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"Gheorghe Asachi" Technical University of Iasi, Romania

REMOVAL OF OIL FROM OILY SLUDGE BY MICRO-EMULSION METHOD

Lanlan Yu[1*], Shilong Xing[1], Chunhong Nie[1], Kai Zheng[2]

[1]*College of Chemistry and Chemical Engineering, Northeast Petroleum University, Daqing 163318, Heilongjiang Province, China*
[2]*The No.2 Petroleum Production of Daqing Oil Field, Daqing 163414, Heilongjiang Province, China*

Abstract

At present, the production of oily sludge is huge, and the micro-emulsion method can effectively separate crude oil and water from the oily sludge by reducing the interfacial tension between oil and cement. In this paper, the micro-emulsion was prepared by using surfactants, such as sodium dodecyl benzene sulfonate (SDBS), cetyltrimethylammonium chloride (CTAB), sodium dodecyl sulfonate (SDS), sodium cetyl sulfate (CAS), and alkylphenol polyoxyethylene ether (OP-10) as the main raw materials. The influence of the following on the deoiling effect were investigated: amount of micro-emulsion added, type and formulation of the surfactant; and treatment temperature, centrifugation period and speed. Results showed that the micro-emulsion prepared from SDBS and OP-10 had the best deoiling effect on oily sludge. Under 45°C treatment temperature, 10 min centrifugation period and 3600 r/min centrifugation speed, the deoiling rate reached 97.35%, when the micro-emulsion was compounded at a ratio of 2:1. Moreover, the deoiling effect was better than that of other surfactants and composite surfactants. The surfactant type and micro-emulsion treatment temperature considerably influenced the deoiling effect. The micro-emulsion conditioning and centrifugation treatment could effectively separate the three phases (oil, water, and mud). Thermal analysis and SEM microscopic analysis showed that crude oil and water in the oil sludge were largely removed by treatment with quenching and tempering centrifugation with microemulsion.

Keywords: deoiling, micro-emulsion, oily sludge quenching, tempering-mechanical centrifugation

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1. Introduction

Oily sludge is solid oily waste generated during oil extraction, storage, transportation, refining, and treatment of oily sewage. It is a major pollutant in the petrochemical industry (Guangji et al., 2013), and its production increases with the development of oil and natural gas (Bingcheng et al., 2017; Egazar'yants et al., 2015; Ju et al., 2013; Shahi et al., 2017). According to a recent estimate of global crude oil production, 20 million tons of oily sludge is produced each year (He et al., 2017; Ping et al., 2012). Oily sludge is listed as solid waste in the National Hazardous Waste List (Wanfu et al., 2012). Its danger and potential development and utilization value as an energy substance have received increasing attention (Bingcheng et al., 2017). The various kinds of harmful substances contained in oily sludge, such as petroleum hydrocarbons, benzene, naphthalene, and phenanthrene, cause atmospheric, soil, and groundwater pollution, seriously threaten human health if not handled properly (Fan et al., 2013; Hong and Sanglan, 2011; Vasudevan and Rajaram, 2001). The reasonable recycling of oil can allow resource utilization and the reduction of pollution, as well as benefit the resources themselves and the environment. Extraction (Gumerov et al., 2017), chemical cleaning (Jiling et al., 2017; Ming et al., 2018), mechanical separation (Song et al., 2015), ultrasonic demulsification (Fang et al., 2013; Yingxin et al.,

*Author to whom all correspondence should be addressed: e-mail: lanlanyucn@163.com; Phone: +86-459-6617603

2018), microwave demulsification (Xianbu and Likun, 2011), and pyrolysis (Yirong, 2016; Shahraki et al., 2018; Zhentong et al., 2018) are the main resource utilization methods for oily sludge. In addition, thermal washing technology, which is a promising sludge treatment method, can enable thorough bulk processing, recover oil and gas resources, and solidify heavy metals in sludge while emitting only a small amount of pollutant gases. Mechanical separation technology is an important technical method that includes pre-treatment, quenching, tempering, and centrifugation. The three-phase separation of oil, water, and mud and considerable improvement of the recovery rate of crude oil are possible with this technology.

Micro-emulsion reduces interfacial tension well (Bera et al., 2014), and an important application is the improvement of oil recovery (Jeirani et al., 2014). Because the micro-emulsion is compatible with water and oil at the same time and has the property of solubilization, the treatment of oily sludge can effectively realize the three-phase separation of oil-cement, the deoiling rate is high and the raw material is easy to be obtained, and the energy consumption is low, it is also widely used in tertiary oil recovery and crude oil removal from oil sand (Dantas et al., 2010; Viana et al., 2015). In the study of Keliang et al. (2010), the deoiling rate of crude oil for a middle phase micro-emulsion system under optimal conditions can reach 98.9%. The research of Dongmei et al. (2006) found that the best middle phase micro-emulsion used in oil sand washing can reach an oil washing rate of 88.9%. However, the cost of preparing micro-emulsions is high, and the selection and development of surfactants with high efficiency and low cost still needs to be improved. This goal will be a future hot spot in research.

In this study, xylene was utilized as the oil phase to prepare a micro-emulsion. N-Pentanol was the cosurfactant. The surfactants sodium dodecyl benzene sulfonate (SDBS), cetyltrimethylammonium chloride (CTAB), sodium dodecyl sulfonate (SDS), sodium cetyl sulfate (CAS), and alkylphenol polyoxyethylene ether (OP-10) were the main raw materials. The prices of the surfactants were in order: sodium cetyl sulfate (CAS), cetyltrimethylammonium chloride (CTAB), sodium dodecyl sulfonate (SDS), sodium dodecyl benzene sulfonate (SDBS) and alkylphenol polyoxyethylene ether (OP-10). The surfactant-to-cosurfactant ratio was determined by drawing a pseudoternary phase diagram. The influences of the amount of micro-emulsion, type and formulation of surfactants, and the operation conditions of the centrifugation process on the deoiling effect were investigated. The oily sludge before and after treatment was analyzed by electron microscopy and thermal analysis to explore the mechanism underlying the deoiling process.

2. Material and methods

2.1. Reagents and instruments

The reagents used were xylene (analytical grade; Liaoning Quanrui Reagent Co., Ltd., China), n-pentanol (analytical grade; Shanghai Macklin Biochemical Co., Ltd. China), SDBS (analytical grade; Shanghai Macklin Biochemical Co., Ltd. China), alkyltrimethylammonium chloride (analytical grade; Shanghai Macklin Biochemical Co., Ltd. China), SDS (analytical grade; Shanghai Macklin Biochemical Co., Ltd. China), CAS (analytical grade; Shanghai Macklin Biochemical Co., Ltd. China), OP-10 (analytical grade; Shanghai Macklin Biochemical Co., Ltd. China), oily sludge and gasoline.

The instruments used were HH-S26S digital display constant temperature water bath pot (Chunlan Instrument Factory, China); 722 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); DJ1C enhanced electric agitator (Jiangsu Jintan Dadi Automation Instrument Factory, China); TSH-O-4000 centrifugal precipitator (Tianjin Medical Equipment Factory, China); DuPont 2100 thermal analyzer (Perkin Elmer Company, USA); S-4800 scanning electron microscope (Hitachi High Technologies Corporation, Japan); D/max-2200pc X-ray diffractometer (Science and Technology Corporation, Japan).

2.2. Analysis of the basic properties of oily sludge

2.2.1. Property determination of oily sludge

In this study, the oil content of the oily sludge in Daqing Oilfield was determined by spectrophotometer. At 420-nm wavelength, the absorbance was measured with gasoline as the reference for drawing the standard curve, which was the basis for determining the corresponding oil content and for calculating the oil rate. The determination of water content was done with the national standard method of measuring the water content of the mixed system of water and oil (Yong et al., 2008). The remaining impurities were filtered, washed, and dried for standing, and the amount of mud sand (i.e., the mud rate) was weighed.

2.2.2. Drawing of standard curve and determination of oil content in sludge

In this step, 0.5 g of the dehydrated crude was weighed (Yong et al., 2008), placed in a 500 mL volumetric flask, and diluted with gasoline to set a standard solution with a concentration of 1000 mg/L. Then, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0 mL of the standard solution were added to 10 volumetric flasks (each with 50 mL capacity). A volumetric flask without any of the standard solutions was utilized as a blank control. The volume was adjusted with gasoline, the absorbance *E* was measured at a wavelength of 420 nm in comparison with that of the blank sample, and the standard curve was drawn (Fig. 1).

Calculation formula of oil content is given by Eq.(1):

$$X_0 = \frac{EV_0 \times N}{KG} \quad (1)$$

where, X_0 - oil amount, mg/L; E - absorbance, cm^{-1}; V_0 - gasoline volume, mL; G - weight of oily sludge sample, g; K - absorptivity, L/mg·cm ($K=E_i/C_i$, E_i is the average value of absorbance; C_i is the average concentration.); N - dilution multiple.

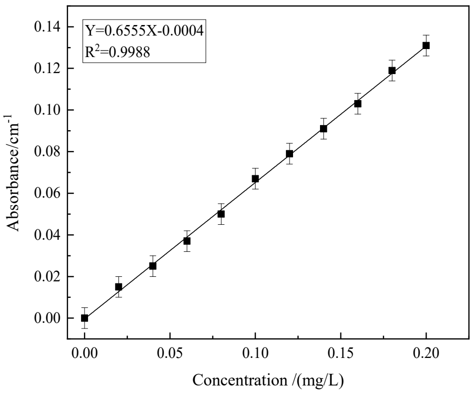

Fig. 1. Standard curve of oil content

2.2.3. XRD and thermal analyses of oily sludge

The instrument was a Cu target, the working voltage was 40 kV, and the working current was 30 mA. The sample was scanned at a speed of 10°/min to clarify its physical and chemical properties and analyze the components of the oily sludge. The thermal analysis procedure was started at 10°C and ramped to 800°C at a rate of 10°C per minute for 10 min. The relationship between the decomposition rate of the oily sludge and the temperature was tested in air to analyze the change in the oily sludge in each temperature section.

2.3. Preparation of micro-emulsion

The oil phase selected for the experiment was xylene; the cosurfactant was n-pentanol; and the surfactants were analytically pure SDBS, CTAB, SDS, CAS, and OP-10. At room temperature, 1 g of surfactant and 5 g of cosurfactant were obtained, mixed, and stirred uniformly, and a certain amount of distilled water was added to the mixture until the system was clear and transparent.

2.3.1. Complex formulation of micro-emulsion

Many variables are involved in the preparation of micro-emulsion, and intuitively presenting in the form of phase diagrams is difficult. Therefore, a pseudo-ternary phase diagram was used, because it was accurate, intuitive, and comprehensive. In accordance with the experimental purpose, a ternary phase diagram was drawn by the mass ratio of the fixed surfactant to the alcohol or the mass ratio of the fixed brine to the oil. The pseudo-ternary phase diagram was drawn in the form of the mass ratio of the fixed surfactant to the alcohol.

The micro-emulsion was prepared by the Shah method (Yonghong et al., 2015). The oil phase was mixed with the surfactant and the co-surfactant at room temperature, and distilled water was then added to the mixture until the entire system was clear and transparent. Different kinds of surfactants were mixed and compounded by changing the mixing ratio. The micro-emulsion after compounding was compared with the micro-emulsion prepared by a single surfactant, and a suitable micro-emulsion was selected for the deoiling experiment on the oily sludge.

2.3.2. Screening of micro-emulsion

After the micro-emulsion was completed, the micro-emulsion with a stable system and optimal deoiling effect was screened out, and the optimal deoiling condition of oily sludge was determined through experiments.

2.4. Determination of deoiling conditions of oily sludge

The following four factors that affect the deoiling rate of oily sludge were studied: solid–liquid ratio, micro-emulsion dosage, treatment temperature, and centrifugation (speed and time). The optimal deoiling conditions for the micro-emulsion treatment of the oily sludge were determined through the control experiment.

2.4.1. Optimal solid–liquid ratio determination

A certain amount of oily sludge was obtained and mixed with distilled water at a certain mass ratio, and the micro-emulsion prepared by SDS was added to determine the deoiling rate. Then, the optimal solid-liquid ratio of the oily sludge to the distilled water was identified.

2.4.2. Determination of centrifugation conditions

The solid-liquid ratio was fixed as 1:2, at which the oily sludge and the micro-emulsion were thoroughly mixed. The mixture was then centrifuged at speeds of 3000, 3600, and 4000 r/min for 5, 10, and 15 min, respectively. The optimal centrifugation speed and time were determined, and the experiment was conducted three times under the same experimental conditions.

2.4.3. Determination of treatment temperature and micro-emulsion dosage

The temperature and the micro-emulsion dosage can affect the deoiling rate of oily sludge and the quality of the oil from oily sludge. The deoiling effect was compared through a preliminary trial test, and the treatment temperatures of the experiment were finally determined as 30°C, 40°C, 45°C, 50°C and 55°C (Daiyin et al., 2018). The micro-emulsion dosages were 1, 2, 3, 4 and 5 mL. The optimal operating conditions of the oily sludge micro-emulsification treatment were determined by comparing the deoiling rate. Three experiments were repeated under the same experimental conditions.

2.5. Mechanism analysis of treatment with micro-emulsion

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

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 and irritating volatile odor. The measured oil content in the oily sludge was 37.28%, the moisture content was 27.10%, and the mud content was 35.62%.

3.1.1. XRD analysis of oily sludge

The XRD spectrum of the oily sludge is shown in Fig. 2. The diffraction peak of the silica crystal is the largest in the spectrum. Silica, an inorganic mineral, comprises the sample. The XRD pattern has a few small diffraction peaks, thereby suggesting that the oily sludge sample also contained minerals, such as calcite and albite. Organic substances, such as oil-containing alkanes and aromatic hydrocarbons, may also exist.

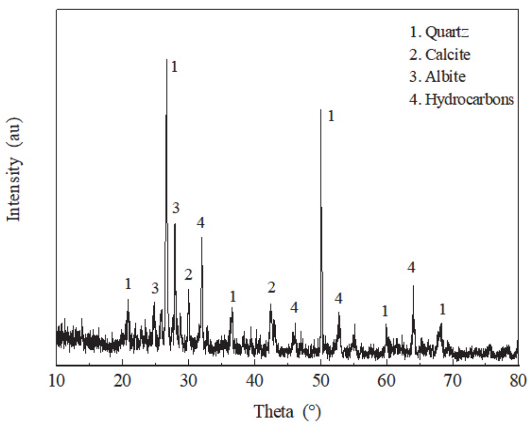

Fig. 2. XRD spectrum of oily sludge

3.1.2. Thermal analysis of oily sludge

Differential thermal analysis (DTA) and thermogravimetric (TG) analysis were performed on the ground oily sludge. The results of TG/DTA are shown in Fig. 3. As can be seen from Fig. 3, the weightlessness of the oily sludge sample from the normal temperature to 800 °C is as follows:

(1) 30~100℃: In this stage, the dehydration and degassing of the sample, the evaporation of water in the sample by heat and the precipitation of adsorbed gas lead to the weightlessness stage corresponding to the precipitation of water and gas in this region on the TG diagram.

(2) 100~240℃: The weight loss rate of light hydrocarbon components is controlled by the volatilization temperature of light hydrocarbon components, which account for more than 50% of oily sludge. There may also be some non-volatile water that continues to evaporate.

(3) 240~480℃: This stage is called volatilization stage. At this stage, the oily sludge contains volatile organic compound, which is the main component of the weightless components, and has a large amount of volatilization. This is because some alkanes undergo pyrolysis reaction, and the weightless rate decreases rapidly. The peak value of DTA curve shows obvious endothermic peak.

(4) 480~700℃: that is the fix carbon combustion stage, it is mainly the pyrolysis process of heavy components of petroleum hydrocarbon and a small amount of residual organic matter in the oil sludge.

The above analysis shows that the oily sludge sample contained water, light and heavy hydrocarbon components and some volatile organic compound.

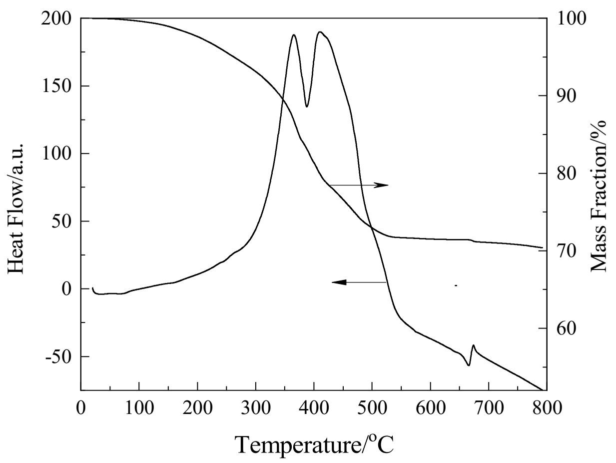

Fig. 3. TG/DTA spectrum of oily sludge

3.2. Preparation and complex formulation of micro-emulsion

3.2.1. Drawing of pseudo-ternary phase diagram

The ratio of each component in the micro-emulsion was determined by drawing a pseudo-ternary phase diagram, and the preparation of the micro-emulsion is shown in Fig. 4. The right half of the curve and one side of the triangle in the figure were a co-dissolved area where the single micro-emulsion was prepared. The red dot was selected as the matching point. Under this system, the surfactant-to-cosurfactant ratio was 1:5 (Nong and Qingluo, 2015), and the mass fraction of the entire system after mixing was 44%, the mass fraction of the oil phase xylene was 36%, and the mass fraction of the distilled water was 20 %. The prepared micro-emulsion was O/W micro-emulsion (Yuhua et al., 2013).

The principle of micro-emulsion treatment for oily sludge is as follows. Micro-emulsion is obtained as a product of a dispersion system, in which a number of micro-emulsion components are uniformly mixed and spontaneously formed under certain conditions. The micro-emulsion is thermodynamically stable, isotropic, and transparent or translucent in appearance. After components are dissolved completely and have reached stability, the micro-emulsion is added to the oily sludge for stirring. The micro-emulsion has good solubilization and extremely low interfacial tension, it can weaken the adhesion of oil, water and clay, and thus be used to wash and dissolve the organic components in the oily sludge by external force, such as mechanical agitation, to separate and recover the oil from the sludge (Bera and Mandal, 2015).

3.2.2. Screening of micro-emulsion

Preparation of single and compound micro-emulsions is shown in Table 1 and Table 2. The micro-emulsion was centrifuged in accordance with the experimental operation to observe whether the layer was separated (Chun et al., 2019), and its stability was determined as shown in Table 3, which shows that the micro-emulsion does not show any delamination after centrifugation, thereby indicating that the ratio selected in this experiment has good stability. The oily sludge was treated by the micro-emulsion and centrifugation, and the deoiling data are shown in Table 4.

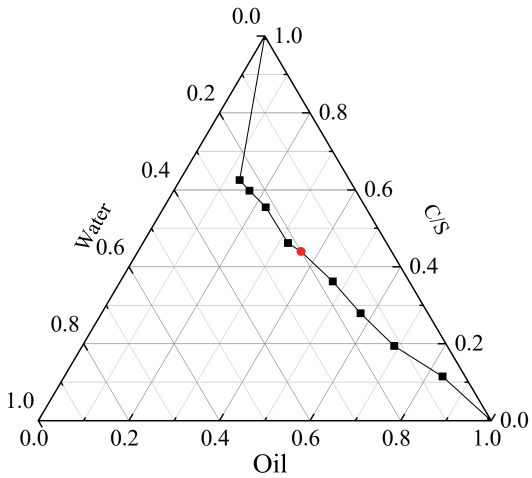

Fig. 4. Preparation of pseudo-ternary phase diagram by micro-emulsion

The cationic surface active agent CTAB is based on the physical adsorption of dipole-dipole interaction at the oil-water-mud interface; that is, the positive groups in CTAB and the negative carboxylic groups in crude oil form ion pairs due to gravitational action, which plays a role in solubilizing and reducing interfacial tension (Baofeng et al., 2015).

Table 1. Preparation table of single micro-emulsion

Micro-emulsion number	*Surfactant type*	*Dosage (g)*	*N-pentanol (g)*	*Xylene (g)*	*Water (g)*
1-1	SDS	1.00	5.00	4.90	2.68
1-2	SDBS	1.00	5.01	4.90	2.72
1-3	CAS	1.01	5.00	4.91	2.73
1-4	CTAB	0.99	5.00	4.89	2.80
1-5	OP-10	0.99	4.99	4.88	2.71

Table 2. Preparation table of compound surfactant micro-emulsion

No.	*Different surfactant ratio*	*Surfactant Species*		*Surfactant Total mass/g*	*N-pentanol (g)*	*Xylene (g)*	*Distilled water (g)*
		SDS	OP-10				
2-1.1	1:2	0.34	0.66	1.00	5	4.90	2.70
2-1.2	1:1	0.51	0.58	1.10	5	4.93	2.66
2-1.3	2:1	0.67	0.36	1.03	5	4.92	2.80
		SDBS	OP-10				
2-2.1	1:2	0.30	0.62	0.93	5	4.95	2.73
2-2.2	1:1	0.61	0.50	1.11	5	4.97	2.71
2-2.3	2:1	0.66	0.32	0.98	5	4.88	2.77
		CAS	OP-10				
2-3.1	1:2	0.33	0.66	1.00	5	4.95	2.82
2-3.2	1:1	0.51	0.51	1.02	5	4.89	2.81
2-3.3	2:1	0.66	0.33	0.99	5	4.95	2.71
		CTAB	OP-10				
2-4.1	1:2	0.34	0.66	1.01	5	4.90	2.75
2-4.2	1:1	0.51	0.51	1.02	5	4.86	2.77
2-4.3	2:1	0.68	0.34	1.02	5	4.89	2.71

Table 3. Experimental data of centrifugation for micro-emulsion

Micro-emulsion number	*Centrifugation speed (r/min)*	*Centrifugation period (min)*	*Post-centrifugation phenomena*
1-1	3000	10	No stratification
1-2	3000	10	No stratification
1-3	3000	10	No stratification
1-4	3000	10	No stratification
1-5	3000	10	No stratification
2-1.1	3000	10	No stratification
2-1.2	3000	10	No stratification
2-1.3	3000	10	No stratification
2-2.1	3000	10	No stratification
2-2.2	3000	10	No stratification
2-2.3	3000	10	No stratification
2-3.1	3000	10	No stratification
2-3.2	3000	10	No stratification
2-3.3	3000	10	No stratification
2-4.1	3000	10	No stratification
2-4.2	3000	10	No stratification
2-4.3	3000	10	No stratification

Table 4. Deoiling data of micro-emulsion on oily sludge

Mass of oily sludge (g)	*Micro-emulsion number*	*Dosage (g)*	*Distilled (g)*	*Absorbance (m)*	*Oil rate of bottom (%)*	*Deoiling (%)*
5	1-1	5	15	0.031	4.37	88.25
5	1-2	5	15	0.017	2.40	93.56
5	1-3	5	15	0.034	4.80	87.12
5	1-4	5	15	0.094	13.27	64.39
5	1-5	5	15	0.019	2.68	92.80
5	2-1.1	5	15	0.025	3.53	90.53
5	2-1.2	5	15	0.020	2.82	92.42
5	2-1.3	5	15	0.026	3.67	90.15
5	2-2.1	5	15	0.016	2.25	93.93
5	2-2.2	5	15	0.018	2.54	93.18
5	2-2.3	5	15	0.011	1.55	95.83
5	2-3.1	5	15	0.023	3.24	91.28
5	2-3.2	5	15	0.021	2.96	92.04
5	2-3.3	5	15	0.017	2.40	93.56
5	2-4.1	5	15	0.037	5.22	85.98
5	2-4.2	5	15	0.060	8.47	77.27
5	2-4.3	5	15	0.040	5.64	84.84

The anionic surfactants SDBS, SDS, and CAS are for chemical adsorption, which forms chemical bonds by electron transfer and exchange or sharing between the adsorbed molecules and surface atoms. The strong adsorption and stable membrane structure are beneficial for reducing interfacial tension. Unlike other anionic surfactants, SDBS contains a unique phenyl group in the hydrophobic chain; the structure of this group is similar to that in the oil phase and can reduce interfacial tension (Ying et al., 2005).

The nonionic surfactant OP-10 does not dissociate when dissolved in water, and no ions are generated. The lipophilic group in the molecule is the same as the ionic surfactant, and it is composed of polyoxyethylene chain and water; thus, it can form hydrogen bonds with hydrogen ions in water. The water affinity of anionic surfactants is formed by the dipolar action of ions and polar water molecules to generate an oil-water interfacial film, which is poor in stability. Nonionic surfactants have good compatibility with other types of surfactants, and the treatment effect of oily sludge is enhanced when they interact with each other.

Table 4 reveals that the deoiling rate of the oily sludge after treatment with different micro-emulsions reached 95.83%, and the micro-emulsion was prepared by the surfactants SDBS and OP-10.

The nonionic surfactants contain a certain amount of oxygen-containing groups. Thus, the nonionic surfactants have excellent hydrophilicity and can enhance the stability of the emulsion. The wide hydrophilic base of the nonionic surfactants enlarges the inter-molecular space, and the arrangement of the interface film molecules loosens the mechanical strength of the interface film, thereby reducing the interfacial tension. Charged particles are generated when the ionic surfactant dissociates in an aqueous solution. Consequently, electrostatic repulsion between the droplets hinders polymerization between the droplets. Furthermore, the interface film is loosely arranged because adjacent molecules on the interface adsorption layer repel each other due to electrostatic repulsion, thereby reducing the mechanical strength of the interface film and the interfacial tension.

The materials in the centrifuge tube were divided into three layers after micro-emulsification and centrifugation of the oily sludge. The upper, middle, and bottom layers were oil, water, and ash, respectively. The last layer comprised two layers, namely, an upper layer similar to floc and a lower one comprising sediment, as shown in Fig. 5a. The upper layer after the experimental treatment can be used for crude oil treatment, the sewage of the middle layer was treated, and the oil content in the bottom ash of the lowest layer was measured to calculate the oil removal rate and selected the micro-emulsion with the best deoiling effect. Number 1-5 is a polyoxyethylene nonionic micro-emulsion. Thus, the molecules are not charged, and no electrostatic repulsion occurs between the molecules. Consequently, the molecules become increasingly likely to accumulate. Moreover, the molecular weight of the hydrophilic group can rely only on hydrogen bonds to interact with water molecules, and ultra-low interfacial tension cannot easily form between the oil and water interfaces. However, the ionic surfactant has chemical and hydrogen bonds. Hence, the nonionic sludge has less force than the ionic sludge and cannot separate the oily sludge effectively. The experimental phenomenon after the treatment of oily sludge with No. 1-5 micro-emulsion was different from that of other types of micro-emulsion treatment. The middle layer (water) was transparent; the floc in the bottom slag floats above the water layer, mixed with the oil, and cannot be easily separated. As shown in Fig. 5b, the colloid and asphaltenes can be replaced from the oil-water interface to strengthen the hydrogen bonding effect between the polar groups because the polar group of OP-10 has a stronger polarity than the colloidal and asphaltene polar groups, and it can be tightly bound to the colloidal and asphaltene molecules (Meirong et al., 2013). Therefore, this floc is a mixture of colloid, asphaltenes, and some impurities in crude oil, which is colloidal. The floc absorbs a small amount of water in the ionic environment and sinks to the bottom.

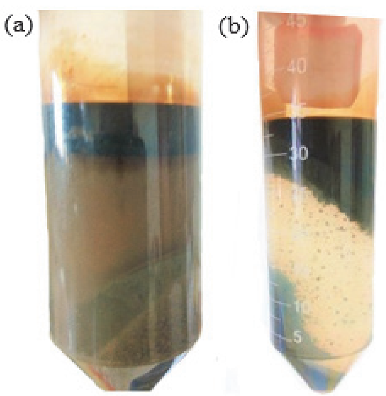

Fig. 5. Effects of different micro-emulsions on: (a) Other micro-emulsion treatment of oily sludge, and (b) No.1-5 micro-emulsion treatments of oily sludge

3.3. Determination of solid–liquid ratio

Fig. 6 shows that the initial solid–liquid ratio was 1:1. The deoiling rate increases with the solid-liquid ratio and reaches the peak value when the solid–liquid ratio was 1:2. After reaching the peak value, the deoiling rate began to decrease. Therefore, the optimal solid–liquid ratio was 1:2.

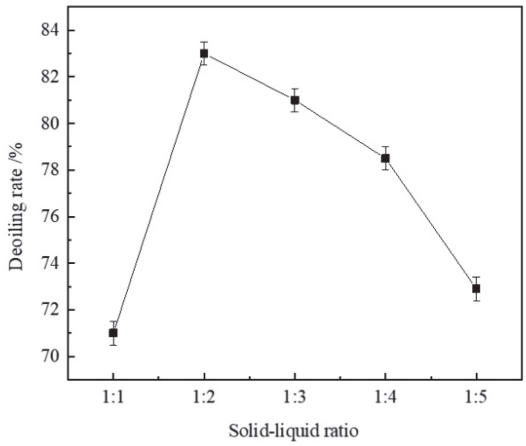

Fig. 6. Deoiling rate of oily sludge under different solid–liquid ratios

3.4. Determination of centrifugation speed and time

The micro-emulsion can well penetrate into the solid surface and the pores of the particles because of its ultra-low interfacial tension and strong wetting, emulsifying, and solubilizing capabilities. When added to the sludge, the film at the oil-water interface can be destroyed, thereby destroying the emulsified state of the oil surrounding the water. At the same time, the oil-bearing sludge can be effectively quenched and tempered to promote the separation of oil sludge, and the three-phase separation of oil-cement can be effectively realized by centrifugal separation and sedimentation (Kuchlyan et al., 2016; Meili et al., 2012). As seen in Fig. 7, prolonged centrifugation period improved the deoiling effect.

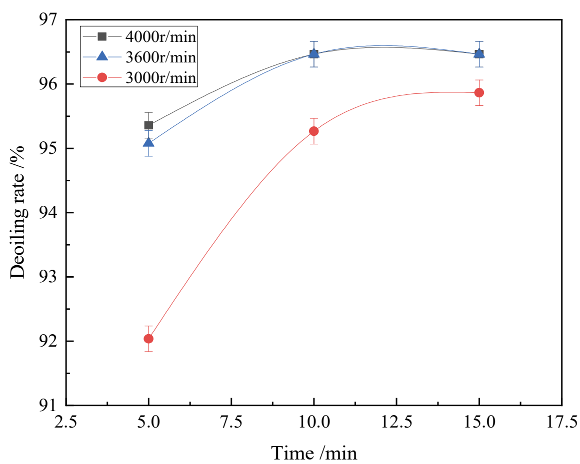

Fig. 7. Relationship between centrifugation speed and centrifugation period

Within the same centrifugation period a high rotation speed enhanced the deoiling effect. When the centrifugation period was 10 min and the rotation speed was 3600 r/min, the deoiling rate reached the maximum value. From the aspects of energy saving and treatment efficiency, the centrifugation period in the micro-emulsification treatment of oily sludge should be determined as 10 min, and the centrifugation speed was 3600 r/min.

3.5. Determination of treatment temperature and micro-emulsion dosage

The space for solubilization in the micelles increases with temperature due to the enhanced thermal motion of the ionic surfactant molecules. Nonionic surfactants have a cloud point and are temperature-sensitive. For nonionic surfactants containing polyoxyethylene groups, when the temperature increases, the hydrogen bonds between the polyoxyethylene groups and the water molecules are destroyed, hydration decreases, the micelles are easily formed, and the number of aggregations increases. Fig. 8 shows that at a fixed temperature, the deoiling rate of oily sludge increased with the micro-emulsion dosage, but the high magnitude decreased. The deoiling effect of the oily sludge was the best at 45°C. From the viewpoint of resource utilization, the amount of the micro-emulsion added was determined to be 3 mL. At this time, the deoiling rate of the oily sludge reached 97.35%.

In summary, the optimal temperature for the micro-emulsification treatment process of 5g oily sludge was 45°C, and the most reasonable dosage of the micro-emulsion was 3 mL.

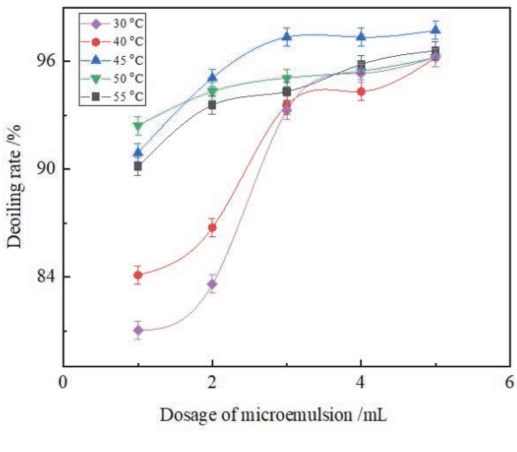

Fig. 8. Relationship between micro-emulsion dosage, treatment temperature, and deoiling rate

3.6. Thermal analysis and scanning electron microscopy (SEM) analysis of oily sludge after addition of micro-emulsion

3.6.1. Thermal analysis of oily sludge before and after addition of micro-emulsion

TG analysis was performed on the oily sludge sample before and after micro-emulsion centrifugation treatment, and the results are shown in Fig. 9.

The oily sludge considerably changes after the micro-emulsion treatment. When the initial temperature increases to 180°C, the weight loss is slower, and this condition characterizes the free water volatilization stage in the oily sludge. After treatment, the moisture content of the oily sludge is reduced, indicating that the free water of the sludge is removed after treatment. At 180°C~350°C, the weight loss is fast because of the thermal volatilization of the light oil in the oily sludge and the removal of the combined water in the microorganism, thereby indicating that some crude oil and bound water in the oily sludge are removed after micro-emulsion centrifugation. The weight loss rate after micro-emulsion treatment has reached 8.7%, slightly lower than 9.4% before treatment, which indicates that after treatment of oily sludge, binding water is released and crude oil is removed. At 350°C~550°C, the weight loss is severe, and the weight loss rate before treatment is 31.1%. With increasing temperature, the heavy oil in the oily sludge decomposes with a large amount of volatile organic compounds, the weight loss of the oily sludge is accelerated, and a large amount of crude oil in the oily sludge is removed, and the weight loss rate after treatment is only 15.6%, which proves that a large amount of crude oil in the oil sludge is removed after adding micro-emulsion and centrifugation. At 550°C or above, the weight loss is slower.

This condition characterizes the stage of fixed carbon combustion in the sludge, and some minerals are thermally decomposed. The results show that crude oil and free water in the oil sludge were largely removed by treatment with quenching and tempering centrifugation with microemulsion.

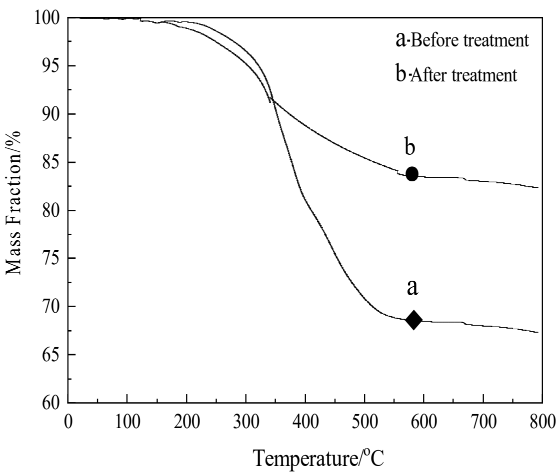

Fig. 9. TG curve of oily sludge

3.6.2. SEM analysis of oily sludge before and after addition of micro-emulsion

Fig. 10 (a-b) shows that the oily sludge samples before and after the micro-emulsion was added are significantly different. In Fig. 10a, the untreated oily sludge was loosely structured and has many pores between the particles. The particles in the oily sludge had no fixed shape.

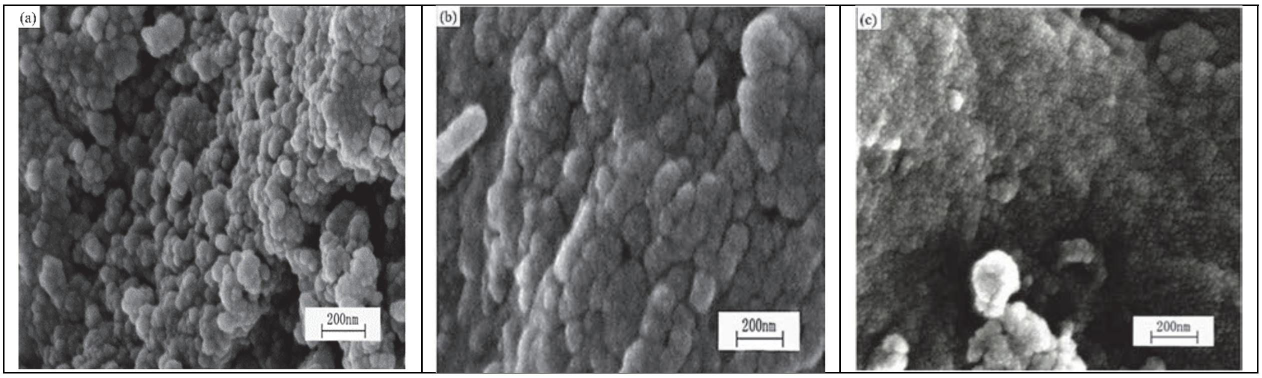

Fig. 10. SEM images of oily sludge with (a) No micro-emulsion added, (b) Micro-emulsion added and (c) Treatment with quenching and tempering centrifugation with micro-emulsion

They did not aggregate to form a bulk material. In Fig. 10b, after a certain amount of micro-emulsion was added, the micro-emulsion destroyed the rigid skeleton structure of the oily sludge sample. Therefore, the combination of oil and clay occurred only because of the existence of surface tension, and the ultra-low interfacial tension of the micro-emulsion cannot be neglected. Most of the water in the oily sludge was removed because of the dehydration of micro-emulsion, and the oil was precipitated and aggregated to form large particles and a large volume of oil beads. However, the oil was not separated from the clay but adsorbed onto it. The addition of micro-emulsion can reduce the interfacial tension between oily sludge and cement, weaken the binding force of the three, and promote the separation of oily sludge. At this time, the oily sludge can be applied to processes such as centrifugation.

Fig. 10c shows that the oily sludge changed from being loose small particles before treatment into a large volume of dense mud cake after centrifugation, and the structure changed from loose to compact, thereby indicating that after subjecting the oily sludge to quenching and tempering-centrifugation of micro-emulsion, the water and oil contents decreased gradually with increasing cake thickness.

4. Conclusions

The characteristics of the oily sludge were as follows: the oil content was 37.28%; the moisture content was 35.62%; and the mud content was 27.10%. Oily sludge contained water, inorganic mineral such as silica, light and heavy hydrocarbon components and some volatile organic compound.

Through an experiment, a pseudo-ternary phase diagram was drawn to guide the preparation of the micro-emulsion. The calculated mass ratio of the surfactant to the cosurfactant was 1:5. The mass fraction of the two was 44%. The mass fraction of xylene was 36%. The mass fraction of distilled water was 20%.

The micro-emulsion prepared by SDBS and OP-10 was obtained through a comparison experiment. The deoiling effect on the oily sludge was the best when the solid–liquid ratio was 2:1. The deoiling rate of the oily sludge reached 97.35% when the centrifugation speed was 3600 r/min. The centrifugation period was 10 min, the treatment temperature was 45°C, the amount of treated oily sludge was 5 g, and the amount of added micro-emulsion was 3 mL. After the oily sludge was treated by quenching and tempering-centrifugation of the micro-emulsion, the oil, water, and mud are separated effectively, and the sewage oil was effectively removed and recovered.

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