Rapid and continuous oxidation of organic contaminants with ascorbic acid and a modified ferric/persulfate system

Yang Lei, Hui Zhang *, Jiawen Wang, Jia Ai

Department of Environmental Engineering, Wuhan University, Wuhan 430079, China

HIGHLIGHTS

- A novel $Fe^{3+}/H_2A/PS$ system was proposed to oxidize organic pollutants.
- Ascorbic acid could enhance the efficiency of iron activated persulfate process.
- The pollutants could be removed quickly and continuously.
- The system is efficient in a wide pH_0 range (2.0–6.2).
- The reduction and chelating ability of H_2A are responsible for the good performance.

GRAPHICAL ABSTRACT
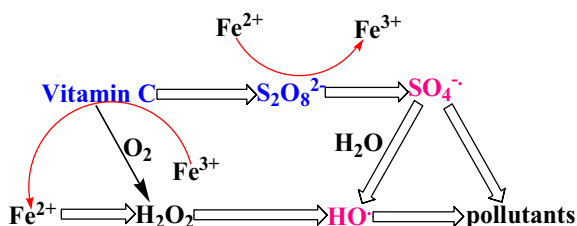
ABSTRACT

An eco-friendly reagent, Vitamin C (ascorbic acid, H_2A), has been introduced into a traditional iron activated persulfate (PS) process (Fe^{2+}/PS). The modified $Fe^{3+}/H_2A/PS$ system exhibits a rapid and continuous oxidation of organic contaminants, and shows great advantages over the conventional Fe^{2+}/PS process by enhanced removal efficiency and wide working initial pH (pH_0 2.0–6.2). This can be attributed to both the reduction and chelating ability of ascorbic acid. The optimal dosages of ascorbic acid, ferric ion and persulfate were determined by batch experiments. Radical quenching experiments show that SO_4^- and $HO^.$ are the main reactive species in the $Fe^{3+}/H_2A/PS$ process. Based on these results, a plausible degradation mechanism is proposed. The modified system may provide a simple and effective technology for the decomposition of refractory organics in water.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Advanced oxidation processes (AOPs) have been widely used in wastewater treatment and soil/groundwater remediation [1–3]. Particularly, sulfate radical (SO_4^-) based AOPs have received increasing attention. This is because persulfate (PS, the source of SO_4^-) is more stable than other oxidants such as ozone and has a higher oxidation ability after being activated [4]. Generally, persulfate can be activated by various methods, including ultrasound,

heat, ultraviolet energy, alkaline, transition metals and some natural organic compounds [4–7].

Among the various activation methods, great attention has been paid to the iron activated persulfate [8–10]. This is because iron is the second most abundant metal element in the earth's crust and it may be readily applied for the activation of persulfate to form SO_4^-. Although the traditional iron activation method of generating SO_4^- via Eq. (1) still remains the most favorable route, especially when taking the practical industrial application into consideration, it has some drawbacks. First of all, ferrous ion (Fe^{2+}) is difficult to be regenerated when it is oxidized to ferric ion (Fe^{3+}) (Eq. (1)). This may lead to the formation of large amounts of iron sludge as a high

concentration of Fe^{2+} is needed. Secondly, the reaction is only effective at pH around 3.0 [11]:

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\cdot-} \quad (1)$$
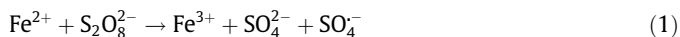
To overcome these problems, heterogeneous iron catalysts were employed to activate persulfate under wide pH range [12–15], chelating agents were used to complex with Fe^{2+} [11,16–18], and electrochemical method was utilized to enhance the regeneration of Fe^{2+} [19–23]. Nevertheless, the main drawbacks of these methods lie in the complexity of catalyst preparation, the potential environmental effects of the chelating agents and the extra cost of electrical energy [24,25]. Recently, the reducing agents were introduced to the Fe^{2+}/PS process to promote Fe^{3+}/Fe^{2+} cycles. Liang et al. reported that the addition of sodium thiosulfate into Fe^{2+}/PS process improved the destruction of trichloroethylene [26]. Zou et al. introduced hydroxylamine (HDA) into the Fe^{2+} activated peroxymonosulfate system, and observed that the HDA could accelerate the degradation of benzoic acid [27]. Han et al. also reported the enhanced decolorization of Orange G by HDA in Fe^{2+}-EDDS activated PS system [28]. Unfortunately, HDA and its degradation products are toxic [27]. So environmentally friendly reducing regents would be more preferable and we now propose the use of ascorbic acid as an alternative.

As an eco-friendly reducing agent, ascorbic acid ($C_6H_8O_6$, H_2A), also named as Vitamin C, has shown great promise in water and wastewater treatment [29–31]. For example, Xu et al. reported the reduction of Cr(VI) by H_2A in aqueous solutions [30]. The chlorinated solvents such as tetrachloroethene and carbon tetrachloride could be degraded by H_2A via reductive dechlorination [29,31]. More recently, Fukuchi et al. observed that H_2A could enhance the degradation of 2,4,6-tribromophenol in Fenton-like processes [32]. To the best of our knowledge, there was little work on the use of H_2A in $SO_4^{\cdot-}$ based AOPs. Consequently, the use of H_2A in AOPs was herein reported and a novel Fe^{3+}/H_2A/PS process was proposed for the effective oxidation of organic pollutants. Secondly, the factors that affect the oxidation process have been investigated and a possible mechanism was suggested. Acid Orange 7 (AO7) was chosen as the model pollutant since AO7 containing aromatic molecules are extremely stable and resistant to conventional wastewater treatment methods [15]. In addition, it is easy to monitor and has previously been well studied by other researchers as well as our group [14,15,20,33–36].

2. Materials and methods

2.1. Materials

Acid Orange 7 (4-(2-hydroxynaphthylazo)-benzenesulfonic acid sodium salt), ascorbic acid, sodium persulfate and ferric chloride were purchased from Shanghai No. 3 Reagent Factory (China). Clofibric acid ($C_{10}H_{11}ClO_3$, CFA) was offered by Accela ChemBio Co., Ltd. (Shanghai, China). All the solutions were freshly prepared with deionized water before each run.

2.2. Experimental

The batch trials were performed in a glass beaker with working volume of 200 mL. A magnetic stirrer provided mixing of the solution in the reactor. The initial pH was adjusted using H_2SO_4 (0.1 M) or NaOH (0.1 M) after ferric chloride, ascorbic acid and AO7 were transferred to the reactor. The reaction was initiated with the addition of PS and performed at ambient temperature (20 ± 2 °C). At predetermined time intervals, samples were taken and mixed with excess methanol (v/v = 1:1) to quench the reaction before analysis.
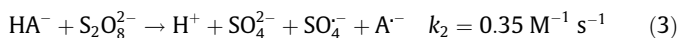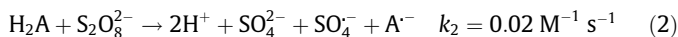
2.3. Analysis

The absorbance of AO7 was measured at the maximum wavelength of 485 nm using a Rayleigh UV-9100 spectrophotometer (Rayleigh Co., China). In the test for AO7 mineralization, an Analytik Jena multi N/C 3100 analyzer was applied. The carrier gas was high purity oxygen with a flow rate of 150 mL/min and the detector was a non-dispersive infrared absorption detector. Note here that methanol was replaced with sodium sulfite (0.1 M) to quench the reaction. The concentrations of persulfate and iron ion were determined according to the iodometric titration method [37] and the modified phenanthroline spectrophotometric method [38], respectively. H_2A was measured by a selective spectrophotometric method [39].

3. Results and discussion

3.1. Decolorization efficiency of AO7 in different systems

In order to compare color removal in different systems, several preliminary experiments were performed. It can be seen from Fig. 1 that neither PS nor its coupling with Fe^{3+} can lead to the decolorization of AO7. This illustrated that persulfate was not able to oxidize AO7 and it could not be activated before Fe^{3+} was reduced to Fe^{2+}, which can be verified by a very small percentage of PS decomposition (1.3%) after 20 min reaction (Fig. S1). Although H_2A is a reducing agent, it could not destroy the azo double bond. Fig. 1 indicated that insignificant color removal was achieved by H_2A with/without Fe^{3+}. A slightly improved decolorization efficiency of 14.6% and PS decomposition of 13.3% was achieved in the H_2A/PS system. This is because H_2A can react with PS to generate $SO_4^{\cdot-}$, as shown in Eqs. (2) and (3) [40]:

$$H_2A + S_2O_8^{2-} \rightarrow 2H^+ + SO_4^{2-} + SO_4^{\cdot-} + A^{\cdot-} \quad k_2 = 0.02 \text{ M}^{-1} \text{ s}^{-1} \quad (2)$$

$$HA^- + S_2O_8^{2-} \rightarrow H^+ + SO_4^{2-} + SO_4^{\cdot-} + A^{\cdot-} \quad k_2 = 0.35 \text{ M}^{-1} \text{ s}^{-1} \quad (3)$$

where H_2A, HA^- and $A^{\cdot-}$ are the symbols of ascorbic acid, hydrogen ascorbate, and oxidized dehydroascorbic acid radical, respectively.

The combination of Fe^{3+}, PS and H_2A achieved 94.2% of AO7 decolorization in 20 min, as illustrated in Fig. 1. But when Fe^{3+} was replaced with Fe^{2+}, the removal percentage of AO7 declined to 60.0% though nearly the same amount of PS was decomposed
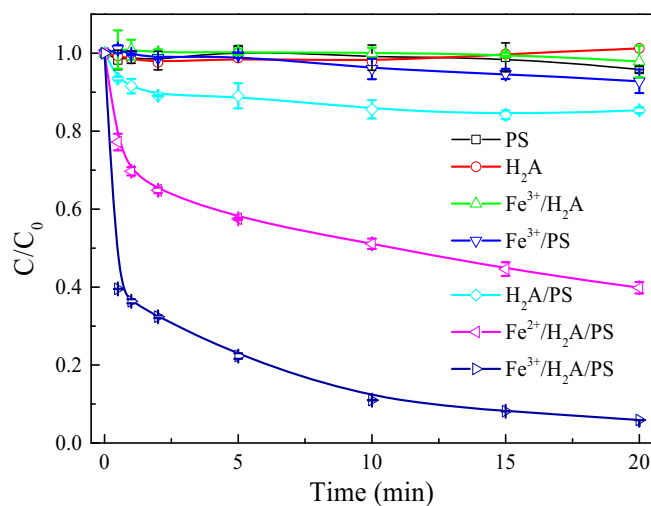

Fig. 1. Decolorization efficiency of AO7 in different systems. Conditions: [PS] = 5.0 mM; [Fe^{3+}] = [Fe^{2+}] = 1.0 mM; [H_2A] = 0.5 mM; pH_0 = 3.0; [AO7] = 50 mg/L. Data expressed as means ± standard deviations (n = 3).