Oxidative degradation of propachlor by ferrous and copper ion activated persulfate

C. S. Liu, K. Shih, C. X. Sun, F. Wang

Abstract

The process of in situ chemical oxidation (ISCO) by persulfate (S\(_2\)O\(_8\)\(^{-}\)) can be accelerated by metal ion activation, which more effectively degrades subsurface pollutants by enhancing sulfate radical (SO\(_4\)\(^{2-}\)) generation. This study compared the results of propachlor degradation by Cu\(^{2+}\) and Fe\(^{2+}\) activated persulfate and revealed differing degradation kinetics and mechanisms between the two types of activation systems. The activation of persulfate by Fe\(^{2+}\) ions generally resulted in rapid degradation in the early stage, but was accompanied by a dramatic decrease in efficiency due to the rapid depletion of Fe\(^{2+}\) by the sulfate radicals generated. In contrast, the Cu\(^{2+}\) activated persulfate had a longer lasting degradation effect and a proportionally greater degradation enhancement at elevated Cu\(^{2+}\) concentrations. An optimal Fe\(^{2+}\) concentration should be sought to activate the persulfate, as a high Fe\(^{2+}\) concentration of 2.5 mM or above, as was used in this study, may inhibit propachlor degradation due to the competitive consumption of sulfate radicals by the excess Fe\(^{2+}\) ions. Higher temperatures (55 °C compared with 30 °C) resulted in enhanced metal activation, particularly with the Cu\(^{2+}\) activated system. Furthermore, acidic conditions were found to be more favorable for propachlor degradation by metal activated persulfate. The ecotoxicity of degraded propachlor samples, which was indicated by average well color development (AWCD) for its microbial community activity, was confirmed to be decreased during the degradation processes with these two ions activated persulfate.

1. Introduction

Chloroacetanilide herbicides are among the most popular and commonly used pesticides worldwide, and are primarily employed for the preemergence control of annual grasses and broadleaf weeds in corn and rice plots. The annual usage of chloroacetanilide herbicides active ingredients in many countries, such as the European Union (Eurostat, 2007), United States (Grube et al., 2011), and China (Zheng and Ye, 2002), even exceed one million kilogram. As expected, the comprehensive use of these herbicides has resulted in serious nonpoint contamination in groundwater and soils. For example, metolachlor is among the top five most frequently detected pesticides in groundwater in the United States (Kolpin et al., 2000). Chloroacetanilide herbicides are reported to be of moderate to high chronic toxicity to aquatic vertebrates and invertebrates, and of high toxicity to aquatic plants and some green algae (Bian et al., 2009; Samtani et al., 2010). Many chloroacetanilide herbicides have been demonstrated to be carcinogenic (Oosterhuis et al., 2008). The development of strategies to remove chloroacetanilide herbicides from contaminated groundwater and soil sites is thus a timely and important task.

Although chloroacetanilides may be subject to natural attenuation and biotransformation in water and soils, such processes are often very slow, particularly under nutrient-limited conditions such as in subsurface soils or groundwater (Krause et al., 1985; Potter and Carpenter, 1995). Hydrolysis through nucleophilic substitution reaction is considered the main natural process by which chloroacetanilides are decomposed in soils and groundwater (Carlson et al., 2006; Cai et al., 2007). However, there is still a toxicity threat due to the considerable amount of intermediates generated, some of which may be even more toxic than their parent compounds (Kocsis et al., 2005). Similar shortcomings also exist in chloroacetanilide remediation technologies that rely on iron-bearing clay minerals, iron oxides, or organic matter to carry out reduction processes in anaerobic soils and groundwater (Boparai et al., 2006; Greer et al., 2010). It is thus necessary to explore more effective chloroacetanilide decomposition technology that is effective in oxygen-depleted conditions for soil and groundwater remediation.

In the past 20 years, in situ chemical oxidation (ISCO) has become a promising remediation technology for soils and groundwater. ISCO is usually performed by injecting chemical oxidants, such as hydrogen peroxide, permanganate, ozone, or persulfate (Seol et al., 2003), into the soil or water. Among the various oxidants available for this process, persulfate is the newest and least studied, but has received increasing attention (Tsitonaki et al., 2010). In addition to its high oxidative potential (E\(_0\) = 2.01 V), persulfate is moderately stable at...
the subsurface environments and has the potential to be transported from the point of injection to target pollutants in field sites.

Persulfate is usually activated by heat (Liang et al., 2009), UV light (Saient et al., 2011), bases (Furman et al., 2010), transition metals (Xu and Li, 2010), soil minerals (Liang et al., 2010), and radiolysis (Criquet and Leitmer, 2011) to form sulfate radicals (SO₄⁻²), which have an even greater oxidative potential (E° = 2.6 eV) than persulfate. In soils and groundwater, the sulfate radicals are free to react with a wide range of contaminants, which can further generate other reactive species, such as hydroxyl radicals (OH·), peroxymonosulfate (HSO₅⁻), and hydrogen peroxide (H₂O₂) (Liang et al., 2010), that are critical to the destruction of organic pollutants in soils and groundwater.

However, exploring a feasible activation method for ISCO is a major challenge, and the primary limitation is insufficient knowledge of the reaction pathways of activated persulfate in subsurface environments (Liang et al., 2009; Furman et al., 2010). Certain earth minerals found in soil, such as pyrite (FeS₂), birnessite (α-MnO₂), and goethite (α-FeOOH), may be efficient and appropriate activators of persulfate activation in subsurface environments (Liang et al., 2010). However, conditions of extreme acidity or basicity may sometimes be needed for the effective degradation of target pollutants (Costanza et al., 2010). Metal ions, especially ferrous metals, have been proven to be efficient persulfate activators and can be easily injected into soils and groundwater for ISCO (Zhang et al., 2010). Significant amounts of Fe²⁺ are adsorbed onto mineral surfaces through the anaerobic reduction of iron minerals in soil (Li et al., 2008), and copper ions enter into soil either as one kind of metal pollutant or a co-existing component through the application of herbicides and fertilizers (Gimeno-García et al., 1996) even to levels of several hundred ppm (Martley et al., 2004). Both metal ions may be used as the in situ persulfate activators in the remediation of soils and groundwater. To our knowledge, limited work has been carried out to investigate persulfate activation by metal ions to degrade chloroacetanilide herbicides, especially by copper ions. Propachlor, one of the most widely used chloroacetanilide herbicides in China and with the longest field life, and its degradation was attempted to evaluate propachlor degradation efficiency at pH 4. The first system was conducted by using different initial concentrations of ferrous and copper ions (1.0, 2.5, 5.0, and 10 mM) to activate persulfate (5.0 mM) for propachlor (10 mg L⁻¹) degradation at pH 4. The second system attempted to evaluate propachlor degradation efficiencies at temperatures 20 °C, 30 °C and 55 °C through ferrous- and copper-ion (2.5 mM) activation. The third system performed the degradation experiments under different pH (4, 7, and 10) to observe such influence on ferrous- and copper-ion activation processes. All of the experiments were carried out in two replicates, the mean values of which are reported.

2.3. Analytical methods

The propachlor concentration in aqueous solution was determined by high performance liquid chromatography (HPLC) (Shimadzu, Japan) conducted with a LC-10A pump, a SIL-10A automatic injector, and an SPD 10A-UV – vis detector. An Alltima™ C18 column (5 μm beads, 250 × 4.6 mm ID) with a mobile phase (70% methanol:30% water) and a flow rate of 1.0 mL min⁻¹ was used for the propachlor separation. A maximum absorption wavelength of 215 nm was used for the propachlor determination. The sodium persulfate concentration was determined by the iodometric method (Kolthoff and Stenger, 1947), and the concentrations of the sulfate ions were determined by a Dionex ICS-90 IC (Sunnyvale, CA, USA), with a mobile phase aqueous solution of 1.0 mM of NaHCO₃-8.0 mM Na₂CO₃ at a flow rate of 1.0 mL min⁻¹.

2.4. Ecological toxicity test of the degraded propachlor samples

Community level physiological profiles (CLPP) of the soil microbial community was assessed as described in a modified method reported previously (Kong et al., 2006). Briefly, the microbial communities in 10 g soil sample (dry weight equivalent; red soil collected to a depth of within 20 cm from a field site in Guangzhou City, Guangdong, China) was extracted by 100-mL sterile saline solution (0.85%) containing 5 g of 3-mm glass beads on a 300-rpm rotary
shaker for 20 min at 25 °C. After being diluted 100-fold and settled for 10 min, the 10 mL extraction solution was added to the propachlor degradation sample that had been degraded by activated persulfate for 10 h with an initial propachlor concentration of 10 mg L\(^{-1}\), consistent with the initial concentrations used in kinetics studies. For controlled experiments, 2.5 mM of Fe\(^{2+}\) or Cu\(^{2+}\) solutions and 10 mg L\(^{-1}\) of original propachlor solution, instead of propachlor degradation sample, was applied here. The mixture was then added to 90 mL of sterilized water to facilitate the incubation process. Then, 150 μL of the solution was added to each of the cells of a Biolog-ECO plate. The light absorbance at 590 nm was measured by an automated Biolog Microplate Reader (Hayward, CA, U.S.A.), and the data were collected by using Microlog 4.01 software (Hayward, CA, USA). The plates were then sealed inside a plastic bag and incubated at 25 °C in the dark and monitored every 24 h for 5 d, during which no contamination of control wells (only water) was found. Well absorbance values were adjusted by subtracting the absorbance of the controlled well (water only). Average well color development (AWCD), calculated as the average optical density across all wells per plate, was used as an indicator of general microbial activity (Garland and Mills, 1991). CLPP diversity was calculated for the Shannon index by subtracting the control from each substrate absorbance and then dividing this value by the recorded total color change (Zak et al., 1994).

3. Results and discussion

3.1. Propachlor degradation by Fe\(^{2+}\) and Cu\(^{2+}\) activated persulfate

Fig. 2 shows the results of the oxidative degradation of propachlor (10 mg L\(^{-1}\)) by persulfate activated with ferrous or copper ions at 30 °C. Without Fe\(^{2+}\) and Cu\(^{2+}\) in the solution, the propachlor underwent a steady but slow degradation possibly due to the direct electron transfer oxidation from persulfate anion to propachlor. A 13.1% removal for the initial propachlor was observed after 66 h. Iron has been widely reported as an efficient activator, and indeed the propachlor was found to be efficiently degraded by Fe\(^{2+}\) activated persulfate, which removed 60% of the initial propachlor in the first 32 h. However, observation of the kinetics results showed a dramatic decrease in the propachlor degradation rate after the initial stage. In contrast, the propachlor degradation with Cu\(^{2+}\) activated persulfate exhibited a different trend, showing steady degradation behavior throughout the reaction period, with 69.6% of the initial propachlor removed in 66 h.

Ferrous ions can rapidly activate persulfate to form sulfate radicals (SO\(_4^{2-}\)) at a high rate constant (k) of 2.7×10\(^{10}\) M\(^{-1}\) s\(^{-1}\). However, the high reduction potential of Fe\(^{2+}\) ions and the high oxidation potential of the sulfate radicals generated may initiate an even stronger interaction (k = 4.6×10\(^{9}\) M\(^{-1}\) s\(^{-1}\)) between Fe\(^{2+}\) and sulfate radicals (Liang et al., 2010). Ferrous ions were converted simultaneously by both persulfate and sulfate radicals, and the final reaction product (SO\(_4^{2-}\)) remained in the system, as shown in Fig. 3. The reaction equations were as follows (Liang et al., 2010).

\[
\begin{align*}
\text{Fe}^{2+} + S_2O_8^{2-} & \rightarrow \text{Fe}^{3+} + S_2O_4^{2-} + \text{SO}_4^{2-} \quad k = 2.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \quad (1) \\
\text{Fe}^{2+} + \text{SO}_4^{2-} & \rightarrow \text{Fe}^{3+} + \text{SO}_2^{2-} \quad k = 4.6 \times 10^{9} \text{ M}^{-1} \text{ s}^{-1} \quad (2)
\end{align*}
\]

As the reaction rate constant of Eq. (2) is much higher than that of Eq. (1), significant amounts of sulfate radicals should have been consumed by ferrous ions. Consequently, the behavior of propachlor degradation dramatically decreased following the complete depletion of Fe\(^{2+}\) in the system in the later stage, although the degradation efficiency was considerably enhanced in the early stage (Ahmad et al., 2010; Xu and Li, 2010). The SO\(_4^{2-}\) concentrations (Fig. 3) produced in the system show a corresponding trend to the propachlor degradation. A faster production of SO\(_4^{2-}\) was found in the early stage and the rate slowed down when Fe\(^{2+}\) was depleted in the later stage.

The result of activating persulfate by copper was clearly reflected by the substantial enhancement of propachlor degradation in Fig. 2. Propachlor underwent a steady and efficient degradation behavior in the studied reaction period. This may suggest that Cu\(^{2+}\) activates persulfate to form sulfate radicals and sulfate ions. Copper ions can be oxidized to become Cu\(^{3+}\), although at a lower reaction rate and with a higher energy barrier to overcome (Xu et al., 2008):

\[
\text{Cu}^{2+} + S_2O_8^{2-} \rightarrow \text{Cu}^{3+} + S_2O_4^{2-} + \text{SO}_4^{2-} \quad (3)
\]

However, copper ion is more stable as a result, and the sulfate radicals generated may be mainly consumed by propachlor oxidation, instead of copper ions compared to ferrous ions. Another potential mechanism of enhanced propachlor oxidation may be the generation of Cu\(^{3+}\), which is unstable and may act as an oxidant for propachlor degradation (Chandra and Yadava, 1970). The recurrent Cu\(^{2+}\) ions in this process were capable of activating persulfate, which may explain the well-maintained propachlor degradation efficiency throughout the entire reaction. Therefore, the trend of propachlor degradation...
and the corresponding sulfate generation derived from persulfate activation by Cu$^{2+}$ ions was apparently different from those generated by activation with Fe$^{2+}$ ions. At the end of the reaction period (66 h), the propachlor removal rate was greater when with Cu$^{2+}$ activated persulfate. In addition, a lower consumption of persulfate was observed with Cu$^{2+}$ activation, indicating the more efficient use of persulfate for the degradation of propachlor than the case when activation was by Fe$^{2+}$ ions.

### 3.2. Effects of different Fe$^{2+}$ and Cu$^{2+}$ concentrations

Using 5.0 mM of persulfate at 30 °C, different concentrations (0–10 mM) of Cu$^{2+}$ and Fe$^{2+}$ were added separately to investigate their effect on propachlor (10 mg L$^{-1}$) degradation (Fig. 4). It can be clearly concluded that the metal ions alone generally do not provide any degradation effect for propachlor as shown by the control experiments in Fig. 4. As discussed in the previous section, persulfate activation by Cu$^{2+}$ generally resulted in a continuous degradation process throughout the reaction period. A higher Cu$^{2+}$ concentration was also found to facilitate the degradation rate. At Cu$^{2+}$ concentrations of 1.0, 2.5, 5.0, and 10 mM, the rates of propachlor removal in 66 h were 52.5%, 69.6%, 75.0%, and 76.3%, respectively. According to Eq. (3), 5.0 mM of persulfate can be activated with 5.0 mM of Cu$^{2+}$ ions. This proposed activation can also explain the result of limited increase in propachlor degradation when using 10 mM Cu$^{2+}$, which only resulted in ~2% increase of propachlor degradation compared to that by 5 mM Cu$^{2+}$ (Fig. 4A).

For persulfate activation by Fe$^{2+}$ ions, a stoichiometric concentration of 5.0 mM or higher did not result in the best propachlor degradation effect. Instead, 2.5 mM was found to be the optimized iron concentration, removing 60.5% of the propachlor in 66 h (Fig. 4B). This observation is consistent with the reported strong interaction between the sulfate radicals and the Fe$^{2+}$ ions, whereby the available Fe$^{2+}$ in solution acts as a sulfate radical scavenger (Tsianou et al., 2010) to decrease the propachlor degradation rate. When the Fe$^{2+}$ concentration was increased to 10 mM, only 18.3% of the propachlor was removed due to the consumption of generated sulfate radicals by excess Fe$^{2+}$ ions, which is only slightly higher than that in the experiment using persulfate without metal activation.

### 3.3. Effect of temperature on propachlor degradation

Fig. 5 demonstrates the results for 10 mg L$^{-1}$ propachlor degradation at 20 °C, 30 °C and 55 °C through persulfate (5 mM) activated by 2.5 mM Cu$^{2+}$ or Fe$^{2+}$ ions. Heat has also been reported as another important and efficient method of activating persulfate (Liang and Su, 2009). In the absence of a metal activator, the propachlor degradation rate at 55 °C was significantly increased compared with that at 30 °C and 20 °C, achieving a 76.8% propachlor removal rate in 66 h. However, under a higher temperature, metal activation by Fe$^{2+}$ was only capable of enhancing propachlor degradation within the first 40 h. At 55 °C, persulfate was activated by both Fe$^{2+}$ and heat to generate sulfate radical, but the rapid interaction between Fe$^{2+}$ and SO$_4^{•-}$ (k = 4.6 × 10$^{9}$ M$^{-1}$ s$^{-1}$) (Eq. (2)) quickly consumed the sulfate radicals. The propachlor removal efficiency by Fe$^{2+}$ activated persulfate was thus lower than that without metal activation after 65 h of reaction (Fig. 5). The adverse effect of Fe$^{2+}$ and sulfate radical interaction is clearly a primary concern when considering Fe$^{2+}$ activation of persulfate at elevated temperatures.

With the Cu$^{2+}$ activated persulfate, a higher temperature was found to be more beneficial to propachlor degradation, with complete propachlor degradation (100% removal) being achieved in 32 h at 55 °C. In this system, both Cu$^{2+}$ and heat activate persulfate to generate more SO$_4^{•-}$ radicals for propachlor degradation. A much higher propachlor degradation rate was obtained at higher temperatures due to the stable coexistence of SO$_4^{•-}$ and Cu$^{2+}$. Persulfate may be more readily decomposed at higher reaction temperatures, and Cu$^{2+}$ ions can thus more efficiently activate persulfate to generate SO$_4^{•-}$ radicals for propachlor degradation. The overall propachlor removal rates by Cu$^{2+}$ activated persulfate at the higher temperature of 55 °C were 26.3%, 37.2%, 68.3%, and 100% for reaction times of 5, 10, 20 and 32 h, respectively. These removal rates are clearly significantly higher than the corresponding propachlor depredation rates when at 20 °C and 30 °C (Fig. 5).

### 3.4. Effect of solution pH

The reaction pH commonly plays an important role in the degradation of organic pollutants in ISCO processes. The degradation behavior of propachlor was investigated by using 5.0 mM of persulfate activated with 2.5 mM of Cu$^{2+}$ or Fe$^{2+}$ ions under acidic (pH 4), neutral (pH 7), and alkaline (pH 10) conditions at 30 °C (Fig. 6). In general, the rate of propachlor degradation decreased with an increase in pH with metal ion activated persulfate. However, different persulfate activation mechanisms may dominate in different pH environments. For example, the metal ion activation mechanism may be responsible for sulfate radical generation under acidic conditions, which leads to the degradation of propachlor. When the reaction pH is increased...
to neutral or even alkaline levels, the strong hydrolysis of Cu$^{2+}$ and Fe$^{2+}$ ions may significantly interfere with persulfate activation (Xu and Li, 2010) and decrease propachlor degradation rates. At high pH values, base-activated persulfate may be mainly responsible for the generation of sulfate radicals for propachlor degradation. This base activation mechanism has been confirmed to be as follows (Furman et al., 2010):

$$2S_2O_8^{2-} + 2H_2O \rightarrow SO_4^{2-} + SO_4^{2-} + O_2^{-} + 4H^+$$  \( (4) \)

Under strongly alkaline conditions, sulfate radicals can also react with hydroxyl anions to generate hydroxyl radicals (OH$^\cdot$), which have a little higher oxidation potential than sulfate radicals (Kolthoff and Miller, 1951):

$$SO_4^{2-} + OH^- \rightarrow SO_4^{2-} + OH^\cdot$$  \( (5) \)

As a result, low propachlor degradation rates were observed in the experiments at pH 10, regardless of the type of metal ions (Cu$^{2+}$ or Fe$^{2+}$) used to activate the persulfate.

3.5. Ecotoxicity during propachlor degradation

The ecotoxicity of propachlor degradation intermediates toward bacteria should be further investigated, and the average well color development (AWCD) can be used as an indicator of microbial activity in soils, in which a higher AWCD value indicating a lower ecotoxicity of the incubation sample (Garland and Mills, 1991). Such information is important in the development of effective ISCO remediation strategies by metal ion activated persulfate. In this study, the AWCD was used to evaluate the effect of propachlor degradation samples (after reaction with persulfate for 10 h) on microbial activity (Garland and Mills, 1991). As shown in Fig. 7, the AWCD values of the control sample (with water only) increased rapidly after 24 h and achieved a value of 1.74 within 120 h of incubation, while the AWCD value with 10 mg/L of propachlor was only 0.41 at the end of the incubation time, which indicates that propachlor has a strongly negative effect on microbial activity. The metal ions themselves also pose some toxic on the soil microbial communities, as shown in Fig. 7, the AWCD values of the control sample (with 2.5 mM metal ion solution only) within 120 h of incubation decreased slightly to 1.62 and 1.53 for Fe$^{2+}$ and Cu$^{2+}$, respectively. Compared with that with original propachlor sample, incubation with propachlor after being treated by Cu$^{2+}$/Fe$^{2+}$ activated persulfate resulted in an increase in AWCD values and a corresponding decrease in the adverse impact of propachlor on the microbial community. With the Cu$^{2+}$ activated persulfate, the AWCD value reached 1.26 in the 120 h of incubation, which is consistent with the higher propachlor degradation rate by Cu$^{2+}$ activated persulfate observed in Fig. 2. Overall, the ecotoxicity of propachlor sample was confirmed to be decreased during the process of persulfate oxidation, and thus metal ion activated persulfate may be a promising ISCO strategy to facilitate the detoxification of contaminated soils or groundwater.

4. Conclusions

In this study, two types of metal ions, Cu$^{2+}$ and Fe$^{2+}$, were used to activate persulfate for propachlor degradation. When activated by Fe$^{2+}$, propachlor underwent an initially fast degradation, but then quickly slowed down. Copper ion activated persulfate was proven to generate a more steady and efficient degradation of propachlor. For the same propachlor and persulfate concentrations, the rate of propachlor degradation increased when the higher Cu$^{2+}$
concentration was used for persulfate activation. In contrast, when the concentration of Fe²⁺ was above 2.5 mM, a further increase in Fe²⁺ concentration was found to inhibit propachlor degradation, potentially due to the consumption of sulfate radicals by the excess Fe²⁺ ions. This result clearly indicates that an optimal Fe²⁺ concentration needs to be determined to efficiently initiate the persulfate degradation process for target compounds. Higher temperatures generally enhance the degradation rate, as the activation of persulfate degradation process for target compounds. However, the Cu²⁺ generally enhance the degradation rate, as the activation of persulfate: proposed reaction kinetics. J Contam Hydrol 2010;49:8858–64.


