

Comparison of Persulfate Activation and Fenton Reaction in Remediating an Organophosphorus Pesticides-Polluted Soil



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ABSTRACT

Organophosphorus pesticides (OPs) are one of the most regular pollutants and frequently detected in the contaminated sites, so developing an efficient method for the treatment of OPs is highly required. The aim of the present study was to compare the effectiveness of persulfate (PS) activation and Fenton reaction in remediating the soil polluted with OPs. The polluted soil used in this study was sampled from an abandoned insecticide factory in Nantong, Jiangsu Province of China, mainly containing chloropyrifos (CP) and 4-bromo-2-chlorophenol (BCP, the raw material of profenofos) with total concentration of about 30 000 mg kg⁻¹. The results showed that both BCP and CP were efficiently degraded by base activation of PS, and increasing the ratio of NaOH/PS enhanced CP degradation, but slightly decreased BCP degradation. The greatest degradation rates for CP and BCP were 92% and 97%, respectively, with 7.0 mol L⁻¹ NaOH and 0.21 mol L⁻¹ PS and a soil-to-liquid ratio of 1:1. Furthermore, ferrous iron activation of PS also degraded BCP efficiently, but only 60% of CP was degraded under the same reaction conditions. These results indicated that base activation of PS was more feasible than Fe²⁺ activation and Fenton reaction in remediating the soil polluted with OPs. The high degradation rate for CP may be linked to the initial hydrolyzation of CP by base to 3,5,6-trichloro-2-pyridinol, which can be further rapidly degraded by free radicals generated from base activation of PS.

Key Words: base activation, 4-bromo-2-chlorophenol, chloropyrifos, degradation rate, ferrous iron

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INTRODUCTION

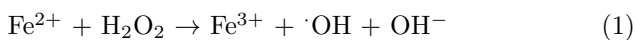
Organophosphorus pesticides (OPs) have been widely used to control agricultural and household pests since the 1970s. The consumption of OPs was about 3 × 10⁵ t, which accounted for about 72% of the total consumption of pesticides in China in 2010 (Hao *et al.*, 2010). However, because of being extensively used, OPs can be released into the natural environment and are frequently detected in the water, soil and sediments (Lacorte and Barcelo, 1994; Simcox *et al.*, 1995; Liu *et al.*, 2001). OPs have received an increasing concern due to their potential risk for wildlife and human health (Smith, 1987; Loewenherz *et al.*, 1997; Fenske *et al.*, 2000; Bai *et al.*, 2006; Wang *et al.*, 2016). It has been reported that the toxicity of OPs is initiated by inhibiting the enzyme acetylcholinesterase in the central and peripheral nervous systems (Pope *et al.*, 1999). OPs are

recalcitrant to biodegradation especially in soil with high concentrations, which can be found in agricultural soil and chemical plant (especially in pesticides factory) (Aislabie and Lloyd-Jones, 1995). Therefore, it is imperative to develop an efficient method for the remediation of OPs-contaminated soil.

In the past decades, advanced oxidation processes (AOPs) have been widely used for the remediation of contaminated soil and water (Yang *et al.*, 2014; Cheng *et al.*, 2016). Among AOPs, Fenton-based oxidation has attracted much attention due to its high effectiveness for the mineralization of organic pollutants with environment-friendly products (*e.g.*, H₂O) (Cai *et al.*, 2012; Li *et al.*, 2016). Fenton process encompasses reaction of H₂O₂ with ferrous ions yielding hydroxyl radical ([•]OH), which can degrade a wide range of contaminants with the second reaction rate constant of about 10⁶–10¹⁰ mol L⁻¹ s⁻¹ (Hoigné and Bader, 1976). The

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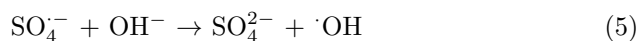
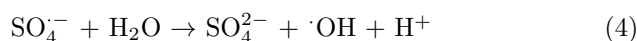
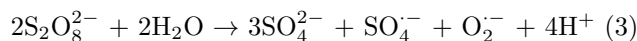
main mechanism of Fenton process can be described *via* the following reactions (Eqs. 1 and 2):



However, Fenton reaction is highly pH-dependent with the optimal pH value around 3.0 (Neyens and Baeyens, 2003; Burbano *et al.*, 2005), which limits its field applications. Furthermore, H_2O_2 is quite active and easily consumed with the natural organic matter (*e.g.*, humic substances) when it is applied for *in situ* remediation of contaminated soil. Compared with H_2O_2 , persulfate (PS) with a redox potential (E^0) of 2.1 V is an emerging and more stable oxidant in the subsurface environment and has received considerable attention in the remediation of contaminated soil and groundwater in recent years (Tsitonaki *et al.*, 2010). More importantly, PS can be activated by ultraviolet (Xiao *et al.*, 2016), heat (Fang *et al.*, 2013b), base (Furman *et al.*, 2010), transition metal (Fang *et al.*, 2013a, 2017; Zhu *et al.*, 2016), and certain organics (Fang *et al.*, 2013c) to produce sulfate radical ($\text{SO}_4^{\cdot-}$), a stronger oxidant with E^0 of 2.5–3.1 V, and can degrade organic pollutants selectively. However, up to now, most of PS activation methods focused on the degradation of contaminants in aqueous solution, and little attention has been paid to remove pollutants in soil, particularly for the degradation of pollutants in soil sampled from polluted sites.

Among the activators, ferrous iron and base were the most commonly used for *in situ* remediation of groundwater (Siegrist *et al.*, 2011). Similar to Fenton process, Fe^{2+} could activate PS to generate $\text{SO}_4^{\cdot-}$, and it is cheap, non-toxic, naturally abundant, and environmental-friendly (Liang *et al.*, 2004a). However, Fe^{2+} activation of PS generally requires a high concentration of Fe^{2+} , but excess Fe^{2+} would then result in rapid scavenging of $\text{SO}_4^{\cdot-}$, lowering the remediation percent of contaminants (Liang *et al.*, 2004b). By contrast, PS activated with base has also been applied frequently, and accounts for about 60% of the total activation methods for PS in *in situ* chemical oxidation (Crimi and Taylor, 2007; Furman *et al.*, 2011; Marchesi *et al.*, 2013; Zhao *et al.*, 2013). It has been reported that base-activated PS would generate multiple reactive species, including hydroxyl radical, sulfate radical, and superoxide radical. Furman *et al.* (2010) investigated the mechanism of base-catalyzed decomposition of PS and found that both superoxide radical anions and sulfate radicals were generated from this system

(Eq. 3). Also, $\cdot\text{OH}$ was formed from the reaction of $\text{SO}_4^{\cdot-}$ and H_2O or OH^- (Eqs. 4 and 5), and both $\text{SO}_4^{\cdot-}$ and OH were responsible for the degradation of organic contaminants in the PS activation system (Liang *et al.*, 2007).



Therefore, the main purposes of this study were to investigate the effectiveness of PS activation and Fenton reaction and to find an optimal condition for the remediation of OPs-polluted soil.

MATERIALS AND METHODS

Contaminated soil

The OPs-polluted soil was sampled at a depth of 1.0 m from an insecticide factory in Nantong, Jiangsu Province, China (32°01' N, 120°51' E), and stored in a refrigerator until use. The pollutants in the soil were analyzed by using a gas chromatography-mass spectrometer (GC-MS) (Varian CP 3800/Saturn 2200, USA). Briefly, 10 mL solvent (hexane:acetone = 1:1, volume:volume) was added to 40-mL glass vials containing 5.0 g polluted soil, which were then placed on a reciprocating shaker at 200 r min⁻¹ for 1.0 h. The supernatant was then analyzed with a GC-MS for the detection of pollutant components. Helium was used as the carrier gas at a flow rate of 1.0 mL min⁻¹. The sample injection volume was 1.0 μL and the initial temperature for the injector was 280 °C. The initial temperature of the oven was 60 °C and was kept for 3.0 min, and then the temperature increased to 260 °C at a rate of 5 °C min⁻¹ and was kept for 5.0 min. As shown in Fig. 1, two main pollutants were detected in the soil, including 4-bromo-2-chlorophenol (BCP) and chlorpyrifos (CP) with a concentration of about 10 000 and 11 000 mg kg⁻¹, respectively. They were selected as the target pollutants in the different oxidation remediation processes. CP is an organophosphate insecticide, which can be used on a variety of crops to control pest insect, and human exposure to CP may cause neurological effects and developmental disorders. BCP is the raw material of profenofos. The physicochemical properties of BCP and CP are listed in Table I.

Experimental procedures

The experiment was conducted in a 250-mL brown

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