Compound Cleaning Agent for Oily Sludge from Experiments and Molecular Simulations

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ABSTRACT: This paper reported a new oily sludge compound cleaning agent formula, which used a combination of molecular simulation and experimental methods to study its interfacial formation energy (IFE), and exciting results were obtained. From a total of 24 surfactants in five categories, sodium silicate (Na_2SiO_3), sodium dodecylbenzene sulfonate, and fatty alcohol polyoxy-ethylene polyoxypropylene ether (JFC-SF) were screened out because of their excellent washing oil effect. Under a reasonable orthogonal system, when the mass ratio of the three surfactants was 3:1:1, the oil desorption effect was the best, the oil residual rate could reach 2.13%, and the oil removal efficiency could reach 93.53%. Verified by the molecular dynamics simulation module, the absolute value of the interface binding energy was the largest at this compound ratio, which was 465.71 kcal/mol. More importantly, we have discussed in depth the mechanism of adsorption and permeation of oily sludge by cleaning agents. Through single-factor influence experiments, the following optimized working condition parameters of the cleaning agent were determined: cleaning conditions with an agent content of 4%, a temperature of 70 °C, a stirring speed of 400 rpm, a cleaning time of 30 min, and a liquid−solid ratio (L/S) of 4:1. The research results laid the foundation for resource utilization, harmlessness, and reduction of oily sludge in the Liaohe oilfield.
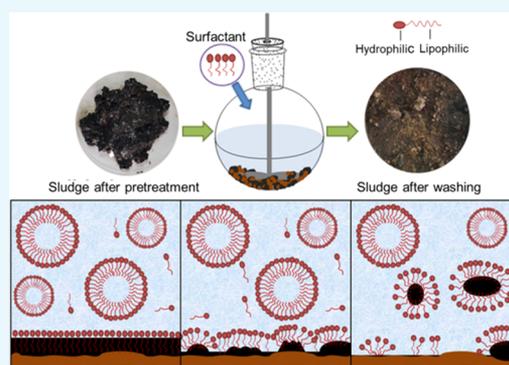
1. INTRODUCTION

In recent years, with the development and progress of the petrochemical industry, the amount of oily sludge produced in the processes of oil field exploitation, oil and gas transportation, and oil-refining wastewater treatment has gradually increased. It is known as one of the main pollutants in the petrochemical industry, usually in the form of water-in-oil (W/O). Oil sludge is a composite emulsion composed of various petroleum hydrocarbons, water, heavy metals, and solid particles[1] and is a national hazardous waste. It will cause stratum blockage and excessive suspended solid content in the reinjected water,[2,3] which seriously causes a waste of economic resources and environmental pollution.[4] The way to treat oily sludge efficiently, in a pollution-free manner, and at low cost is considered as a research hotspot of environmental protection in the petrochemical industry.

At present, technologies such as solvent extraction, conditioning-mechanical separation, incineration, ultrasonic radiation, pyrolysis, electrolytic air flotation, and chemical cleaning are commonly used to treat oily sludge.[5] The process of chemically cleaning sludge is to make the surfactant act on the sludge interface through the action mechanism of the cleaning agent's adsorption, emulsification, and dissolution and the interaction between the surfactant chain containing ester groups and the oil leads to surface activity.[6] The adsorption of the agent on the oil surface reduces the interfacial tension of the oil-cement and the contact force of the oil sludge, quickly strips the oil from the oil sludge, and realizes the three-phase separation.[7,8] Due to its convenient operation, simple process flow, excellent oil washing effect, and low treatment cost, chemical sludge cleaning technology has been widely used.

The physical properties of different sludges vary greatly, and the purification effect of oily sludge is greatly affected by the critical micelle concentration (CMC) of a single surfactant, which often leads to unsatisfactory cleaning of oily sludge. However, a compound surfactant can combine the characteristics of multiple types of surfactants to better perform cleaning, which has broad application prospects. Posocco et al.[9] investigated the oil−water interfacial tension of Tween 80 and Span 20 and found that Tween 80 and Span 20 have a significant synergistic effect under a certain compound ratio.

Jing et al.[10] studied the oil-washing ability of four surfactants on sludge and found that anionic surfactants and sodium silicate have better washing effects, with oil residual rates of 2.66 and 1.6%. Chen et al.[11] used sodium nonylphenol polyoxyethylene ether sulfate (AEOS) and KOH as sludge cleaning agents and found that surfactants and alkalis have a synergistic effect. Surfactant plays the role of wetting and hydrophobic, reducing interfacial tension, and alkali plays the role of a dispersant. Duan et al.[12] found that the surface tension of the compound cleaning agent was the lowest when the ratio of sodium carbonate, AEO-9, and rhamnolipid was 5:1:0.5. When the mixing concentration is 2 wt %, the ratio of detergent aqueous solution/sludge is 3:1, the cleaning time is 40 min, and the cleaning temperature is 50 °C, the oil content after cleaning can be reduced to about 0.5 wt %.

It is an effective technical method to use molecular dynamics simulations to integrate multidimensional basic experimental data for unified analysis and to find universal principles and regularities. At present, many scholars apply molecular dynamics simulations to oil−water interface analysis to guide experimental research. Liu et al.[13] used molecular dynamics simulations to calculate the interface formation energy of different systems, and the adsorption behavior of sulfonate-type anionic Gemini surfactants at the oil−water interface was explored, laying the foundation for tertiary oil recovery technology. Alonso et al.[14,15] used molecular dynamics simulations to experimentally measure the interfacial properties of several combinations of surfactants, salts, and oils, and the existence of synergistic effects was confirmed. To deeply understand the effect of surfactant sodium dodecylbenzene sulfonate (SDBS) on the efficiency of oil−water separation, Yang et al.15 studied its adsorption behavior by the method of combining molecular simulations and experiments, and the results showed that SDBS effectively reduced the surface tension and interfacial formation energy (IFE) value.

Oily sludge has strong selectivity for cleaning agent formulations and traditional experiments were associated with limitations in exploring the action mechanism of surfactants, and the application and development of molecular dynamics simulations in the oil−water interface has become more and more mature. Therefore, this paper focuses on the typical oily sludge of the Liaohe oilfield, and a new oily sludge compound cleaning agent formula was proposed. The experimental research was analyzed and guided by molecular dynamics simulations to further explore the mechanism of the compound system and the surfactant cleaning oily sludge, so as to strengthen the understanding of the molecular structure relationship and the understanding of the surface aggregation morphology, and the optimized conditions of cleaning agents were determined by measuring the oil removal efficiency and oil residual rate.

2. RESULTS AND DISCUSSION

2.1. Preliminary Screening of Cleaning Agents. At present, the commonly used oily sludge cleaning agents are mainly divided into inorganic salt type and organic salt type.[16] Among them, organic salt surfactants can be divided into cationic surfactants, anionic surfactants, nonionic surfactants, and amphoteric surfactants according to the properties of the hydrophilic head. Due to the complex and diverse structures of surfactants, surfactants with different structures have different adsorption characteristics, critical micelle concentration values, and solubilization capabilities.[17] Therefore, three or more

surfactants were selected from the above five categories as representative monomers, and the surfactants with the best susceptibility to the oil sludge of the Liaohe oilfield were selected and compared in sequence.

The oil removal efficiency of 24 kinds of surfactants is shown in Figure 1. We can observe that the oil removal efficiency of
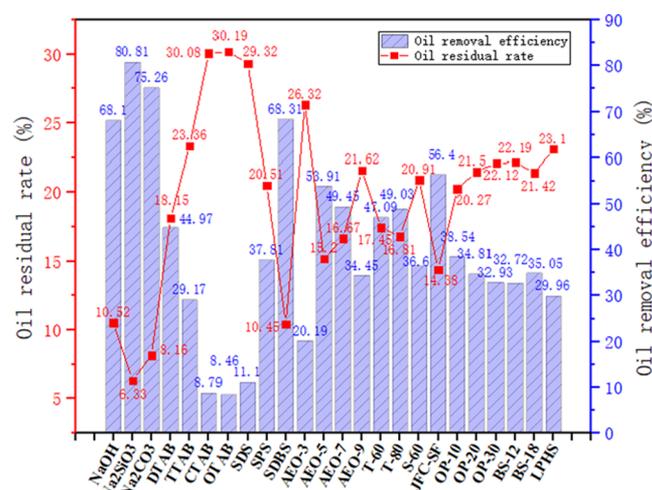
Figure 1. Comparison of oil removal efficiency of surfactants.

inorganic salt-type surfactants is better than most other types of surfactants. This is because Na_2SiO_3 dissolves in water to generate strong alkali (NaOH) and weak acid (silicic acid). Both constantly neutralize the acid and alkali, and the final solution becomes alkaline. Na_2CO_3 and NaOH also exhibit alkalinity in aqueous solutions. Inorganic salt surfactants can work together with polar molecules such as colloids and asphaltenes in petroleum to increase the solubility of solutes, and the interfacial tension between the liquid−liquid interface and the solid−liquid interface can be effectively reduced.[18] However, the unstable structure and irritation of Na_2CO_3 and NaOH are characterized by strong corrosiveness and deliquescent in the air. Therefore, Na_2SiO_3, which has the best oil removal efficiency and convenient storage, is selected as the next step compound formula.

From the aspects of oil removal efficiency and oil residual rate, it can be observed that Na_2SiO_3, SDBS, and JFC-SF have the best washing effect. SDBS is an anionic surfactant, which is sensitive to water hardness, has strong foaming power and high detergency, and is easy to compound with various additives. JFC-SF is a nonionic surface-active agent with good penetrating performance and strong washing ability and can easily wash off various oil stains. The results showed that the deoiling abilities of Na_2SiO_3, SDBS, and JFC-SF reduced in turn. Therefore, the three surfactants were compounded in the next step to obtain a cleaning agent with a better oil removal efficiency (Tables 1 and 2).

2.2. Compound Experiment. *2.2.1. Compound Experimental System.* In the compound system, there are interaction forces between surfactant molecules of different types and structures, and the performance and compound effect of the entire system are affected by the interaction forces.[19] According to research, the increase of the force between surfactant molecules can increase the system's activity, and the greater the probability of synergism. However, the compound system of cationic and polyoxyethylene-based nonionic surfactants can only achieve additive synergistic

Table 1. Surfactant Information

Name	Sodium metasilicate	Sodium dodecyl benzene sulfonate	Fatty alcohol polyether
Abbreviation	Na_2SiO_3	SDBS	JFC-SF
HLB	-	10.6	11~13
Appearance	White particle	Light yellow crystal	White translucent liquid
Structure			

Table 2. Orthogonal Test System and Evaluation of Oil Removal Efficiency[a]

test	test sample formulation	oil residual rate (%)	oil removal efficiency (%)
1	Na_2SiO_3 + SDBS	8.71	73.58
2	Na_2SiO_3 + JFC-SF	10.65	67.71
3	SDBS + JFC-SF	13.24	59.87
4	Na_2SiO_3 + SDBS + JFC-SF	3.21	84.82

[a]It is concluded that the fourth orthogonal test system is adopted to determine the best ratio.

effects when the surfactant has a specific structure.[20,21] Therefore, the surfactants with the best oil removal efficiency were selected in this study: A(Na_2SiO_3), B(SDBS), and C(JFC-SF). According to the oil residual rate and oil removal efficiency obtained by different systems, the final orthogonal test system was determined.

2.2.2. Compound Experiment. The Na_2SiO_3 + SDBS + JFC-SF compound experimental system was adopted, and Na_2SiO_3 (A), SDBS (B), and JFC-SF (C) with the highest oil removal efficiency were used as research objects. The oil removal efficiency and oil residual rate of the compound cleaning agent under different ratio conditions were measured. The results are shown in Table 3.

The degreasing effect of the cleaning agent and the oil residual rate after oil sludge washing under the conditions of different proportions was different from each other, indicating that the synergistic effects of the three single surfactants were

Table 3. Effect of Compound Washing Oil

test	orthogonal experimental system	ratio	oil residual rate (%)	oil removal efficiency (%)	average oil removal efficiency (%)
1	Na_2SiO_3 (A):SDBS (B):JFC-SF (C)	1:1:1	3.21	90.28	90.24
2			3.15	90.45	
3			3.30	89.99	
4		3:1:1	2.10	93.63	93.53
5			2.27	93.12	
6			2.03	93.84	
7		2:2:1	3.38	89.75	89.5
8			3.49	89.42	
9			3.52	89.33	
10		6:3:1	2.76	91.64	91.64
11			2.93	91.12	
12			2.59	92.15	
13		2:1:2	3.60	89.10	89.03
14			3.55	89.24	
15			3.71	88.75	
16		1:1:2	4.56	86.17	86.48
17			4.37	86.75	
18			4.45	86.51	
19		1:2:1	5.01	84.82	85.18
20			4.53	86.26	
21			5.13	84.45	
22		1:6:3	8.05	75.58	75.63
23			7.87	76.14	
24			8.19	75.17	

Table 4. Simulation System and System Composition of Different Compound Ratios

system	proportion	SiO$_3$	SDBS	JFC-SF	water	decane	Na$^+$	Cl$^-$
A1B1C1	1:1:1	40	40	40	2400	500	120	0
A3B1C1	3:1:1	72	24	24	2400	500	168	0
A2B2C1	2:2:1	48	48	24	2400	500	144	0
A6B3C1	6:3:1	72	36	12	2400	500	180	0
A2B1C2	2:1:2	48	24	48	2400	500	120	0
A1B1C2	1:1:2	30	30	60	2400	500	90	0
A1B2C1	1:2:1	30	60	30	2400	500	120	0
A1B6C3	1:6:3	12	72	36	2400	500	96	0

Table 5. Total Energy and IFE of Mixed Systems

system	proportion	E_{total} (kcal/mol)	IFE (kcal/mol)
A1B1C1	1:1:1	−54 934.99	−40.05
A3B1C1	3:1:1	−55 885.27	−465.71
A2B2C1	2:2:1	−53 485.95	−445.71
A6B3C1	6:3:1	−54 625.37	−455.21
A2B1C2	2:1:2	−53 148.06	−442.90
A1B1C2	1:1:2	−52 653.30	−438.78
A1B2C1	1:2:1	−51 578.19	−429.82
A1B6C3	1:6:3	−43 776.99	−364.81
E_{ref} = −42 933.07 kcal/mol	$E(Na_2SiO_3)$ = −0.19 kcal/mol	$E(SDBS)$ = −139.07 kcal/mol	$E(JFC\text{-}SF)$ = −40.63 kcal/mol

unequal under the conditions of different proportions. The experimental results prove that when the ratio of Na$_2$SiO$_3$, SDBS, and JFC-SF is 3:1:1, the residual oil rate after cleaning is the lowest, and the adsorption and permeation effects are fully utilized to realize the desorption of oil in the sludge. The oil removal efficiency can reach an average value of 2.13% and the oil residual rate can reach an average value of 93.53%. Therefore, it is recommended that the mass ratio of the three agents should be controlled at 3:1:1 during the field application in the Liaohe oilfield.

2.2.3. Molecular Dynamics Simulations of the Compound System. The interfacial formation energy (IFE) module of the molecular dynamics simulation was applied to the oil-containing compound high-efficiency cleaning agent for further research. Na$_2$SiO$_3$, SDBS, JFC-SF, and the compound ratio were recorded as A, B, C, and AxByCz, and the molecular mole fraction in the solvent was represented by x, y, and z (x = 0−6, y = 0−6, and z = 0−6). Combined with the experimental research, the following eight compound ratios were explored by molecular dynamics simulations. The composition of the simulation system at different compound ratios is shown in Table 4.

Interfacial formation energy (IFE) refers to the reduced energy of the system after surfactant molecules enter the oil−water interface layer, which can be used to investigate the stability of the interface. Its value is closely related to the interaction force between surfactants and water molecules, between surfactant molecules, and between surfactants and oil-phase molecules.[22,23] IFE can be obtained by eq 1.

$$\text{IFE} = \frac{E_{total} - (n_1 \times E_A + n_2 \times E_B + n_3 \times E_C + E_{ref})}{n_1 + n_2 + n_3} \tag{1}$$

where E_{total} is the total energy of the system after the surfactant reaches an equilibrium at the oil−water interface (kcal/mol); E_{ref} is the energy of the oil−water interface system when no surfactant is added (kcal/mol); n_1, n_2, and n_3 are the number of Na$_2$SiO$_3$, SDBS, and JFC-SF in each system, respectively; and

E_A, E_B, and E_C are the potential energies of Na$_2$SiO$_3$, SDBS, and JFC-SF, respectively (kcal/mol). The interface generation performance of the eight complex schemes is shown in Table 5.

The increase and decrease of system energy are represented by the positive and negative values of IFE, respectively.[24] When the cleaning agent acts on both the oil and water phases, the total interface energy and the oil−water interfacial tension are reduced.[25] The greater the absolute value of the IFE of the composite detergent, the greater the ability of the surfactant to reduce the total energy of the interface, which proves that the composite detergent has a better oil removal efficiency and the stronger the synergy between the formulations. According to the experimental data of the molecular dynamics simulation, A3B1C1 can reduce the interfacial tension the strongest to −465.71 kcal/mol, and the oil removal efficiency is the best.

2.3. Optimization of Cleaning Conditions. The oil removal efficiency of a cleaning agent is affected by the temperature, washing time, stirring speed, solid−liquid ratio, cleaning agent content, etc.[26−28] Now, experimental research on the influence of different factors on the effect of washing oil to determine the optimal cleaning conditions of the cleaning agent applied on the spot is carried out.

2.3.1. Influence of Temperature on Oil Removal Efficiency. Under the cleaning conditions with a solid−liquid ratio of 1:3, an agent content of 5%, a stirring speed of 500 rpm, and a cleaning time of 30 min, the temperature was controlled as the only single variable, and the experiment on the influence of temperature on the oil removal efficiency was carried out. The experimental results are shown in Figure 2. When the temperature is low, the oil washing effect is not ideal. As the temperature increases, the oil residual rate drops rapidly. This is due to the increase in temperature that accelerates the thermal movement of oil molecules, reduces the viscosity of crude oil, and weakens the adhesion of the oil film, making it easy to separate from oil and mud. When the temperature is between 65−75°C, the residual oil rate has the lowest value of about 2%. The excessive temperature has
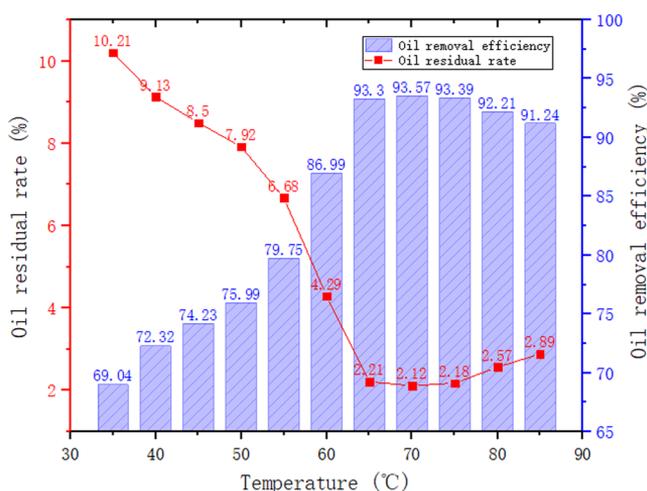
Figure 2. Influence of temperature on oil removal efficiency.

basically no effect on the oil removal efficiency and also causes a waste of resources, so the optimal washing temperature was set at 70 °C.

2.3.2. Influence of Cleaning Time on Oil Removal Efficiency. Under the cleaning conditions with a temperature of 70 °C, a solid−liquid ratio of 1:3, an agent content of 5%, and a stirring speed of 500 rpm, the time was controlled as a single variable, and the experiment on the influence of washing time on the oil residual rate was carried out. The experimental results are shown in Figure 3. When the stirring time is too
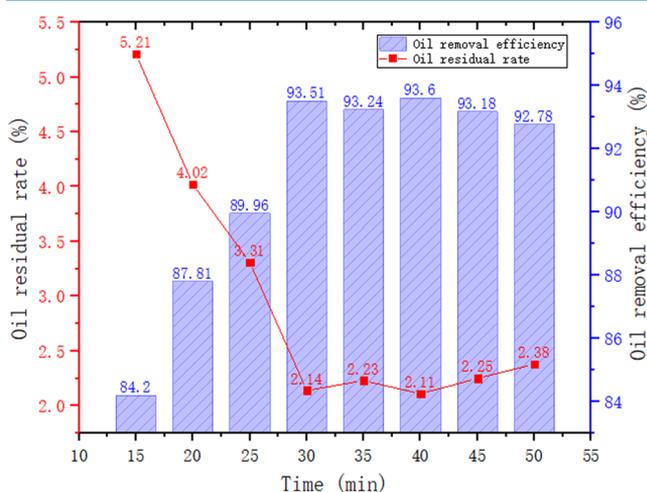
Figure 3. Influence of time on oil removal efficiency.

short, the oil washing effect is not ideal. As the washing time increases, the residual oil rate drops rapidly. This is because the sludge and the cleaning agent are slowly and fully contacted, and the surfactant molecules penetrate into the oil film, and the oil removal efficiency increases rapidly. The residual oil rate is basically stable and there is a minimum value of about 2%. Considering that excessive cleaning may increase the emulsification of sludge and affect the washing effect,[29] as well as power consumption and other issues, the washing time is determined to be 30 min.

2.3.3. Influence of Stirring Speed on Oil Removal Efficiency. Under the cleaning conditions with a temperature of 70 °C, a solid−liquid ratio of 1:3, an agent content of 5%, and a cleaning time of 30 min, the stirring speed was controlled

as a single variable, and the experiment on the influence of the speed on the oil residual rate was investigated. The experimental results are shown in Figure 4. When the rotation
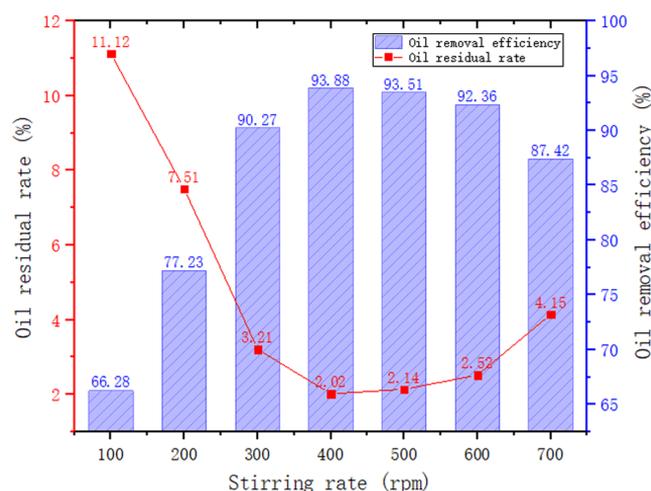
Figure 4. Influence of stirring speed on oil removal efficiency.

speed is too small, the oil washing effect is not ideal. As the rotation speed increases, the solid and liquid phases are fully mixed, and the oil residual rate drops rapidly. When the speed is about 400 rpm, the oil residual rate has a minimum value of 2.1%. With the continuous increase of the stirring intensity, the oil washing effect is significantly reduced. This is because the excessive stirring intensity will aggravate the mechanical collision between the oil molecules, causing the oil to re-emulsify and easily form an oil-in-water emulsion with water, which hinders three-phase separation.[30] Considering the consumption of power resources, it is more appropriate to choose the stirring intensity at about 400 rpm.

2.3.4. Influence of S/L Ratio on Oil Removal Efficiency. Under the cleaning conditions with a temperature of 70 °C, an agent content of 5%, a stirring speed of 400 rpm, and a cleaning time of 30 min, the S/L ratio was controlled as a single variable, and the experiment on the effect of the S/L ratio on the residual oil rate was carried out. The experimental results are shown in Figure 5. If the liquid−solid ratio is too small, the fluidization of sludge cannot be achieved,[31] which is
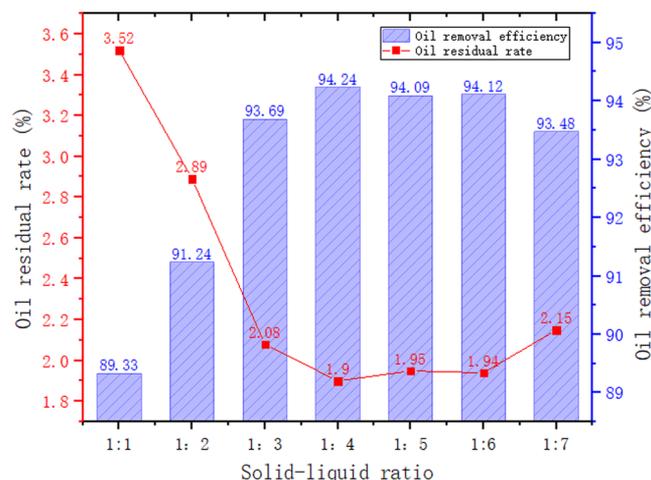
Figure 5. Influence of S/L ratio on oil removal efficiency.

not conducive to the separation of oil and sludge. With the decrease of the S/L ratio, the washing oil effect has been significantly improved. When the S/L ratio is about 1:4, the oil removal efficiency tends to be stable, and the oil residual ratio has a minimum of 1.9%. As the S/L ratio continues to decrease, it has little effect on the efficiency of washing oil. Taking into account the cost of medicament and the amount of circulating water treatment,[32] it is more appropriate to control the S/L ratio at about 1:4.

2.3.5. Influence of Cleaning Agent Content on Oil Removal Efficiency. Under the cleaning conditions with a temperature of 70 °C, a solid−liquid ratio of 1:4, a stirring speed of 400 rpm, and a cleaning time of 30 min, the cleaning agent content was selected as a single variable, and the experiment on the effect of the cleaning agent concentration on the residual oil rate was carried out. The experimental results are shown in Figure 6. If the concentration of the
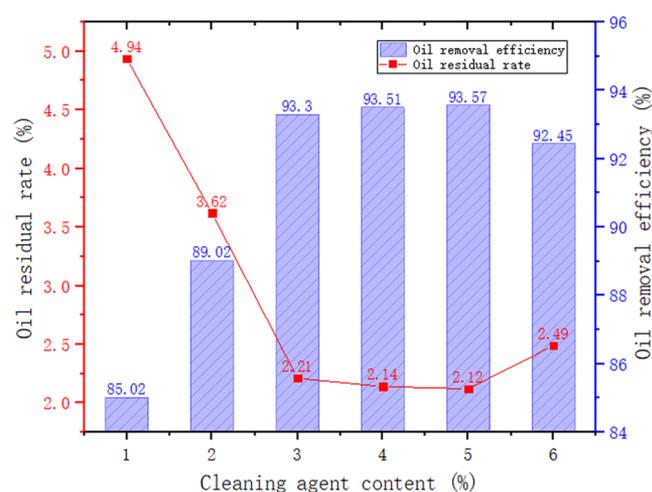
Figure 6. Influence of cleaning agent content on oil removal efficiency.

cleaning agent is too small, the effect of washing oil is not ideal. As the concentration increases, the residual oil rate drops rapidly. When the concentration ranges from 3 to 5%, the sludge residual oil rate reaches the lowest value of about 2%. As the concentration continues to increase, the residual oil rate increases from 2 to 4.5%. This is because when the concentration of the cleaning agent reaches its critical micelle concentration, the increase in the concentration of the cleaning agent will result in the formation of a large number of micelles, and the fluidity of the cleaning agent will be weakened, which is not conducive to the separation of the two phases.[33] Therefore, the cleaning agent content of 4% is the most suitable.

2.4. Oil Removal Mechanism Analysis. In this paper, based on the characteristics of the interaction between the three surfactants and the oil and the interfacial formation energy in the molecular dynamics simulation, adsorption and permeation are assumed to be the mechanism of compound cleaning agents. The sludge was mixed with the cleaning agent as shown in Figure 7. Among them, Na_2SiO_3 can work together with polar molecules in petroleum to increase the solubility of the solute, and some acidic substances may be saponified to form surfactants. In addition, the charge of the polar groups of anionic surfactants can be neutralized by Na_2SiO_3, compressing the electric double layer and reducing
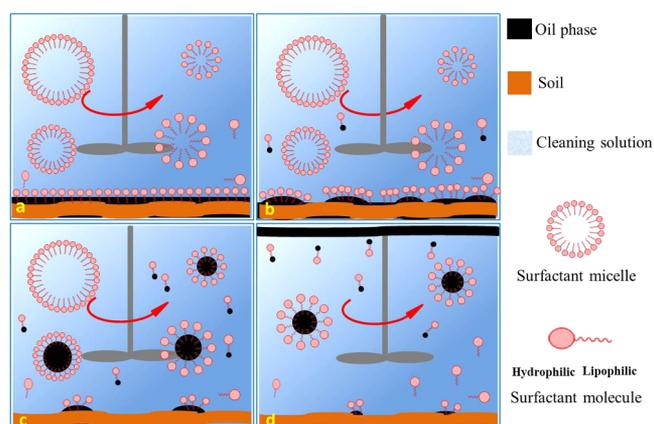
Figure 7. Proposed mechanism for cleaning sludge.

the charge density and colloidal repulsion, which is conducive to colloidal coalescence and oil−water separation. The anionic surfactant SDBS and the nonionic surfactant JFC-SF mainly play the role of adsorption and permeation. As shown in Figure 7a, the surfactant molecules in the lotion exist in the form of lamellar micelles and spherical micelles. Because of their "lipophilic−hydrophilic" amphiphilic nature, surfactant molecules were adsorbed on the oil−water interface, the lipophilic group was rooted in the oil phase, and the hydrophilic group was embedded in the water phase, with an oriented arrangement at the oil−water interface to form a stable adsorption layer, which produced a tensile force at the oil−water interface as shown in Figure 7b, further reducing the oil−water interfacial tension. As shown in Figure 7c,d, a part of the oil phase is gradually decomposed by the surfactant, and the oil droplets were prevented from coalescing again by the repulsion between the polar groups of the surfactant molecules. The other part of the oil phase was heated and stirred, and the oil droplets are stripped from the sludge and dissolved in the center of the spherical micelle, or the surfactant molecules pull the oil molecules to remove the sludge to achieve the two-phase separation of oil and sludge.

3. CONCLUSIONS

In this paper, the oil sludge of the Liaohe oilfield was treated as harmless and resourced by chemical cleaning methods. Combined with molecular dynamics simulation analysis, a compound cleaning agent with excellent susceptibility to oil sludge in the Liaohe oilfield was proposed, and exciting results were obtained. From a total of 24 kinds of surfactants in five categories, three kinds of surfactant monomers with a better washing oil effect were selected. The results showed that the deoiling abilities of Na_2SiO_3, SDBS, and JFC-SF reduced in turn. Under a reasonable orthogonal system, when the mass ratio of Na_2SiO_3, SDBS, and JFC-SF is 3:1:1, the oil residual rate can reach 2.13%, and the oil removal efficiency can reach 93.53%, which has achieved exciting results. Verified by the molecular dynamics simulation module, the absolute value of the interfacial formation energy (IFE) is the largest under this compound ratio, which can reach 465.71 kcal/mol. Finally, we not only clarified the mechanism of adsorption and penetration of the cleaning agent but also found that the cleaning effect of the cleaning agent can reach the peak at the agent content of 4%, the temperature of 70 °C, the stirring speed of 400 rpm, the cleaning time of 30 min, and the liquid−solid ratio (L/S)

of 4:1. This work will provide a new and efficient cleaning agent for the treatment of oily sludge in the Liaohe oilfield.

4. EXPERIMENTAL SECTION

4.1. Materials. The sludge samples were provided by the Liaohe oilfield. The oil sludge of the Liaohe oilfield is characterized by large particles, more silt, less oil content, and hard sludge. Therefore, the oil sludge should be pretreated first, and quantitative amount of hot water at 90 °C should be added to the oil sludge and thoroughly stirred. The measured oil content of the uniform sludge after dehydration is 32.98%. The effect diagram before and after mixing is shown in Figure 8.
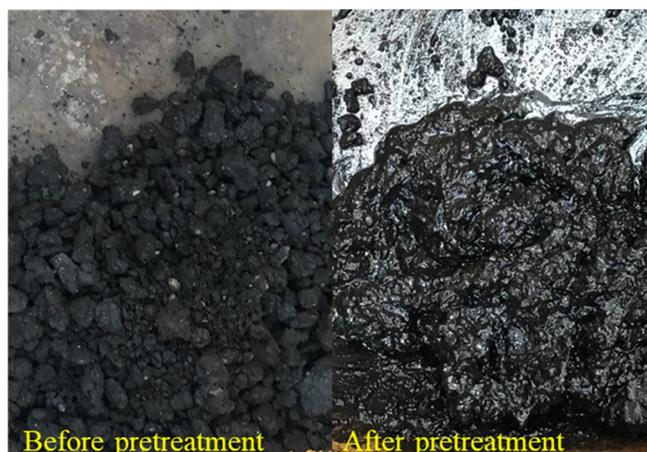
Figure 8. Effect picture of sludge pretreatment.

NaOH, Na_2SiO_3, and Na_2CO_3 were provided by Tianjin Hongyan Reagent Factory. Dodecyl trimethyl ammonium bromide (DTAB), tetradecyl trimethyl ammonium bromide (TTAB), cetyl trimethyl ammonium bromide (CTAB), and octadecyl trimethyl ammonium bromide (OTAB) were obtained from Zhengzhou Qixiang Chemical Factory. Sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (SDBS), and sodium petroleum sulfonate (SPS) were purchased from Wuxi Yatai United Company. Fatty alcohol polyoxyethylene ether (AEO-3, AEO-5, AEO-7, AEO-9), Tween 60, Tween 80, and Span 60 were provided by China Sasol Co., Ltd. Fatty alcohol polyoxyethylene polyoxypropylene ether (JFC-SF) was obtained from Linyi Lusen Reagent Factory. Polyoxyethylene octylphenol ether (OP-10, OP-20, OP-30), dodecyl dimethyl betaine (BS-12), octadeyl dimethyl betaine (BS-18), and lauramidopropyl hydroxysultaine (LPHS) were purchased from Guangzhou Churen Chemical Co., Ltd.

4.2. Experimental Method. The surfactant was put into a flask containing oily sludge and mechanically stirred under the conditions of the set detergent concentration, temperature, time, stirring speed, and S/L ratio. After allowing the mixture to stand and settle, the bottom mud was taken out and placed in an oven to dry. The dried sludge was subjected to Soxhlet extraction experiments with petroleum ether, a mixed solvent of benzene and ethanol, and chloroform. Then, the volatile solvent was continuously distilled out using a rotary evaporator, and finally, the oil phase was obtained.

The oil residual rate and oil removal efficiency can be obtained by eqs 2, 3 and 4.

$$K_1 = \frac{m_1}{m_2} \times 100\% \tag{2}$$

$$K_2 = \frac{m_3}{m_2} \times 100\% \tag{3}$$

$$K = \frac{K_1 - K_2}{K_1} \times 100\% \tag{4}$$

where m_1 is the oil content of the sample sludge (g), m_2 is the mass of the sample sludge before treatment (g), m_3 is the oil content after treatment (g), K_1 is the original oil content of the sludge (%), K_2 is the oil residual rate of the sludge after treatment (%), and K is the oil removal efficiency (%).

5. COMPOUND SYSTEM MODEL AND SIMULATION DETAILS

5.1. Model and Simulation Settings. This simulation was completed under the molecular dynamics software Materials Studio2018 program platform. First, the 3D model structure of n-decane, sodium dodecylbenzene sulfonate, sodium silicate, JFC-SF, and water molecules in the Visualizer module was built. The interaction parameters of surfactants come from the molecular force field optimized by condensed matter—COMPASS force field, and its potential energy includes two parts of energy: bonding interaction and nonbonding interaction. Then, the Dmol3 module was used to optimize the optimal molecular structure of the three surfactants, so that the energy of the surfactant molecular system reached the minimum. The optimized molecular conformation and schematic diagrams of the distribution of each atom are shown in Figures 9 and 10.
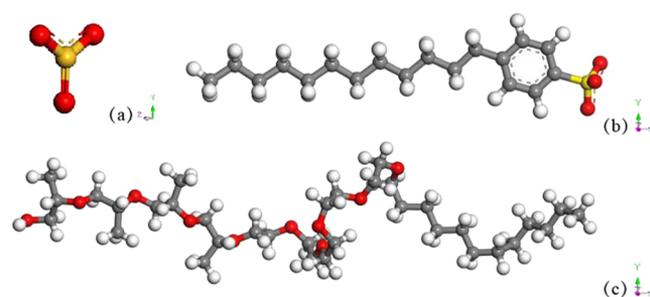
Figure 9. Optimized molecular structure: (a) Na_2SiO_3, (b) SDBS, and (c) JFC-SF. Si: yellow; S: orange; O: red; N: blue; and C: gray.

5.2. Complex System Model Construction and Simulation Details. Using the construction tool under the amorphous cell module, under the temperature condition of 273 K, the COMPASS force field was selected to establish the crude oil system model, the compound surfactant model, and the water phase system model. The simulation system was built with the build layers module, centered on the origin, and the size of the system box in the x, y, and z directions is 4 nm × 4 nm × 16 nm, using periodic cell periodic boundary conditions. Each layer has 500 n-decane molecules and 60 surfactant molecules with different compound ratios distributed at both ends of the box, and the middle water phase contains 1200 water molecules and different numbers of Na atoms. The front view of the system model is shown in Figure 11.

After the initial system model is established, the Forcite module is used to optimize the energy, structure, and dynamics
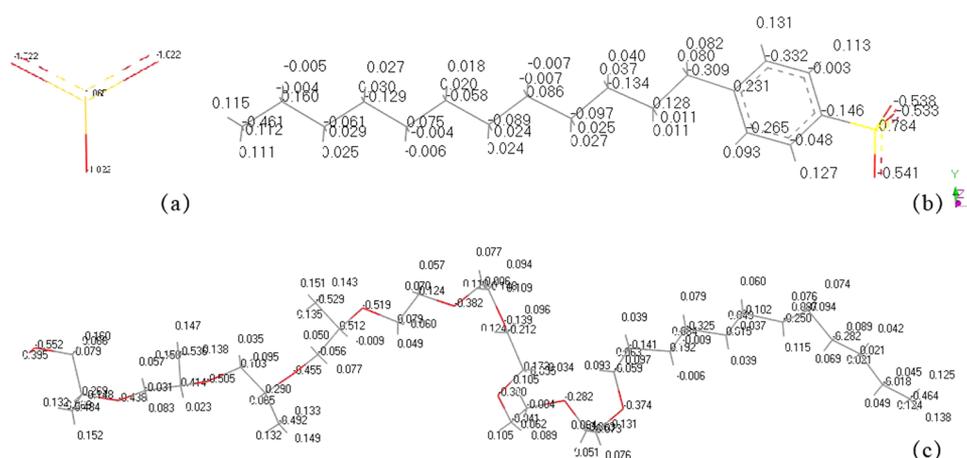
Figure 10. Schematic diagram of atomic distribution: (a) Na_2SiO_3, (b) SDBS, and (c) JFC-SF.
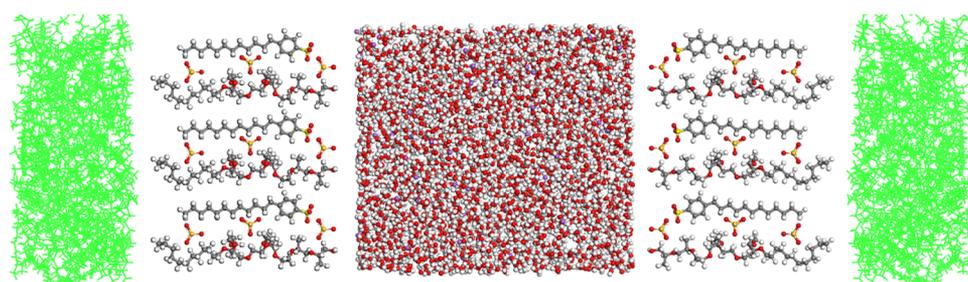
Figure 11. Compound system model. Si: yellow; S: orange; O: red; N: blue; C: gray; Na^+: purple; and oil: green.
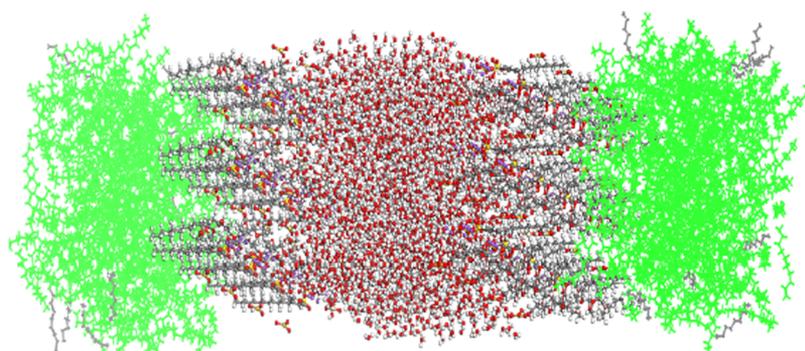
Figure 12. Equilibrium structure diagram of the surfactant in the oil–water system after the simulation.

of the system. The simulation level is MEDIUM, using the NPT ensemble, 0.0001 GPa is set as the conditional pressure, the van der Waals interaction force and electrostatic interaction are calculated by the atom-based method, and the cutoff distance is 1.25 nm. The Andersen and Berendsen method is chosen to control the temperature and pressure, 1.0 fs is set as the time step, a 500 ps molecular dynamics simulation is performed, the total number of steps is 500 000, and the calculation output is obtained every 500 steps. The equilibrium structure diagram of the surfactant in the oil–water system after the simulation is shown in Figure 12.

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Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Hu, G.; Li, J.; Zeng, G. Recent development in the treatment of oily sludge from petroleum industry: A review. *J. Hazard. Mater.* **2013**, *261*, 470−490.

(2) Hui, K.; Tang, J.; Lu, H.; Li, J.; et al. Status and prospect of oil recovery from oily sludge: A review. *Arabian J. Chem.* **2020**, *13*, 6523−6543.

(3) Wang, J.; Yin, J.; Ge, L.; Shao, J. H.; Zheng, J. Z. Characterization of Oil Sludges from Two Oil Fields in China. *Energy Fuels* **2010**, *24*, 973−978.

(4) Heidarzadeh, N.; Gitipour, S.; Abdoli, M. A. Characterization of oily sludge from a Tehran oil refinery. *Waste Manag. Res.* **2010**, *28*, 921−927.

(5) Duan, M.; Li, C. C.; Wang, X. D.; Fang, S. W.; Xiong, Y.; Shi, P. Solid separation from the heavy oil sludge produced from Liaohe Oilfield. *J. Pet. Sci. Eng.* **2019**, *172*, 1112−1119.

(6) Moncayo-Riascos, I.; Farid, B. C.; Bibian, A. H. Chemical Alteration of Wettability of Sandstones with Polysorbate 80. Experimental and Molecular Dynamics Study. *Energy Fuels* **2017**, *31*, 11918−11924.

(7) Nundy, S.; Ghosh, A.; Mallick, T. K. Hydrophilic and Superhydrophilic Self-Cleaning Coatings by Morphologically Varying ZnO Microstructures for Photovoltaic and Glazing Applications. *ACS Omega* **2020**, *5*, 1033−1039.

(8) Gong, X.; He, S. Highly Durable Superhydrophobic Poly-dimethylsiloxane/Silica Nanocomposite Surfaces with Good Self-Cleaning Ability. *ACS Omega* **2020**, *5*, 4100−4108.

(9) Posocco, P.; Perazzo, A.; Preziosi, V.; Laurini, E.; Pricl, S.; Guido, S. Interfacial tension of oil/water emulsions with mixed non-ionic surfactants: comparison between experiments and molecular simulations. *RSC Adv.* **2016**, *6*, 4723−4729.

(10) Jing, G. L.; Chen, T. T.; Luan, M. M. Studying oily sludge treatment by thermo chemistry. *Arabian J. Chem.* **2016**, *9*, S457−S460.

(11) Chen, G.; Cheng, C.; Zhang, J.; Sun, Y.; Hu, Q.; Qu, C.; Dong, S. B. Synergistic effect of surfactant and alkali on the treatment of oil sludge. *J. Pet. Sci. Eng.* **2019**, *183*, 106420−106428.

(12) Duan, M.; Wang, X.; Fang, S.; Bo, Z.; Li, C.; Xiong, Y. Treatment of Daqing oily sludge by thermochemical cleaning method. *Colloids Surf., A* **2018**, *554*, 272−278.

(13) Liu, M. T.; Pu, M. F.; Ma, H. W. Molecular Dynamics Simulation on Adsorbing Behavior of Anionic Gemini Surfactants at Decane/Water Interface. *Chem. Res. Chin. Univ.* **2012**, *33*, 1319−1325.

(14) Alonso, G.; Gamallo, P.; Mejía, A.; Sayós, R. Assessing salt-surfactant synergistic effects on interfacial tension from molecular dynamics simulations. *J. Mol. Liq.* **2020**, *299*, 112223−112259.

(15) Yang, Y.; Ma, Z. K.; Xia, F. J.; Li, X. B. Adsorption behavior of oil-displacing surfactant at oil/water interface: Molecular simulation and experimental. *J. Water Process Eng.* **2020**, *36*, 101292−101300.

(16) Liang, J.; Zhao, L.; Hou, W. Solid effect in chemical cleaning treatment of oily sludge. *Colloids Surf., A* **2017**, *522*, 38−42.

(17) Liu, C. H.; Zhang, Y.; Sun, S. S.; Huang, L. X.; Yu, L.; Liu, X. N.; Lai, R. Q.; Luo, Y. J.; Zhang, Z. Y.; Zhang, Z. Z. Oil recovery from tank bottom sludge using rhamnolipids. *J. Pet. Sci. Eng.* **2018**, *170*, 14−20.

(18) Liu, X. N.; Yao, T. T.; Lai, R. Q.; Xiu, J. L.; Huang, L. X.; Sun, S. S.; Luo, Y. J.; Song, Z. Z.; Zhang, Z. Z. Recovery of crude oil from oily sludge in an oilfield by sophorolipid. *Pet. Sci. Technol.* **2019**, *37*, 1582−1588.

(19) He, D. Q.; Chen, J. Y.; Bao, B.; Pan, X. L.; Li, J.; Qian, C.; Yu, H. Q. Optimizing sludge dewatering with a combined conditioner of Fenton's reagent and cationic surfactant. *J. Environ. Sci.* **2020**, *88*, 21−30.

(20) Guan, R. P.; Yuan, X. Z.; Wu, Z. B.; Wang, H.; Jiang, L. B.; Li, Y. F.; Zeng, G. M. Functionality of surfactants in waste-activated sludge treatment: A review. *Sci. Total Environ.* **2017**, *609*, 1433−1442.

(21) Wang, L. F.; He, D. Q.; Tong, Z. H.; Li, W. W.; Yu, H. Q. Characterization of dewatering process of activated sludge assisted by cationic surfactants. *Biochem. Eng. J.* **2014**, *91*, 174−178.

(22) Yang, Y.; Ma, Z. K.; Xia, F. J.; Li, X. B. Adsorption behavior of oil-displacing surfactant at oil/water interface: Molecular simulation and experimental. *J. Water Process Eng.* **2020**, *36*, 101292−10300.

(23) Meng, J. Q.; Yin, F. F.; Li, S. C.; Zhong, R. Q.; Sheng, Z. Y.; Nie, B. S. Effect of different concentrations of surfactant on the wettability of coal by molecular dynamics simulation. *Int. J. Min. Sci. Technol.* **2019**, *29*, 577−584.

(24) Gao, S. M.; Kang, Z. H.; Yuan, R. X.; Liu, N. N.; Zhu, P.; Wang, B. H. Molecular dynamics study of nonylphenol-substituted dodecyl sulfonate at air/water interface: Role of steric effect of surfactant headgroups. *J. Mol. Struct.* **2019**, *1192*, 35−41.

(25) Xu, J. F.; Zhang, Y.; Chen, H. X.; Wang, P.; Xie, Z. H.; Yao, Y. J.; Yan, Y. G.; Zhang, J. Effect of surfactant headgroups on the oil/water interface: An interfacial tension measurement and simulation study. *J. Mol. Struct.* **2013**, *1052*, 50−56.

(26) Urum, K.; Steve, G.; Turgay, P.; Sean, M. M. A comparison of the efficiency of different surfactants for removal of crude oil from contaminated soils. *Chemosphere* **2006**, *62*, 1403−1410.

(27) Hu, G. J.; Li, J. B.; Zeng, G. M. Recent development in the treatment of oily sludge from petroleum industry: A review. *J. Hazard. Mater.* **2013**, *261*, 470−490.

(28) Sivagami, K.; Deeksha, A.; Govindaraj, D.; Indumathi, N. Treatment of petroleum oil spill sludge using the combined ultrasound and Fenton oxidation process. *Ultrason. Sonochem.* **2019**, *51*, 340−349.

(29) Yang, T. H.; Liu, X. S.; Li, R. D.; Li, B. S.; Kai, X. P. Hydrothermal liquefaction of sewage sludge to produce bio-oil: Effect of co-pretreatment with subcritical water and mixed surfactants. *J. Supercrit. Fluids* **2019**, *144*, 28−38.

(30) Bergero, M. F.; Lucchesi, G. I. Degradation of cationic surfactants using immobilized bacteria: Its effect on adsorption to activated sludge. *J. Biotechnol.* **2018**, *272−273*, 1−6.

(31) Jin, Y. Q.; Zheng, X. Y.; Chu, X. L.; Chi, Y.; Yan, J. H.; Cen, K. Oil recovery from oil sludge through combi ned ultrasound and thermochemical cleaning treatment. *Ind. Eng. Chem. Res.* **2012**, *51*, 9213−9217.

(32) Viana, F. F.; Neuma, D.; Rossi, C.; Neto, A.; Silva, M. Aged oil sludge solubilization using new microemulsion systems: Design of experiments. *J. Mol. Liq.* **2015**, *210*, 44−50.

(33) Ramirez, D.; Collins, C. D. Maximisation of oil recovery from an oil-water separator sludge: Influence of type, concentration, and application ratio of surfactants. *Waste Manage.* **2018**, *82*, 100−110.