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Mechanism and Characteristics of Oil Recovery from Oily Sludge by Sodium Lignosulfonate Treatment

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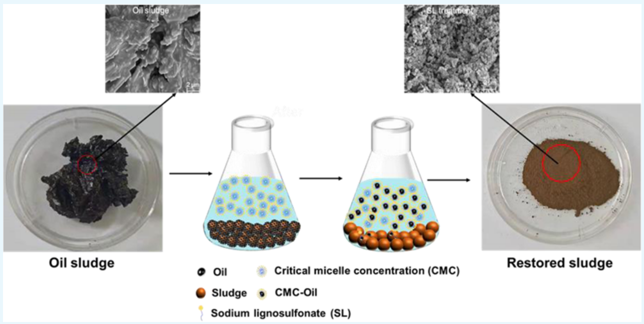
ABSTRACT: The separation of oil components from oily sludge is an important component of soil remediation and energy recovery. Therefore, establishing a green and efficient separation technology is of great significance. In this study, oily sludge was separated using sodium lignosulfonate (SL) treatment. The effects of temperature, SL concentration, rotate speed, time, and pH on the oil removal rate were studied. The optimal conditions were as follows: temperature, 30 °C; SL concentration, 2.0 $g \cdot L^{-1}$; rotate speed, 200 rpm; time, 60 min; and pH 11. The maximum oil removal rate was 83.21%. The physicochemical properties of oily sludge were analyzed. The soil was looser, and the contact angle (55°) of the soil surface was reduced. Alkanes, aldehydes, ketones, carbonic acids, benzene rings, and alicyclic ethers were removed. The result shows that the SL treatment removed a wider range of petroleum hydrocarbon and had a stronger oil removal capacity. It provides a new method for the green and efficient separation of oily sludge.



INTRODUCTION

Oily sludge is a sludge mixed with crude oil, all kinds of refined oil, residual oil, and other heavy oil. It is mainly produced in the exploitation, processing, and transportation of oil by oil spilling to the ground.[1,2] The annual production of oily sludge from the petroleum industry is up to billions of tons.[1,3] The ecological environment was seriously threatened by the presence of oily sludge, and oil resources were wasted.[4] The oil phase in oily sludge is mainly crude oil, which is mainly composed of hydrophobic petroleum hydrocarbons (PHCs) (e.g., saturated hydrocarbons, aromatic hydrocarbons, colloids, and asphaltenes). Asphaltenes and colloids have the greatest viscosity and the lowest liquidity. They are also the most stubborn components in the separation process of oily sludge. Therefore, the effective separation of PHCs from oily sludge has attracted the attention of researchers. At present, the treatment methods of oily sludge include solvent extraction,[5,6] incineration, the biological method, the coking method, profile control of oily sludge, and comprehensive utilization of oily sludge.[7,8] Traditional chemical methods including solvent extraction (chloroform, dichloromethane, chloroform, acetone, n-hexane, and n-heptane) were hazardous to the environment due to the addition of large quantities of chemicals. The subsequent pollution treatment load was large.[9] A large amount of energy was consumed in the incineration and coking. The biological method was a green treatment technology; however, the process control requirements were high. A low concentration of oily sludge was difficult to be treated with a biological method.[10] Physicochemical methods have the characteristics of high separation efficiency. They mainly include ultrasonic, flotation, and hot washing treatments.[11−14] In particular, hot washing has become a mainstream technology.

The interfacial tension of PHCs at the solid−liquid interface was reduced, and micellar dissolution was enhanced using surfactants during hot washing.[15] The migration and dissolution of PHCs in aqueous solutions were facilitated. Three-phase separation of PHCs, soil, and water in oily sludge was realized.[16] The surfactants mainly include biological surfactants and chemical surfactants. Biosurfactants mainly include glycolipids, fatty acids, and neutral lipids.[17,18] They are nontoxic and biodegradable.[19] Compared with chemical surfactants, the research of biosurfactants is in its infancy. The chemical surfactant in hot washing has the advantages of simple operation and a high oil removal rate. Sodium dodecyl

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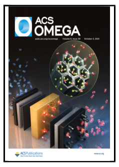

sulfate (SDS) was a typical chemical surfactant. The concentration of PHCs in the aqueous phase was increased by SDS treatment.[20] Duan et al.[21] studied the separation mechanism of oily sludge during SDS treatment. It was found that the water-soluble polyelectrolyte complex was destroyed by SDS. Finally, a water-soluble cationic flocculant−SDS complex was formed. The chemical surfactant, represented by SDS, has a high degreasing efficiency. However, the environment and organisms were seriously damaged owing to its poor biodegradation.[7] Therefore, it is very important to study green and efficient surfactants for oily sludge separation. Sodium lignosulfonate (SL) is an important byproduct of sulfite pulping,[22,23] and is also an anionic surfactant. This was attributed to the fact that SL contains numerous anionic polar groups (such as phenol, aliphatic hydroxyl, carbonate, and sulfonic acid groups). It is an amphiphilic molecule.[24,25] Therefore, it can be used as a washing surfactant for oily sludge. In addition, SL has the advantages of low cost and environmental friendliness. The pollution load of oily sludge after hot washing will be effectively reduced.

In this study, the PHCs in oily sludge were removed by SL treatment. The effects of reaction temperature, SL concentration, rotate speed, reaction time, and pH on the oil removal rate were studied. The apparent morphology of the oily sludge with and without treatment was analyzed by scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDX), and contact angle measurements. The main components of oily sludge with and without treatment were analyzed using infrared spectroscopy (FTIR) and gas chromatography−mass spectrometry (GC−MS). It provides a new method for the green and efficient separation of oily sludge.

■ RESULTS AND DISCUSSION

Effect of Temperature on the Oil Removal Rate. The surfactant micelle with a maximum adsorption binding force was formed at the Kraft point (temperature).[26] Therefore, the effect of the reaction temperatures (20, 30, 40, 50, 60, and 70 °C) on the oil removal efficiency during the separation of oily sludge by SL treatment was studied. The other reaction conditions were as follows: SL concentration, 1.0 g·L^{-1}; rotate speed, 150 rpm; pH = 7.0; and time, 60 min. The results are presented in Figure 1. The oil removal rate increases slowly with temperature in the control experiment. It increased from 8.49 to 13.21%. Compared with the control experiment, the oil removal rate has a significant change in the SL treatment. It increased from 37.60 to 54.11% when the reaction temperature increased from 20 to 30 °C. The maximum oil removal rate was obtained at 30 °C, indicating that the Kraft point of SL was 30 °C.[26] First, larger diameter micelles were formed. The combination of the nonpolar end of SL to PHCs in the oily sludge was promoted. This results in reduced interfacial tension between sand grains and PHCs. The mass transfer rate of SL from the soil phase to the water phase was increased, which promoted the removal of PHCs from the sediment surface. However, the oil removal rate decreased with increasing temperature above 30 °C and was 31.52% at 60 °C and 33.00% at 70 °C. The softening degree of colloid and asphaltene increases with the increase of temperature. The interfacial tension between them and the sand surface was increased. A large number of PHCs adhered to their surfaces. The solubility of PHCs was reduced, and the activity of the combination of the nonpolar end of SL with hydrocarbon substances was inhibited.[27] Therefore, the optimal temperature for oily sludge separation by SL treatment was 30 °C.

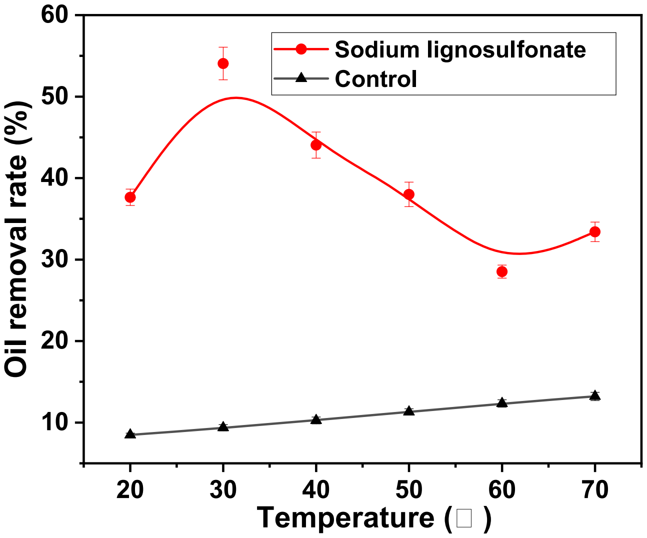

Figure 1. Effect of temperature on the oil removal rate during oily sludge separation by sodium lignosulfonate treatment.

Effect of SL Concentration on the Oil Removal Rate. The effect of SL concentration (0.5, 1.0, 2.0, 3.0, and 4.0 g·L^{-1}) on the oil removal rate was studied. The other reaction conditions were as follows: temperature, 30 °C; rotate speed, 150 rpm; pH = 7.0; and time, 60 min. The results are presented in Figure 2. The oil removal rate was low without SL addition (9.37%). The removal of PHCs was facilitated by increasing the SL concentration at low SL concentrations. The oil removal rate increased from 49.21 to 63.25% when the concentration of SL increased from 0 to 2.0 g·L^{-1}. This was attributed to the critical micelle concentration of SL at 2.0 g·L^{-1}, which reduced the surface tension of the oily sludge. The details are shown in Figure 3. The dissolution of PHCs was accelerated at this concentration. They were efficiently removed from the oily sludge as a large number of micelles entered the solution.[28,29] In particular, the oil removal rate

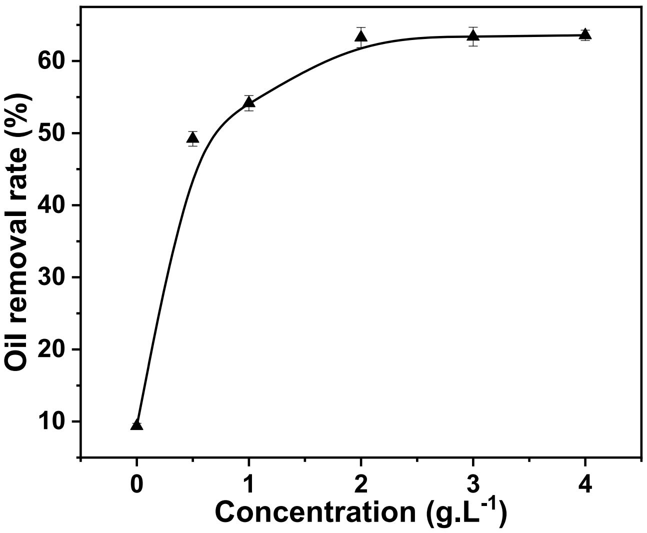

Figure 2. Effect of sodium lignosulfonate concentration on the oil removal rate during oily sludge separation by sodium lignosulfonate treatment.

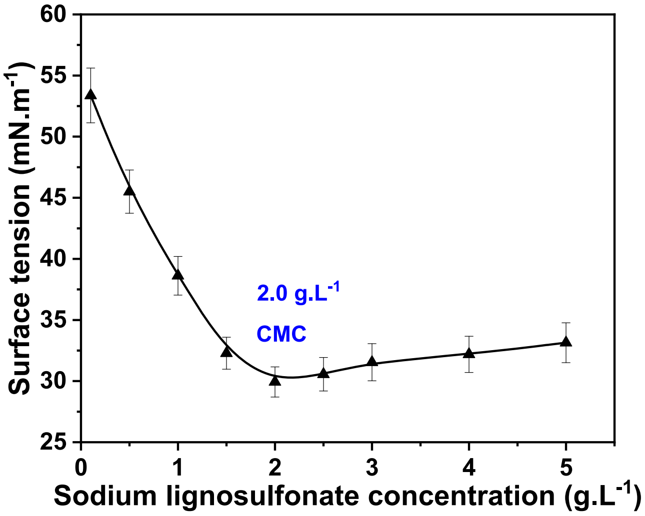

Figure 3. Effect of sodium lignosulfonate concentration on surface tension during oily sludge separation by sodium lignosulfonate treatment.

remains constant as the SL concentration continues to increase. Therefore, the optimal SL concentration was 2.0 g·L^{-1}.

Effect of Rotate Speed on the Oil Removal Rate. The adequate mixing of chemicals and oily sludge was one of the main prerequisites for ensuring the separation of oily sludge.[7] Agent permeation at the interface between the sludge and PHCs was promoted at a suitable rotate speed. Therefore, the effect of rotate speed (50, 100, 150, 200, 250, and 300 rpm) on the oil removal rate of oily sludge was studied. The other reaction conditions were as follows: temperature, 30 °C; SL concentration, 2.0 g·L^{-1}; pH = 7.0; and time, 60 min. The results are presented in Figure 4.

The oil removal rate increased from 6.33 to 12.03% with the increase of revolution in the control experiment. This means that the removal of oil components from oily sludge by rotate speed alone was limited. It has a significant effect on the oil removal rate after the addition of SL. It increased from 44.27 to 68.51% as the rotate speed increased from 50 to 200 rpm. This was attributed to the decrease of the bonding force between the sludge surface and PHCs with the increase of friction. The PHCs were removed with the gradual shrinkage of the oil droplets.[30] In addition, the foaming property of the SL solution was improved by the increase in vibration generated by increasing the rotate speed.[31] The contact probability of the hydrophobic PHCs with SL increased, and the PHCs were adsorbed by the air bubbles. The removal of PHCs was promoted. However, it was reduced to 50.27% at 300 rpm. This was attributed to the enhanced readsorption and polymerization of the removed PHCs on the sludge surface. Therefore, the optimal rotate speed was 200 rpm.

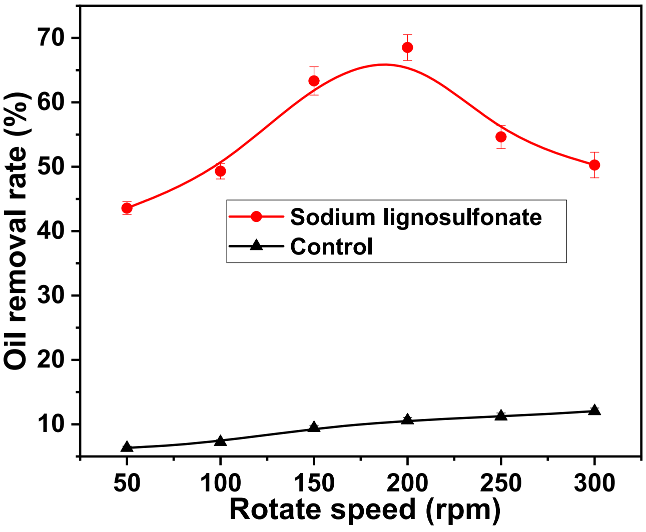

Figure 4. Effect of rotate speed on the oil removal rate during oily sludge separation by sodium lignosulfonate treatment.

Effect of Time on the Oil Removal Rate. The effect of reaction time (30, 40, 50, 60, 120, and 180 min) on the oil removal rate was studied. The other reaction conditions were as follows: temperature, 30 °C; SL concentration, 2.0 g·L^{-1}; rotate speed, 200 rpm; and pH = 7.0. The results are presented in Figure 5.

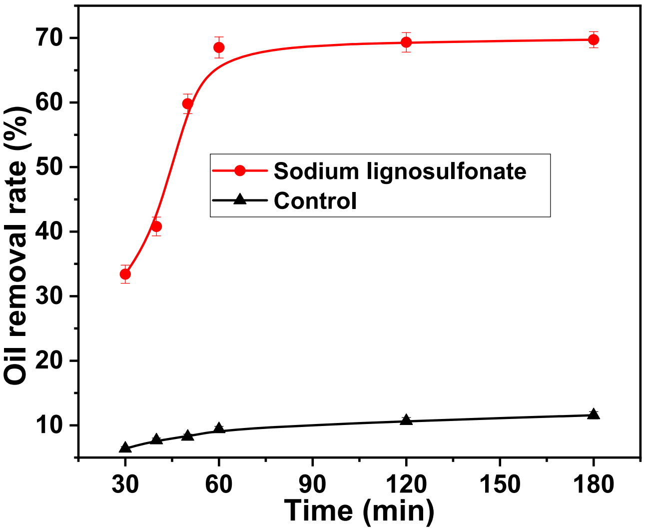

Figure 5. Effect of time on the oil removal rate during oily sludge separation by sodium lignosulfonate treatment.

The results of the control experiment showed that the oil removal rate increased from 6.39 to 11.56% with time. This indicates that it was difficult to effectively remove PHCs from oily sludge by increasing the reaction time without SL addition. However, it increased rapidly from 33.21 to 68.56% between 30 and 60 min after adding SL. Then, it remained essentially unchanged after 60 min (69.03 and 69.89% at 120 and 180 min, respectively). This means that extending the reaction time only provided limited improvement in oily sludge separation under the fixed reaction conditions. In fact, the stripping effect of PHCs mainly comes from the combination of SL adsorption and hydraulic shear.[32] However, the adsorption force and hydraulic shear force would not change with the reaction time under fixed reaction conditions. Therefore, the optimal reaction time was 60 min.

Effect of pH on the Oil Removal Rate. The physicochemical properties of SL (including solubility, surface activity, foaming, and foam stability) were affected by the pH of the solution.[33] Therefore, the effect of the solution pH (3, 5, 7, 9, 11, and 13) on the oil removal rate was studied. The other reaction conditions were as follows: reaction temperature, 30

°C; SL concentration, 2.0 g/L; rotate speed, 200 rpm; and reaction time, 60 min. The results are presented in Figure 6.

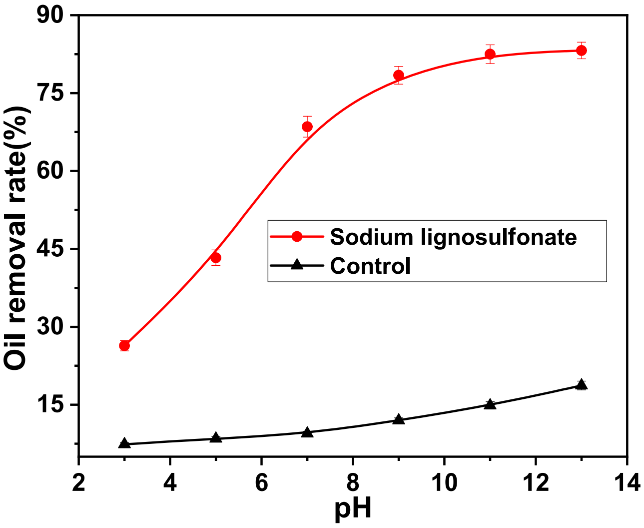

Figure 6. Effect of pH on the oil removal rate during oily sludge separation by sodium lignosulfonate treatment.

Obviously, the removal rate of oil components changed significantly with and without SL addition. It increases from 7.37 to 18.70% as the pH increases, which is due to the fact that some PHCs are alkali-soluble. In particular, most of the aromatic hydrocarbons have good alkali solubility. Moreover, the oil removal rate was significantly increased with the synergistic effect of SL. It was positively correlated with the pH of the solution. The oil removal rate was low under acid conditions (26.12 and 43.63% at pH 3.0 and 5.0, respectively). In contrast, higher oil removal rates were obtained under alkaline conditions (68.49 and 83.21% at pH values of 7.0 and 11.0, respectively). Then, it increased slightly with the continuous increase in pH. This was attributed to the conformational curling and microaggregation of SL in solution under low pH conditions. The ionization degree of carboxylic acid and phenolic hydroxyl groups increased with increasing pH. The electrostatic repulsion increased, while the molecular elongation and the microarea aggregation of SL were reduced.[34] Therefore, SL has a more stable structure and stronger reactivity under alkaline conditions, which leads to a better binding force with nonpolar substances. In addition, the acids in the PHCs were removed due to their saponification with the alkali.[35] The combination force between PHCs and soil was further weakened, allowing the PHCs to be stripped from the surface of oily sludge. The optimal pH was 11.

The optimal conditions for SL treatment were obtained through a single-factor analysis, which were as follows: a reaction temperature of 30 °C, SL concentration of 2.0 g·L^{-1}, rotate speed of 200 rpm, the reaction time of 60 min, and pH of 11. Under these conditions, the oil removal rate was as high as 83.21%, which was increased by 12.86% compared with that of the traditional SDS treatment. Subsequently, the physicochemical properties and removal components of the oily sludge were analyzed.

Physicochemical Properties of Oily Sludge with and without Treatment. Oily sludge is a type of water-in-oil emulsion that mainly includes water, solid particles, PHCs, and metals. It is very stable, primarily because the protective film formed by the oil on the surface of the water droplets prevents polymerization between the water and water droplets. This interfacial film is formed by natural emulsifiers, such as some PHCs, asphaltenes and colloids, fine solid particles, oil-soluble organic acids, and other uniformly dispersed substances.[1] The difficulty in separating oily sludge is due to its stable emulsion structure. However, green efficient separation was achieved by the SL treatment. The contact angles of the different oily sludges are shown in Figure 7.

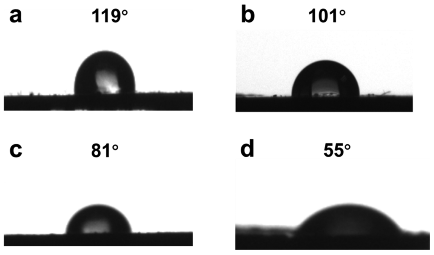

Figure 7. Contact angle of the oily sludge surface with and without treatment ((a) oily sludge; (b) control experiment; (c) SDS treatment; (d) SL treatment).

The wetting behavior of a droplet in contact with a solid surface depends on the contact angle. The wettability between the liquid and solid was controlled by their chemical properties and surface microstructure.[36] The contact angle of the original oily sludge was 119°. This indicates that the original sludge was highly hydrophobic. The sludge surface was covered with PHCs, which made it difficult for the surface to be wetted by water. The contact angle of the oily sludge treated with SDS was 81°. The surface of the sludge changed from hydrophobic to hydrophilic. However, it was not very hydrophilic. This proves that the separation degree of the oily sludge by SDS treatment was not high. The contact angle of the oily sludge surface was substantially reduced to 55° with the SL treatment. In particular, the contact angle of the oily sludge surface in the control experiment was 101°. This indicates that the surface of the soil was strongly hydrophilic and a large number of PHCs in the oily sludge were removed by the SL treatment. The morphological and structural features of the oily sludge with and without treatment were analyzed by SEM. The results are presented in Figure 8.

The original oily sludge appeared to be agglomerated in bulk. It had distinct oil-coated soil morphology with a bright color. In fact, oily sludge mainly forms by the adsorption of PHCs on hydrophilic solid particles at the water−oil interface.[37] There were two reasons leading to the strong stability of the oily sludge. First, the larger solid particles were heavy and rough, which lead to settling. The fine solid particles were lighter, which allows them to float on the surface of the water. Second, the oil solid particles in the oily sludge adsorb onto the soil. This results in the formation of a strong protective layer on the surface of the particles,[38] which generates charge repulsion from polar organic compounds in the oily sludge and promotes the formation of homogeneous oily sludge. The dispersion of the soil was improved by the SDS treatment. Its surface appeared as a dense black sheet. This was attributed to the fact that SDS contains not only polar hydrophilic groups but also nonpolar hydrophobic groups (lipophilic groups). SDS was adsorbed on the interface between soil and PHCs. The interfacial tension between soil and PHCs was reduced, which was beneficial to the removal of

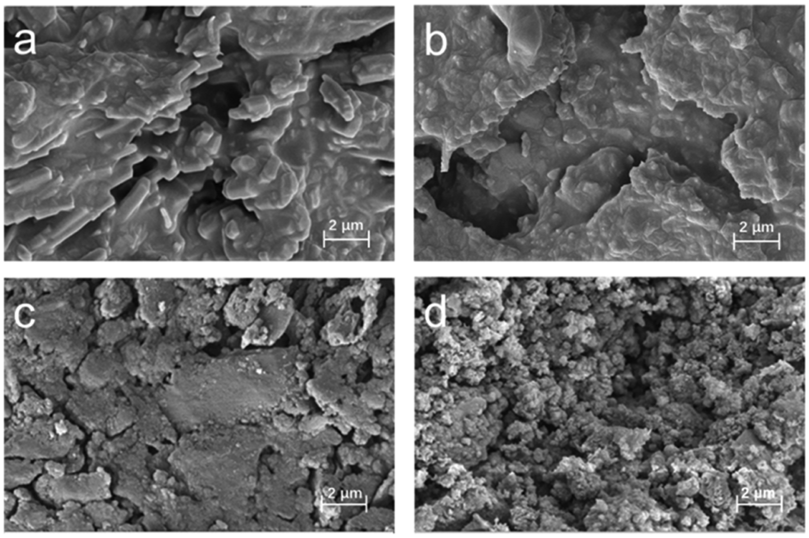

Figure 8. Micromorphology of the oily sludge with treatment ((a) oily sludge; (b) control experiment; (c) SDS treatment; (d), SL treatment).

PHCs.[39] Small amounts of residual PHCs were responsible for the formation of flaky soil. Compared with the soil treated with SDS, the soil treated with SL was more dispersed. Its shape was dark and loose, indicating that more PHCs had been removed. Moreover, the surface morphology of the oily sludge in the control experiment without SL addition was similar to that of the original oily sludge. This was attributed to the fact that SL is an anionic amphiphilic polymer with good wettability, adsorption, and dispersion. It was readily adsorbed to the surface of liquids, which changed the surface properties. Therefore, higher oil removal rates were obtained.

The surface elemental composition of the different oily sludge was analyzed by EDX. The percentages of surface atoms in the oily sludge are listed in Table 1. Oily sludge is a type of water-in-oil emulsion that mainly includes water, solid particles, PHCs, and metals.[30] The solid was mainly composed of silica, inorganic metal salt, and carbonate.[15] Therefore, the main components of the oily sludge were carbon, hydrogen, oxygen, sulfur, and silicon. In fact, the oily sludge was covered by a large amount of PHCs while other elements were not detected. The atomic percentage of carbon in the oily sludge decreased from 81.65 to 56.07% with SDS treatment. This indicates that the PHCs were removed. The atomic percentage of oxygen increased from 13.41 to 35.16%. PHCs also contain a certain amount of nitrogen, sulfur, and oxygen (NSO) compounds.[20] The NSO content decreased with the removal of PHCs. The atomic percentage of sulfur on the surface of the oily sludge decreased from 5.03 to 2.65%. A large amount of sand surface was exposed after the removal of PHCs from the oily sludge. As a result, the atomic percentages of Si and Al increased. Compared with the oily sludge with SDS treatment, the surface composition of the oily sludge with SL treatment contained more types of elements. The change in the atomic percentage was more significant. The atomic percentages of carbon and oxygen were 48.15 and 25.99%, respectively. The results of the control experiment showed that the contents of C, H, and O were the same as those of the original oily sludge. This indicates that control experiments without SL addition do not have effective removal capability of PHCs. The SL treatment had a substantial oil removal effect, and a large number of PHCs were removed. More elements were detected in the soil, and the atomic percentages of Mg, Al, Si, K, and Ti increased significantly. The main functional groups of the different oily sludges were analyzed by FTIR, and the results are presented in Figure 9.

Table 1. Elemental Distribution and Composition Changes of Oily Sludge with and without Treatment

			samples	
element	oily sludge (%)	control experiment (%)	SDS treatment (%)	SL treatment (%)
C	81.65	81.32	56.07	48.15
H	4.20	4.31	13.09	10.45
O	9.05	9.15	22.07	15.54
Mg				1.53
Al			2.64	6.90
Si	0.07	0.08	3.48	11.60
S	5.03	4.98	2.65	2.42
K				2.19
Ti				1.22

As expected, most bands in the oily sludge with and without treatment had similar spectral distributions and relative intensities. However, some special functional groups migrated or disappeared in the different oily sludges. This indicates that the main components of PHCs in the oily sludge were changed with and without treatment. The absorption at 3427 cm^{-1} was attributed to the O−H stretching vibration from the hydroxyl groups of the PHCs and water. The sharp absorption peak at 2920 cm^{-1} was attributed to the C−H stretching vibration of alkanes.[40] Similarly, the band at 2850 cm^{-1} was attributed to the C−O stretching vibration of the aldehyde group. The band at 1616 cm^{-1} was attributed to the C−H deformation of olefins. The weak absorption peak at 1452 cm^{-1} was attributed to the C═C stretching vibration of the benzene skeleton. The small band at 1045 cm^{-1} was attributed to the C−O−C stretching vibration of fatty ether. The adsorption band at 792 cm^{-1} was attributed to the stretching vibration of the C−H substituted bond of the benzene ring. The adsorption band at 532 cm^{-1} was attributed to the bending vibration of C−C═O in aliphatic aldehydes. The absorption band at 470 cm^{-1} was attributed to the lattice vibrations of Mg−O and Al−O.[41] The

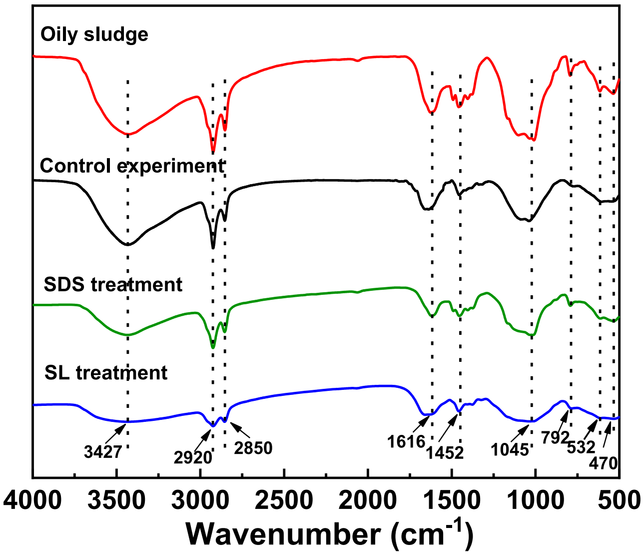

Figure 9. FTIR of the oily sludge with and without treatment.

results show that the PHCs in the oily sludge mainly consisted of aliphatic and aromatic hydrocarbons.

The above absorption peaks of the oily sludge were weakened to different degrees by the SDS treatment. This shows that the SDS treatment has a certain oil removal ability. The main functional group characteristics of the oily sludge in the control experiment were similar to those of the original oily sludge. This means that PHCs in the oily sludge cannot be effectively removed without SL addition. Compared with that treated with SDS, there were some clear changes in the absorption spectra of the oily sludge treated with SL, which were summarized as follows. The absorption intensity at 3427 cm^{-1} decreased substantially. This indicates that a larger total amount of PHCs was removed by the SL treatment. The peak intensities at 2920, 2850, 1452, 1045, 792, 532, and 469 cm^{-1} were significantly reduced. This was attributed to the efficient removal of asphaltenes (*e.g.*, alkanes, aldehydes or ketones, carboxylic acids, benzene rings, and alicyclic ethers). In fact, it was the most difficult component of the oily sludge to treat. This means that the SL treatment of the oily sludge was more efficient than that of the SDS treatment.

PHCs in Oily Sludge with and without Treatment. Typically, an oily sludge is composed of 40−52% alkanes, 28−31% aromatics, 15−32% asphaltenes, and colloids.[4] At present, the organic solvents used for the oil component extraction mainly include chloroform, dichloromethane, chloroform, acetone, *n*-hexane, and *n*-heptane. In particular, *n*-heptane has the extraction effect on all components.[42] Therefore, the organic compounds in the different oily sludge samples were extracted using *n*-heptane. Changes in the PHCs in the oily sludges that underwent different treatments were analyzed using GC−MS. The results are presented in Figure 10.

Figure 10 shows the chemical compositions of the extracts from the oily sludge with and without treatment. The details are presented in Table 2. The main components of the oily sludge were saturated and aromatic hydrocarbons, naphthenic acid, benzoic acid, mercaptan, and pyridine. These results were consistent with those of the previous studies.[43] The saturated and aromatic hydrocarbons accounted for 75% of the total PHCs in the oily sludge. The chemical composition of these hydrocarbons mainly included alkanes, cycloalkanes, benzene, toluene, phenols, and a variety of polycyclic aromatic hydrocarbons (PAHs). The pectin contained polar components (*e.g.*, naphthenic acid, mercaptan, thiophene, and pyridine). Asphaltene is a mixture of n-pentane-insoluble substances and colloidal substances, and its main components include alkyl substitutes for aromatic and aliphatic hydrocarbons.[3] The content of 2,6,10,14-tetramethylpentadecane was significantly reduced, and other saturated hydrocarbons

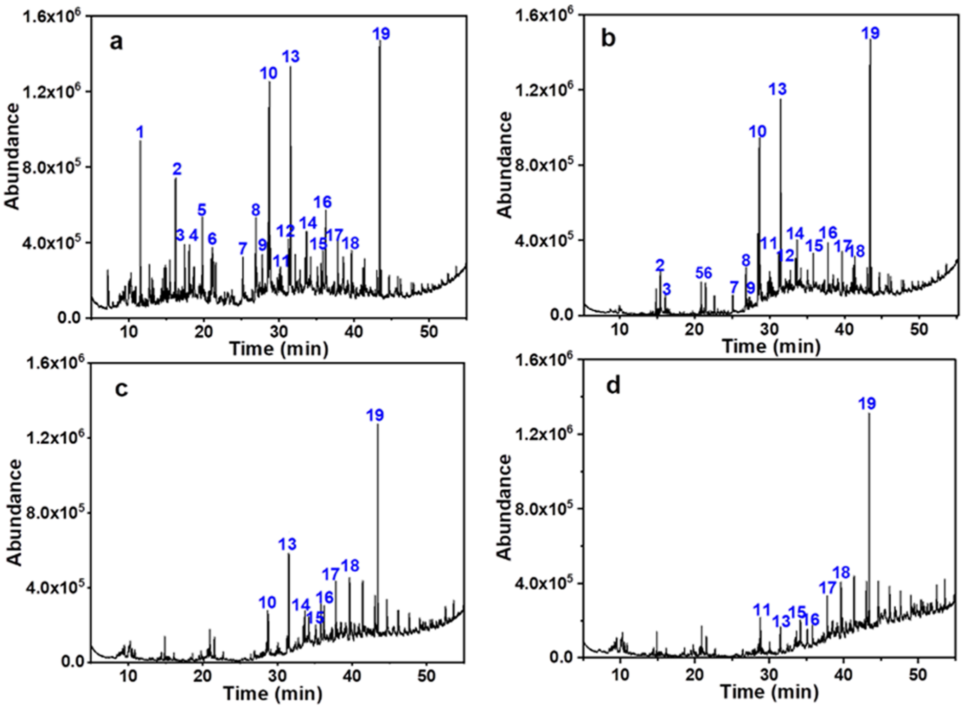

Figure 10. GC−MS of the oily sludge with and without treatment ((a) oily sludge; (b) control experiment; (c) SDS treatment; (d) SL treatment).

Table 2. Chemical Compositions of Different Oily Sludges

			retention time (min)		
array	oily sludge	control experiment	SDS treatment	SL treatment	components
1	11.507				diethyldimethyl-plumbane 2,3-dihydroxybenzoic acid
2	16.216	16.216			cyclohexasiloxane, dodecamethyl-
3	17.424	17.424			dodecane, 2,6,10-trimethyl-
4	18.024				tetradecane
5	19.775	19.775			2,6,10-trimethyltridecane
6	21.080	21.080			pentadecane carbonic acid, eicosyl vinyl ester
7	25.177	25.177			hexadecane
8	26.905	26.905			tridecane, 5-propyl-
9	28.518	28.518			heptadecane
10	28.690	28.690	28.690		2,6,10,14-tetramethylpentadecane
11	28.810	28.810		28.810	*n*-eicosane
12	31.271	31.271			octadecane
13	31.505	31.505	31.500	31.500	hexadecane, 2,6,10,14-tetramethyl-
14	33.668	33.668	33.668		Octadecane, 2-methyl-
15	35.820	35.820	35.820	35.820	*n*-eicosane
16	36.226	36.226	36.226	36.615	cyclic octaatomic sulfur, hexathiane, 4-phenylpyridine
17	37.800	37.800	37.800	37.800	*n*-eicosane, eicosane, 2-methyl-
18	39.653	39.653	39.653	39.653	docosane
19	43.413	43.413	43.413	43.413	phenol

and aromatic hydrocarbons below C_{18} were completely removed by the SDS treatment. The ability of the SDS treatment to remove PHCs decreased with the increasing length of the molecular chain. There was a slight decrease in the contents of 2,6,10,14-tetramethylcetane, 2-methyl-octadecane, n-eicosane, cyclooctatomic sulfur, hexathiane, and 4-phenylpyridine, while the contents of n-eicosane, 2-methyl-eicosane, docosanediane, and 2,2′-methylene-bis-(4-methyl-6-tert-butyl phenol) remained essentially unchanged. This indicates that the SDS treatment had a better removal effect on the light PHCs. It was difficult to remove heavy PHCs, represented by pectin. Figure 10b shows the results of the control experiment without SL. The contents of most PHCs were basically unchanged. This means that the control experiment has no effect on the separation of oily sludge. Compared with the oily sludge treated with SDS, all light hydrocarbons (including C_{20} and below) were completely removed by the SL treatment, except for a small amount of n-eicosane and 2,6,10,14-tetramethylhexadecane. Therefore, it had a stronger removal effect on light PHCs. This confirms the above conclusion. The ability of the SDS treatment to remove light PHCs was lower than that of the SL treatment. Except for 2,2′-methylene-bis-(4-methyl-6-tert-butyl phenol) (whose content remained unchanged), the heavy PHCs were effectively removed by the SL treatment. This means that the range of PHCs removed by the SL treatment was wider and the removal ability was stronger than those by the SDS treatment. The separation mechanism of oily sludge mainly consists of solubilization and migration. SDS has high reactivity under alkaline conditions,[34] and the CMC of SDS was formed at lower temperatures. The interactions between SDS molecules and PHC molecules were enhanced, which resulted in reduced interfacial tension between soil and PHCs. The fluidity of PHCs in oily sludge was increased, which promoted the migration of PHCs from the oily sludge. The efficient separation of PHCs from the oily sludge was realized.

■ CONCLUSIONS

A green and efficient method for separating oily sludge with SL treatment was developed, which achieved an oil removal rate of up to 83.21%. The oily sludge treated with SL had better hydrophilicity and higher dispersibility. The atomic percentage of carbon in the sample was significantly reduced owing to the efficient removal of PHCs. Compared with the oily sludge treated with SDS, more light PHCs were removed by SL treatment. It also had a significant effect on heavy PHCs. This indicates that the SL treatment removed a wider range of PHC and had a stronger removal capability.

■ MATERIALS AND METHODS

Materials. Oily sludge was collected from Xinjiang, China. The chemical composition of the oily sludge was analyzed using an automatic ash moisture analyzer (AG, CH-8953, Dietikon, Switzerland). The water, oil, and solid contents were 55.50, 32.50, and 12.00%, respectively. SL and SDS were purchased from Sigma-Aldrich (Milwaukee, WI). Other analytical chemicals were purchased from Aladdin (Shanghai, China).

Hot Washing of the Oily Sludge. The hot washing of the oily sludge was conducted in a conical flask. Various concentrations of SL solution were added to 2.0 g of oily sludge. The solid−liquid ratio was 1:20. The pH of the mixture was adjusted using a sodium hydroxide solution, and various reaction temperatures and rotate speeds were used. The oily sludge was left standing for 4 h after the reaction. The solid and liquid were completely stratified, and the supernatant was removed. Finally, the precipitated oily sludge was placed in an oven at 60 °C for 6 h. The water and oil contents were determined using an automatic ash moisture analyzer (prepASH 219, Precisa, Zurich, Switzerland). Two grams of oily sludge was added to the crucible. The first heating rate was 5 $°C\cdot min^{-1}$. The temperature was kept at 100 °C for 4 h. The weight loss is the moisture content. The second heating rate was 8 $°C\cdot min^{-1}$. The temperature was kept at 600 °C for 4 h. The solid content in oily sludge was obtained. The total weight of oily sludge was the sum of oil content, water content, and solid content. Therefore, the oil content of the oily sludge was calculated.

The separation effect of the oily sludge without adding SL was analyzed in the control experiment. Hot washing with the SDS chemical surfactant was used.[44] The specific method and steps were as follows: 2.0 g·L^{-1} SDS solutions were added to 2.0 g of the oily sludge. The solid−liquid ratio was 1:20. The reaction was conducted at 50 °C for 40 min. The fixed speed was 200 rpm. The oil removal rate was calculated in a manner similar to eq 1

$$QR(\%) = (O_1 - O_2)/O_1 \quad (1)$$

where QR was the removal rate of the oily sludge (%), O_1 was the oil content of the original oily sludge (%), and O_2 was the oil content of sludge after treatment (%). The oil removal rate with SDS was 70.35%.

Physicochemical Properties of the Oily Sludge. The lipophilicity and hydrophilicity of the different oily sludges were analyzed using a droplet shape analyzer (DSA100M, KRÜSS, Hamburg, Germany).[45] The average values were obtained from three measurements. The surface morphologies of the different oily sludges were analyzed using SEM (Quanta FEG 250, FEI, Hillsboro, Oregon). The elements in the oily sludge were determined using an energy-dispersive X-ray spectrometer installed on a JSM-6700F.[46] The oily sludge was dried in an oven at 60 °C. A relatively flat sheet of sludge was selected, which was attached to a conductive adhesive. Gold was sprayed on the sample for 50 s after a nitrogen purge. The magnification was 6000.

The changes in the main functional groups in the oily sludge were analyzed using FTIR (TENSOR27, Bruker, Karlsruhe, Germany). The specific method and steps were described by Wang et al.[47] The organic matter in the oily sludge was analyzed using GC−MS (QP2010SE, Shimadzu, Kyoto, Japan).[43] First, 500 mg of the oily sludge was extracted with n-heptane. Second, ultrasonic treatment was applied at 3000 rpm for 10 min, and the sample was centrifuged for 5 min. After centrifugation, the ultraviolet spectrum of the supernatant was measured at 400 nm. The above steps were repeated several times until the absorbance of the supernatant did not change. The supernatant was filtered through a 0.22 μL microporous membrane. The GC sample column was an HP-5 fused silica capillary column. The operating conditions were as follows. The injection port was maintained at 280 °C in a splitless mode, and 1 μL of the extracted sample was injected. The initial temperature was set to 60 °C with a hold time of 2 min. The temperature was increased to 140 °C at 5 °C·min^{-1}, with a hold time of 5 min. Subsequently, the temperature was increased to 300 °C at 5 °C·min^{-1}, with a hold time of 5 min.

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Notes

The authors declare no competing financial interest.

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