Hydroxyl radical generation linked with iron dissolution and dissolved oxygen consumption in zero-valent iron wastewater treatment process

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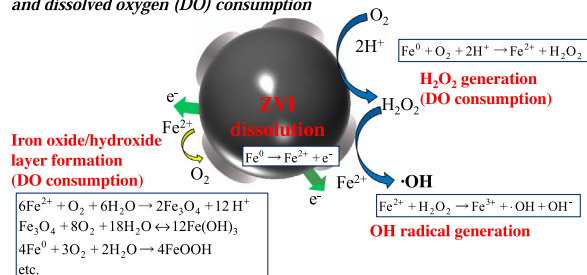
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HIGHLIGHTS

- The OH radical generated by zero-valent iron (ZVI) was systematically examined.
- The iron dissolution dominantly controlled OH radical generation by ZVI.
- The OH radical generation was also largely affected by the passive layer formation.
- The amount of generated OH radical increased with ZVI dosage and decreased with pH.
- The OH radical generation by ZVI could be simulated by the proposed kinetic model.

GRAPHICAL ABSTRACT

ABSTRACT

In zero-valent iron (ZVI) wastewater treatments, organic pollutants are degraded by hydroxyl radical (OH radical) generated via the Fenton reaction besides by the reductive reaction. The generation of OH radical is initiated by the dissolution of ZVI. The strong linkage of OH radical generation by ZVI with eluted ferrous ion and dissolved oxygen (DO) through the iron dissolution and the formation of passive iron oxide/hydroxide layer on the ZVI surface was found. While OH radicals were gradually generated by microscale ZVI (mZVI) until the termination of iron dissolution, the OH radical generation by nanoscale ZVI (nZVI) was very quick at the initial phase, subsequently slowed down and terminated. Although the rate of OH radical generation with nZVI was much faster than that with mZVI, the amount of generated OH radical with nZVI was less than mZVI under the same iron dosage conditions. With increasing ZVI dosage and controlled solution pH value, the amount of generated OH radical for both mZVI and nZVI increased and decreased, respectively. For nZVI under the oxic condition, the quick depletion of DO at the initial phase accompanied with the sequential recovery to the saturation concentration was found. A reaction kinetic model was developed to quantify a linkage of OH radical generation with the iron dissolution and the formation of passive iron oxide/hydroxide layer on the ZVI surface. The linkage could be reasonably simulated by the proposed kinetic model with the correlation coefficient of >0.828.

1. Introduction

Zero-valent iron (ZVI) particulates have been extensively used for the treatment of contaminated groundwater and wastewater since they are inexpensive and environmentally friendly strong

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reducing agents [1–4]. It is generally accepted that four mechanisms, reductive degradation, oxidative degradation, precipitation and adsorption, are responsible for removal of pollutants by ZVI (Fig. 1) [2,3]. ZVI particulates are composed of the core providing reducing power for reactions and the shell consisting of iron oxides and hydroxides which offer sites for adsorption and chemical complex formation. In aquatic systems, a passive layer consisting of iron oxides and hydroxides is formed on ZVI surface as a result of oxidation of metallic iron [2,5–7]. In our previous study [8], XRD patterns confirmed the formation of iron oxides and hydroxides such as $FeOOH$, Fe_3O_4 and Fe_2O_3 on the surface of ZVI in the oxic aqueous solution. The passive iron oxide/hydroxide layer on the ZVI surface causes a decrease in reactivity of ZVI. On the other hand, it enhances adsorption and precipitation. Therefore, the core-shell structure is very important to elucidate the reactivity of ZVI for various wastewater treatment processes. While the elution of iron ions promotes reductive degradation and oxidative degradation or OH radical generation, the formation of iron oxide/hydroxide layer encourages adsorption and precipitation. They compete with each other and their competitive superiority strongly depends on solution pH. Nevertheless, very little quantitative information on the mechanisms for removal of pollutants by ZVI is available in the literature. The reductive degradation is very effective but sometimes it is not capable of mineralization of organic pollutants. On the other hand, the oxidative degradation, in which hydroxyl radical (·OH) being strong, non-selective and highly reactive oxidant plays a significant role, has potential for mineralization of organic pollutants [9–15]. However, the contribution of oxidative degradation by ZVI is still indistinct. The pollutants can be more effectively degraded by the oxidative pathway besides the reductive degradation in oxic solutions. To date, little systematic information on the generation of OH radical by ZVI is available whereas the potential roles of OH radical in ZVI treatment under the oxic condition have been pointed out. This study focused on the OH radical generation dominating the oxidative degradation by ZVI.

In this study, the OH radical generation rate by ZVI in the oxic condition was measured using the coumarin fluorescence probing technique, which has been widely used to estimate the amount of generated OH radical [16–18] and is more rational for measurements of OH radical concentration as compared with the techniques based on the oxidation of methanol, ethanol, 2-propenol and benzoic acid as probe components [11,14].

Although several studies in the literature have concerned the behaviors of Fe ions in the OH radical generation process [12,14], the change in dissolved oxygen (DO) playing important roles in

the OH radical generation and the formation of passive iron oxide/hydroxide layer on ZVI surface has been scarcely paid attention.

Iron dissolution initiates OH radical generation by ZVI in aqueous solutions (Fig. 1). An electrochemical corrosion of ZVI provides electrons for the reduction of pollutants.

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \tag{1}$$

In both oxic and anoxic conditions, Fe^{2+} is a primary product from the aqueous corrosion of ZVI. In anoxic conditions, iron corrosion is written as [2,5]:

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \tag{2}$$

In the absence of DO, ZVI can react with H_2O to form soluble Fe^{2+} and then iron oxides and hydroxides as described below.

The reductive degradation of organic pollutants adsorbed onto the ZVI surface is induced by the electrons emitted through ZVI corrosion. In the anoxic condition, the reductive degradation dominates the degradation of pollutants by ZVI.
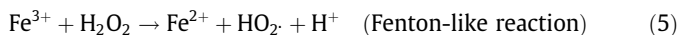
In oxic solutions, iron corrosion under acidic conditions generates hydrogen peroxide besides Fe^{2+} [3,11].

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \tag{3}$$
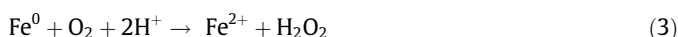
H_2O_2 generated by Reaction (3) reacts with Fe^{2+} and produces highly reactive hydroxyl radical.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \quad \text{(Fenton reaction)} \tag{4}$$

The regeneration of Fe^{2+} takes place by the following reactions [5,7,13,17]:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\cdot + H^+ \quad \text{(Fenton-like reaction)} \tag{5}$$

$$2Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+} \tag{6}$$

The iron redox cycling consisting of oxidation of Fe^{2+} and reduction of Fe^{3+} is established by Reactions (4)–(6). The established iron redox cycle promotes OH radical generation. The oxidative degradation by OH radical generated in the oxic condition may strongly facilitate the mineralization of organic pollutants. Incidentally, the oxidation potential of perhydroxyl radical is rather weak as compared with that of the hydroxyl radical [8].

The formation of iron oxide/hydroxide layer on the ZVI surface occurs simultaneously as the dissolution of ZVI progresses. The formation of iron oxide/hydroxide layer includes many reactions such as follows [1,3,5]:
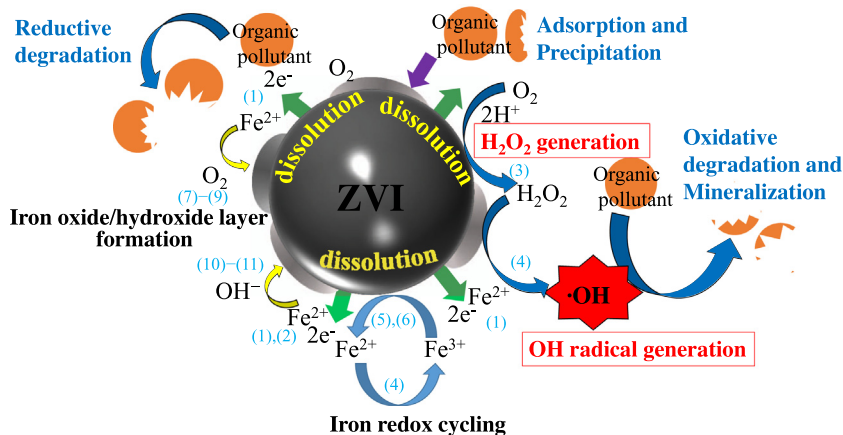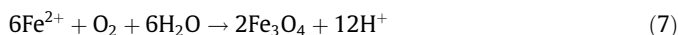
$$6Fe^{2+} + O_2 + 6H_2O \rightarrow 2Fe_3O_4 + 12H^+ \tag{7}$$

Fig. 1. Mechanisms in removal of organic pollutants by ZVI (The numbers in the figure represent Reaction Numbers in the text).