Fenton's process for simultaneous removal of TOC and Fe^{2+} from acidic waste liquor

Yingxin Gao^a, Min Yang^{a*}, Jianying Hu^b, Yu Zhang^a

^aState Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, PO Box 2871, Beijing 100085, China

Tel. +86 (10) 6292-3475; Fax: +86 (10) 6292-3543; email: yangmin@mail.rcees.ac.cn

^bDepartment of Urban and Environmental Sciences, Peking University, China

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Abstract

The potential of Fenton's reagent for the removal of organic substrates and ferrous ions, which are the main pollutants in acidic waste liquor, was assessed. The optimum molar ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ for the removal of Fe^{2+} was 0.72–0.76, which could be indicated by variations of ORP. Under optimal H_2O_2 dose, the minimum Fe^{2+} concentration ($1.2\text{--}1.3\text{ mg/l}^{-1}$) appeared at 45 min under a pH of 3.27–4.50. Under an H_2O_2 dose of 95 mg/l^{-1} , nearly 80% of TOC removal was caused by adsorption for a total TOC removal of 49%, and the contribution of oxidation was not over 20%. At 380 mg/l^{-1} H_2O_2 , more than 76% of TOC removal was contributed by oxidation, for a total TOC removal of 65%.

Keywords: Fenton's process; Acidic waste water; Fe^{2+} ; TOC; Oxidation; Coagulation

1. Introduction

Acidizing, a technique for improving the permeation ability of rock layers of wells using diluted inorganic acids such as hydrochloric acid (HCl), has long been one of the most common forms of stimulation to increase the production rate of oil and gas reservoirs [1,2]. For acidizing one well, about 200–500 m³ waste acidic liquid returns to the surface, containing high concen-

compounds, etc. [2,3]. Because of the wide distributions of HCl, ferrous ions (Fe^{2+}), and organic distribution of oil wells and the increased frequency of acidizing, the waste acidic liquids have brought about a severe environmental problem in China [4].

Some physical and chemical processes such as oilfield pit closure, neutralization–coagulation and underground injection have been employed to treat acidic waste liquids [3]. Oilfield pit closure, which was once extensively used,

*Corresponding author.

especially in China, causes severe damage to soil and plant growth [5]. Underground injection technology, on the other hand, must meet strict regulations for both construction and operation of disposal wells, and is receiving stringent restrictions in Europe and the US because of its potential damage to reservoirs [6]. The neutralization–coagulation method has gradually been accepted as the primary choice because it could reduce the damage to the environment to a minimum level. By neutralizing the acidity of the waste liquid, ferrous ions can be hydrolyzed to form iron hydroxide precipitates, resulting in partial removal of ferrous ions (Fe^{2+}) and organic substances from the liquid. However, this method produces a large amount of incompact ferrous sludge with bad settleability [7]. And the residual Fe^{2+} and TOC of the effluent usually require further treatment. For Fe^{2+} removal, oxidation of Fe^{2+} to Fe^{3+} with air is a conventional method. Nevertheless, a long oxidation time and sedimentation time for incompact ferric complexes are necessary because of the very low reaction rate even at a pH of 8.0 [8] and poor deposition.

On the other hand, Fenton's reagent, which produces hydroxyl radicals catalyzed by Fe^{2+} by Eq. (1), has long been used for decomposition of refractory compounds in wastewater [Eqs. (3) and (4)] [9–13]. Fe^{3+} formed through oxidization by H_2O_2 [Eqs. (1) and (2)] can be reduced to Fe^{2+} via Eqs. (5) and (6). Compared with the reaction rate of Eq. (1), however, the rate of Eq. (5) is very low [14], and therefore most of the iron in the solution exists in the form of Fe^{3+} , which could easily be hydrolyzed through Eq. (7). When H_2O_2 is added into the Fe^{2+} -bearing acidic waste solution, Fenton's reaction possibly occurs, resulting in oxidation of Fe^{2+} and organic substances. Subsequently, almost all iron removal could be realized by adjusting the pH of the solution to neutral to form ferric hydroxide precipitates. And further removal of organic substances is also possible through adsorption by the ferric hydroxide precipitates formed [15,16].

In this study, the possibility of using Fenton's reaction to realize simultaneous removal of Fe^{2+} and TOC from acidic waste liquor was explored by adding H_2O_2 to the solution. Experiments were conducted to investigate the effects of various operation conditions on performance of the treatment system by using oxygen reduction potential (ORP) as a parameter to indicate the transformation of the $\text{Fe}^{3+}/\text{Fe}^{2+}$. The results derived from the present study could provide useful information for practical purposes.

2. Materials and methods

2.1. Acidic waste liquor and synthetic solution

Samples of acidic waste liquor were collected from an acidic waste liquor pond from the Jidong Oilfield, China, and stored at 4°C before use. Its characteristics are: pH 1.4, TOC 94 mg/l⁻¹, Cl^- 20,000 mg/l⁻¹, Ca^{2+} 1480 mg/l⁻¹, Mg^{2+} 435 mg/l⁻¹, Fe^{2+} 208 mg/l⁻¹, Fe^{3+} 5 mg/l⁻¹, and chroma 104°.

A stock synthetic ferrous solution was prepared by dissolving ferrous sulfate into deionized water to give a final Fe^{2+} concentration of 1000 mg/l⁻¹.

2.2. Reagents

H_2O_2 (30%), ferrous sulfate, sodium hydroxide, and all of the other reagents were purchased

from the Beijing Chemical Company, Beijing. All of the chemicals were reagent grade and used without further purification.

2.3. Experimental procedure

All experiments were conducted in a thermostat batch reactor (volume: 1.0 L, $20 \pm 0.2^\circ\text{C}$) and in the absence of light. The initial pH of the acidic waste liquor was modulated to given levels by using 1 mol/L NaOH solution, and the reactions were initiated by adding H_2O_2 to the solution under vigorous magnetic-stirring. For the experiment of titration of H_2O_2 , variations of pH, ORP and dissolved oxygen (DO) were monitored continuously. Samples were taken for the analysis of Fe^{2+} concentration. For the experiment of kinetics study, samples were withdrawn with a syringe for the analysis of Fe^{2+} , H_2O_2 and TOC.

For tests using synthetic ferrous sulfate solution, the pH of the solution was adjusted to given values with 1 mol/l H_2SO_4 while the DO was controlled below 1.0 mg/l^{-1} by bubbling N_2 continuously. Then the given amount of FeSO_4 solution was added into the synthetic solution, and a Fenton's reaction was initiated by adding H_2O_2 . Reaction conditions were the same with the acidic waste liquor.

2.4. Sample analysis

Hydrogen peroxide was determined iodometrically (at $\text{H}_2\text{O}_2 > 10^{-3} \text{ M}$) or spectrophotometrically using the TiCl_4 method [17] (at $\text{H}_2\text{O}_2 < 10^{-3} \text{ M}$; $= 730 \text{ M}^{-1}\text{cm}^{-1}$). No interference was noticed in the Fe^{3+} concentration range of this study. The concentrations of Fe^{2+} and Fe^{3+} were determined by using the *o*-phenanthroline colorimetric method at 510 nm [18]. The pH was measured with a portable pH meter (pH14M, TOA, Japan) and calibrated with standard buffers between pH 1.0 and 3.0. DO and ORP were determined with a portable DO meter (DO10,

TOA, Japan) and ORP meter (DO10, TOA, Japan) respectively. In the experiment for determining the respective contribution of adsorption by ferric hydroxo complexes and oxidation by hydroxyl radicals to TOC removal, samples were centrifuged without pH adjustment, and the TOCs of supernatants and sediments were measured on a TOC 500 (Shimadzu, Japan) and Apollo 9000 (Tekman-Dohrmann, USA), respectively.

3. Results and discussion

3.1. Effects of H_2O_2 dosage on Fe^{2+} removal

Generally, Fenton's reaction is widely applied to the removal of organic substances, and the effects of different factors on the removal of organics have been carefully investigated. For the purpose of TOC removal, the dose of H_2O_2 was generally several times that of Fe^{2+} in molar ratio [10,11]. For the removal of Fe^{2+} , however, the required H_2O_2 has not been investigated. In order to investigate the effects of H_2O_2 on Fe^{2+} removal, titration of H_2O_2 to the acidic waste liquor was used, and variations in Fe^{2+} , DO, pH and ORP levels with an increase of the H_2O_2 dose were followed. As shown in Fig. 1, Fe^{2+} almost linearly decreased from 208 mg/l^{-1} to 3.84 mg/l^{-1} when the dose of H_2O_2 was gradually added to 95 mg/l^{-1} . A continuous decline of pH during the titration process was observed, which was considered to be the result of the hydrolysis of Fe^{3+} [Eq. (7)] following oxidation of Fe^{2+} . When the dose of H_2O_2 was increased further from 95 mg/l^{-1} , however, further oxidation of Fe^{2+} became negligible. Fig. 2 shows variations of ORP and DO in the course of H_2O_2 titration. It is interesting that the plot of ORP vs. H_2O_2 dose shows a flex point at an H_2O_2 dose of 95 mg/l^{-1} . The ORP swiftly increased with the increase of the H_2O_2 dose before the flex point, and then remained almost unchanged with further increase of H_2O_2 . On the other hand, a flex point of the

Fig. 1. Effect of H₂O₂ on variations of Fe²⁺ and pH for acidic waste liquor. Conditions: initial pH 3.25, [Fe²⁺]₀: 208 mg/l⁻¹, T = 20°C.

Fig. 2. Effect of H₂O₂ on variations of ORP and DO (acidic waste liquor). Conditions: initial pH 3.25, [Fe²⁺]₀: 208 mg/l⁻¹, T = 20°C.

plot of DO vs. H₂O₂ was also observed at almost the same time. DO values had no evident increase before the flex point. A sudden rise in DO was observed when the dose of H₂O₂ was near 95 mg/l⁻¹, accompanied with an obvious release of O₂. The possible pathways of O₂ releasing reactions have been proposed by many researchers [Eq. (8)] [9,19]. From Eq. (1), it is clear that O₂ was not released through oxidation of Fe²⁺. Production of O₂ through H₂O₂ decomposition began only when Fe²⁺ was nearly depleted and Fe³⁺ was reduced back to Fe²⁺. The above facts suggest that both ORP and DO indicate the progress of the oxidation of Fe²⁺ to Fe³⁺, and could be used as indicators of Fe²⁺ abundance during reaction. At the flex point, the molar ratio of H₂O₂ added to Fe²⁺ in the solution was about 0.75.

Assuming that Eqs. (1) and (2) were the dominating reactions for Fe²⁺ oxidation, the theoretical consumption of H₂O₂ for oxidizing 1 mole Fe²⁺ to Fe³⁺ should be 0.5 moles (not taking into account the reaction of OH radicals with peroxide and with organic solutes), which was much lower than the ratio of H₂O₂ to Fe²⁺ observed in this

study. In order to see if the existence of organic substances affected the consumption of H₂O₂, titration of H₂O₂ to synthetic ferrous solutions free of organic compounds was used. Variations of ORP under different initial Fe²⁺ concentrations are shown in Fig. 3. It was found that while different inflexions were observed for different initial Fe²⁺ concentrations (94 mg/l⁻¹, 163 mg/l⁻¹, 390 mg/l⁻¹), the molar ratios of H₂O₂ titrated (41 mg/l⁻¹, 75 mg/l⁻¹, 173 mg/l⁻¹) to Fe²⁺ corresponding to the inflexions were, respectively, 0.72, 0.76 and 0.73, giving an average value of 0.74. It is clear that the molar ratio of H₂O₂ to Fe²⁺ corresponding to inflexions of ORP was not obviously affected by the coexisting organic compounds in wastewater. Thus, it is reasonable to suppose that consumption of H₂O₂ was not only caused by the oxidation of Fe²⁺, but also due to some side reactions like decomposition of H₂O₂ to H₂O and O₂ by ferric ions [19].

3.2. Effects of initial pH and reaction time on Fe²⁺ removal

It is well known that the optimum pH of Fenton's reaction is 2.5–3.5 for the removal of organic substances [9]. The effects of pH on Fe²⁺ removal, however, were not quite clear. The pH

of four different groups was adjusted to 3.28, 3.65, 3.90 and 4.5, respectively, with 1.0 mol/l^{-1} NaOH solution, and chronological variations of residual Fe^{2+} were monitored under a constant molar ratio of H_2O_2 to Fe^{2+} of 0.75 (Fig. 4). More than 98% of Fe^{2+} was removed in 1 min after the addition of H_2O_2 under each pH level, although the residual Fe^{2+} increased slightly with the increase of pH. The residual Fe^{2+} then decreased with time, and reached a minimum value of $1.2\text{--}1.3 \text{ mg/l}^{-1}$ following a 45-min reaction. It is assumed that the oxidation of Fe^{2+} by H_2O_2 [Eq. (1)] coexisted with the reduction of Fe^{3+} by organoradicals [Eq. (9)] [9]. When H_2O_2 was depleted, Eq. (9) will become the dominating reaction, which resulted in the increase of Fe^{2+} .

In order to verify the above hypothesis, a variation of residual Fe^{2+} in a ferrous sulfate solution free of organic compounds was followed with the addition of H_2O_2 (the molar ratio of the added H_2O_2 to Fe^{2+} being 0.75), and the result is shown in Fig. 5. It was found that when no organic compounds existed in Fenton's solution, the residual Fe^{2+} arrived at a stable level of about 1 mg/l^{-1} following a 500-min reaction. The residual Fe^{2+} did not increase even by extending the reaction time to 1500 min. The result shown in Fig. 5 indirectly supports the hypothesis that the re-increase of Fe^{2+} in the acidic waste liquor resulted from the reaction between Fe^{3+} and organoradicals as in Eq. (9). From the viewpoint of Fe^{2+} removal, extension of reaction time is not preferable when the solution contains organic compounds.

3.3. Effects of H_2O_2 on TOC removal

Fig. 6 shows the effects of pH on TOC removal. Significant removal of TOC was achieved soon after addition of H_2O_2 , perhaps mainly due to adsorption by ferric hydroxides.

Fig. 3. Effect of H_2O_2 on variations of ORP (ferrous sulfate solution). Conditions: initial pH 3.25, $T = 20^\circ\text{C}$.

Fig. 4. Effect of initial pH levels on Fe^{2+} removal (acidic waste liquor). Conditions: $[\text{H}_2\text{O}_2]_0: 95 \text{ mg/l}^{-1}$; $[\text{Fe}^{2+}]_0: 208 \text{ mg/l}^{-1}$; $T = 20^\circ\text{C}$.

Fig. 5. Variation of Fe^{2+} in the absence of organic compounds. Conditions: initial pH 3.25; $[\text{Fe}^{2+}]_0: 163 \text{ mg/l}^{-1}$, $[\text{H}_2\text{O}_2]_0: 76 \text{ mg/l}^{-1}$, $T = 20^\circ\text{C}$.

Fig. 6. Effect of pH on the removal of TOC (acidic waste liquor). Conditions: $[H_2O_2]_0$: 95 mg/l⁻¹, $[Fe^{2+}]_0$: 208 mg/l⁻¹, T : 20°C.

Fig. 7. Effect of H_2O_2 on the removal of TOC (acidic waste liquor). Conditions: initial pH 3.25, T : 20°C; $[Fe^{2+}]_0$: 208 mg/l⁻¹.

Fig. 8. Decomposition of H_2O_2 at different H_2O_2 dosage (acidic waste liquor). Conditions: initial pH 3.25, T : 20°C, $[Fe^{2+}]_0$: 208 mg/l⁻¹.

Fig. 9. Effect of H_2O_2 on the removal efficiency of TOC by oxidation and coagulation. Conditions: initial pH 3.25, $[Fe^{2+}]_0$: 208 mg/l⁻¹, T : 20°C; reaction time: 120 min.

Further extending the reaction time contributed little to TOC removal because Fenton's reaction could not proceed with the low residual H_2O_2 (below 0.2 mg/l⁻¹ 1 min after the start of the reaction). Variations of pH from 3.28 to 3.90 did not much affect TOC removal. A pH of 4.5 or higher, however, is apparently not preferable for TOC removal.

Since the dose of H_2O_2 determines the amount of $OH^\bullet$ produced, it is easy to speculate that the TOC removal performance in the Fenton's reaction system is, to a large extent, affected by the H_2O_2 dose. TOC removal at increasing H_2O_2

dosage was investigated as shown in Fig. 7. The TOC removal for the first minute was about 49% under each H_2O_2 dose, further demonstrating that the TOC removal in the first minute was mainly effected by adsorption. It is clear from the results shown in Fig. 8 that the consumption of H_2O_2 in the first minute was of almost the same value (90–95 mg/l⁻¹) for each H_2O_2 dose, indicating that this portion of H_2O_2 was mainly used for Fe^{2+} oxidation. Figs. 7 and 8 show that the TOC removal changed little with time under an H_2O_2 dose of 95 mg/l⁻¹ because no more H_2O_2 was available soon after the start of the reaction. At

an H_2O_2 dose of 190 mg/l^{-1} , however, the TOC removal increased gradually with time until the residual H_2O_2 was almost completely consumed at time 120 min. For an H_2O_2 dose of 380 mg/l^{-1} , the reaction continued for ca. 240 min. It should be noted, however, that an increase of H_2O_2 dose from 95 mg/l^{-1} to 380 mg/l^{-1} only resulted in an increase of TOC removal of no more than 20%. The residual Fe^{2+} was almost constantly lower than 1.0 mg/l^{-1} at an H_2O_2 dose of 190 mg/l^{-1} or higher. The slow declines of residual TOC and H_2O_2 shown in Figs. 7 and 8 indicated that the decomposition rate of H_2O_2 catalyzed by the $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle [Eqs. (6)–(8)] was very low.

It is well known that Fenton's system has dual functions of oxidation and coagulation for organics removal during wastewater treatment. With the addition of excessive H_2O_2 , most ferrous ions were quickly oxidized to ferric ions that had a strong hydrolyzing potential, and were believed to have a high capacity for absorbing organics. The respective contribution of adsorption by ferric oxides and oxidation by hydroxyl radicals to TOC removal after a 120-min reaction were investigated under different H_2O_2 dosages, as shown in Fig. 9. It was found that the contribution of oxidation to TOC removal increased with the increase of H_2O_2 dosage. Under an H_2O_2 dose of 95 mg/l^{-1} , nearly 80% of TOC removal was caused by adsorption for the total TOC removal of 49%, and the contribution of oxidation was not over 20%. At 380 mg/l^{-1} H_2O_2 , more than 76% of TOC removal was contributed by oxidation for the total TOC removal of 65%.

It should be noted that the significantly increased contribution from oxidation with the increase of H_2O_2 dosage from 95 mg/l^{-1} to 380 mg/l^{-1} did not produce a significant increase in total TOC removal. The oxidation intermediates formed during Fenton's reaction were mainly some polar compounds like alcohols and organic acids. These kinds of organic compounds are not easily removed through adsorption. However, they are more susceptible to micro-

organisms and could be removed through biodegradation.

4. Conclusions

Removal of Fe^{2+} and TOC from acidic waste liquor through a Fenton's reaction system was investigated, and some interesting phenomena were observed. According to the experimental results obtained in this study, some conclusions can be drawn as follows:

1. Fe^{2+} in wastewater can be effectively removed by adding H_2O_2 with a ratio of H_2O_2 to Fe^{2+} of 0.75 or higher, and ORP is a good indicator for addition of H_2O_2 .

2. TOC removal is affected by adsorption as well as oxidation. TOC removal was dominated by adsorption at a molar ratio of H_2O_2 to Fe^{2+} of 0.75, and by oxidation at a molar ratio of H_2O_2 to Fe^{2+} of 3.0.

3. The Fenton's reaction system can be effectively utilized for acidic waste liquor treatment.

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