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Enhanced nitrobenzene adsorption in aqueous solution by surface silylated MCM-41

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ABSTRACT

To improve the adsorption of nitrobenzene from aqueous solution, surface silylation of MCM-41 (hexagonal mesoporous silica) with trimethylchlorosilane was conducted. The silylated MCM-41 (CH_3-MCM-41) was characterized by X-ray diffraction (XRD), transmission electron micrograph (TEM), N_2 adsorption-desorption, Fourier transform infrared spectroscopy (FTIR), and thermogravimetric/differential thermalanalysis (TG/DTA) techniques. Adsorption of nitrobenzene onto CH_3-MCM-41 was investigated with respect to contact time, initial nitrobenzene concentration, temperature, pH and ionic strength. The results indicated that surface modification of MCM-41 significantly enhanced its adsorption capacity for nitrobenzene. Adsorption isotherms were well described by Langmuir and Freudlich models. The maximum adsorption capacity of CH_3-MCM-41 was 375.5 μmol/g, one order of magnitude higher than that of MCM-41 (25.8 μmol/g). Negative thermodynamic constant values ($\Delta G_0 < 0$, $\Delta H_0 < 0$ and $\Delta S_0 < 0$) suggested that the adsorption reaction of nitrobenzene onto CH_3-MCM-41 was thermodynamically favorable, spontaneous and exothermic under the examined conditions. Moreover, adsorption of nitrobenzene by CH_3-MCM-41 was independent of pH within a range of 3.0–9.5. Increasing ionic strength can apparently enhance nitrobenzene adsorption by CH_3-MCM-41. Compared to other adsorbents, CH_3-MCM-41 showed a relatively higher adsorption capacity and shorter equilibrium time. Therefore, surface sylilated MCM-41 has a potential and promising application in the removal of nitrobenzene from water.

1. Introduction

As one of the typical nitroaromatic compounds (NACs), nitrobenzene is widely used during chemical processes producing dyes, explosives, pesticides and synthetic rubber [1]. Due to its mutagenicity, recalcitrance, and tendency to accumulate in the environment, many countries have listed it as a priority pollutant. The U.S. Environmental Protection Agency (USEPA) recommends that human health consumption of water and organism for nitrobenzene should not be greater than 17 μg/L [2]. Therefore, it is essential to remove nitrobenzene before discharge.

In our previous study, MCM-41 has shown a great promise as adsorbent for nitrobenzene removal from aqueous solution [3]. MCM-41, one type of ordered mesoporous silica materials, is widely used in shape-selective catalysis, selective adsorption and separation processes, chemical sensors, as well as nanotechnology, due to its high surface area, narrow pore-size distribution and impressive ordered mesoporosity [4]. It was reported that MCM-41 displayed a quite short equilibrium time (even less than 1 min) to reach its maximum capacity for nitrobenzene adsorption [3], which is crucial for its practical application. Similarly, quick equilibrium was also observed for other organic pollutants adsorption such as pharmaceuticals [5], microcystins [6] using ordered mesoporous silica adsorbents. However, MCM-41 has a relatively low adsorption capacity for the removal of nitrobenzene. The possible reason is that the structure of MCM-41 could collapse by mechanical compression through the hydrolysis of siloxane bonds in the presence of adsorbed water, which may decrease the amount of active adsorption sites [7]. Moreover, lots of silanol groups on the surface of MCM-41 make it highly hydrophilic, leading to a low adsorption capacity for hydrophobic pollutants. Thus, it is necessary to modify MCM-41 to improve its hydrothermal stability and adsorption capacity for application.

In general, modification can be conducted by grafting the surface of MCM-41 by means of silanols groups reaction with a

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silylation reagent, such as 3-aminopropyltrimethoxysilane [8,9], hexamethyldisilazane [10] and trimethylchlorosilane [11,12]. Among the silylation reagents used, it has been reported that trimethylchlorosilane is effective for surface silylation to improve the stability of porous silica materials to moisture and compression [7]. The silylated MCM-41 has been verified to have a greater adsorption capacity for organic pollutants removal from aqueous solution, such as ultraviolet filters [11] and benzene [12]. It is believed that decreasing the amount of surface hydroxyl groups on MCM-41 can successfully reduce the amount of adsorbed water, and finally can improve the stability and hydrophobicity of MCM-41 [13,14]. Therefore, it could be reasonably assumed that surface silylation of MCM-41 would substantially enhance the efficacy of nitrobenzene removal from aqueous media.

The main purpose of the present study was to determine the enhancement of nitrobenzene adsorption by surface silylated MCM-41 using trimethylchlorosilane (TMCS). The achieved silylated MCM-41 was characterized using X-ray diffraction (XRD), transmission electron micrograph (TEM), N_2 adsorption-desorption, Fourier transform infrared spectroscopy (FTIR), and thermogravimetric/differential thermalanalysis (TG/DTA) techniques. Furthermore, the influences of several operating parameters such as contact time, initial nitrobenzene concentration, temperature, pH and ionic strength on the adsorption capacity of silylated MCM-41 were investigated.

2. Materials and methods

2.1. Materials

Nitrobenzene (98%; without further purification) was purchased from Tianjin Third Chemical Factory. Cetyltrimethylammonium bromide (CTAB) was obtained from Xilong Chemical. Tetramethyl orthosilicate (TMOS) was purchased from Tianjin Kermel Chemical. TMCS was purchased from Shanghai Oule Chemical. The initial pH of background solution was adjusted by introducing appropriate amounts of acid (HCl) or base (NaOH) solutions. Deionized distilled water was purified by Millipore Milli-Q system. Unless otherwise stated, all reagents used in this study were analytical grade (>99%).

2.2. Preparation of modified MCM-41

The MCM-41 was synthesized in classical alkaline medium using conventional literature recipes [15]. Typically, CTAB was dissolved in NaOH solution, followed by adding TMOS solution dropwise. The molar gel composition was as the following: CTAB: TMOS: NaOH: H_2O = 0.12: 1: 0.24: 66.7. The white precipitate was homogenized by vigorous stirring for 2 h at ambient temperature and then heated at 100 °C in a Teflon-coated stainless-steel autoclave for 48 h under autogenous pressure. Subsequently, the white precipitate was filtered off, washed with distilled water, and dried at 80 °C overnight followed by calcination in flowing air at 540 °C for 4 h to remove the surfactant molecules.

Before silylation, the calcined MCM-41 powder was heated at 120 °C for 2 h to remove the adsorbed moisture in an air oven. Then, modification of calcined MCM-41 with TMCS was conducted as described previously [7]. In brief, 12 mL of TMCS was mixed with 1 g of MCM-41 powder in 100 mL of anhydrous toluene (for 24 h under reflux conditions and a nitrogen atmosphere). The resulting modified MCM-41 was filtered off and sequentially washed with toluene and acetone each for three times. Finally, the product was heated for 12 h at 120 °C under vacuum condition and was designated as CH_3-MCM-41.

2.3. Characterization of MCM-41 and CH_3-MCM-41

Before characterization, MCM-41 and CH_3-MCM-41 were heated at 120 °C for 2 h to remove the adsorbed moisture and were kept sealed under dry air in desiccator. Transmission electron micrograph (TEM) of the samples was taken on a Hitachi H-8100 TEM, operated at 200 kV. Powder X-ray diffraction (XRD) patterns were recorded on a Philips PW1710 diffractometer using Cu $K\alpha$ radiation. Nitrogen adsorption isotherms were measured at 77 K on a Micromeritics ASAP 2020 sorptometer, with the samples outgassed for 16 h at 110 °C and 10^{-6} Torr prior to measurement. Fourier transform infrared spectroscopy (FTIR) spectra were performed on the Spectrum One spectrometer from 400 to 4000 cm^{-1} by dried KBr pellet. Thermal analysis of the samples was performed on a Netzsch STA 449 C Simultaneous DTA-TG apparatus from 30 to 800 °C with a heating rate of 10 °C/min. The total carbon content was determined by a PerkinElmer Series II CHNS/O 2400 elemental analyzer.

2.4. Adsorption experiments

The effect of contact time on nitrobenzene adsorption onto MCM-41 and CH_3-MCM-41 was studied at pH 5.8. The adsorption experiments were carried out by mixing 0.5 g of MCM-41 (0.25 g for CH_3-MCM-41) with a 100 mL aqueous solution containing 16 μmol/L nitrobenzene in a 500 mL stirred flask at temperature of 25 °C. Samples were taken out and filtrated by a glass fiber with 0.7 μm pore size at appropriate time intervals. Then the residual concentration of nitrobenzene was determined.

The adsorption isotherm experiments of nitrobenzene were performed using a batch experiment. A certain amount of adsorbent (0.05 g for MCM-41 and 0.01 g for CH_3-MCM-41) was placed in a 50-mL flask, into which 10 mL of nitrobenzene solution with varying initial concentrations were added. The experiments were performed in a temperature-controlled water bath shaker for 4 h at a mixing speed of 180 rpm. When the equilibrium was thought to be established, the solutions were filtered and analyzed for the remaining concentration of nitrobenzene. Solid-phase nitrobenzene concentrations at equilibrium, q_e (μmol/g), were calculated according to Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{1}$$

where C_0 (μmol/L) and C_e (μmol/L) are the initial and equilibrium aqueous-phase concentrations of nitrobenzene, respectively; V (L) is the volume of the aqueous solution; M (g) is the mass of dry adsorbent used in the experiments.

The effect of solution pH on nitrobenzene adsorption was investigated according to the following procedure. A mass of 0.01 g of CH_3-MCM-41 (0.05 g for MCM-41) was added to a series of 25 mL flasks containing 10 mL of 10 μmol/L nitrobenzene solution. The solution pH was adjusted to a pH range from 3.0 to 9.5 using 0.1 mol/L HCl or 0.1 mol/L NaOH solutions. NaCl (0.1 mol/L) was used to keep constant ionic strength. The flasks were then sealed and placed in the shaker at 24.5 ± 0.5 °C for 4 h. To evaluate the effect of ionic strength on nitrobenzene adsorption, NaCl was used at various concentrations, ranging from 0.01 to 1 mol/L. Initial nitrobenzene concentration of 10 μmol/L and 1 g of CH_3-MCM-41 (5 g for MCM-41) per liter of solution was examined. The initial pH of the solution was adjusted to 5.8. The suspensions were then sealed and placed in the shaker at 24.5 ± 0.5 °C for 4 h. To check reproducibility, all nitrobenzene adsorption tests were carried out in duplicate. The coefficient of variations (CV) of the data was in most cases below 5%.