Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20349

67 (2017) 140–144
March

Treatment of waste cutting fluid enhanced by combining emulsion-breaking coagulation with sponge iron/Fenton oxidation processes

Yanxiang Liu[a,*], Xiaoxue Wang[a], Liangming Yu[b]

[a]*School of Chemical and Environmental Engineering, Jianghan University, Wuhan 430056, China, Tel. +86-27-82644662; Fax: 86-27-51253048; emails: yxliujd@163.com (Y. Liu), 1002105914@qq.com (X. Wang)*
[b]*College of Arts & Science of Jianghan University, Wuhan 430056, China, email: 475657278@qq.com*

Received 27 May 2016; Accepted 16 November 2016

ABSTRACT

Machining cutting fluid wastewater is difficult to treat because of its degree of emulsification, high chemical oxygen demand (COD) concentration, complex composition, and low biodegradability. A combination of emulsion-breaking coagulation with sponge iron/Fenton oxidation processes was used to treat waste machining cutting fluid. The treatment process was optimized using single- and orthogonal-factor tests, and the feasibility of reusing the effluent was investigated. The results showed that the optimum operating parameters were a twofold dilution, 1.5% D03, 0.01‰ polyacrylamide, and pH 8. The COD removal efficiency of sponge iron/Fenton oxidation reached 99.2%. The same removal efficiency was obtained when reusing the effluent under the experimental conditions when the dilution multiple exceeded threefold. The process is an efficient, environmentally friendly method for treating waste cutting fluids.

Keywords: Cutting fluid waste; Emulsion breaking; Coagulation; Sponge iron/Fenton oxidation; Reuse

---

1. Introduction

Cutting fluid is a coolant and lubricant designed for metalworking processes. It has a bad odor and cannot be recycled. Therefore, cutting fluid wastewater is listed as hazardous waste [1]. It contains chemicals such as surfactants and preservatives, which are extremely difficult to degrade due to their high stability, and some cutting fluids contain toxic and carcinogenic ingredients. Cutting fluid wastewater can destroy ecosystems and pose a threat to human health if discharged directly into natural water systems. Therefore, its treatment and final disposal must be handled carefully [2,3]. Current cutting waste treatment methods are divided into physical (e.g., flotation, adsorption, and membrane filtration), chemical (e.g., chemical de-emulsification and supercritical water oxidation), and biological (e.g., aerobic and anaerobic biological treatments) methods [4–9]. However, it is impossible to remove the various environmentally unacceptable chemicals using a single treatment process. Therefore, a combination of two or more of these techniques is required [5]. This work investigated a combination of emulsion-breaking/Fenton oxidation processes to enhance the treatment of cutting waste. In addition, the treatment effluent was reused instead of clean water, which should benefit the environment, reduce processing costs, and achieve clean production.

2. Experimental setup

2.1. Materials and instruments

The polyacrylamide (PAM; Sinopharm Chemical Reagent, Beijing, China), sponge iron (Henan Gongyi Renyuan Water Treatment Plant, Henan, China), combination reverse demulsifier D03 (Guangzhou ZhenQing Environmental Protection Technology, Guangdong, China), and 30% (w/v) hydrogen peroxide (Sinopharm Chemical Reagent, Beijing, China) obtained were of industrial grade. Cutting waste fluid was obtained from an auto company in the Wuhan Economic and Technological Development Zone; the waste was highly

---

* Corresponding author.

1944-3994/1944-3986

emulsified and turbid with a strong milky appearance and a bad odor; it contained about 6% black oil, initial pH = 5.2, and had a chemical oxygen demand (COD) concentration of 125,660 mg/L. A YP-302N six-joint blender (Beijing Venture Technology, Beijing, China) and CM-02 COD analyzer (Beijing Double-Hui Cheng Electronics, Beijing, China) were used in the laboratory analysis.

2.2. Experimental methods

Most emulsion treatment processes combine chemical and physical treatments that depend on various process capabilities and meet the basic requirements for water quality. We examined a reverse de-emulsification–PAM coagulation–sponge iron/Fenton oxidation treatment process in our experiments (Fig. 1). The experiments were performed in test jars at room temperature and involved the following steps: dilute the wastewater using fresh water; add the reverse demulsifier D03; adjust the pH with calcium hydroxide solution; add the polymer coagulant PAM; stir with the six-joint blender; flocculate; separate the supernatant for the sponge iron/Fenton process; and reuse the effluent for wastewater dilution. Single-factor and orthogonal experiments were used to determine the influence of dilution, D03 dosage, and PAM dosage on the COD removal efficiency.

The pH was measured with a pH electrode. The COD concentration was measured using a fast digestion-spectrophotometric method using the procedures described in standard methods [10]. The %COD removal ratio (%COD RR) was calculated using the following equation:

$$\%\text{COD RR} = \frac{C_0\text{-}C_t}{C_0} \times 100 \qquad (1)$$

where C_0 is the initial COD concentration of the cutting waste, and C_t is the COD concentration of the experimental effluent.

3. Results and discussion

3.1. De-emulsification–coagulation pretreatment experiments

3.1.1. Single-factor experiments

3.1.1.1. Influence of raw waste dilution Experiments conducted using undiluted raw cutting waste showed that de-emulsification–coagulation and precipitation were difficult. Therefore, experiments were conducted at different dilutions. The same volume of raw waste was diluted onefold, twofold, threefold, or fourfold with freshwater. Then, we added 1.5% (vol/vol) D03, adjusted the pH to 8 with 20% calcium hydroxide, and added 0.05‰ (m/m) PAM in a 1:1 (vol/vol) ratio. The results are shown in Table 1. Although the amount of COD removed increased with the dilution, the %COD removal decreased from 97% to 89%. This can be attributed to the decrease in the concentration of organics at a lower concentration (due to dilution), and hence a higher %COD removal. Considering the %COD removal and operating costs, a twofold dilution was used for further studies of the process.

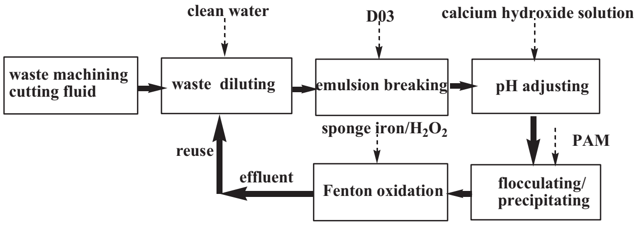

Fig. 1. Treatment process of waste cutting fluid.

3.1.1.2. Influence of D03 dosage The same volume of raw waste was diluted twofold with freshwater, and 1.0%, 1.5%, 2.0%, and 4.0% volume ratios of D03 were added. The pH was adjusted to 8 with 20% calcium hydroxide, and 0.05‰ PAM added according to 1:1 (vol/vol). The alum blossom was weak, and no layer phenomenon was obvious in sample No. 1. There was a strong alum blossom and separate layers with a clear supernatant in samples Nos. 2–4. Table 2 shows that the COD removal rate increased with the D03 dosage. A 1.5% volume ratio of D03 was the best based on practical and cost considerations.

Because cutting waste consists of a complex mixture of water, oil, and additives such as emulsifiers, corrosion inhibitors, and antifoaming and extreme pressure agents, these emulsions are very stable [7]. The standard method for treating emulsions is chemical de-emulsification. A demulsifier can balance or offset the surface tension of the film on both sides of the interface, and stabilize the charge, leading to precipitation of the emulsifier and oil–water separation.

D03 is a cationic polymer with good reverse de-emulsification properties in oil-in-water systems. Its mechanism of action is mainly charge neutralization and adsorption bridging.

3.1.1.3. Influence of pH The pH can influence the coagulation process. In order to study its effect on the treatment, the initial pH of the waste was adjusted to between 7.0 and 9.0. The same volume of raw waste was diluted twofold, and then 1.5% D03 was added. Then, the pH was adjusted to 7, 8, or 9 with 20% calcium hydroxide and 0.05‰ PAM was added. The COD of the supernatant was measured, and the %COD RR was calculated. The results are shown in Table 3. Based on practical and cost considerations, pH 8 was determined to be the best.

Table 1
Effect of diluted multiple on the %COD removal (%COD RR)

Dilution times	1	2	3	4
%COD RR	89.8	95.1	96.9	97.1

Table 2
Influence of reverse demulsifies rate on the %COD removal

Volume ratio of demulsifier (%)	COD (mg/L)	%COD RR
1.0	9,934.5	87.7
1.5	6,737.0	94.6
2.0	5,543.0	95.6
4.0	5,498.6	95.6

3.1.1.4. Influence of PAM concentration The coagulation/flocculation method is widely used to destabilize and aggregate colloids. PAM is a commonly used polymeric flocculant because it is possible to synthesize PAMs with various functionalities (positive, neutral, or negative charges), which can be used to achieve a good settling performance at relatively low cost [11]. Three equal volumes of raw waste were diluted twofold, and 1.5% volume D03 was added, and the pH was adjusted to 8 with 20% calcium hydroxide. Then, 0.01‰, 0.05‰, or 0.1‰ PAM was added. All of the samples produced a strong alum blossom and separate layers with a clear supernatant. The results are shown in Table 4. This result indicates that the %COD removal is not influenced by the PAM concentration. Furthermore, the percentage removal of COD with PAM was significant even at the lowest dosage of 0.01‰, which resulted in the removal of more than 95.1% of the COD. Therefore, the optimum PAM dosage was 0.01‰ concentration.

3.1.2. Orthogonal test and range analysis

Many factors can affect the %COD RR in the de-emulsification–coagulation pretreatment process, and each factor has a wide range of variation. The orthogonal test method can be used to optimize the operating parameters [12]. Based on the numbers of experimental factors and levels, L9 (3^4) orthogonal experiments (Table 5) were chosen. The results and analysis are shown in Table 6.

Table 6 shows that the order of factors was as follows: dilution > D03 concentration > pH > PAM concentration. Considering the costs, the optimum processing conditions were: a threefold dilution, pH = 8, 1.5% D03, and 0.05‰ PAM. The COD of the effluent was 6,203.5 mg/L, and the removal rate was 95.1%. However, the high COD values and light yellow color of the effluent limit the reuse/recycling of water. The Fenton process is widely used to reduce the COD. Therefore, an attempt was made to reduce the COD of the effluent in an economical way and reuse/recycle it within the industry.

Table 3
Effect of pH on the %COD removal

pH	COD (mg/L)	%COD RR
7	8,137.5	93.5
8	6,796.5	94.6
9	7,888.5	93.7

Table 4
Effect of PAM concentration on the %COD removal

PAM (g/mL)	COD (mg/L)	%COD RR
0.01‰	6,742.5	95.8
0.05‰	6,196.0	94.6
0.1‰	6,492.0	94.8

3.2. Advanced treatment and effluent reuse

3.2.1. Sponge iron/Fenton oxidation advanced treatment

Sponge iron is a versatile new water-treatment material with a large specific surface area, good physical adsorption and electrochemical flocculation performance, low cost, and easy regeneration. It has many applications, such as the treatment of oily, phosphorus, and coking wastewater, and the removal of organic matter and nitrate [13,14].

Sponge iron and H_2O_2 are added in Fenton experiments. Fenton oxidation improves with a large number of Fe^{2+} ions, which are created by a micro-electrolysis process [15].

3.2.1.1. Influence of reaction time Reaction time is an important factor in the Fenton process. Fig. 2 shows the COD removal rate at different times when the concentrations of sponge iron and H_2O_2 were 30 g/L and 10 mL/L, respectively. The COD removal rate increased with time and stabilized after 60 min. This is mainly because few hydroxyl radicals (·OH) were generated at the beginning of the reaction, which accounted for the limited effect on the COD removal rate. As the reaction proceeded more completely, the COD removal rate increased with the reaction time. However, the COD removal rate decreased after 60 min because of H_2O_2 depletion. Therefore, the optimal reaction time was 60 min.

Table 5
Orthogonal experimental factors level

Factor	Dilution times	pH	D03 concentration (%)	PAM (g/mL)
1	1	7	1.5	0.01‰
2	2	8	2.2	0.0‰
3	3	9	3.0	0.1‰

Table 6
Orthogonal experimental results on the treatment of waste cutting fluid

No.	Dilution times	D03	pH	PAM	%COD RR
1	1	1	1	1	85.1
2	1	2	2	2	87.1
3	1	3	3	3	92.9
4	2	1	2	3	93.7
5	2	2	3	1	94.8
6	2	3	1	2	95.1
7	3	1	3	2	95.8
8	3	2	1	3	96.2
9	3	3	2	1	97.2
K_1	264.99	274.53	276.36	276.99	
K_2	283.59	278.13	277.95	277.98	
K_3	289.17	285.09	283.44	282.78	
Y_1	88.33	91.51	92.12	92.33	
Y_2	94.53	92.71	92.65	92.66	
Y_3	96.39	95.03	94.48	94.26	
R	8.06	3.52	2.36	1.93	

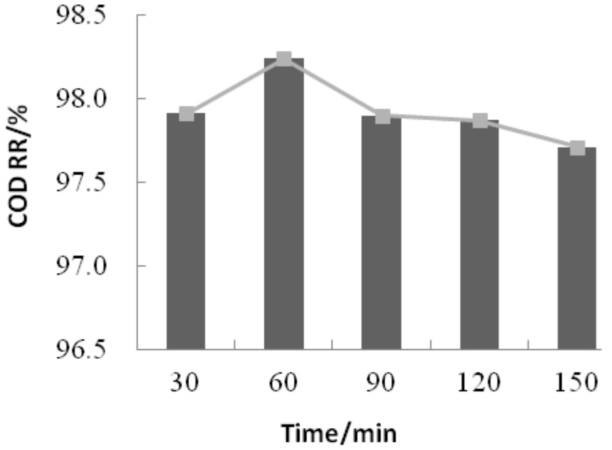

Fig. 2. Effect of Fenton oxidation reaction time on the %COD removal.

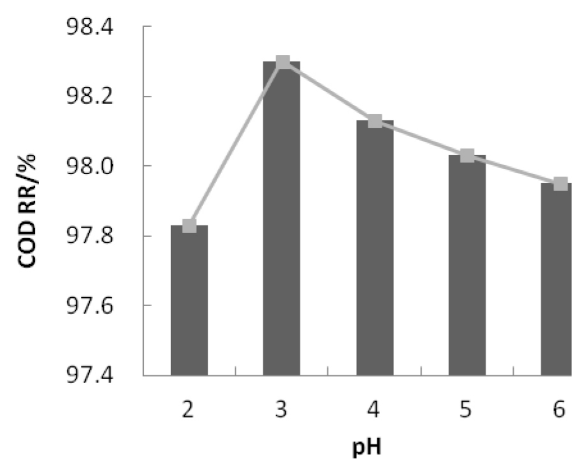

Fig. 3. Effect of pH on the %COD removal.

3.2.1.2. Influence of pH Because the Fenton oxidation reactions are pH-dependent, it is necessary to investigate the effect of pH on the removal efficiency of COD. Therefore, a series of experiments was conducted at initial pH values ranging from 2 to 6. As shown in Fig. 3, the removal efficiency of COD decreased continuously as the pH increased from 3 to 6. This could be attributed to the production of larger amounts of ·OH from the Fenton reaction due to more iron ions leaching from the micro-electrolysis process in acidic conditions. Therefore, the optimum pH was 3.

3.2.1.3. Influence of H_2O_2 dosage Fig. 4 shows the COD removal rate for a reaction time of 60 min, pH of 3, and H_2O_2 dosages of 2, 4, 10, 16, and 20 mL/L. With increasing H_2O_2 dosage, the COD removal rate increased with time, reached a peak, and then decreased. When the H_2O_2 dosage was 16 mL/L, the %COD removal reached 99.2% because more ·OH was generated as the H_2O_2 concentration increased, and ·OH accelerated the oxidation process. When the concentration of H_2O_2 was excessive, the H_2O_2 quickly turned Fe^{2+} into Fe^{3+}, which depressed the oxidation process.

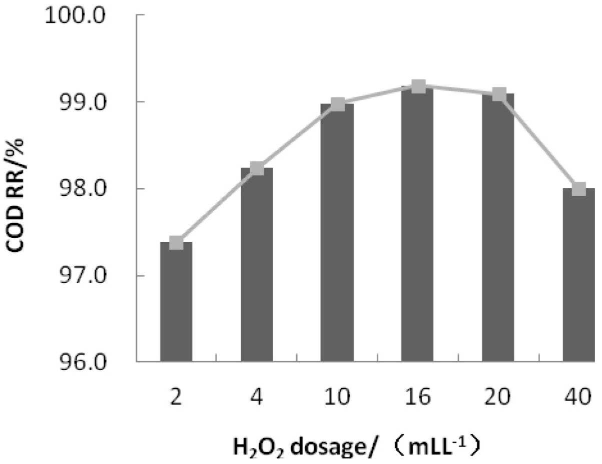

Fig. 4. Influence of H_2O_2 dosages on the %COD removal.

Table 7
Results of reused the effluent under the experimental conditions

Dilution times	1	2	3	4
COD of outflow (mg/L)	11,966	9,787	6,792	5,134

3.2.2. Effluent reuse

The effluent treated by breaking coagulation/Fenton oxidation was clear and odorless. The COD was approximately 1,022.4 mg/L. The cutting waste was diluted with the effluent, and the experiments were completed under the optimum processing conditions. The results are shown in Table 7. This shows that the COD removal rate using recycled effluent with a threefold dilution was similar to that using clean tap water diluted twofold.

4. Conclusions

- The optimized process conditions were obtained in single- and orthogonal-factor experiments and were pH = 8, a twofold dilution, 1.5% demulsifier volume ratio concentration, and 0.01‰ PAM. The COD removal efficiency from cutting wastewater treated with the sponge iron/Fenton oxidation treatment reached 99.2% when the reaction time was 120 min, pH = 3, and the concentrations of sponge iron and hydrogen peroxide were 30 g/L and 16 mL/L, respectively.
- The same result was obtained when using the effluent instead of freshwater, which will not only reduce the costs, but also realize “zero liquid effluent”.

Acknowledgments

This study was financed by the Natural Science Foundation of P.R. China (No. 201477091) and the Science Project of Education Bureau of Wuhan, China (No. 2012c02). The authors thank the anonymous reviewers for their comments, and also thank the professional editors from “Textcheck” for improving the English quality in this document.

References

[1] Ministry of Environmental Protection of the People’s Republic of China, The National Development and Reform Commission of the People’s Republic of China, National Hazardous Waste List, 2008. (in Chinese)

[2] C. Cheng, D. Phipps, R.M. Alkhaddar, Treatment of spent metalworking fluids, Water Res., 39 (2005) 4051–4063.

[3] J. Samaly, A. Giwa, S.W. Hasan, Recent improvements in oily wastewater treatment: progress, challenges, and future opportunities, J. Environ. Sci., 37 (2015) 15–30.

[4] N. Moulai-Mostefa, M. Frappart, O. Akoum, L.H. Ding, M.Y. Jaffrin, Separation of water from metal working emulsions by ultrafiltration using vibratory membranes, J. Hazard. Mater., 177 (2010) 978–982.

[5] K. Bensadok, M. Belkacem, G. Nezzal, Treatment of cutting oil/water emulsion by coupling coagulation and dissolved air flotation, Desalination, 206 (2007) 440–448.

[6] K. Piyamongkala, L. Mekasut, S. Pongstabodee, Cutting fluid effluent removal by adsorption on chitosan and SDS-modified chitosan, Macromol. Res., 16 (2008) 492–502.

[7] J. Sánchez-Oneto, J.R. Portela, E. Nebot, E.M. de la Ossa, Hydrothermal oxidation: application to the treatment of different cutting fluid wastes, J. Hazard. Mater., 144 (2007) 639–644.

[8] J.V.G. Christopher, P.I. Thompson, Effects of pH amendment on metal working fluid wastewater biological treatment using a defined bacterial consortium, Biotechnol. Bioeng., 89 (2005) 357–366.

[9] C. Cheng, D. Phipps, R.M. Alkhaddar, Thermophilic aerobic wastewater treatment of waste metalworking fluids, Water Environ. J., 20 (2006) 227–232.

[10] State Environmental Protection Administration of China, The Environmental Protection Industry Standards of the People’s Republic of China, HJT399, 2007. (in Chinese)

[11] Y. Zeng, C. Yang, J. Zhang, W. Pua, Feasibility investigation of oily wastewater treatment by combination of zinc and PAM in coagulation/flocculation, J. Hazard. Mater., 147 (2007) 991–996.

[12] M. Matos, C.F. García, M.A. Suárez, C. Pazos, J.M. Benito, Treatment of oil-in-water emulsions by a destabilization/ultrafiltration hybrid process: statistical analysis of operating parameters, J. Taiwan Inst. Chem. Eng., 59 (2016) 295–302.

[13] N. Ma, Y. Wang, J. Li, Y. Zhang, Application of new water treatment material sponge iron in wastewater treatment, Environ. Sci. Manage., 39 (2014) 71–73. (in Chinese)

[14] P.R. Rout, P. Bhunia, R.R. Dash, Effective utilization of a sponge iron industry by-product for phosphate removal from aqueous solution: a statistical and kinetic modelling approach, J. Taiwan Inst. Chem. Eng., 46 (2015) 98–108.

[15] Y. Yu, Research on treatment of petrochemical wastewater by microelectrolysis-Fenton process, Jiangxi Chemical Industry, 3 (2010) 109–112. (in Chinese)