Removal of DDT from aqueous solutions using mesoporous silica materials

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Abstract

BACKGROUND: There are few reports about adsorbents for the effective removal of large-molecule pesticides such as DDT (1,1,1-trichloro-2,2' bis(*p*-chlorophenyl)ethane). Some mesoporous silica materials and their modified derivatives might serve as good adsorbents for these large organic molecules because of their large pore diameter and special pore structures. In this work, the adsorption processes of DDT in aqueous solutions were investigated using different mesoporous silica materials, including HMS, MCM-41, SBA-15 and MCM-48.

RESULTS: All these materials exhibit efficient DDT removal, and the adsorption is a rapid process with over 50% of DDT removed within approximately 2 h. The efficiency of DDT removal is influenced by the adsorbent characteristics, such as pore volume, pore diameter, connectivity between pore channels and surface OH groups. The influences of water/acetone ratio and initial DDT concentration in solution were also explored. It was found that with enhancing DDT solubility, the addition of acetone in the reaction solution had no evident impact on DDT adsorption efficiency. Increasing the initial concentration of DDT resulted in a decrease of DDT adsorption efficiency. The adsorption kinetics of DDT on mesoporous silica material is shown to be pseudo-second-order. After thermal treatment at a relatively low temperature of 450 °C, the adsorbed DDT was completely decomposed and the adsorbents, except MCM-41, were regenerated well.

CONCLUSION: The results demonstrate the potential of a simple and efficient new approach for the removal of OCPs (organochlorine pesticides), especially large OCP molecules from surface water or groundwater.

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Keywords: mesoporous silica; removal; adsorption; DDT

INTRODUCTION

1,1,1-trichloro-2,2' bis(*p*-chlorophenyl)ethane (DDT), discovered in 1939, was used extensively in agriculture because of its high effectiveness, low cost, and persistence in the environment.¹ However, chemical stability and associated lipophilicity result in large accumulations of DDT in the environment. High concentrations of DDT and its metabolites DDD (1,1-dichloro-2,2-bis(4-chlorophenyl) ethane) and DDE (1,1-dichloro-2,2-bis(4-chlorophenyl) ethylene) are found in soils, water and air at many locations,^{2,3} even after prohibition of its use by many countries in the 1970s. Because of their lipophilicity, DDT residues tend to accumulate in the fatty tissues of ingesting organisms through the food chain,^{4,5} and act on the central neural systems to produce microscopic changes in the liver and kidneys, and cause reproductive disorders.⁶

To remove DDT residues from water, soil or air, many methods have been developed, including biological treatments,⁷ photochemical reactions⁸ and reductive dechlorination.⁹ However, limitations such as low adsorption efficiency, long reaction time, rigorous reaction conditions, and toxic byproducts produced, exist. These limitations have inhibited their applications in the practical environment. Compared with the methods mentioned above, adsorption has been found to be an effective, simple, and environmental friendly method.

Various adsorbents, such as activated carbon, polymeric resins, and organoclays, have been explored.^{10–12} However, these

materials are efficient only for adsorbing small organic molecules. Until now, there have been few reports about materials used to adsorb and remove large-molecule pesticides effectively, such as DDT (the molecule diameter is about 2.5 nm). Some mesoporous silica materials and their modified derivatives could serve as adsorbents for large organic molecules because of their large pore diameter and specific pore structure. However, very little research has been reported on mesoporous silica materials used to adsorb DDT. One exception, Sawicki *et al.*,¹³ removed various pesticides from aqueous solutions using mesoporous cyclodextrin–silica nanocomposites. Those materials were found to have a specific adsorption affinity toward the pesticides, particularly specific toward *p,p'* substituted diphenyl-based pesticides such as DDT and DDE. One of their results showed that HMS, an unmodified adsorbent ('pristine' HMS silica), also displayed relatively good adsorption efficiency. Further research work is needed to find

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more promising water treatment agents for the removal of large-molecule pesticides, especially DDTs.

This work was undertaken to explore the adsorption processes of DDT on various 'pristine' mesoporous silicas: HMS, MCM-41, SBA-15, and MCM-48, which are representative mesoporous silica materials with different topologies (the way the pores connect in space). The framework nanopores of HMS are wormholelike,¹⁴ MCM-41 is described as a regular cylindrical silica nanopore, and SBA-15 is assumed to be made up of cylindrical nanopores that are connected through lateral microporous channels.¹⁵ The 3D-connected topology of MCM-48 is described using a gyroid periodic minimal surface.¹⁶

In this work the adsorption processes of these four mesoporous silica materials were investigated. The effects of experimental parameters such as water/acetone ratio and initial DDT concentration in solution were also studied. The adsorption kinetics were determined with the help of the adsorption processes and tracer analyses.

The regeneration of adsorbents and the post-treatment of adsorbates are important in practical applications. In this work, a thermal decomposition method was used for the regeneration of the mesoporous silica adsorbents, which can completely decompose organic contaminants without producing toxic by-products. It was found that at a relatively low temperature (450 °C), almost 100% DDT can be degraded. Compared with MCM-41 and MCM-48, HMS and SBA-15 retained better physical structure after regeneration.

MATERIALS AND METHODS

Materials

DDT (p,p'-dichlorodiphenyltrichloroethane) was purchased from Aldrich (USA). A composite stock standard solution of DDTs including p,p'-DDE, p,p'-DDD, o,p'-DDT, p,p'-DDT was obtained from National Research Center for Certified Reference Materials of China. The concentration of each pesticide in the stock standard solution was 100 µg mL⁻¹. Calibration standards of DDTs were prepared by diluting the stock standard solution in n-hexane (Tedia Company, USA) using high performance liquid chromatography (HPLC). Dodecylamine (chemical grade) was purchased from Sinopharm Chemical Reagent Co., Ltd, China. All other chemicals were analytical grade and purchased from Beijing Chemical Reagent Factory. Sodium sulphate (Na₂SO₄) was oven-dried at 150 °C for 2 h to act as a desiccant.

Synthesis of adsorbents

HMS

HMS was synthesized by employing slightly modified literature procedures.¹⁷ Tetraethoxysilane (TEOS) 0.2 mol was dissolved into a mixture of water 5.92 mol, dodecylamine 0.054 mol and ethanol 1.818 mol under vigorous stirring. After stirring for 10 min, the reaction mixture was aged at ambient temperature for 18 h, then filtered, washed with distilled water and dried on a glass plate at ambient temperature for 12 h. The product was calcined in air under static conditions at 650 °C for 4 h to remove organic template.

MCM-41

In a typical synthesis, 30 mL TEOS was added dropwise to NaOH solution, which was prepared by adding 2.7 g NaOH to 150 mL H₂O at room temperature, then 5.3 g CTAB was gradually added under vigorous stirring. Finally, 1.488 g NH₄F was added to the gel

mixture. After 1 h of mixing at ambient temperature, the resulting gel was transferred to an autoclave and aged at 110 °C for 10 h. The molar composition of the gel mixture was 1.0 SiO₂: 0.25 Na₂O: 0.65 CTAB: 62 H₂O: 0.3 NH₄F. The solid products were collected by filtration and dried in air. The as-synthesized sample was calcined at 550 °C for 6 h to remove the template CTAB.

SBA-15

A typical preparation procedure for SBA-15 materials is described as follows: pluronic P123 (10 g) and NH₄F (0.125 g) were dissolved in 400 mL HCl solution (pH = 1) with stirring at ambient temperature for 1 h. TEOS (23 mL) was added to the solution. After stirring for 1 h, the mixture was aged at 35 °C for 24 h. Then it was transferred into an autoclave, aged at 100 °C for 48 h, and a white powder was recovered through filtration, washed with distilled water thoroughly, and dried at 100 °C for 24 h. Finally, the product was calcined at 550 °C for 6 h in air.

MCM-48

MCM-48 was synthesized by the conventional hydrothermal pathway similar to the procedure described by Wang.¹⁸ First, 3.734 g CTAB was dissolved in 25 mL H₂O, then after adding 0.485 g NaOH, 5.258 g TEOS was added dropwise to the solution. After stirring for 0.5 h, the mixture was transferred to an autoclave and crystallized at 110 °C for 72 h. The molar composition of the gel was 1.0 SiO₂/0.24 Na₂O/0.4 CTAB/55 H₂O. The solid products were collected by filtration and dried at 60 °C. Finally, the as-synthesized sample was calcined at 550 °C for 6 h.

Characterization and measurement

The textural properties of materials were measured by nitrogen adsorption-desorption at liquid nitrogen temperature, using a gas sorption analyzer NOVA 1200 (USA). X-ray diffraction (XRD) analysis was performed to identify the characteristics of the mesoporous materials on a Siemens (Karlsruhe, Germany) D5005 X-ray diffractometer. Diffraction patterns were recorded with Cu Kα radiation (40 mA, 40 kV).

Adsorptions of DDT

DDT stock solution (100 µg mL⁻¹) was prepared in analytical-grade acetone, and diluted in 500 mL distilled water to achieve aqueous DDT stock solution. 50 mg samples of each material were placed in 40 mL glass vials with Teflon-lined septa caps. Then 35 mL of the aqueous DDT stock solution was added in each vial. Reaction vials were tightly sealed with Teflon-lined screw caps to prevent any loss of solution. To minimize the aggregation of adsorbent and decrease the influence of diffusion on the DDT removal rate, vials were placed on magnetic stirrers for continuous stirring.

At predetermined time intervals, vials were removed from the magnetic stirrers and centrifuged at 4000 rpm for 5 min. 20 mL of supernatant solution was removed and serially extracted with n-hexane three times (4 mL, then 2 mL, and 2 mL) to recover DDT. After each extraction, vials were held still in an upright position for about 5 min to achieve complete phase separation. The combined n-hexane phases were passed through a glass column containing about 1 g anhydrous Na₂SO₄. Then 1 mL aliquots of the extracts were diluted in 4 mL n-hexane. Approximately, 1 mL aliquots from the diluted hexane solutions were removed in 2 mL glass vials. The vials were immediately sealed with Teflon-lined septa caps and later analyzed using gas chromatography-mass spectrometry (GC-MS).

Figure 1. N₂ adsorption-desorption isotherms of materials.

Figure 2. BJH pore size distributions of materials.

To test the impact of acetone in solution on DDT adsorption, several reactors with different water/acetone ratios were established using a reaction system consisting of 50 mg of SBA-15 and 1.5 $\mu\text{g mL}^{-1}$ of DDT. The water/acetone ratios were varied from 9:1 to 49:1 (v/v), and a reaction time of 12 h was chosen to analyze the extent of DDT removal.

The adsorption efficiency of DDT in solution was calculated from the following equation:

$$\text{Removal}(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

The DDT concentration retained on the adsorbent phase (q_e , $\mu\text{g mg}^{-1}$) was calculated from

$$q_e = \frac{V(C_0 - C_e)}{W} \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations of DDT ($\mu\text{g mL}^{-1}$), respectively, V is the volume of the solution (mL), and W is the mass of adsorbent (mg).

DDT decomposition and adsorbent regeneration

The DDT decomposition and adsorbent regeneration were carried out in a sealed glass tube (10 cm length, 0.4 cm i.d.). The adsorption

Table 1. Textural parameters of materials before and after adsorption-desorption experiments

Sample	Surface area ($\text{m}^2 \text{g}^{-1}$)		BJH pore diameter (nm)		Pore volume ($\text{cm}^3 \text{g}^{-1}$)	
	Before ^a	After ^b	Before	After	Before	After
HMS	851.1	740.3	4.725	4.391	1.005	0.813
SBA-15	640.6	620.8	6.719	6.294	1.076	0.977
MCM-41	1297	569.5	3.457	2.292	1.121	0.326
MCM-48	979.1	682.1	3.419	2.569	0.898	0.438

^a The data of materials parameters before adsorption experiments.

^b The data of materials parameters after heating at 450 °C for 2 h.

Figure 3. Effect of water/acetone ratio on DDT adsorption efficiency. Experimental conditions: initial DDT 1.50 $\mu\text{g mL}^{-1}$, 50 mg SBA-15, reaction for 12 h.

experiment procedures were similar to those described above, the reaction system was 50 mg SBA-15 and 4 $\mu\text{g mL}^{-1}$ of DDT. After 12 h of adsorption, the adsorbents were dried at 70 °C for 6 h. For all decomposition reactions, 8 mg of adsorbents were ground in the glass tubes, sealed under air atmosphere, and then heated at specified temperatures for 2 h. After finishing the experiments, the glass tubes were carefully crushed, 15 mL of 25 mmol L^{-1} NaOH was added to the solid residue to dissolve the mesoporous materials and stirred for 1 h. Then each sample was extracted with hexane as in the method described above. The combined hexane phases were then taken for GC-MS analysis.

GC-MS analysis

GC-MS analysis was conducted on an Agilent (USA) 6890 gas chromatograph equipped with an Agilent 5973 mass selective detector. An HP-5 capillary column (30 m $\times$ 0.25 mm, 0.25 μm film thickness) was used. Ultra high purity helium (flow rate of 1.0 mL min^{-1}) was used as the carrier gas. The injection volume was 1 μL . The column temperature was ramped as follows: initial temperature 70 °C for 2 min following the injection, increased at 20 °C min^{-1} to 200 °C and then at 10 °C min^{-1} to 280 °C, and maintained at the final temperature for 1.5 min. The net run time for the whole analyses was 18 min. The identification and quantification of DDT and its metabolites were done using selective ion monitoring.

Figure 4. Kinetics of DDT and its metabolites (DDD and DDE) removal by adsorbents in water/acetone (49:1) phase.

Figure 5. Pseudo-first-order (a) and pseudo-second-order (b) adsorption kinetics of DDT uptake by different mesoporous silica materials.

RESULTS AND DISCUSSION

Features of adsorbents

N_2 adsorption–desorption isotherms (Fig. 1) of HMS, MCM-41, SBA-15 and MCM-48, are similar to those reported previously.^{19–22} There are two hysteresis loops occurring in the N_2 adsorption–desorption isotherm of MCM-48, which are attributed to two kinds of mesoporous silica pores of different pore sizes.²³ This is reflected in the corresponding pore size distribution in Fig. 2. The BET surface areas, Barrett–Joyner–Halenda (BJH) pore diameters

and pore volumes are summarized and listed in Table 1. MCM-41 has the largest BET surface area, while SBA-15 has the largest pore diameter and smallest surface area.

Removal of DDT in aqueous solutions by mesoporous silica materials

Effect of water/acetone ratio

As a screening test to identify different adsorbents for DDT removal in aqueous solution, a higher concentration of DDT in solution than

Figure 6. Influence of adsorbent on DDT adsorption efficiency. Experimental conditions: water/acetone ratio 49:1, initial DDT $1.03 \mu\text{g mL}^{-1}$, 50 mg adsorbent, reaction for 36 h.

that found in a natural system is needed. It is reported that acetone could be used as a solubilizing agent.²⁴ However, at the same time as enhancing DDT solubility and mass transfer, whether acetone could influence the adsorption efficiency of DDT was still not clear. So the impact of water/acetone ratio on the efficiency of DDT adsorption by SBA-15 was examined first. It is noted from Fig. 3 that high efficiency DDT removal (>88 %) can be obtained with different ratios. Varying the water/acetone ratio does not lead to obvious changes of removal efficiency. From this, perhaps one can deduce that the DDT solubility in aqueous system can be enhanced to $1.5 \mu\text{g mL}^{-1}$ with a water/acetone ratio of 49:1.

Kinetics of DDT removal by different adsorbents

The kinetics of removal of DDT and its metabolites by various mesoporous silica adsorbents are shown in Fig. 4. In each chart of Fig. 4, the first point versus time 0 h represents the blank sample, determined before the addition of adsorbent.

It is noteworthy that the adsorption of DDT is initially a rapid process with over 50% of DDT being removed within approximately 2 h, indicating a high affinity between the DDT molecules and the mesoporous silica surface. Afterwards, the adsorption rate slows, with a little undulation in DDT concentration for a certain time, then reaching the final equilibrium. The undulation of DDT concentration is attributed to the loss in some porosity of the mesoporous silica.^{25,26} The porous structure of mesoporous silica degrades to some extent upon extended exposure to water.^{26,27}

As shown in Fig. 4, the adsorption equilibrium time depends on the adsorbents (34, 34, 6 and 16 h for HMS, MCM-41, SBA-15 and MCM-48, respectively). This could be due to the differences in the pore size and pore connectivity of adsorbents. As listed in Table 1, SBA-15 has the largest pore diameter, which is favorable for the diffusion of DDT molecules into the inner surface of the pore channels. So the equilibrium time of DDT on SBA-15 is the shortest. Although the main nanopores are the smallest, MCM-48 has some nanopores with larger diameter (Fig. 2). Meanwhile, the pore channels of MCM-48 are connected with each other, differently from MCM-41 and HMS.²⁸ The larger pores and better connectivity of the pore channels benefit the transfer of DDT molecules, and lead to a shorter equilibrium time for DDT adsorption on MCM-48 than MCM-41. In addition, the difference in the adsorption

equilibrium time might also be due to physiochemical properties of the material surface.^{28,29} The densities of OH groups on the surface of mesoporous silica are usually different.²⁸ Hydrophilic organic molecules can be adsorbed onto inner pore surface of mesoporous silica by hydrogen bonding. The greater the number of surface OH groups, the faster the adsorption process. It was reported that the surface OH densities of both SBA-15 and MCM-48 are higher than that of MCM-41.^{29,30} So SBA-15 and MCM-48 exhibit shorter equilibrium times than HMS and MCM-41.

A pseudo-first-order model and a pseudo-second-order model have been used to describe DDT adsorption kinetics. The integrated pseudo-first-order rate equation is written as

$$\log(q_e - q_t) = \log q_e - k_1 t \quad (3)$$

where q_e and q_t are the amounts of adsorbed DDT at equilibrium and any time t ($\mu\text{g mg}^{-1}$), respectively, k_1 is the equilibrium rate constant of the first-order sorption.

The pseudo-second-order equation is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where k_2 represents the pseudo-second-order rate constant.

Figure 5(a) and 5(b) present the results of fitting the experimental data with pseudo-first-order and pseudo-second-order models, respectively. Figure 5(b) shows that the pseudo-second-order model fits the adsorption kinetics data very well.

The regression coefficients of HMS, SBA-15 and MCM-48 are all extremely high (0.999) except for MCM-41 (0.939), which indicates good compliance with the pseudo-second-order model for the adsorption mechanism.

Influence of adsorbent

The efficiencies of DDT removal by different adsorbents were also evaluated (Fig. 6). From Fig. 6 and Table 1, one can conclude that the materials with larger pore volume and pore diameter have greater adsorption efficiency. As discussed above, big pore size favors the diffusion of DDT molecules. By diffusing DDT molecules through channels of adsorbents with smaller pore sizes, a higher degree of pore congestion might occur, making it difficult for later molecules to arrive at deeper inner pores. In addition, SBA-15 with the smallest surface area displays the highest adsorption efficiency (approximately 95% in 36 h), indicating that surface area is not the ruling factor for determining the adsorption capacity of DDT. So we can conclude that the DDT adsorption in aqueous solution is a multilayer adsorption; more adsorption layers can be formed in bigger pores, and larger pore volume is favorable for the accumulation of more DDT molecules.

Influence of DDT concentration

Figure 7 shows the influence of the initial DDT concentration in aqueous solution on adsorption efficiency. The processes of DDT removal with different initial DDT concentrations are similar except for various adsorption rates (Fig. 7(a)). After treatment for 36 h, the adsorption equilibrium is reached almost simultaneously. It indicates that the initial DDT concentration does not impact on the equilibrium time for adsorption. At lower initial DDT concentration, the adsorption efficiency is affected insufficiently in the concentration range of about $2\text{--}8 \mu\text{g mL}^{-1}$. With the increase of initial DDT concentration to $10 \mu\text{g mL}^{-1}$, the adsorption

Figure 7. Influence of initial concentration of DDT. Experimental conditions: (a) water/acetone ratio of 29:1, 50 mg HMS; (b) water/acetone ratio of 9:1, 50 mg SBA-15, reaction for 12 h.

efficiency slightly decreases from 99% to 96% (Fig. 7(b)), but the equilibrium adsorption amount (q_e) still increases. This observation reveals that the adsorption is less than saturation when the initial DDT concentration is lower than 10 µg mL⁻¹, which indicates that SBA-15 has an excellent adsorption capacity for DDT.

Proposed scheme for DDT adsorption

Based on the above results, the model for the adsorption processes of DDT on mesoporous silica is proposed as follows. First, by forming hydrogen bonds between the hydrophilic part of DDT with OH groups in the inner surfaces of mesoporous silica,³¹ DDT molecules are adsorbed on the pore surface of mesoporous silica. This phase is a rapid process, and corresponds with the adsorption phase within the first 2 h (Fig. 4). After the pore surface is almost full of adsorbed DDT molecules, the electrostatic effect between DDT molecules contributes the primary interaction, and multilayer adsorption seems to start. With the increase of adsorbed molecules, insufficient space exists to accommodate the latter molecules and the access difficulty is indicative of restricted diffusivity through the narrow pore channels. In addition, the bottleneck trend in the pore channels increases with more adsorbed DDT molecules, reducing the diffusion into deep pore channels. On the other hand, smaller pore diameter and pore volume, sequentially, cause the adsorption amount to decrease. So the adsorption capacity in MCM-48 with smaller pore volume should be smaller than that in MCM-41, while SBA-15 with the largest pore diameter and pore volume has the highest adsorption capacity (Fig. 6 and Table 1).

DDT decomposition and adsorbent regeneration

Decomposition reactions were carried out in the temperature range 250 to 450 °C for 2 h. The elimination efficiencies of DDT and its metabolites formed in the reactions are shown in Fig. 8. The first point versus the reaction temperature of 0 °C represents the blank sample before heating. The decomposition efficiencies of DDT and DDD increase with rising reaction temperature. When the reaction temperature is increased to 350 °C, DDT is completely converted. The main metabolite produced is DDE. The largest residues of DDE are detected at 250 °C, and then degraded continuously when the temperature further increases. It is concluded that the pesticide

Figure 8. Influence of reaction temperature on the DDT decomposition efficiency of SBA-15.

molecules adsorbed on mesoporous silica can be easily destroyed by heating.

The initial materials and the materials used (after adsorbing in aqueous solution for 36 h and heating at 450 °C for 2 h) were characterized by nitrogen adsorption–desorption. The results are shown in Table 1. Among these mesoporous materials, SBA-15 is most stable, retaining its high surface area, large pore diameter and large pore volume after regeneration. HMS retains most of its porosity after regeneration. In contrast, the pore structures of MCM-41 and MCM-48 are seriously damaged after regeneration. With MCM-41, more than half of its surface area and pore volume is lost due to its low hydrothermal stability.^{32,33}

CONCLUSIONS

The present work indicates that mesoporous silica HMS, MCM-41, SBA-15 and MCM-48 are able to remove DDT from aqueous solutions effectively. The DDT removal process on mesoporous silica is rapid and obeys a pseudo-second-order model. SBA-15 has the shortest equilibrium time (6 h) and the highest adsorption efficiency of approximately 95% (in 36 h using 49:1 water/acetone

ratio). Larger pore diameter and larger pore volume are favorable to higher adsorption capability, and better pore connectivity provides a higher adsorption rate. After thermal treatment of the adsorbents at 450 °C for 2 h, almost 100% DDT can be decomposed. The textual properties of SBA-15 and HMS remain good after recovery.

Due to high-efficiency and lack of harm to the environment, these mesoporous silica materials can be used as a new adsorbent for the removal of large OCP molecules, which are difficult to remove using traditional adsorbents.

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