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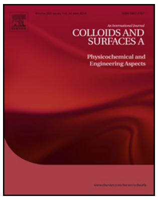

Preparation of amine-modified silica foams and their adsorption behaviors toward TNT red water

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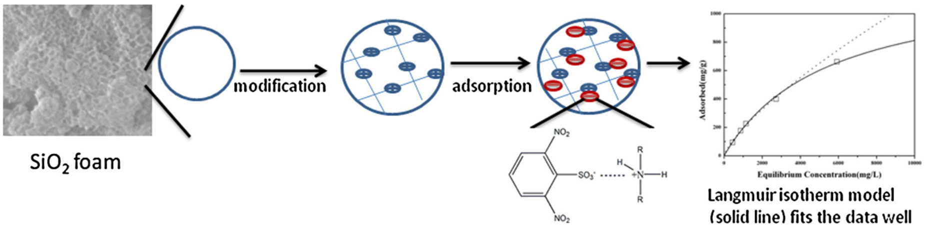
HIGHLIGHTS

- Amine containing SiO_2 foams are prepared for specific organic treatment.
- Secondary amine modified foams show excellent COD removal capacity.
- Adsorption behavior fit the pseudo-second-order dynamic and Langmuir adsorption models well.
- Adsorption bases on the attraction between amine groups on foam and the negative organic pollutants.

GRAPHICAL ABSTRACT



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ABSTRACT

Secondary and primary amines containing silica foams ($F–SiO_2$) were prepared by using silane coupling agents, (3-aminopropyl) triethoxysilane (KH-550) and bis(3-triethoxysilicyl propyl)-amine (KH-270), as modifiers. Not only Brunauer–Emmett–Tell (BET) surface and pore size of $F–SiO_2$ are greatly reduced after modification, but also increased chemical oxygen demand (COD) removal efficiency to trinitrotoluene (TNT) red water is obtained. Among the series of $F–SiO_2$, the secondary amine modified silica foams possess higher COD removal capacity. Controlled experiments indicate the adsorption mainly derives from the attraction of amine groups toward the negative organic pollutants in TNT red water rather than the effect of the large BET surface and hydroxyl groups on the surface of $F–SiO_2$. The adsorption model studies show the pseudo-second-order dynamic adsorption model and Langmuir isotherm model well fit the experimental data. The prepared amine-modified $F–SiO_2$ is an efficient adsorbents of organic pollutants in TNT red water.

1. Introduction

Mesoporous silicas are considered as promising materials for bimolecular loading [1,2], supports of catalyst [3], absorbents of wastewater [4] and greenhouse gases [5,6] due to their attractive properties, such as large surface area, tunable pore structure, and high thermal stability. In which mesocellular foams [7,8], mesoporous silica with textural (interparticular) mesoporosity [9], and hierarchical monoliths [10] show more efficient properties than related bulk mesoporous silica materials.

In order to tailor the properties of mesoporous silica, mesoporous silicas have been functionalized with $-NH_2$ [4,11], -COOH [12], $-SO_3H$ [13] and so on. Therefore, a series of solid-supported sorbents, based on bulk mesoporous silicas including MCM-41,

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MCM-48, SBA-12, SBA-15, SBA-16, and KIT-6 have been prepared via wet impregnation and systematically evaluated [11,14–17].

Among the main applications of mesoporous silicas, removal of heavy metals for environmental cleanup is the essential one [18,19]. The earliest report on this topic is the removal of mercury in wastewater using propylthiol-functionalized mesoporous silicas [18]. Since then, there have been a large number of works dealing with metallic species, primarily cations, in wastewater [4,11]. Heavy metals are more efficiently adsorbed on mesostructured silicas modified with amino groups [20–23]. For example, amine containing mesoporous silica, SBA-15, has been prepared to develop efficient adsorbents of Cu^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+} from wastewater [24]. In addition, SBA-15 functionalized with 3-aminopropyltrimethoxy-silane is studied as potential absorbent for Cd^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Al^{3+} and Cr^{3+}. The adsorption capacity and selectivity of the materials are investigated in mono-mental and multi-metal solutions. The amine-modified SBA-15 adsorbent exhibits an excellent selectivity against sodium, potassium, and calcium [25]. But until now, reports on the organic pollutant treatment by mesoporous silica are few, only works on the organic pollutant removal by thiol and sulfonic acid-functionalized silica foams are reported [13]. Study on the organic pollutant removal by amine modified mesoporous silica based on the composition of the wastewater has not been performed.

EP Geiannes group [26] has synthesized a more cost-effective silica foam with ultra large mesopores. The CO_2 adsorption behavior of the silica foam after incorporation of polyetherimide has been studied. In the present work the silica foam was modified with amine-containing silanes and its specific removal behaviors to trinitrotoluene (TNT) red water, which was produced during the purification of crude TNT by sodium sulfate and contained large amount of negative organic pollutants, was studied. Silica foam modified by secondary amine showed excellent chemical oxygen demand (COD) removal to the TNT red water. Under optimum conditions, its COD removal achieved 165.9 mg/g toward the TNT red water with initial COD of 1800 mg/L due to the specific interaction of amine groups in the foam with the negative groups of the pollutants. The adsorption dynamic and isotherm models were used to fit the data. The modified foams are excellent adsorbents of negative charge containing organic pollutants.

2. Experimental

2.1. Materials

SiO_2 foam was afforded by the group of EP Giannelis and its synthesis had been reported elsewhere [26]. Tetraethyl orthosilicate (TEOS) was from Beijing Chemical Co. (Beijing China). (3-Aminopropyl) triethoxysilane (99%, KH-550) and bis(3-triethoxysilicyl propyl)-amine (99%, KH-270) were purchased from Aladdin Industrial Corporation. TNT red water [27], which was reddish brown and opaque, with a high concentration of dinitrotoluene sulfonates (2,4-dinitrotoluene-3-sulfonate and 2,4-dinitrotoluene-5-sulfonate) and high COD, was supplied by Dongfang Chemical Corporation (Hubei Province, China). All the other reagents used in this study were analytical grade, and distilled water was used to prepare the solutions.

2.2. Modification of SiO_2 foam

The grafting of amine groups onto SiO_2 foam was carried out as follows. 0.25 g of silica foam was introduced in a three neck flask with 30 ml of ethanol and 10 ml of water and stirred at room temperature for 1 h for complete dispersion, then oxalic acid was dropped in to adjusted the pH of the dispersion to 4, followed by dropwise addition of 0.5 ml of silane coupling agents (KH-550, KH-270) in half an hour. The dispersion was further stirred at room temperature and then 60 °C for 4 h, respectively. The solid was filtered and washed with distilled water and ethanol for two times respectively and dried in vacuum at 80 °C. In the target samples the weight ratio of initial silica foam and that from silane coupling agent component is approximate to 1.

The controlled sample, bulk SiO_2 particles were prepared by sol–gel process. 15 ml of ethanol solution containing 7.5 ml of TEOS was added dropwise to 100 ml of ethanol/water mixture (2/1) (containing 0.5 mol/l ammonium hydroxide) at a rate of 0.5 ml/min as the solution was heated to 60 °C under stirring, where the reaction was continued for 2 h. SiO_2 particles were obtained after subsequent steps of centrifugation, washing with water, ethanol, and drying in vacuum at 70 °C

For clear understanding, bulk SiO_2 particles, SiO_2 foam, KH-550 and KH-270 modified SiO_2 foam were assigned as SiO_2, F-SiO_2, NH_2-F-SiO_2 and NH-F-SiO_2, respectively.

2.3. Adsorption experiments

The adsorption experiments were carried out in 100 ml of conical flasks. Certain amounts of the adsorbents were separately introduced into a series of conical flasks with 25 ml of TNT red water. Then, the flasks were shaken in a SHA-BA water bath at a speed of 150 rpm for a certain time (5, 10, 20, 40, 60, 90, and 120 min) at room temperature. Then, the samples were filtered and dried in vacuum at 70 °C for 8 h. For dynamic study, the amount of NH-F–SiO_2 used was 0.125 g toward 25 ml of TNT wastewater. For adsorption isotherm study, 0.125 g of NH-F-SiO_2 was added into 25 ml of TNT wastewater with initial COD of 10,800, 5400, 2700, 1800 and 1080 mg/L, respectively, for 1 h.

2.4. Characterization

The Fourier transform infrared (FT-IR) spectrum in the 4000–400 cm^{-1} region was performed using a Perkin Elmer Spectrum 100 FT-IR spectrometer. KBr was used as a background material and disks of sample/KBr mixtures were prepared to obtain the FT-IR spectra. Transmission electron microscopy (TEM) images were obtained by a JEM-3010 of the Japanese electronics company. Samples were prepared by dispersing the samples in ethanol under sonication. A few drops of the dispersions were loaded onto a carbon coated copper microgrid and dried in air. Field emission scanning electron microscopy (FE-SEM) images were acquired from a LEO-1530 field emission scanning electron microscope operated at 5 kV. N_2 adsorption–desorption isotherms were obtained on a micromeritic instrument (Autosorb-IQ-2MP, USA) at liquid nitrogen temperature. The silica foam and NH-F–SiO_2 were degassed prior to analysis under high vacuum at 60 °C for at least 4 h. Their specific surface areas were determined using the multipoint Brunauer–Emmett–Teller (BET) method. The pore size distributions derived from the adsorption and desorption branches of the isotherms and calculated based on the Barrett-Joyner-Halenda (BJH) model.

The COD of the filtrates were analyzed by the COD rapid detector (5B-6, Lian-Hua Tech. Co., China) with a precision of ±5% to determine the adsorption efficiency of adsorbents. The adsorbed amount, q_e (mg/g), by per unit mass of NH-F-SiO_2 was calculated based on Eqs. (1):

$$q_e = \frac{(COD_O - COD_e)^V}{W} \quad (1)$$

where COD_o and COD_e(mg/L) are the COD values of the initial TNT red water and treated red water after reaching equilibrium, respectively. V (L) is the volume of the TNT red water and W(g) is