The flocculation mechanism and treatment of oily wastewater by flocculation

Zhenchao Zhang

ABSTRACT

In the present study, the performance of compound flocculants composed of different concentrations of polyaluminum chloride (PAC) and cationic polyacrylamide (CPAM), the influencing mechanism of the flocculation process and the effects of temperature, settling time, and speed and time of stirring were investigated. The results show that the poor water quality with high concentrations of oil, suspended solids (SS) and polymer greatly increases the oily wastewater emulsion stability and the difficulty of the flocculation treatment process. The compound flocculant in oily wastewater treatment can achieve best results at optimum conditions of temperature 45 °C, settling time 60 min, and two stirring stages, 250 $r{\cdot}min^{-1}$ for 3 min followed by 100 $r{\cdot}min^{-1}$ for 7 min. At the PAC dosage of 80 $mg{\cdot}L^{-1}$ and the CPAM dosage of 0.8 $mg{\cdot}L^{-1}$, the turbidity of oily wastewater is reduced from 153.8 NTU to 11.2 NTU, and the turbidity removal rate reaches 92.69%. Through further measurements, oil content and SS content are less than 10 $mg{\cdot}L^{-1}$, which meets the requirement of the Daqing oilfield re-injection standard.

Key words | compound flocculants, flocculation, mechanism analysis, oily wastewater

Zhenchao Zhang
College of Chemistry and Chemical Engineering,
Northeast Petroleum University,
Daqing 163318,
China
E-mail: *891775276@qq.com*;
grayhelmet@foxmail.com

INTRODUCTION

With the application of tertiary oil recovery, petroleum exploitation generates large volumes of wastewater, especially oily wastewater containing large quantities of polymers (mainly hydrolyzed polyacrylamide, HPAM), crude oil, and suspended solids (SS). The produced wastewater needs to be further treated before being re-injected into the stratum again for reuse. The presence of polymers can significantly increase the viscosity of the wastewater and stabilize oil–water emulsions, leading to great difficulties in the flocculation process and the subsequent treatment (Lu & Wei 2011). The high concentrations of oil and SS require the dosages of flocculants to be increased significantly. These conditions lead to increased stability of oily wastewater, making subsequent treatment more difficult. Thus, oily wastewater treatment has become an urgent concern. Oily wastewater is usually treated by gravity sedimentation (Deng *et al.* 2002), coagulation (Verma *et al.* 2010; Birjandi *et al.* 2013; López-Maldonado *et al.* 2014), flotation (Suarez *et al.* 2009; Maruyama *et al.* 2012), coagulation composite flotation (Santo *et al.* 2012), demulsification (Kishi *et al.* 2005; Martínez-Palou *et al.* 2013), membrane separation (Zhong *et al.* 2003; Masuelli *et al.* 2009; Liang *et al.* 2014), flocculation treatment (Gao *et al.* 2010; Lee *et al.* 2010; Gao *et al.* 2011; Kang *et al.* 2012; Wen *et al.* 2015), and biotechnology (Huang *et al.* 2009; Yu *et al.* 2013).

Flocculation is one of the most effective methods of oilfield wastewater treatment. It is a physical–chemical treatment process that uses continuously recycled media and a variety of additives to improve the settling properties of SSs through improved floc bridging (Borchate *et al.* 2014). Flocculation is employed for the treatment of high-phosphorus hematite flotation wastewater with a mixture of ferric chloride, poly-aluminum chloride (PAC), and polyacrylamide (PAM) and achieved high turbidity removal efficiency (Yang *et al.* 2010). Flocculants neutralize the repulsive electrical charges surrounding particles, causing them to stick together, creating flocs (Borchate *et al.* 2014). Pulp mill wastewater was treated by using coagulation/flocculation with aluminum chloride and starch-g-PAM-g-PDMC (Wang *et al.* 2011a, 2011b). Flocculation for oily wastewater serves to increase floc formation and settling velocity and

doi: 10.2166/wst.2017.414

facilitate the agglomeration of the coagulated particles to form larger flocs and thereby hasten gravitational settling (Sarkar *et al.* 2006). A high-flocculation composite flocculant was prepared by sodium alginate, polyaluminum ferric chloride, and cationic polyacrylamide (CPAM); the dosage of the composite flocculant was 20 $mg \cdot L^{-1}$, and the removal efficiency of chemical oxygen demand and turbidity reached 89.6% and 99.2%, respectively (Zeng *et al.* 2011). The efficiency of organic–inorganic compound flocculants for oily wastewater has been confirmed by many studies. A great variety of flocculants are used for oily wastewater, including Al-Fe-Mg composite flocculants (Li *et al.* 2015), polymer flocculant (Lu *et al.* 2016), biological modified flocculants (Liu *et al.* 2014), PAM and PAC. Flocs sizes were larger in the presence of anionic PAMs than cationic PAMs because of repulsive forces between the anionic PAM and particle surface, which lead to the formation of open structures for flocs (Nasser *et al.* 2013). The concentrations of multivalent cations in pellets are important indicators for activating sludge flocculability. Multivalent (especially trivalent) cations have greater binding ability (Li *et al.* 2014).

In this work, a series of experiments were conducted to study the efficiency of composite flocculants and the influential factors for the treatment of oily wastewater from Daqing oilfield, China. According to changes of turbidity and its removal rate, the optimum conditions for oily wastewater treatment were obtained to provide theoretical guidance for the optimization and modification of wastewater treatment technology. In addition, the mechanism of the flocculation process is described and analyzed.

EXPERIMENT

Materials

PAC (industrial grade) and CPAM (industrial grade) were obtained from Daqing oilfield.

Wastewater samples

Oily water was collected from the Daqing oilfield. Table 1 compares the characteristics of the oily wastewater from Daqing oilfield and Liaohe oilfield. It is obvious that the oily wastewater from Daqing oilfield has a worse water quality.

Instruments and analytic methods

The pH was measured by a precision acidity meter (PHS-3C, Shanghai Leici Precision Instrument Co. Ltd, China).

A Brookfield rotational viscometer (DV-II + pro, Brookfield Company, USA) was employed to measure the oily wastewater viscosity.

The conductivity of oily wastewater was measured by a digital conductivity meter (DDS-11A, Shanghai Leici Precision Instrument Co. Ltd, China).

The zeta potential measurement was performed on a Zetaplus zeta apparatus (Brookhaven Company, USA).

UV spectrophotometry (SL93.2-1994) was used to measure the oil contents of samples at an optimum absorption wavelength of 430 nm. Oil content was then obtained

Table 1 | The characteristics of the oily wastewater from Daqing oilfield and Liaohe oilfield

Item	Sample from Daqing oilfield	Sample from Liaohe oilfield
pH	7.3–8.1	7.8–8.0
Appearance	Dark yellow	Light yellow
Density (293 K) ($g \cdot cm^{-3}$)	0.991	0.997
Viscosity (293 K) (mPa·s)	3.92	1.93
Conductivity ($S \cdot cm^{-1}$)	1.181	0.892
Interfacial tension ($mN \cdot m^{-1}$)	75.4	51.6
Zeta potential (mV)	−88.9	−53.2
Oil concentration ($mg \cdot L^{-1}$)	628.3	393.6
Size of oil droplets (μm)	3.6	6.8
SS concentration ($mg \cdot L^{-1}$)	320.8	195.6
Polymer concentration ($mg \cdot L^{-1}$)	389	282
Polymer type	HPAM, original molecular weight 2.8×10^7	HPAM, original molecular weight 2.2×10^7
Polymer molecular weight	8.0×10^6	8.0×10^5

according to

$$A = 0.00289 \times C - 0.00823$$

where A is absorbency and C is the oil content ranging from 0 mg·L^{-1} to 100 mg L^{-1}.

A high definition digital biological microscope (YYS-100, Shanghai Yiyuan Optical Instrument Co., Ltd, China) was used to observe oil droplets in the wastewater, and the size and distribution of oil droplets were calculated.

SS concentrations were determined by filtering a known volume of water on a pre-weighed and pre-combusted (450 °C for 30 min) glass fibre filter. After filtration, the filters were dried at 60 °C for 2 days and weighed again.

The HPAM concentration was measured by starch-CdI_2 spectrophotometry, wherein the Cl^- interference was eliminated by adjusting the wastewater pH to 3.5 with 0.1 M H_2SO_4, and the influence of Fe^{3+} was eliminated by maintaining a constant excess of Al^{3+} in the solution (Lu *et al.* 2012).

The turbidity was determined by using a turbidity meter (WGZ-2000, Shanghai Leici Precision Instrument Co. Ltd, China).

A full automatic surface/interface tensiometer (JK99B, Shanghai Zhong Chen Corp., China) was employed to measure the oily wastewater interfacial tension by the ring method (ISO 6295-1983).

The transmission electron microscopy (TEM) of micro-organism flocs was carried out by a 100 kV electron microscope (JEM-1400, Japan). Microstructures were examined in the TEM using bright-field and selected area electron diffraction crystallographic analysis.

A laser particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd, UK) was used to determine the particle size and the distribution of the SS and flocs.

Flocculation experiments

The compound flocculants were composed of different concentrations of PAC and CPAM. A certain amount of PAC and CPAM was dissolved into distilled water, respectively. The reaction container was a beaker equipped with stirring; oily wastewater after preheating was added into the beaker. PAC was added into the beaker and then CPAM was added after 1 min. The process of stirring had two stages. First was the rapid mixing stage, lasting 5 min at the speed of 250 r·min^{-1}. The second was the reaction stage, lasting 5–10 min at the speed of 60 r·min^{-1}. Then the mixtures were transferred into a water bath set at 45 °C, and allowed to settle for 2 h. At the end of the settling period, the supernatant was taken from the beaker and the flocs were taken from the bottom of the beaker. Oil content and SS in the oily wastewater, as well as droplet distributions, zeta potential and interfacial tension, were measured. And then repeated extractions were performed for flocs by petroleum ether until the oil in flocs was removed entirely. In order to get more accuracy of the experiment results, all experiments in this study were performed in quintuplicate, and the results are reported as the mean values of five parallel experiments.

RESULTS AND DISCUSSION

Effect of flocculants

For comparison, PAC or CPAM was added to the oily wastewater as the only flocculant as a conventional flocculation. Figure 1 shows the effect of PAC and CPAM dosage on the removal rate of turbidity respectively. When PAC dosage was below 80 mg·L^{-1}, the removal rate of turbidity increased with the increase of PAC dosage. But when the PAC dosage was higher than 80 mg·L^{-1}, the removal rate of turbidity slightly decreased. Thus, the optimum dosage was 80 mg·L^{-1}, in which the removal rate reached 66.51%. The employment of CPAM results in a trend similar to that of PAC for oily wastewater, although the augmentation amplitude is lower than that. When CPAM dosage was 0.8 mg·L^{-1}, turbidity removal rate reached 56.42%, which was higher than for the other dosages.

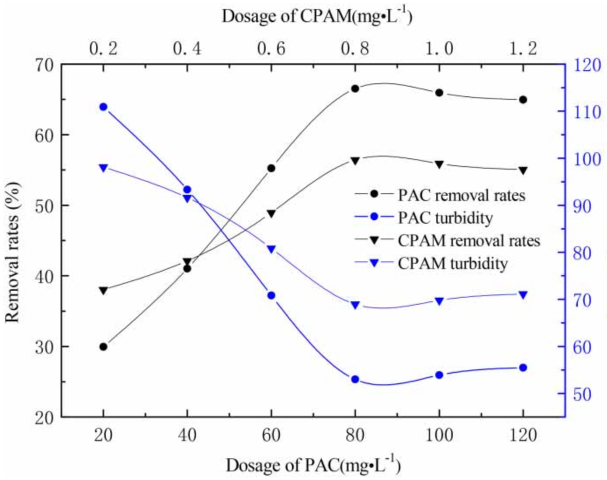

Figure 1 | Variation of the turbidity and removal rates with the dosage of PAC and CPAM respectively.

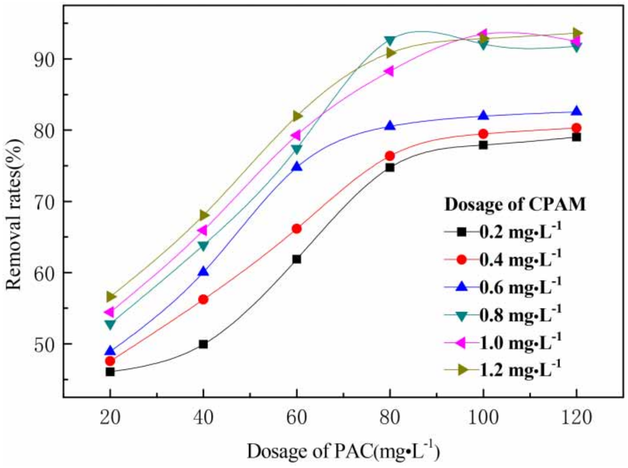

Figure 2 | Variation of the turbidity with the dosage of compound flocculants.

Figure 2 show the turbidity removal rate with different dosage of compound flocculants, composed of PAC and CPAM. It can be seen that as the dosages of compound flocculant increased, the removal rate increased. However, note that there was no remarkable change of removal rate with higher dosages of compound flocculant; at higher dosage of flocculants the degree of flocculation decreased as the particles may be completely covered by the absorbed polymer layer. At the PAC dosage of 80 mg·L^{-1} and the CPAM dosage of 0.8 mg·L^{-1}, the removal rate of turbidity reached 92.69%. Comparing with the conventional flocculation with PAC or CPAM only, the use of the two mixed coagulants in oily wastewater treatment can achieve better result.

Effect of temperature

The effect of temperature on turbidity removal rate is shown in Figure 3. When temperature is lower than 45 °C, the removal rate of turbidity increased with the increase of temperature. But when the temperature is higher than 45 °C, the removal rate of turbidity slightly decreased. In the temperature range of 45 to 65 °C, the removal rate decreased from 88.02% to 84.23%. During the range of temperature, particles moved too fast in the reaction system, resulting in the formation of flocs with a smaller size, and inducing hydration. The optimum temperature of 45 °C was shown to remove SS and oil from oily wastewater, achieving a turbidity removal rate of 88.02%. When the temperature is lower than about 15 °C, the contact time for flocculation is increased because of the formation of flocs, resisting velocity and Brownian forces in the oily wastewater.

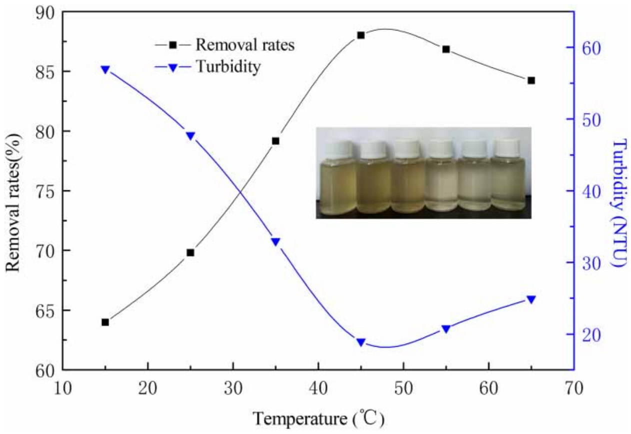

Figure 3 | Variation of the turbidity and removal rates with the temperature.

Effect of stirring time and speed

The process of stirring was divided into two stages after adding the compound flocculants. The first was the mixing stage, and the second was the reaction stage. During the first stage, the speed of particle collision increased excessively with strong stirring. Floc formation, between flocculants and SS was suppressed in oily wastewater. However, stirring with slower speed would result in inadequate reactions between flocculants and SS. Also, during the second stage, stirring that was too fast caused lighter and smaller flocs to form and grow unreasonably. Stirring slowly in this stage could lead to less adsorption efficiency. A recent study (Zhou *et al.* 2016) illustrated that the first stage was the mixing rapidly, lasting 5 min with stirring speed of 200 r·min^{-1}, and second was the reaction stage, lasting 5–10 min with 30 r·min^{-1}.

The relationship between removal rates and different combinations of fast and slow stirring speed was investigated by design of an orthogonal experiment, in which the dosage of flocculants was 0.1 g·L^{-1} at 45 °C. The results are shown in Figure 4(a). When fast stirring speed is 250 r·min^{-1} and slow stirring speed is 100 r·min^{-1}, turbidity removal rate reached 90.96%, which was higher than for the other combinations.

The effect of different combinations of fast and slow stirring time on turbidity removal rates was investigated by design of an orthogonal experiment, in which the dosage of flocculants was 0.1 g·L^{-1} at 45 °C. As is shown in Figure 4(b), it can be concluded that fast stirring lasting 3 min combined with slow stirring for 7 min made the removal rates achieve 91%.

Effect of settling time

The relationship between removal rates and settling (or sedimentation) time was investigated; results are shown in

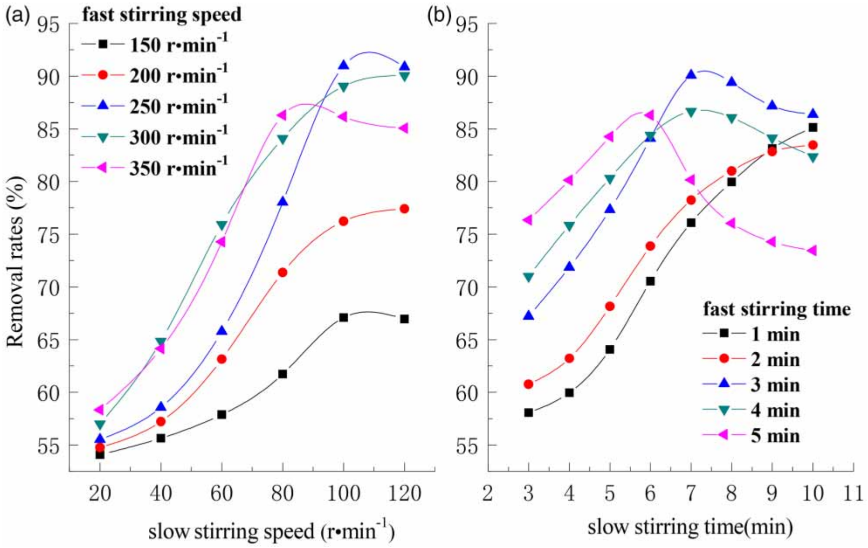

Figure 4 | Variation of the turbidity with two stages of (a) stirring speed and (b) time.

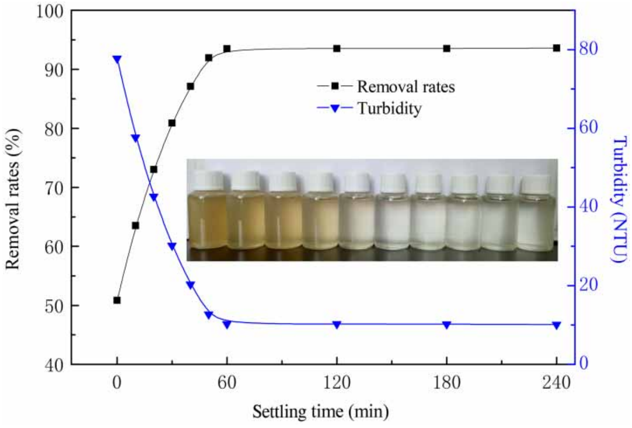

Figure 5 | Variation of the turbidity and removal rate with the settling time.

Figure 5. When settling time is lower than 60 min, settling time shows a remarkable effect on the removal rate of turbidity. With the increasing of settling time from 0 to 60 min, the removal rate of turbidity was increased from 50.87% (0 min) to 93.49% (60 min). When the settling time increased beyond 60 min, the removal rate of turbidity would not change obviously.

MECHANISM ANALYSIS

Mechanism of flocculant effect on the flocculation efficiency

PAC is used as inorganic polymer flocculant; its molecular formula is $[Al_2(OH)_nCl_{6-n}]_m$, and it can produce Al-polyhydric complexes, such as $[Al_6(OH)_{14}]^{4+}$, $[Al_7(OH)_{17}]^{4+}$, and $[Al_8(OH)_{20}]^{4+}$ (Yang *et al.* 2009). These complexes have a large net structure and can sweep flocs in the flocculation process. Additionally, PAC can form positively charged complex compounds through hydrolyzation, which diffuses to the oil–water interface and are characteristically absorbed onto the double layer at the oil–water interface (Guo *et al.* 2013). These adsorbed complex compounds can neutralize some of the negative charges on the oil–water interface.

CPAM is a cationic flocculant that can neutralize negative charge of oil drops and lower zeta potential and electric double-layer thickness, reducing the repulsion between the oil drops and destroying their stability. Mainly, the applications of PAM include treatment of natural water, wastewater, and ore flotation tailings. The molecular formula of CPAM is C_3H_5NO. The major consideration for wide use of CPAM is high formation efficiency of a high molecular mass polymer. Also, CPAM has proved to be nontoxic for humans, animals and plants (Choi *et al.* 2005). The effects of polymer molecular weight on flocculation are best described in terms of bridging and electrostatic patch character mechanisms, which help the resulting flocs to become larger, allow their aggregation with each other (Borchate *et al.* 2014).

With the combined use of PAC and CPAM, more positive charges are integrated into the floc hydroxide, which is capable of electrostatic adhesion. Therefore, colloidal particles can be quickly precipitated because of their adhesion to these net structures. In addition, PAC is an inorganic flocculant that can produce a complementary effect of flocculation when used with organic flocculants. Thus, comparing with the conventional flocculation with PAC or

CPAM only, the compound flocculant exhibits good effects with reduced dosage and has reduced corrosion effects on equipment (Zhao *et al.* 2008). The description of the compound flocculation mechanism is presented in Figure 6.

Mechanism of temperature effect on the flocculation efficiency

The settling velocity of water droplets may be raised by heating the water and surrounding oil, which reduces both the oil–water interfacial tension and viscosity of the oil (Binner *et al.* 2014). So the temperature directly influences wastewater treatment. When the temperature was lower than about 15 °C, the contact time for flocculation was increased because of the formation of flocs, resisting velocity and Brownian forces in the oily wastewater. However, at the higher temperature of flocculation, particles moved too fast in the reaction system, resulting in the formation of flocs with a smaller size, and inducing hydration. Thus, a moderate temperature of 45 °C achieves the best treatment result.

Mechanism of stirring effect on the flocculation efficiency

According to the experiment of the flocculation process, it was observed that the added flocculation spread through the oily wastewater under rapid stirring. During this stage, a hydrolysis reaction occurred between flocculants and oil droplets, and suspension particles on destabilization formed colloidal particles that aggregated to produce micro-flocs, and stirring with slower speed would result in inadequate reactions. In the second stage with slower stirring, the micro-flocs grew further, forming larger and denser particles. The particles on destabilization began to aggregate, indicating that the flocs grew and formed larger and looser flow-like flocs, and stirring that was too fast caused lighter and smaller flocs to form and grow unreasonably. Flocculants facilitate the agglomeration of the colloidal particles to form larger floccules and thereby hasten gravitational settling.

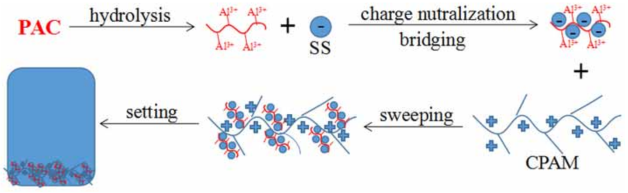

Figure 6 | Mechanism of compound flocculation.

Mechanism of gravitational settling effect on the flocculation efficiency

With increased settling time, the turbidity removal rate increased remarkably and then became nearly constant. In flocculation process that the oil droplets and SS attach to the flocs formed by flocculants and then form large flocs from small ones, which need a longer time to settle. Thus, 90 min was determined as the optimal settling time.

Mechanism of water quality effect on the flocculation efficiency

The characteristics of the oily wastewater from Daqing oilfield are shown in Table 1 and in Figure 7. Oily wastewater usually has a poor water quality with high concentrations of oil, SS and polymer. In addition, the zeta potential of oily wastewater is relatively high. The magnitude of zeta potential gives an indication of the potential stability of an emulsion system. A higher zeta potential indicates a stronger electrostatic repulsive force between particles and thus better dispersion stability of the emulsion solution (Wang *et al.* 2011a, 2011b).

The SS had a high zeta potential and small particle size. Small particle sizes can be absorbed on the oil–water interface and increase the oil–water interfacial strength and the high zeta potential, which greatly enhances the oil-in-water emulsion stability (Spinelli *et al.* 2007).

It is reported that the adsorption of polymer on oil droplets can increase the density of negative electric charge on the surface of oil droplets (Zhang *et al.* 2006). Additionally, the high stability of these polymer-contained oily

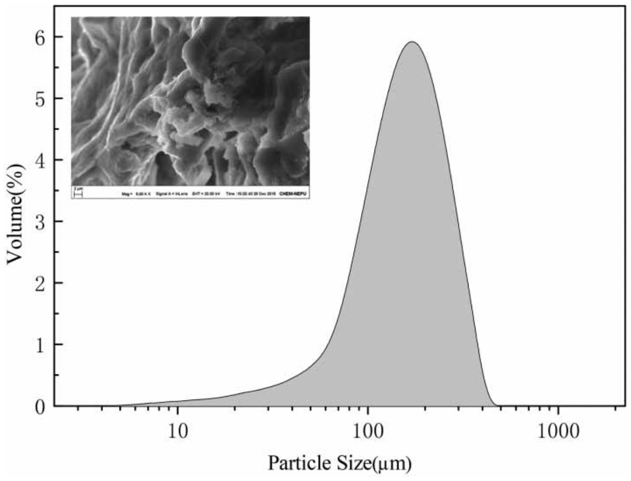

Figure 7 | Size and size distribution of SS flocs.

wastewaters is based on both an associative thickening mechanism caused by the alkyl chains of polymer molecules and the adsorption of polymer at the oil–water interface, which can form a solid film to prevent the Ostwald ripening of emulsion droplets (Yang *et al.* 2014).

CONCLUSION

The results of the present study demonstrate that the integration of an effective flocculation process and appropriate flocculants is a promising and efficient approach for polymer-contained oily wastewater treatment. In this paper, the effect of dosage of flocculants, temperature, stirring time and speed, and settling time are investigated for optimizing the parameters of the flocculation process. Together with the analysis of the flocculation process, the flocculation influence mechanisms have been discussed. The compound flocculant (PAC and CPAM) neutralized charge, bridged and swept flocs, and reduced the turbidity of oily wastewater. High concentrations of oil, SS and polymer greatly increases the oily wastewater emulsion stability and the difficulty of the treatment process. Optimal experimental conditions were determined as follows: PAC dosage of 80 mg·L^{-1} and CPAM dosage of 0. 8 mg·L^{-1}, settling temperature of 45 °C, settling time of 60 min and two stirring stages, 250 r·min^{-1} for 3 min followed by 100 r·min^{-1} for 7 min. Under these conditions, the turbidity of oily wastewater was reduced from 153.8 NTU to 11.2 NTU, and the turbidity removal rate reached 92.69%, which meets the requirement of the Daqing oilfield re-injection standard.

REFERENCES

Binner, E. R., Robinson, J. P., Silvester, S. A. & Lester, E. H. 2014 Investigation into the mechanisms by which microwave heating enhances separation of water-in-oil emulsions. *Fuel* **116** (1), 516–521.

Birjandi, N., Younesi, H., Bahramifar, N., Ghafari, S., Zinatizadeh, A. A. & Sethupathi, S. 2013 Optimization of coagulation-flocculation treatment on paper-recycling wastewater: application of response surface methodology. *Journal of Environmental Science & Health Part A Toxic/Hazardous Substances & Environmental Engineering* **48** (12), 1573–1582.

Borchate, S. S., Kullkarni, G. S., Kore, V. S. & Kore, S. V. 2014 A review on applications of coagulation-flocculation and ballast flocculation for water and wastewater. *International Journal of Innovations in Engineering and Technology* **4** (4), 216–222.

Choi, K., Kimmerer, W., Smith, G., Ruiz, G. & Lion, K. 2005 Post-exchange zooplankton in ballast water of ships entering the San Francisco Estuary. *Journal of Plankton Research* **27** (7), 707–714.

Deng, S., Bai, R., Chen, J. P., Jiang, Z., Yu, G., Zhou, F. & Chen, Z. 2002 Produced water from polymer flooding process in crude oil extraction: characterization and treatment by a novel crossflow oil–water separator. *Separation & Purification Technology* **29** (3), 207–216.

Gao, B. Y., Wang, Y. & Yue, Q. Y. 2010 The chemical species distribution of aluminum in composite flocculants prepared from polyaluminum chloride (PAC) and polydimethyldiallylammonium chloride (PDMDAAC). *CLEAN: Soil, Air, Water* **33** (4), 365–371.

Gao, B., Jia, Y., Zhang, Y., Li, Q. & Yue, Q. 2011 Performance of dithiocarbamate-type flocculant in treating simulated polymer flooding produced water. *Journal of Environmental Sciences* **23** (1), 37–43.

Guo, J., Cao, J., Li, M. & Xia, H. 2013 Influences of water treatment agents on oil-water interfacial properties of oilfield produced water. *Petroleum Science* **10** (3), 415–420.

Huang, X., Liu, J., Lu, L., Wen, Y., Xu, J. C. & Yang, D. H. 2009 Evaluation of screening methods for demulsifying bacteria and characterization of lipopeptide bio-demulsifier produced by *Alcaligenes* sp. *Bioresource Technology* **100** (3), 1358–1365.

Kang, W., Guo, L., Fan, H., Meng, L. & Li, Y. 2012 Flocculation, coalescence and migration of dispersed phase droplets and oil–water separation in heavy oil emulsion. *Journal of Petroleum Science & Engineering* **81** (1), 177–181.

Kishi, R., Sata, F., Yoshioka, E., Ban, S., Sasaki, S. & Konishi, K. 2005 Treatment of waste filature oil/water emulsion by combined demulsification and reverse osmosis. *Separation & Purification Technology* **63** (2), 264–268.

Lee, K. E., Teng, T. T., Morad, N., Poh, B. T. & Hong, Y. F. 2010 Flocculation of kaolin in water using novel calcium chloride-polyacrylamide ($CaCl_2$-PAM) hybrid polymer. *Separation and Purification Technology* **75** (3), 346–351.

Li, H., Wen, Y., Cao, A., Huang, J. & Zhou, Q. 2014 The influence of multivalent cations on the flocculation of activated sludge with different sludge retention times. *Water Research* **55** (2), 225–232.

Li, S., Yang, S., Yi, P. & Zhang, J. H. 2015 Preparation of aluminum-ferric-magnesium polysilicate and its application on oily sludge. *Journal of the Serbian Chemical Society* **80**, 57–57.

Liang, C. Z., Sun, S. P., Li, F. Y., Ong, Y. K. & Chung, T. S. 2014 Treatment of highly concentrated wastewater containing multiple synthetic dyes by a combined process of coagulation/flocculation and nanofiltration. *Journal of Membrane Science* **469** (11), 306–315.

Liu, Q. Y., Zhang, Y. B. & Zhao, C. C. 2014 The isolation of bioflocculant-producing strains and the application in the oily wastewater treatment process. *Petroleum Science & Technology* **32** (23), 2807–2814.

López-Maldonado, E. A., Oropeza-Guzman, M. T., Jurado-Baizaval, J. L. & Ochoa-terán, A. 2014 Coagulation-flocculation mechanisms in wastewater treatment plants through zeta potential measurements. *Journal of Hazardous Materials* **279**, 1–10.

Lu, M. & Wei, X. 2011 Treatment of oilfield wastewater containing polymer by the batch activated sludge reactor combined with a zerovalent iron/EDTA/air system. *Bioresource Technology* **102** (3), 2555–2562.

Lu, M., Wu, X. & Wei, X. 2012 Chemical degradation of polyacrylamide by advanced oxidation processes. *Environmental Technology* **33** (9), 1021–1028.

Lu, Q., Yan, B., Xie, L., Huang, J., Liu, Y. & Zeng, H. 2016 A two-step flocculation process on oil sands tailings treatment using oppositely charged polymer flocculants. *Science of the Total Environment* **565**, 369–375.

Martínez-Palou, R., Cerón-Camacho, R., Chávez, B., Vallejo, A. A., Villanueva-Negrete, D. & Castellanos, J. 2013 Demulsification of heavy crude oil-in-water emulsions: a comparative study between microwave and thermal heating. *Fuel* **113** (2), 407–414.

Maruyama, H., Seki, H. & Satoh, Y. 2012 Removal kinetic model of oil droplet from o/w emulsion by adding methylated milk casein in flotation. *Water Research* **46** (9), 3094–3100.

Masuelli, M., Marchese, J. & Ochoa, N. A. 2009 SPC/PVDF membranes for emulsified oily wastewater treatment. *Journal of Membrane Science* **326** (2), 688–693.

Nasser, M. S., Twaiq, F. A. & Onaizi, S. A. 2013 Effect of polyelectrolytes on the degree of flocculation of papermaking suspensions. *Separation & Purification Technology* **103** (3), 43–52.

Santo, C. E., Vilar, V. J. P., Botelho, C. M. S., Bhatnagar, A., Kumar, E. & Rui, A. R. B. 2012 Optimization of coagulation–flocculation and flotation parameters for the treatment of a petroleum refinery effluent from a Portuguese plant. *Chemical Engineering Journal* **183** (5), 117–123.

Sarkar, B., Chakrabarti, P. P., Vijaykumar, A. & Kale, V. 2006 Wastewater treatment in dairy industries – possibility of reuse. *Desalination* **195** (1), 141–152.

Spinelli, L. S., Pires, R. V., Barboza, E. M., Louvisse, A. M. T., Aquino, A. S. & Lucas, E. F. 2007 Influence of polymer bases on the synergistic effects obtained from mixtures of additives in the petroleum industry: performance and residue formation. *Journal of Petroleum Science & Engineering* **58** (1), 111–118.

Suarez, S., Lema, J. M. & Omil, F. 2009 Pre-treatment of hospital wastewater by coagulation-flocculation and flotation. *Bioresource Technology* **100** (7), 2138–2146.

Verma, S., Prasad, B. & Mishra, I. M. 2010 Pretreatment of petrochemical wastewater by coagulation and flocculation and the sludge characteristics. *Journal of Hazardous Materials* **178** (1–3), 1055–1064.

Wang, B., Wu, T., Li, Y., Sun, D., Yang, M. & Gao, Y. 2011a The effects of oil displacement agents on the stability of water produced from ASP (alkaline/surfactant/polymer) flooding. *Colloids & Surfaces A Physicochemical & Engineering Aspects* **379** (1–3), 121–126.

Wang, J. P., Chen, Y. Z., Wang, Y., Yuan, S. J. & Yu, H. Q. 2011b Optimization of the coagulation-flocculation process for pulp mill wastewater treatment using a combination of uniform design and response surface methodology. *Water Research* **45** (17), 5633–5640.

Wen, Y., Zheng, W., Yang, Y., Cao, A. & Qi, Z. 2015 Influence of Al^{3+} addition on the flocculation and sedimentation of activated sludge: comparison of single and multiple dosing patterns. *Water Research* **75** (5), 201–209.

Yang, Z. H., Huang, J., Zeng, G. M., Ruan, M., Zhou, C. S. & Li, L. 2009 Optimization of flocculation conditions for kaolin suspension using the composite flocculant of MBFGA1 and PAC by response surface methodology. *Bioresource Technology* **100** (18), 4233–4239.

Yang, Y., Li, Y., Zhang, Y. M. & Liang, D. W. 2010 Applying hybrid coagulants and polyacrylamide flocculants in the treatment of high-phosphorus hematite flotation wastewater (HHFW): optimization through response surface methodology. *Separation & Purification Technology* **76** (1), 72–78.

Yang, Q., Xin, X., Wang, L., Lu, H., Ren, H. & Tan, Y. 2014 Modification of the stability of oil-in-water nano-emulsions by polymers with different structures. *Colloid and Polymer Science* **292** (6), 1297–1306.

Yu, L., Han, M. & He, F. 2013 A review of treating oily wastewater. *Arabian Journal of Chemistry* **265**, 1913–1922.

Zeng, D., Hu, D. & Cheng, J. 2011 Preparation and study of a composite flocculant for papermaking wastewater treatment. *Journal of Environmental Protection* **2** (10), 1370–1374.

Zhang, R., Liang, C., Wu, D. & Deng, S. 2006 Characterization and demulsification of produced liquid from weak base ASP flooding. *Colloids & Surfaces A Physicochemical & Engineering Aspects* **290** (1–3), 164–171.

Zhao, X., Liu, L., Wang, Y., Dai, H., Wang, D. & Cai, H. 2008 Influences of partially hydrolyzed polyacrylamide (HPAM) residue on the flocculation behavior of oily wastewater produced from polymer flooding. *Separation & Purification Technology* **62** (1), 199–204.

Zhong, J., Sun, X. & Wang, C. 2003 Treatment of oily wastewater produced from refinery processes using flocculation and ceramic membrane filtration. *Separation & Purification Technology* **32** (1–3), 93–98.

Zhou, Z., Liu, S. & Jia, L. 2016 Flocculation kinetics mechanism and floc formation prepared by poly aluminum chloride coupled with polyacrylamide for ship ballast water. *Water Science & Technology* **74** (1), 57–64.

First received 13 May 2017; accepted in revised form 30 June 2017. Available online 24 July 2017