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Degradation of organic compounds during the corrosion of ZVI by hydrogen peroxide at neutral pH: Kinetics, mechanisms and effect of corrosion promoting and inhibiting ions

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ABSTRACT

The corrosion of zero valent iron (ZVI) by hydrogen peroxide (H_2O_2) generates hydroxyl (•OH) and other radical oxygen species (ROS) that degrade organic materials. To better understand the factors that govern the ROS formation during the H_2O_2-induced corrosion, we investigated the degradation of an organic probe compound (acesulfame (ACE)) in slurries of ZVI powder in unbuffered laboratory water at pH 6.5 ± 0.5. Chloride ions accelerated the corrosion of ZVI by H_2O_2 and the formation ROS and, therefore, the degradation of organic materials. Conversely, slowing corrosion by phosphate buffer inhibited ROS formation and the degradation of organic compounds. The rate of H_2O_2 decomposition was correlated with the liberation of Fe^{2+}(aq) and the ACE degradation rate. The kinetics of H_2O_2 decomposition was pseudo-first-order and zero-order at low (<0.04 mM/mg) and high $[H_2O_2]/[ZVI]$ initial ratios, respectively, and was consistent with Langmuir kinetics. The H_2O_2 decomposition rate was proportional to the ZVI reactive surface area (SA) and nearly independent of the extent of ZVI oxidation, the presence of a Fe^{2+}(aq) chelating agent, and •OH quenchers (methanol and *tert*-butanol). Kinetic data suggest a mechanism involving rapid cathodic reduction of H_2O_2 at the metallic ZVI surface which causes the liberation of Fe^{2+}(aq) that generate •OH via the homogeneous Fenton reaction. The stoichiometric efficiency (SE) of organics degradation ranged from 0.0008% to 0.014% and increased with decreasing H_2O_2 decomposition rate.

1. Introduction

Hydrogen peroxide (H_2O_2) is an environmentally friendly oxidant widely used for disinfection, biofouling control and as a bulk oxidant in industrial, medical and environmental applications. H_2O_2 and other peroxides are evaluated as a replacement for chlorine-based disinfectants to avoid pollution with toxic chlorination byproducts, for instance in membrane-based water treatment systems (Ling et al., 2017, Ling et al., 2018) and as a bleaching agent in the paper production (Rotash et al., 2014). In the presence of iron and other transition metal compounds, H_2O_2 generates transient reactive oxygen species (ROS) while decomposing to oxygen, especially at elevated pH (>5) and temperature (Bremner et al., 2006; De Laat and Le, 2006; Kwan and Voelker, 2002; Teel et al. 2001, 2007; Watts et al., 1999). ROS include the extremely reactive hydroxyl radical (•OH) (Buxton et al., 1988) and the more selective hydroperoxyl radical (•O_2H), superoxide radical anion (•O_2^-) and hydroperoxide (HO_2^-) (Kwan and Voelker, 2003; Valentine and Ann Wang, 1998; Watts et al., 1999). In acidic solution, the classical Fenton reaction involves the Fe(II/III)-catalyzed disproportionation of H_2O_2 generating •OH and HO_2^- (Goldstein et al., 1993). ROS can be formed in biological systems and elicit toxicity (Stohs and Bagchi, 1995). In membrane-based water treatment systems, ROS can attack the polymeric separation layer (Gabelich et al., 2005; Ling et al., 2018). Fenton-generated ROS are exploited for the destruction of environmental pollutants (Neyens and Baeyens, 2003; Pignatello et al., 2006). ROS are transient intermediates during the corrosion of zero-valent iron (ZVI) by dioxygen as the bulk oxidant (Chiou et al., 1990; Duesterberg et al., 2005; Katsoyiannis et al., 2008; Keenan and Sedlak, 2008). The

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composition and the rate of corrosion products (rust) formation depend on many factors, including pH and the presence of anions (Guo et al., 2016; Sun et al., 2016; Zou et al., 2016). Corrosion products consist of various ferric oxyhydroxides (mainly α-FeOOH (goethite), γ-FeOOH (lepidocrocite), and Fe_3O_4 (magnetite)) with the average composition $2Fe_2O_3 \cdot H_2O$ (Landolt, 2007). Fe oxides catalyze the decomposition of H_2O_2 and ROS generation (Kwan and Voelker, 2003; Valentine and Ann Wang, 1998). ROS formation and the degradation of organic materials during ZVI corrosion in dilute H_2O_2 (Bergendahl and Thies, 2004; Jia et al., 2017; Namkung et al., 2005) and the effect of ions that can promote or inhibit corrosion (e.g., chloride and phosphate, respectively) (Li et al., 1999) on the process are still poorly understood.

In Table S1, the stoichiometry of the most significant reactions involved in ZVI oxidation, homogeneous (classical) and heterogeneous Fenton reactions and rust formation processes are summarized. Additional reactions and more detailed descriptions of the chemistry involved can be found in text books, e.g (Landolt, 2007)., and reviews (Neyens and Baeyens, 2003; Pignatello et al., 2006). In the presence of ZVI, H_2O_2 decomposition can occur via four pathways (Bergendahl and Thies, 2004): (1) cathodic oxidation of $Fe^0(s)$ and reduction of H_2O_2 (R 1.4) by two-electron transfer, (2) the classical Fenton (R 2.1) reaction, (3) the Fenton-like reaction, which is initiated by R 2.2, and (4) reaction with $\cdot OH$ (R 2.5). Corrosion of $Fe^0(s)$ is coupled to the generation of solid Fe(II) (rust) and soluble $Fe^{2+}(aq)$ (R 1.1). The spatial separation of cathodic and the anodic processes lead to the formation of cavities (pitting) (Landolt, 2007). The Fenton reaction is affected by numerous factors, most importantly by the $Fe^{2+}(aq)$ concentration, the pH and the presence of complexing agents. As indicated in Table S1, $Fe^{2+}(aq)$ is the key reactant involved in the formation of $\cdot OH$. It can be formed by the oxidation of $Fe^0(s)$ (R 1.1), the reduction of Fe(III) by H_2O_2 (R 2.2) and $\cdot O_2H$ (R 2.3). $Fe^{2+}(aq)$ is consumed by the homogeneous Fenton reaction (R 2.1), the precipitation and co-precipitation as oxyhydroxide (R 3.1, 3.4) and by reacting with $\cdot OH$ (R 2.4). Oxidation reactions of ZVI by H^+, Fe^{3+}, and $\cdot OH$ are indicated in R 1.7 to 1.9.

Previous studies reported that the rate of ROS production is accelerated by H^+ and inhibited by various ligands such as phosphate and natural organic matter (NOM) (De Laat and Le, 2006; Pignatello et al., 2006; Sun et al., 2016). Increasing pH to >3.5 causes Fe(III) to form solid ferric oxyhydroxides. The latter are weaker activating agents than $Fe^{2+}(aq)$. Studies with selective organic probes indicated that the yield of $\cdot OH$ yield decreased with increasing pH while that of the less reactive Fe(IV) (ferryl) and Fe(V) species increased, e.g., by R 2.10 (Keenan and Sedlak, 2008; Pignatello et al., 2006). Increasing $[H_2O_2]$ at constant solution conditions increases the rate of corrosion and the rate of ROS generation (Kwan and Voelker, 2003). In the presence of an excess of O_2, the dominant cathodic process is R 1.2 (reduction of O_2 to H_2O while a small fraction is converted to H_2O_2 (R 1.3). H_2O_2 so formed can form ROS and degrade organic materials (Keenan and Sedlak, 2008).

The stoichiometric efficiency (SE) indicates the molar ratio of degraded probe P to H_2O_2 consumed during exposure to ZVI/H_2O_2 (Eq. (1)):

$$SE(t) = \frac{[P]_0 - [P]_t}{[H_2O_2] - [H_2O_2]_t} \quad (1)$$

where $[P]_0$, $[P]_t$, $[H_2O_2]_0$, and $[H_2O_2]_t$ are the molar concentrations of probe compound P and H_2O_2 at time 0 and t, respectively. SE depends on the structure of P and reaction conditions and time: it is lower if the products formed consume additional H_2O_2. Published SE data are scarce and difficult to compare. A correction is needed if P is removed due to adsorption to the iron surface (Huang et al., 2001; Namkung et al., 2005). SE was determined for the decolorization of Rhodamine B in H_2O_2/Fe(II,III) oxide systems and was found to depend on the type of oxide (Xue et al., 2009). Depending on the oxide, SE decreased with increasing surface area (SA) from a maximum of approximately 14% to less than 2%. The decrease was attributed to the quenching of $\cdot OH$ by surface reactions. In a nano-ZVI/H_2O_2 system, the rate of organics oxidation increased as the pH decreased (Li and Zhu, 2014; Wang et al., 2016). Methyl *t*-butyl ether (MTBE) was transformed more efficiently at $pH = 4$ than at $pH = 7$ and 3 in a ZVI/H_2O_2 system (Bergendahl and Thies, 2004). The kinetic model suggested that $Fe^{2+}(aq)$ was formed by the oxidation of $Fe^0(s)$ and fed into the Fenton reaction cycle.

Because the decomposition of H_2O_2 by ZVI and the release of $Fe^{2+}(aq)$ are accelerated by corrosion promoters, i.e., H_3O^+, Cl^-, O_2, H_2O_2, corrosion promoters are accelerating the Fenton reaction and thus the degradation of organics (Bergendahl and Thies, 2004). Studies with trichloroethylene (TCE) as the electron acceptor indicated that pretreatment of ZVI with chloride ions accelerated electrochemical processes by increasing surface roughness via pitting corrosion, dissolving the passivation layer and generating reactive sites (Gotpagar et al., 1999). By contrast, corrosion is suppressed by phosphate ions binding strongly to the iron species formed during the ZVI oxidation, which occurs even in the presence of chloride ions (De Laat and Le, 2006; Refaey et al., 2000; Reffass et al., 2009). Assessing the degradation of organic materials during ZVI corrosion by H_2O_2 in a variety of matrices requires detailed data that document the effects of chloride and phosphate ions on ROS formation. This laboratory study quantified the effect of chloride and phosphate ions on the degradation of organic compounds by ROS formed during the corrosion of ZVI and aimed to gain mechanistic insight into the process. Acesulfame (ACE) was used as the probe compound because it occurs ubiquitously in the environment (Lange et al., 2012), is poorly sorbing (Tran et al., 2015) and its reaction rate with $\cdot OH$ was determined previously (Toth et al., 2012; Urban, 2015).

2. Materials and methods

2.1. Chemicals

All chemicals used were of reagents grade. Iron powder was obtained from Sigma-Aldrich Pte. Ltd., Singapore. The SEM images of iron powder are presented in the Supplementary Data (Fig. S1). The diameter of iron powder ranged from 50 to 150 μm. The artificial sweeteners, acesulfame (ACE), saccharin (SAC), cyclamate (CYC) were purchased from Sigma-Aldrich Pte. Ltd., Singapore. Mass-labeled internal standards, ACE-d4, SAC- 13C, CYC-d11, were purchased from Toronto Research Chemicals, Inc., Canada. HPLC grade methanol (MeOH) and ammonium acetate, hydrogen peroxide (30% wt/wt), sodium phosphate, sodium chloride, 2,2′-bipyridine (BPY), *tertiary*-butanol (tBuOH) were purchased from Sigma-Aldrich Pte. Ltd, Singapore.

2.2. Experimental set-up

All experiments were carried out at room temperature (25 ± 1 °C) in 100 ml acid-washed glass bottles wrapped in aluminum foil to exclude light. Initial concentrations of ZVI powder, H_2O_2, chloride and phosphate were adjusted by amending appropriate aliquots of concentrated standard stock solutions. Aliquots of artificial sweeteners were added to obtain an initial concentration of 100 μg/L each. ZVI powder was kept in suspension by rotary shaking the flasks at 150 rpm. Samples were collected at predetermined time intervals with a 5 ml syringe and filtered immediately by a 0.22 μm-nylon syringe filter. To study the effect of