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Technical Note

Remediation of 1,2,3-trichlorobenzene contaminated soil using a combined thermal desorption–molten salt oxidation reactor system

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HIGHLIGHTS

- Soil remediation using a TD–MSO system has not yet been widely used or analyzed.
- The chlorinated species were not detected in the emissions.
- The destruction mechanism and reaction pathway were proposed.

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ABSTRACT

A combined thermal desorption (TD)–molten salt oxidation (MSO) reactor system was applied to remediate the 1,2,3-trichlorobenzene (1,2,3-TCB) contaminated soil. The TD reactor was used to enrich the contaminant from soil, and its dechlorination of the contaminant was achieved in the MSO reactor. The optimum operating conditions of TD, and the effects of MSO reactor temperatures, additive amounts of the TCB on destruction and removal efficiency (DRE) of TCB and chlorine retention efficiency (CRE) were investigated. The reaction mechanism and pathway were proposed as well. The combined system could remediate the contaminated soil at a large scale of concentration from 5 to 25 g kg^{-1}, and the DRE and CRE reached more than 99% and 95%, respectively, at temperatures above 850 °C. The reaction emissions included C_6H_6, CH_4, CO and CO_2, and chlorinated species were not detected. It was found that a little increase in the temperature can considerably reduce the emission of C_6H_6, CH_4, and CO, while the CO_2 level increased.

1. Introduction

Contamination of soils with organic compounds like chlorinated organic chemicals is a wide spread problem arising from the extensive use of pesticides in agriculture or from industrial chemical wastes (Yeung and Gu, 2011). Various biological (Saichek and Reddy, 2005), physical (Rivas, 2006) and chemical (Wang et al., 1998) techniques have been initiated to decontaminate these contaminated soils. Thermal desorption (TD) method has attracted interests as a remediation technology for the effective removal of volatile and semi-volatile organic matter, especially, chlorinated compounds from contaminated soils (Zhao et al., 2012a,b). This technology is removing the contaminant from the soil, rather than destroy it. The desorbed organic compounds need to be further treated. Molten salt oxidation (MSO) is one of the promising alternative destruction technologies for chlorinated organics because it is capable of trapping chlorine atoms during organic destruction (Hsu et al., 2000; Yao et al., 2013a). MSO is a robust thermal treatment process for destroying organic-containing wastes. The operating temperature of MSO is hundreds of degrees lower than that of normal incineration, it generates less off-gas, since the process is an exothermic reaction and does not require supplemental fuel to sustain a flame, and the process is easy to operate (Yao et al., 2011, 2013b). Traditional MSO method usually added wastes to the molten salt directly, and there is a problem of waste production, more consumption of molten salt and secondary pollution. Therefore, proper pretreatment and purification of waste is very important to reduce the burden of subsequent processing molten salt and improve the treatment effect.

The objective of this study is to use the combination of TD and MSO technologies, the TD reactor could enrich contaminant from soil, and its destruction was achieved in MSO reactor. The combination TD–MSO technology could reduce the waste production and consumption of molten salt, and also prevent secondary pollutant.

Chlorobenzenes are widely used for industrial and domestic purposes such as solvents, degreasers, pesticides, herbicides, dyes, pharmaceuticals, disinfectants, rubbers, plastics and electric goods (Schroll et al., 2004; Zhang et al., 2012) and as intermediate in the

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production of other chemicals, and they have become ubiquitous pollutants (Wu et al., 2002; Song et al., 2011). These toxic compounds are environmentally stable and easily distributed to different environmental settings due to their volatility and resistance to degradation, therefore they have been ranked as prior pollutants by USEPA (Karnofsky, 1997). Trichlorobenzene (TCB) is a kind of typical chlorinated organics, highly volatile and fat-soluble, very stable in natural environment. In this study, 1,2,3-TCB contaminated soil was selected to evaluate the treatment effect of TD–MSO technology.

In the study, the molten salt selection, optimum conditions of TD, the effects of MSO reactor temperatures and additive amounts of TCB on destruction and removal efficiency (DRE) and chlorine retention efficiency (CRE) were investigated. And the reaction mechanism and pathway were proposed as well.

2. Experimental material and methods

2.1. The TD–MSO reactor system

The lab-scale TD–MSO reactor was produced by Ocean Glory GH (Beijing, China) Technology and its schematic diagram is shown in Fig. 1. The system consists of a screw feeding, air injection, TD reactor, MSO reactor, temperature control, and off-gas treatment system. The temperature of two reactors was controlled by the temperature control system. The feeding system is combined with air injection system and TD reactor system. The MSO reactor is connected with TD reactor system and off-gas treatment system. The off-gas leaving the MSO reactor is cooled down by a vertical air-to-gas heat-exchanging condenser, and then scrubbed by NaOH solution, *n*-hexane and subsequently vented. The NaOH solution and *n*-hexane were used mainly for absorbing the acid gas and organic components in off-gas. The TD reactor and MSO reactor with a capacity of 3 and 2 L, respectively. They are made of 304 stainless steel and 310S stainless steel to withstand both high temperature and chlorine attack.

The device operation includes the following steps: (1) the chlorinated organic compound contaminated soil is added to the TD reactor by screw feeder. (2) Through the temperature control system, the molten salt is melted. (3) Open the air injection system, heat the TD-reactor, the chlorinated organic compound desorbs from the contaminated soil and enter into MSO reactor. (4) The emissions let off after adsorption by alkaline solution and organic solvent. (5) Replace the material of TD-reactor after reaction. (6) Replace molten salt after multiple reaction. Each series of experiments included at least three repetitions.

Two indexes were involved to evaluate the effect of dechlorination by the combined system, the DRE and CRE, these two indicators' expressions are given below:

$$\mathrm{DRE}\ \% = M_{in} - M_{out}/M_{in} \quad (1)$$

M_{in} is the amount of TCB placed in the thermal desorption reactor (g); and M_{out} is amount of TCB absorbed in *n*-hexane (g).

$$\mathrm{CRE}\ \% = Y_{Cl}/S_{Cl} - J_{Cl} - W_{Cl} \quad (2)$$

S_{Cl} is the amount of chlorine atoms in TCB (g); Y_{Cl} is the amount of chlorine atoms in drained salt (g); J_{Cl} is the amount of chloride atoms in alkaline solution (g); and W_{Cl} is amount of chlorine atoms in TCB absorbed in *n*-hexane solution (g).

2.2. Materials

In this study, the appropriate molten salt system in treatment of 1,2,3-TCB was selected by experiment. A binary salt mixture consisting of 71 mol% Na_2CO_3 and 29 mol% K_2CO_3 with eutectic temperature of 573 °C was selected. The selected solvents in the study is *n*-hexane. All involved chemicals are analytical pure and were purchased from Beijing chemical reagents company. The pollutant 1,2,3-TCB (99% + pure) were supplied by Chengdu Xiya Chemical (China).

2.3. Sample preparation

The soil used in the experiment was collected at depth of 0–10 cm from suburb of Beijing (China). After removal of rubble, leaves and large sundry and freeze drying, then the soil was sieved through a 0.83 mm sieve to obtain a fraction of the soil with uniform physical properties.

Selected soils were artificially contaminated by dissolving 5, 15and 25 g of TCB in 100 mL of hexane, respectively, and adding the mixture to 1 kg of the soil. After mixing by shaker for 72 h in 500 mL flask, the wet soil mixture was then placed in a fuming cupboard at room temperature until the *n*-hexane totally evaporate. The corresponding contaminant concentration was 5, 15 and 25 g kg^{-1}, respectively.

2.4. Test methods and analysis

Preliminary experiment was performed to determine the optimum temperature and residence time of TD reactor.

About 20 g contaminated soil was placed in TD reactor, then heated to selected temperature, and stayed for 10–50 min. The

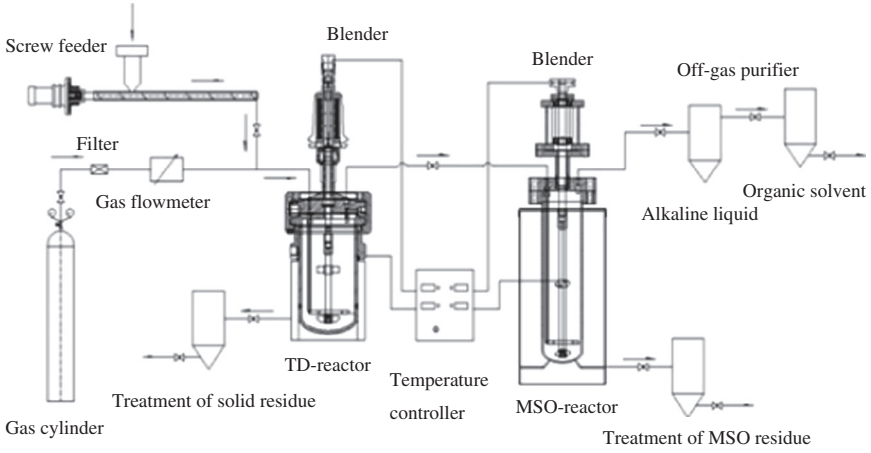

Fig. 1. The schematic diagram of the TD–MSO system.