

Research Article

Treatment of Cutting Oil-in-Water Emulsion by Combining Flocculation and Fenton Oxidation

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Recently, the disposal of waste oil-in-water cutting emulsion has become an urgent issue because of its extremely high chemical oxygen demand (COD). The present work focuses on treating the waste cutting emulsion generated from the Samsung Thai-Nguyen factory in Vietnam. This work used multistage methods to treat the waste cutting emulsion to meet the wastewater disposal requirement and characterize the oil recovered. The multistage methods consist of the flocculation method (stage 1) and Fenton oxidation (stage 2). The wastewater after stage 1 treatment has a COD reduction efficiency of 98.24% at the condition of pH 5, $\text{Al}_2(\text{SO}_4)_3$ 2 g/L, C-PAM 12 mg/L, stirring speed 50 rpm, and stirring time 15 minutes. At that condition, the COD value decreased from 147200 mg/L to 2484 mg/L. After stage 2, the COD value further decreased from 2484 mg/L to 85.4 mg/L with total COD removal efficiency increasing to 99.9% at the optimum conditions of pH 3, H_2O_2 : FeSO_4 concentration ratio of 10:1, and FeSO_4 concentration of 14.04 g/L. After the stage 2 treatment, the wastewater with the COD value of 85.4 mg/L and BOD_5 value of 30 mg/L satisfied the Vietnam standard grade B and grade A, respectively, for industrial wastewater. The oil recovered from the treatment has a heating value of 38095 ± 8 kJ/kg, and thus, it could be reusable as fuel gas.

1. Introduction

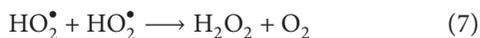
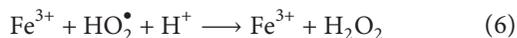
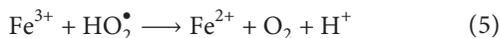
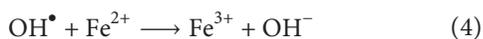
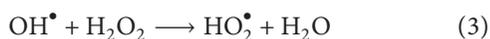
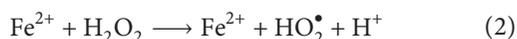
Metal cutting emulsions or cutting fluids play an important role in the machining process. They are frequently used in metalworking industries for several reasons, such as lubricating and cooling the machine. It also helps to increase the cutting tool efficiency and its lifetime and improve the surface of the workpiece and protect them from corrosion [1, 2]. Among various types of cutting emulsions, oil-in-water emulsions are the most preferred in the industry due to their longer period and easier preparation [3, 4]. These emulsions are formed by blending oil and water for about 3–15% oil concentration and the emulsifiers for more stable emulsion [5].

Despite their huge advantages, cutting emulsions is becoming the main source of oil-contaminated wastewater in metal industries. They contain chemical ingredients toxic

to human health and cause some symptoms such as skin irritation, respiratory diseases, or cancers [6]. The composition of the used cutting emulsion was probably denatured and become more toxic than before using. If disposal techniques are not appropriate, they will lead to secondary contamination and harm to the environment. The serious issues on the treatment were due to the complicated composition and the high volume of the wastewater disposal. It is estimated that more than 1000 million gallons of the cutting emulsions are disposed of each year in the USA, and the amount of wastewater may increase a lot after using [7, 8]. It brings about more challenges for the treatment to meet the requirement of the standard for discharging fluids.

There are many methods used for the treatment of the O/W cutting emulsion. They are physical separation [9], chemical treatment [10, 11], biodegradation [12, 13], and advanced oxidation process (AOP) [14, 15]. In recent years,

AOP is gaining attention for its high efficiency, simple process, and ability to handle nonbiodegradable fluids. AOP is a technology that uses hydroxyl free radicals (OH^\bullet) that break down toxic organic compounds into harmless compounds such as CO_2 and water [16, 17]. The Fenton method is being most widely applied with a series of advantages such as no need for stimulating reactive energy, easy-to-obtain chemicals, fast processing time, and high efficiency [17]. In general, the Fenton oxidation process consists of the primary reaction between H_2O_2 and Fe^{2+} in an acidic medium to generate OH^\bullet , the radical species necessary for organic pollutant degradation. The reaction mechanism is complex followed by equations (1)–(7) [18, 19]. It demonstrates that the Fenton process is closely dependent on the pH of solution, ferric concentration, and hydrogen peroxide concentration. Therefore, to obtain the best treatment by Fenton oxidation, it is necessary to determine the suitable conditions for the treatment:



Previous work reported that the combinations of several methods lead to enhanced treatment. For instance, the electrochemical method could be combined with membrane filtration [20, 21]. Another work from Kaur and Sodhi reported treating cutting emulsion by adsorption from the agricultural waste [22]. Su et al. reported that a combination of flocculation and absorption by the heterogeneous Fenton system could remove 99.8% of chemical oxygen demand (COD) for wastewater [23]. However, the heterogeneous Fenton system is very difficult to apply at a larger scale due to the high cost and difficulty to scale up. The demand for cheap and efficient methods to treat waste-cutting emulsion is still more urgent. If the oil concentration is too high, it is necessary to recover and recycle the separated oil.

In this work, the aim is to treat cutting fluids discharged from Samsung Thai-Nguyen company in Vietnam to pass the Vietnam standard for treated wastewater. COD was selected as the target standard for the treatment. At first, the cutting emulsion was characterized to determine some physiochemistry properties. Secondly, stage 1 was carried out by the flocculation method using flocculants. Then, it is treated further using a homogenous Fenton process to increase the treatment's efficiency at a large scale. A flotation technique was applied to obtain a better recovery of oil. The flocculation was selected due to the suitability and low cost

as compared to other methods. Also, at high COD of the cutting emulsion, the flocculation will remove oils, a major cause of the high COD of cutting emulsion wastewater. Two flocculation agents that are $\text{Al}_2(\text{SO}_4)_3$ and cationic polyacrylamide (C-PAM) were used. C-PAM is a positively charged organic polymer used as a water treatment flocculant aid [23]. The Fenton oxidation was selected as stage 2 for the treatment. The hydroxyl radical produced from advanced oxidation can decompose the residual oil and other contaminants into harmless substances such as CO_2 and water [24].

2. Experimental

2.1. Characterization of Oil-in-Water Emulsion. Cutting emulsions were provided by Samsung Thai-Nguyen, Vietnam. The oil concentration in the emulsion was determined by the steam distillation method. The heat value of the recovered oil was determined with Parr 6300 (USA) according to ASTM D240. The pH of the sample was determined using Titra Lab machine, TIM 900 of France. Particle size distribution and zeta potential of the emulsion were determined by dynamic laser scattering technique using Horiba SZ-100.

2.2. Stage 1: Flocculation Process. Stage 1 treatment of waste cutting O/W emulsion by flocculation method was conducted as follows: first, $\text{Al}_2(\text{SO}_4)_3$ (initial concentration of 35 wt.%) was added slowly into a beaker containing about 200 mL of waste cutting emulsion under constant stirring. Simultaneously, the pH of the reaction was adjusted using NaOH 1 M or H_2SO_4 0.5 M and continued stirring for 5 minutes. After that, C-PAM (initial concentration of 0.2 wt.%) was injected under gentle stirring for 15 minutes. The oil and the sludge were separated with a separating funnel, and the oil was recovered. The water after filtration was bubbled for 30 minutes (with air compression at pressure $P = 5$ bar, gas flow 5 mL/min) and filtered again. COD of the wastewater after this step was determined to evaluate the COD removal efficiency of the process. The detailed procedure is given in Figure 1.

2.3. Stage 2: Fenton Oxidation. The wastewater after stage 1 was subjected to stage 2 treatment with Fenton oxidation as shown in Figure 1. About 100 mL of the cutting emulsion was placed in a beaker under stirring. The pH of the solution was adjusted with H_2SO_4 0.5 M, then, adding iron (II) sulfate salt ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) with content 14.04 (g/L) followed by hydroperoxide solution (H_2O_2 , 30 wt.%). The reaction was allowed to proceed for 20 minutes. After completing the reaction, the pH of the solution was neutralized to 7 using NaOH 1 M (to meet the requirement before discharging into the environment) and stirred for 2 hours to remove the residual H_2O_2 , letting it set down for another 3 hours before filtration. The clear solution after filter was subjected to COD measurement.

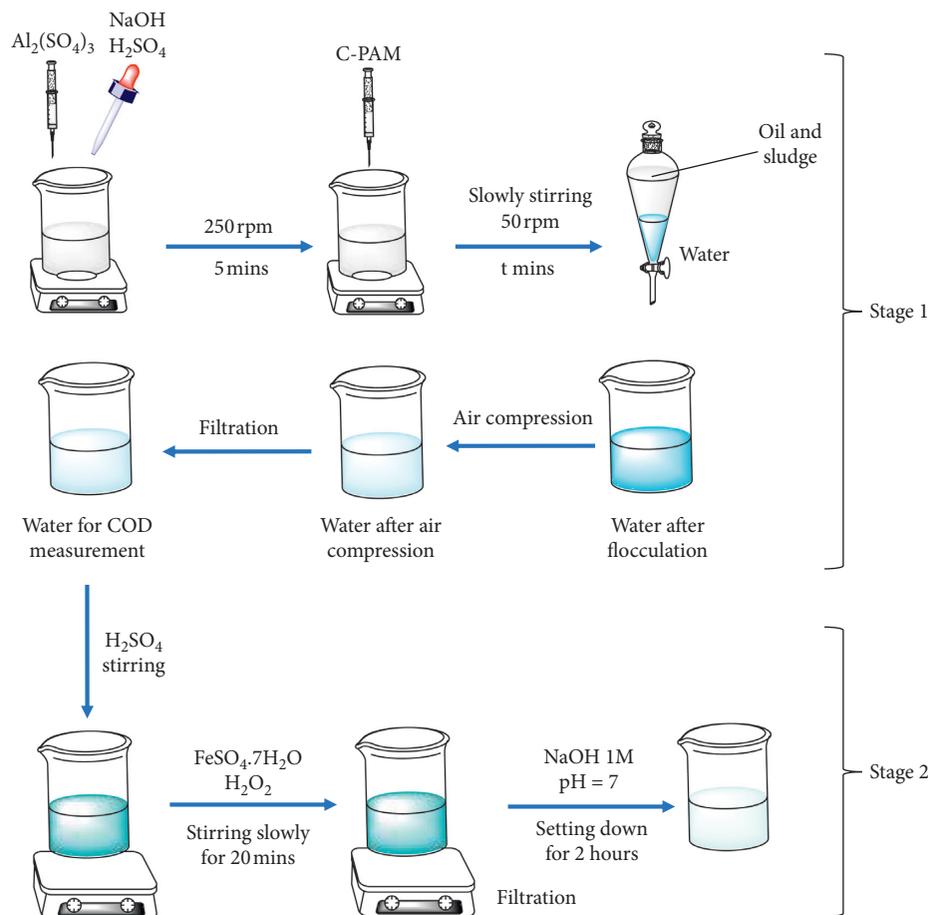


FIGURE 1: Treatment process with stage 1 (floculation) and stage 2 (Fenton oxidation).

2.4. Determination of COD. The chemical oxygen demand (COD) is the quantity of oxygen required to oxidize the organic compounds in a wastewater sample. In this work, the organic compounds are oxidized by potassium dichromate in sulfuric acid solution 0.5 M at reflux temperature. Silver sulfate is used as a catalyst and mercuric sulfate is added to prevent the effect of chloride substance. The excess dichromate is titrated with standard ferric ammonium sulfate, using ferroin as an indicator. The COD of wastewater after treatment was determined as the following equation:

$$\text{COD} = \frac{8000 \cdot C \cdot (V_1 - V_2)}{V_0} \left(\frac{\text{mg}}{\text{L}} \right), \quad (8)$$

in which C is the concentration of ferric ammonium sulfate (mol/L), V_0 is the volume of wastewater sample before dilution (mL), V_1 is the volume of ferric ammonium sulfate to titrate the blank sample (mL), and V_2 is the volume of ferric ammonium sulfate to titrate the sample (mL).

2.5. Determination of BOD. Biochemical oxygen demand (BOD) is the amount of oxygen taken up by the microorganisms that decompose the organic compounds in wastewater. In this case, BOD represents the type of organic water pollution. BOD is calculated by keeping a sample of

water containing a known amount of oxygen for five days at 20°C according to the method described in TCVN 7325 (ISSO 5814) and the formula is shown as follows:

$$\text{BOD}_5 = \left[(p_1 - p_2) - \frac{V_t - V_s}{V_t} (p_3 - p_4) \right] \frac{V_t}{V_s}, \quad (9)$$

in which p_1 is the dissolved oxygen concentration of the solution at zero (mg/L), p_2 is the dissolved oxygen concentration of the sample solution after 5 days (mg/L), p_3 is the dissolved oxygen concentration of the blank solution at zero (mg/L), p_4 is the dissolved oxygen concentration of the blank solution after 5 days (mg/L), V_s is the volume of the original sample (mL), and V_t is the total volume of the sample (mL).

3. Results and Discussion

3.1. Characterization of Waste Cutting Emulsion. Characterization of the waste cutting emulsion was performed to determine its characteristic physiochemical parameters. Figure 2 shows the appearance of the emulsion, its size distribution, and zeta potential. Several parameters characteristics for the emulsion are shown in Table 1.

As can be seen, the emulsion has a milky white color with an oil concentration of 5.35%. The size distribution of the

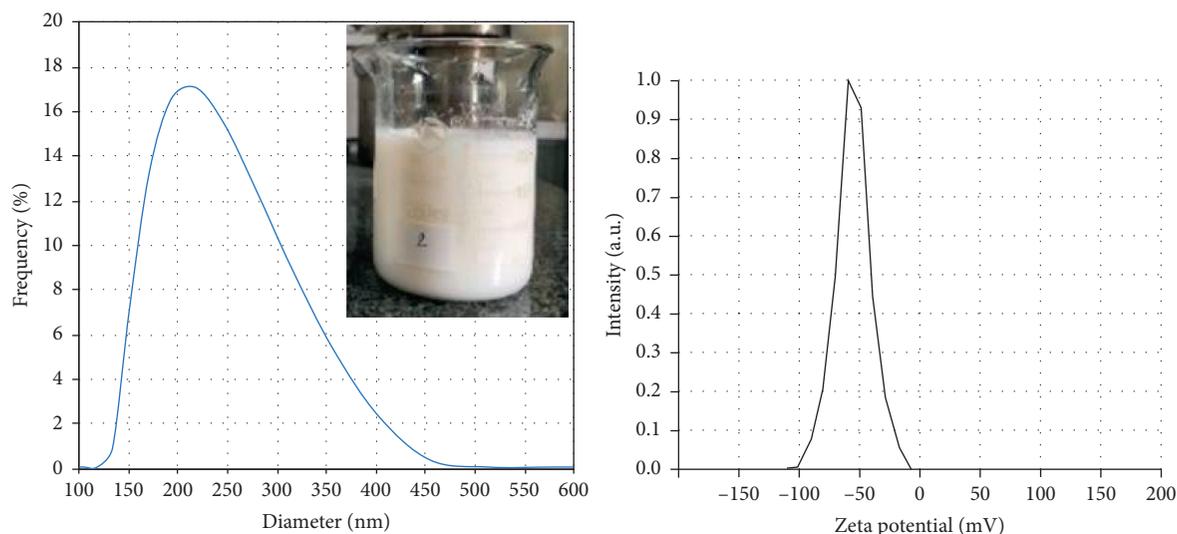


FIGURE 2: Size distribution and zeta potential of waste cutting emulsion.

TABLE 1: Characteristic parameters for waste cutting O/W emulsion.

Parameter	Value
Oil concentration, %	5.35 ± 0.22
pH	8.721 ± 0.005
COD, mg/L	147200 ± 100
Particle size (mean), nm	216.7 ± 3.4
Zeta potential, mV	-53.3 ± 1.4

emulsion was unimodal with an average size of oil drops of about 216.7 nm. It indicated that the oil droplets were very small and evenly distributed in the water phase. The stability of the emulsion was evaluated by zeta potential. The zeta potential of the O/W emulsion was -53.3 mV, suggesting that the oil droplet surface is a negative charge. The high negative zeta potential of the O/W emulsion subsequently enhanced the stability of the emulsion. In this case, if they were discharged into the environment, it would not be easy to treat them. In addition, due to the very high COD value, it is necessary to combine several methods for the treatment to obtain the maximum decrease in COD value before discharging into the environment.

3.2. Results from Stage 1: Flocculation Treatment. The flocculation treatment of the oil cutting emulsion was carried out using $\text{Al}_2(\text{SO}_4)_3$ and cationic polyacrylamide (C-PAM) as the flocculant and flocculant aid, respectively. Several factors will be investigated, including pH, the dosage of $\text{Al}_2(\text{SO}_4)_3$, and the dosage of C-PAM. The flotation will be used during the flocculation process to increase the efficiency of the oil-water separation.

3.2.1. Effect of pH. Effect of pH on the treatment of emulsions using $\text{Al}_2(\text{SO}_4)_3$ and C-PAM as a flocculant and flocculant aid was performed at the same dosages of $\text{Al}_2(\text{SO}_4)_3$ (3.5 g/L), C-PAM (10 mg/L), stirring speed

(80 rpm), and stirring time (25 minutes). The pH was adjusted from 3 to 10. The efficiency of the treatment was evaluated through COD reduction.

Table 2 shows the COD of wastewater after treatments at various dosages and pH conditions. As can be seen, the treatment using the only $\text{Al}_2(\text{SO}_4)_3$ as a flocculant achieved the best efficiency at pH equal to 5. The COD value for treated water was 5024 mg/L, corresponding to the COD removal efficiency of 96.58%. Simultaneously, the flocculation treatment with $\text{Al}_2(\text{SO}_4)_3$ and C-PAM gets the best efficiency at a pH of 5. In this case, the COD value of water after the treatment was 4168 mg/L. This is the lowest COD value among all the treatment conditions. The highest COD removal efficiency of 97.17% was obtained.

The dependence of pH on the flocculation pretreatment is depicted in Figure 3. It illustrated that when increasing pH from 3 to 5, the treatment efficiency increased. The best pH for the flocculation pretreatment was around 5 to 6. At pH higher than 6, the efficiency of the treatment decreased.

The effect of pH on the flocculation treatment may probably be explained due to the formation of colloidal particles from $\text{Al}_2(\text{SO}_4)_3$ as flocculant. In the water medium, aluminum sulfate was dissociated into Al^{3+} cation. Then, ion Al^{3+} was hydrolyzed to produce several common colloidal particles, such as $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, and $\text{Al}(\text{OH})_4^-$, or solid polymer colloidal particles, $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$, and $\text{Al}(\text{OH})_3$ [25], in which $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ is known as the best coagulant agent among all. However, the amount of the solid polymer colloidal particles (i.e., $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$, and $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$) is less than the common colloidal particles.

On the other hand, the hydrolysis of Al^{3+} ion is suppressed in the acidic medium (pH from 3 to 4). Only a small amount of Al^{3+} ion was hydrolyzed to form colloidal flocculant agents. Thus, the COD removal efficiency obtained in this case was not so high. When the pH of the medium increased to 5 and 6, the hydrolysis of Al^{3+} increased favorably. Various colloidal particles, such as $\text{Al}(\text{OH})^{2+}$ and

TABLE 2: COD values and COD removal efficiencies of wastewater after treatment at various dosages and pH (stirring speed 80 ppm, stirring time 25 minutes).

pH	Al ₂ (SO ₄) ₃ (g/L)	C-PAM (mg/L)	COD of treated water (mg/L)	COD removal efficiency (%)
3	3.5	0	7284	95.05
	3.5	10	5582	96.20
4	3.5	0	5704	96.12
	3.5	10	4878	96.68
5	3.5	0	5024	96.58
	3.5	10	4164	97.17
6	3.5	0	5092	96.54
	3.5	10	4298	97.08
7	3.5	0	5512	96.25
	3.5	10	4749	96.67
8	3.5	0	6022	95.91
	3.5	10	4934	96.64
9	3.5	0	9682	93.42
	3.5	10	7012	95.34
10	3.5	0	12268	91.66
	3.5	10	11842	91.95

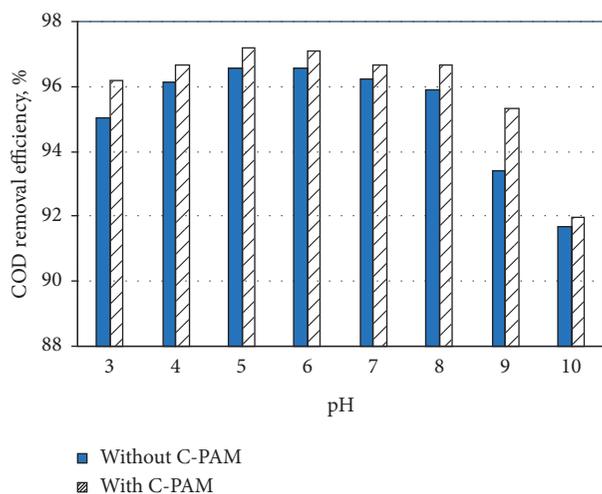


FIGURE 3: COD removal efficiency with and without C-PAM (10 mg/L) ([Al₂(SO₄)₃] = 3.5 g/L, stirring speed 80 rpm, stirring time 25 minutes).

Al(OH)₂⁺, were formed. Besides, some polymer colloidal particles with high positive oxygen numbers, that is, Al₂(OH)₂⁴⁺, Al₃(OH)₄⁵⁺, and Al₁₃O₄(OH)₂₄⁷⁺, could be formed via the condensation process. The formation of these polymer colloidal particles helps to neutralize suspended particles and oil particles in the emulsion more efficiently.

At a basic pH medium (pH from 7 to 10), the hydrolysis equilibrium moved to the right to form the positive charge particles. So far, the hydrolysis of Al³⁺ resulted in the formation of Al(OH)₃ precipitate. These precipitated Al(OH)₃ will absorb a small number of positive charge ions from the water medium, giving a small reduction in treatment efficiency. When pH is higher than 8, Al(OH)₃ interacted with OH⁻ to form AlO₂⁻ anion. It will further stabilize the O/W emulsion due to the same electrical charge with oil droplets. Consequently, the COD removal efficiency decreased at pH from 7 to 10.

From Figure 3, when Al₂(SO₄)₃ and C-PAM were used, COD treatment efficiency increases by about 20% compared to when using Al₂(SO₄)₃ alone. It was because C-PAM is a cationic polymer macromolecule. It will decrease the negative charge of oil droplets and increase the speed of the sedimentation process. Thus, the optimum condition for the pretreatment process was at pH 5, Al₂(SO₄)₃ dosage of 3.5 g/L, C-PAM dosage of 10 mg/L, stirring speed 80 rpm, and stirring time of 25 minutes. The best treatment efficiency was 97.17%, corresponding to the reduction in COD of wastewater from 147200 mg/L to 4164 mg/L.

3.2.2. Effect of Al₂(SO₄)₃. The effect of the dosage of Al₂(SO₄)₃ on the COD removal efficiency was investigated at the conditions as follows: pH 5, C-PAM of 10 ppm, stirring speed of 80 rpm, and stirring time of 25 minutes. The amount of Al₂(SO₄)₃ was adjusted from 0.5 to 5 g/L. Figure 4 shows the result obtained.

As we can see, the treatment efficiency reached the highest at the Al₂(SO₄)₃ concentration of 2 g/L. In particular, COD value reduced to 3527 mg/L, yield 97.6%. At the concentration of Al₂(SO₄)₃ higher than 2 g/L, the removal efficiency decreased. It may be because, at the concentration of 2 g/L, the cations generated from hydrolysis of Al³⁺ and C-PAM were enough to neutralize the oil droplets in the emulsion. At Al₂(SO₄)₃ concentration less than 2 g/L, the cation was not neutralized completely during the flocculation process. Therefore, the electrostatic interaction force between the oil droplets may still be large; thus, the emulsion is still stable, yielding the low treatment efficiency. Similarly, when the Al₂(SO₄)₃ concentration is higher than 2 g/L, the cation is hydrolyzed excessively, giving an excess of positive charge. At this time, the emulsion is reversely stabilized; thus, the treatment efficiency decreased.

3.2.3. Effect of C-PAM. The concentration of C-PAM used for the treatment was varied from 2 ÷ 20 mg/L. Figure 5

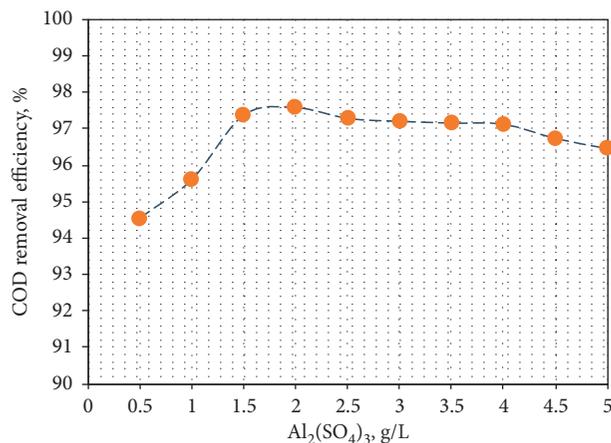


FIGURE 4: Effect of $\text{Al}_2(\text{SO}_4)_3$ dosages on COD removal efficiency (pH 5, C-PAM: 10 mg/L, stirring speed 80 rpm, and stirring time 25 minutes).

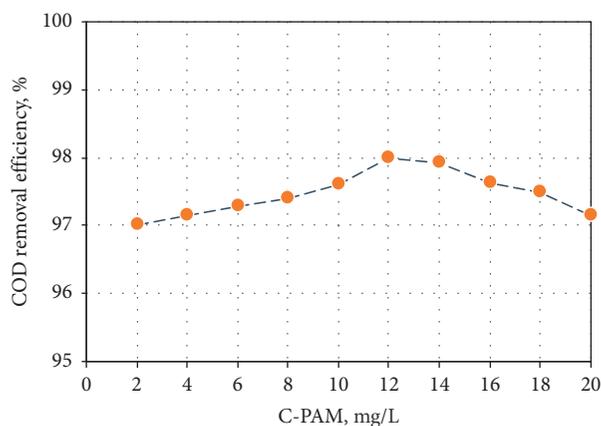


FIGURE 5: COD removal efficiencies at different C-PAM concentrations ($[\text{Al}_2(\text{SO}_4)_3] = 2$ g/L, stirring speed 80 rpm, stirring time 25 minutes).

shows the effect of C-PAM concentration on the COD removal at the conditions: pH = 5, $\text{Al}_2(\text{SO}_4)_3$ 2 g/L, stirring speed 80 rpm for 25 minutes. At the C-PAM concentration of 12 mg/L, COD reduced to the lowest value, that is, 3020 (mg/L), corresponding to the highest yield of 97.98%. It may be because that the C-PAM content of 12 mg/L is the optimum amount of the C-PAM needs to attach to the oil droplets. When the amount of C-PAM is less than 12 mg/L, the number of polymer molecules is not enough to cover the oil particles' surface. Therefore, there existed a vacant position that has not been neutralized. The repulsion force made the emulsion difficult to be coagulated. Hence, COD is still high. When the amount of C-PAM is higher than 12 mg/L, the particle surface is saturated with C-PAM molecules. And therefore, the surface of oil droplets again was stabilized.

3.2.4. Effect of Stirring Rate. During the flocculation process, the stirring rate is a very important factor that affects the COD removal. In this work, we investigate the stirring rate

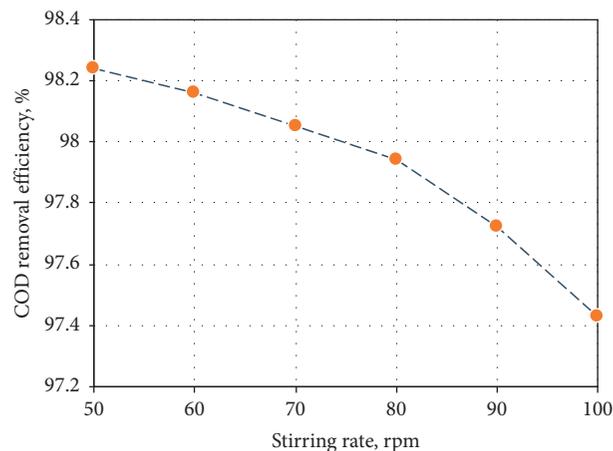


FIGURE 6: Effect of stirring rate on COD removal efficiency (C-PAM 12 mg/L, $[\text{Al}_2(\text{SO}_4)_3]$ 2 g/L, stirring time 25 minutes).

from 50 to 100 rpm for about 25 minutes. Figure 6 shows the results about the effect of stirring on the removal efficiency. As we can see, the highest COD removal efficiency was obtained at the speed of 50 rpm. The COD value decreased to 2568 mg/L with regard to the COD removal efficiency of 98.24%. At a higher stirring rate, the oil droplet was more separated due to the strong stirring force. The aggregation of the oil droplets decreased under a high stirring speed. The stirring rate of 50 rpm was enough for the attraction force to form large aggregates necessary for coagulation.

3.2.5. Effect of Stirring Time. The slow stirring step may affect the flocculation treatment. The time for stirring was altered from 5 to 55 minutes under the condition, that is, pH 5, $\text{Al}_2(\text{SO}_4)_3$ 2 g/L, C-PAM 12 mg/L, and stirring speed 50 rpm. The obtained results are given in Table 3.

From the results, when the stirring time is less than 15 minutes, the collision between the oil droplets was not enough to form larger oil droplets. However, if the stirring time is longer than 15 minutes, the large oil droplets may be broken into smaller ones. It may prevent the cumulation of oil from the wastewater. Therefore, the optimum stirring time is determined to be 15 minutes. At that condition, the COD of wastewater obtained was 2484 mg/L, equivalent to the COD removal efficiency of 98.31%.

Overall, after stage 1 treatment with flocculation, the COD of waste cutting emulsion decreased from 147200 mg/L to 2484 mg/L under the optimum condition: pH 5, $\text{Al}_2(\text{SO}_4)_3$ 2 g/L, C-PAM 12 mg/L, stirring speed 50 rpm, and stirring time 25 minutes. This treated wastewater will be used for further treatment (step 2) with Fenton oxidation.

3.2.6. Heat Value of Oil Recovered. The oil recovered after the flotation process was characterized by determining the heat value. The heat value of the oil recovered was 38095 ± 8 kJ/kg. This value is comparable to the heat value of biodiesel (~ 41000 kJ/kg) [26] and higher than that of brown coal (~ 19575 kJ/kg) [27]. It shows that the used oil could be recycled and used as fuel gas for heat generation. It will

TABLE 3: COD value and COD removal efficiency.

Stirring time (minutes)	COD (mg/L)	COD removal efficiency (%)
5	2938	98.00
15	2484	98.31
25	2586	98.24
35	2702	98.16
45	2768	98.12
55	2992	97.96

increase the cost-effectiveness for the treatment of cutting waste oil emulsion containing high oil concentration.

3.3. Result for Stage 2 Treatment by Fenton Process

3.3.1. Effect of $H_2O_2/FeSO_4$ Concentration Ratio. The concentration ratio $H_2O_2 : FeSO_4$ was varied from 3:1 to 15:1 at the same conditions: initial pH of 3 and $FeSO_4$ concentration of 11.23 (g/L). The results are shown in Figure 7.

Figure 7 shows that the concentration ratio of $H_2O_2 : FeSO_4$ increased from 3:1 to 10:1, and the COD removal increased. It is found that COD decreased when the concentration ratio increased to 12:1 and 15:1. Hence, the optimum concentration ratio of $H_2O_2 : FeSO_4$ was 10:1. The lowest COD value obtained was 172.2 (mg/L), with a COD removal efficiency of 93.06%. This observation may be explained as follows: at lower $H_2O_2 : FeSO_4$ concentration ratios, the H_2O_2 was not enough to oxidize the organic pollutants; therefore, the COD removal was low. However, when concentration ratios were too high, H_2O_2 may contribute to the COD and exhibit as hydroxyl radical scavenger [19, 28, 29] as shown by equation (3). The product, hydroperoxyl radical, is an oxidizing radical, but its oxidizing ability is lower than that of hydroxyl radical (OH^\bullet), leading to a decrease in treatment efficiency. Therefore, the suitable concentration ratio between H_2O_2 and $FeSO_4$ was applied for the next treatment step.

3.3.2. Effect of $FeSO_4$ Concentration. The concentration of $FeSO_4$ was varied from 8.42 to 19.66 g/L for the treatment of the emulsion and the result is shown in Figure 8.

The effect of $FeSO_4$ concentration on the treatment was performed at the conditions as follows: pH 3 and the ratio $H_2O_2 : FeSO_4$ of 10:1. The optimum $FeSO_4$ concentration was determined to be 14.04 g/L, with the lowest COD value of 84.1 mg/L, achieving 96.61% removal efficiency. At the concentration of $FeSO_4$ less than 14.04 g/L, it was not enough to catalyze the H_2O_2 degradation to form OH^\bullet radical. However, with too much $FeSO_4$, more radicals were lost by the excess of ion Fe^{2+} due to the reaction (4). Therefore, a suitable amount of $FeSO_4$ was important to accelerate the Fenton reaction for the treatment.

3.3.3. Effect of pH. For the Fenton reaction, the pH is a critical factor, since it affects the generation of radical. In this work, the pH of the treatment was investigated ranging from 2 to 5. The result for the effect of pH is plotted in Figure 9.

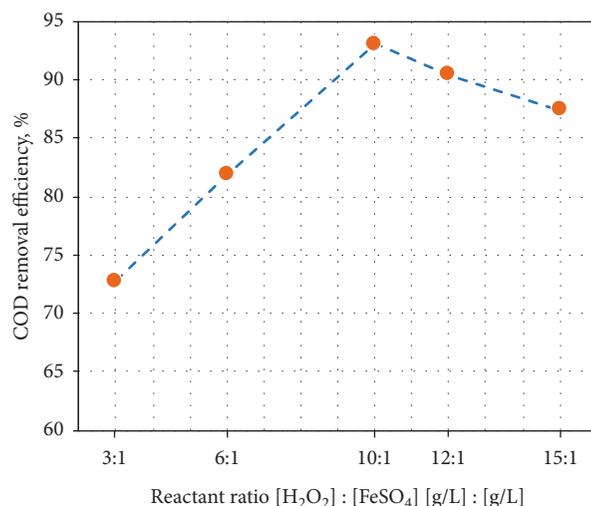


FIGURE 7: COD removal efficiency at different $H_2O_2 : FeSO_4$ concentration ratios.

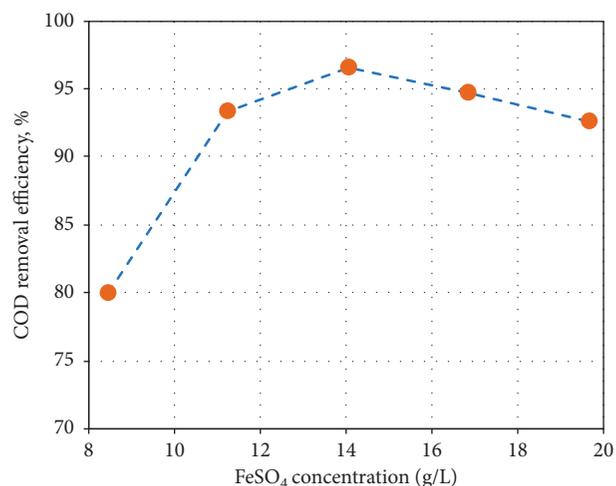


FIGURE 8: COD removal efficiency at different $FeSO_4$ concentrations (g/L).

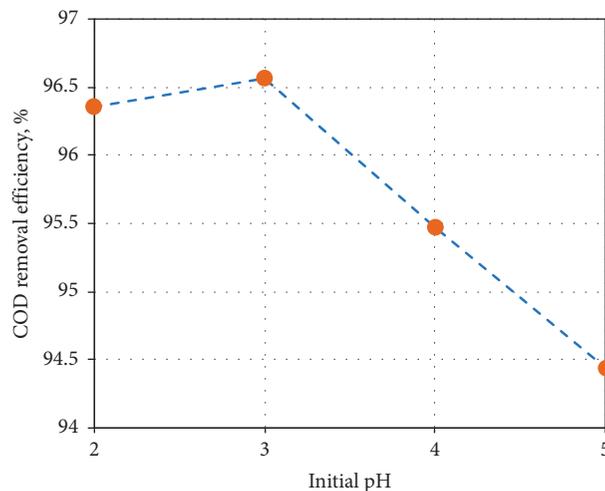
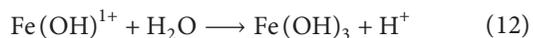
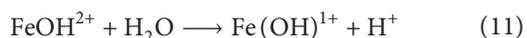


FIGURE 9: COD removal efficiency at different initial pHs.

TABLE 4: COD and BOD₅ of the waste cutting oil after stage 1 and stage 2 treatment.

Parameter	Stage 1+ stage 2 treatment	Standard A	Standard B
COD (mg/L)	85.4	75	150
BOD ₅ (mg/L)	30	30	50

As we can see, the low pH value gave higher COD removal efficiency than at the high pH. In particular, the best COD removal was obtained at a pH of 3, with the lowest COD value of 85.4 mg/L. The COD efficiency was 96.56%. It could be explained that when pH is higher than 3, ion Fe³⁺ may tend to dissociate with water to form Fe(OH)₃ (equations (10)–(12)) and, therefore, it produced less OH[•] radical. At pH less than 3, the amount of OH[•] radical was decreased due to hydrate ion formation, that is, [Fe(H₂O)₆]²⁺, which reacts slowly with H₂O₂ [30]. Another possibility is that, at low pH, H⁺ ion will act as a hydroxyl radical scavenger as shown by equation (13) [30]:



Thus, the best condition for treatment by the Fenton process was pH 3, concentration ratio H₂O₂: FeSO₄ of 10:1, and FeSO₄ concentration of 14.04 g/L. At that condition, the COD of wastewater obtained was 85.4 mg/L.

Table 4 shows COD and BOD₅ of wastewater after the treatment compared to Vietnam standard A and standard B for wastewater. As can be seen, the COD of the wastewater from cutting emulsion meets standard B, and the BOD₅ value meets the requirement of standard A. It showed that the treatment utilized in the present work could treat efficiently the waste-cutting emulsion. Thus, the wastewater could be discharged into the environment without any concern.

4. Conclusions

The waste oil-in-water cutting fluids were effectively treated in this work by combining the flocculation and Fenton processes. Under the best condition, the COD value was reduced from 147200 mg/L to 2484 mg/L after stage 1, flocculation treatment, and to 85.4 mg/L after stage 2, Fenton process. The COD removal efficiency of the overall treatment process was up to 99.94%. The COD and BOD₅ values of the treated wastewater sample satisfied grade B and grade A level for industrial wastewater standards of Vietnam. Our result demonstrated that a combination of conventional flocculation and traditional homogenous Fenton process could be practically applied for the large-scale treatment of waste cutting emulsion. The cost may be

minimized by using cheap chemical reagents and simple setting equipment. Moreover, with the support of the flotation technique, the oil was accumulated more effectively. It could be recovered and utilized as fuel gas for heat generation.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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