2,4-Dichlorophenoxyacetic acid (2,4-D) degradation promoted by nanoparticulate zerovalent iron (nZVI) in aerobic suspensions

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ABSTRACT

Reactive species generated by Fe^0 oxidation promoted by O_2 (catalyzed or not by ligands) are able to degrade contaminant compounds like the herbicide 2,4-dichlorophenoxyacetic acid. The degradation of 2,4-D was influenced by the concentrations of zero valent iron (ZVI) and different ligands, as well as by pH. In the absence of ligands, the highest 2,4-D degradation rate was obtained at pH 3, while the highest percentage degradation (50%) was achieved at pH 5 after 120 min of reaction. Among the ligands studied (DTPA, EDTA, glycine, oxalate, and citrate), only ethylenediaminetetraacetic acid (EDTA) and *diethylenetriaminepentaacetic acid* (DTPA) significantly enhanced oxidation of 2,4-D. This increase in oxidation was observed at all pH values tested (including neutral to alkaline conditions), indicating the feasibility of the technique for treatment of contaminated water. In the presence of EDTA, the oxidation rate was greater at pH 3 than at pH 5 or 7. Increasing the EDTA concentration increased the rate and percentage of 2,4-D degradation, however increasing the Fe^0 concentration resulted in the opposite behavior. It was found that degradation of EDTA and 2,4-D occurred simultaneously, and that the new methodology avoided any 2,4-D removal by adsorption/coprecipitation.

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1. Introduction

Zerovalent iron (ZVI) is widely used as a reactive material in permeable barriers employed for groundwater remediation, whereby inorganic contaminants (such as Cr(VI) or NO_3^-) and organochlorine compounds (such as trichloroethylene or perchloroethylene) can be reduced to less toxic products (Katsenovich and Miralles-Wilhelm, 2009; Su and Puls, 2004), that is possible due to the low redox potential of ZVI ($E_{red}^0 = -0.44$, vs SHE) under anoxic conditions.

However, in the presence of oxygen, a reducing system can be converted into an oxidizing system, and the reductive power of iron can be used for oxidative reactions. Oxygen reacts with ZVI generating O_2^{2-}, which can react further through two routes (Scheme 1). The usefulness of this process for oxidative degradation of contaminants depends on the extent to which the branching process favors hydroxyl radical formation (route II), as first reported by Noradoun et al. (2003) and Roy et al. (2003).

The reduction of O_2 proceeds through a $4e^-$ pathway on bare iron, with production of H_2O_2 as an intermediate, and a $2e^-$ pathway, with formation of H_2O_2 as product, on a passivated iron layer. The most likely rate-determining step on bare iron involves the formation of O_2^-, while on a passive layer the reaction rate is determined by chemisorption of oxygen (Jovancicevic and Bockris, 1986).

Using the oxidative power of the Fe^0/O_2 system, Noradoun et al. (2003) observed the complete degradation of 4-chlorophenol and pentachlorophenol in the presence of metallic iron, EDTA and O_2. All three reagents were shown to be essential for contaminant oxidation, and the formation of an Fe(II)-EDTA complex was proposed to be responsible for the reaction with hydrogen peroxide, in a modified Fenton reaction. The same was reported by Sanchez et al. (2007) during phenol degradation. On the other hand, Feitz et al. (2005), studying the influence of EDTA on oxidation of benzoic acid and molinate, observed that degradation occurred even in the absence of EDTA, albeit to a lesser extent. This same research group compared the oxidation rates of compounds with different affinities for the iron surface, such as aniline and phenol, and investigated the formation of oxidizing species, such as the hydroxyl radical. However, no relationship was observed between the charge of the compound studied and the relative rate of oxidation, so a direct interaction between the metal surface and the contaminant was considered to be of low importance for degradation since even weakly adsorbed

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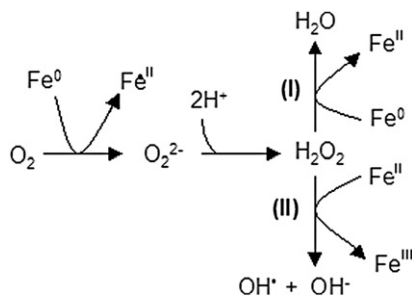
Scheme 1. Oxygen reduction promoted by reaction with ZVI.

compounds were degraded, indicating that hydroxyl radical generation, as well as contaminants degradation, occurs in the bulk solution (Joo et al., 2005).

Degradation of different kinds of pollutants has been conducted by use of ZVI in aerobic conditions as, for example, the pharmaceutical diazepam (Bautitz et al., 2012) and anthraquinone dyes (Chang et al., 2009). However the adsorption/coprecipitation process has usually been neglected leading to a possible TOC and COD overestimation.

Since the use of ZVI to oxidize pollutant compounds is a fairly new technology, there is a lack of information concerning the application of ZVI nanoparticles for environmental remediation as, for example, the effect of using different iron ligands to enhance the process efficiency or which is the role of adsorption/coprecipitation phenomenon on contaminants removal or yet, the effect of keeping the system pH at known values. This work therefore presents some results about parameters that have been uncovered by literature using for that the degradation of the model contaminant 2,4-D, which is the second pesticide more used in Brazil and has the advantage of being non volatile.

The parameters investigated included the pH of the medium, the presence of different iron ligands (glycine, EDTA, DTPA, citrate and oxalate), different concentrations of iron and EDTA, and the effect of air bubbling. A dissolution methodology was also developed in order to avoid overestimation of mineralization.

2. Materials and methods

2.1. Reagents and particle characterization

2,4-D (99%, Sigma–Aldrich), EDTA (analytical grade, Mallinckrodt), 2,4-dichorophenol (2,4-DCP) (99%, Acros), and all other reagents were used without any special purification. ZVI nanoparticles were prepared by reduction of ferrous iron using sodium borohydride, according to the procedure of Ponder et al. (2000). After synthesis, the nanoparticles were stored refrigerated in nitrogen-saturated water slurry (5% w/v) for at most one week.

The sizes of individual particles were determined by Field Emission Gun – Scanning Electron Microscopy analysis (FEG-SEM), using a JEOL Model JSM7500F instrument.

2.2. Chemical analysis

The decay of 2,4-D and EDTA concentrations, and changes in the chemical compositions of the solutions, were measured using a Shimadzu HPLC system equipped with a Phenomenex Luna C_{18} column (4.6 mm $\times$ 25 cm) and a PDA detector set at 230 nm. Determination of 2,4-D and 2,4-dichlorophenol employed isocratic elution with a mobile phase consisting of water (35%) and methanol containing 1% acetic acid (65%), at a flow rate of 1.0 mL min^{-1}. The analysis of EDTA followed the methodology described by Venezky and Rudzinski (1984).

Mineralization of the compounds was evaluated by total organic carbon analysis (TOC), using a Shimadzu TOC 5000A instrument, immediately after sample preparation.

2.3. Batch experimental setup

Experiments were carried out at room temperature (25 $\pm$ 2 °C) under air bubbling (using an aquarium pump and rate of 35 L h^{-1}) and magnetic stirring at 530 rpm. The pH was controlled when necessary to within $\pm$0.5 pH units, by addition of H_2SO_4 2 M. The degradation experiments were conducted in a 300 mL beaker, using a total suspension volume of 50 mL. The required quantity of a 5% (w/v) ZVI suspension was added to the beaker, with water, and sonicated (60 Hz) for 1 min to disperse the particles. Appropriate volumes of ligand and 2,4-D solutions were then added to the ZVI suspension under magnetic stirring and air bubbling.

A new procedure was adopted in order to avoid overestimation of degradation due to adsorption of organic compounds onto the Fe^0 or iron oxy/hydroxy particles. In a first step, 5 mL aliquots of reaction suspension were withdrawn, raised the pH to 11 (to quench the reaction) and centrifuged at 3000 rpm for 4 min. The supernatant was then transferred to a 10 mL volumetric flask and kept in a fridge while the solid was dissolved by addition of dilute H_2SO_4 solution, with sonication. The dissolved iron was then added to the volumetric flask, and the pH was adjusted to 2 for subsequent HPLC and TOC analyzes.

3. Results and discussion

3.1. ZVI characterization

The FEG-SEM analyses showed that the sizes of individual particles ranged from 25 to 120 nm, with an average of 75.6 nm, and that there was formation of aggregates larger than 1 μm (Supplementary material), what is in accordance with the followed methodology of preparation (Ponder et al., 2000).

3.2. Influence of the experimental procedure on degradation

The mechanism of contaminant removal by Fe^0/H_2O has been discussed in the literature (Noubactep, 2010). The great majority of reports concerning ZVI suggest the existence of a purely reduction or oxidation mechanism, depending on conditions, with no mention of an adsorption/coprecipitation process. However, passivation of the surface of metallic iron is well known, as well as the sorption of many different organic compounds onto iron oxides (Clausen and Fabricius, 2001; Kung and McBride, 1991). It was therefore important to ensure that the data reported here resulted from chemical oxidation, rather than any other process.

It is known that 2,4-D, at pH values lower than 5 (Clausen and Fabricius, 2001), and chlorophenols adsorb physically and chemically to the surfaces of iron oxides (Kung and McBride, 1991) so an experimental procedure was developed based on dissolution of the remaining Fe^0 and iron oxides in dilute sulfuric acid in order to avoid overestimation of degradation and mineralization rates.

The effect of adsorption of 2,4-D onto Fe^0 and iron oxide surfaces was not significant (Fig. 1A). However, the mineralization results provided evidence of adsorption/coprecipitation (Fig. 1B), emphasizing the importance of adopting a procedure to avoid overestimation of mineralization. Once the final pH of the reaction mixture has never reached values lower than 4.6 (Fig. 2A), and given that the pKa of 2,4-D is 2.64 (Clausen and Fabricius, 2001), the herbicide remains ionized and therefore is less liable to sorption. On the other hand, 2,4-dichlorophenol, the first intermediate identified during 2,4-D oxidation, has a pKa of 7.85 (Kung and