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Mary Kay Camarillo

University of the Pacific, mcamarillo@pacific.edu

William T. Stringfellow

Lawrence Berkeley Lab, wstringfellow@lbl.gov

C. Feng

H. Sun

University of the Pacific, hsun@pacific.edu

S. Li

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Treatment of oil–water emulsion from the machinery industry by Fenton’s reagent

Chao Feng, Henghu Sun, Suqin Li, Mary Kay Camarillo,
William T. Stringfellow and Yangyang Liang

ABSTRACT

An oil–water emulsion from the machinery industry was treated using Fenton’s reagent. The objective was to reduce the high chemical oxygen demand (COD) of this waste stream so that it would meet the COD effluent limit of Chinese Standard JS-7740-95. The optimal $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ ratio for COD removal was 3. An orthogonal experimental design was developed based on the optimal $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ ratio to evaluate the significance of four parameters relevant to the treatment process, namely, H_2O_2 dosage, initial pH, oxidation time and coagulation pH. The influence of the four parameters on COD removal efficiency decreased as follows: H_2O_2 dosage > oxidation time > coagulation pH > initial pH. The COD removal efficiency was further investigated based on the most important single-factor parameter, which was H_2O_2 dosage, as discovered in the orthogonal test. A well-fitted empirical correlation was obtained from the single-factor analysis and up to 98% COD removal was attained using 50 mM H_2O_2 . Using the doses and conditions identified in this study, the treated oil–water emulsion can be discharged according to Chinese Standard JS-7740-95.

Key words | Fenton’s reagent, H_2O_2 dosage, oil–water emulsion, orthogonal test

Chao Feng

Henghu Sun (corresponding author)

Mary Kay Camarillo

William T. Stringfellow

Pacific Resources Research Center,
School of Engineering and Computer Science,
University of the Pacific,
3601 Pacific Avenue,
Stockton, CA 95211, USA
E-mail: hsun@pacific.edu

Henghu Sun

Green Construction Materials and Circulation
Economy Center,
Architectural Design and Research Institute of
Tsinghua University Co., Ltd,
Haidian District, Beijing 100084, China

Suqin Li

Yangyang Liang

Ecological Engineering Department,
School of Metallurgical and Ecological Engineering,
University of Science and Technology Beijing,
30 Xueyuan Road, Haidian District,
Beijing 100083, China

William T. Stringfellow

Earth Science Division,
Lawrence Berkeley National Laboratory,
1 Cyclotron Road,
Berkeley, CA 94720, USA

INTRODUCTION

Oil–water emulsions are used extensively in many industries, including the metal working industry and in hydrometallurgy (Hu *et al.* 2002; Hilal *et al.* 2004a; Mostefa & Tir 2004; Hesampour *et al.* 2008). These emulsions contain a mixture of free and emulsified oils, surfactants, co-surfactants, which are weakly amphiphilic molecules that support aggregation of the primary surfactants (Chennamsetty *et al.* 2005), and various additives. The emulsions are employed to cool and lubricate the tool/workpiece interface to increase tool life and improve the overall finish of the workpiece (Hu *et al.* 2002; Hilal *et al.* 2004a; Hesampour *et al.* 2008). These oil–water emulsions must be replaced periodically due to the effects of thermal degradation, particulate contamination, and biological contamination (Chazal 1995; Hilal *et al.* 2004b). Therefore, a large amount of hazardous liquid is produced that requires treatment. Due to the presence of oils, surfactants and co-surfactants,

the oil–water emulsions are very stable with high chemical oxygen demand (COD) and difficult to treat, especially when the oil droplets are finely dispersed (Hu *et al.* 2002; Hilal *et al.* 2004a; Mostefa & Tir 2004). In this study, alternatives were sought for the current treatment process that employs coagulants to treat the oil–water emulsion, producing an effluent with a COD of around 300 mg/L. This effluent does not meet the discharge standard, which requires that COD be less than 100 mg/L. Therefore, more effective pretreatment is required before discharging this machinery wastewater to the sewer.

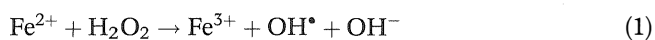
Conventional treatment methods are not typically effective for an oil–water emulsion due to the presence of surfactants and co-surfactants (Mostefa & Tir 2004). The standard treatment approach is chemical de-emulsification followed by gravity settling or air flotation (Mostefa & Tir 2004; Li *et al.* 2008). Various chemicals are used in this

process and the effluent from chemical treatments requires secondary purification (Burke 1991; Mostefa & Tir 2004). During the last few decades, several methods have been developed to treat oil–water emulsions, such as membrane technologies and electroflotation techniques (Hilal *et al.* 2004a; Mostefa & Tir 2004).

Membrane treatment is a promising method and several studies have reported that membrane microfiltration and ultra-filtration are effective processes in oil–water emulsion treatment (Lin & Lan 1998; Scott *et al.* 2001; Miyagi & Nakajima 2002; Hilal *et al.* 2004a). However, fouling via deposition, microbial growth, pore blocking and macromolecular adsorption can limit the applicability of membrane treatments. Suspended particles captured at the membrane surface can cause gradual fouling and a consequential reduction in permeability (Hilal *et al.* 2004a).

Electroflotation is adequate for the separation of oil from oily wastewater (Osasa *et al.* 1992; Hosny 1996; Il'in & Sedashova 1999; Mostefa & Tir 2004; Ben Mansour & Chalbi 2006). However, the main disadvantage of this process is the high cost of electrode materials (Hosny 1996; Ben Mansour & Chalbi 2006). A few studies have reported on the use of an insoluble anode to reduce treatment costs (Ho & Chan 1986; Hosny 1996). Nevertheless, the main disadvantage of this method is low separation efficiency (Hosny 1996; Mostefa & Tir 2004). The inclusion of a chemical process with electrochemical methods would result in better treatment, but at a higher cost.

In the last few decades, treatment by Fenton's reagent has proved to be an effective technology for the removal of recalcitrant organic pollutants in aqueous solutions (Sedlak & Andren 1991; Legrini *et al.* 1993; Neyens & Baeyens 2003; Lee *et al.* 2013). The main advantage of Fenton's reaction is the destruction of pollutants to harmless compounds, e.g. CO₂, water and inorganic salts (Neyens & Baeyens 2003). Fenton's reagent is added as a mixture of hydrogen peroxide (H₂O₂) and ferrous iron (Fe²⁺). Strong oxidative hydroxyl radicals OH• (oxidation potential: 2.8 V (Legrini *et al.* 1993; Szpyrkowicz *et al.* 2001)) are generated due to Fenton's reagent and Fe²⁺ is oxidized to ferric iron (Fe³⁺) according to the following reaction (Kitis *et al.* 1999; Lu *et al.* 2001; Yoon *et al.* 2001):

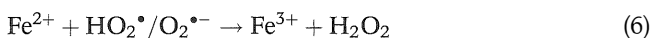
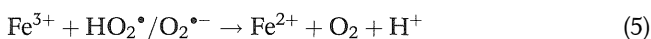
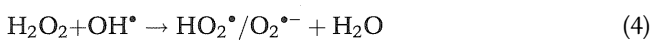
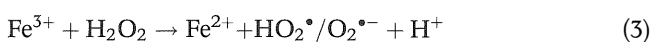


According to Equation (1), the Fe²⁺ acts as a catalyst to initiate the decomposition of H₂O₂, resulting in the generation of hydroxyl radicals (Neyens & Baeyens 2003).

Hydroxyl radicals can be scavenged by reacting with Fe²⁺ according to Equation (2) (Chamarro *et al.* 2001; Neyens & Baeyens 2003).



Ferric iron (Fe³⁺) will also catalyze the decomposition of H₂O₂. Simultaneously, Fe²⁺ is regenerated through the so-called Fenton-like reaction between Fe³⁺ and H₂O₂. Reactions following the initial reaction of the Fenton's reagents (Equation (1)) are shown in Equations (3)–(6) (Kwan & Voelker 2002; Duesterberg & Waite 2006).

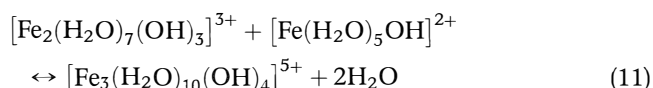
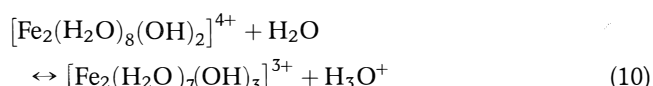
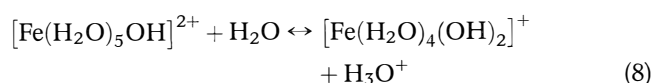
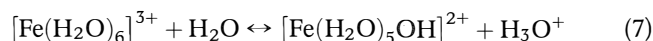


As shown in Equation (1), Fe²⁺ and H₂O₂ can collectively initiate hydroxyl radical formation. Ferrous iron (Fe²⁺) and H₂O₂ can also react with the generated hydroxyl radicals (Equations (2) and (4)). Hydroperoxyl radicals (HO₂•) and its conjugate base superoxide (O₂•[−]), can both reduce oxide iron ions and thus affect the cycling of iron between Fe³⁺ and Fe²⁺. These species can propagate the chain of reactions by reducing Fe³⁺ (Equation (5)) or terminate it by oxidizing Fe²⁺ (Equation (6)). The kinetic constants of Equations (3)–(6) are dependent on pH, demonstrating its importance in determining which reactions are predominant (Gallard *et al.* 1998; Kwan & Voelker 2002; Duesterberg & Waite 2006).

The hydroxyl radicals generated in Equation (1) can oxidize organics by abstraction of hydrogen atoms to produce organic radicals (R•), which are reactive and can be further oxidized, and thus causes chemical decomposition of compounds by conversion to CO₂, water and inorganic salts (Venkatadri & Peters 1993; Lin & Lo 1997; Szpyrkowicz *et al.* 2001; Neyens & Baeyens 2003).

Ferric hydroxyl-complexes can be formed during the Fenton process according to Equations (7)–(8). These reactions are dependent on pH. The complexes will polymerize with increasing pH according to Equations (9)–(11), which account for the coagulation capability of Fenton's reagent

by the formation of iron complexes (Lin & Lo 1997; Szpyrkowicz *et al.* 2001; Neyens & Baeyens 2003).



Fenton's reagent has the dual functions of oxidation and coagulation in the treatment process, and the extent of each treatment mechanism will depend on the $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ ratio (Lin & Lo 1997; Gulkaya *et al.* 2006). If the $[\text{H}_2\text{O}_2]$ dose is higher, there tends to be a more oxidative effect. When the $[\text{Fe}^{2+}]$ dose is higher, coagulation is the more important treatment mechanism. As it functions as both a strong oxidant and a coagulating agent, Fenton's reagent has been successfully used as treatment method for textile wastewater (Lin & Lo 1997; Szpyrkowicz *et al.* 2001; Kang *et al.* 2002), pulp and paper treatment effluents (Perez *et al.* 2002), cosmetic wastewater (Bautista *et al.* 2007), cork cooking wastewater (Guedes *et al.* 2003), municipal landfill leachate (Deng 2007) and carpet dyeing wastewater (Gulkaya *et al.* 2006). However, few research studies have been conducted on the treatment of oil–water emulsion by Fenton's reagent (Tony *et al.* 2009a; b). In the previous studies, a photo-Fenton treatment method was used that combined a UV light source and Fenton's reagent. The goal of this research was to demonstrate the use of Fenton's reagent to treat oil–water emulsion from the machinery industry. Specifically, the research objectives were to: (1) determine the optimal $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ ratio for COD reduction; (2) design an orthogonal test at optimal $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ ratio to evaluate the significance of four parameters: H_2O_2 dosage, initial pH; oxidation time and coagulation pH; and (3) investigate the COD removal efficiency based on the most important single factor.

MATERIALS AND METHODS

Materials

The oil–water emulsion used in this research was obtained from a machinery plant located in Xiaodian District, Taiyuan, Shanxi, China (Table 1). Fenton's reagent was prepared using H_2O_2 (30%wt, density = 1.11 g/cm³) and ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), which were from Sinopharm Chemical Reagent Co., Ltd and Beijing Chemical Works, respectively. Sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) were used for pH adjustment, which were from Beijing Chemical Works. Distilled water was obtained from the University of Science and Technology, Beijing. All chemicals used were reagent-grade.

Experimental procedure

The experiments were conducted in 100 mL flasks containing 100 mL of oil–water emulsion sample (at 30 °C and 1 atm). Initially, the pH of the wastewater sample was adjusted to between 2 and 5 with 0.1 N H_2SO_4 and NaOH. Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was added to the sample followed by H_2O_2 , and then the wastewater sample was mixed by magnetic stirrer for 10–40 minutes, depending on the designated oxidation time. After oxidation, the pH of the sample was raised to 5–8 with 0.1 N NaOH. After 1 minute of slow mixing, the sample was allowed to settle. Based on previous studies (Lin & Lo 1997; Szpyrkowicz *et al.* 2001; Kang *et al.* 2002), the experiment time was sufficient for the decomposition and release of H_2O_2 , which was important since residual H_2O_2 interferes with COD analysis. Lin and Lo (Lin & Lo 1997) found that all H_2O_2 was completely degraded after 120 minutes in their study. Therefore, we conservatively waited 4 hours before collecting supernatant for the COD test. COD was measured according to Chinese Standard HJ/T399-2007, using a 5B-3B automatic COD analyzer (Lianhua Ecotech Co.,

Table 1 | Oil–water emulsion characteristics

Parameter	Original sample	Treated sample	Discharge standard
Petroleum hydrocarbons (mg/L)	4.5	1.25	10
COD (mg/L)	1,610	29	100
TSS (mg/L)	479	1.4	200
pH	9.73	6.55	6~9

COD: chemical oxygen demand; TSS: total suspended solids.

Ltd, Beijing, China). Each experiment was performed twice and the mean value was used for analysis.

Data analysis

The COD removal efficiency (Re) is defined as follows:

$$\text{Re}(\%) = ((\text{COD}_0 - \text{COD}_F) / \text{COD}_0) \times 100$$

where COD_0 is the COD of the original oil–water emulsion, which was 1,610 mg/L in this study, and COD_F , which is the COD of the treated samples.

An orthogonal experimental test design was employed, which is used for solving multiple-factor optimization problems while minimizing the number of tests that need to be performed (Fan *et al.* 2004). The use of an orthogonal experimental test design allowed for the significance of different factors to be evaluated. The statistical software packages SPSS and Origin were used for statistical analyses.

RESULTS AND DISCUSSION

Effect of $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ ratio

To determine the optimal $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ ratio for the orthogonal test, all other parameters were held constant

($[\text{FeSO}_4 \cdot 7\text{H}_2\text{O}] = 40 \text{ mM}$, initial $\text{pH} = 3.0$, 30 minutes oxidation period and a coagulation $\text{pH} = 7.0$), while the $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ ratio was varied between 0.5:1 and 6:1 (Figure 1). The highest COD removal of over 99% occurred at $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}] = 3$. The COD removal efficiency decreased when the $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ ratio was lower or higher than 3, which may be attributed to the scavenging effects of ferrous ions or peroxide on hydroxyl radicals according to Equations (2) and (4), respectively. This result coincides with the observation that the COD removal of municipal landfill leachate by Fenton's reagent was highest at $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}] = 2\text{--}3$ (Deng 2007). In the present study, $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}] = 3$ was considered optimal and was used in the subsequent tests. The optimal $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ ratio was confirmed following the experiments of the orthogonal test.

Evaluation of the significance of parameters by orthogonal test

The orthogonal test was designed to allow determination of the remaining parameters (Table 2). There are four factors and four levels, such that 16 samples were oxidized by Fenton's reagent. COD removal efficiency was used as the optimization metric. Table 3 shows the experimental design and results of the orthogonal test. Test results were evaluated for COD removal efficiency in each experiment, as well as the

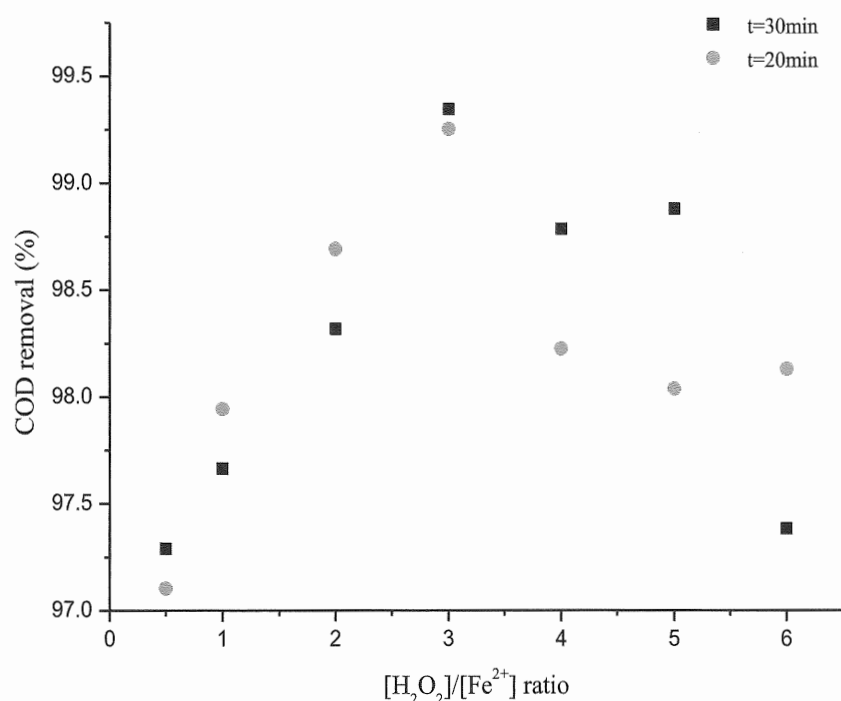


Figure 1 | The effect of $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ ratio on COD removal efficiency (conditions: $[\text{FeSO}_4 \cdot 7\text{H}_2\text{O}] = 40 \text{ mM}$; initial $\text{pH} = 3.0$; oxidation time = 20 or 30 minutes; coagulation $\text{pH} = 7.0$).

Table 2 | The orthogonal test factors and levels

Level	Test factors			
	A H ₂ O ₂ (mM)	B Initial pH	C Oxidation time (min)	D Coagulation pH
1	30	4	10	7
2	150	3	20	6
3	110	2	40	5
4	70	5	30	8

average COD removal efficiency at the i th test level (k_i). The range in removal efficiency for the test levels (k_i) was also reported. The 16 experiments were performed to test different combinations of factors (Table 3). For example, in experiment No. 10, the sample was handled under A level = 3, B level = 2, C level = 4 and D level = 3, which was equivalent to a 110 mM dosage of H₂O₂, initial pH = 3, 30 minutes oxidation

Table 3 | Configuration and results of the orthogonal test

Test no.	Test factors				
	A H ₂ O ₂ (mM)	B Initial pH	C Oxidation time (min)	D Coagulation pH	Removal efficiency (%)
1	1	1	1	1	95.1
2	1	2	2	2	97.2
3	1	3	3	3	94.5
4	1	4	4	4	95.3
5	2	1	2	3	97.9
6	2	2	1	4	96.9
7	2	3	4	1	99.2
8	2	4	3	2	97.5
9	3	1	3	4	95.4
10	3	2	4	3	97.7
11	3	3	1	2	97.4
12	3	4	2	1	98.1
13	4	1	4	2	98.4
14	4	2	3	1	98.4
15	4	3	2	4	98.1
16	4	4	1	3	95.8
k_1	95.5	96.7	96.3	97.7	
k_2	97.9	97.5	97.9	97.6	
k_3	97.1	97.3	96.5	96.5	
k_4	97.7	96.7	97.6	96.4	
Range	2.4	0.8	1.6	1.3	

period and coagulation pH = 5, respectively. The COD removal efficiency was 97.7% in experiment No. 10. The k_1 in factor A is the average removal efficiency of tests 1 to 4. Range refers to the difference between the maximum and minimum removal efficiency values.

To collect data for the orthogonal test, experiments were conducted where each parameter was altered sequentially and the effect of the four parameters was observed with respect to COD removal (Figure 2). Initial pH for the first point is level 3, which is 2 for this parameter. The experiments for which initial pH level is 3 are experiments 3, 7, 11 and 15. The performance characteristics value for the first data point is thus the average of those values obtained from experiments 3, 7, 11 and 15, which is 97.3%. The numerical value of the maximum point in each plot represents the best factor-level condition in terms of COD removal efficiency. Therefore, the optimum conditions were 150 mM for H₂O₂ dosage, initial pH = 3, 20 minutes oxidation time and coagulation pH = 7. In addition, the greater the differences in COD removal, the greater the influence of that factor on COD removal efficiency, and the more important the factor. Therefore, the influence on COD removal efficiency decreases in the following order: H₂O₂ dosage > oxidation time > coagulation pH > initial pH (Figure 2 and Table 3).

In order to further confirm whether the process parameters (H₂O₂ dose, initial pH, oxidation time, and coagulation pH) were statistically significant or not, an analysis of variance (ANOVA) test was performed (Table 4). The H₂O₂ dosage, oxidation time and coagulation pH were all significant in influencing COD removal, while initial pH was not significant. After oxidation, the pH in all cases was around 2.3, regardless of the initial pH. However, the coagulation pH was significant due to the pH dependence of the complexation reactions (Equations (7)–(11)). The significance of these four parameters can be ranked as follows: H₂O₂ dosage > oxidation time > coagulation pH > initial pH, which is consistent with the results in Figure 2 and Table 3. Therefore, H₂O₂ dosage was found to be the most important determinant of COD removal.

The effect of H₂O₂ dosage on COD removal efficiency

The COD removal efficiency was investigated based on the most important single factor, which was H₂O₂ dosage, as was confirmed in the orthogonal test. However, the optimal [H₂O₂]/[Fe²⁺] ratio was further confirmed under optimum experimental conditions, as the optimal molar [H₂O₂]/[Fe²⁺] ratio of 3 was originally obtained under different

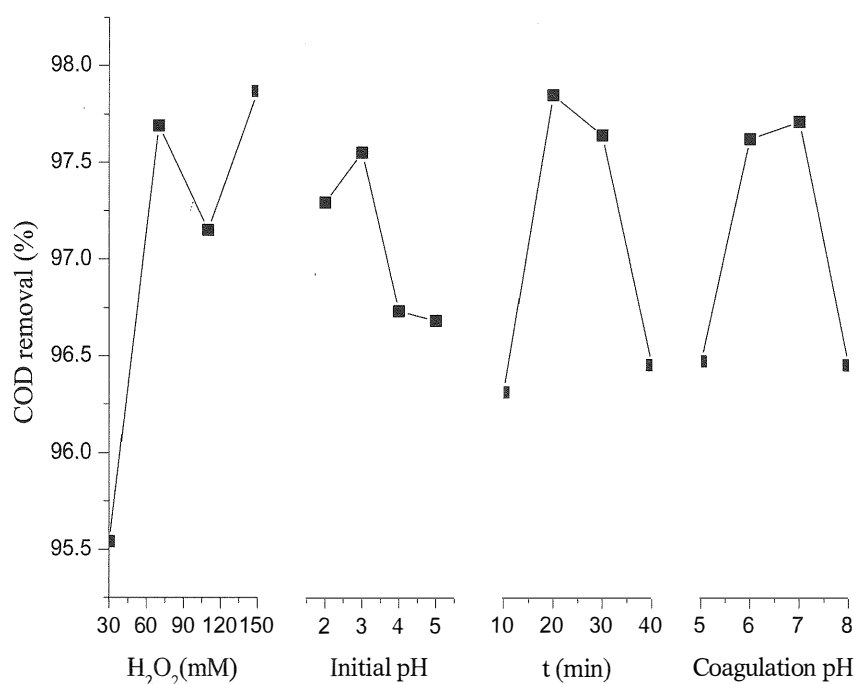


Figure 2 | The effect of each parameter on COD removal efficiency.

Table 4 | ANOVA table

Factors	Sum of squares	Degrees of freedom	Mean of squares	F	Significance ^a
H_2O_2	13.53	3	4.51	43.44	** ($p < 0.01$)
Initial pH	2.17	3	0.72	6.96	Not significant
Oxidation time	7.60	3	2.53	24.40	* ($p < 0.05$)
Coagulation pH	5.81	3	1.94	18.65	* ($p < 0.05$)

^aCritical F value is 9.28 ($p < 0.05$) and significance level is '**', if F value is larger than 9.28; critical F value is 29.46 ($p < 0.01$) and significance level is '***', if F value is larger than 29.46.

conditions (initial pH = 3.0; oxidation time of 30 minutes; coagulation pH = 7.0), compared with the optimum experimental conditions (initial pH = 3.0; oxidation time of 20 minutes; coagulation pH = 7.0). Further experiments confirmed that the optimal $[H_2O_2]/[Fe^{2+}]$ ratio is still 3 (Figure 1).

It is important to determine the H_2O_2 dosage needed since it represents a significant component of the cost for this type of treatment system. The COD removal efficiency increased dramatically at low H_2O_2 doses, but leveled off around $[H_2O_2] = 50$ mM (Figure 3). In the experiments, the

COD removal efficiency was as high as 86% even without the addition of Fenton's reagent. The inherent reduction in COD may be attributed to the pH adjustment and stirring that caused the oil–water emulsion to destabilize (Dyab 2012). This was confirmed by the formation of flocs at the bottom of the reactor when the pH was adjusted to 3. The destabilization of flocs may be the result of the solution reaching the zero-point of charge for oil droplets, which is reported to occur within the pH range of 2–5 (Crittenden *et al.* 2012). Some of these flocs were re-suspended into the solution when the pH was subsequently increased to 7. The increased H_2O_2 dosage up to 50 mM caused the COD removal efficiency to rise rapidly, likely the result of increased generation of hydroxyl radicals. In addition, more ferric hydroxyl-complex was likely produced because of the constant $[H_2O_2]/[Fe^{2+}]$ ratio, and hence, COD removal was enhanced by coagulation. However, this beneficial effect of oxidation and coagulation becomes less significant as the dosage of H_2O_2 increases. This may be because the formation of hydroperoxyl/superoxide radicals (Equation (4)) becomes more prominent with higher dosage of H_2O_2 . Although hydroperoxyl/superoxide radicals are generated, the subsequent reactivity of hydroperoxyl/superoxide radicals towards iron ions results in a faster oxidation of Fe^{2+} (Equation (6)) than reduction of Fe^{3+} (Equation (5)) at pH 3 or even lower, which leads

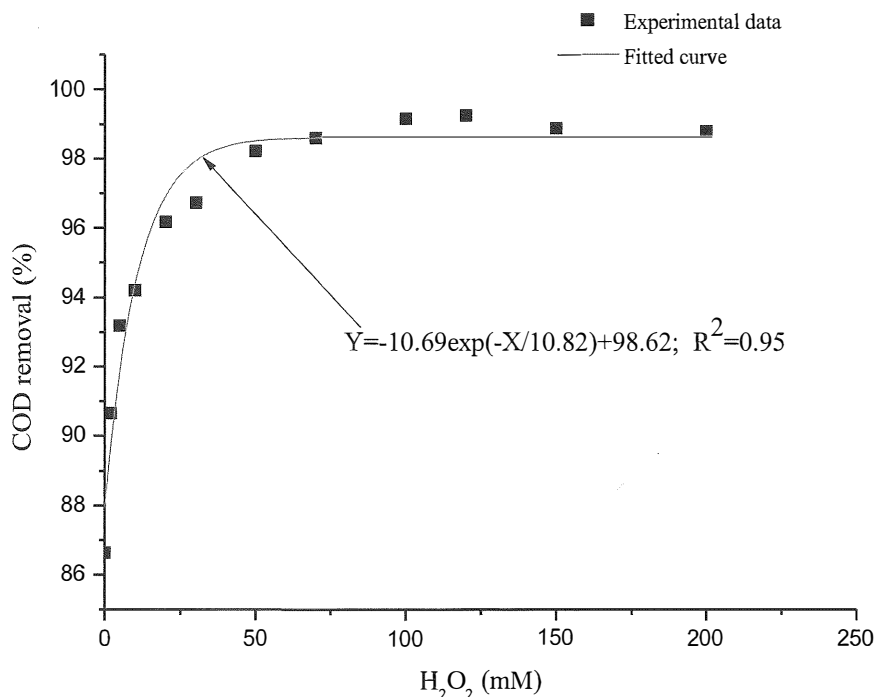


Figure 3 | The effect of H₂O₂ dosage on COD removal efficiency (conditions: [H₂O₂]/[Fe²⁺] ratio = 3; initial pH = 3.0; oxidation time = 20 minutes; coagulation pH = 7.0).

to chain termination (Kwan & Voelker 2002; Duesterberg & Waite 2006). This limiting of further hydroxyl radicals generation is similar to the findings presented by Mandal *et al.*, Gulkaya *et al.* and Bautista (Gulkaya *et al.* 2006; Bautista *et al.* 2007; Mandal *et al.* 2010). A higher dose of H₂O₂ did not lead to any further improvement in terms of COD removal in wastewater treatment because of the occurrence of the auto-scavenging reaction.

An empirical correlation was obtained for the relationship between H₂O₂ dosage and COD removal (Figure 3), using the nonlinear curve fit function 'ExpDec1' in Origin 8.0, where X refers to H₂O₂ dosage (mM) and Y refers to COD removal (%). The empirical formula is specific to the conditions of the experiments here: [H₂O₂]/[Fe²⁺] ratio = 3, initial pH = 3.0, oxidation time = 20 minutes and coagulation pH = 7.0. According to Figure 3, the use of concentrations over 50 mM will not yield improved COD removal and will result in added cost. An excess of reagent would also produce more sludge, increasing the cost of treatment and disposal. Therefore, 50 mM of H₂O₂ is recommended. Table 1 shows the oil-water emulsion characteristics after treatment by Fenton's reagent using 50 mM H₂O₂. The COD is much lower than the standard (100 mg/L COD) and the removal efficiency is 98.2%, which is slightly lower than the value calculated by the empirical correlation. According to Chinese Standard JS-7740-95, the treated

oil-water emulsion can be discharged directly to the sewer. However, from an economic standpoint view, only 8.6 mM H₂O₂ is needed to meet the discharge standard, which will produce an effluent with 100 mg/L of COD.

CONCLUSIONS

In this study, compared with existing coagulation-flocculation methods, which do not sufficiently reduce COD, Fenton's reagent was confirmed as an effective treatment technology for oil-water emulsion from the machinery industry. An orthogonal test was successfully used to determine the optimal parameters for COD removal. The H₂O₂ dose was the most important parameter for improving COD removal. Future research should focus on a complete cost analysis and life cycle assessment, including sludge treatment and handling requirements.

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