



# Heterogeneous Fenton oxidation of 2,4-dichlorophenol using iron-based nanoparticles and persulfate system



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## HIGHLIGHTS

- Nanoscale zero-valent iron (nZVI) was used as the heterogeneous catalyst.
- Fe<sup>2+</sup>, nZVI, and nano-Fe<sub>3</sub>O<sub>4</sub> (nFe<sub>3</sub>O<sub>4</sub>) used as the catalysts were compared.
- nZVI generated sulfate radicals for oxidation of 2,4-dichlorophenol (DCP).
- nZVI has two functions – dechlorination and Fenton oxidation.

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## ABSTRACT

Nanoscale zero-valent iron (nZVI) has received attention for its potential applications in contaminated site remediation due to its reactivity. However, it is still unclear how nZVI acts as a catalyst to generate sulfate radicals in heterogeneous Fenton oxidation of 2,4-dichlorophenol (DCP). In this paper, various Fe materials such as Fe<sup>2+</sup>, nano-ZVI, and nano-Fe<sub>3</sub>O<sub>4</sub> (nFe<sub>3</sub>O<sub>4</sub>) were used as heterogeneous catalysts, where the removals of DCP by Fe<sup>2+</sup>, nZVI, and nFe<sub>3</sub>O<sub>4</sub> were 11.9%, 9.0%, and 5.5%, while the degradation of DCP in the presence of persulfate increased to 34.4%, 37.8%, and 5.8%, respectively. These data indicate nZVI can potentially generate sulfate radicals. UV, SEM, EDS and XRD demonstrated that changes on the surface of nZVI occurred owing to the Fe<sup>2+</sup> leaching. It was further observed that DCP degradation increased when the dosage of nZVI and persulfate concentration also increased. However, it decreased when the initial pH and DCP concentration increased. More than 98% of DCP degradation was achieved within 180 min under optimum conditions, but less than 40% of chemical oxygen demand (COD) was removed. The degradation of DCP follows the pseudo-first-order kinetics and it is a chemical control reaction with an activation energy of 91.5 kJ mol<sup>-1</sup>. Finally, a possible mechanism of DCP degradation using the nZVI/PS system was proposed.

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## 1. Introduction

Chlorophenols are characterized by high toxicity, high chemical oxygen demand (COD) and weak biodegradability, and hence they constitute a toxic group that is harmful to organisms and people's health at low concentrations. Apart from their noxious effects, chlorophenols impart taste and odor to water and create an oxygen demand in receiving waters [1,2]. In particular, 2,4-dichlorophenol (DCP) is a persistent contaminant frequently found in agricultural sites, water disinfected by chlorination, and pulp and paper mill

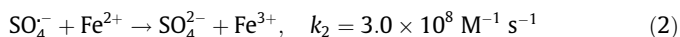
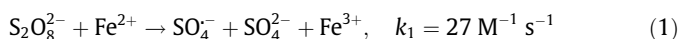
effluents. The main method for removing DCP has been either adsorption on activated carbon or oxidative destruction. However, the adsorption process using activated carbon only transfers DCP from one phase to another phase without degrading the DCP, while wet oxidation using high temperatures and pressures is not economically viable for remediation [3]. Advanced oxidation processes (AOPs) such as heterogeneous Fenton processes have been the focus of attention in recent years due to their potential effectiveness in the degradation and mineralization of organic contaminants [3,4].

The Fenton reagent (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>) is used for the oxidation of organic contaminants at low pH values (pH < 3.0) to avoid hydrolysis and precipitation of Fe<sup>3+</sup>, which is one of the limitations of the Fenton process for treating wastewater. Recently, persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) (PS, E<sup>0</sup> = 2.01 V) has emerged as an alternative oxidant

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because its activation results in the generation of strongly oxidizing sulfate-free radicals ( $\text{SO}_4^{\cdot-}$ ,  $E^0 = 2.6 \text{ V}$ ). The redox potential is higher than  $\text{H}_2\text{O}_2$  ( $E^0 = 1.76 \text{ V}$ ), giving it the potential to oxidize organic contaminants due to the advantages of high solubility and wide operative pH range [4,5]. The chemical activation of persulfate is generally carried out by using transition metal ions as activators, and ferrous ions are the most widely used. The generally accepted mechanism for ferrous ions activating persulfate involves the following steps [6,7]:



A report has proved that organic pollutants can be degraded efficiently by persulfate activated by microwave, ultraviolet, thermal, and photochemical methods [5]. For example, the degradation of amoxicillin using sulfate radicals under ultrasound irradiation can remove more than 98% COD [5]. Although these methods can achieve a high rate of COD removal, they need more energy and sophisticated facilities, which will increase costs and limit their application. Metal ions such as  $\text{Fe}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{V}^{3+}$  and  $\text{Ru}^{3+}$  were used as effective catalysts for Fenton oxidation of organic contaminants [8], and the reaction of persulfate with  $\text{Fe}^{2+}$  to generate sulfate-free radicals is the most preferable for environmental applications since other metal ions are toxic. However, the generation of sulfate-free radicals by the reaction of  $\text{Fe}^{2+}$  with persulfate is too fast to control, meaning less use of free radicals, and excessive amounts of iron ion need further treatment [1,2].

Nanoscale zero-valent iron (nZVI) due its due to size, large surface area, and high reactivity, is now considered useful for removing organic contaminants such as chlorophenols [9]. nZVI can also serve as a slow-releasing source of dissolved  $\text{Fe}^{2+}$  in the Fenton system, which will activate  $\text{H}_2\text{O}_2$  to produce hydroxyl-free radicals [10]. The nZVI-Fenton oxidation integrates nZVI reduction and Fenton oxidation is regarded as an effective process for degrading organic contaminants, where it is usually preceded by an nZVI reduction process [10–12]. Subsequently,  $\text{H}_2\text{O}_2$  reacts with the  $\text{Fe}^{2+}$  to generate hydroxyl radicals, which start the oxidation of an organic contaminant and its degraded products. The key issues associated with the conventional Fenton oxidation can be addressed by nZVI as a heterogeneous catalyst, i.e. the consumption of chemical reagents and the production of significant quantities of chemical sludge. Both of these processes entail increased operational costs.

nZVI used as a catalyst for heterogeneous Fenton-like oxidation of biocide 4-chloro-3-methyl phenol (CMP) has been reported, where the heterogeneous nZVI/ $\text{H}_2\text{O}_2$  system proved to be efficient and rapid when oxidizing CMP under neutral pH conditions. This is superior to commercial reductive iron/ $\text{H}_2\text{O}_2$  systems and provides a potential alternative and novel heterogeneous Fenton catalyst for environmental remediation [11]. Additionally, the sulfate radical is more stable than the hydroxyl radical and can be transported greater distances in the sub-surface where it can persist for weeks [13]. To date, the reactivity of nZVI used as a heterogeneous catalyst to generate a sulfate radical for oxidation for DCP has not been explored.

For these reasons, the degradation kinetic and mechanisms must be understood since nZVI/persulfate is a potential method for treating water [13]. Therefore, the main objectives of this study were to: (1) evaluate the feasibility of nZVI, nano- $\text{Fe}_3\text{O}_4$  (n $\text{Fe}_3\text{O}_4$ ) and  $\text{Fe}^{2+}$  for dechlorination of DCP and for activation of persulfate in oxidation of DCP; (2) determine the efficiency of Fenton oxidation of DCP using nZVI in various conditions; and (3) analyze nZVI

oxidation using various techniques such as SEM, EDX to elucidate the DCP degradation mechanism by nZVI/PS system.

## 2. Materials and methods

### 2.1. Materials and chemicals

nZVI particles less than 50 nm in size with a specific surface area of 40–60  $\text{m}^2/\text{g}$  and a purity of >99.5%, were purchased from Hongwu Nano Material Co. Ltd. (Guangdong, China). The n $\text{Fe}_3\text{O}_4$  particles less than 30 nm in size with a specific surface area of 50–70  $\text{m}^2/\text{g}$  and a purity of >99.9%, were purchased from Hongwu Nano Material Co. Ltd. (Guangdong, China). Sodium persulfate (PS) and Ferrous sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) were purchased from Guangdong Guanghua Chemical Factory Co. Ltd. (Guangdong, China). A solution containing DCP was prepared by dissolving DCP with deionized water to the desired concentration. All chemicals used in this study were of analytical grade and did not require further purification.

### 2.2. Characterizations

The surface morphology and elemental composition of freeze-dried powders of nZVI were analyzed by scanning electron microscopy (SEM) (JSM 7500F, Japan) with an operating voltage of 5 kV. The elemental loadings on the surface of nZVI before and after reaction were analyzed using INCA EDS (Oxford Instruments, UK) in conjunction with SEM. X-ray diffraction (XRD) patterns of nZVI powders were recorded operating at 40 kV and 40 mA. XRD signals were collected with diffraction angles ranging from  $10^\circ$  to  $80^\circ$  of  $2\theta$  with a step width of  $0.05^\circ$  and a counting time of 30 s per  $0.1^\circ$ . The solutions before and after reaction were measured using a UV Spectrophotometer (722 N, Shanghai, China) with wavelength ranging from 250 nm to 800 nm.

### 2.3. Batch experiments

To compare the degradation of DCP by various materials, batch experiments were carried out using  $\text{Fe}^{2+}$ , nZVI, and n $\text{Fe}_3\text{O}_4$  added to a solution of 30  $\text{mg L}^{-1}$  (15 mL) DCP on a rotary shaker in darkness. The temperature and rotary shaker speed were 298 K and 250 r/min, respectively. The initial pH of the DCP solution was adjusted by 1.0 mol/L  $\text{H}_2\text{SO}_4$  and 1.0 mol/L NaOH and pH was detected using a pH meter (PHS-3, Shanghai, China). Mixed solutions were filtered through 0.45  $\mu\text{m}$  membranes at different time intervals. Following this the filtrates were extracted by adding ethyl acetate ( $V_{\text{filtrate}}:V_{\text{ethyl acetate}} = 1:1$ ) as an extraction solvent to determine the residual concentration of DCP at 285 nm using the UV-752 spectrophotometer [14]. Chemical oxygen demand of the filtrates was detected by COD analyzer (Lian-hua Tech. Co. Ltd, China). The degraded products were identified by GC-MS (Agilent GC, USA) using a HP-5MS column (length 30 m, diameter 0.25 mm, thickness 0.25 mm) at temperature programmed mode from 60 to 280  $^\circ\text{C}$  (26 min) [1]. Concentrations of DCP were determined based on the calibration curves and accordingly the removal efficiency ( $R(\%)$ ) of DCP was calculated using the following equation:

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \quad (3)$$

where  $R(\%)$  represented the DCP removal efficiency,  $C_0$  (mg/L) was the initial concentration of DCP in the solution, and  $C_t$  (mg/L) stood for the concentration of DCP at  $t$  min.

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