica (Non-SiO_2—OH)

6.7 mL of concentrated ammonia and 5.1 mL deionized water were mixed into ethanol solution (70 mL) under a continuous stirring. 3.76 g of TEOS was added. After 40 min, the temperature of the system was heated to 55 °C. 0.64 mL of deionized water and 3.76 g of TEOS were added dropwisely. In addition, the last step was repeated after 40 min. Then, the product was collected by centrifugation, washed with ethanol and distilled water, respectively, dried at 60 °C for 12 h.

2.1.2. Synthesis of mesoporous SBA-15-OH

2 g of Pluronic P123 was dissolved in a solution containing deionized water (14.9 g) and 2 M HCl (60 g) at 35 °C. 4.3 g of TEOS was added dropwisely and constantly agitated for 24 h. Subsequently, the mixture was transferred into a stainless autoclave and aged at 100 °C for 24 h [25]. The white powder was filtrated, followed by washing with deionized water and ethanol respectively, dried at 60 °C for 12 h. Finally, the template was removed by calcination at 550 °C for 6 h in air.

2.1.3. Synthesis of mesoporous KIT-6-OH

2 g of Pluronic P123 was added into 68.2 g of distilled water including 3.8 g of 36.5% HCl to form a homogeneous solution at 35 °C. 2 g of N-butanol was added under stirring. After 1 h, 4.3 g of TEOS was added dropwisely. Then, the mixture was stirred for 24 h, and aged at 100 °C for 24 h in an autoclave [26]. The collection, cleaning, desiccation and calcinations procedures were same as those described at 2.1.2.

2.1.4. Synthesis of mesoporous SBA-12-OH

Brij76 (1.5 g) was dissolved in 28.7 g of distilled water to a clear solution at 35 °C and then 4.4 g of sodium silicate was added. After 1 h, 8.85 g of 36.5% HCl was quickly added into the solution with vigorous stirring. The mixture was agitated for a day and hydrothermal treatment at 140 °C for 24 h [27]. Collection, clean and calcinations procedures were same above. SBA-12-T (SBA-12-80, SBA-12-100, SBA-120) were synthesized with same procedures just at different hydrothermal temperature, corresponding 80 °C, 100 °C, 120 °C, respectively.

2.2. Surface modification of silica

2.2.1. Preparation of amine-functionalized silica

1 g of prepared silica above was dispersed in 100 mL toluene and 4 mL of 3-aminopropyltriethoxysilane (APTES) were added. Then the mixture was refluxed for 24 h at 80 °C [28]. Then, materials were separated by vacuum filtered and cleaned by acetone, dichloromethane and ethanol, dried at 60 °C for 12 h. In this work, the corresponding amine-grafted silica material was respectively recorded as Non-SiO_2—NH_2, SBA-15-NH_2, SBA-12-NH_2, KIT-6-NH_2, SBA-12-80-NH_2, SBA-12-100-NH_2, SBA-12-120-NH_2.

2.2.2. Preparation of nitro-functionalized silica

0.5 g of prepared amine-functionalized silica was dispersed in 20 mL concentrated HNO_3 solution with stirring for 4 h. Then solid was filtered and cleaned by distilled water to neutral, dried at 60 °C for 12 h. Finally, the corresponding nitro-grafted silica material was labeled as Non-SiO_2—NO_2, SBA-15-NO_2, SBA-12-NO_2, KIT-6-NO_2, respectively.

2.3. Batch adsorption experiments

Batch adsorption experiments were carried out by vibrating the solution containing 25 mg adsorbent and 50 mL predetermined concentration of MB, Cu^{2+} in a shaker. Mixtures were shaking for 24 h at 30 °C to achieve equilibrium, and then filtered with a syringe filter of 0.22 μm. Residual concentration of MB and Cu^{2+} was analyzed through UV–vis spectrophotometer, Atomic adsorption spectroscopy (AAS), respectively. Equilibrium adsorption capacity of adsorbent, q_e ($mg\ g^{-1}$) was computed by following equation:

$$q_e = \frac{C_o - C_e}{m} \times \frac{V}{1000} \tag{1}$$