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Treatment of Cutting Oily-Wastewater by Sono Fenton Process: Experimental Approach and Combined Process

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***Abstract*—**Conventional coagulation, advance oxidation process (AOPs), and the combined process were evaluated and compared for its suitability to treat the stabilized cutting-oil wastewater. The 90% efficiency was obtained from the coagulation at $Al_2(SO_4)_3$ dosage of 150 mg/L and pH 7. On the other hands, efficiencies of AOPs for 30 minutes oxidation time were 10% for acoustic oxidation, 12% for acoustic oxidation with hydrogen peroxide, 76% for Fenton, and 92% sono-Fenton processes. The highest efficiency for effective oil removal of AOPs required large amount of chemical. Therefore, AOPs were studied as a post-treatment after conventional separation process. The efficiency was considerable as the effluent COD can pass the standard required for industrial wastewater discharge with less chemical and energy consumption.

***Keywords*—**Cutting oily-wastewater, Advance oxidation process, Sono-Fenton, Combined process.

I. Introduction

CUTTING oil is mostly used in metalworking industries; for example, cooling, lubrication, welding resistance, and disposal of metal chip. Oily waste emitted from industry is normally in form of oil-in-water emulsion with surfactant, which could become fuming and odorous. This emulsion normally contains high stability with small oil-droplets and difficult to treat by a conventional physical process. An effective technique is required in order to separate oil-droplets from the oily wastewater. Physical processes are widely used for oil removal, e.g. coalescer, flotation, coagulation, and membrane processes [1]-[4]. Moreover, other advanced separation and destruction processes such as dissolved air flotation, acoustic oxidation, and thermal oxidation, for oily wastewater were proposed by various researchers [5]-[9]. Oxidation processes, for example, chemical oxidation, acoustic oxidation, and advance oxidation processes, have been studied for its application such as treatment of non-degradable materials like aromatic carbon constituents. Especially advance oxidation processes which have the high efficiency for oil separation. The main concept of the processes is to generate hydroxyl radical (·OH), which is a very strong oxidant, to virtually oxidize any compound present in the water matrix, often at a diffusion controlled reaction speed. Consequently, ·OH reacts unselectively once formed. Contaminants will be quickly and efficiently fragmented and converted into small inorganic molecules.

Fenton process is one of the advance oxidation processes using $FeSO_4$, known as Fenton's reagent, to catalyze hydroxyl radical production. In addition, the treatment efficiency of Fenton can be enhanced by ultrasonic irradiation, which is called as sono-Fenton process. In this study, four different advance treatment processes were applied to separate cutting-oil including acoustic oxidation, chemical oxidation, Fenton, and sono-Fenton processes. Effects of size, concentration, and component of cutting oil to the treatment efficiency were also investigated. Moreover, impacts of different operating factors (i.e. pH, H_2O_2 concentration, Fe^{2+}/H_2O_2 ratio, and initial oil concentration) were analyzed on the efficiency of cutting oil removal. In addition, the synergistic effects between acoustic oxidation and Fenton process were studied.

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II. Experimental Procedure

A. Sample Preparation

Cutting-oil wastewater was synthesized by diluting 1 mL of concentrated cutting oil (Castrol Cleancut) in 1 L of tap water. Characteristics of the wastewater are shown in Table I and the size distribution of oil droplets is exhibited in Fig. 1.

TABLE I
CHARACTERISTICS OF THE CUTTING OIL EMULSION

Parameter	Unit	1 g/l of cutting oil
pH	-	7.4
Conductivity	(μs/cm)	275
Turbidity	(NTU)	1,356
COD	mg/l	3,051
TDS	mg/l	183

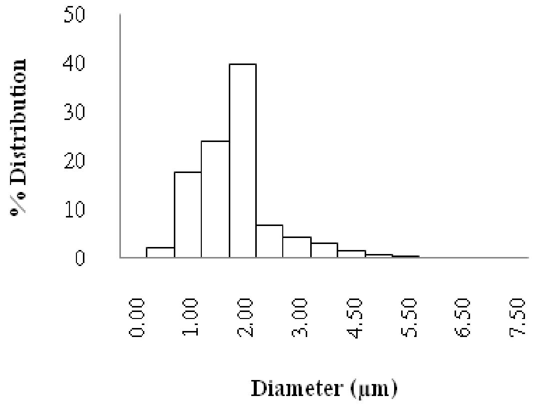

Fig. 1 Size distribution of cutting-oil droplet

The wastewater contains the COD value of 3051±120 mg/L and turbidity of 1356±56 NTU. The average droplet sizes of the cutting oil were in the range of 0.1 - 10μm. The wastewater contains the COD value of 3051±120 mg/L and turbidity of 1356±56 NTU. The average droplet sizes of the cutting oil were in the range of 0.1 - 10μm.

B. Acoustic Oxidation

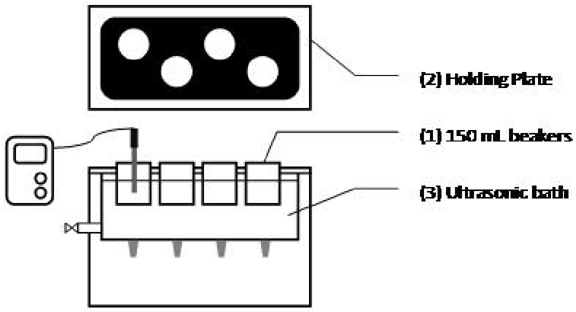

Fig. 2 Acoustic oxidation set-up

The experimental set-up in this study is shown in Fig. 2. Four 150-ml beakers containing degassed tap water were placed in the ultrasonic cleaner bath. The temperature of the experiment was controlled. Furthermore, a beaker was reserved for measuring the oxidation reduction potential (ORP) as a control system. Oxidants and reagents prepared in a separated vessel were added into the sample and the ultrasonic irradiation was immediately turned on.

C. Chemical Oxidation

1. Acoustic Oxidation with Hydrogen Peroxide

Several concentrations of hydrogen peroxide were added in the acoustic oxidation process. Samples were collected at different irradiation time and analyzed for COD values.

2. Acoustic Oxidation + Air Bubbling

Oxygen, which could be simply supplied by air bubbling, was added as an oxidation enhancement. Several aeration rates were used in the acoustic oxidation process. The samplings were conducted with the same procedure in Section III *A*.

D. Advance Oxidation Processes

Fenton and sono-Fenton processes were investigated in 100-ml beakers. The irradiation was performed at power input and frequency of 400 W and 28 kHz, respectively. The optimum hydrogen peroxide and ferrous ion dosages were either experimentally determined or obtained from previous literatures [10]. Samples were collected at 30 and 60 minutes of reaction time and analyzed for COD value.

E. Analytical Method

Analytical parameters in this study were determined by methods displayed in Table II.

TABLE II
ANALYTICAL PARAMETERS AND DETERMINATION METHODS

Parameter	Method
Chemical Oxygen Demand (COD)	Close reflux titration
Turbidity	Infrared light-scattering method by Lovibond PC Checkit Turbidimeter
pH	EXTECH pH/mV/Temperature meter 4072208
Oxidation Reduction Potential (ORP)	HANNA Standard hydrogen ORP probe
%COD removal	$\%COD_{Removed} = 100\% \times \left(1 - \frac{COD_t}{COD_0}\right)$ where COD_t = COD value at time t, mg/L; COD_0 = Initial value of COD, mg/L

III. RESULTS AND DISCUSSION

A. Treatment Processes

Numerous separation techniques were applied for removal of cutting-oil wastewater in several literatures. Furthermore, several destruction techniques were investigated in the mentioned conditions. The description and efficiency of these processes are displayed in Table III.

TABLE III
TECHNOLOGIES PROPOSED TO TREAT CUTTING OIL WASTEWATER

Separation processes			
Technique	Description	Efficiency	Sources
Coagulation	Using metal salts to destabilize oil droplets	90 - 95%	[11]
Coalescer	Enhance the separation of oil droplets by enlarging droplets' size	30%	[4]
Dissolved Air Flotation (DAF)	Increase the rising rate of droplets by reducing density of droplets	80%	[12]
Electro coagulation	Similar to coagulation but metal ions were supplied by electrochemical reaction	90%	[6]
Ultrafiltration	Separate most suspended substances by filtering through membrane	95%	[7], [8]
Destruction processes			
Technique	Description	Operating condition	Efficiency
Acoustic oxidation	Use of ultrasonic irradiation to break down oil droplets	Irradiate the sample using 100, 150, 200, 300, and 400 W power input	~ 0
Acoustic oxidation + H_2O_2	Use of hydroxyl radicals (·OH) to enhance the rate of acoustic oxidation	Ultrasonic was irradiated using 400 W power input and added 14 g/l of H_2O_2	13.6%
Acoustic oxidation + air bubbling	Use of air bubble to enhance the rate of acoustic oxidation	Ultrasonic was irradiated using 400 W power input and supplied oxygen by air bubbling rate of 0.3 L/min	4.5%

It can be seen that separation processes can provide high removal efficiency but the effluent COD still exceeded the industrial effluent standard of 120 mg/L. On the other hand, destruction processes had low efficiency (less than 15%), which is not sufficient to treat the wastewater. AOPs were therefore studied for treatment of cutting oil wastewater.

B. Advance Oxidation Processes (AOPs)

1. Effect of pH value

In this part, effects of pH on COD removal efficiency were investigated in the similar condition as in Seo et al. [10], i.e. 3 g/L of $FeSO_4$ and 14 g/L of H_2O_2. The results are displayed in Fig. 3 showing the 75.1% and 94.3% removal efficiency can be achieved at the acidic pH range (pH = 1.0 - 2.0). At pH 2.0, the efficiency was obviously higher when peroxide is absent due to the precipitation of iron. The pH, therefore, should be retained extremely low for (1) prevent the formation of ferrous and ferric hydroxide those induces sweep flocculation, and (2) the radical-production of Fenton chemistry prefers lower pH.

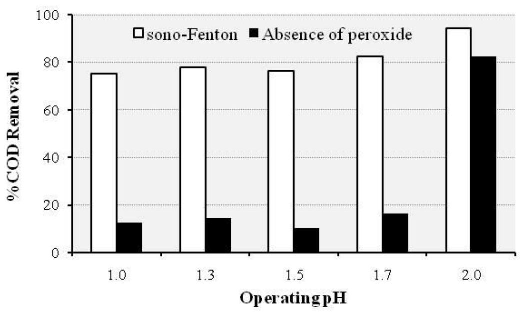

Fig. 3 Efficiency of sono-Fenton process obtained at different pH

2. Effect of Fe^{2+}:H_2O_2 ratio

The sono-Fenton process was applied for treating 1 g/l cutting oil wastewater with initial pH of 1.7. The optimum ratio of ferrous ion to hydrogen peroxide was determined for a constant 14 g/L H_2O_2 and varied Fe^{2+} concentrations. Fig. 5 exhibits the results indicating the increase of efficiency at Fe^{2+}/H_2O_2 of 1:143 until reaching the highest value of 91.3% at Fe^{2+}/H_2O_2 of 1:28 (i.e. 500 mg/L Fe^{2+} and 14 g/L H_2O_2). The efficiency was slightly decreased at the Fe^{2+}/H_2O_2 of 1:19. The reason responsible for poor COD removal at low Fe^{2+}/H_2O_2 was no catalytic decomposition of hydrogen peroxide occurs due to inadequate amount of Fe^{2+} [13]. On the other hand, high dosage of Fe^{2+} could negatively affect the oxidation process since Fe^{2+} is a known radical scavenger, which could react with the hydroxyl radical according to the following reaction [13]:

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^-$$

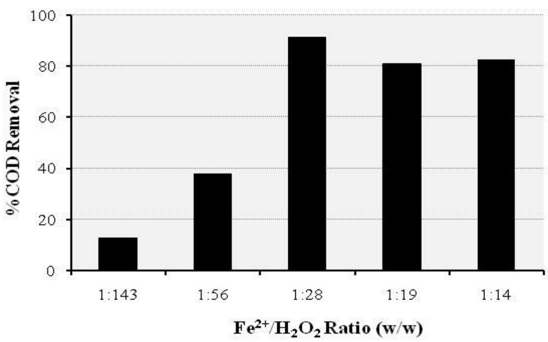

Fig. 4 One-hour COD removal efficiencies at different Fe^{2+}/H_2O_2 ratio

C. Analyze of Synergistic Effects

Synergistic effects are examined by comparing the efficiency from kinetic constants between two processes (i.e. Fenton and sono-fenton) at 10.5 g/L of H_2O_2 and 375 mg/L of Fe^{2+} without ultrasonic irradiation. The COD reduction is exhibited in Fig. 5.

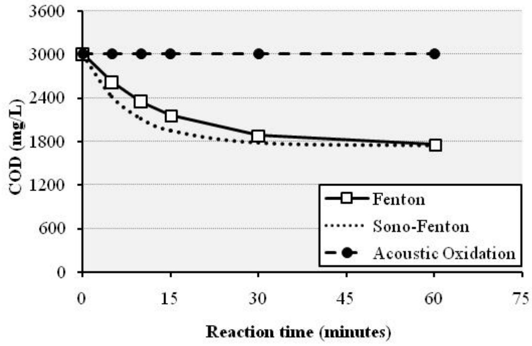

Fig. 5 Comparison between COD reduction Acoustic Oxidation, Fenton and Sono-Fenton

The synergistic index can be calculated by the following equations.

$$f = {k_{sono-Fenton}}/{(k_{Fenton} + k_{Acoustic\ oxidation})}$$

$$f = {0.123}/{(0.074 + 0.0)} = 1.66$$

D. AOPs Applied as Post-Treatment Process

The study of Fenton and sono-Fenton as the post-treatment of separation processes were conducted for 0.1% cutting-oil wastewater. The constant Fe^{2+}/H_2O_2 ratio of 1:28 was applied. The remaining COD at 30 and 60 minutes after the oxidation is shown in Fig. 6. Similar residual COD was obtained from all three processes, which can pass the effluent standard. Nevertheless, the 1:28 Fe^{2+}/H_2O_2 ratio was still high causing a large amount of chemical consumption. Effects of Fe^{2+}/H_2O_2 ratios on the oil removal were then examined.

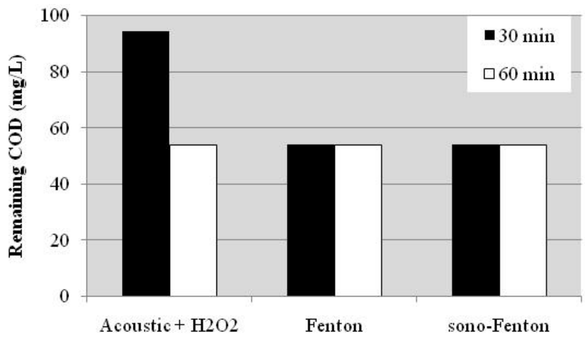

Fig. 6 Remaining COD for AOPs as a post-treatment process at 30 and 60 minutes

E. Effect of Fe^{2+}/H_2O_2 ratio in Fenton process

Effects of Fe^{2+}/H_2O_2 ratios in the range of 2.5 - 25 on efficiencies were investigated as exhibited in Fig. 7. As can be seen, the effluent COD was rapidly decreased in the first 15 minutes. The generated Fe^{2+} can effectively react with H_2O_2 producing hydroxyl radical that can oxidize stabilized oil-droplets. The highest treatment efficiency was obtained at the F/H ratio of 1:10, which corresponded to other works [14], [15]. The appropriate ratio of supplied H_2O_2 to the oil concentration is required for an effective separation with less chemical and energy consumptions.

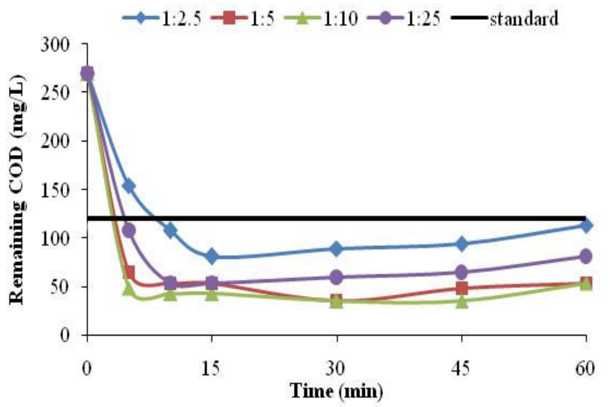

Fig. 7 Effect of Fe^{2+}: H_2O_2 ratio on COD remaining

F. Combined Process

From previous studies, the treatment of 1% cutting-oil wastewater by the sono-Fenton process (Fig. 8) had a drawback from the high consumption of chemical and energy. Therefore, the sono-Fenton should be applied as a post-treatment process after separation processes, which normally contain 90% removal efficiency. The effluent COD can pass the industrial standard with less chemical and energy usages. The schematic diagram of this concept is depicted in Fig. 9.

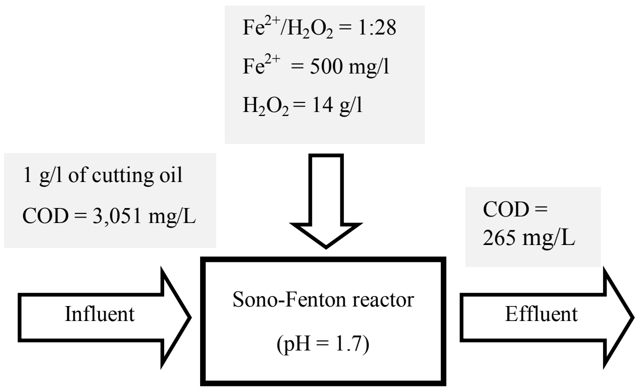

Fig. 8 Schematic diagrams of sono-Fenton process

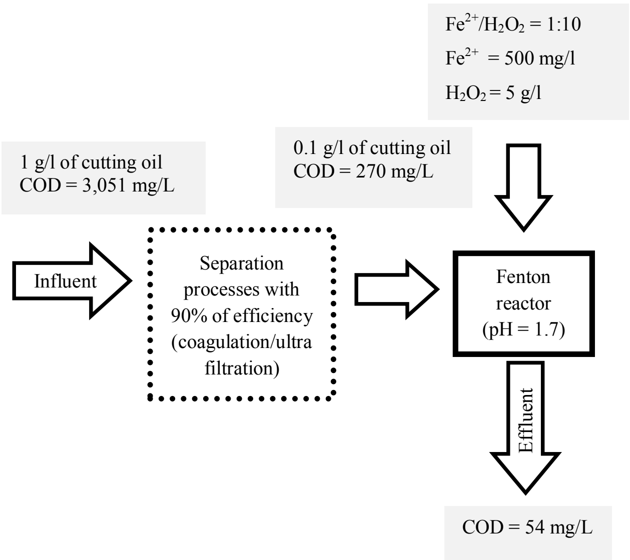

Fig. 9 Schematic diagrams of combined processes

IV. Conclusion

In this study, the possibility of using sono-Fenton processes for cutting oil wastewater treatment was assessed. Effects of various parameters on the oil removal were investigated, including pH, H_2O_2 concentration, Fe^{2+}/H_2O_2 ratio, and initial oil concentration. Conclusions can be drawn as following.

- Optimal pH for sono-Fenton process is 1.0 - 1.7, which can prevent the $Fe(OH)_3$ precipitation and encourage the hydroxyl radical production.
- The ferrous ion to hydrogen peroxide ratio can affect the cutting oil removal efficiency. The optimal Fe^{2+}/H_2O_2 ratios for 1% and 0.1% cutting oil wastewater were 1:28 and 1:10, respectively. Conventional separation processes were therefore required to reduce the consumption of chemical and energy with effective treatment performance.

Numerous studies should be further conducted, for instance, (1) continuous system experiment, (2) electrocoagulation with iron electrodes and electro-Fenton for cutting oil removal, and (3) treatment of different types of oily wastewater by combined processes.

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