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Feasibility investigation of oily wastewater treatment by combination of zinc and PAM in coagulation/flocculation

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Abstract

Poly-zinc silicate (PZSS) is a new type of coagulant with cationic polymer synthesized by polysilicic acid and zinc sulfate. It has been used in several sorts of wastewaters treatment, but not used in oily wastewater treatment. In this study, we investigated the coagulation/flocculation of oil and suspended solids in heavy oil wastewater (HOW) by PZSS and anion polyacrylamide (A-PAM). The properties of PZSS cooperated with A-PAM were compared with PAC and PFS in dosages, PAMs amount, settling time, pH value and flocs morphology. The results showed that PZSS was more efficient than PAC and PFS. Under the optimum experimental conditions of coagulation/flocculation (dosage: 100 mg/L, A-PAM dosage: 1.0 mg/L, settling time time: 40 min and pH 6.5–9.5), more than 99% of oil was removed and suspended solid value less than 5 mg/L by using PZSS cooperated with A-PAM, which could satisfy the demands of the pre-treatment process for HOW to be reused in the steam boiler or recycled into the injecting well.

Keywords: Heavy oil wastewater; Poly-zinc silicate; Coagulation; Flocculation; Polyacrylamide

1. Introduction

Heavy oil wastewater (HOW) contains oil droplets, suspended solids and dissolved salts, which is main pollution source for local water in Xinjiang, China [1,2]. Recycling such wastewater by heavy oil wastewater treatment is strongly desirable and of great challenge for heavy oil industry. Compared with other types oily wastewater, HOW belongs to the colloidal suspension which contains large amount of chemical oxygen demand (COD), suspended solids (including clay particles, pressure crack sands, residues of broken colloid and indissolvable particles), soluble organic compounds, microorganisms, and inorganic salts as shown in Table 1. In the heavy oil recovery, HOW needs to be reused in steam boiler or recycled into the injecting well for enhancing the crude oil exploitation after treatment. The maximum allowable limit for recycling wastewater, required by China Department of Petroleum (CDP), is 2 mg/L oil and suspended solids for reused in the boiler inlet, and 10 mg/L oil and 5 mg/L suspended solids for injecting well [3]. Several techniques, e.g. coagulation/flocculation, floatation, centrifugation and biological methods, have been developed to remove pollutants from oily waters [4–6]. But the coagulation/flocculation method is widely used for its capability of destabilizing and aggregating colloids [7,8]. For example, poly-ferric sulfate (PFS) and poly-aluminum chloride (PAC) are widely used as coagulants in wastewater treatment [9–11]. However, these inorganic coagulants are easy to form smaller flocs with low settling speed. In addition, the corrosive coagulants usually result in a large amount of hazardous sludge with residual metal, and increase the treating load [12]. The organic polyacrylamide has the excellences of lower dosage and rapid settling speed for flocs, but with limited effect by oneself [13,14]. As using these conventional methods could not satisfy the requirement for HOW treatment, it is important to find more efficient method [15,16].

Recently, poly-zinc silicate (PZSS), a new type of coagulant, has received much attention in wastewater treatment because of its non-toxicity and specific characteristics of the charge-

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Table 1
Characteristics of HOW

Parameter	Concentration
Density of oil–water (g/cm^3)	0.05
pH	6.5–6.8
Suspended solid (mg/L)	90–300
COD (mg/L)	500–1000
Phenols (mg/L)	10–20
Sulfides (mg/L)	15–30
Viscosity (mPa S)	0.678
Oil (mg/L)	400–1000
Turbidity (NTU)	150–350
Silica (mg/L)	100–150
Total iron (mg/L)	5.0–10.0
Total dissolvable solid (mg/L)	3000–5000

neutralization and the bridging effect [17,18]. It has been widely used to purify drinking water and wastewaters in various industries, such as, cane sugar, dye, tannery, amylon, brewery, paper, and electric power. It showed more efficient flocculating effect than the conventional ferric and aluminum coagulants [19–22]. However, there have been few reports in the treatment of oily wastewater by using PZSS with PAM. Herein, we used PZSS with A-PAM as coagulating and flocculating chemicals for HOW treatment. They showed very good performance with more than 99% removal efficiency of suspended solid and oil.

2. Materials and methods

2.1. Materials and experimental set-up

Samples of HOW were collected into a mixing jar from the outlet of oily water separator in HOW factory. PZSS, PAC and PFS were provided by Youbang Co., China. The coagulants were in the powder form and were prepared as 5% solutions. The polyacrylamide anionic (A-2350), cationic (C-100), and non-ionic (N-08), obtained from SNF Co., were used as flocculants. The molecular weights of A-2350, N-08 and C-100 are in the range of 10–12 × 10^6, 10–12 × 10^6 and 6–8 × 10^6, respectively. Sodium hydroxide, purchased from Chinese Company, was also used for pH adjustments.

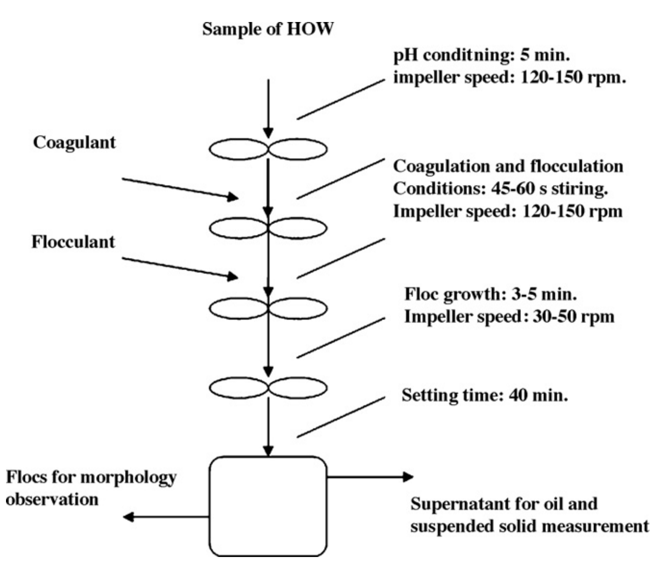


Fig. 1. Experimental set-up.

2.2. Experimental procedure

Fig. 1 illustrated the experimental procedure. A conventional jar apparatus with six beakers was used to coagulate the samples. Each beaker filled with 1–2 L of sample can be simultaneously stirred at the same speed. HOW was adjusted to the desired pH value at 120 rpm for 5 min, and then the coagulants with different dosages of 0–600 mg/L were added to the HOW. After rapidly mixing for 45–60 s at 120–150 rpm, 0.2–3.0 mg/L PAMs were added. Then, the stirring rate slowed down to 30–50 rpm for 3–5 min to allow the growth of flocs. Finally, the stirring stopped and the flocs settled for known time. All tests were carried out at 70 ± 1°C.

2.3. Analysis methods

The pH meter used was pHS–3C (ShangHai, China). The oil concentrations were determined using a UV spectrophotometer (Model DR/3000, Hach Co., USA) to measure absorbency [23]. The suspended solid concentration was measured by the standard methods [24]. The morphology of flocs was observed through TEM (JEM-100CXII, Japan).

3. Results and discussion

3.1. Effect of coagulant dosage

The effect of coagulant varying dosage was analyzed with 1.0 mg/L A-PAM at all times at pH 6.8. The original oil concentration in HOW was 500–1000 mg/L. Fig. 2 shows the curves of different coagulants dosage against the percentage of oil removal and suspended solid value. It was noticed that 100 mg/L of PZSS removed 95% of oil. But for PFS and PAC, 600 and 450 mg/L removed 51% and 95% of oil, respectively. The dosages needed by the conventional coagulants were four to six times more than

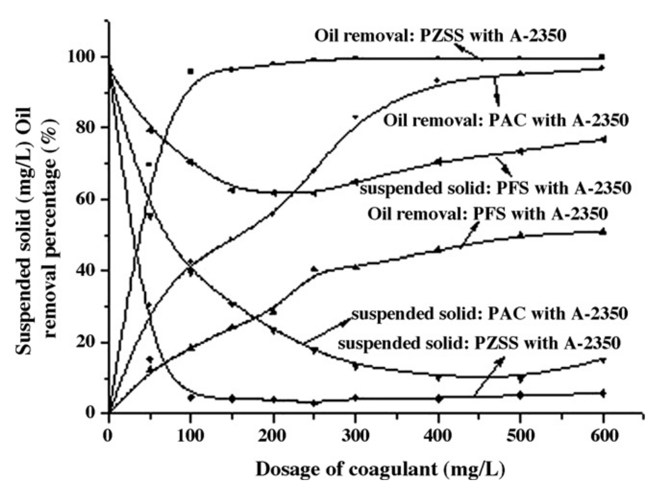


Fig. 2. Effect of coagulant dosage on the removal of oil and suspended solid.

PZSS. Furthermore, PZSS is proved to be a better coagulant compared with PAC and PFS even at lower dosage; 50 mg/L of PZSS could remove 70% of oil.

These results can be explained based on charge density. The oil removal is sensitive to the coagulant dosage since the colloidal stability of the oily water emulsion is a function of the quantities [25]. PZSS is a positive charge polyelectrolyte with acidity and high charge density compared with other coagulants [22], but HOW belongs to the emulsive suspension trending to neutral pH value. Therefore, this condition could easily stimulate PZSS to coagulate the oil from HOW. The bigger adsorption area of PZSS results in the bigger flocs adsorbing more charges, which increases the surface activation and enhances the capabilities of adsorption and charge neutralization. Hence, PZSS destabilizes the negative charge colloids of oil and emulsion from HOW by charge neutralization and adsorption mechanism [18,22]. In addition, the polysilicate radicle in PZSS, which neutralizes the charge of oil droplets to bind and bridge, helps to coagulate and adsorb the oil droplets. As a result, it requires lower dosage to destabilize the emulsive oil.

As shown in Fig. 2, PZSS had the best effect on removing suspended solids. The flocs formed by PZSS appeared rapidly and grew very fast to form a larger size, which could easily settled. The flocs with chain-net structure formed large entangled mass resembling cobwebs. This might due to the bridging mechanism. Almost 99% of the suspended solids were removed by PZSS with A-PAM. Nevertheless in Fig. 2, it is also noticed that the suspended solid value increased at 300 mg/L of PZSS and 600 mg/L of PAC. This shows the restabilization of oil and suspended solids in HOW. At high doses of coagulant, a sufficient degree of over-saturation occurs to produce a rapid precipitation of large quantity of coagulant. A number of works on restabilization of colloidal suspensions due to excessive treatment with polyelectrolytes have been done [26].

3.2. Effect of polyacrylamide dosage

Based on the reduction of suspended solids and removal efficiencies of the oil by the PAMs, the flocculating properties of the PAM are influenced by its molecular weight and charge density as seen from Fig. 3. The oil removal efficiency increased with the PAM dosage. The efficiency of oil removal by A-PAM was impressive, even at low dosage. More than 90% of oil removal could be achieved at 0.2 mg/L by A-PAM. A-2350 is an anion PAM with very high molecular weight and low charge density. It removed oil with the best effect among the PAMs as it achieved 99% of oil removal at 1 mg/L. As shown in Fig. 3, the reduction of suspended solid increased with PAM's dosage except C-100. The effect of C-100 was not sensitive in the removal of suspended solid, implying that C-100 had no efficiency in improving flocculating effect. A-2350 is the most efficient to reduce the suspended solid among these PAMs, by which the suspended solid concentration decreased from 23.5 mg/L by PZSS oneself to 4.6 mg/L.

Although the cationic polymer C-100 may be a suitable choice according to the electrostatic interaction, the molecular weight of PAM is more important [27]. C-100 has lower molecular weight compared with A-2350 and N-08. Thus, the flocs bridged by C-100 are weak with slow-settling speed. The polymers with high molecular weight are extremely effective in promoting flocs growth [28]. The A-2350 with high molecular weight performed better than N-08 and C-100 with medium and low molecular weight, respectively. Consequently, A-2350 can strongly flocculate the negative charge particles. Further increase in the dosage of PAM does not improve the reduction efficiency. This behavior suggests that flocs breakup occurs due to charge reversal and dispersion when there is an excessive or overdosing of flocculants [29]. However, the percentage reduction of oil and suspended solid with A-2350 was very significant even at the lower dosage of 0.5 mg/L.

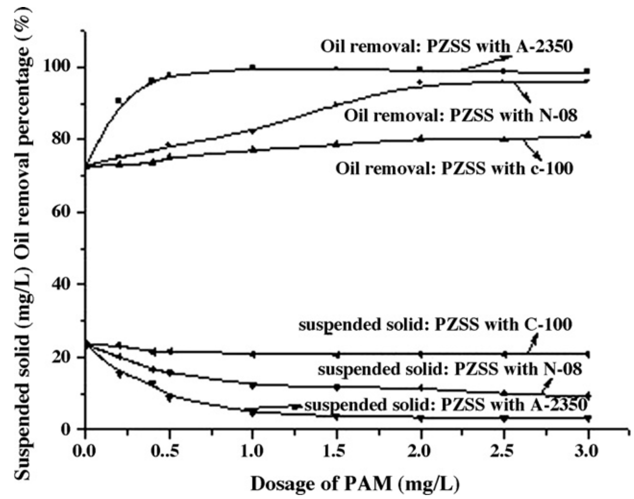


Fig. 3. Removal oil and suspended solid at various dosages of PAM (PZSS: 100 mg/L).

3.3. Effect of settling time

Effect of settling was analyzed at different settling time at optimum dosage of PZSS, PAC and A-PAM. The settling rate of flocs by PZSS was faster compared to PAC. PZSS coagulated HOW produced flocs of better quality, namely larger flocs with faster settling velocity. Fig. 4 shows that settling for 20 min by PZSS combined with A-PAM could remove 99% of oil. Nevertheless, PAC with A-PAM needing settle 60 min or even longer could achieve the same oil removal. Before settling for 5 min, it was observed that the percentage of oil removal was low for PAC. This proves that the oil droplets attached to the flocs formed by PAC needs take longer time to settle, which causes the oil removal unfavorable at early stage. This is because the chances of the oil droplets and coagulant particles meet were lower to result in the removal efficiency inadequate. At longer time of settling, breakage of the oil droplets are enhanced, thus reduces the diameter of the oil droplets resulting in the larger interfacial area available for the coagulation and adsorption to happen [30].

As shown in Fig. 4, for PZSS with A-PAM, it needs only 40 min to reach 4.6 mg/L of suspended solid. For PZSS, the

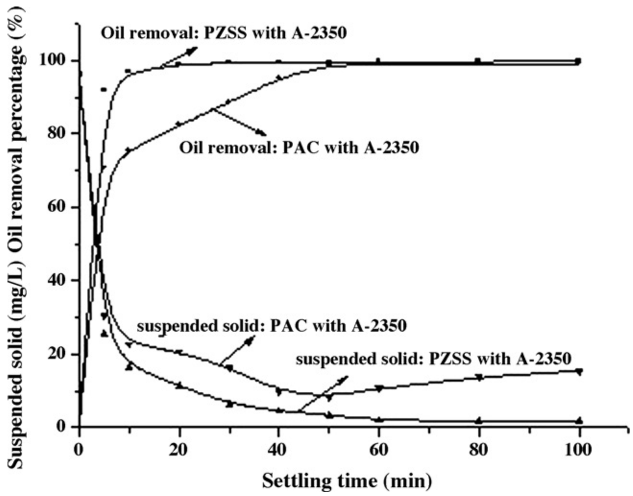


Fig. 4. Effect of settling time on oil removal and suspended solid reduction (PZSS: 100 mg/L; A-2350: 1.0 mg/L; PAC: 450 mg/L).

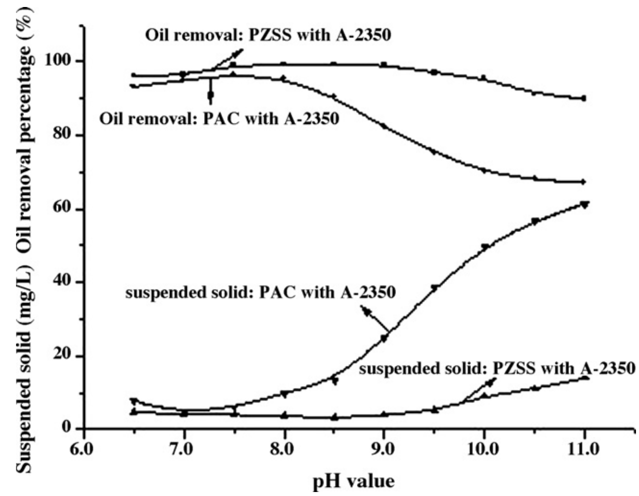
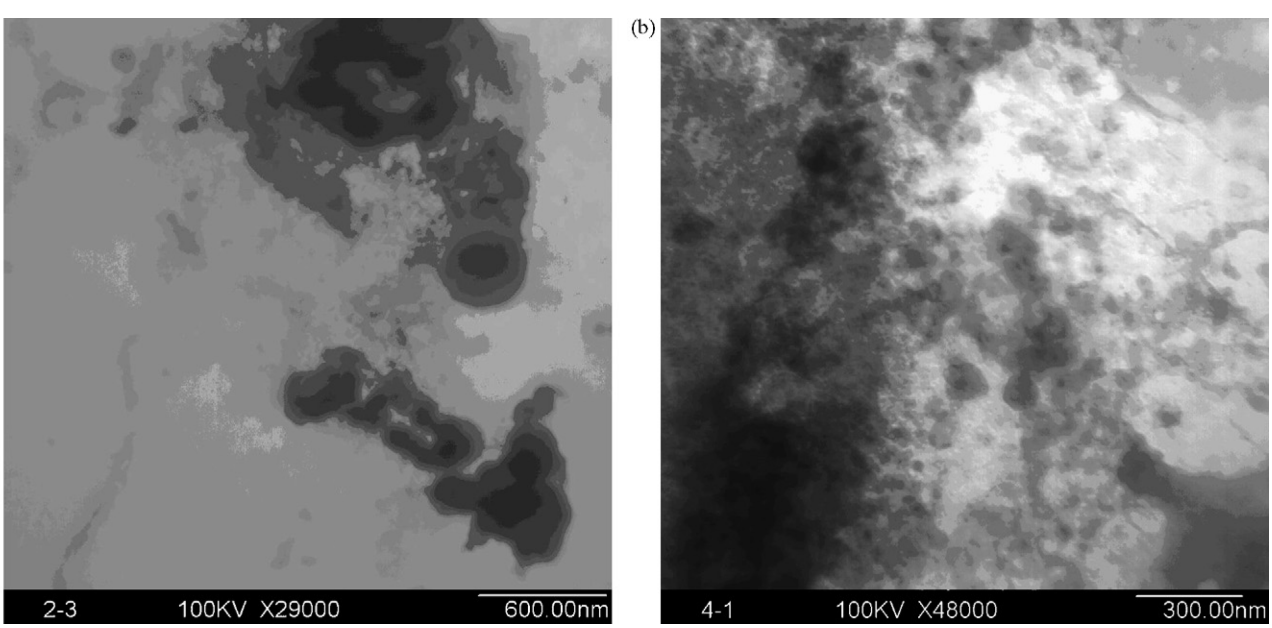


Fig. 5. Oil and suspended solid removal using PZSS and PAC vs. different pH value (PZSS: 100 mg/L; A-2350: 1.0 mg/L; PAC: 450 mg/L).

changes was small compared with PAC. This illuminates that PZSS bridges the flocs more firmly and tightly than PAC. After settling for 60 min, PAC's suspended solid increased from 10.7 to 15.5 mg/L. The flocs formed by PAC seemed to be easily dispersed in the sample if the settling time was prolonged. The breakage of the flocs caused the sample to be turbid again. This indirectly caused the suspended solid to disperse in the sample. It is clearly noticed that PAC acts only as a coagulant which coagulates the suspended oil and solid in HOW and settle it by gravity settling, and PAC does not adsorb the emulsive oil nor bind the flocs strongly. The flocs formed by PZSS are larger and denser causing the suspended solid to settle faster. PZSS with A-PAM promotes the aggregation of colloids, bridges between the dispersed oil droplets and suspended solids, and conduces the particles to form sufficient size, which can settle quickly and easily [22].

3.4. Determination of the optimal pH

Emulsion breaking is usually brought about by changing the pH value of samples or inorganic coagulants [31]. The relationships between the pH value and the oil removal and suspended solid are shown in Fig. 5. Almost 96% and 93% of oil removal could be achieved at the original pH value by PZSS and PAC. Oil removal efficiency was over 95% at the broad pH value 6.5–10.0 by PZSS. But for PAC, the pH value at 7.0–8.0 achieved the same degree. PZSS helps to demulsify and increase the droplet size and enhance the adsorption of oil in the neutral and alkalescent condition [22]. Therefore, the electrostatic attractions among the oil droplets and the adsorption increase and improve the adsorption of oil onto PZSS. As shown in Fig. 5, PZSS and PAC with A-PAM had an effective removal of suspended solid at pH 6.5–10.5 and 6.5–8.0,

(a)


(b)

Fig. 6. TEM photographs of flocs formed by PZSS (a) and PAC (b).

respectively. The suspended solid by PZSS was 3.1 mg/L at the optimum pH 8.5, but it was 4.6 mg/L at the optimum pH 7.0 for PAC. When pH value was over 10.5 and 8.0 for PZSS and PAC, respectively, the suspended solids increased drastically. It may be that the coagulants hydrolyze to form the flocs to settle slowly and result in the flocs formed by $Al(OH)_4^-$ dispersing, which increases the suspended solid as pH value is over 8.0 for PAC [9].

3.5. Observation of flocs morphology

Fig. 6(a) and (b) show the flocs morphology by TEM. As shown in Fig. 6(a) that the hydrolyzing aggregation produced by PZSS with A-PAM was adhered to the particle surface of HOW. The particles congregated to form the big flocs and massed further. The adhering and bridge could be observed. The flocs settled easily and rapidly and had a good flocculability. Fig. 6(b) displays the flocs by PAC was loosed, which proves the settling speed was slower than PZSS. Because zinc ion is easy to aggregate with PSA and form the chain-net structure, the positive charge through the hydrolization and aggregation is adsorbed on the particles, as a result, the charge neutralization takes the colloidal particles off stability and bridges in PZSS and A-PAM molecules to adhere big flocs.

4. Conclusions

This investigation demonstrated that the coagulation/flocculation with PZSS and anionic polyacrylamide (A-PAM) cooperation was an effective method for HOW treatment by reducing oil and suspended solid concentration. The results show that PZSS were more effective than PAC and PFS. At the optimum conditions (dosage: 100 mg/L, A-PAM dosage: 1.0 mg/L, settling time: 40 min and pH 6.5–9.5), more than 99% of suspended solid and oil was removed by using PZSS cooperated with A-PAM. The dosages needed by PAC and PFS were four to six times more than PZSS. A-PAM (A-2350) with high molecular weight and low charge density was more effective than C-PAM (C-100) and N-PAM (N-08) in removing oil and suspended solid. The settling time using PZSS with A-PAM in mixing jar was 40 min and it was quite enough for flocs to settle. There was a broad pH range between 6.5 and 10.0 by PZSS with A-PAM that the oil removal could reach above 95% and suspended solid less than 5 mg/L. The flocs morphology by TEM proved that PZSS with A-PAM formed the firm and tight flocs and could settle rapidly. Accordingly, PZSS with A-PAM can be favourable in removing oil and suspended solids in the pre-treatment of HOW before reused in steam boiler or recycled into the injecting well.

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