Environment Protection Engineering

Vol. 48 2022 No. 4

DOI: 10.37190/epe220403

LANLAN YU (ORCID: 0000-0002-7063-0716)[1]
PENG LIU (ORCID: 0000-0002-7357-7068)[1]
KAI ZHENG (ORCID: 0000-0002-5539-0080)[2]

PREPARATION OF POLYMERIC FERRIC SULFATE –QUATERNARY AMMONIUM CATIONIC-MODIFIED STARCH COMPOSITE FLOCCULANT AND ITS APPLICATION IN OILY SLUDGE TREATMENT

Inorganic-organic compound flocculant of PFS-quaternary ammonium cation-modified starch composite flocculant was prepared by etherification and compounding method, with corn starch, sodium hydroxide (NaOH), cationic etherifying agent 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTMA), polymeric ferric sulfate (PFS) as raw materials. The best preparation conditions were the rate of PFS and quaternary ammonium cation-modified starch mass 4:1, pH of the solution 2, temperature 60 °C, and the reaction time of 4 h. The factors were ranked according to the influence degree as follows: mass ratio > reaction time > pH > temperature. The flocculant prepared under optimal preparation conditions was applied to the treatment of oily sludge in the oil field. When pH of the oily sludge–flocculant mixture was 7 and the dosage at 110 mg/dm^3, the deoiling rate of the oily sludge reached 82.25%, which was an effective conditioning flocculant for oily sludge. SEM analysis showed that the mechanisms of flocculant were mainly net catching and adsorption bridging action. Thermogravimetry (TG) and energy dispersive spectroscopy (EDS) analyses showed that crude oil and bound water were removed by the composite flocculant.

1. INTRODUCTION

With the increasing exploitation of petroleum and natural gas, the output of oily sludge also increases. The treatment of oily sludge mainly involves sludge conditioning by adding high-efficient and appropriate flocculant [1–3]. Flocculants mainly include

[1]College of Chemistry and Chemical Engineering, Northeast Petroleum University, Daqing 163318, Heilongjiang Province, China, corresponding author L. Yu, email address: yxskcn@sina.com

[2]The No. 2 Petroleum Production of Daqing Oil Field, Daqing 163414, Heilongjiang Province, China.

inorganic, organic and microbial flocculants [4, 5]. Some researchers use organic flocculants such as polyacrylamide, alkyl benzene sulfonate, and alkyl phenol ether and inorganic flocculants such as silicate, iron salt and aluminum salt in oily sludge conditioning to promote the effective deoiling of oily sludge to maximise the recovery of crude oil [6].

Traditional flocculant causes extensive corrosion to the equipment and results in high concentrations and specific weights of residual heavy metals. These disadvantages are becoming increasingly obvious in production. Starch is a natural polymer compound, which is non-toxic, pollution-free, and cheap. It has high selectivity, thus attracting high attention it has been widely used [7]. Starch has a wide range of sources, including potato, wheat, and corn. At present, a breakthrough has been made in synthetic starch. The sources of starch are diverse [8]. China is a large, agricultural country with rich starch resources. Starch has diverse polymer structure chains and strong reaction activity on the sub-chain. The required modified starch can be obtained through esterification, oxidation and graft copolymerization, or the composite flocculant can be obtained by compounding starch with inorganic and organic substances [9–11]. Some researchers modified starch via etherification and graft copolymerization for application in sludge dewatering and wastewater treatment, achieving good results [12, 13]. The modified starch, as a natural organic polymer flocculant, has a strong role in capturing and promoting the sedimentation of suspended particles in water [14]. The modified starch flocculant has been widely used in sewage treatment, drinking water purification and for removal of dyes and heavy metals [15–17].

Inorganic-organic composite flocculant can overcome the shortcomings of a single flocculant. It has both characteristics of inorganic and organic polymer flocculant. Inorganic flocculant is characterised by rapid demulsification and strong electric neutralisation ability, while organic polymer flocculant is characterised by obvious absorption bridging effect, rapid floc sedimentation and less flocculant dosage, and it can lower the concentration of residual metal ions and reduce secondary pollution [18]. It is widely used in sewage treatment because of its highly efficient flocculation performance at low temperatures and its wide range of applications [19, 20]. The inorganic-organic modified starch composite flocculant can also be used in sludge dewatering, treatment of oil sand tailings and improvement of oil field recovery [21–23].

In the present study, a cheap and abundant starch was modified and compounded with polymeric ferric sulphate (PFS) flocculant. After chemical modification by cationic etherifying agent (CHPTAM), polyhydroxy starch and PFS formed a composite flocculant. By changing the chemical structure of the inorganic polymer flocculant, the effect of PFS-quaternary ammonium type cationic-modified starch composite flocculant on the oil removal from oily sludge was studied innovatively. The novel inorganic-organic polymer composite flocculant has many advantages such as ease of obtaining raw materials, easy operation, mild reaction, and high application value. The composite flocculant was applied to the centrifugal conditioning treatment of oil-bearing sludge in the oil field for the first time, and good treatment effects were obtained.

2. EXPERIMENTAL

Reagents and instruments. The reagents include corn starch (grade I edible product, No. 2 Branch, Beijing Gusong Economic & Trade Co., Ltd.), polymeric ferric sulfate (PFS), analytical pure, Tianjin Damao Chemical Reagent Factory, cationic etherifying agent 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAM, 69% liquid, Dongying J&M Chemical Co., Ltd.), glacial acetic acid (analytical pure, Shenyang Huadong Reagent Factory), absolute alcohol (analytical pure, Shenyang Huadong Reagent Factory), potassium bromide (analytical pure, Shenyang Huadong Reagent Factory), sodium hydroxide (analytical pure, Shenyang Huadong Reagent Factory), sulfuric acid (analytical pure, Shenyang Huadong Reagent Factory) and oily sludge (Daqing Oil Field, gasoline 93#).

The instruments include HH-S26S digital constant water bath (Jiangsu Jintan Earth Automation Instrument Factory, China), UV-1750 Shimadzu ultraviolet-visible spectrophotometer (Japan), 202-Type constant drying oven (Shanghai Shengqi Instrument Co., Ltd., China), FA-N/JA-N series electronic balance (Shanghai Minqiao Precision Scientific Instrument Co., Ltd., China), DJ1C amplified motor agitator (Jiangsu Jintan Earth Automation Instrument Factory, China), TG18G type electric centrifuge (Jiangsu Hi-Tech Instrument Factory, China), Tensor 27 type Fourier infrared spectrometer (Bruker Spectral Instruments, Germany), JSM-6360LA scanning electron microscope (JEOL, Japan), DuPont 2100 type thermal analyser (Perkin Elmer, USA) and 5000ESCA X-ray photoelectron spectrometer (Bruker Spectral Instruments, Germany).

Properties of oily sludge. Soxhlet-extraction spectrophotometry was adopted to measure oil content. At the wavelength of 420 nm, the standard curve was generated using $93^{\#}$ gasoline as the reference. The corresponding oil content was determined from the standard curve. The oil content of oily sludge was measured before and after treatment with flocculant, and the oil removal efficiency from oily sludge was calculated. The property of water content was determined according to the national standard method for the determination of water content of a water–oil mixed system. After the remaining impurities were filtered, washed, dried, left standing and weighed, the content of mud and sand was obtained.

The oily sludge before and after adding PFS-modified starch composite flocculant was analyzed using scanning electron microscopy, thermal analysis and an X-ray photoelectron spectrometry for EDS analysis to explore the mechanism of composite flocculant action on the oily sludge.

Preparation of composite flocculant. Quaternary ammonium-type cationic-modified starch flocculant was prepared by dissolving 20 g of NaOH in 100 cm^3 of distilled water. NaOH solution and etherifying agent CHPTAM were placed in an ice bath (temperature lower than 10 °C) according to the mass ratio of 3:1, stirred fully and activated for 10 min. Then, 30 g of dry starch was weighed. The activated drug was sprayed on corn starch. The mixture was stirred evenly, allowed to stand for 30 min and air-dried. Water content was less than 5%. Then, the sample was placed in the microwave oven and reacted for 3 min at a power of 300 W. After the reaction, the crude product was obtained and soaked in an ethanol solution containing 20% glacial acetic acid by a mass fraction, and then filtered, washed, and dried. Finally, quaternary ammonium-type cationic starch (CMS) was obtained.

PFS-modified starch composite flocculant was prepared by weighing 1 g of PFS and placing it in 100 cm^3 of distilled water to stir it fully. 1 g of the prepared quaternary ammonium-type cationic starch was transferred into 100 cm^3 of distilled water. It was stirred fully to dissolve it. Then, it was added into a 100 cm^3 flask. The dissolved PFS solution was placed in the flask. After being reacted for some time at a certain temperature, a PFS-modified starch composite flocculant was obtained.

By considering the oil removal efficiency from oily sludge by PFS-quaternary ammonium type cationic-modified starch composite flocculant, the effect of the following parameters was evaluated: the mass ratio PFS:CMS (modified starch) of 1:1, 2:1, 3:1, 4:1 and 5:1; the mixed solution pH of the reaction system (1, 1.5, 2, 2.5, and 3), the temperature of 40, 50, 60, 70, and 80 °C; the reaction time of 1, 2, 3, 4, and 5 h. A single-factor experiment was conducted. At the same experimental conditions, the experiment was repeated thrice.

Based on the single-factor experiment results, by using the oil removal efficiency from oily sludge by the composite flocculant as the index, the corresponding orthogonal table comprising four-factor (mass ratio PFS:CMS, flocculant reaction system pH, temperature, and reaction time) and three-level $L_9(3^4)$ was formulated. Nine groups of experiments were conducted to determine the best process conditions for the composite flocculant.

The functional groups of the composite flocculant products in KBr wafers were analyzed using Fourier infrared spectrometer for structural representation. The scanning wavenumber was in the range of 500–4000 cm^{-1}.

Performance evaluation of composite flocculant. Oily sludge of 5 g was put into a beaker of 100 cm^3 and distilled water of 20 cm^3 was added. The oily sludge was treated with composite flocculants of 60, 90, 110, 140, and 170 mg/dm^3. Adding different concentrations of flocculant into the beaker, stirring at 50 °C for 30 min, and pouring into a centrifuge tube to control centrifuge time for 30 min and centrifuge speed for 3600 rpm. The sediment after bottom treatment was taken to measure its oil content, the oil removal efficiency from oily sludge was calculated, and the optimal dosage of composite flocculant was determined. The experiment was repeated thrice under the same experimental conditions.

A sulfuric acid solution (15 wt. %) was used to adjust the pH of the solution of the oily sludge–flocculant mixture. Oily sludge samples were treated at pH of 5, 6, 7, 8, 9, and 10. The experiment was repeated thrice under the same experimental conditions.

In the treatment of oily sludge under the same conditions, when the optimum dosage was 110 mg/dm^3, and pH of the oily sludge–flocculant mixture was 7, the effect of the prepared PFS-modified starch composite flocculant was compared with the effect of a single flocculant of PFS and quaternary ammonium type cationic starch (CMS) before modification, to observe the treatment effect of oily sludge.

3. RESULTS AND DISCUSSION

3.1. DETECTION OF BASIC PROPERTIES OF OILY SLUDGE

The oily sludge used in the experiment was black and viscous and had a strong volatile pungent odour. It was generally composed of oil in water, water in oil and suspended solid particles. The suspended solids and colloidal particles were emulsified with oil and water to form a relatively stable suspended emulsion glue system, which was very viscous and difficult to settle down [24, 25]. In the oily sludge, the water content measured was 24.58%, the oil content was 13.13%, and the mud content was 59.89%.

3.2. SINGLE-FACTOR EXPERIMENT

Figure 1 shows that when the mass ratio of PFS to cationic-modified starch was 3:1, the oil removal efficiency from oily sludge by composite flocculant reached the maximum. When the mass ratio increased until the dosage of PFS was excessive, the oil removal efficiency did not increase. With the increase of PFS, the oil removal efficiency increased, because iron has a strong affinity for –OH, and it can polymerise with modified cationic starch very quickly to form a polynuclear polymer. In addition, the modified quaternary ammonium cationic starch has a special net structure. The flocculant with complete composite reaction has a strong ability of electric neutralization and strong absorption bridging ability, which can improve the oil removal efficiency from oily sludge and achieve an ideal de-oiling effect. Therefore, the composite flocculant was prepared with a mass ratio PFS:CMS of 3:1.

Figure 2a shows that pH of reaction systems greatly affects the oil removal efficiency from oily sludge. In the preparation of the composite flocculant, considering that the pH of the PFS solution is different from that of the cationic-modified starch solution, the gel was present in the composite process. Therefore, pH should first be adjusted to make it similar for both solutions used and then compound it [26]. In the reaction system of mixed solution at pH 2, the oil removal efficiency from oily sludge reached the highest value, which was 79.59%. Therefore, the composite flocculant was prepared in the reaction system.

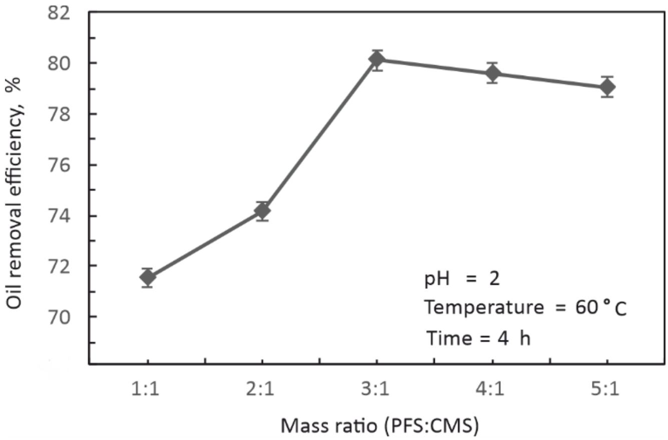

Fig. 1. The effect of mass ratio (PFS:CMS) on the oil removal efficiency (flocculant dosage 90 mg/dm^3, pH of oil sludge–flocculant mixture 7)

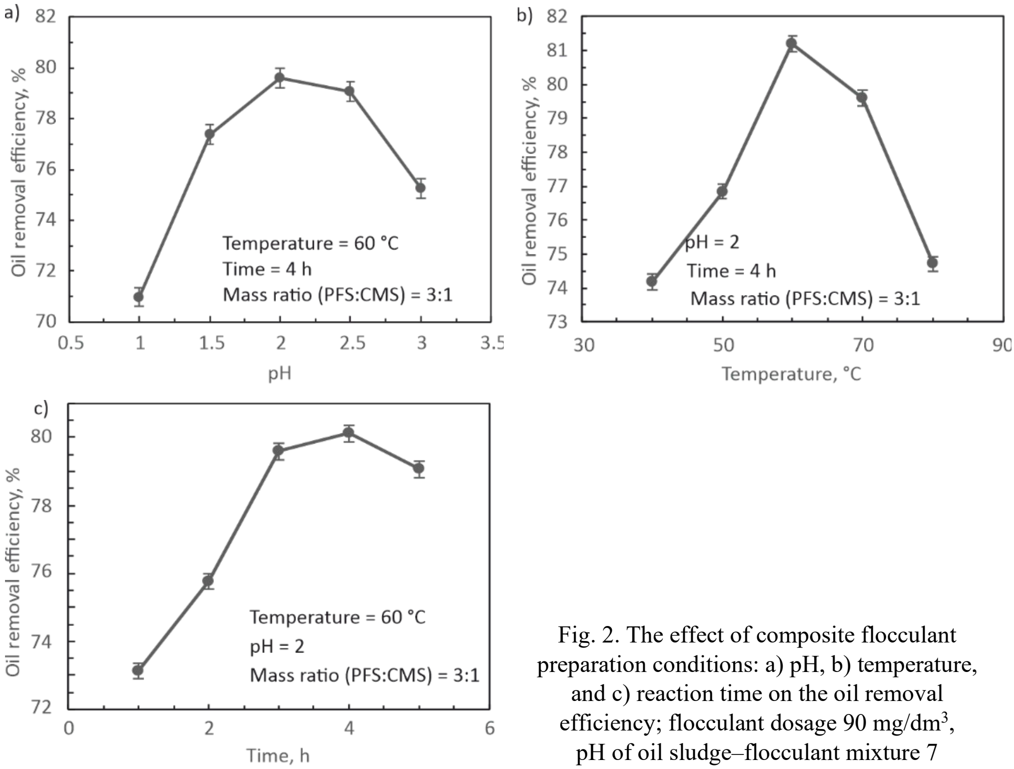

Fig. 2. The effect of composite flocculant preparation conditions: a) pH, b) temperature, and c) reaction time on the oil removal efficiency; flocculant dosage 90 mg/dm^3, pH of oil sludge–flocculant mixture 7

Figure 2b shows that with the increase of the temperature in the course of composite flocculant preparation at 40–60 °C, the oil removal efficiency from oily sludge by the flocculant increased gradually. When the temperature was 60 °C, the oil removal efficiency reached the highest value of 81.19% and then decreased. When the temperature was low, the modified starch can only be compounded with PFS partially, and the reaction was incomplete. As a result, the netting and bridging function of the modified starch skeleton structure could not be fully played through coordination with the rapid sedimentation of PFS. Therefore, the oil removal efficiency was relatively low. When the temperature was too high, the modified starch might lose efficacy, resulting in an incomplete reaction [27]. Therefore, the temperature was set to 60 °C.

Figure 2c shows that when the reaction time of composite flocculant preparation increased from 1 to 4 h, the oil removal efficiency increased gradually. When the reaction time was 4 h, the oil removal efficiency reached the highest value of 80.12%. Upon increasing the reaction time, the oil removal efficiency decreased. Therefore, the reaction time was determined to be 4 h.

3.3. ORTHOGONAL EXPERIMENT

The factor level table of the orthogonal test is formulated according to the single-factor experimental result, as shown in Table 1.

Table 1

Orthogonal experiment results

No.	Mass ratio PFS:CMS	pH	Temperature [°C]	Reaction time [h]	Oil removal efficiency [%]
1	2:1	1.5	50	3	72.58
2		2.0	60	4	74.18
3		2.5	70	5	75.78
4	3:1	1.5	60	5	80.12
5		2.0	70	3	78.52
6		2.5	50	4	76.85
7	4:1	1.5	70	4	79.06
8		2.0	50	5	81.72
9		2.5	60	3	80.65
K_1	74.18	77.25	76.96	77.25	
K_2	78.50	78.14	78.32	76.70	
K_3	80.48	77.76	77.79	79.21	
R	6.3	0.89	0.53	2.51	

K_n represents the average of the sum of the test indicator values corresponding to the n level.

R represents the difference between the maximum and minimum of K_n.

Table 1 shows that the effects of the range *R* of 4 factors rank can be arranged as mass ratio PFS:CMS > reaction time > reaction system pH > temperature. Based on the comprehensive analysis of the single factor result and the values of orthogonal factors, the optimum synthesis conditions are determined as follows: mass ratio PFS:CMS 4:1, pH 2, temperature 60 °C and reaction time 4 h. Under the best conditions, three sets of parallel verification experiments were carried out, and the oil removal efficiency was determined as 82.19, 83.08 and 82.31%, 82.53% on average.

3.4. INFRARED SPECTRUM ANALYSIS OF COMPOSITE FLOCCULANT

The infrared spectrum of the flocculant prepared under the best conditions (Fig. 3) shows an absorption peak at 3443.92 cm^{-1} corresponding to hydrogen bond –OH stretching vibration. A strong peak at 1638.31 cm^{-1} was assigned to Fe–OH bending vibration. The absorption peak at 1252.33 cm^{-1} corresponds to C–N stretching vibration of the quaternary ammonium group, and the absorption peak at 1010.28 cm^{-1} to –C–O–C– stretching vibration.

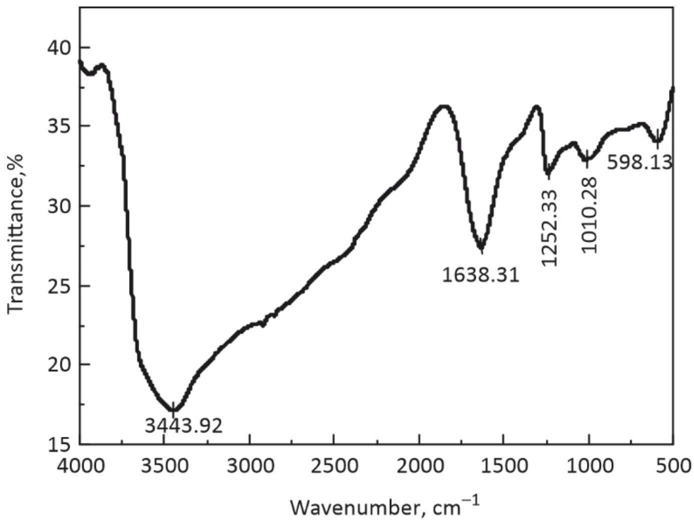

Fig. 3. FTIR spectrum of the compound flocculant

A weak absorption peak at 598.13 cm^{-1} appeared after introducing PFS into the modified starch when part of –OH groups was replaced by oxygen in the modified starch coordinated with ether oxygen bond on the cationic starch under the effect of the hydrogen bond of –OH. Therefore, a simple physical mixture was not formed, but the molecules were connected by chemical bonds. Quaternary ammonium cationic modified starch was etherified, and then reacted with PFS to form a new inorganic-organic composite flocculant.

3.5. TREATMENT OF OILY SLUDGE WITH COMPOSITE FLOCCULANT

Upon increasing the dosage of the flocculant, the oil removal efficiency from oily sludge increased first and then decreased (Fig. 4). When the flocculant dosage increased to 110 mg/dm^3, the oil removal efficiency reached a maximum of 82.25%.

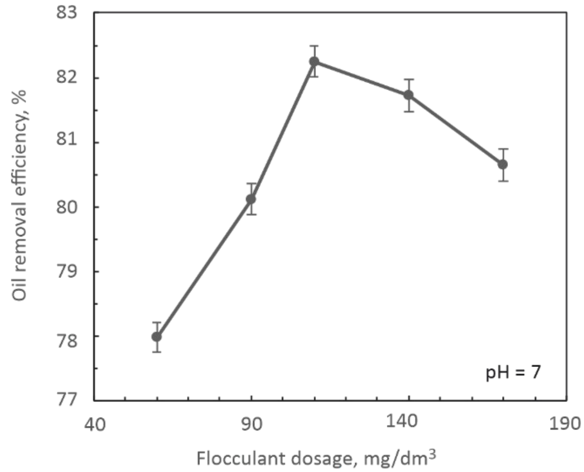

Fig. 4. The effect of composite flocculant dosage on the oil removal efficiency; PFS:CMS 4:1, pH 2, temperature 60 °C, and reaction time 4 h

By etherification, the cationic groups of the quaternary ammonium group were introduced into the starch molecule, which made the molecular chain increase. The cationic surface had a positive charge, and the complex iron salt also enhanced the positive charge, which further enhanced the deoiling ability of the flocculant. The composite flocculant has a larger molecular weight, longer molecular chain and more chances to contact and collide oil in oily sludge, thus increasing the number of oil molecules adsorbed and the oil removal efficiency as well. Therefore, the effect can be achieved by adding a small amount of reagent. The composite flocculant prepared in the experiment can achieve an ideal deoiling result with the use of its high-efficiency coordination effects such as adsorption bridging, netting, electric neutralization, and flocculation. An appropriate amount of flocculant was added to make oily sludge conditioning, which is helpful to improve the oil removal efficiency. However, the excessive dosage would reduce the oil removal efficiency. The experimental result shows that the optimal flocculant dosage was 110 mg/dm^3.

At pH 7 of the oily sludge–flocculant mixture, the oil removal efficiency from oily sludge was the highest (Fig. 5). At pH < 7, the oil removal efficiency was relatively low because cationic-modified starch has a good flocculation effect on the negatively charged inorganic or organic suspension. However, the surface of the oil phase was negatively charged in this experiment. In the acidic system, the oily sludge particles are wrapped by opposite charges. Considering the positive charge, the electrostatic repulsion between oil phases is enhanced, which is not conducive to the agglomeration and precipitation of particles. At pH > 7, the oil removal efficiency from oily sludge is also low. Consequently, in the alkaline system, the electronegativity of oily sludge particles increases. At the same time, the positively charged group in the flocculant will be partially neutralised and no longer interact with oily sludge particles, and the flocculation effect decreases. Therefore, the optimum application system is at pH 7.

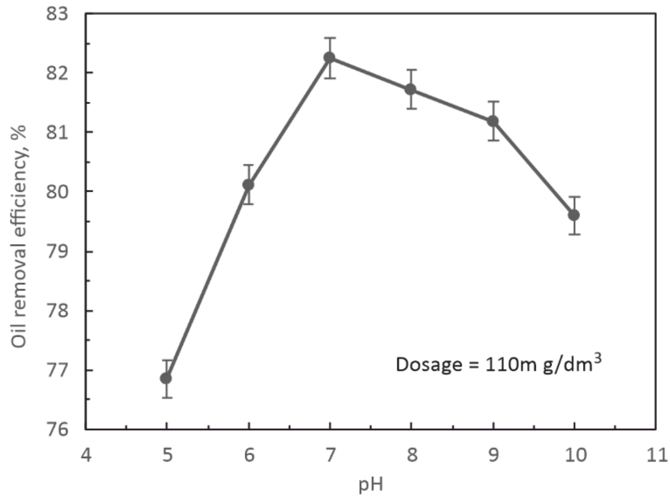

Fig. 5. The effect of oily sludge pH on the oil removal efficiency; PFS:CMS 4:1, pH 2, temperature 60 °C, and reaction time 4 h

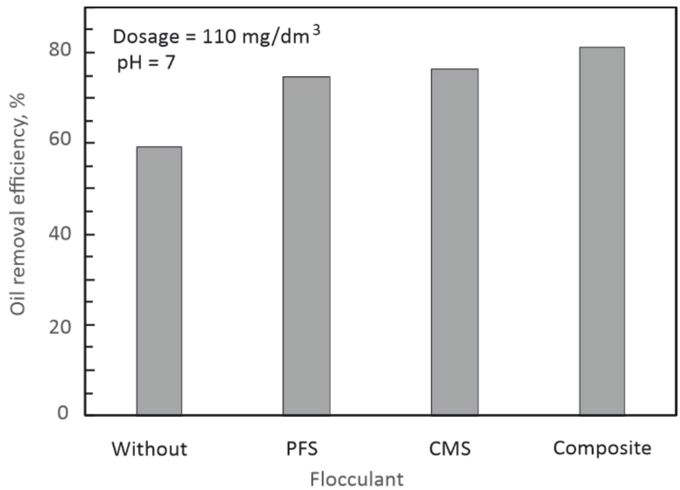

Fig. 6. The effect of flocculant type on the oil removal efficiency

By considering the oil removal efficiency as the index, the deoiling effect of PFS--modified starch composite flocculant was compared with that of the single flocculant of polymeric ferric sulphate (PFS) and CMS before composite. The experimental results are shown in Fig. 6, the inorganic-organic composite flocculant has higher oil removal efficiency from oily sludge and better flocculation and de-oiling effect than the single inorganic flocculant PFS and quaternary ammonium cationic-modified starch flocculant CMS. The composite flocculant prepared in the experiment as PFS-quaternary ammonium cationic-modified starch can be used as a flocculant for the treatment of oily sludge. The results confirm that the composite flocculant has a better application effect than the single flocculant, The research and application of composite flocculants are the development direction in the future.

3.6. MECHANISM OF THE OIL REMOVAL FROM OILY SLUDGE AFTER COMPOSITE FLOCCULANT ADDING

Figure 7 shows the microstructure of oily sludge before and after treatment with composite flocculant. The oily sludge before treatment is loose and granular, with many pores between particles that are irregularly arranged, and its oil and water contents are high. After treatment, sludge particles aggregate to form dense mud cake with small pores. Their intrinsic viscosity and molecular number increased, and their adsorption bridging performance was remarkably improved.

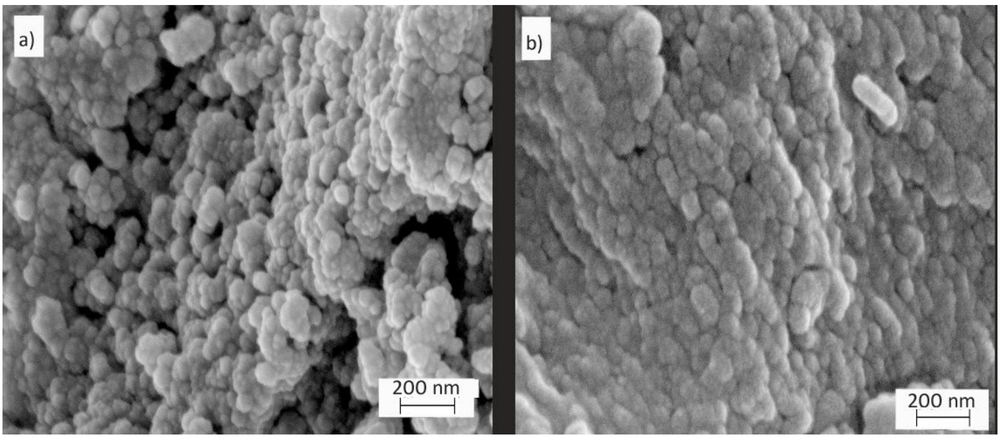

Fig. 7. SEM images of oily sludge before (a) and after adding flocculant (b)

This result shows that a remarkable amount of water and oil phases in oily sludge are after sludge conditioning and flocculation. Under the function of flocculant, the oil phase molecules in oily sludge can be removed from the sludge surface to the greatest extent through adsorption bridging and netting oil phase particles, and high oil removal efficiency and ideal de-oiling effect are achieved.

3.7. THERMAL ANALYSIS OF OILY SLUDGE BEFORE AND AFTER ADDING OF COMPOSITE FLOCCULANT

The oily sludge after treatment with composite flocculant was greatly changed compared with that before treatment (Fig. 8). The initial temperature was 180 °C, and the weight loss was slow. This stage involved the volatilization stage of free water in oily sludge. After treatment, the water content of the oily sludge decreased, indicating that free water was removed. At 180–320 °C, the weight loss was fast due to heat volatilization of light oil and the removal of bound water in microorganisms. This indicates that some crude oil and bound water in oily sludge were removed after adding a flocculant for conditioning.

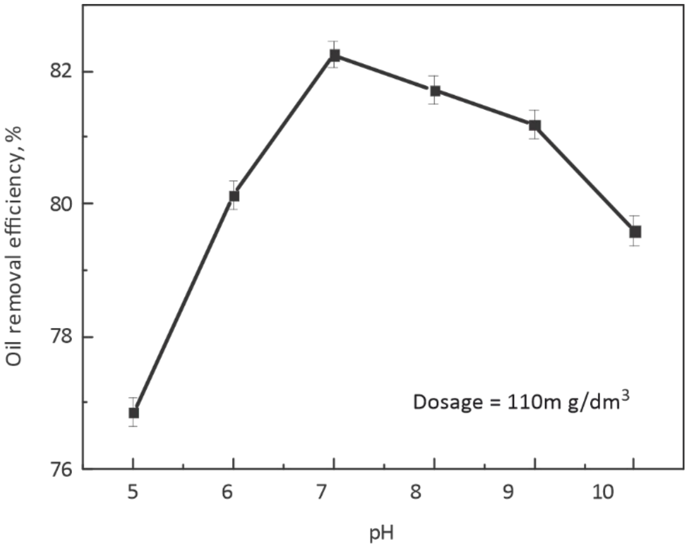

Fig. 8. TG curves of oily sludge

At 320–550 °C, the weight loss was severe. With the increase in temperature, the heavy oil and a large amount of volatile organic compounds were decomposed, thus accelerating the weight loss of the sludge. After adding flocculant treatment, a large amount of crude oil was removed. Above 550 °C, the weight loss was slow, and at this stage, fixed carbon was burnt, and some minerals decomposed thermally.

3.8. EDS ANALYSIS OF OILY SLUDGE BEFORE AND AFTER ADDING COMPOSITE FLOCCULANT

X-ray photoelectron spectroscopy was used to analyze the elemental composition before and after the treatment of oily sludge with PFS–quaternary ammonium cationic starch composite flocculant. The results are shown in Table 2 and Fig. 9. It could be seen that carbon was greatly reduced after treatment because the oil was separated from the oily sludge when the flocculant was added.

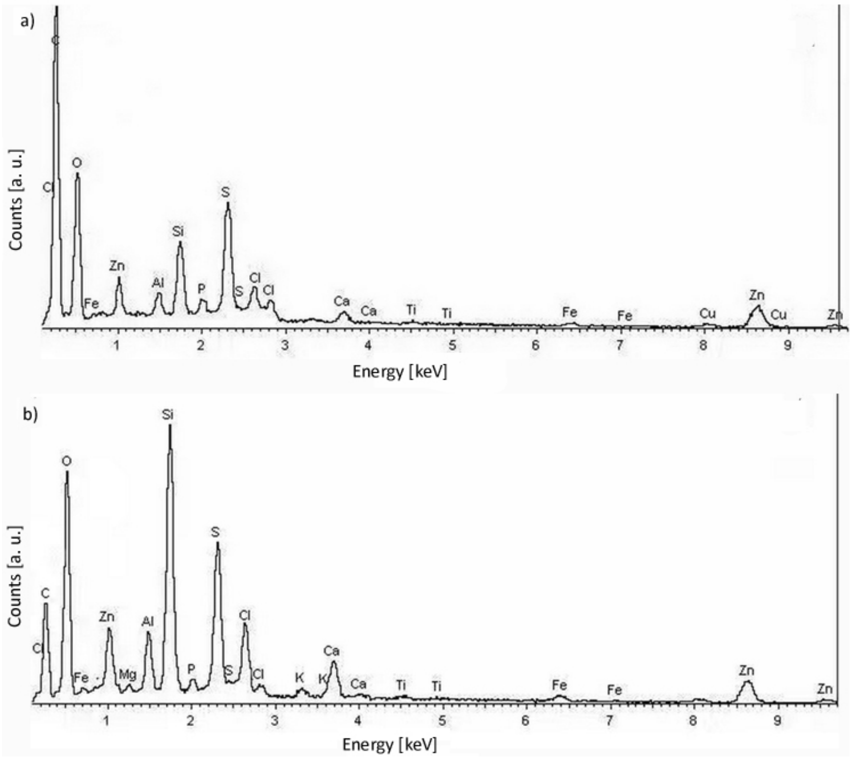

Fig. 9. EDS images of oily sludge before (a) and after adding flocculant (b)

Table 2

Elemental content in oily sludge
before and after treatment [wt. %]

Element	Before	After	Element	Before	After
C	48.2	28.6	Ca	1.1	4.6
O	28.5	28.4	Mg	0.2	2.3
Si	8.2	15.1	K	0.5	2.5
Fe	3.1	5.4	S	2.4	2.5
Al	2.2	3.9	P	2.5	2.6
Zn	3.1	4.1			

The main element of sediment was silicon, as well as other inorganic salts, such as magnesium salt, carbonate, etc. After the oily sludge was treated, a large amount of crude oil was removed from the oily sludge, leaving most of it as inorganic salts and a small amount of organic matter. Thus, the flocculant was characterized by a good separation degree of oily sludge and less oil content in sludge after treatment.

4. CONCLUSIONS

In the oily sludge treatment at pH = 7, 110 mg/dm^3 composite flocculant was applied. The oil removal efficiency was 82.25%, and this condition promoted the deoiling effect of oily sludge. PFS-quaternary ammonium cationic-modified starch composite flocculant was added to make oily sludge conditioning. The comparison and analysis of the SEM images showed that in oily sludge conditioning, the synergistic effect of strong charge neutrality and bridging and netting of long network chain macromolecules made the oil phase separate from oily sludge. After treatment, the sludge particles were closely arranged, and the water and oil phases were removed. Thermal and EDS analysis results show that the crude oil and bound water can be removed from oily sludge after treatment with composite flocculant.

REFERENCES

[1] ALTIERI G., DI RENZO G.C., GENOVESE F., *Horizontal centrifuge with screw conveyor (decanter): Optimization of oil/water levels and differential speed during olive oil extraction*, J. Food Eng., 2013, 119 (3), 561–572. DOI: 10.1016/j.jfoodeng.2013.06.033.

[2] CHEN Y., TIAN G., LIANG Y., ZHANG Q., LI J., *Ammonium persulfate-initiated polymerization of cationic starch-grafted-cationic polyacrylamide flocculant for the enhanced flocculation of oil sludge suspension*, J. Disp. Sci. Technol., 2019, 40 (9), 1246–1255. DOI: 10.1080/01932691.2018.1505526.

[3] TIAN G., CHEN Y., LIANG Y., GAO Y., *Synthesis of nanocomposites from cationic polyacrylamide and modified carbon black: Application as flocculants for oily sludge suspension*, Appl. Organomet. Chem., 2019, 33 (1), e4620. DOI: 10.1002/aoc.4620.

[4] GERDE J.A., YAO L., LIU J., WEN Z., WANG T., *Microalgae flocculation, impact of flocculant type, algae species and cell concentration*, Algal Res., 2015, 3, 30–35. DOI: 10.1016/j.algal.2013.11.015.

[5] MIYAHARA M., SAKAMOTO A., KOUZUMA A., WATANABE K., *Poly iron sulfate flocculant as an effective additive for improving the performance of microbial fuel cells*, Biores. Technol., 2016, 21, 331–335. DOI: 10.1016/j.biortech.2016.09.046.

[6] CHIRWA E.M.N., MAMPHOLO T., FAYEMIWO O., *Biosurfactants as demulsifying agents for oil recovery from oily sludge performance evaluation*, Water Sci. Technol., 2013, 67 (12), 2875–2881. DOI: 10.2166 /wst.2013.207.

[7] CHANG Y., HU Z., WANG P., ZHOU J., *Synthesis, characterization, and flocculation performance of cationic starch nanoparticles*, Carb. Polym., 2021, 269, 118337. DOI: 10.1016/J.CARBPOL.2021.118337.

[8] MOHSENI A., FAN L., RODDICK F., LI H., GAO Y., LIU Z., *Cationic starch: an effective flocculant for separating algal biomass from wastewater RO concentrate treated by microalgae*, J. Appl. Phycol., 2021, 33, 917–928. DOI: 10.1007/S10811-020-02348-1.

[9] LIN Q., LIANG R., ZHONG F., YE A., SINGH H., *Interactions between octenyl-succinic-anhydride-modified starches and calcium in oil-in-water emulsions*, Food Hydrocol., 2018, 77, 30–39. DOI: 10.1016 /j.foodhyd.2017.08.034.

[10] SHARMA M., AGUADO R., MURTINHO D., VALENTE A.J.M., DE SOUSA A.P.M., FERREIRA P.J.T., *A review on cationic starch and nanocellulose as paper coating components*, Int. J. Biolog. Macromol., 2020, 162, 578–598. DOI: 10.1016/j.ijbiomac.2020.06.131.

[11] WEI C., QIANG L., HUANG Y., ZHU X., XIA A., ZHU X., *Simultaneous enhancing the sedimentation and adsorption performance of Chlorella vulgaris with montmorillonite modified cationic starch*, Biochem. Eng. J., 2020, 164, 107785. DOI: 10.1016/j.bej.2020.107785.

[12] LIU M., ZHU P., YANG W., CHEN Y., LAN J., REN S., *Synthesis and evaluation of a novel inorganic-organic composite flocculant., consisting of chitosan and poly-ferric cerium silicate*, J. Chem. Technol. Biotechnol., 2019, 94 (1), 79–87. DOI: 10.1002/jctb.5747.

[13] HU P., SHEN S., YANG H., *Evaluation of hydrophobically associating cationic starch-based flocculants in sludge dewatering*, Sci. Rep., 2021, 11, 11819. DOI: 10.1038/S41598-021-91323-Y.

[14] LI X., YANG B., LI F., ZHENG H., ZENG G., WU P., *Research progress of natural polymers in wastewater treatment*, Mini-Rev. Org. Chem., 2019, 16 (4), 335–344. DOI: 10.2174/1570193X15666180326120151.

[15] PAL S., MAL D., SINGH R.P., *Cationic starch: An effective flocculating agent*, Carbohydr. Pol., 2014, 59 (4), 417–423. DOI: 10.1016/j.carbpol.2004.06.047.

[16] YANG Z., YUAN B., HUANG X., ZHOU J., CAI J., YANG H., LI A., CHENG R., *Evaluation of the flocculation performance of carboxymethyl chitosan-graft-polyacrylamide. A novel amphoteric chemically bonded composite flocculant*, Water Res., 2012, 46 (1), 107–114. DOI: 10.1016/j.watres.2011.10.024.

[17] LIU W., MA J., PANG H., WANG Z., YAO X., *Synthesis of a polyamine-modified starch flocculant and its application*, Iran Pol. J., 2021, 30, 675–683. DOI: 10.1007/S13726-021-00921-0.

[18] YANG Z., SHANG Y., LU Y., CHEN Y., HUANG X., CHEN A., JIANG Y., GU W., QIAN X., YANG H., CHENG R., *Flocculation properties of biodegradable amphoteric chitosan-based flocculants*, Chem. Eng. J., 2011, 172 (1), 287–295. DOI: 10.1016/j.cej.2011.05.106.

[19] LIU L., HE A., LI X., *Study on the flocculating performance of modified starches*, Adv. Mater. Res., 2014, 955–959, 532–536. DOI: 10.4028/www.scientific.net/AMR.955-959.532.

[20] NNAJI P.C., OKOLO B.I., MENKITI M.C., *Nephelometric performance evaluation of oxidized starch in the treatment of coal washery effluent*, Nat. Res., 2014, 5 (3), 79–89. DOI: 10.4236/nr.2014.53009.

[21] LIU J., JIA S., XU L., ZHU F., SHAN R., LIU Y., SUN Z., *Application of composite degradable modified starch-based flocculant on dewatering and recycling properties*, Water Sci. Technol., 2020, 82 (10), 2051–2061. DOI: 10.2166/WST.2020.464.

[22] DAI C., YANG S., WU X., LIU Y., PENG D., WANG K., WU Y., *Investigation on polymer reutilization mechanism of salt-tolerant modified starch on offshore oilfield*, En. Fuels, 2016, 30 (7), 5585–5592. DOI: 10.1021/acs.energyfuels.6b00840.

[23] ZHAO N., BITAR H.A., ZHU Y., XU Y., SHI Z., *Flocculation performance of anionic starch in oil sand tailings*, Water Sci. Technol., 2018, 78 (5–6), 1268–1275. DOI: 10.2166/wst.2018.405.

[24] ZHANG Z.Y., LI L.H., ZHANG J.S., MA C., WU X., *Solidification of oily sludge*, Petr. Sci. Technol., 2018, 36 (4), 273–279. DOI: 10.1080/10916466.2017.1419482.

[25] LI C., ZHAO Y., GAN Z., NIE M., *Method of smoldering combustion for refinery oil sludge treatment*, J. Hazard. Mater., 2021, 409, 124995. DOI: 10.1016/J.JHAZMAT.2020.124995.

[26] LI Y., ZHANG H., WANG X., MA J., LIAN L., LOU D., *Preparation and flocculation performance of polysilicate aluminum-cationic starch composite flocculant*, Water Air Soil Poll., 2020, 231 (7), 1–7. DOI: 10.1007/s11270-020-04711-x.

[27] CHU Z., GONG Z., WANG Z., ZHANG H., LIU L., WU J., WANG J., *Experimental study on gasification of oil sludge with steam and its char characteristic*, J. Hazard. Mater., 2021, 416, 125713. DOI: 10.1016 /J.JHAZMAT.2021.125713.