Studies on remediation of DDT-contaminated soil and dechlorination of DDT

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Abstract

A practical and efficient disposal method for 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT)-contained soil is reported. The treatment process was a combination technique: first to extract DDT in the soil, and then to hydrogenate the extract containing DDT. 4,4'-DDT was effectively extracted in the soil and hydrodechlorinated in this treatment process. Additionally, solvent media and extracting time for DDT removal were investigated. An efficient heterogeneous catalytic method was also developed by comparing the rates of dechlorination of DDT over two different catalysts in organic-aqueous heterogeneous system. Compared to Raney Ni, Pd/C is a more efficient catalyst in disposing DDT.

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1. Introduction

DDT (1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane) was widely used on a variety of agricultural crops and for the pest control in the management of malaria. However, its use has been prohibited in most countries because of its negative impact on wildlife and its toxic effects on human health via the food chain [1]. The United States Environmental Protection Agency (EPA) has classified DDT and its metabolite products, DDD (1,1-dichloro-2,2-bis(4-chlorophenyl)ethane) and DDE (1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene), which are extremely stable in the environment, as priority pollutants [2].

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However, despite risks from DDT and its related compounds, DDT is still used for essential public health purpose in some tropical countries [3]. Moreover, DDT-contained soils due to chemical factories have long been a significant problem in most countries. Considering its negative effects, it is necessary to find a practical and efficient disposal method for DDT-contained soil.

The removal of DDT from contaminated soils has intrigued many scientists in recent year, and numerous of remediation disposal routes, including low temperature thermal desorption [4], microwave heating [5], surfactant enhanced elution [6, 7], supercritical fluid extraction [8] and sulfuric acid treatment [9], have been studied. Through these remediation disposal routes, DDT was extracted from the soil. In order to reduce the toxicity of the extract effectively, it is necessary to degradation of DDT. To date, a number of methods for the degradation of DDT under relatively mild conditions have been extensively studied, including photo remediation [10-12], bioremediation [13-15], hydrodechlorination [16, 17], reductive dechlorination using metals [18, 19] and electrolysis [20].

The present study comes up with a combination technique, which is a practical and efficient disposal method for DDT-contained soil. In order to reduce the toxicity of the DDT-contained soil completely, thermal desorption was introduced to extract DDT in the soil, and then hydrodechlorination was introduced to hydrogenate the extract containing DDT.

2. Author Artwork

2.1. Materials

Catalysts (Raney Ni) used in this study were purchased from C&P Chemical Co., China. The catalysts were not pre-treated before all the experiments and only kept in a desiccator. DDT-contained soil was obtained from heavy pollution sites of DDT, China. The other reagents, such as solvents and bases, were analytical grade. The purities of hydrogen and nitrogen used in the experiments were more than 99.99%.

2.2. Analysis

The intermediate products in the hydrodechlorination reaction were determined by GC - MS (Thermo Fisher Trace Ultra ITQ-900) with a column of DB-5 (30m in length, 0.25 mm ID, 0.25 μm film thickness). The concentration of hydrodechlorinated products was analyzed by GC - FID (Agilent - 7890A) with a column of HP-5 (30m in length, 0.32 mm ID, 0.25 μm film thickness). The temperature program used for analysis was: 50 °C, held for 5 min to 265 °C at a rate of 5 °C/min, with a final hold time of 5 min. The injection port and detector temperature were set at 265 °C.

3. Results and discussion

3.1. General procedure of the thermal desorption of DDT - contained soil

DDT-contained soil (20 g, accurately weighed) was placed in a cellulose extraction thimble. A round bottomed flask was filled with 100 mL of solvent (acetone, dichloromethane, n-hexane, petroleum ether). The extraction was performed for 4-8 h. The liquid extract was quantitatively transferred to a round bottomed flask. The content of DDT and its metabolite products in the soil was determined using GC-MS. In addition, according to the above scheme, the soil was also extracted with a mixture of petroleum ether - acetone (1:1, v/v) as shown in Fig. 1. In petroleum ether/acetone (50/50), complete desorption could be finished within 4h.
3.2. Catalytic hydroreduction of the DDT extract from the soil

In a typical example, a solution of the extract in solvent (80 mL) was added to a 100mL three-necked flask attached with a thermometer, a condenser and a hydrotreater (including a hydrogen cylinder, hydrogen flowmeter, triple valve and a nitrogen cylinder). After the air in the flask was completely replaced by nitrogen, a catalytic amount of catalyst was added. The reaction mixture was stirred vigorously with a magnetic stirrer and was kept at a desired temperature (30 °C) using a thermostated water bath.

The catalytic activities of Raney Ni were examined in the hydrodechlorination reaction of the DDT extract at 30 °C. The initial concentration of the substrate was 2.5 g/L and the quantity of Raney Ni added to the reaction system was 200 mg. The efficiencies of the dechlorination of the extract from the soil are shown in Fig. 2. It can be seen that DDT can be hydrodechlorinated over Raney Ni under different conditions. As the DDT completely dechlorinated, the end products formed was diphenylethane, which was confirmed by GC-MS analysis. Moreover, the influence of the temperature and pressure was investigated. It was found that DDT can be completely dechlorinated under higher pressure (0.6 MPa) and
temperature (80 °C). Hence, the combination technique is a practical and efficient disposal method, which can effectively remove and degrade DDT of the heavy pollution sites.

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