



## Degradation of alachlor with zero-valent iron activating persulfate oxidation



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### ABSTRACT

Alachlor, a commonly used herbicide in agriculture, has been selected as a target pollutant to evaluate the oxidative performance of zero-valent iron (ZVI) coupling with persulfate (PS) for the first time. Compared with  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ , ZVI achieved the best degradation effect. Bench-scale kinetics tests were conducted to demonstrate the impacts of several key factors controlling the treatment performance, including ZVI dosage, PS dosage, initial pH, temperature, nature organic matter (NOM), citrate and anions. The alachlor degradation followed a pseudo-first-order kinetics pattern and was effective in a broader pH range. The optimum ZVI to PS molar ratio was found to be 2:1. Heat could facilitate production of sulfate radicals and thus enhance the alachlor degradation. Sodium citrate as a chelating agent at an appropriate concentration could improve the alachlor decay in the  $\text{Fe}^{2+}$ +PS and ZVI+PS system. The removal was strongly inhibited in system added NOM, anions of  $\text{Cl}^-$  or  $\text{HCO}_3^-$  while it was not obvious impacted by adding  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$ . Seven proposed degradation pathways were evaluated, using Liquid Chromatography–Mass Spectroscopy (LC–MS) analysis. In conclusion, ZVI+PS can be as a potential technology for purifying alachlor-polluted water.

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### 1. Introduction

Alachlor (2-chloro-N-2,6-diethylphenyl-N-(methoxymethyl)acetamide), a well-known pre- and post-emergence herbicide from the chloroacetanilide family, has been commonly used to control the annual grasses and many broad-leaf weeds in crops [1]. Alachlor has been classified as the carcinogen of B2 group by the Environmental Protection Agency (EPA) and has also been known as a highly toxic endocrine disrupting chemical where the permissible maximum concentration in drinking water is  $20 \mu\text{g/L}$  [1,2]. As chlorine endocrine disruptor, its toxic and genotoxic effects may cause cancer and mutagenicity in laboratory animal and even contribute to infertility [3].

Alachlor has a half-life in soil of 7–38 days [4], and can leach beyond the root zone and migrate to natural waters under certain conditions [5,6]. Therefore, alachlor was frequently detected in the surface water and ground water [7]. Also, alachlor has a low

molecular weight (269.77 Da), a high solubility (240 g/mL, at 25 °C). So the biological pre-treatment [8] and the traditional coagulation–sedimentation–filtration treatment processes in drinking water treatment plants, present the poor treatability for alachlor [9,10]. Therefore, there is urgent need to seek an efficient and economical technique to eliminate alachlor.

Chemical oxidation processes like catalytic and non-catalytic wet air oxidation [11] and advanced oxidation processes (AOPs), including photochemical ( $\text{O}_3/\text{UV}$  and  $\text{H}_2\text{O}_2/\text{UV}$ ) [9] and photocatalytic processes ( $\text{TiO}_2/\text{UV}$ ) [12], Fenton, photo-Fenton [3], ozonation [13], ultrasonic oxidation [14] and PS [15] have shown successful results dealing with these recalcitrant compounds.

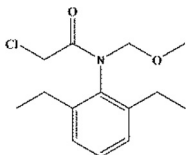
AOPs have shown successful results dealing with the recalcitrant compounds, since it has many advantages such as relative high solubility and stability at room temperature, non-selectively widespread reactivity with environmental contaminants [16]. PS can be activated by heat [17], UV [18] and transition metal ions [19], generating a stronger and non-selective oxidant sulfate radical ( $\text{SO}_4^{\cdot-}$ ,  $E_0=2.6 \text{ V}$ ).

Owing to the advantages of cost effectiveness, high activity and the environmentally friendly nature,  $\text{Fe}^{2+}$  has been commonly selected as the activator of PS to generate  $\text{SO}_4^{\cdot-}$  in practical

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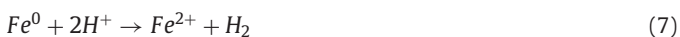
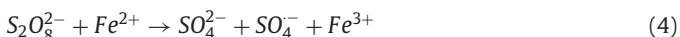
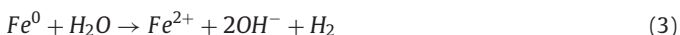
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**Table 1**  
The physicochemical properties of alachlor.

Chemicals formula	Chemical structure	Molecular weight (g/mol)	Water solubility (g/mL, 25 °C)
C <sub>14</sub> H <sub>20</sub> ClNO <sub>2</sub>		269.77	240

application [20]. However, a high concentration of Fe<sup>2+</sup> is required in the iron activated PS system since Fe<sup>2+</sup> is hard to be regenerated after conversion to Fe<sup>3+</sup> [21]. The excessive Fe<sup>2+</sup> can act as a scavenger of SO<sub>4</sub><sup>-</sup> and iron sludge generated at the end of the treatment is not reusable requiring additional treatment and disposal [22].

ZVI is non-toxic, cheap and easily obtained. It can not only be the alternative source of Fe<sup>2+</sup>, but also recycle Fe<sup>3+</sup> on its surface and reduce the precipitation of iron hydroxides during the reaction [23]. The use of ZVI overcomes the disadvantage of Fe<sup>2+</sup> and has the advantage of avoiding the addition of other anions by ferrous salts [24]. ZVI can produce Fe<sup>2+</sup> by the following reactions:



To date, ZVI+PS system has been reported to remove some important organic pollutants such as p-nitrophenol [25], dyes (acid orange II and methyl orange) [24,26] and bisphenol A [27]. However, to the best of our knowledge, very limited information on the ZVI+PS oxidation of herbicides in water is available.

The object of this study was to investigate the performance of ZVI for PS activation. Then, several key influencing factors including initial ZVI dosage, PS dose, initial pH, citrate, NOM and common coexisting ions on the alachlor degradation were evaluated. Finally, the preliminary degradation mechanistic information was provided through the products identification.

## 2. Experimental

### 2.1. Materials

The alachlor was supplied by Sigma-Aldrich (St. Louis, Missouri, USA). The physicochemical properties of alachlor were shown in Table 1. Sources of other chemicals and reagents used in the study were summarized in the supplementary material (Text S1).

### 2.2. Procedures

All the tests were performed in 250 mL glass vessels with 200 mL simulated alachlor-contaminated water. When the PS and ZVI were added into the solution, the mechanical stirrer was switched on to maintain the solution well mixed. As the effect of temperature was considered, the vessels were installed in a water bath apparatus (SHZ-B, Shanghai Yuejin Medical Instruments Co., Ltd.), providing a desirable reaction temperature. At designated time intervals (0, 2, 4, 6, 10, 15, 30, 45, 60 min), 0.8 mL sample was taken out from each replicate vessel and put into 0.2 mL ethanol to quench the oxidation induced by any residual oxidant. After filtering, the filtrate was used for the detection of the residual. All the experiments were carried out in duplicate to ensure accurate data acquisition and interpretation.

### 2.3. Analytical methods

The alachlor concentration was examined by using a high performance liquid chromatography (HPLC, Waters 2010, USA) equipped with a Symmetry C18 column by using a UV-vis detector (Waters 2489) at the absorption wavelength of 200 nm. The details of the alachlor analyses were summarized in the supplementary material (Text S2).

## 3. Results and discussion

### 3.1. Effect of initial ZVI dosage

In this study, three different forms of iron (Fe<sup>3+</sup>, Fe<sup>2+</sup> and ZVI) were used to test the formation of SO<sub>4</sub><sup>-</sup>. The detailed discussion was shown in the supplementary material (Text S3 and Fig. S1). ZVI +PS system achieved the optimal performance in the degradation of alachlor compared with Fe<sup>3+</sup>+PS and Fe<sup>2+</sup>+PS system.

Also, noted that ZVI alone did not have significant influence on the degradation of alachlor and less than 18% of alachlor was degraded under the PS alone (Fig. S2).

Fig. 1a illustrated the alachlor removal under different ZVI to PS molar ratio. As observed, the alachlor removal was significantly influenced by the molar ratio of ZVI to PS and the best alachlor removal was obtained at the molar ratio of 2:1 for ZVI to PS. Of note, the alachlor degradation well followed a pseudo-first-order kinetics pattern (R<sup>2</sup> > 0.95) with any particular ZVI dosage in 60 min (Fig. 1b). The overall rate law and the degradation efficiency for the alachlor degradation could be expressed as Eqs. S1 and S2.

The pseudo-first-order reaction rate constant increased from 0.0711 to 0.1271 min<sup>-1</sup> when the molar ratio of ZVI to PS increased from 0.5 to 2, but gradually decreased to 0.0671 min<sup>-1</sup> as the molar ratio further increased to 4. The significant enhancement in degradation efficiency appeared to be attributed to production of more active radical species after introduction of the catalyst [19]. Excess ZVI dosage likely provided too much Fe<sup>2+</sup> which could scavenge SO<sub>4</sub><sup>-</sup> produced in the ZVI +PS system (Eq. 5), leading to reduce the overall degradation efficiency. In general, the optimum

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