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Influence of particle size of zero-valent iron and dissolved silica on the reactivity of activated persulfate for degradation of acid orange 7

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HIGHLIGHTS

- Different ZVI types exhibited respective level of ability to activate persulfate with an order of nano-ZVI > micro-ZVI > milli-ZVI.
- The presence of SiO_2 decreased the AO7 degradation ratio and prolonged the persulfate half-life.
- The iron oxides of α-Fe_2O_3, Fe_3O_4, α-FeOOH and $Fe_8O_8(OH)_6SO_4$ was found on the ZVI surface after reaction.
- The complexes of $\equiv FeH_3SiO_4$ or $\equiv FeH_2SiO_4^-$ were formed on the surface of nano-ZVI in the presence of SiO_2.

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ABSTRACT

The environmental impact caused by azo dyes such as acid orange 7 (AO7) is currently a major concern, mainly due to their toxicity, potential carcinogenic nature and difficult degradation. This research described the heterogeneous reactions of persulfate with milli-ZVI (1 mm), micro-ZVI (150 μm) and nano-ZVI (50 nm) under various experimental conditions. The results demonstrated that the combination of persulfate with ZVI was efficient in promoting the degradation of AO7 with the pseudo first-order and second-order kinetics reaction, and different ZVI types exhibited respective level of ability to activate persulfate to degrade acid orange 7, which was ranged as nano-ZVI > micro-ZVI > milli-ZVI. However, the presence of dissolved SiO_2 decreased the AO7 degradation ratio and prolonged the persulfate half-life. The iron corrosion products coating on the ZVI after reaction was comprised of α-Fe_2O_3, Fe_3O_4 and α-FeOOH with some $Fe_8O_8(OH)_6SO_4$, which was identified by Raman spectroscopy, X-ray diffraction (XRD) and Fourier transform infrared (FTIR). With the presence of SiO_2, surface complexes of $\equiv FeH_3SiO_4$ or $\equiv FeH_2SiO_4^-$ for binding of silicates were formed. These observations indicated that the dissolved SiO_2 in the ZVI activated persulfate system affected the corrosion of iron, altered the surface area with the adsorption of SiO_2, and appeared to influence the decomposition of persulfate and AO7.

1. Introduction

Advanced oxidation processes (AOPs) have been proven particularly effective to oxidize recalcitrant, toxic and non-biodegradable compounds to various by-products and eventually to inert end-products by the intermediacy of hydroxyl and other radicals [1–4]. In recent years, the application of AOPs based on activation of persulfate ion ($S_2O_8^{2-}$) to generate the sulfate radicals ($SO_4^{-\cdot}$) with a redox potential (E_0 = 2.5–3.1 vs. NHE) [5] exhibits a great potential in destroying many refractory contaminants [6–8]. Sulfate radicals can be generated from the activation of persulfate by UV, heat, high pH, hydrogen peroxide, and transition metal ions [9–11]. Although the degradation of contaminants with sulfate radicals appears to be promising, the homogeneous reaction of ferrous ion by persulfate exhibites an obstacle of maintaining available ferrous ion during the degradation process [12]. Because the persulfate activation with Fe^{2+} is unlike the Fenton's reaction where an adjustment of pH in the range of 3–4 is satisfactory for continuous recycling of Fe^{2+} and Fe^{3+} due to reductants formation (e.g., hydroperoxide anion and superoxide radical) [13].

Consequently, in order to achieve complete degradation, excess ferrous salts are necessary, which will make high dissolved iron in the solution. However, it has been found that Fe^{2+} can activate persulfate but also can further react with $SO_4^{-\cdot}$ at an even higher rate [Eq. (1)] than that for $SO_4^{-\cdot}$ generation [Eq. (2)] [14,15].

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$$SO_4^{-\cdot} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} \quad (1)$$

$$k = 4.6 \times 10^9\ M^{-1}\ s^{-1}, 22\ ^\circ C$$

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{-\cdot} + SO_4^{2-} \quad (2)$$

$$k = 2.0 \times 10^1\ M^{-1}\ s^{-1}, 22\ ^\circ C$$

Obviously, maintaining proper quantities of Fe^{2+} to slow generation of $SO_4^{-\cdot}$ and enhance oxidative efficiency toward target contaminants is crucial. A potential alternative to ferrous ion activation is zero-valent iron (ZVI) activation of persulfate to produce sulfate radicals. The use of ZVI not only overcomes the disadvantage of Fe^{2+} but also has the advantage of avoiding the addition of other anions by ferrous salts. ZVI can produce Fe^{2+} by the following reactions [Eqs. (3)–(5)] [16].

$$Fe^0 \rightarrow Fe^{2+} + 2e^- E^0 = 0.447\ V(vs\ S.H.E.) \quad (3)$$

$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \quad (4)$$

$$Fe^0 + S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{2-} \quad (5)$$

Moreover, Bremner et al. [17] proposed faster recycling of ferric iron on the ZVI surface through the electron transferring to Fe^{3+}, which can keep suitable Fe^{2+} concentration in solution [Eq. (6)].

$$Fe^0 + 2Fe^{3+} \rightarrow 3Fe^{2+} \quad (6)$$

Recently, researchers have used ZVI to activate persulfate to control the rate of sulfate radical formation, therefore, enhancing the reaction efficiency [16,18,19]. Seok et al. [16] hypothesized that the mechanism may be heterogeneous activation of persulfate, involving direct electron transfers from ZVI or surface-bound Fe^{2+} [Eqs. (2) and (7)]. ZVI activation not only serves as a slow-releasing source of dissolved Fe^{2+}, but also provides another way that does not involve aqueous Fe^{2+} to produce sulfate radicals

$$Fe^0 + 2S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{2-} + 2SO_4^{-\cdot} \quad (7)$$

Kusic et al. [20] reported that at the determined optimal conditions, the $Fe^0/S_2O_8^{2-}$ process yielded 53.36% mineralization, whereas only 34.89% mineralization was achieved by the $Fe^{2+}/S_2O_8^{2-}$.

However, in light of the findings from the previous studies, most studies have investigated the effect of some variation parameters, such as pH, dosage of persulfate on the efficiency of removing contaminants. As groundwater contains dissolved SiO_2 at concentrations ranging from 5 mg/L to 85 mg/L (0.08–1.42 mM SiO_2) [21], and SiO_2 is typically considered as a corrosion inhibitor, the presence of dissolved SiO_2 in water may have a significant influence on both iron corrosion and iron releasing to water [22]. The effect of dissolved SiO_2 and the particle size of ZVI on the reactivity of activated persulfate in the ZVI-persulfate system have never been reported. Moreover, the role of the morphology and structure of the iron oxides on the ZVI surface after persulfate reaction have not been evaluated. Therefore, an understanding of the effect of particle size of ZVI and dissolved SiO_2 on the degradation of AO7 in the ZVI-persulfate system will help to predict its fate and could lead to an ability to improve the performance of persulfate oxidation on recalcitrant organic pollutants.

Acid orange 7 was chosen as the target contaminant because it is present in many chemical industry wastewaters from textile, pulp and paper, cosmetic and other industries. It is not only aesthetically displeasing, but also toxic, potential carcinogenic nature and difficult degradation by biological treatment methods due to its complex structure and stability [23]. This research objective is to gain insight into: (1) the effect of particle size of ZVI including 1 mm (named millimeter-size ZVI, milli-ZVI), 150 μm (named micro-size ZVI, micro-ZVI), and 50 nm (named nano-size ZVI, nano-ZVI) on the degradation of AO7, (2) the effect of dissolved SiO_2 on the degradation of AO7 and (3) the influence of particle size of ZVI and dissolved SiO_2 on the changes of the morphology and structure of ZVI after treatment.

2. Materials and methods

2.1. Materials

All chemicals used in this study were reagent grade and ultrapure water was produced by a Millipore milli-Qsystem. The milli-ZVI (purity >95%, approx. 1 mm) was purchased from Tianjin Kemiou chemical Reagent Co., Ltd. (Tianjin China), the micro-ZVI (purity >99%, approx. 150 μm) and nano-ZVI (purity >99.9%, approx. 50 nm) were obtained from Aladdin chemistry Co., Ltd. (Shanghai, China). As determined by N_2 isothermal adsorption (the BET surface area) presented the total surface area (a_s) of these ZVI were 0.071 m^2/g, 0.389 m^2/g and 28.637 m^2/g for milli-ZVI, micro-ZVI and nano-ZVI, respectively. AO7 (purity >99.0%) was purchased from Tokyo Chemical Industry (Japan). All other chemicals used were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China).

2.2. Experimental procedure

Stock solution of AO7 (0.4 mM) and persulfate (4 mM) were prepared by adding a required amount of pure AO7 and sodium. Fifty millilitres of the prepared AO7 and persulfate stock solutions were added simultaneously to a 250-mL Erlenmeyerl flask to give initial concentrations of AO7 and persulfate of 0.2 mM and 2.0 mM, respectively. The flask was open to the atmosphere and shaken at 150 rpm in a rotary shaker (ZHWY-20102C, Shanghai, China) at 25 ± 0.2 °C. To assess of the effect of particle size of ZVI on activation persulfate, milli-ZVI (1 mm), micro-ZVI (150 μm), nano-ZVI (50 nm) were used. For determining effect of the dosages of the three particle size of ZVI on the degradation of AO7, 0.1 g/L, 0.3 g/L, 0.5 g/L, 0.8 g/L, 1.0 g/L ZVI were studied. All reactions were initiated by adding persulfate solution. All samples were withdrawn in the predetermined time intervals by ethanol (1.0 mL of ethanol for each 1.0 mL sample), a well-known quenching agent for sulfate radicals [24], and the residual ZVI was separated by centrifugation for 5 min at 10,000 rpm in 2 mL polypropylene microcentrifuge tubes, then the supernatant was filtered through a 0.45-μm membrane filter and analyzed for AO7, persulfate, dissolved Fe^{2+} and total dissolved iron. ZVI particle was easily oxidized because of its strong reducing capacity. Therefore, a comparative study was performed using acid-washed and unwashed ZVI (date not shown). The results indicated that there was no significant difference on the degradation of AO7 between acid washed ZVI (milli-ZVI, micro-ZVI) and unwashed ZVI. However, the unwashed nano-ZVI always showed no effect on the activation of persulfate. That was due to the forming of iron oxides that will decrease its reactivity on the surface of unwashed nano-ZVI. Therefore, all nano-ZVI used in the experiment all were washed by acid, and the milli-ZVI and micro-ZVI were unwashed. Partial ZVI were washed in N_2-sparged HCl (1:100) for 1 h to remove the surface oxides or other contaminants, and then rinsed with N_2-sparged acetone and ultrapure water for several times until the Cl^- which were adsorbed on the surface of ZVI was removed.

To evaluate the impact of dissolved SiO_2 on the degradation of AO7 in the ZVI activated persulfate system, the decomposition of