

Oil removal in tight-emulsified petroleum waste water by flocculation

L L Pan^{1,3,4}, Y Chen^{1,3,*}, D Chen^{1,3}, Y Q Dong², Z T Zhang¹ and Y X Long⁴

¹ Institute of Petrochemical and Energy Engineering, Zhejiang Ocean University, Zhoushan, Zhejiang 316022, China

² Institute of Petroleum Engineering, Changzhou University, Changzhou, Jiangsu 213016, China

³ United National-Local Engineering Laboratory of Harbor Oil & Gas Storage and Transportation Technology, Zhoushan, Zhejiang 316022, China

⁴ China Petroleum Group Engineering Design Co., Ltd. Qinghai Branch, Dunhuang, Gansu 736200, China

*Corresponding author. Tel.: 1-365-682-3036.

E-mail addresses: chenying9468@126.com (Ying Chen).

Abstract. In this study, the emulsified oily wastewater was collected from a petrochemical plant. The size distributions of the emulsified oil particles in the wastewater and the supernatant liquid generated from the wastewater flocculation were conducted using scattered light, and routine analyses of COD and oil content in the wastewater were performed. This paper studied the oil removal process during flocculation using PAC and/or PAM and discussed the reason of low degreasing rate of the tight-emulsified petroleum wastewater. Experimental results show that the emulsified petroleum wastewater is a kind of high-concentration (COD, 9,600.0 mg·L⁻¹) tight-emulsified (weighted average oil particle size, 440 nm) oil-containing (553.0 mg·L⁻¹) wastewater. Compared with that in treating ordinary emulsified wastewater, the oil removal efficiency of the flocculation method based on PAC and PAM in treating tight-emulsified petroleum wastewater is relatively low (the highest oil removal rate is only about 85%). It is speculated that the reasons may be that the PAC and PAM form small oil alum flocs that do not sediment easily in water.

1. Introduction

The higher oil content of emulsified petroleum wastewater intensifies the difficulty of the secondary biochemical treatment of wastewater, and the high-efficiency oil removal pre-treatment of wastewater remains a huge challenge^[1]. At present, the main oil removal pre-treatment methods for emulsified petroleum wastewater are gravity sedimentation^[2], acidification^[3], heating^[2], centrifugal sedimentation^[2], extraction^[4], filtering^[5], air flotation^[6], and chemical coagulation or flocculation^[3,7]. Among these methods, chemical flocculation has been extensively used because of its advantages, such as simple operation, strong adaptability, high efficiency, and economy^[7]. The main flocculants used in this method are inorganic flocculants^[3-4,8] (e.g., polyaluminum chloride (PAC), polyferric silicate, and polymeric ferric sulfate) and organic flocculants^[3-4,7-8] (e.g., polyacrylamide (PAM), polyvinylamine, polyvinylsulfonate). PAC and PAM have received considerable attention because of their advantages,



including abundant sources, low cost, and good flocculation effect^[4,8-9]. Zhang^[3] used PAC ($140 \text{ mg}\cdot\text{L}^{-1}$) to treat emulsified wastewater (oil content, $35.5 \text{ mg}\cdot\text{L}^{-1}$; chemical oxygen demand (COD), $625 \text{ mg}\cdot\text{L}^{-1}$) from a union station of Shengli Oil Field, and the oil removal efficiency was 83%. Daud^[10] used PAC ($300 \text{ mg}\cdot\text{L}^{-1}$) to treat emulsified biodiesel wastewater (oil content, $2,680 \text{ mg}\cdot\text{L}^{-1}$; COD, $5,900 \text{ mg}\cdot\text{L}^{-1}$; suspended solid concentrations, $2,680 \text{ mg}\cdot\text{L}^{-1}$, $5,900 \text{ mg}\cdot\text{L}^{-1}$, and $348 \text{ mg}\cdot\text{L}^{-1}$) and achieved an oil removal efficiency of 97%. Zeng^[7] used PAC and PAM (PAC, $450 \text{ mg}\cdot\text{L}^{-1}$; PAM, $1.0 \text{ mg}\cdot\text{L}^{-1}$) to treat emulsified wastewater with thickened oil (oil content, $400\text{--}1000 \text{ mg}\cdot\text{L}^{-1}$; COD, $500\text{--}1000 \text{ mg}\cdot\text{L}^{-1}$; suspended solid concentration, $90\text{--}300 \text{ mg}\cdot\text{L}^{-1}$; turbidity, $150\text{--}350 \text{ NTU}$); the maximum oil removal efficiency was 95%. These studies show that, as the crude oil becomes heavier, the pollutant content of petroleum wastewater increases during oil exploitation, and the emulsification intensifies. Petroleum wastewater even reaches the tight-emulsified state^[9] in certain instances. However, there is no clear presentation of the concept of tight-emulsified oily wastewater, and few reports on the oil removal pre-treatment of tight-emulsified petroleum wastewater have been published. Thus, this paper studied the oil removal pre-treatment technologies based on PAC and PAM and the flocculation schema, analyzed on tight-emulsified high-concentration petroleum wastewater from a petrochemical plant and discussed the reasons that the degreasing rate of the tight-emulsified oily wastewater is lower than that of ordinary emulsion. The first paragraph after a heading is not indented (Bodytext style).

2. Experimental process

2.1. Reagents and instruments

Reagents: The wastewater was collected from a petrochemical plant. The reagents used included petroleum ether (boiling range, $30\text{--}60\text{ }^{\circ}\text{C}$; analytically pure), anhydrous sodium sulfate (analytically pure), sulfuric acid (guaranteed reagent), PAC (industrial grade; alkalization degree, 45%; the molecular weight range, $5000\text{--}8000$ Dalton; surface charge density, 2.44 mmol/g), PAM (industrial grade; cationic degree, 30%; the molecular weight range, $3,000,000\text{--}8,000,000$ Dalton; surface charge density, 3.56 mmol/g), and deionized water (prepared in the laboratory).

Instruments: TU-1810PC ultraviolet–visible spectrophotometer (Persee General Instrument Co., Ltd., Beijing, China), Zetasizer Nano ZS90 nanoparticle size and Zeta potentiometric analyzer (Malvern Corporation, UK), 722S visible spectrophotometer (INESA Analytical Instrument Co., Ltd., Shanghai, China), WGS-800 turbidimeter (Xinrui Instruments Co., Ltd., Shanghai, China), OxiTop® Control 12 infrared remote-controlled Laboratory BOD automatic analyzer (WTW Corporation, Germany) were used in the experimental analyses. JYW-200A liquid table and interface tensiometer (Chengde peak testing machine testing equipment Co., LTD.)

2.2. Flocculation experiment

A wastewater sample (200 mL) was collected and placed in a beaker. Its pH level was adjusted to a pH level by adding sulfuric acid ($0.05 \text{ mL}\cdot\text{L}^{-1}$ aqueous solution). PAC and PAM (2% aqueous solution) were added into the sample, which were then stirred and allowed to set for 20 min. After alum flocs formed and their sedimentation state was observed, the supernatant was collected to analyze the oil content. When PAC was used, the sample was rapidly stirred for 2 min (200 r/min). When PAM was used, the sample was slowly stirred for 10 min (50 r/min). When both PAM and PAC were used, PAC was added, the sample was rapidly stirred for 2 min (200 r/min), PAM was added, and then the water sample was slowly stirred for 10 min (50 r/min).

2.3. Analytical method

In the petroleum ether extraction, ultraviolet spectroscopy was used to analyze the oil content (wavelength, 255 nm)^[11]. Scattered light was used to measure the particle size^[12]. Potassium dichromate rapid spectrophotometric method was employed to analyze the COD^[11]. Pressure differential method was adopted to measure the biochemical oxygen demand (BOD₅)^[11]. The weight

method was utilized to determine the suspended solid concentration^[11]. A turbidimeter was used to measure turbidity.

3. Results and discussions

3.1. Wastewater characteristic analysis

Figure 1 presents external views of the emulsified petroleum wastewater samples. Figure 1 (a) shows that the wastewater was translucent and brown. Its turbidity was 268 NTU, as presented in table 1. It contains black solid particles and presents a slightly unpleasant petroleum odor. After the wastewater was allowed to set for 18 d, it presented two distinct layers, as shown in Figure 1(b). The upper layer was brown in color with a slight milky white appearance (turbidity, 204 NTU). The lower layer exhibited the sedimentation of solid particles. After 30 d, the milky white color of the upper layer became more obvious (turbidity, 181 NTU), and the lower layer presented the sedimentation of more solid particles, as presented in Figure 1(c). These results indicated that the wastewater could be a three-phase oil–water–solid system. The turbidity of the wastewater was caused by the suspended solids and emulsified oil. The suspended solids gradually sedimented during the setting process, and the turbidity of the wastewater in the upper layer decreased. The emulsion was generally milky white in color, and the size of its particles in the dispersion phase was generally smaller than 2×10^4 nm^[5]. Particle size affects the transparency degree of the wastewater. When the particle size of a mini-emulsion in the dispersion phase does not exceed 500 nm^[13], the tight-emulsion is translucent. By contrast, when the particle size of an ordinary emulsion in the dispersion phase is at least 500 nm^[14], the ordinary emulsion is not transparent. Therefore, the oil particle size of the petroleum wastewater could be within the particle size range of a mini-emulsion in the dispersion phase because the wastewater was translucent. During the setting process, the oil particle size gradually increased in accordance with the Ostwald ripening phenomenon^[15], and the white color of the wastewater intensified.

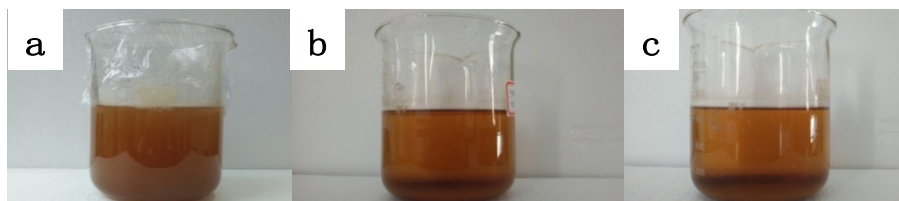


Figure 1. External view of wastewater.

(a) Wastewater upon collection, wastewater samples after setting times of (b) 18 d and (c) 30 d.

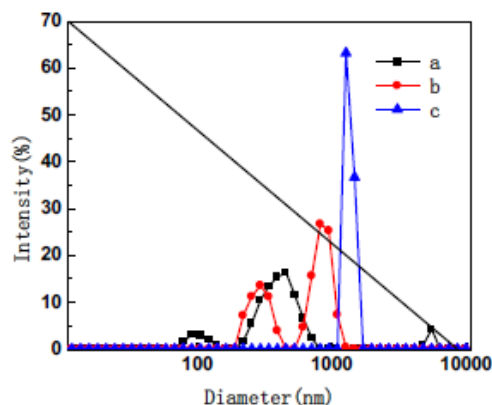


Figure 2. Size distribution of the particles in wastewater.

a—Wastewater upon collection. b—Wastewater allowed to set for 18 d. c—Wastewater allowed to set for 30 d.

Figure 2 shows the particle size distribution in the wastewater. The 18 d and 30 d particle size distributions were obtained in the upper layer of the sample. The size distribution of the particles in the wastewater upon collection presented three peaks at 90, 460 and 5,560 nm. After 18 d, the particle size distribution presented two peaks at 295 nm and 825 nm. After 30 d, the particle size distribution had a single peak at 1,280 nm. The first and second peaks could be assigned to the oil particles, whereas the third peak could be attributed to the solid particles. The solid particles easily sedimented and separated because of their large sizes; thus, after the wastewater was allowed to set for 18 d, the third peak disappeared. As a consequence of the Ostwald ripening phenomenon^[15], small oil drops were initially absorbed by the large liquid drops and subsequently disappeared, whereas the large ones increased in size. Furthermore, the first and second peaks shifted to the right, that is, the average oil particle sizes increased from 90 nm to 295 nm and from 460 nm to 825 nm. After the setting time was extended to 30 d, the small liquid drops were completely absorbed by the large ones, and the first peak disappeared. As a result, the second peak became narrower and higher. The peak continued to shift to the right, that is, the average oil particle size further increased from 825 nm to 1,280 nm. In summary, the wastewater contained solid particles and oil particles; the former sedimented during the setting process because of their large sizes, whereas the latter were relatively small. The wastewater was translucent within tight-emulsion particle size range in the dispersion phase, as shown in Figure 1(a). As the setting time extended, the particle sizes of the oil drops gradually enlarged, and the wastewater slowly became milky white, as shown in Figures 1(b) and (c). Therefore, the wastewater was tight-emulsified wastewater containing solid particles and oil.

The formation conditions for tight-emulsions are as follows: the system should contain a large quantity of surfactants besides oil and water, and a high shear force in the emulsion formation process should be present^[13]. In this study, we examined whether the petroleum wastewater generation process exhibits the same formation conditions as that for tight-emulsions.

Table 1 shows the results of the wastewater characteristic analysis. The COD of the wastewater was 9,600.0 mg·L⁻¹, its BOD₅ was 897.1 mg·L⁻¹, its oil content was 553.0 mg·L⁻¹, its BOD₅/COD ratio was 0.093, and the contribution of the oil content in wastewater to COD was 17.2% (if per gram of petroleum-like matter was equivalent to 3 g of COD^[3]). Heavy oil is known to contain many natural surfactants, such as pectin and asphaltene^[16]. Various surfactants are added during petroleum exploitation and processing. Consequently, heavy oil wastewater contains many organic pollutants, which are difficult to degrade^[17]. These surfactants not only increase the COD in the wastewater but also decrease the BOD₅/COD ratio. Under the effect of high shear force during petroleum processing, such as the coal carbonization of residual oil, the surfactants form high-stability tight-emulsified petroleum wastewater.

Table 1. Wastewater characteristics.

Parameter	Turbidity /NTU	Solid Suspension /(mg·L ⁻¹)	COD / (mg·L ⁻¹)	BOD ₅ /(mg·L ⁻¹)	Oil content /(mg·L ⁻¹)	pH
Value	268	2,804.4	9,603.8	897.1	553.3	8

Table 1 shows that the solid suspension content of the wastewater was high (2,804.4 mg·L⁻¹), and the large quantity of coke powders generated during heavy oil processing may be the major cause of the high solid suspension content. In this study, the coke powders sedimented and formed a black solid sedimentary layer during the wastewater setting process, as shown in Figures. 1(b) and (c).

In summary, the wastewater was a tight-emulsion with a high COD concentration (9,600.0 mg·L⁻¹). It contains suspended solids and oil (oil content, 553.0 mg·L⁻¹). According to a previous study^[2], the flocculation method can gather oil drops with particle sizes ranging from 100 nm to 2×10⁴ nm. Thus, PAC and PAM were used in the oil removal pre-treatment of the wastewater sample in the current study.

3.2. PAC/PAM-based flocculation as oil removal pre-treatment

In the oil removal of wastewater via flocculation, PAC and PAM are usually used simultaneously^[4,6]. Thus, the influences of the PAC and PAM dosages on the oil removal efficiency were studied, as shown in Figure 5.

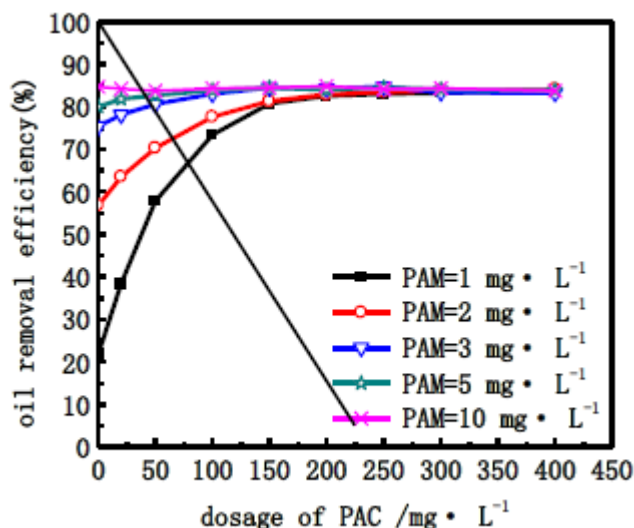


Figure 3. Influences of PAC and PAM Dosages on Oil Removal Efficiency.

(Other conditions: Temperature: 45 °C; pH: 8).

Figure 3 shows the variation trends when the PAC dosage was increased from 20 mg·L⁻¹ to 150 mg·L⁻¹. When the PAM dosages were 1, 2, 3, 5, and 10 mg·L⁻¹, the oil removal efficiency rapidly increased from 38.4% to 80.7%, rapidly increased from 63.5% to 81.3%, slowly increased from 78.1% to 84.5%, slowly increased from 81.8% to 84.5%, and fluctuated at 84%, respectively. These results indicated that when the PAC dosage was low (e.g., 20 mg·L⁻¹), the oil, which cannot be removed because of the insufficient PAC dosage, could be removed by PAM flocculation; thus, the oil removal efficiency increased as the PAM dosage increased. When the PAC dosage was sufficient (e.g., 200 mg·L⁻¹), PAM dosage had no influence on the oil removal efficiency. Similarly, when PAM dosage was insufficient, the oil removal efficiency increased as the PAC dosage increased. When the PAM dosage was sufficient (e.g., 10 mg·L⁻¹), the PAC dosage had no influence on the oil removal efficiency.

Therefore, the PAC and PAM dosages should be 150 mg·L⁻¹ and 3 mg·L⁻¹ to ensure high oil removal efficiency, good operating performance, and low slag production. Emulsified oil droplets were not easily destabilized due to their high stability, but had been significantly reduced when the first dosing of PAC. After the cationic organic flocculant was added, the oil droplets mixed slowly so that the cationic electricity can be better promoted to emulsify and the oil droplets were further destabilized. Thus, adding a small amount of cationic organic flocculants can significantly reduce the amount of inorganic flocculants, thereby saving drug costs.

3.3. Brief analysis of the flocculation schema of tight-emulsified petroleum wastewater

The experimental results presented in Section 2.4 showed that the oil removal efficiency was not high when PAC and PAM were used to treat the tight-emulsified petroleum wastewater in this study, with the maximum efficiency being only 84.5%. The emulsified wastewater collected from a union station of Shengli Oil Field and treated by Zhang^[5] is tight-emulsified petroleum wastewater because Shengli Oil Field exploitation had entered the tertiary oil recovery phase. During this phase, substantial amounts of chemical reagents, such as surfactants, are used to remove oil during the recovery process. Consequently, the contribution of oil content in wastewater to the COD was minimal in the study of Zhang^[3], that is, only 16.9%, which is similar to the result obtained in the current study. The

emulsified biodiesel (whose raw material is palm oil) wastewater treated by Daud^[10] is not tight-emulsified oil-containing wastewater because the variety and quantity of the surfactants (mainly being fatty acid salt) during biodiesel production are low and a high shear force or the formation conditions for tight-emulsion are absent. The oil content was the main source of the COD in the wastewater treated by Daud^[10] (if the oil content and COD were $2,680 \text{ mg}\cdot\text{L}^{-1}$ and $5,900 \text{ mg}\cdot\text{L}^{-1}$, respectively, then the contribution of oil to COD value was 136%); as a result, the oil removal efficiency of the PAC flocculation could reach as high as 97%. The emulsified thickened oil wastewater treated by Zeng^[7] could also not be considered tight-emulsified petroleum wastewater; its oil content was the main source of the COD (oil content, $400\text{--}1,000 \text{ mg}\cdot\text{L}^{-1}$; COD, $500\text{--}1,000 \text{ mg}\cdot\text{L}^{-1}$), and the oil removal efficiency with PAC/PAM flocculation reached 95%.

A comparison of these results necessitates an investigation as to why the oil removal efficiency of the flocculation of tight-emulsified petroleum wastewater is not as high as that of the flocculation of ordinary emulsified wastewater. Thus, the PAC and/or PAM were added respectively to deionized water and the tight-emulsified petroleum wastewater to flocculate, the particle size analysis was carried out with the Master2000 laser particle size analyzer for the preliminary analysis of the reasons for the relatively low oil removal efficiency of the flocculation of tight-emulsified petroleum wastewater.

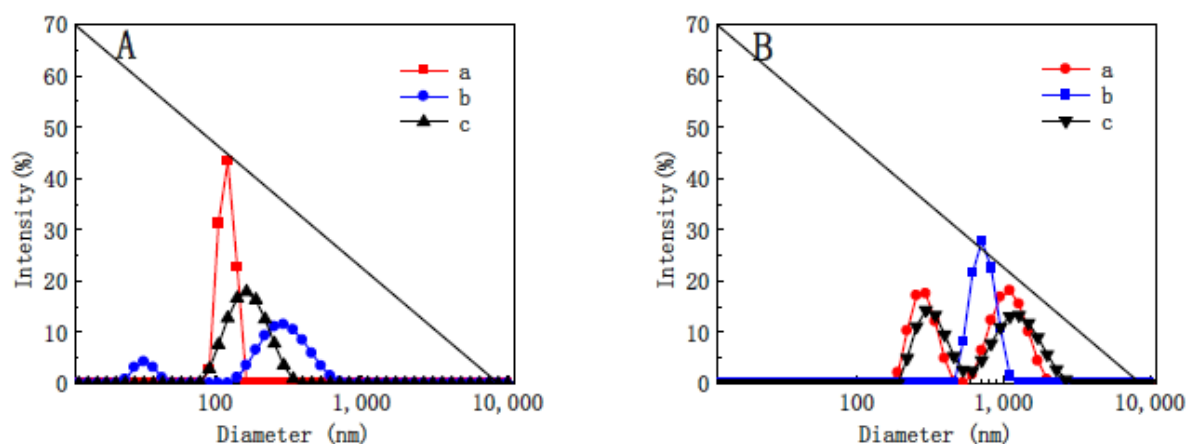


Figure 4. Particle size distribution in the supernatant after flocculation.

(the supernatant was diluted with 10 times, Mechanical stirring at the speed of $950 \text{ r}\cdot\text{min}^{-1}$, the circulating pump speed is $2400 \text{ r}\cdot\text{min}^{-1}$, and then was centrifuged).

A—Pure water system; B—Tight-emulsified petroleum wastewater system.

a: PAC dosage, $200 \text{ mg}\cdot\text{L}^{-1}$; temperature, 40°C ; pH, 7.5; setting time, 20 min.

b: PAM dosage, $10 \text{ mg}\cdot\text{L}^{-1}$; temperature, 45°C ; pH, 8; setting time, 20 min.

c: PAC dosage, $150 \text{ mg}\cdot\text{L}^{-1}$; PAM dosage, $3 \text{ mg}\cdot\text{L}^{-1}$; temperature, 45°C ; pH, 8; setting time, 20 min.

Figure 4 shows the particle size distribution in the supernatant layer after flocculation. Figure 4A shows that when PAC was added to deionized water, floc particles appeared in the supernatant layer, and their size distribution peaked at 120 nm. When PAM was added, the size distribution of the flocs in the supernatant liquid presented two peaks at 30 nm and 300 nm. When PAC and PAM were simultaneously used, the floc particles in the supernatant layer exhibited a single-peak distribution, and its peak position was 160 nm. These results indicated that the floc density was high, and only small (particle size, 300nm) PAC floc particles existed in the supernatant layer because PAC is an inorganic agent. By contrast, PAM is an organic matter; thus, the floc density was low, and the PAM floc particles were large (particle size, 300 nm) in the supernatant layer. In summary, both PAC and PAM generated small alum flocs that do not easily sediment in water. All the floc particles exhibited

sizes smaller than several hundreds of nanometers, whereas the sizes of large floc particles that can rapidly sediment were larger than 1×10^4 nm.

Figure 4B shows that when PAC flocculation was used to treat the tight-emulsified petroleum wastewater, the particle size distribution in the supernatant liquid presented two peaks at 270 nm and 1,100 nm. When PAM flocculation was used, the particle sizes exhibited a single-peak distribution, whose peak position was 700 nm. When PAC and PAM were simultaneously used, the particle size distribution presented two peaks at 300 nm and 1,200 nm. These results indicated that small oil-containing alum flocs could exist in the supernatant liquid resulting from wastewater flocculation.

It can be found from Figure 4 that the flocs are very small, and the particle size of the flocs is the most basic unit of the flocs, the particle size of the microflocs. This indicates that there is no more complex bonding effect in the process of processing, and mainly the adsorption energy of the weak electrostatic adsorption. As can be seen from Figure 4, the PAC+PAM has a larger particle size than PAC after handling the same water sample. This is because the PAC can act as an electrically neutral, compressed double layer and a certain net trap when it is added to the PAC, resulting in a small and loose flocculation and slow deposition rate. And PAC + PAM, not only on the surface of positive charge, electrostatic adhesion ability enhancement, and volume of hydrolyzate and branches also increase, the ability of adsorption bridging improvement, coupled with large floc sedimentation in the process of sweep, significantly improve the treatment effect.

The bonding between the oil particles and floc particles was assumed planar to simplify the descriptions. If two 90 nm oil particles bonded with two 120 nm PAC floc particles, then oil-containing flocs with particle sizes of approximately 295 nm would be formed. These sizes are approximate to the value of the first peak in Figure4B (a) (i.e., 270 nm). If four 440 nm oil particles bonded with 120 nm PAC floc particles, then oil-containing alum flocs with particle sizes of approximately 960 nm would be formed. These sizes are approximate to the value of the second peak in Figure4B(a) (i.e., 1,100 nm). Furthermore, if four 440 nm oil particles bonded with five 30 nm PAM floc particles, then oil-containing alum flocs with particle sizes of approximately 710 nm would be formed. These sizes are approximate to the value of the peak of the particle size distribution in Figure4B(b) (i.e., 700 nm). Similarly, if two 90 nm oil particles bonded with two 160 nm small PAM/PAC alum flocs, then oil-containing alum flocs with particle sizes of approximately 350 nm would be formed. These sizes are approximate to the value of the first peak in Figure4B(c) (i.e., 300 nm). If four 440 nm oil particles bonded with five 160 nm PAM/PAC alum flocs, then oil-containing alum flocs with particle sizes of approximately 1,075 nm would be formed. These sizes are approximate to the value of the second peak in Figure4B(c) (i.e., 1,200 nm). Therefore, if the oil-containing alum flocs formed from the bonding of tight-emulsified oil particles and small floc particles were sufficiently small, then the oil-containing flocs can neither sediment nor separate within a limited time. Consequently, these oil particles cannot be removed by the flocculation method. This phenomenon could be main cause of the relatively low oil removal efficiency of the flocculation method in treating tight-emulsified petroleum wastewater.

4. Conclusions

The water quality analysis results indicate that petroleum wastewater in a petrochemical plant is high-concentration (COD, $9,600.0 \text{ mg} \cdot \text{L}^{-1}$) tight-emulsified wastewater with suspended solids and oil ($553.0 \text{ mg} \cdot \text{L}^{-1}$).

Tight-emulsified petroleum wastewater can be pre-treated for oil removal by the flocculation method, and the influence laws of the different operating parameters on the oil removal efficiency are similar to those in the flocculation-based pre-treatment of ordinary emulsified wastewater. However, the aggregation of small alum flocs and tight-emulsified oil particles can form oil-containing alum flocs smaller than several hundreds or thousands of nanometers. Due to the poor sedimentation of these flocs, the degreasing efficiency of tight-emulsified oily wastewater treated by PAC and PAM is lower than that of ordinary emulsion.

Acknowledgments

This study was supported by the Science and Technology Program Project of Zhejiang Province (2016C33031), the Zhoushan City Science and Technology Program Project of Zhejiang Province (2015C41017), and the Dinghai District Science and Technology Program Project of Zhejiang Province.

References

- [1] Jamaly S, Giwa A & Hasan S W 2015. Recent improvements in oily wastewater treatment: progress, challenges, and future opportunities. *J Environ Sci (English version)*. **37**: 15- 30.
- [2] Pintor A M A, Vilar V J P, Botelho C M S, & Rui A R B 2016. Oil and grease removal from wastewaters: sorption treatment as an alternative to state-of-the-art technologies. *Chemical Engineering Journal*. **297**: 229-255.
- [3] Zhang Y, Gao B, Lu L, Yue Q, Wang Q, & Jia Y 2010. Treatment of produced water from polymer flooding in oil production by the combined method of hydrolysis acidification-dynamic membrane bioreactor-coagulation process. *Journal of Petroleum Science & Engineering*. **74**: 14-19.
- [4] Chai S L, Robinson J & Mei F C 2014. A review on application of flocculants in wastewater treatment. *Process Safety & Environmental Protection*. **92**: 489-508.
- [5] Otitoju T A, Ahmad, A L, & Ooi, B S 2016. Polyvinylidene fluoride (pvdf) membrane for oil rejection from oily wastewater. *Journal of Water Process Engineering*. **14**:41-59.
- [6] Santo C E, Vilar V J P, Botelho C M S, Bhatnagar A, Kumar E & Boaventura R A R 2012. Optimization of coagulation–flocculation and flotation parameters for the treatment of a petroleum refinery effluent from a portuguese plant. *Chemical Engineering Journal*. **183**: 117-123.
- [7] Zeng Y, Yang C, Zhang J & Pu W 2007. Feasibility investigation of oily wastewater treatment by combination of zinc and pam in coagulation/flocculation. *Journal of Hazardous Material*. **147**: 991-996.
- [8] Lee K E, Morad N, Teng T T & Poh B T 2012. Development, characterization and the application of hybrid materials in coagulation/flocculation of wastewater: a review. *Chemical Engineering Journal*. **203**: 370-386.
- [9] Gao R, Li F, Li Y & Wu T 2017. Effective removal of emulsified oil from oily wastewater using in-situ generated metallic hydroxides from leaching solution of white mud. *Chemical Engineering Journal*. **309**: 513-521.
- [10] Daud Z, Awang H, Latif A A A, Nasir N, Ridzuan M B, & Ahmad Z 2015. Suspended solid, color, cod and oil and grease removal from biodiesel wastewater by coagulation and flocculation processes. *Procedia - Social and Behavioral Sciences*. **195**:2407-2411.
- [11] The State Environmental Protection Administration 2002. Water and wastewater monitoring and analysis method. Fourth Edition. *Beijing: Environmental Science Press Journal of Polymer Science Part A Polymer Chemistry(in Chinese)*.
- [12] Malvern instrument Corporation.LTD 1999. Laser particle size analyzer Mastersize 2000 operating manual.
- [13] Ugelstad J, El-Aasser M S & Vanderhoff J W 1973. Emulsion polymerization: initiation of polymerization in monomer droplets. *Journal of Polymer Science Part C Polymer Letters*. **11**: 503-513.
- [14] Schmitt V, Cattelet C, & Lealcalderson F 2004. Coarsening of alkane-in-water emulsions stabilized by nonionic poly(oxyethylene) surfactants: the role of molecular permeation and coalescence. *Langmuir the Acs Journal of Surfaces & Colloids*. **20**: 46-52.
- [15] Lin C T, Wu J M & Chern C S 2013. Effects of the molecular weight of polymeric costabilizers on the ostwald ripening behavior and the polymerization kinetics of styrene miniemulsions. *Colloids & Surfaces A Physicochemical & Engineering Aspects*. **434**:178-184.

- [16] Chen C, Guo J, An N, Ren B, Li Y & Jiang Q 2013. Study of asphaltene deposition from tahe crude oil. *Petroleum Science*. **10**: 134-138.
- [17] Zolfaghari R, Fakhru'L-Razi A, Abdullah L C, Elnashaie S S E H & Pendashteh A 2016. Demulsification techniques of water-in-oil and oil-in-water emulsions in petroleum industry. *Separation & Purification Technology*. **170**: 377-407.