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Application of nanoporous silicas as adsorbents for chlorinated aromatic compounds. A comparative study

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ABSTRACT

The removal of two selected environmental pollutants such as 2,4-dichlorophenoxyacetic acid (2,4-D) and Triclosan (TC) was examined by adsorption experiments on the modified SBA-15 and MCF mesoporous silicas. Mesoporous adsorbents were modified by a grafting process with (3-aminopropyl)triethoxysilane (APTES) and 1-[3-(trimethoxysilyl)propyl]urea (TMSPU). Mesoporous materials were synthesized and characterized by N_2 adsorption–desorption experiment, transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), elemental analysis and adsorption studies. The results show that both APTES-functionalized SBA-15 and MCF nanoporous carriers are potentially good adsorbents for the removal of 2,4-D in a wide range of concentrations from 0.1 to 4 mg/cm^3. Maximum adsorption capacity of as-modified adsorbents for 2,4-D estimated from the Langmuir model was ~280 mg/g. The ionic interaction between the adsorbent and 2,4-D seems to play a key role in the adsorption process of the pollutant on APTES-modified siliceous matrices. The efficiency of TC sorption onto all prepared mesoporous adsorbents was significantly lower as compared to the entrapment of 2,4-D. Experimental data were best fitted by the Langmuir isotherm model. The results of this study suggest that mesoporous silica-based materials are promising adsorbents for the removal of selected organic pollutants.

1. Introduction

Mesoporous materials are defined as porous structures with a pore size of 2–50 nm [1]. Among these materials, mesoporous silicas such as MCM-41, SBA-15, SBA-16 and MCF have attracted considerable research attention due to their large specific surface area, high pore volume, homogeneous pore distribution and chemical inertness [2]. The presence of silanol groups allows surface modification of these nanoporous matrices [3]. Mesoporous materials have potential applications in many fields of science including their use as catalysts [4], gas sensors [5], battery components [6], capacitors [7], drug carriers [8], vehicles in molecular biology [9], tissue scaffolds [10], cell markers [11], biomolecule immobilization [12], and in separation [13] and purification [14] processes.

Recently, mesoporous silicas have been demonstrated to serve as a good material for the applications in the field of environmental science. In particular, mesoporous materials are emerging as an ideal agent for adsorption of organic and inorganic pollutants [15].

Mesoporous materials have been developed and described in the literature as suitable adsorbents of many hazardous substances such as heavy metal ions [16], insecticides [17], eutrophic agents [18], organic dyes [19] and many other organic compounds [20]. Application of these mesoporous silicas for the removal of environmental pollutants is of significant importance as it offers a simple, rapid, convenient and inexpensive method to get rid of many harmful chemical compounds. Among different toxic environmental pollutants, the precise removal of chlorinated aromatic compounds such as 2,4-dichlorophenoxyacetic acid (2,4-D) and 5-chloro-2-(2,4-dichlorophenoxy)phenol (Triclosan, TC) seems to be particularly significant due to their wide application in agriculture, cosmetics and the chemical industry. 2,4-Dichlorophenoxyacetic acid is widely used in agriculture to control weeds and as a plant growth promoter [21]. Although the herbicide is moderately toxic, the high-quantity usage of 2,4-D creates a lot of pollution problems due to its translocation to residential areas [22]. Triclosan is commonly used as an antimicrobial agent over the past half century [23]. This biocide is widely used in a large number of daily use products such as soaps, shampoos, deodorants, skin creams and toothpastes. Its increased use for such a long time makes this chlorinated aromatic compound frequently detected in the aquatic

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environment. In certain conditions Triclosan derivatives could serve as a source of toxic polychlorinated dioxins in the environment [24]. The toxicity of chlorinated aromatic compounds to biological systems makes the design of new adsorbents for removal of these toxic analytes significantly important in environmental science.

In the present study, Santa Barbara amorphous type material (SBA-15) and mesocellular siliceous foam (MCF) mesoporous materials have been chosen as the adsorbents for environmental pollutants. The surface of siliceous materials has been modified with (3-aminopropyl) triethoxysilane (APTES) and 1-[3-(trimethoxysilyl)propyl]urea (TMSPU) by a grafting method. The aim of the investigation was to compare the adsorption properties of pure and modified silicas for chlorinated aromatic compounds. Therefore, we evaluated whether the modification of the aforementioned mesoporous materials might improve their adsorption of 2,4-dichlorophenoxyacetic acid and Triclosan. The results of these preliminary studies may provide a foundation for developing simple and convenient methods for environmental pollutant adsorption using nanoscale mesoporous silicas.

2. Experimental details

2.1. Chemicals and materials

Tetraethyl orthosilicate (≥99.0%), polyethylene-glycol-*block*-poly-propylene-glycol-*block*-polyethylene-glycol (Pluronic P123, Mw = 5800), hydrochloric acid (purum p.a. ≥32.0%), 1,3,5-trimethylbenzene (98%), ammonium fluoride (puriss. p.a. ≥98%), (3-aminopropyl) triethoxysilane (99%), 1-[3-(trimethoxysilyl)propyl]urea (97%), 2-propanol (puriss. p.a. ≥99.8%), 2,4-dichlorophenoxyacetic acid (≥98%) and Triclosan (≥97%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Dichloromethane (puriss. p.a. ≥99.9%) was supplied from Fluka. Commercial anhydrous toluene (99.8%, Sigma-Aldrich) was finally redried on A4 molecular sieves.

2.2. Synthesis of SBA-15 and MCF materials

SBA-15 material was prepared according to the procedure described by Zhao et al. [25] with modifications. In a typical synthesis, 48.0 g of poly(ethylene glycol) and poly(propylene glycol) block copolymer (Pluronic P123) was dissolved in 1800 cm^3 of aqueous HCl (1.6 M) at 35 °C. After about 3 h, 102.0 g of tetraethylorthosilicate (TEOS) was added. The mixture was magnetically stirred at 35 °C for 20 h followed by an aging step at 110 °C for 24 h. The suspension was filtered and washed with distilled water. The precipitate was dried in air and calcined at 500 °C for 6 h with a heating rate of 1 °C/min.

MCF silica was synthesized as reported by Schmidt-Winkel et al. [26] with modifications. In a typical procedure, 36.0 g of Pluronic P123 was dissolved in 1350 cm^3 of 1.6 M HCl at room temperature. After surfactant dissolution, 0.414 g of ammonium fluoride and 36.0 g of 1,3,5-trimethylbenzene were added. After 1 h of stirring at 35 °C, 79.2 g of TEOS was added and the mixture was magnetically stirred at 35 °C for 20 h. The suspension was aged at 100 °C for 24 h. The precipitated solid was isolated by filtration, washed with distilled water and dried in air. As-prepared material was calcined at 500 °C for 8 h (heating step 1 °C/min).

2.3. Surface modification of mesoporous materials

SBA-15 and MCF silicas were modified by a grafting strategy using (3-aminopropyl)triethoxysilane (APTES) and 1-[3-(trimethoxysilyl) propyl]urea (TMSPU) dissolved in water-free toluene. The functionalization procedure was as follows: 5.0 g of calcined silica (SBA-15 or MCF) was mixed with 100 cm^3 of 0.15 M trialkoxysilane solution. The reaction was performed in a borosilicate bottle with a PTFE stopper at 110 °C for 24 h. After the reaction was complete, the mixture was cooled down, filtered and rinsed with anhydrous toluene (4×150 cm^3) and dichloromethane (4×150 cm^3). The resulting product was dried at 80 °C for 24 h. The samples functionalized with APTES were denoted as SBA-15-A, MCF-A, while silicas modified with TMSPU were designed as SBA-15-U and MCF-U.

2.4. Adsorption studies

Adsorption experiments have been carried out in glass vials containing 0.200 g of silica immersed in 10 cm^3 of suitable pollutant (2,4-D or Triclosan) solution in 2-propanol. The interval of examined pollutant concentration was from 0.1 mg/cm^3 to 8 mg/cm^3. The samples were stirred at 25 °C for 24 h. After the adsorption equilibrium was attained, the amount of adsorbed compound was evaluated using the expression:

$$Q_e = [(C_0 - C_e)x\ V]/m \quad (1)$$

and the efficiency of pollutant adsorption was evaluated from the formula:

$$E_a = [(C_0 - C_e)/C_0]\ x\ 100\% \quad (2)$$

where Q_e (mg/g) is the amount of adsorbed pollutant in the equilibrium state, C_0 (mg/cm^3) and C_e (mg/cm^3) are the initial and equilibrium concentrations of the adsorbate, V (cm^3) is the volume of pollutant solution and m (g) is the mass of the carrier. E_a (%) represents the efficiency of the adsorbed compound.

The amount of adsorbate was evaluated spectrophotometrically. Prior to the measurement, the suspension was centrifuged (15,000 ×*g*) for 15 min and the supernatant was diluted with 2-propanol. The absorbance of 2,4-D and Triclosan were measured at 209 and 283 nm, respectively.

The equilibrium experimental points for 2,4-D and TC adsorption were fitted to the linear forms of Langmuir (3) and Freundlich (4) isotherm equations [27]:

$$1/Q_e = [1/(Q_m x\ K_L x\ C_e)] + 1/Q_m \quad (3)$$

$$\log Q_e = \log K_F + (1/n)\log C_e \quad (4)$$

where Q_e (mg/g) and Q_m (mg/g) are the amount of adsorbed pollutant and maximum adsorption capacity, respectively; C_e (mg/dm^3) is the equilibrium pollutant concentration; K_L (dm^3/mg) and K_F ($mg^{1-1/n}\ dm^{3/n}$/g) represent Langmuir and Freundlich constant, respectively; and n is the exponential constant of Freundlich equation related to the intensity of sorption.

2.5. Kinetic studies

A typical procedure in kinetic adsorption studies was as follows. A mass of 0.200 g of mesoporous adsorbent was immersed in 10 cm^3 of suitable pollutant (2,4-D or Triclosan) in 2-propanol. The adsorption experiment was performed at 25 °C and the initial concentration of pollutants was 1.0 mg/cm^3. The samples were stirred and the concentration of organic compounds was determined at different time intervals ranging from 5 to 360 min to ensure the adsorption equilibrium state. The amount of adsorbed 2,4-D and TC was measured spectrophotometrically at 209 and 283 nm, respectively. Prior to the absorbance measurement the samples were filtered and diluted with 2-propanol. The sorption kinetic data were fitted to the pseudo-second-order model [28] and were expressed as:

$$t/Q_t = 1/\left(k\ Q_e^{\ 2}\right) + t/Q_e \quad (5)$$

where Q_e (mg/g) and Q_t (mg/g) are the amounts of adsorbed organic compounds onto mesoporous adsorbent at equilibrium state and at