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Short Communication

Experimental Study on Removal of Emulsified Oil by Electrocoagulation with a Rotating Container

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Electrocoagulation (EC) was proved to be highly effective to remove the oil from oily sewage in an oilfield. However, much work still needs to be done to improve the oil removal performance and to reduce the energy consumption of the EC device. In this text, a rotating container method was employed for the purpose of strengthening the mass transfer process in the EC device. Firstly, the effect of different rotation rates and APEs on the oil removal process was determined, showing that the rotation of the container decreases the effect of EC on oil removal. Then, the effect of the current density on oil removal was investigated, showing that the oil removal efficiency rises with increasing current density. Lastly, the effect of the rotation rate on the appearance time of flotation was investigated, showing that the rotation of the container slows down the formation of floating floc, resulting in a lower oil removal efficiency.

Keywords: Electrocoagulation; oily sewage; oil removal efficiency; rotation container.

1. INTRODUCTION

The oily sewage that is produced in large volumes during the crude oil extraction and refining process is attracting more and more attention, as it causes pollution of the environment [1]. Globally, 250 million barrels of water are produced daily from both oil and gas field [2]. Furthermore, oily sewage has the characteristics of high oil content, high salinity and micron-sized oil droplets, resulting in high stability. Therefore, oily sewage should be treated for recycling or direct discharge [3]. In the past decade, many traditional treatment methods to remove oil of micron size have been applied, including physical methods, chemical methods, biological methods and so on.

The conventional methods, including physical methods, chemical methods and biological methods, are not ideal for the treatment of oily sewage, and are especially unfit for removing emulsified oil from sewage [4]. Electrochemical methods are clean and efficient water purification methods, especially EC technology. EC is not only an environmentally friendly and efficient, water demulsification technology, but also combines the advantages of chemical coagulation, flotation and electrochemistry [5].

For a given current density, the energy consumption is mainly related to the potential difference of the electrodes. Chen [6] proposed a theoretical model of electrolysis voltage considering the overpotential, current density, voltage, conductivity of the solution, plate spacing, and surface of the electrodes. The anode overpotential, cathode overpotential, equilibrium potential difference and IR-drop of the solution can be overcome when current passes through the EC reactor. The concentration overpotential, also called the diffusion or mass transfer overpotential, is caused by the difference in electroactive species concentration between the bulk solution and the electrode surface. When the reaction rate is much smaller than the process of mass transfer, the concentration overpotential presented is much smaller [7]. The concentration overpotential can be decreased by promoting the metal ions mass being released to the emulsion via turbulence. Some experts [7,8] investigated the effect of the flow rate and flow patterns on the mass transfer process in a continuous system and found that the water flow improves the mixing conditions, thereby speeding up the transport process of metal ions and minimizing the concentration overpotential. Some mechanical means can also help in transporting the electrolyte solution from anode to cathode at a higher speed. In some of the literature, rotors were employed in the EC process, mainly in a batch system, and the results showed that as the stirring rate increases, the removal efficiency II first increases and then decreases. A moderate stirring rate achieves the maximum removal efficiency as the mixing can firstly improve the mass transfer of coagulants within the EC reactor, then facilitate effective aggregation of oil droplets under mild conditions. However, this method can only improve the oil removal efficiency in the rotor action area, while most of the remaining areas are unaffected.

In this work, to eliminate the passivation phenomenon so as to reduce the energy consumption, a rotating container method was applied to improve the mass transfer process. The effects of the rotation rate on the removal efficiency under different tilt angles of parallel-plate electrodes (APEs) were investigated and ultimately the removal rates under static and rotating conditions at the optimum APE were compared.

2. EXPERIMENTAL

2.1 Characteristics of sewage

Oily sewage is characterized by a high oil concentration, droplets with micro size and high salinity. To every 1.0 L tap water was added successively 2.0 g of sodium dodecyl benzene sulfonate (SDBS) and 3.0 g of No. 0 diesel taken from Sinopec. Then the solution was mixed using a high shear machine for about 10 min. 2.0 g of NaCl was applied to increase the conductivity of the solution. The pH was adjusted to 7.0 ± 0.2 with 0.1 M NaOH or 0.1 M H_2SO_4, [9] the best treatment effect with the help of the amphoteric nature of aluminium hydroxide under a neutral pH. The types of experimental reagents used in the experiments are shown in Tab. 1.

Table 1. Main experimental reagents

Reagent	Level
Diesel	0#
Sodium dodecyl benzene sulfonate	AR
NaCl	AR
H_2SO_4 (strong)	AR
Petroleum ether	AR
NaOH	AR
HCl	AR
KCl	AR

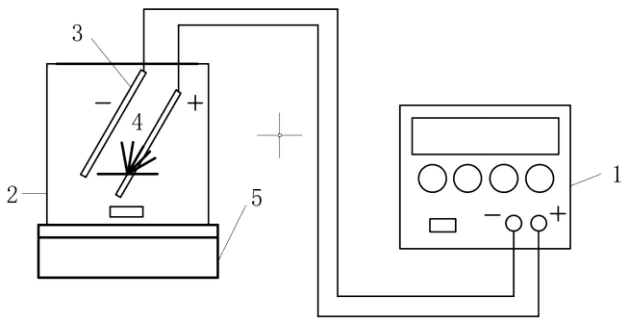
The oil concentration in the wastewater was analyzed using a UV-spectrophotometer, the conductivity was measured using a conductivity meter, and the pH value was monitored with a pH meter.

The oil removal efficiency is calculated by Eq. (1):

$$\eta(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}$$

where C_0, C_t are the initial oil concentration (mgL^{-1}); and the oil concentration after the treatment time (mgL^{-1}).

2.2 Experimental method



1—DC power supply. 2—Electrocoagulation container. 3—Aluminium plate. 4—Emulsion oil wastewater. 5—Rotating platform.

Figure 1. Device principle and photo of experiment

The experimental apparatus used in this study is shown in Fig. 1. Constructed of perspex, the rectangular reactor has an effective volume of 2.5 L. In this experiment, aluminium plates were used as electrodes. The electrodes, one aluminium anode and one aluminum cathode, were 80.0×80.0×2.0 mm, and the plate spacing was 4.0 cm. An insulating bar was used to fix the two plates and to hang the two plates on the iron rack table. The inclination angle of the plates was fixed through the bonding of insulating tape and the insulating bar.

In this work, all experiments were performed with the same cathode and anode. In each run, the electrodes were rubbed with sandpaper to remove the passivation film, then submerged in acetone and washed with 5% (v/v) hydrochloric acid for 10 min successively. Finally, rinse 3 times in tap water. The oil content was measured 3 times and the average of the three results was calculated to ensure experimental reliability, and the error was controlled at 5%. The experimental instruments used are shown in Tab. 2.

Table 2. Main experimental instruments

Name	Type	Manufacturer
DC power supply	PS-305DM	Hong Kong Lung Wai Instruments Co. Ltd
Digital shear emulsion mixer	JRJ300-SH	Shanghai Specimen Factory
pH meter	PHSJ-4F	Shanghai Yidian Scientific instrument Co. Ltd
Electronic balance	FA1004	Shanghai Shunyu Hengping Scientific instrument Co. Ltd
Electromagnetic agitator	RG-18	Gongyi Yuhua Instrument Co. Ltd
Spectrophotometer	A360	Ao Art Instruments
Electric rotary	MT200KL20	Shenzhen Kangxin Technology Co. Ltd

3. RESULTS AND DISCUSSION

For each EC experiment conducted under standard conditions (pH=7.0 ± 0.2, plate spacing of 4.0 cm, treatment time of 24 min), 25.0 ml samples were taken every 4.0 minutes to measure the oil content.

3.1. Effect of different rotation rate and APE

In order to evaluate the effect of the rotation rate of electrocoagulation container on the oil removal process, rotation rates of 0 rad/s and 0.05 rad/s with current density of 119.8 Am^{-2} were used to investigate different APEs (0°, 68°, 90°) [10]. The other operational parameters such as pH, treatment time and plates space were kept constant.

At each rotation rate, the samples under different APEs were taken after the treatment time of 24 min and allowed to stand for 1h. The oil removal efficiency of different APEs with the change of electrolytic time is shown in Figs. 2 and 3.

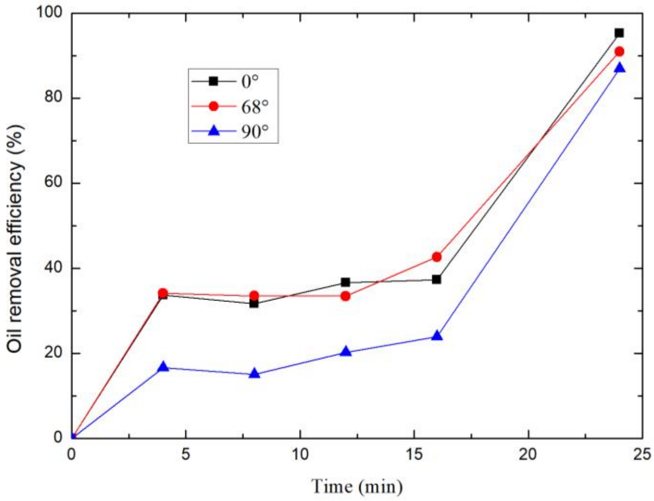


Figure 2. Oil removal efficiency with the treatment time at different APEs (pH=7 ± 0.2, *d*=4.0 cm, *J*=119.8 Am^{-2}, *r*=0 $rads^{-1}$)

For a given APE, the removal processes in Fig. 2 have two stages: lag stage and reactive stage. In the lag stage from 0 to 16 min, with the increasing treatment time, the oil removal efficiency increased slowly or fluctuated. At the beginning, the shorter treatment time leads to the appearance of hydrolyzates in the form of $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_3$ and a little bit of polymer [6]. The main demulsification mechanism is electrostatic neutralization, resulting the raising in the oil removal rate limited.. Subsequently, the removal rate significantly increases (16–24 min). This might be attributed to the following aspects: (i) according to Faraday's law, a longer treatment time leads to the increment of the amount of Al^{3+} and H_2 bubbles; (ii) the effect of flotation is enhanced with a higher bubble density; (iii) convection can improve the anode concentration polarization and facilitate the hydrolysis reaction. A higher coagulant dosage tends to increase the frequency of collisions, thereby causing more aggregation.

Besides, the oil removal efficiency under different APEs showed that at APEs of 0° and 68°, the treatment effect is much higher than at an APE of 90°. These results are consistent with the studies of Liu [11]. A small APE provides better oil removal, because at a smaller tilt angle the distribution coverage strongly enhances the interaction between coagulation and flotation. In addition, the diffusion layer is weakened by the bubbles, increasing the flux of Al^{3+} [12]. The existence of the special angle 68° might due to the following aspects: (i) with accumulation of Al^{3+} and bubbles, the nucleates are reduced at the surfaces of electrode; (ii) the bubbles and flocs tend to be dispersed evenly; (iii) the bubbles carrying impurities can rise to the surface of the solution without obstructions [13].

As shown in Fig. 3, for the greater treatment time, the oil removal in the early stage increased slowly before 16 min and rose rapidly after 16 min. The oil removal efficiencies with APE 0° and APE 68° are higher than that of APE 90°.This is similar to the trend shown in Fig. 3, for the reasons explained above. To sum up, by comparing the oil removal efficiency of the intermediate sample points at different APEs we find that the oil removal efficiency with APE 0° and APE 68° is higher than that of APE 90° at all rotation rates studied.

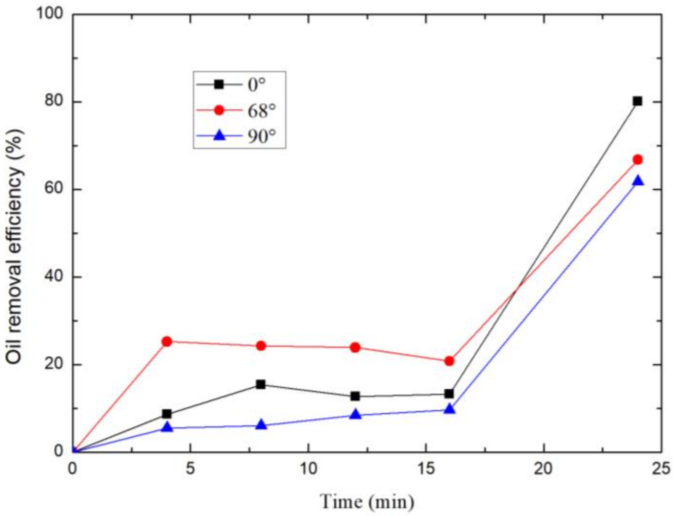


Figure 3. Oil removal efficiency with the treatment time at different APEs (pH=7 ± 0.2, d=4.0 cm, J=119.8 Am^{-2}, r=0.05 $rads^{-1}$)

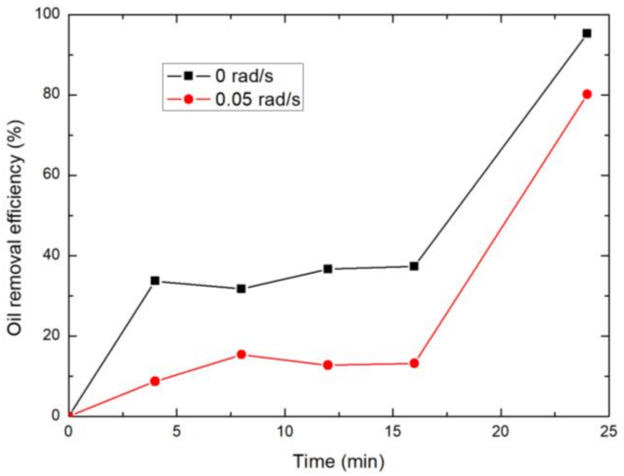


Figure 4. Oil removal efficiency with the treatment time at different rotation rates (pH=7 ± 0.2, d=4.0 cm, J=119.8 Am^{-2}, APE=0°)

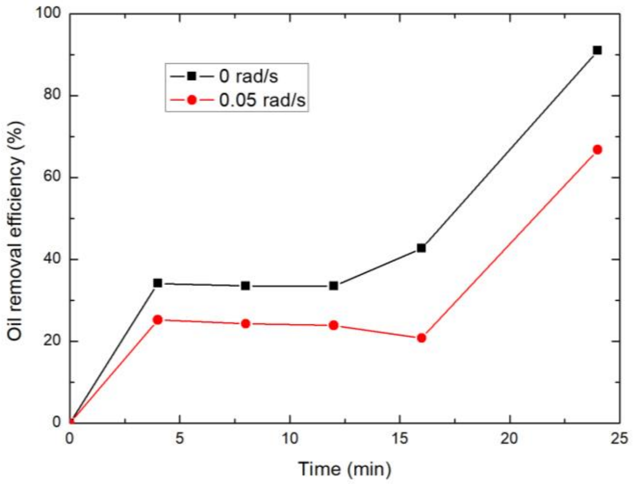


Figure 5. Oil removal efficiency with the treatment time at different rotation rates (pH=7 ± 0.2, d=4.0 cm, J=119.8 Am^{-2}, APE=68°)

According to Figs. 4 to 6, the oil removal efficiency with the rotation rate of 0.05 rad/s is always lower than the container without rotation, whatever the APE selected. According to the principle of the electrocoagulation process, this is for the following reasons: (i) the rotation of the container might block the bubble rising process, reducing the flotation effect; (ii) the rotation of the container might block the floc growth process.

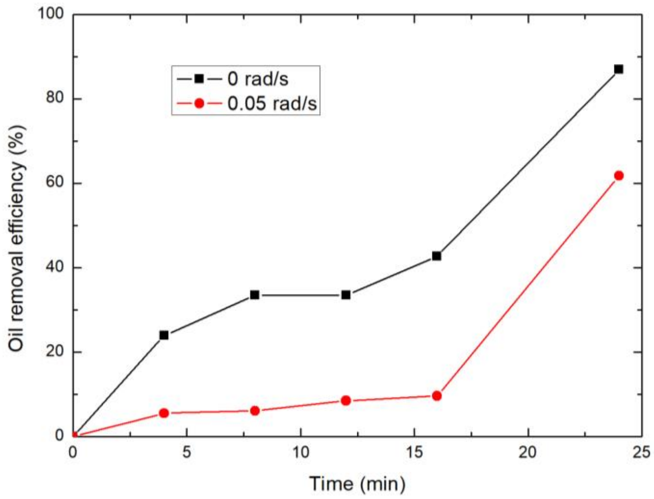


Figure 6. Oil removal efficiency with the treatment time at different rotation rates (pH=7 ± 0.2, *d*=4.0 cm, J=119.8 Am^{-2}, APE=90°)

To sum up, through comparing the oil removal efficiency experiments with different rotation rates and APEs, the oil removal efficiency with APE 0° and APE 68° is higher than that of APE 90°, and the rotated container affecting the reformation of flocs decreases the oil removal.

3.2. Effect of current density

To investigate the effects of the current density on oil removal, the current density was adjusted to 218.8 A m^{-2}. The experiment was repeated under the above experimental conditions, and Fig. 7 provides the results.

As Fig. 7 shows, the oil removal increases rapidly to about 95% at 16 min at current density of 218.8 A m^{-2}, while the oil removal efficiency increases slowly to no more than 90% at 24 min when the current density is 119.8 Am^{-2}. This is because the increment of the generation rate of Al^{3+} and bubbles at higher current density results in the enhancement of flocculation and flotation. Increasing the current density is an effective measure to cut the processing time during the EC process.

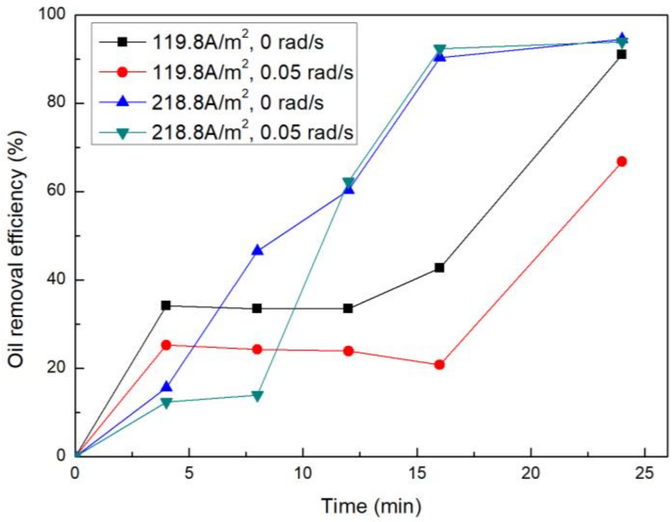


Figure 7. Oil removal efficiency with the treatment time at different current densities (pH=7 ± 0.2, d=4.0 cm, J=218.8 A m^{-2}, APE=68°)

3.3. Effect of rotation rate

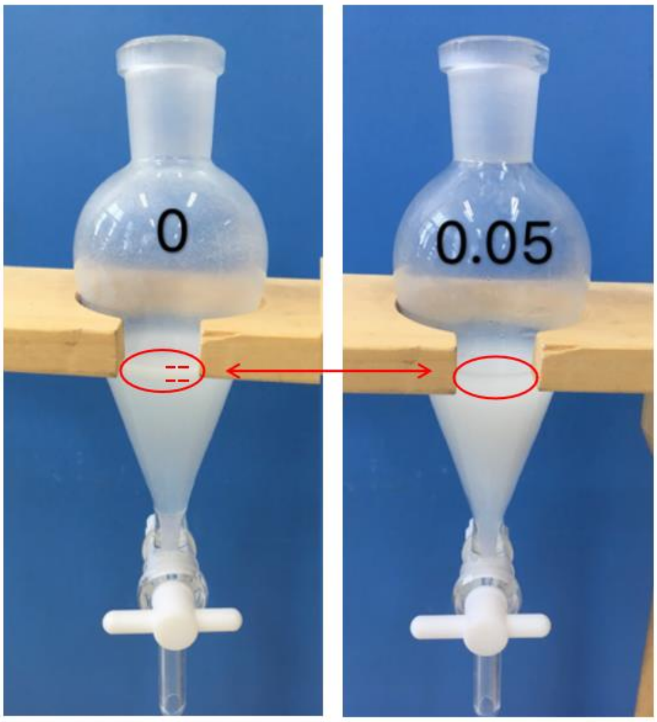


Figure 8. The stratification of the solution after sampling for 12 min

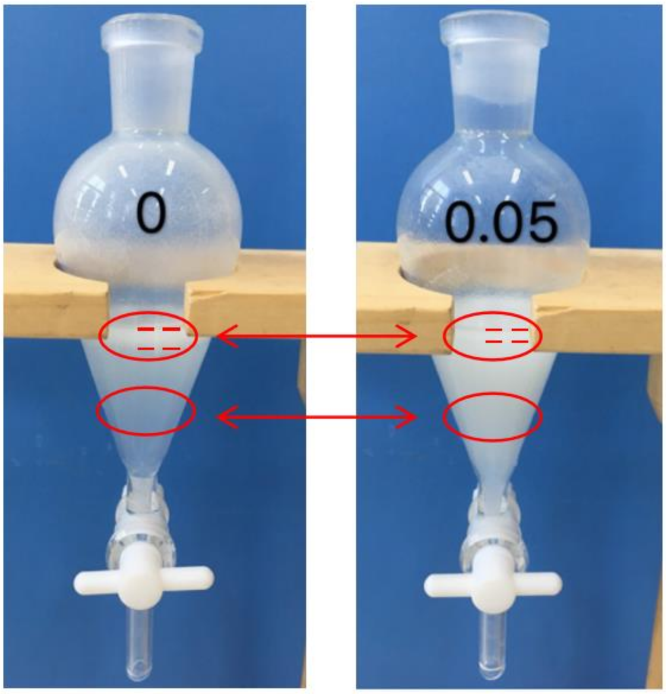


Figure 9. The stratification of the solution after sampling for 16 min

To investigate the effect of the rotation rate on the appearance time of flotation, the rotation rate was adjusted to 0 rad/s and 0.05 rad/s at the APE of 68°. The experiment was repeated under the above experimental conditions, and the stratification of samples at 12 min and 16 min at different speeds is shown in Fig. 8 and Fig. 9.

After sampling and static settling, it can be observed from Fig. 8 that floating floc has appeared in the water samples with the speed of 0 rad/s at 12 min, but not in the water samples with the speed of 0.05 rad/s. As can be seen in Fig. 9, floating floc began to appear in the water sample of 0.05 rad/s at 16 min, while lots of floating floc was generated in the water sample of 0 rad/s. This contrastive experiment indicated that the rotation of the container slows down the formation of floating floc to a certain extent, which may be one reason explaining the lower oil removal efficiency.

4. CONCLUSIONS

The study examines the effect of container rotation on the oil removal performance of an electrocoagulation device.

Firstly, the effects of different rotation rates and APEs on oil removal process were determined, showing the oil removal efficiency with APE 0° and APE 68° is higher than that at APE 90°, and the rotation of the container decreases the effect of electrocoagulation on oil removal.

Also, the effect of the current density on oil removal was investigated. The results indicated that the oil removal efficiency rises with increase of the current density, and it is an effective measure to shorten the processing time of electrocoagulation by increasing the current density.

Finally, the effect of the rotation rate on the time of flotation appearance was investigated. The results indicated that the rotation of the container slows down the formation of floating floc to a certain extent, which may be one reason for the lower oil removal efficiency.

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