

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)**SciVerse ScienceDirect**

Procedia Environmental Sciences 16 (2012) 289 – 292

**Procedia**

Environmental Sciences

The 7<sup>th</sup> International Conference on Waste Management and Technology

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

Chuanhai Xia<sup>a,\*</sup>, Xuanxuan Ma<sup>a,b</sup>, Sujing Liu<sup>a,b</sup>, Ping Fan<sup>c</sup><sup>a</sup> *Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China*<sup>b</sup> *University of Chinese Academy of Sciences, Beijing 100049, China*<sup>c</sup> *College of Chemistry, Liaoning University, Shenyang 110036, China*

### Abstract

A practical and efficient disposal method for 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT)-contaminated 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.

© 2012 Selection and/or peer-review under responsibility of Basel Convention Coordinating Centre for Asia and the Pacific and National Center of Solid Waste Management, Ministry of Environmental Protection of China.

*Keywords:* 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT); remediation technique; heterogeneous catalytic dechlorination; Raney Ni, Pd/C

### 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].

\* Corresponding author. Tel.: +86-0535-2109173; Fax: +86-0535-2109000.

E-mail address: [chxia@yic.ac.cn](mailto:chxia@yic.ac.cn)

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 photoremediation [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  $\mu\text{m}$  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  $\mu\text{m}$  film thickness). The temperature program used for analysis was: 50  $^{\circ}\text{C}$ , held for 5 min to 265  $^{\circ}\text{C}$  at a rate of 5  $^{\circ}\text{C}/\text{min}$ , with a final hold time of 5 min. The injection port and detector temperature were set at 265  $^{\circ}\text{C}$ .

## 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.

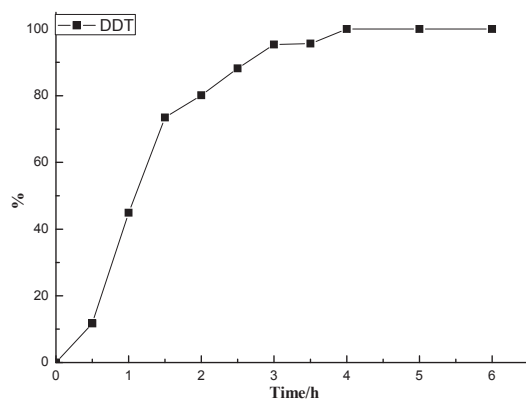


Fig. 1. The thermal desorption of DDT - contained soil

### 3.2. Catalytic hydrotreatment 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.

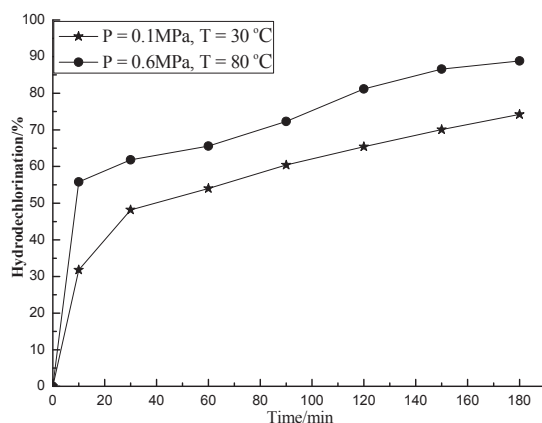


Fig. 2. Hydrodechlorination reaction of the extract over Raney Ni under

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.

## Acknowledgements

This study was financially supported by the Knowledge Innovation Program of Chinese Academy of Sciences (KZCX2-EW-206), National Natural Science Foundation of China (21007088) and Research Grant for Outstanding Young Scientists of Shandong Province (BS2009CL006).

## References

- [1] Kale SP, Murthy, NBK, Raghu K, Sherkhane PD, Carvalho FP. Studies on degradation of 14C-DDT in the marine environment. *Chemosphere* 1999;39:959-968.
- [2] Sayles GD, You G, Wang M, Kupferle MJ. DDT, DDD, and DDE dechlorination by zero-valent iron. *Environmental Science & Technology* 1997;31:3448-3454.
- [3] Foght J, April T, Biggar K, Aislabie J. Bioremediation of DDT-contaminated soils: a review. *Bioremediation Journal* 2001;5:225-246.
- [4] Norris G, Al-Dhahir Z, Birnstingl J, Plant SJ, Cui S, Mayell P. A case study of the management and remediation of soil contaminated with polychlorinated biphenyls. *Engineering Geology* 1999; 53(2):177-185
- [5] Kawala Z, Atamanczuk T. Microwave-enhanced thermal decontamination of soil. *Environmental Science & Technology* 1998;32:2602-2607.
- [6] Kile DE, Chiou DT. Water solubility enhancements of DDT and trichlorobenzene by some surfactants below and above the critical micelle concentration. *Environmental Science & Technology* 1989;23:832-838.
- [7] Mirnader G, Edward M, Hua S, William A, Paul-André D. Remediation of DDT-contaminated soil using optimized mixtures of surfactants and a mixing system. *Remediation Journal* 2010;20(4):119-132.
- [8] Demessie S, Richardson ET. Cleaning up pesticide contaminated soils: Comparig effectiveness of supercritical fluid extraction with solvent extraction and low temperature thermal desorption. *Environmental Technology* 2000,21(4):447-456.
- [9] Singh DK, Agarwal HC. Chemical release and nature of soil-bound DDT residues. *J. Agric. Food Chem.* 1992,40(9):1713-1716.
- [10] Sherman WV, Evans R, Nesyto E, Radlowski C. Dechlorination of DDT in Solution by Ionizing Radiation. *Nature* 1971;232:118-119.
- [11] Hendrik CA, Van B, Henk J. Vander S, Herman VO, Jitze VL. Photochemical radical chain dechlorination of DDT in 2-propanol. *Industrial & Engineering Chemistry Product Research and Development* 1982;21(1):123-125.
- [12] Shimakoshi H, Tokunaga M, Baba T, Hisaeda Y. Photochemical dechlorination of DDT catalyzed by a hydrophobic vitamin B12 and a photosensitizer under irradiation with visible light. *Chemical Communications* 2004;16:1806-1807.
- [13] Purnomo AS, Mori T, Takagi K, Kondo R. Bioremediation of DDT contaminated soil using brown-rot fungi. *International Biodeterioration & Biodegradation* 2011;65(5):691-695.
- [14] Quan X, Zhao X, Chen S, Zhao H, Chen J, Zhao Y. Enhancement of p,p'-DDT photodegradation on soil surfaces using TiO<sub>2</sub> induced by UV-light. *Chemosphere* 2005;60(2):266-273.
- [15] Mo CH, Cai QY, Li HQ, Zeng QY, Tang SR, Zhao YC. Potential of different species for use in removal of DDT from the contaminated soils. *Chemosphere* 2008;73(1):120-125.
- [16] Piechocki W, Gryglewicz G, Gryglewicz S. Hydrodechlorination of DDT and chloroalkanes over carbon-supported Ni-Mo catalyst. *Journal of Hazardous Materials* 2009;163(2-3):1397-1402.
- [17] Zinoviyev SS, Shinkova NA, Perosa A, Tundo P. Liquid phase hydrodechlorination of dieldrin and DDT over Pd/C and Raney-Ni. *Applied Catalysis B: Environmental* 2005;55(1):39-48.
- [18] Gautam SK, Suresh S. Dechlorination of DDT, DDD and DDE in soil (slurry) phase using magnesium/palladium system. *Journal of Colloid and Interface Science* 2006;304(1):144-151.
- [19] Tian H, Li J, Mu Z, Li L, Hao Z. Effect of pH on DDT degradation in aqueous solution using bimetallic Ni/Fe nanoparticles. *Separation and Purification Technology* 2009;66(1):84-89.
- [20] Karagunduz A, Gezer A, Karasuloglu G. Surfactant enhanced electrokinetic remediation of DDT from soils. *Science of The Total Environment* 2007;385(1-3):1-11.