Combined Fenton oxidation and aerobic biological processes for treating a surfactant wastewater containing abundant sulfate

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ABSTRACT

The present study is to investigate the treatment of a surfactant wastewater containing abundant sulfate by Fenton oxidation and aerobic biological processes. The operating conditions have been optimized. Working at an initial pH value of 8, a Fe^{2+} dosage of $600\,mg\,L^{-1}$ and a H_2O_2 dosage of $120\,mg\,L^{-1}$, the chemical oxidation demand (COD) and linear alkylbenzene sulfonate (LAS) were decreased from 1500 and $490\,mg\,L^{-1}$ to 230 and $23\,mg\,L^{-1}$ after 40 min of Fenton oxidation, respectively. Advanced oxidation pretreatment using Fenton reagent was very effective at enhancing the biodegradability of this kind of wastewater. The wastewater was further treated by a bio-chemical treatment process based on an immobilized biomass reactor with a hydraulic detention time (HRT) of 20 h after Fenton oxidation pretreatment under the optimal operating conditions. It was found that the COD and LAS of the final effluent were less than 100 and $5\,mg\,L^{-1}$, corresponding to a removal efficiencies of over 94% and 99%, respectively.

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1. Introduction

A surfactant detergent plant in Guangzhou of China generates wastewater containing chemical oxidation demand (COD), surfactant, suspended solids (SS), fat and oil [1,2]. Besides, sulfate concentration is high in the most detergent plant effluent because of the sulphonation process.

For economic reasons, it is still usual to treat the wastewater from these plants by anaerobic processes [3]. If this kind of wastewater containing abundant sulfate is treated by an anaerobic process, the sulfate will be converted to sulfides by sulfate reducing bacteria (SRB) [4,5]. The prevailing SRB inhibit the performance of acidogenic and methanogenic bacteria, so it will affect anaerobic treatment processes [6]. Consequently, most of the sulfides can be converted to sulfur under aerobic condition. This will subsequently consume a lot of dissolved oxygen. And sulfur is also harmful to aerobic bacteria in aerobic process. As a result of the high residual surfactants, the wastewater will foam during aerobic biological process. Therefore, it is not feasible to destroy the surfactant by aerobic treatment process directly. Pretreatment should be used such as flocculation, adsorption, foam separation and so on. There is a need to consider how to provide adequate treatment efficiency with an acceptable operating cost. Fenton oxidation is an alternative pretreatment.

Fenton reagent is a mixture of hydrogen peroxide (H_2O_2) solution and ferrous iron, which generates hydroxyl radicals according to a complex reaction sequence in an aqueous solution [7,8]. The purpose of this study was to investigate the feasibility of using Fenton's reagent as a pretreatment prior to biological treatment of this kind of wastewater. The objective of the present investigation was to examine the effects of operating variables on the performance of Fenton oxidation. The effectiveness of Fenton's reagent pretreatment on the biodegradability of this kind of wastewater was also examined. The results derived from a pilot plant study could provide significant information for industrial applications.

2. Materials and methods

2.1. Materials

In this work, Fenton oxidation had been employed to remove organic matter from a detergent wastewater characterized by high concentrations of surfactants and sulfate. The wastewater came from a Chinese detergent factory whose effluents were treated by means of coagulation–flocculation, anaerobic and aerobic biological process in its own industrial wastewater treatment plant (WWTP). The WWTP did not run well, so there was a lot of foam during aeration and the effluent could not meet the local discharge standards. The COD of influent, the wastewater pretreated by coagulation–flocculation, and effluent in this WWTP during the experimental period are presented in Fig. 1. In this phase, a sample of wastewater with a representative COD value around $1500\,mg\,L^{-1}$

Table 1
Parameter value from a detergent industry wastewater and emission limit values

Analyzer parameter	A sample used in the Fenton oxidation test[a]	Wastewater during the pilot plant[b]	Limit value[c]
COD (mg L^{-1})	1500 ± 47	1533 ± 334	100
BOD$_5$ (mg L^{-1})	332 ± 13	367 ± 125	20
SS (mg L^{-1})	213 ± 8	255 ± 173	70
LAS (mg L^{-1})	490 ± 11	417 ± 96	5
Oils and fats (mg L^{-1})	129 ± 5	121 ± 39	10
pH	8.0 ± 0.1	8.6 ± 1.2	6–9

[a] Data are average of three determinations.
[b] Number of samples analyzed = 10.
[c] Allowable limit for industrial wastewater discharges of Guangdong Province of PR China, based on Standard DB44/26-2001.

and the sulfate concentration around 2100 mg L^{-1} was used in the Fenton oxidation test in the laboratory, and its characteristics are shown in Table 1. A representative analysis of the wastewater during a pilot plant study is also given in Table 1, together with the provincial allowable limits for industrial wastewater discharges.

2.2. Analytical methods

Laboratory methods used for this study were from either standard methods [9] or were specified by the manufacture of the instrument. COD was analyzed following the standard method with potassium dichromate. Linear alkylbenzene sulfonate (LAS) concentration was determined by the standard method using a 752N UV/vis spectrophotometer (Shanghai Precision & Scientific Instrument Co. Ltd., China). pH was measured using a pH meter (model Ecoscan-pH6). In addition, the biodegradation curve for COD was plotted to estimate the aerobic biodegradability of wastewater [10].

2.2.1. Definitions and units of biodegradation curve

The amount of degradation attained at the end of the test was reported as the biodegradability in the Zahn–Wellens test:

$$D_T = \left[1 - \frac{C_T - C_B}{C_A - C_{BA}}\right] \times 100$$

where

D_T = biodegradation (%) at time T, C_A = COD value in the test mixture measured 3 h after the beginning of the test (mg L^{-1}), C_T = COD value in the test mixture at time T of sampling (mg L^{-1}), C_B = COD value of the blank at time T of sampling (mg L^{-1}), C_{BA} = COD value of the blank, measured 3 h after the beginning of the test (mg L^{-1}).
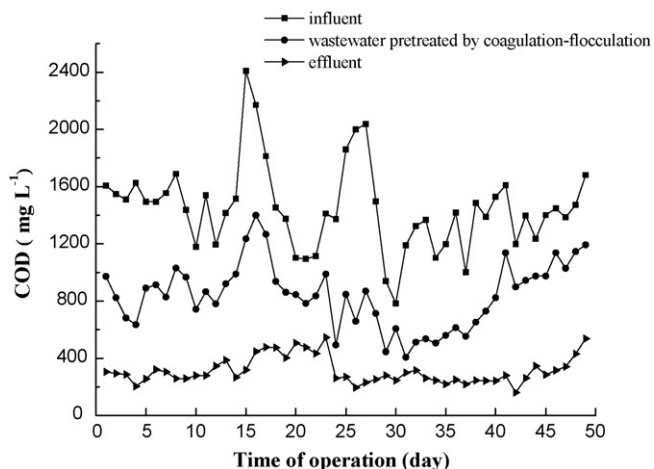

Fig. 1. The COD of influent, the wastewater pretreated by coagulation–flocculation, and effluent in this WWTP during the experimental period.

2.2.2. Plot of biodegradation curve

Activated sludge obtained from the WWTP, mineral nutrients and the test material as the sole carbon source in an aqueous solution were placed together in a glass vessel equipped with an agitator and an aerator. The mixture of activated sludge, nutrients and the test material was agitated and aerated at 20–25 °C by compress air for 28 days. The degradation process was monitored by determination of the COD values in the filtered solution daily. The ratio of eliminated COD after each interval to the value 3 h after the start was expressed as percentage biodegradation which served as the measure of the extent of degradation at this time. All bioassays were quantified by plotting the COD removal efficiency versus time.

2.3. Fenton oxidation test

Fenton oxidation was carried out in a batch mode using a 500-mL jar with a test wastewater volume of 250 mL. The reaction temperature was 24(±1) °C for all Fenton experiments. pH adjustments were performed using HCl or NaOH solutions. First, granular ferrous sulfate (FeSO$_4$·7H$_2$O) was added. 30% (w/w) H$_2$O$_2$ was subsequently added with 1 min of stirring. After the designated oxidation time, calcium oxide (CaO) was added and the aqueous solution was stirred rapidly to increase the pH to approximately 5. Then, 10 M NaOH solution was added to adjust the pH to 7–8, and a small amount of 0.2% (w/w) polyacrylamide solution was added for flocculation. The flocs were allowed to settle for half an hour. The supernatant COD and LAS were measured.

2.4. A pilot plant study

The reactions were scaled-up in a pilot plant. It consisted of two parts. One was a Fenton oxidation reactor and the other was a biomass reactor. The Fenton oxidation reactor equipped with a stirrer was a 150-L tank. The bench-scale upflow biomass reactor was constructed from a cylindrical container with an internal diameter of 20 cm, an overall height of 200 cm, and an available volume of 20 L. At the bottom of the reactor, a filter plate was laid to support the expanded ceramic medium with mean particle sizes between 3 and 5 mm. Air was introduced into the reactor through perforated pipes with an orifice diameter 3 mm.

Fenton oxidation was carried out in batch mode under the optimal conditions determined by the previous laboratory test. After 40 min of Fenton oxidation, CaO and NaOH solution were added and the aqueous solution was stirred at 150 rpm for 5 min to increase the pH to 7–8. This was followed by 5 mg L^{-1} polyacrylamide addition with 50 rpm mixing speed to promote flocs formation for 5 min. After 2 h of precipitation, the supernatant was collected into an influent tank located after Fenton oxidation reactor for further biological treatment. To ensure that the wastewater after precipitation contains adequate nutrition for microorganisms, 4 mg L^{-1} sodium tri-polyphosphate was added into the influent tank. Then, the wastewater was fed into the upflow immobilized biomass reac-

Table 2
Results of wastewater treatment using pilot plant combined Fenton and aerobic biological processes (mean of three samples)

Influent		Fenton's reagent pretreatment		Biotreatment		
COD (mg L^{-1})	LAS (mg L^{-1})	COD (mg L^{-1})	LAS (mg L^{-1})	HRT (h)	COD (mg L^{-1})	LAS (mg L^{-1})
				5	131 ± 4	7.9 ± 0.2
1652 ± 42	528 ± 17	235 ± 5	24.7 ± 0.6	10	92 ± 3	4.0 ± 0.1
				20	84 ± 4	4.0 ± 0.1
				5	151 ± 7	8.1 ± 0.2
2412 ± 73	561 ± 11	362 ± 8	39.5 ± 0.7	10	105 ± 5	4.7 ± 0.1
				20	92 ± 3	4.5 ± 0.1

tor and the overall flow rate through the reactor was controlled by a metering pump.

Thickened activated sludge was obtained from the WWTP with a concentration of 4000 mg L^{-1}. 2 L activated sludge was added into the upflow biomass reactor without pretreatment and then completely mixed with medium. After inoculation, the medium bed was first aerated with an airflow rate of 40 L h^{-1} for 3 days. At last, the system was operated with a continuous influent at a certain flow rate controlled by the metering pump. Changing the influent flow rate allowed control of the hydraulic detention time (HRT). 3–7 days of acclimation were needed when the immobilized reactor was operated at different HRTs.

3. Results and discussion

3.1. Optimum operating conditions of Fenton oxidation

A series of experiments were conducted to examine the effect of initial pH on the efficiency of wastewater treatment. Because the Fe^{2+} dosage was significantly high in this study, the pH value was always between 3 and 5 due to the hydrolyzation of the excessive ferrous iron. And the pH value between 3 and 5 was in favor of Fenton oxidation. Hence, we kept the initial pH unchanged for all the subsequent tests.

Fig. 2(a–c) shows the removal efficiencies referred to COD and LAS which were obtained at different initial Fe^{2+} concentrations after 40 min of reaction, corresponding to an initial H$_2$O$_2$ dosage of 60, 120, 180 mg L^{-1}, respectively. At an initial H$_2$O$_2$ dosage of 60, 120, 180 mg L^{-1}, there was a strong correlation ($r = 0.99$, 0.98 and 0.99, respectively) between LAS removal and COD removal efficiencies. Also, there was a very important improvement on the efficiency of COD and LAS removal when increasing the Fe^{2+} dosage up to a certain level. According to the results, looking at the final COD and LAS removal efficiencies achieved (approximately 85% and 95%, respectively), more attention should be paid to the Fe^{2+} dosage rather than to the H$_2$O$_2$ dosage for an efficient application of the Fenton treatment to the wastewater used in this work, coincided reasonably well with results reported by Sheng et al. [11] and Bautista et al. [12]. On the other hand, it is not advisable to use too much ferrous iron in practice, not only because it entails a higher cost of reagent but also because it needs subsequent treatment to remove any residual ferrous iron. The higher the iron dosage, the more sludge produced and the higher its disposal cost. The results presented in Fig. 2(a) and (b) indicated that Fe^{2+} dosage of about 600 mg L^{-1} would be sufficient in most cases.

Fig. 3 shows the residual COD and LAS varied with the dosage of H$_2$O$_2$ after 40 min of Fenton oxidation. The Fe^{2+} dosage was 1200 mg L^{-1} in all cases to make sure ferrous iron was sufficient. Both the COD and LAS removal curves tended to level off above 120 mg L^{-1} H$_2$O$_2$ dosage. A higher dosage of H$_2$O$_2$ means a higher production of hydroxyl radicals and this enhances the rate of mineralization. Nevertheless, this effect was less significant as the H$_2$O$_2$ dosage increases due to the auto-scavenging effect of peroxide on hydroxyl radicals.
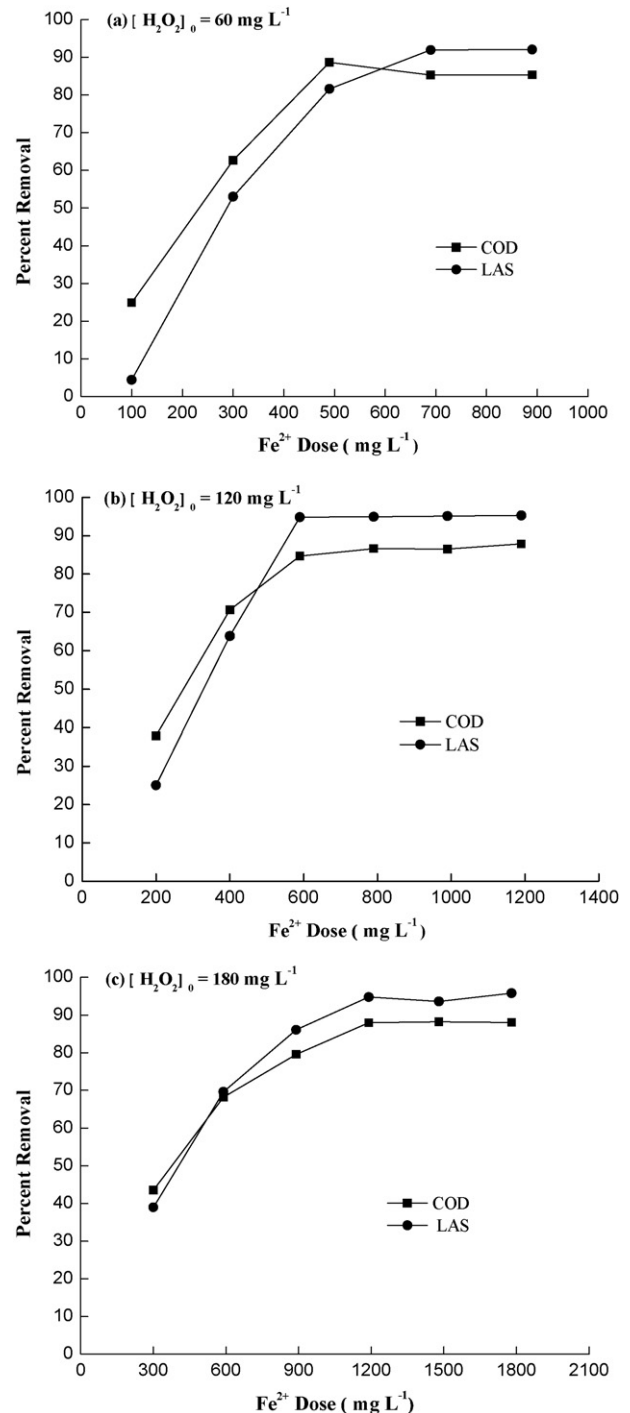

Fig. 2. Effect of initial Fe^{2+} concentration on the LAS and COD removal with different dosages of H$_2$O$_2$.
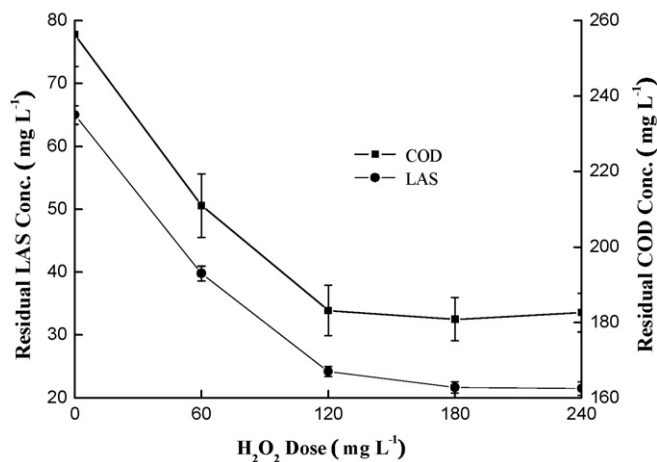
Fig. 3. The residual LAS and COD concentrations varied with the dosage of H_2O_2 ($COD_0 = 1500$ mg L^{-1}; $LAS_0 = 490$ mg L^{-1}; $[Fe^{2+}]_0 = 1200$ mg L^{-1}).

Fig. 4 shows the residual COD and LAS as a function of oxidation time after the application of 600 mg L^{-1} Fe^{2+} and 120 mg L^{-1} H$_2$O$_2$. It can be observed a very important improvement on the efficiency of COD and LAS removal after 5 min of oxidation. And the COD and LAS removal curves tended to level off after 40 min of oxidation. The reason for this is that a high (600 mg L^{-1}) Fe^{2+} dosage will enhance the decomposition of H$_2$O$_2$, giving rise to a very rapid generation of hydroxyl radicals and a high concentration of this species in the early stages of the process [12,13]. Hence, 40 min of Fenton oxidation with 600 mg L^{-1} Fe^{2+} would be sufficient to oxidize COD and LAS from the initial values of 1500 and 490 mg L^{-1} to 230 and 23 mg L^{-1}, respectively.

3.2. Biodegradability enhancement

Although some anionic surfactants can easily be biodegraded by aerobic microorganisms [14], it still seems worthwhile to investigate the effects of Fenton's reagent pretreatment on the biodegradability of this type of wastewater [13,15]. Fig. 5 shows the COD removal efficiencies with three different treatments. It was interesting to note that, for the wastewater pretreated by Fenton oxidation, application of 60 and 120 mg L^{-1} H$_2$O$_2$ resulted in an increase in COD$_B$/COD from 0.3 to 0.9 and from 0.3 to 0.7, respectively. (COD$_B$ is the total COD which can be biodegraded in the Zahn–Wellens test.) Therefore, a small amount of H$_2$O$_2$ significantly increased both the rate and the extent of biodegra-
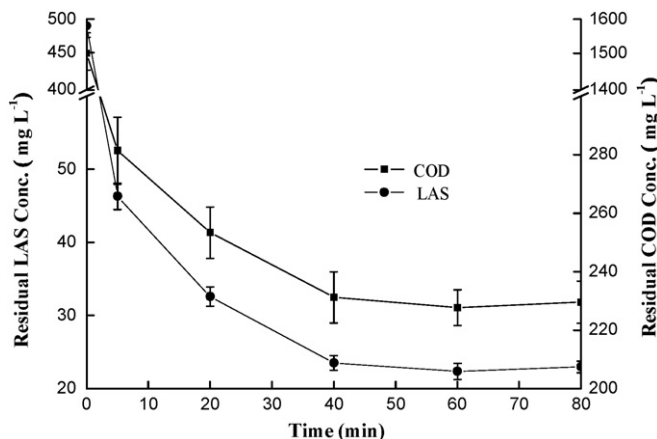

Fig. 4. The residual LAS and COD concentrations varied with the reaction time ($[Fe^{2+}]_0 = 600$ mg L^{-1} and $[H_2O_2]_0 = 120$ mg L^{-1}).
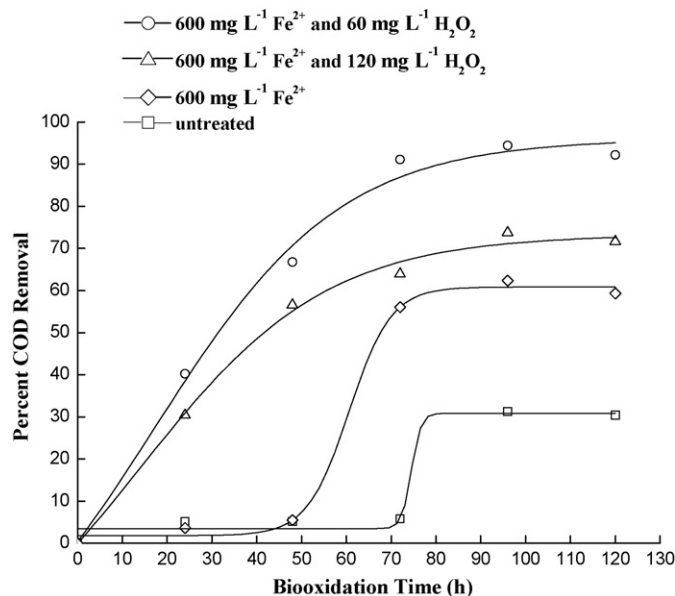

Fig. 5. Biodegradation plot for the untreated and pretreated wastewater.

dation of the test wastewater. For the wastewater pretreated by means of coagulation–flocculation with 600 mg L^{-1} Fe^{2+}, the value of COD$_B$/COD increased from 0.3 to 0.6 after 2 days' acclimation period. However, since there was still a large amount of residual surfactants in the wastewater after the application of only 600 mg L^{-1} Fe^{2+} (without any H$_2$O$_2$ dosage), as seen in Fig. 3, it was impractical to treat the wastewater by aerobic biological process directly after only coagulation–flocculation as a pretreatment because of foam problem.

3.3. Wastewater treatment by combined Fenton oxidation and aerobic biological processes

Influent and effluent qualities for the pilot plant are shown in Table 2.

Two samples of wastewater with significantly different values of COD (1652 and 2412 mg L^{-1}) were traced in the pilot plant. The COD in wastewater after Fenton oxidation under the optimal operating conditions were deceased from 1652 and 2412 mg L^{-1} to 235 and 362 mg L^{-1}, respectively, while the majority of the LAS was also removed. With further biotreatment, it was found that maintaining HRT at 10 h significantly reduced the residual COD and LAS compared with the results obtained with HRT of 5 h. When the HRT reached 20 h, the residual COD and LAS were approximately 90 and 4 mg L^{-1}, corresponding to overall COD and LAS removal efficiencies of over 94% and 99%, respectively.

4. Conclusions

- Fenton oxidation was a feasible treatment for wastewater containing a large amount of surfactants and sulfate, allowing a significant decrease of COD and LAS. The optimum operating conditions for the Fenton oxidation process were 600 mg L^{-1} Fe^{2+}, 120 mg L^{-1} H$_2$O$_2$ and 40 min of treatment time. More attention should be paid to the Fe^{2+} dosage rather than to the H$_2$O$_2$ dosage for this type of wastewater treatment.
- Fenton oxidation pretreatment was also highly effective at enhancing the biodegradability of wastewater. It was found that a small amount of H$_2$O$_2$ can significantly increase both the rate and the extent of biodegradation of wastewater. The effluent COD and LAS were below 100 and 5 mg L^{-1}, respectively, after aerobic

biological process based on an immobilized biomass reactor with a HRT of 20 h.

- Wastewater containing a large amount of surfactants and sulfate cannot be easily treated by conventional physicochemical and biological processes. Combining Fenton oxidation and aerobic biological processes provided an elegant and cost-effective way to solve this problem.

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