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PREPARATION OF NEW INORGANIC POLYMER FLOCCULANT AND ITS APPLICATION IN OILY SLUDGE

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Abstract

Sodium silicate, iron sulfate, magnesium sulfate, and zinc sulfate were used as the raw materials to prepare a new inorganic polymer flocculant, polysilicate ferric magnesium zinc (PSFMZ), using direct recombination. The effects of molar ratio of zinc to silicon, ratio of iron to magnesium, reaction temperature, and reaction time on deoiling rate were explored. The optimal synthesis conditions for the flocculant for the thermal-washing treatment of oily sludge were determined. Results showed that when the added amount of flocculant was 40 mg/L, the deoiling rate of oily sludge reached 82.83%, which was higher than those obtained when using polyaluminium chloride, sodium silicate, and on-site flocculant. Thus, the prepared flocculant was effective. Scanning electron microscopy analysis showed that when the flocculant was added to the oily sludge, the microstructure of the sludge particles became flat and compact. Consequently, the sludge was effectively flocculated and oil molecules were successfully removed. Thermal analysis showed that crude oil and free water in the oil sludge were largely removed by treatment with thermal washing with polysilicate metal flocculant.

Keywords: deoiling, inorganic polymer flocculant, oily sludge, polysilicate metal polymer

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1. Introduction

With the development of oil- and gas-extraction methods, the output of oily sludge is increasing gradually (Egazaryants et al., 2015; Lin et al., 2017; Shahi et al., 2017; Zhang et al., 2013). Adding effective and appropriate flocculants to sludge for quenching and tempering is key to oily-sludge treatment. Through wetting, emulsifying, dissolving and solubilizing, the flocculant can change the force between oil, water, and mud, and this process is conducive to the removal of the oil phase from the sludge phase, ultimately leading to three-phase separation (De Castro et al., 2010; Jing et al., 2010; Khan et al., 2019; Sorlini et al., 2018).

Flocculants include inorganic, organic, and microbial types (Gerde et al., 2014; Miyahara et al., 2016; Sun et al., 2017; Valverde et al., 2018; Zhang et al., 2014). Some researchers use the organic flocculants polyacrylamide, alkylbenzenesulfonate, alkylphenol ether, and microbial flocculant to quench and temper oily sludge, remove oil in the oily sludge, and realize the recycling of crude oil to the maximum extent (Chirwa et al., 2013; Meng et al., 2013). Inorganic composite flocculants are prepared by physical or chemical methods with inorganic flocculants in a targeted way aimed at improving the electrical neutralization, bridging, and coordination complexing ability of the flocculant by introducing hydroxyl, sulfate, and highly charged ions based on aluminum and iron salt (Saifuddin and Refal 2014; Wei et al., 2016); To enhance flocculant ability and effect, silicate has been combined with iron salt, aluminum salt, or other inorganic salt ions to form a new flocculant (Sun et al., 2011). Polysilicate metal salt flocculants are new inorganic polymer-composite flocculants. Due to their electrical neutralization and adsorption bridging and netting, these flocculants have

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desirable effects and have thus become research hotspots because of their abundance, innocuity, low cost, and easy preparation (Li et al., 2013a; Wei et al., 2015). At present, polysilicate metal flocculants were mostly used in the treatment of pollutants in sewage, but their application in the oil recovery of oily sludge was seldom reported (Li et al., 2015). The flocculent effect of polysilicate metal-salt flocculant is related to various factors, including the type of metal, the molar ratio between metals and ratio of metal to silicon, which greatly influences the flocculent effect. Iron-salt flocculant has the advantages of compact flocs and rapid settlement. Adding magnesium salt can decrease the chromaticity of treated water and achieve a decolorizing effect. Adding zinc salt can change the structure of flocculant to enhance the electrical-neutralization ability; the formed flocs are denser and can form a good chain network structure. Considering the synergistic effect of various metal salts, polysilicate metal-salt flocculant has good flocculent ability (You et al., 2018). The flocculent effect is influenced by the application system to a large extent. Therefore, flocculants have certain application range. The flocculants can be used to prepare inorganic–organic composite flocculants that combine each component's advantages so that the flocculent effect can be improved and the application range can be increased (Liu et al., 2016).

In this paper, an inorganic polymer flocculant of polysilicate ferric magnesium zinc (PSFMZ) was prepared with raw materials of iron sulfate, magnesium sulfate, zinc sulfate, and sodium silicate by direct recombination. In this method, sulfate is introduced to polysilicic acid (Psi) to trigger a synergistic reaction among iron salt, magnesium salt, and zinc salt. To examine the effects of the single-factor molar ratio of zinc to silicon, molar ratio of iron to magnesium, molar ratio of iron to magnesium to silicon, reaction temperature, and reaction time on deoiling rate, we used the orthogonal test to determine the optimal process conditions. The infrared characterization of the flocculant was carried out and the flocculant was applied to the treatment of oily sludge by thermal washing to investigate its effect on deoiling rate.

2. Material and methods

2.1. Reagents and instruments

The reagents used were sulfuric acid (analytical grade; Shenyang East Reagent Factory, China), sodium hydroxide (analytical grade; Shenyang East Reagent Factory, China), sodium silicate (analytical grade; Shenyang East Reagent Factory, China), iron sulfate (analytical grade; Shenyang East Reagent Factory, China), magnesium sulfate (analytical grade; Harbin Xinda Chemical Plant, China), zinc sulfate (analytical grade; Shenyang East Reagent Factory, China), oily sludge, and gasoline 93#. The instruments used were HH-S26S digital display constant temperature water bath pot (Chunlan Instrument Factory, China), 721 ultraviolet spectrophotometer (Shanghai Jinghua Technology Instrument Co., Ltd., China), 202 constant temperature drying box (Shanghai Shengqi Instrument Co., Ltd., China), FA-N/JA-N electronic balance (Shanghai Minqiao Precision Science Instrument Co. Ltd., China), X85-2 constant temperature magnetic stirrer (Shanghai Meiyingpu Instrument Manufacturing Co. Ltd., China), TSH-O-4000 centrifugal precipitator (Tianjin Medical Equipment Factory, China), MB154S Fourier infrared spectrometer (Bomen Company, Canada); DuPont 2100 thermal analyzer (Perkin Elmer Company, USA), S-4800 scanning electron microscope (Hitachi High Technologies Corporation, Japan),and D/max-2200pc X-ray diffractometer (Science and Technology Corporation, Japan).

2.2. Analysis of the basic properties of oily sludge

This experiment used Soxhlet extraction and spectrophotometry to determine the oil content. Absorbance was measured with 93# gasoline as the reference at a wavelength of 420 nm. The standard curve, where the corresponding oil content was used to calculate the oil content, was drawn.

Natural determination of water content was performed by the method for determining the moisture content of the national standard water–oil mixed system. The remaining impurities were filtered, washed, dried, and left undisturbed. The amount of mud sand, i.e. the mud content, was weighed.

2.3. Preparation of copolymer

2.3.1. Preparation process

A solution containing 5% SiO_2 was prepared by adding distilled water to a certain amount of sodium silicate and activating the mixture for 15 min after full stirring. About 10% of dilute sulfuric acid was added while controlling the reaction temperature at 25°C. pH was adjusted to 2–5 until the solution was slightly blue, and the value was changed to 2 by adding 10% dilute sulfuric acid. The solution was stirred for 30 min at 30–40°C and aged for 24 h, and then 2.5% Psi was obtained.

Iron sulfate, magnesium sulfate, and zinc sulfate solution were added based on the calculation ratio and stirred for a certain period of time at a certain temperature. After aging for 24 h, the new inorganic polymer flocculant, polysilicate ferric magnesium zinc (PSFMZ), was obtained.

2.3.2. Single-factor test

Through the single-control-variable method, the effects of the molar ratio of zinc to silicon $n(Zn)/n(Si)=1:4–2:1$, molar ratio of iron to magnesium $n(Fe)/n(Mg)=1:3–3:1$, and molar ratio of ferromagnesia to silicon $n(Fe+Mg)/n(Si)=1:3–3:1$ on deoiling rate were investigated. The effects of reaction temperature 25–60 °C and reaction times of 10 min to

2 h were also examined. The experiment was repeated three times under the same experimental conditions.

2.3.3. Orthogonal test

According to the results of single-factor test, the deoiling rate of oily sludge by flocculant was used as an indicator for developing a four-factor three-level orthogonal table L_9 (3^4) and determine the optimal synthesis conditions for the flocculant.

2.4. Performance evaluation of flocculant

2.4.1. Structural characterization of flocculant

The polymerized products were characterized by MB154S type Fourier transform infrared spectroscopy and D/max-2200pc type X-ray diffractometer.

2.4.2. Optimal-dosage determination

The flocculant was prepared solutions of 20, 30, 35, 40, 45, 50, and 60 mg/L and applied in oily sludge treated by thermal washing to determine the deoiling rate and optimal dosage of flocculant. The experiment was repeated three times under the same experimental conditions.

2.4.3. Effects of pH on deoiling effect

Different pH values (pH 5–13) were adjusted by 5% sodium hydroxide solution to treat oily sludge of the same weight and draw a deoiling rate curve. Then, the appropriate pH of flocculant was determined. The experiment was repeated three times under the same experimental conditions.

2.4.4. Comparison of deoiling effects

Oily sludge of the same weight was treated under the same conditions of thermal washing. By using the optimal dosage and appropriate pH, flocculant sodium silicate, PAC, and an on-site flocculant were compared. Oily sludge with no flocculant served as the blank control. The deoiling rate was used as an indicator to determine the effect of oily sludge after treatment.

2.5. Mechanism analysis of flocculant action

To explore the mechanism of action, DuPont 2100 type thermal analyzer was used to examine the deoiling performance of oily sludge by thermal washing with flocculant. In addition, S-4800 type scanning electron microscopy was used to perform microscopic analysis on oily sludge treated by thermal washing without and with flocculant.

3. Results and discussion

3.1. Detection of basic properties of oily sludge

The oily sludge adopted in the experiment was black and viscous and had a strong volatile irritating odor. The measured oil content in the oily sludge was 13.13%, the moisture content was 24.58%, the mud content was 59.89%, and other components accounted for 2.4%.

3.1.1. Effect of components of the flocculant on deoiling rate

Fig. 1a shows that when n(Zn)/n(Si) was low, the low content of Zn^{2+} hinders the flocculant from forming a strong chain-network structure. However, the bridging and netting ability of flocculant was reduced, so it can only neutralize part of negative particles in oily sludge and decrease the oiling rate. When n(Zn)/n(Si) was high, the excessive amount of Zn^{2+} can induce the sludge particles to be positively charged, further leading to repulsion between sludge particles and flocculant, attenuating the adsorption of flocculant on sludge particles, and reducing the deoiling rate. Accordingly, only an appropriate amount of n(Zn)/n(Si) can increase the deoiling rate, which reached the maximum value when n(Zn)/n(Si)=1:2, as shown in Fig. 1(a).

Fig. 1b indicated that when n(Fe)/n(Mg) was low, the weak iron ion hydrolysis and low positive charge of magnesium ions resulted in weak neutralization ability of flocculant and low deoiling rate. With increased molar ratio of iron to magnesium, the deoiling rate reached the maximum value when n(Fe)/n(Mg)=1:1. With further increased molar ratio of iron to magnesium, the large amount of iron ions induced the sludge particles to be positively charged, which did not benefit the adsorption bridging of flocculant (Yang et al., 2012). Accordingly, n(Fe)/n(Mg)=1:1 was deemed optimal. Meanwhile, the magnesium salt can also facilitate the treatment of subsequent sewage because of its decolorizing effect.

Fig. 1c shows that when n(Fe+Mg)/n(Si) was low, i.e., the content of metal ions was low, the content of polysilicic acidwas relatively high. The large concentration of silicic acid promoted self-polymerization among silicon molecules, which reduced the binding of silicon and metal ions and attenuated the flocculent effect only with the single adsorption bridging of PSi.

The content of metal ions increased with increased n(Fe+Mg)/n(Si), which enhanced the electric neutralization ability of flocculant and improved the flocculent effect. The metal ions delayed the Psi gel and stabilize the flocculant, and the deoiling rate reached the maximum when n(Fe+Mg)/n(Si)=1:1. With further increased n(Fe+Mg)/n(Si), the high content of metal ions induced the sludge particles to become positively charged from being in a negative state, which led to mutual repulsion among particles and flocculent effect, thereby inhibiting the adsorption of flocculent and reducing the deoiling rate. Accordingly, n(Fe+Mg)/n(Si)=1:1 was deemed optimal.

3.1.2. Effect of the reaction conditions on deoiling rate

Fig. 2a shows that deoiling rate gradually decreased with increased reaction temperature, which was due to the fact that a higher temperature led to a shorter gelation time of Psi.

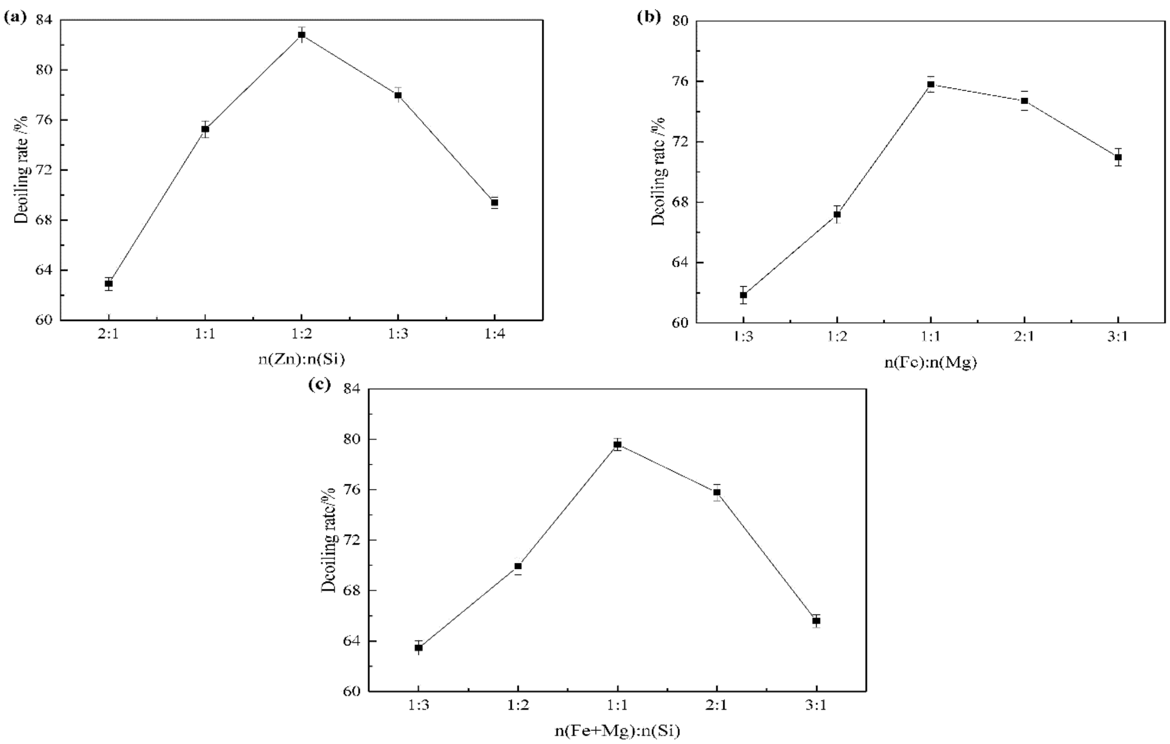

Fig. 1. Effect of molar ratio of (a) zinc to silicon, (b) iron to magnesium, (c) iron and magnesium to silicon on deoiling rate

At the same time, the hydrolysis of magnesium, iron, and zinc salts impeded the binding of PSi; the effective flocculent components decreased and thus the flocculent effect decreased (Shi et al., 2010). Thus, the reaction temperature of 30°C was deemed optimal.

Fig. 2b shows that reaction time reached a high value at 30 min. Over time, the effect of flocculant on deoiling rate became insignificant. Considering that the inorganic reaction was quick, during flocculant preparation, as long as the proportion of Psi, iron salt, zinc salt, and magnesium salt were appropriate, the metal ions coordinated with silicon in a short time to form effective flocculent components. Thus, the reaction time of 30 min was deemed optimal.

3.2. Orthogonal test

Based on single-factor test results, the orthogonal test factor level table was established and is shown in Table 1. The order of range R effect of the four factors from large to small was n(Fe):n(Mg) > n(Zn):n(Si) > reaction temperature>n(Fe+Mg):n(Si). Through comprehensive analysis of the single-factor results and the horizontal values of the orthogonal factors, the optimal synthesis conditions were determined to be A2B2C2D2, i.e., n(Fe+Mg):n(Si)=1:1, n(Fe):n(Mg)=1:1, n(Zn):n(Si)=1:2, and 30°C reaction temperature.

In other words, the polysilicate ferric magnesium zinc sulfate flocculant synthesized under the optimal conditions n(Fe):n(Mg):n(Zn):n(Si)=1:1:1:2, reaction temperature at 30 °C, reaction time for 30 min, and pH 2.0 had a deoiling rate of 83.11% to oily sludge.

3.3. Structural characterization of copolymers

3.3.1. Infrared spectroscopy analysis of copolymers

It can be seen from the Fig. 3 that polysilic acid PSi and polysilicate ferric magnesium zinc flocculant PSFMZ have a wide range of characteristic absorption peaks of -OH at 3450.46 cm^{-1}. At 2083.17 cm^{-1} was the absorption peak of the silica hydroxyl complex Si-O-H, at 1644.85 cm^{-1} was the bending vibration absorption peak of the hydroxyl complex H-O-H, and at 1121.49 cm^{-1} were the absorption peaks of the stretching vibration of the Si-O group. Compared with polysilic acid PSi, the peak area and peak strength of -OH, Si-O-H, H-O-H and Si-O bond were all enhanced of PSFMZ spectrum. Since the metal salts were added to the polysilic acid, a variety of hydrolysis products were formed in the solution, and the content of the hydroxyl group and the hydroxyl group bond increased, increasing its peak strength. The metallic ions and hydroxyl oxygen in the PSi simultaneously undergone hydroxyl bridge polymerization to produce high-charge complex ions with different degree of polymerization, which enhanced the binding strength of silica bonds (Xu et al., 2015). In addition, at 1186.91 cm^{-1} was the Si-O-Fe group absorption peak, and the absorption peak at 971.02 cm^{-1} was the characteristic absorption peak of Si-O-Zn. The absorption peak appearing near 611.21 $cm^{-1}$was the stretching vibration absorption peak generated by Si-O-Mg group and M(metal)-O（Mg-O, Zn-O or Fe-O).

Therefore, the flocculant introduced by metal salt was not simply mixed, but the metal salt chemically bonded with PSi to form complex chemical bonds of Si-O-Zn, Si-O-Mg and Si-O-Fe.

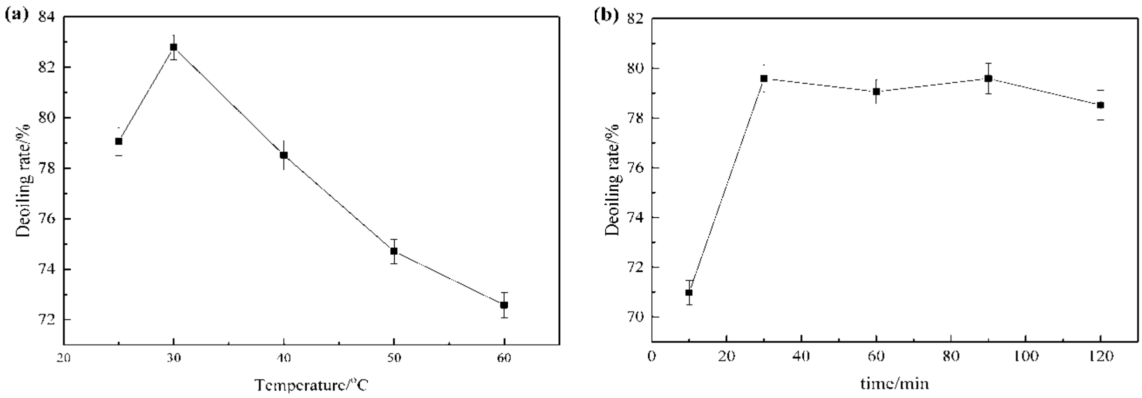

Fig. 2. Effect of a-the synthesis reaction temperature, b-the synthesis reaction time on deoiling rate

Table 1. Orthogonal test results

Serial number	*n(Fe+Mg):n(Si)*	*n(Fe):n(Mg)*	*Reaction temperature (ºC)*	*n(Zn):n(Si)*	*Deoiling rate (%)*
1	1:2	1:1.5	25	1:1	77.38
2	1:2	1:1	30	2:1	72.58
3	1:2	2:1	35	3:1	74.18
4	1:1	1:1.5	35	2:1	75.25
5	1:1	1:1	25	3:1	73.12
6	1:1	2:1	30	1:1	74.71
7	2:1	1:1.5	30	3:1	81.72
8	2:1	1:1	35	1:1	72.05
9	2:1	2:1	25	2:1	70.98
K_1	74.71	78.12	73.83	74.71	
K_2	74.36	72.58	76.34	72.94	
K_3	74.92	73.29	73.83	76.34	
R	0.56	5.54	2.51	3.40	

These findings indicated that in the presence of Psi, the coordination bond formed by metal salts and hydroxyl oxygen in PSi can inhibit the precipitation of the metal-element hydroxide on one hand and slow down the further polymerization of PSi itself on the other. Furthermore, water molecules in the flocculant participated in some complexation reactions with other molecules (Li et al., 2013b).

It can be proved that Fe^{3+}, Mg^{2+}, and Zn^{2+} in the flocculant do not exist as ions alone in the flocculant, but participate in the complexation reaction. Metallic ions were hydroxyl bridged with active silicoxy bonds in activated polysilicate, and new polysilicate ferric magnesium zinc macromolecule polymer were formed by complexing, so the prepared polysilicic metal salt flocculant is bonded and polymerized. Through a series of chemical bond polymers, the components were complexed together, and the efficient flocculation was generated by the adsorption bridging, electric neutralization and roll-sweep net catching after they combine with each other (Moussas and Zouboulis, 2008). It can be inferred from the above analysis that the synthesized polyferric magnesium zinc silicate sulfate is the required target product.

3.3.2. XRD analysis of copolymers

It can be seen from the Fig. 4 that multiple crystal phase diffraction peaks appeared in PSi of polysilicic acid at 15°–40° in 2 thetas, which are crystal diffraction peaks of salts such as Na2SO4 and Na2SiO3, indicating that multiple metal salt crystal phases exist in the amorphous structure of PSi. Compared with PSi, the peak strength of PSFMZ of polysilicate magnesium iron sulfate zinc decreases and the peak width increases, and three crystal packets are generated at 15°–30°.

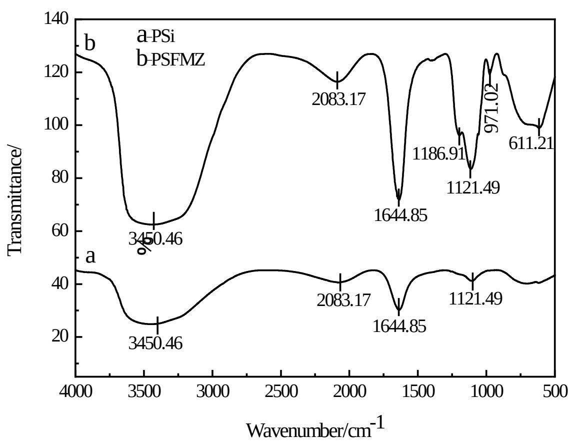

Fig. 3. Infrared spectrum of copolymers

It indicated that Fe^{3+}, Mg^{2+}, Zn^{2+} and SO_4^{2-} have all participated in the reaction and complexed with chain and ring end group hydroxyl of activated silicic acid to form a copolymer with amorphous structure (Zhang et al., 2009). Meanwhile, there are no diffraction peaks of $Fe_2(SO_4)_3$, Fe_2O_3, $Fe(OH)_3$, Na_2SO_4, Na_2SiO_3, SiO_2, $MgSO_4$, $ZnSO_4$ and other salt substances, indicating that the polymerization reaction between iron salt, magnesium salt, zinc salt and silicon salt generated Si-O-Zn, Si-O-Mg, Si-O-Fe and other new structural units, and there were multiple diffraction peaks representing polycrystalline phase coexistence (Liu et al., 2017).

Based on the analyses mentioned above, it can be inferred that metallic ions were hydroxyl bridged with active silica bonds and produce a new silica magnesium zinc macromolecule copolymer. The ions were either adsorbed and adhered to the surface of polysilicic acid, or combined with it by condensation and coordination to connect polysilicic acid into macromolecular polymers after adding iron salt, magnesium salt and zinc salt. Therefore, polysilicate ferric magnesium zinc can play a better role in bridging and sweeping when flocculating (Tang et al., 2019). After pyrolysis centrifuge treatment, the oil content of oily sludge decreased greatly.

3.4. Application of copolymer as flocculant in the thermal washing of oily sludge

3.4.1. Optimal dosage of flocculant

The same amount of oily sludge was treated to investigate the effect of flocculant dosage addition on the deoiling rate of oily sludge, and the results are shown in Fig. 5a. With the addition of flocculant, the deoiling rate of oily sludge initially increased and then decreased, reaching the maximum value of 82.79% when the dosage was 40 mg/L. When the dosage was <40 mg/L, the action of flocculant was insufficient and the deoiling effect was undesirable. When the dosage of flocculant was >40 mg/L, the sludge particles were surrounded by flocculant, which was not conducive to the adsorption bridging and netting of flocculant with the colloidal, resulting in decreased flocculent effect.

The effect decreased with further increased flocculant dosage, which was also a waste of flocculant. Accordingly, the dosage of 40 mg/L was deemed optimal.

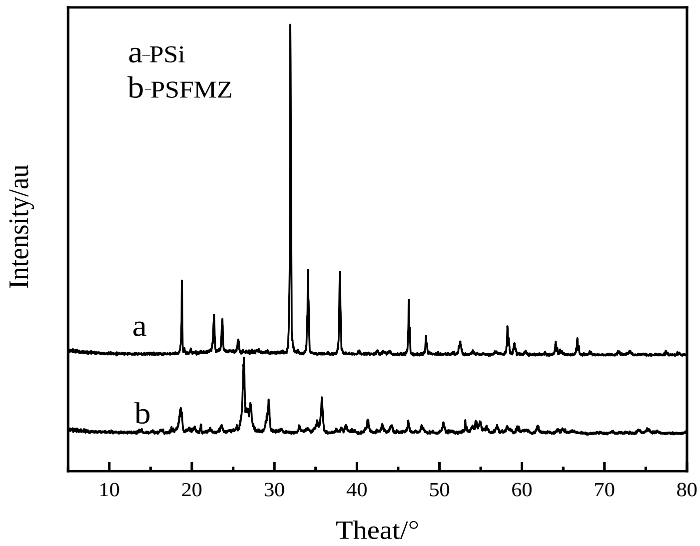

Fig. 4. X-ray diffraction diagrams of copolymers

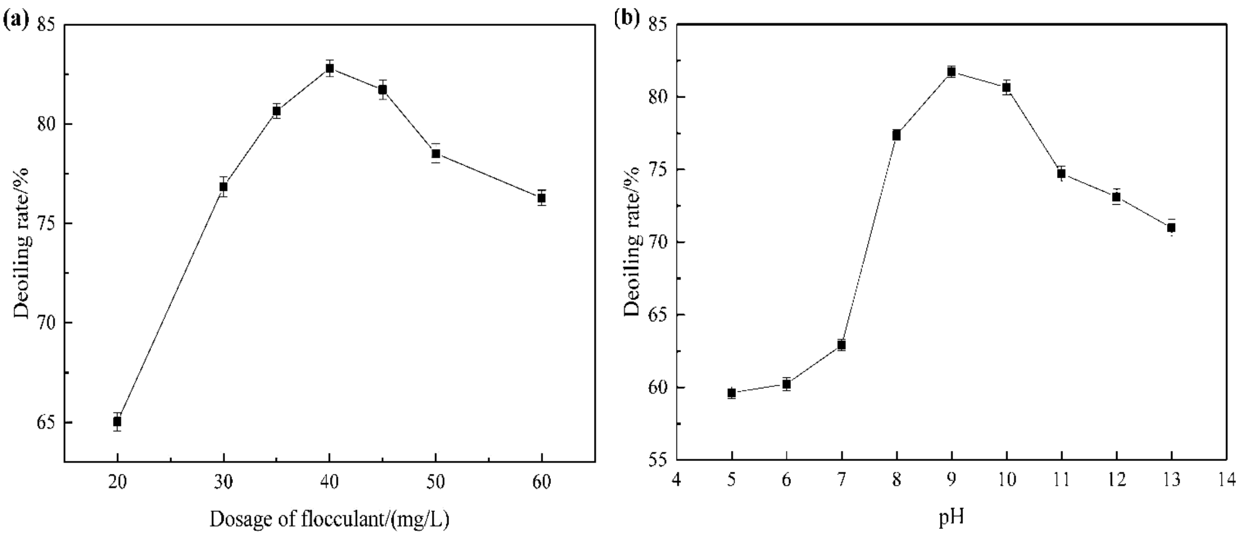

Fig. 5. Effect of (a) flocculant-dosage added, (b) pH on deoiling rate

3.4.2. Effect of pH on deoiling effect

Under different pH values, the deoiling rate of oily sludge of the same amount was investigated to determine the optimal pH, and the results are shown in Fig. 5b. The flocculant agent polysilicate ferric magnesium zinc showed good flocculent effect in the alkaline range. The pH of oily sludge greatly influenced the action of flocculant, and its value directly affected the main forms of iron, magnesium, and zinc while hydrolyzing and polymerizing (Zeng and Park, 2009).

At low pH, Zn hydrolyzed to form oligomers with weak adsorption capacity; when the pH was between 8 and 10, iron, magnesium, and zinc were hydrolyzed to form mononuclear and multinuclear hydroxyl complexed ions, which had electrical neutralization ability. Besides, the Psi had a strong adsorption bridging effect because of its polymer structure. This structure contributed to the optimal flocculent effect of polysilicate ferric magnesium zinc. With further increased pH, the flocculent effect worsened. Thus, pH 9 flocculant polysilicate ferric magnesium zinc was deemed optimal.

3.4.3. Comparison of effects with other flocculants

Two kinds of common flocculants and an on-site flocculant were compared with the experimentally synthesized flocculant. Oily sludge was treated with thermal washing with the deoiling rate as the indicator. The results of comparison are shown in Fig. 6. The deoiling effect of synthesized flocculant reached the effect of others and was even slightly higher, reaching a deoiling rate of 82.79%. Thus, it can be used as the flocculant to treat oily sludge in oil field when using thermal washing.

3.5. Characteristics analysis of oily sludge before and after treatment and mechanism of flocculant

3.5.1. Thermal analysis of oily sludge before and after treatment

Thermogravimetric (TG) analysis of oily sludge samples before and after thermal washing with flocculant is shown in Fig. 7. It can be seen from Fig. 7 that the oil-bearing sludge after thermal washing treatment with flocculant has a great change in characteristics compared with that before treatment. Within the range of initial temperature to 120°C: the weight loss is slow, mainly due to the volatilization of free water in oily sludge, and the moisture content is reduced, indicating that thermal washing treatment with flocculant removes the free water in oil sludge. Within the range of 120–260°C: rapid weight loss, low boiling point oil volatilization in oil sludge, binding water release of microorganisms inside the cell, resulting in weight loss of oil sludge.

The weight loss rate after flocculant treatment has reached 4.2 %, slightly lower than 5.8 % before thermal washing treatment, which indicates that after treatment of oily sludge, binding water is released and crude oil is removed.

In the range of 260–500°C, the weight loss is severe, and the weight loss rate before treatment is 22.9 %. In view of the increase in temperature, volatile aromatic hydrocarbon organic compounds and heavy oil components in the crude oil are easily decomposed by heat to produce low molecular hydrocarbons, and the weight loss rate after treatment is only 11.1%, which proves that a large amount of crude oil in the oil sludge is removed (Cheng et al., 2018;Liu et al., 2018). Above 500°C: gentle weight loss, which is the thermal decomposition of minerals in sludge and the combustion of fixed carbon.

The results show that crude oil and free water in the oil sludge were largely removed by treatment with thermal washing with polysilicate metal flocculant.

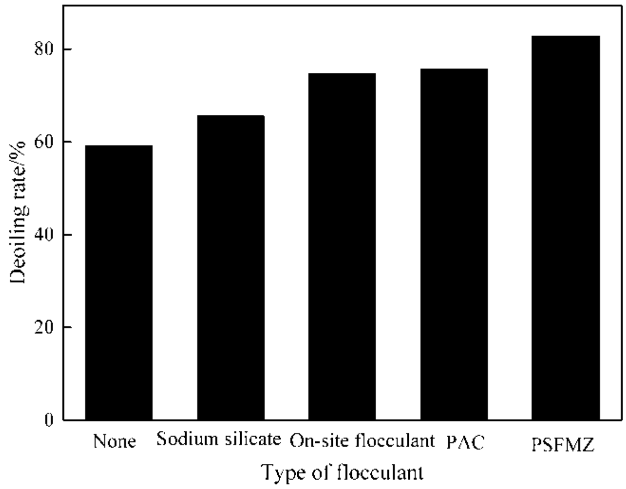

Fig. 6. Effect of compounding among different flocculants and demulsifier 1# in hot washing

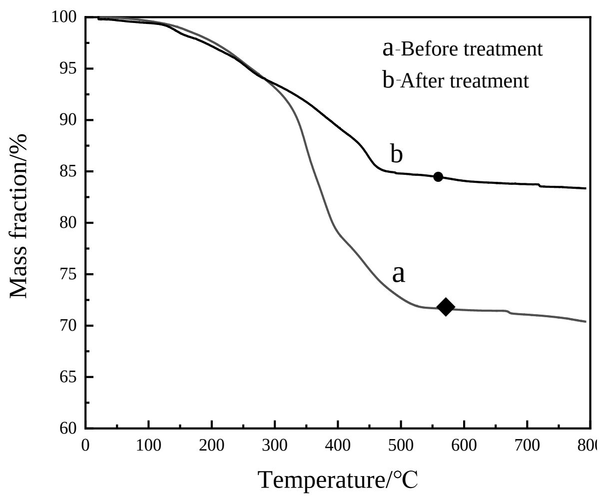

Fig. 7. TG curves of oily sludge before and after treatment

3.5.2. Scanning electron micrographs of oily sludge before and after treatment

A comparison of the scanning electron micrographs of oily sludge before and after adding flocculant is shown in Fig. 8.

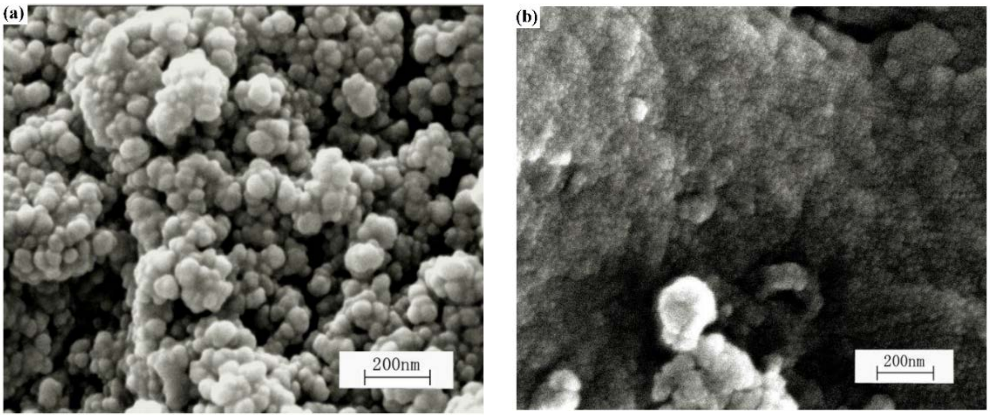

Fig. 8. SEM images of oily sludge (a) before and (b) after treatment

The scanning electron micrographs of oily sludge sample before and after adding flocculant significantly differed. Fig. 8a shows that when a flocculant was not added, the structure of oily sludge was relatively loose, with many pores among sludge particles that were irregularly arranged with no fixed shapes and contained oil and moisture. However, Fig. 8b shows that when a certain amount of flocculant was added for thermal washing, the sludge particles formed a dense mud cake and the pores no longer existed, leading to loss of moisture in the oily sludge and the precipitation and removal of the oil phase to a large extent.

Thus, under the action of flocculant polysilicate ferric magnesium zinc, the electrical neutralization between positive flocculant and negative sludge particles destabilized the negative sludge particles, thereby enabling the absorption bridging and netting of flocculant to absorb more sludge particles and remove more oil molecules from the sludge. Ultimately, the three-phase separation of oil, water, and sludge was achieved (Shi, 2015).

4. Conclusions

(1) The synthesis conditions of flocculant were determined. Through single-factor tests, the optimal synthesis conditions were determined to be as follows: n(Zn):n(Si)=1:2, n(Fe):n(Mg)=1:1, n(Fe+Mg):n(Si)=1:1, reaction temperature at 30 °C, and reaction time for 30 min.

(2) The main and secondary factors affecting the synthesis of flocculants were determined by orthogonal tests. The influence of the factors decreased in the following order: molar ratio of iron to magnesium > molar ratio of zinc to silicon > reaction temperature > amount of iron to magnesium and molar ratio of ferric magnesium to silicon.

(3) When the flocculant dosage was 40 mg/L and pH was 9, the deoiling rate reached 82.79% when oily sludge was treated by thermal washing. The prepared flocculant had better deoiling effect on oily sludge than the other tested flocculants.

(4) Results of scanning electron microscopy showed that when oily sludge was treated by thermal washing, adding polyferric magnesium zinc silicate flocculant can fully exert its adsorption bridging, electric neutralization, and netting function, thereby promoting oil-phase separation from sludge and letting sludge particles flocculate into clusters, which was conducive to settlement and separation.

Acknowledgements

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