ADSORPTION AND CATALYTIC DECHLORINATION OF DDT ON FE-SBA-15

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Abstract

In this work, highly dispersed Fe-SBA-15 was successfully synthesized by a hydrothermal and evaporating method, and used for DDT removal in aqueous media. The synthesized materials possess highly ordered mesostructure and good adsorption efficiency, over 98 % DDT can be removed from aqueous media in 12 h. After separation and thermal catalytic treatment at a relatively low temperature of 350 ^{o}C for 2 h, the trichloromethyl group of DDT adsorbed on Fe-SBA-15 can be completely dechlorinated, whereas on SBA-15, the adsorbed DDT was completely decomposed at 450 ^{o}C for 2 h.

Introduction

1,1,1-Trichloro-2,2' bis(*p*-chlorophenyl)ethane (DDT) was used extensively as a pesticide for agricultural purpose and in public health programs. But its persistence, bioaccumulation, toxicity and long-range atmospheric transport bring many risks to human health and environment. Although it has been regulated under the Stockholm Convention [1], and banned by many countries in the 1970s, DDT and its metabolites are still found at numerous sites in the world [2-4].

Over the past two decades, a number of methods for the DDT degradation have been studied, including biological treatments [5], photochemical reactions [6] and metal-catalyzed reactions [7]. Among these approaches, adsorption has been found to be an effective, simple, and environmental friendly technique. Due to their large surface area, tunable porosity, uniform pore size distribution, controlled morphology, and high thermal stabilities, mesoporous silica materials and their modified derivatives could serve as better adsorbents for large organic molecules. Our previous work [8] indicated that mesoporous silica SBA-15 has rather good efficiency for DDT removal, and the adsorption is a rapid process. After thermal treatment of the adsorbents at 450 ^{o}C for 2 h, almost 100% DDT can be decomposed.

In seeking to find low-temperature decomposition reagents for application in organochlorine remediation, the behavior of CaO, MgO, and Fe_2O_3 has been examined [9-11], respectively. Further studies have revealed that the decomposition efficiencies can be improved by the presence of a small amount of transition-metal oxide as catalyst composition.

In this work, highly dispersed Fe-SBA-15 was successfully synthesized by a hydrothermal and evaporating method, and used for DDT removal in aqueous media. It was found that at relatively low temperature (350 ^{o}C), a high dechlorination efficiency was reached.

Materials and methods

1. Materials

The following chemicals were used without further purification: DDT (p,p'-dichlorodiphenyltrichloroethane, Aldrich); n-Hexane (HPLC, Tedia Company, USA); Dodecylamine (Sinopharm Chemical Reagent Co., Ltd, China). All other chemicals were purchased from Beijing Chemical Reagent Factory. Sodium sulphate (Na_2SO_4) was oven-dried at 150 ^{o}C for 2 h to act as desiccant.

2. Material synthesis

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Typical preparation procedure of Fe-SBA-15 materials is described as follows: Pluronic P123 (2 g) and $Fe(NO_3)_3 \cdot 9H_2O$ (0.123 g) were dissolved in 75 g of 1.6 M HCl aqueous solution. TEOS (4.25 g) was added into the solution at ambient temperature. The mixture was stirred at 40 °C for 24 h and heated at 80 °C for another 24 h under static condition. Then the liquid was evaporated with stirring. Finally, a white powder was recovered and dried at 80 °C. The product was calcined at 550 °C for 6 h in air. The sample is denoted as 2%FeSBA-15, where 2% represents the Fe_2O_3 mass percentage. Similarly, 4%FeSBA-15, 6%FeSBA-15 and SBA-15 samples were also prepared by repeating the above procedure, where SBA-15 was prepared without adding $Fe(NO_3)_3 \cdot 9H_2O$.

3. DDT adsorption and decomposition

DDT adsorptions were conducted in water-acetone (9:1, v/v) phase. Acetone is known as a solubilizing agent [12]. 50 mg samples of each material were placed inside 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. After 12 h of adsorption with continuously stirring, vials were removed from the magnetic stirrers and centrifuged. 20 ml of supernatant solution was removed and serially extracted with n-hexane for GC-MS analysis. 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 certain temperatures for 2 h. After finishing these experiments, the glass tubes were carefully crushed. 15 ml of 25 mM NaOH was added to the solid residue to dissolve the mesoporous materials and stirring for 1 h. Then each sample was extracted with hexane for GC-MS analysis.

4. Material characterizations and GC-MS analysis

XRD analysis was performed to identify the characteristics of the mesoporous materials on a Siemens D5005 X-ray diffractometer. Diffraction patterns were recorded with Cu Ka radiation (40 mA, 40 kV).

To confirm the residual DDT and its metabolites concentration, GC-MS analysis was conducted on an Agilent 6890 gas chromatograph equipped with an Agilent 5973 mass selective detector. An HP-5 capillary column (30 m ×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 column temperature was ramped as follows: initial temperature of 70 °C was kept for 2 min following the injection, increased by 20 °C min^{-1} to 200 °C and by 10 °C min^{-1} to 280 °C, and maintained at the final temperature for 1.5 min.

Results and discussion

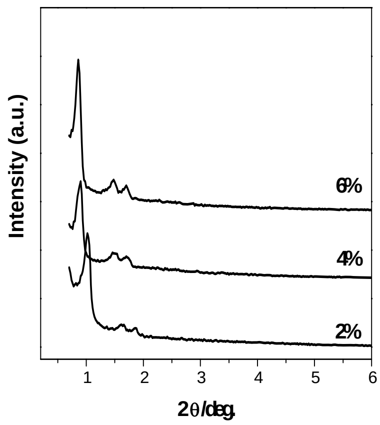

Fig. 1. Low-angle XRD patterns of Fe-SBA-15 with different iron mass contents.

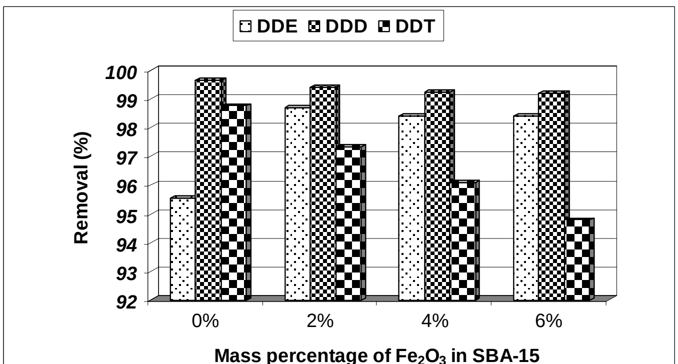

Fig. 2. Effect of iron content on DDTs adsorption efficiency.

Fig. 1 provides the low-angle XRD patterns of as-synthesized 2%FeSBA-15, 4%FeSBA-15 and 6%FeSBA-15, respectively. Three well-resolved diffraction peaks of these synthesized materials, indexed as the (100), (110), (200) diffractions, show typical mesoporous structure of SBA-15 [13]. With increasing the iron mass percentage, the intensity of the characteristic reflection peaks of Fe-SBA-15 enhanced or kept almost constant, indicating the introduction of Fe^{3+} does not decrease scatter contrast between pore walls and pore space [14].

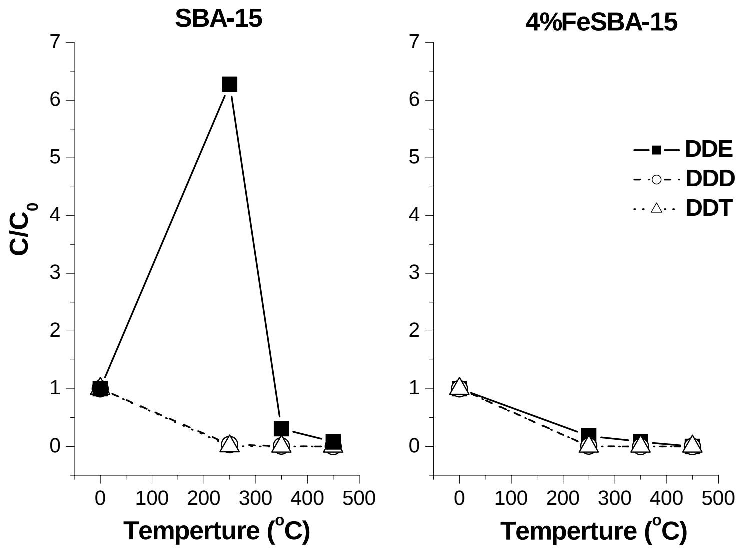

Fig. 3. Effect of reaction temperature on DDT dechlorination efficiency.

The efficiencies of DDT removal by Fe-SBA-15 with different iron contents were evaluated (Fig. 2). It is revealed that all these adsorbents have rather good efficiency for DDT removal, over 98 % DDT can be removed from aqueous media in 12 h. The decomposition efficiencies of DDT and its metabolites adsorbed on adsorbents are shown in Fig. 3. 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 increases to 450 °C, DDT, DDD and DDE is completely converted. 4%Fe-SBA-15 has higher dechlorination efficiency in comparison with SBA-15, indicating iron catalytic dechloriantion effect. After thermal treatment at a relatively low temperature of 350 °C for 2 h, the trichloromethyl group of DDT adsorbed on Fe-SBA-15 can be completely dechlorinated. This demonstrates that iron-containing SBA-15 mesoporous materials have higher dechlorination activity. Due to high-efficiency and harmless to the environment, these mesoporous materials can provide a simple, fast and highly efficient technique to remove DDT and other organic pollutants from aqueous media.

Acknowledgements

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