Application of Zero-Valent Iron Nanoparticles for Diclofenac Removal

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Abstract: Application of zero-valent iron nanoparticles (nZVI) for DCF removal and its mechanism were discussed. With the solids concentration of 0.5 g/L nZVI, more than 30% of DCF could be removed rapidly in 5 min. The pH value and dissolved oxygen (DO) were the important factors of DCF removal by nZVI. Under acidic condition, the DCF removal efficiency was relatively high, during to the oxidation of Fenton-like system. Under neutral and alkaline conditions, the DCF removal efficiency was low, because of the low capacity adsorption of the FeOOH-shell. This study has provided the basis for DCF removal by nZVI-Fenton-like system.

1 INTRODUCTION

Trace level of pharmaceuticals have been reported in natural environments because of the widespread use (Alvarino et al., 2015; Alvarino et al., 2014; Liu et al., 2014). Diclofenac (DCF), a non-steroidal anti-inflammatory drug, is widely applied as a pain killer, which has been one of the most frequently detected pharmaceuticals in surface water and groundwater, due to its' poor treatability in municipal sewage treatment plants (STPs) (Castiglioni et al., 2006; Vieno and Sillanpää, 2014). Studies have shown that DCF residues and their metabolites in water bodies can produce biotoxic effects on different living organisms in water environment, which can lead to microbial resistance and cross resistance. DCF in effluent from STPs may also cause downstream aquatic and terrestrial ecology. The toxic effects of the system pose a great threat to the environment and human health (Stülten et al., 2008; Dai et al., 2009; Boxall et al., 2003). Therefore, DCF removal technologies need to be further discussed.

Nanoscale zero-valent iron (nZVI) has been investigated as a green in-situ tool for the degradation of both organic and inorganic contaminants for more than 10 years (Liang et al., 2014; Han et al., 2016; Hwang et al., 2015; Sheng et al., 2016; Li et al., 2015) The successful application of nZVI in organic contaminants degradation was explored and reported by many researchers (Xia et al., 2014; Machado et al., 2013; Noradoun et al., 2003).

In this study, the DCF removal mechanism by nZVI was investigated based on the operation conditions, including nZVI solids loading, pH value and dissolved oxygen (DO).

2 MATERIALS AND METHODS

2.1 Chemicals and Materials

Diclofenac sodium ($C_{14}H_{10}Cl_2NNaO_2$, 99%), ferric chloride anhydrous ($FeCl_3$, 99%), sodium borohydride ($NaBH_4$, 98%), and sodium hydroxide (NaOH, 99%) were obtained from Aladin. Hydrochloric acid (HCl, 37%) was purchased from Sinopharm Chemical Reagent Shanghai Co., Ltd. Methanol (HPLC grade), acetonitrile (HPLC grade), and acetic acid (HPLC grade) were obtained from Sigma-Aldrich. All chemicals were used without further purification.

Deionized water was prepared with a Milli-Q water purification system (Millipore, Bedford, MA, USA). Microporous membranes (0.22 μm×50 mm) were obtained from CNW (Germany).

2.2 Synthesis of NZVI

The nZVI was synthesized according to the method of liquid-phase reduction of ferric trichloride by sodium borohydride (Sun et al., 2006). The sodium borohydride (NaBH4, 0.5 M) and ferric chloride anhydrous (FeCl$_3$, 0.1 M) with the volume ratio of 1:1 were vigorously reacted. Then the generated jet-black nZVI particles were collected through vacuum filtration and respectively washed with deionized water for three times. Finally, fresh nZVI particles were stored in deionized water by blowing nitrogen at 4 °C.

2.3 Characterization of NZVI

The high-resolution transmission electron microscopy (TEM) observation was performed using a JEOL JEM 2011 HR-TEM operated at 200 kV with an INCA EDS system.

2.4 Batch Experiments

A 1.0 g/L stock solution of DCF was prepared with deionized water. Uptake reactions were initiated by the addition of nZVI particles into 150 mL DCF solution without pH adjusted. The nZVI loading concentration in the solution was 0.1, 0.2, 0.3, 0.4, 0.5, 0.8, 1.0, and 2.0 g/L, respectively, at a DCF concentration of 1 mg/L. After mixing, the reactors were continuously shaken for 2 hours on an orbital shaker. The optimum loading of nZVI was obtained by comparing the results of the above experiments. All the experiments were performed in triplicate.

To investigate the effect of solution pH on DCF removal by nZVI, the initial solution pH was adjusted from 3 to 9 with the initial DCF concentration at 1 mg/L by small amounts of HCl or NaOH solution. Then water samples with different pH values were applied to 0.5 g/L nZVI. All the experiments were performed in triplicate.

The effect of oxygen on DCF removal by nZVI was investigated under the DO-limiting with the optimum nZVI loading and pH value. The oxygen-limiting condition was established by blowing nitrogen over the solution with nitrogen evaporator (N-Evap-111, Organomation Associates, Inc.).

Nitrogen blowing time was kept at least 15 minutes to ensure DO less than 0.5 mg/L. The concentration of DO was monitored by dissolved oxygen meter (HQ-30D, Hach Co.). The initial solution pH value was controlled at 3 and 5. Reaction time was 5, 10, 15, 30, 60, 90 and 120 min, respectively. All the experiments were performed in triplicate.

All solution samples were filtered with 0.22 μm membrane before analysis. The concentrations of DCF in the sample were determined by high performance liquid chromatography (HPLC, Agilent 1260) equipped with an EC-C18 packed column (Agilent). Initial mobile phase of the analysis was a mixture of 30% deionized water (containing 0.1% CH$_3$COOH) and 70% acetonitrile. Final mobile phase ratio was 75%: 25%, within 5 min. The samples were measured at a rate of 1.0 ml/min at a wave length of 275 nm. After measurement, methanol was used to clean the EC-C18 column. All the experiments were performed in triplicate.

2.5 Statistical Analyses

One-way ANOVA was performed to assess the experimental data. Statistical significance was evaluated at $p<0.05$ level. The SPSS software (Ver 20.0) was applied for all statistical analyses.

3 RESULTS AND DISCUSSION

3.1 Characterization Of NZVI

Fresh nZVI particles were analyzed by transmission electron microscopy (TEM). The iron particles were typically less than 100 nm in diameter. Figure 1 showed the smooth sphere surrounded the core structure, indicated that oxidation happened on the surface.
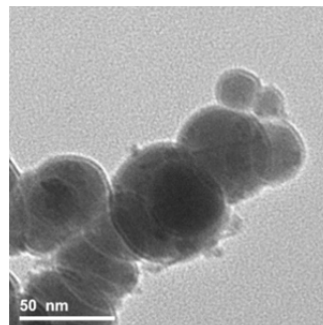

Figure 1: The TEM analysis of fresh nZVI particles.

3.2 DCF Removal By NZVI

Different solids concentration was prepared for the uptake experiments at the ranging from 0.1 to 2 g/L nZVI at a DCF concentration of 1 mg/L, respectively for 2 h. The solution kept the initial pH value of 6.7 without adjusting. As shown in Figure 2, with the increase of nZVI loading, the removal efficiency of DCF was increased. When nZVI loading was higher than 0.4 g/L, the removal efficiency was over 20%. Thus, we defined 0.5 g/L loading as the optimum solids concentration for 1 mg/L DCF treatment. And the loading was adopted in the subsequent experiments.

The nZVI particles have been widely applied in environment remediation due to its complex contaminant removal pathways, including adsorption, complexation, (co)precipitation and surface-mediated chemical reduction (Miehr et al., 2004). As its structure and characteristic, surface-mediated chemical reduction is likely not the reason of DCF removal by nZVI.
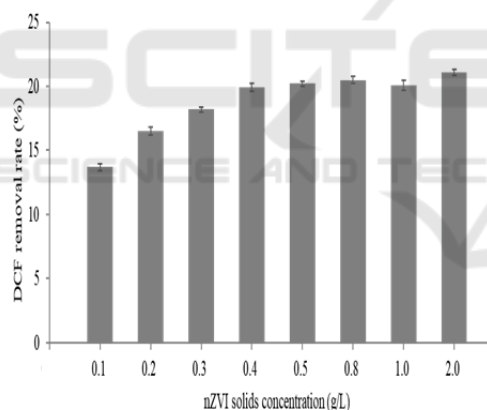
Figure 2: Effect of nZVI solids concentration on DCF removal.

3.3 Effect of Solution PH

The pH is an important factor for DCF removal by nZVI. DCF is a weak acid with a pKa of 4, and as shown in Figure 3, DCF has the carboxylic group and the NH group, which can be act either as proton donor or proton acceptor, so that it possesses a Lewis acid-base character (Žilnik et al., 2007). When the pH of the solution is less than 4, DCF carries positive charge, and negative charge when the pH of the solution is greater than 4.
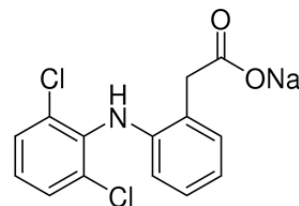
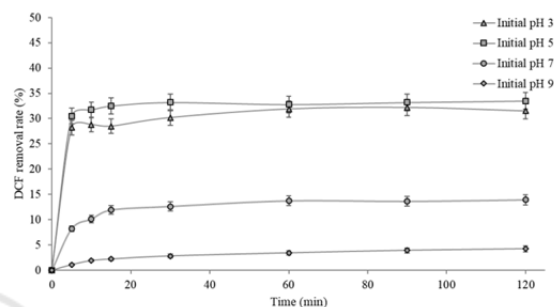Figure 3: Molecular structure of DCF.
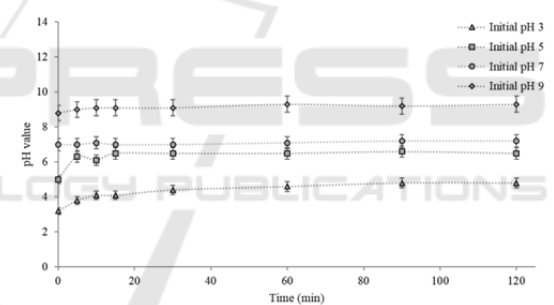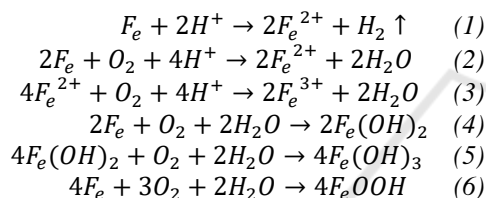
Figure 4: Effect of pH value on DCF removal.

Figure 5: Variation of pH value during DCF removal.

The freshly prepared 0.5 g/L nZVI particles were injected into the sample with 1 mg/L DCF concentration for 2 h. Figure 4 has shown the uptake results at various pH conditions. The removal efficiency in acidic condition was much higher than neutral and alkaline. In acidic condition, the removal efficiency was rapidly reached 30% within 5 min. While under neutral and alkaline conditions, the reaction was carried out relatively slow. In condition of initial pH 5, the best removal result was obtained. The removal trends were similar in condition of initial pH 5 and pH 3. While in condition of initial pH 9, the uptake rate was less than 5% after 2 hours' reaction. The variation of pH in different initial values was shown in Figure 5. A small increase in pH value was observed under neutral and alkaline

conditions. The pH increased relatively under acidic condition, but still below 7.

The nZVI particles were corroded by acid and oxygen. During the corrosion of iron by acid, ferrous iron and ferric iron solution could be generated based on Equations (1), (2) and (3) (Sun et al., 2006; Kishimoto et al., 2011). The present of H^+ inhibited the formation of iron (oxy)hydroxide, resulting in the low contribution of adsorption. In neutral and alkaline conditions, the FeOOH-shell could form based on Equations (4), (5) and (6) (Sun et al., 2006; Kishimoto et al., 2011; Hœrléet al., 2004). According to the equations, the nZVI particles carry positive charge in condition of acid, and negative charge in condition of alkali.

$$F_e + 2H^+ \rightarrow 2F_e^{2+} + H_2 \uparrow \quad (1)$$
$$2F_e + O_2 + 4H^+ \rightarrow 2F_e^{2+} + 2H_2O \quad (2)$$
$$4F_e^{2+} + O_2 + 4H^+ \rightarrow 2F_e^{3+} + 2H_2O \quad (3)$$
$$2F_e + O_2 + 2H_2O \rightarrow 2F_e(OH)_2 \quad (4)$$
$$4F_e(OH)_2 + O_2 + 2H_2O \rightarrow 4F_e(OH)_3 \quad (5)$$
$$4F_e + 3O_2 + 2H_2O \rightarrow 4F_eOOH \quad (6)$$

There could be three main processes for the DCF removal by nZVI: (1) pH in 7-9, both DCF and nZVI carried negative charge, the physical adsorption of FeOOH-shell was the leading reaction; (2) pH in 4-7, DCF carried negative charge, while nZVI carried positive charge, the chemical adsorption might be one of the leading roles; (3) pH in 3-4, both DCF and nZVI carried positive charge, and adsorption could not be the leading roles in acid condition, but in this process high DCF removal efficiency was obtained, so oxidation of Fenton-like system was the leading role, in which the corrosion of iron by acid caused hydrogen peroxide to form, as shown in Equation (7) and (8) (Joo et al., 2004).

$$F_e + O_2 + 2H^+ \rightarrow 2F_e^{2+} + H_2O_2 \quad (7)$$
$$F_e^{2+} + H_2O_2 \rightarrow F_e^{3+} + OH \cdot + OH^- \quad (8)$$
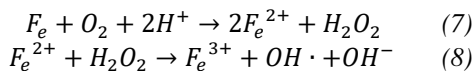
3.4 Effect of Dissolved Oxygen

For further study the DCF removal mechanism by nZVI particles, the effect of dissolved oxygen (DO) was examined.

The freshly prepared 0.5 g/L nZVI particles were injected into the solution with 1 mg/L DCF concentration for 2 h. The DO in system was reduced to less than 0.5 mg/L by blowing nitrogen. As shown in Figure 6, under DO-limiting condition,

both in pH 3 and in pH 5, the removal extent of DCF was obviously reduced. The low efficiency of DCF removal in pH 5 indicated that chemical adsorption was not the leading role in pH 4-7.
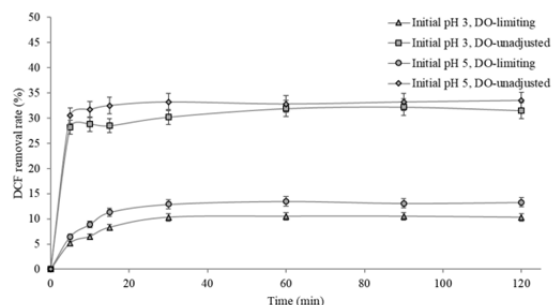

Figure 6: Effect of DO on DCF removal.

3.5 Removal Mechanism

The pH and DO were the main limitation factors. In different pH range, DCF showed different surface charges, and nZVI showed different surface structures. In Fenton-like system, DO was the main donor of hydroxyl radical, and H^+ could corrode iron particles to supply ferrous iron and ferric iron solution. Figure 7 showed the main DCF removal mechanisms by nZVI: (1) in pH 3-7, oxidation of Fenton-like system was the leading role; (2) in pH 7-9, physical adsorption of the FeOOH-shell was the leading role, and less than 5% removal efficiency showed that the capacity of nZVI adsorbed on DCF was very low.
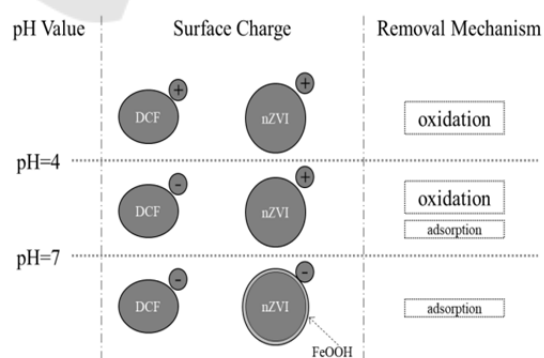

Figure 7: Schematic diagram of DCF removal mechanism by nZVI.

4 CONCLUSIONS

This study demonstrated that nZVI particles had a removal effect on DCF. In pH 5, with the solids concentration of 0.5 g/L nZVI, more than 30% of DCF could be removed rapidly in 5 min. The pH and DO were the main limitation factors. Under acidic condition, the DCF removal efficiency was relatively high, during to the oxidation of Fenton-like system. Under neutral and alkaline conditions, the DCF removal efficiency was low, because of the low capacity adsorption of the FeOOH-shell. This study has provided the basis for DCF removal by nZVI-Fenton-like system. The follow-up study can optimize the reaction conditions and enhance the Fenton-like reaction to improve the removal efficiency of DCF.

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