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Oxalate-enhanced reactivity of nanoscale zero-valent iron under different conditions of O_2, N_2 or without aeration

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ABSTRACT

Being that the influence of organic ligands on contaminant removal by nanoscale zero valent iron (nZVI) has been explored in quite a few studies, there is little information on reaction mechanisms of the ZVI-ligand system under different aeration conditions. The degradation of nitrobenzene (NB) by nZVI-oxalic acids (OA) was investigated under N_2, O_2 and without aeration conditions. From the findings, it was evident that OA dramatically improved NB degradation by nZVI with all of the aeration conditions. Approximately 100% of NB was degraded by nZVI-OA + N_2 system after 60 min of reaction, followed in effectiveness by nZVI-OA + without aeration (95%) as well as nZVI-OA + O_2 (85%). Operation parameters including OA concentration and pH had significant effect on the removal of NB in the nZVI-OA system. 3 mM OA concentration and pH 3.0 were found to be favourable. The Fe^{2+}, total dissolved iron concentrations, pH and ORP values in the nZVI-OA systems had also been monitored. Intermediates and trapping experiments showed that reduction played a fundamental role in the NB degradation by nZVI-OA under N_2 or without aeration conditions. The formation of $Fe(OA)^0$ and $Fe(OA)_2{}^{2-}$ complexes had lower standard ORP, which could improve the strength of reductant in the systems, and thus resulting in an increased degradation efficiency of NB by nZVI-OA + N_2. Under O_2 aeration condition, the NB degradation process could be regarded as an oxidation. In the meantime, OA promoted the production of reactive oxidants species by speeding up the oxidation rates of Fe^{2+} by O_2 and H_2O_2. Summarily, the improved reactivity of nZVI was largely as a result of the strong complexation ability of OA.

1. Introduction

Using ligands to enhance the reactivity of zero valent iron (ZVI or Fe^0) was a significantly scientific discovery for the treatment of organic and inorganic pollutants [1–4]. It has been reported that the transformation of Cr(VI), phenol and aromatic compounds by Fe^0 was enhanced by ethylenediaminetetraacetic acid (EDTA) addition [2,4]. These studies, mainly focusing on the ligands-enhanced degradation rates of Fe^0/dissolved oxygen (DO) system, indicated that more reactive oxidant species (ROS) were produced through an enhanced Fenton-like oxidation [5]. For instance, the addition of oxalate, nitrilotriacetic acid or EDTA to the O_2- containing solution of nanoscale zero valent iron (nZVI) could immensely improve oxidant production by restraining iron precipitation and by accelerating the ferrous iron oxidation rates [3]. Nevertheless, little attention has been paid to the ligand-Fe^0 system under other aeration conditions like N_2 and air. Even though Gong et al. noted that citric acid (CA) could promote reactivity of bismuth-iron system under both aerobic and anaerobic conditions, only the degradation mechanism of 4-chlorophenol with Bi/Fe^0-CA + O_2 was suggested. The authors regarded more ROS to have been produced under both O_2 and N_2 conditions according to the ligand function of CA with Fe^{3+}, as illustrated in Eqs. (1)-(4)

$$Fe(II) + \bullet O_2{}^- + H^+ \rightarrow Fe(III) + H_2O_2 \tag{1}$$

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + \bullet OH \tag{2}$$

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + H^+ + \bullet HO_2 \tag{3}$$

$$Fe(III) + CA \rightarrow Fe(III)(CA) \tag{4}$$

Evidently, H_2O_2 was changed from $^\cdot O_2{}^-$, and was then involved in the following process of ROS ($^\cdot$OH and $^\cdot HO_2$) production. Less certain is how to produce abundant H_2O_2 under the anaerobic conditions. While in the Fe^0-oxalic acids (OA) + N_2 system, it was indicated that OA improved the pentachlorophenol dechlorination by nZVI as a result of its strong ferrous ions chelating and pH buffering properties [6].

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Short-chain organic acids (SOAs) with one to three carboxylic groups including malic, oxalic and citric acids are some examples of the common organic ligands from biological activities [6–8]. As natural products, they occur commonly in the environment and take part in chemical processes through complexation and ligand exchange reactions. Despite enhancing the reactivity of Fe^0, oxalate and citrate were also found to decrease nitrate reduction rates by blocking the Fe^0 reactive sites [7]. It is shown that organic ligands could either promote or inhibit Fe^0 reactivity through adsorption and complexation with the iron surface.

Regardless of some studies having been reported on the Fe^0-SOAs system, the role of SOAs in pollutants removal by Fe^0 under diverse aeration conditions has not systematically been examined. As well, the respective mechanisms have not been completely clarified. In the present study, nitrobenzene (NB) was used as the model organic pollutant, whereas oxalic acid was selected as the representative SOAs. Our objectives were to compare the NB degradation kinetics by nZVI or nZVI-OA with N_2, O_2 as well as without aeration respectively. This was intended for elucidating the effects of aeration and initial pH on the reactivity of nZVI-OA, examining the dynamic behaviours of some indexes in nZVI-OA system with different aeration, and proposing the reactive mechanisms of nZVI-OA + N_2, nZVI-OA + O_2 together with nZVI-OA + without aeration systems.

2. Materials and methods

2.1. Chemicals

All the chemicals reagents were of analytical grade or higher and used as received. The nZVI particles with the average diameter of 50 nm and 99.9% purity were purchased from Aladdin Industrial Co. (Shanghai, China). NB (99%), OA, HCl, NaOH and other reagents were obtained from Sinopharm Chemical Reagent Co. Ltd. (China). Methanol and absolute ethanol were purchased from Merck (Germany). Ultrapure water purified with a Mili-Q system (18 MΩ cm) was used to prepare all solutions.

2.2. Experiments procedure

The degradation of NB was performed in a 150 mL Erlenmeyer flask and at room temperature (22 ± 2 °C). On the other hand, the NB aqueous solution (20 mg L^{-1}) was made ready with and without OA, and the required pH 3.0 adjusted by HCl (0.2 M) or NaOH (1 M). In all the experiments, 100 mL of NB solution along with 0.5 g L^{-1} of nZVI particles or Fe^{2+} (10 ± 0.5 mg L^{-1}) were added then mixed on a rotary shaker at 200 rpm. Samples were withdrawn by a 5 mL syringe at standard intervals, filtered through a 0.45 μm-pore-size membrane filter, then established for residual NB concentration through high performance liquid chromatography (HPLC). To guarantee precise data, all of the experiments were carried out in triplicate. Furthermore, the average values were used to fit the curves. The reactivity of nZVI-OA system could be investigated through the NB degradation efficiencies.

To comprehend the influence of aeration on the reactivity of nZVI-OA, three nZVI-OA systems with various aerations were set up: (i) N_2, (ii) O_2, and (iii) without aeration. For the anoxic/oxic system, the NB solution was purged with N_2/O_2 at flow rate of 1.0 L min^{-1}. For the system without aeration, the free surface of solution was open to the air while the O_2 was transferred to the solution only through the free surface. To circumvent the influence of initial DO in NB solution, solution samples were aerated using N_2 prior to experiments. The DO was also decreased below 0.1 mg L^{-1}.

The degradation of NB as a function of OA concentration was investigated under O_2 aeration condition. Then, OA with various concentrations (0, 1, 2, 3, 4 and 5 mM) were added into the solution. The impact of initial pH (3.0, 5.0 and 7.0) on NB degradation by nZVI-OA was also studied. Unless specified, the nZVI dose was kept constant at 0.5 g L^{-1} in the solution, the initial NB concentration was held at 20 mg L^{-1}, and OA concentration kept at 3 mM while the initial pH maintained at 3.0.

Three defined fractions "degradation" and "precipitation/adsorption" were utilised to characterise the NB removal by chemical reduction/oxidation as well as physical separation processes. The determination was executed after 60 min degradation treatment. The total removal of NB was measured on the basis of the difference value between the initial and the final concentrations of NB solution. The precipitation/adsorption fraction was also established by methanol extraction from suspended solids in the solutions. Meanwhile, the nZVI and degradation fractions were calculated by the differences of the two values.

Additionally, trapping experiments were performed to study the roles of active species involved in the reactions. The radical scavengers utilising *tert*-butyl alcohol (TBA) as the hydroxyl radical scavenger together with benzoquinone (BQ) as the peroxy radical scavenger were further added to the NB solution prior to the reaction.

2.3. Analytical methods

The concentrations of NB were quantitatively measured using HPLC (Agilent 1200, USA) equipped with a C18 reversed-phase column (250 mm × 4.6 mm, 5 μm particles). The mobile phase was 35% water in methanol at a flow rate of 1.0 mL min^{-1}. The detection wavelength was 280 nm.

The degradation products were extracted by liquid-liquid extraction with acetone-hexane mixture (1:1) for three times. The extracted solution was dehydrated using anhydrous sodium sulphate and concentrated to 1 mL by rotary evaporation. A Shimadzu gas chromatography mass spectrometer (GC/MS-QP2100, Shimadzu, Kyoto, Japan) equipped with a CD-WAX fused-silica capillary column (30 m × 0.25 mm i.d, 0.25 μm film thickness) was used for analyzing the samples. The initial temperature of the column oven was 70 °C for 2 min, and then increased up to 210 °C with a heating rate of 5 °C min^{-1}. Helium was used as the carrier gas. Mass spectrometric detection was operated with 70 eV electron impact (EI) mode.

A modified ferrozine method was applied to quantify the concentration of dissolved ferrous ion (Fe^{2+}) and total dissolved iron in the solution [9]. To measure total dissolved iron, a 2 mL aliquot of filtered sample was added into 1 mL of formate buffer (0.005 M sodium formate and 0.015 M formic acid, pH = 3.3). The aqueous pH and oxidation-reduction potential (ORP, mV) values were measured using a pH/ORP meter (PHS-3 C, Leici, Shanghai, China).

3. Results and discussion

3.1. Degradation of NB in different systems

Initial pH of each solution was adjusted to 3.0 with HCl and NaOH. In OA's absence, nZVI reactivity was realised to be relatively low (as illustrated in Fig. 1a). Degradation efficiency of NB by nZVI under various aerations was in the following order: O_2 (35%) > N_2 (29%) > without aeration (10%). This sequence had also been discerned in earlier studies [10,11]. It was reported that the reduction species ($^{\cdot}H$) was significant in the pollutants degradation under anoxic conditions [9]. Different from the nZVI without aeration system, N_2 aeration would decrease the DO in solution. It also facilitated the $^{\cdot}H$ formation, thereby leading to the improved reduction activity of nZVI particles. This is to mean that the presence of DO would compete for electrons from nZVI and form iron oxides on its surfaces. Nonetheless, the degradation efficiency of NB under O_2 aeration condition was higher than the other two. The sufficient DO could be decreased to hydrogen peroxide in nZVI system through two-electron transfer (Eq. (5)) [3]. Under the neutral solution, H_2O_2 might also be generated through the reaction of ferrous iron as well as O_2 (Eq. (1)) [12].