**Zero-valent iron (ZVI) activation of persulfate (PS) for degradation of Para-****chloronitrobenzene in soil**

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**Highlights**

* The p-CNB removal rate increased significantly from 10.8% to 90.1% with an increase of ZVI dosage from 0.1 mmol•g-1 to 1.0 mmol•g-1..
* The p-CNB removal increased with the decrease of initial solution pH and a removal efficiency of 85.3% was obtained.
* the ZVI-persulfate system showed more sufficient p-CNB removal capacity and the removal rate of p-CNB was 88.7%.

**1. Introduction**

Para-chloronitrobenzene (p-CNB) in soil has posed significant health risks because of its persistence and high toxicity. Chemical oxidation by means of persulfate (PS) has received considerable attention for organically contaminated groundwater and soil remediation. Recently, it has been found that Zero-valent iron (ZVI) or metal iron can activate persulfate at room temperature, and it can gradually release Fe2+ to produce sulfate radicals during a long time length, via reactions with water and oxygen in air. ZVI can restore Fe3+ to Fe2+ while reducing hydroxide precipitation during the oxidation. Meanwhile, ZVI is an alternative source of Fe2+ and can serve as an electron donor for the reaction. The objective of this study was to determine the feasibility of p-CNB polluted soil remediation by ZVI-persulfate systems.

**2. Methods**

The naturally contaminated soil of p-CNB were prepared for each batch experiment. Several sets of the experiments were conducted to determine the effects of various parameters on p-CNB degradation. Dynamics experiments were performed to study the difference between the removal of p-CNB by single persulfate, ZVI and ZVI-persulfate system. The reactions were carried out in 100 mL centrifuge tube. Reaction mixtures were obtained by taking an appropriate amount of 50 g contaminated soil and mixed with the 50 mL deionized water on a rotary shaker at 125 rpm and 25°C. During the experiment, 1.0 mL of solution sample was periodically withdrawn from each reactor with a glass syringe and then filtered through a 0.45 µm membrane for immediate analysis. The pH value was monitored by a pH electrode.

**3. Results and discussion**

The results of initial ZVI dosage suggest that the degradation efficiency was heavily influenced by the ZVI when the concentrations of persulfate and p-CNB were fixed. In this system, ZVI play two roles, reducing chloronitrobenzene to chloroaniline and providing Fe2+ for the activation of persulfate (Zhao et al. 2010). Higher initial ZVI dosage provided more active sites on ZVI surface to persulfate, and the persulfate was activated by the release of Fe2+ from Fe0 in the ZVI-persulfate system. Fe2+ is one of the strongest species that can catalyze persulfate to sulfate radicals, the Fe2+ is continuously supplied to the system to ensure the efficiency of degradation of p-CNB. However, at higher initial dosage (1.0 and 1.5 mmol g−1), the degradation rate was similar. Thus, for economic reasons, 1.0 mmol g−1 was chosen as the best dosage.

The removal rate was markedly increased when ZVI and persulfate coexist due to the generation of •OH and SO4−• in combine system. The increased ZVI dosages resulted in enhanced p-CNB degradation benefiting by increased activation of persulfate by ZVI. Combined with the results of SEM, the increase of ZVI could provide more reactive sites for the activation of persulfate, producing more SO4−• and increasing the efficiency of p-CNB degradation. The removal of p-CNB was advantageous in acid condition. At pH 3.0, 90.3% degradation was achieved in 8 h. The results of EPR showed that acidic conditions were beneficial to the activation of persulfate by ZVI to produce more sulfate radicals. In addition, acidic conditions reduce the precipitation of Fe2+ and Fe3+ facilitate reaction. MS analysis in combination with literature review of p-CNB degradation, intermediates identified in this work include p-chloroaniline, 1, 4-benzoquinone and 5-chloro-2-((3-chlorophenyl) diazenyl) phenol..

**4. Conclusions**

The p-CNB removal rate increased significantly from 10.8% to 90.1% with an increase of ZVI dosage from 0.1 mmol•g-1 to 1.0 mmol•g-1. The p-CNB removal increased with the decrease of initial solution pH and a removal efficiency of 85.3% was obtained at an initial pH value of 6.8 in this combined system. Compare three systems, the p-CNB removal rate in the persulfate oxidation system and the single ZVI system was 36.5% and 60.2%, while the ZVI-persulfate system showed more sufficient p-CNB removal capacity and the removal rate of p-CNB was 88.7%. Scanning electron microscopy (SEM) was adopted in order to observe the changes of surface morphology of ZVI before and after reaction. The results showed that with the reaction prolonging, the surface of ZVI changed from smooth to uneven. The generated radical species were identified by Electron paramagnetic resonance (EPR) technique, and the results showed that sulfate radicals (SO4-•) were predominant under acidic condition and hydroxyl radicals (•OH) were predominant under basic condition, revealing the potential reduction and oxidation reaction mechanism responsible for p-CNB removal by ZVI-Persulfate in soil..

**References [Calibri 10]**

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