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Preparation and Application of New Demulsifier for Dirty Oil Sludge

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Abstract
In this study, DW1 as a novel commercial demulsifier was prepared by emulsion copolymerization. The demulsifier DW1 was characterized using five approaches, i.e. (1) FT-IR spectroscopy, (2) gel permeation chromatography (GPC), (3) ^{1}H-NMR, (4) ^{13}C-NMR, and (5) particle size analysis The demulsification experiment using DW1 as a demulsification process was carried out with Xinjiang sludge as the target treatment object, and the sludge before and after treatment was analyzed by scanning electron microscopy.The results showed that the synthetic demulsifier DW1 had the following properties: (1) weight-average molecular weights (Mw) ranging from 454319 to 1388086, (2) number-average molecular weights (Mn) of 801880, (3) molecular weight distribution index of 1.73104, (4) D50 of 26.00 µm, (5) average particle size of 25.00 µm, (6) non-uniform particle size distribution, and (7) good enough stability. The demulsification experiment showed that the oil removal rate of DW1 on a Xinjiang oil field could reach 99.55%.

Keywords: Demulsifier, Oil Sludge, Emulsion Polymerization, Oil Removal Rate.

Introduction
In the process of oil extraction, a large amount of floor sludge and tank bottom sludge will not only cause serious pollution to the environment, but also cause a large amount of waste of funds in the process of its treatment. Up to now, the treatment methods of sludge mainly include physical [1-4], chemical [5-7], biological [8-10], and combined methods [11-13] Demulsification in chemical method has the characteristics of simple operation and quick effect, which will become the most common dehydration and deoiling method in petroleum industry. Effective demulsifier is added in the sewage sludge system, which it makes the demulsifier have dispersed evenly in the sewage sludge system for random movement, when the movement to the oil-water interface will adhere to the oil-water interface, and demulsifier pro-oil base group and hydrophilic group respectively into two phases, resulting in (1) lower interfacial film viscosity and (2) the decrease of strength of oil-water interface, and thereby the results make a shorter film life, the thickness of the oil film, when the film thickness thinning to an extreme, membrane rupture, and lead to successful demulsification. It was found by Zheng Xiaoyuan et al [14] that demulsifier P9935 had the best dehydrating effect when the concentration was 0.3%, and the oil content of treated sludge reached 2.07%. Furthermore, bacteria and yeast in the ocean as demulsifier of oil sludge were used by Fernanda Cristina et al [15], and it was found out that this demulsifier had a strong recovery effect on oil products, and the treated oil sludge had no pollution to the environment. Three demulsifiers were synthesized by Abde-azim et al [16] using nonylphenol ethoxyl compounds as raw materials, among which, the demulsifier based on NP-13 was the best for recovering oil products from dirty oil sludge. In this paper, a kind of demulsifier DW1 was prepared by emulsion polymerization, and the demulsification treatment experiment was carried out on the sludge of a Xinjiang oil field, and good demulsification and oil removal effect were obtained.

Materials and Methods
The Raw Material
In this study, the raw materials used are as follows: Monomer acrylic, pure (AR); Initiator $K_2S_2O_8$, analytically pure (AR); Monomer butyl acrylate, pure (AR); Monomer methyl methacrylate, analytically pure (AR); emulsifier polyoxyethylene octyl phenol ether-10, analytically pure (AR); Polymerization inhibitor

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hydroquinone, analysis of pure (AR); All purchased from Tianjin Damao chemical reagent factory, China

Preparation of Demulsifier DW1

A 1.2 g polyoxyethylene octyl ether -10 emulsifier and a certain amount of water were stirred in a high speed mixer, and then they were transferred to three 500 mL flasks. The temperature rises, and the stirring rate was 300~400 r/min. Nitrogen was injected to remove reactive oxygen species. $K_2S_2O_8$, under 60 °C keeps the temperature warm for 3 minutes. Moreover, the temperature rises to 80 °C, 3 g of monomeric quantitative acrylic acid is alternately added to a certain amount of butyl acrylate equal to 27 g and a certain amount of methyl methacrylate equal to 9 g. After dropping, the reaction lasted 1.5 h. At 60 °C, with an anti-polymerization agent (0.04 g dissolved in 20 mL of water). Hold the heat for half an hour, and then finish the experiment.

Characterization of Demulsifier DW1

FT-IR spectra were tested by the WQF-520 Fourier infrared spectrometer of Rayleigh analytical instruments, Beijing; GPC spectra were tested by the PL-GPC-50 gel permeability chromatograph of Polymer Laboratories UK; ^{1}H-NMR and ^{13}C-NMR spectra were tested by the Bruker Ascend^{Tm}500 NMR spectrometer of Bruker. The particle size analysis diagram was tested by LS-800 laser particle size euramerican technology, which was made or produced by the company LTD.

Demulsification of Dirty Oil Sludge in an Oil Field in Xinjiang

The study on the demulsification process of Xinjiang sludge is mainly based on the influence of stirring time, stirring rate, heating temperature and DW1 amount on the deoiling rate of treated 15 g sludge, so the best demulsification conditions of Xinjiang sludge is obtained. The index of demulsification performance is based on the change of oil content of the sludge before and after treatment. The oil content of the sludge is determined by the determination method of oil content, water content and impurities of the sludge in the oil field of Q/SY LH 0533-2016 [24] according to the enterprise standard of China national petroleum corporation before and after treatment.

SEM Characterization of Oil Sludge Before and After Treatment in a Xinjiang Oil Field

After pretreatment of the sludge before and after treatment, a small number of samples were fixed on the work table with conductive adhesive, and after gold plating, scanning electron microscope S-488 of Shanghai fangrui instrument of the company LTD was used for scanning analysis.

Results and Discussion

FT-IR Spectroscopy Analysis

In Figure 1, the FT-IR spectrum of demulsifier DW1 is shown. It can be seen that the stretching vibration peak of 2850 cm^{-1}-2960 cm^{-1} is methyl, the stretching vibration peak of 1715 cm^{-1} is carbonyl, the bending vibration peaks of 1380 cm^{-1} and 1460 cm^{-1} are the representative of methyl, the bending vibration peak of 1470 cm^{-1} is submethylene, and the peak of 1080 cm^{-1} is the representative of carbon and oxygen absorption peak. In this figure, there is no absorption peak at about 1600 cm^{-1}, but carbonyl peak at 1715 cm^{-1}, indicating that the polymerization reaction of DW1 is conducted by the polymerization of acrylate methacrylate methyl and butyl acrylate through the carbon-carbon double bond, and this polymerization reaction is fully polymerized.

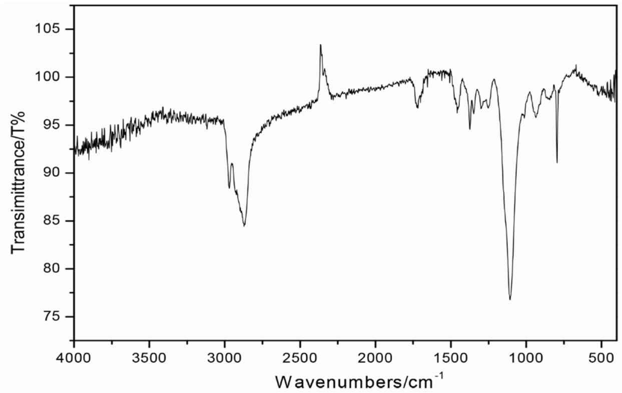

Fig. 1 FT-IR spectra of demulsifier DW1.

Gel Permeation Chromatography (GPC) Analysis

Gel chromatography belongs to liquid chromatography, it is analyzed by the mixture of different components of the different molecular size for separation, mostly used for the analysis of chemical properties of the same molecular volume of different polymer homologues, but at the same time, a variety of average molecular weight and molecular weight distribution can be obtained. Various molecular weights of demulsifier DW1 synthesized in the laboratory were analyzed by gel permeation chromatography, and the results of retention time (RT) and reaction strength (Response) were shown in Fig. 2. Furthermore, the fitting curve of log Mw,GPC and retention time was shown in Fig. 3.

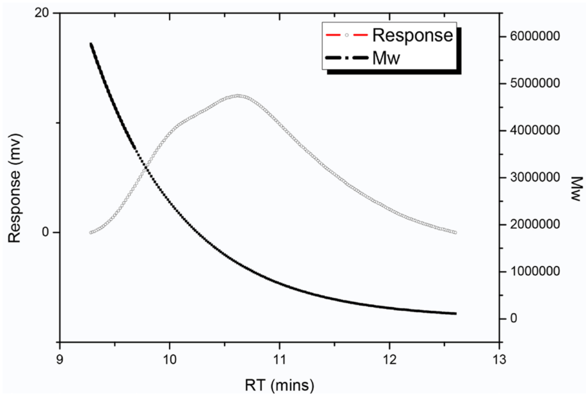

Fig. 2 Gel chromatogram of DW1.

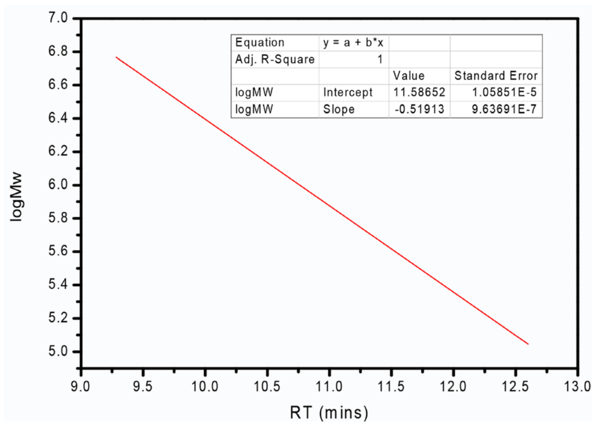

Fig. 3 Fitting diagram of log Mw and RT of DW1.

It can be seen from Figure 2 that the molecular weight distribution of DW1 is shown, and the peak type in the spectrum is symmetrical. According to the logmW value corresponding to retention time and peak type in Figure 3, it can be obtained that the MW (weight average molecular weight) and Mn (number average molecular weight) of DW1 are 454319 to 1388086. The molecular weight distribution index is 1.73, indicating that the polymerization reaction has good controllability and the molecular weight of DW1 is relatively large, that is, the better demulsification performance of the synthesized DW1 is [17-18].

NMR Analysis of Hydrogen and Carbon Spectra of Demulsifier DW1

The chemical shift of hydrogen protons in demulsifier DW1 was determined by using American bruker-500 MHz (DMSO as the solvent and TMS as the internal standard), as shown in Fig. 4 below. The chemical shift of ^{13}C of demulsifier DW1 was measured by bruker-500 MHz (DMSO as solvent and TMS as internal standard) of the United States. The results are shown in Fig. 5 below.

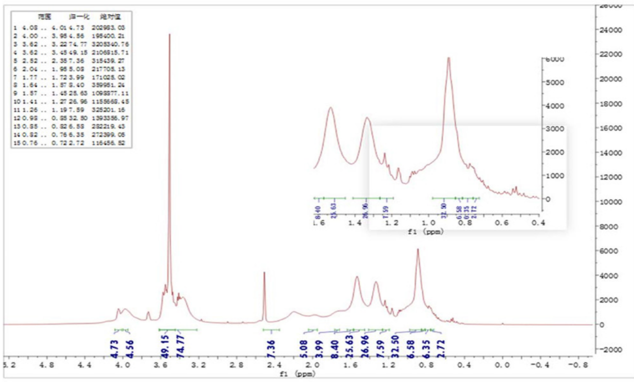

Fig. 4 1H spectrum of demulsifier DW1.

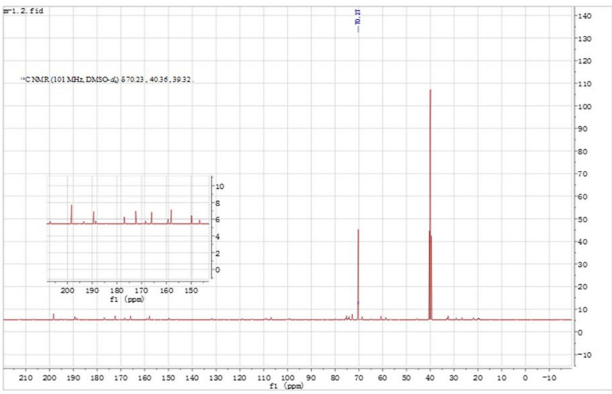

Fig. 5 ^{13}C spectra of demulsifier DW1.

As shown in Fig. 5, ^{13}C NMR (101 MHz, DMSO) δ 39~40 ppm has multiple peaks, indicating the presence of carbon on -CH3, while the single peak at δ 70 ppm, which is weaker than that at δ 39~40 ppm, is seasonal carbon. However, there is no double peak between δ 100 ppm ~ 150 ppm, indicating that there is no double bond of olefin. Furthermore, carbon at δ 170 ~200 ppm is carbonyl.

Analysis of Demulsification Process of Dirty Oil Sludge in an Oilfield in Xinjiang

The study on demulsification of dirty oil sludge in an oil field in Xinjiang is mainly based on the effects of stirring time, stirring rate, heating temperature and DW1 content on oil removal rate, so the optimal demulsification conditions of dirty oil sludge is obtained.

Agitation Time Used to Investigate the Oil Removal Rate of Sludge

The effect of agitation rate on the sludge removal at different stirring times was investigated without demulsifier at constant temperature. The results in Fig. 6 show that the rate of sludge removal decreased by increasing agitation rate.up to 500 r/min and then incresed by further increase of agitation rate.

Fig. 7 shows the effect of agitation time on sludge removal without demulsifier at constant agitation rate of 125 r/min and temperature. As can be seen, the rate of sludge removal increased gradually with the increase of agitation time, and reached the equilibrium state after 30 min. The net oil removal rate of the sludge was 46.37 % at this time. The rate of sludge removal increased slightly by further increase of agitatation time. Considering the cost, 30 min was selected as the best mixing time for the dirty oil sludge removal.

Influence of Temperature on Oil Removal Rate of Sludge

As can be seen from Fig. 8, with the increase in temperature, the net oil removal rate of sludge gradually increases and reaches an equilibrium value. With the increase in temperature, the strength of the oil-mud-water boundary mask decreases, resulting in the rupture of the film [17]. Therefore, at the temperature of 353.15 K (80 °C), the oil removal rate of the sludge reaches the best. When the temperature is greater than 353.15 K, the oil removal rate tends to balance basically. From the perspective of energy consumption cost, the optimal temperature is 353.15 K for the treatment of sludge.

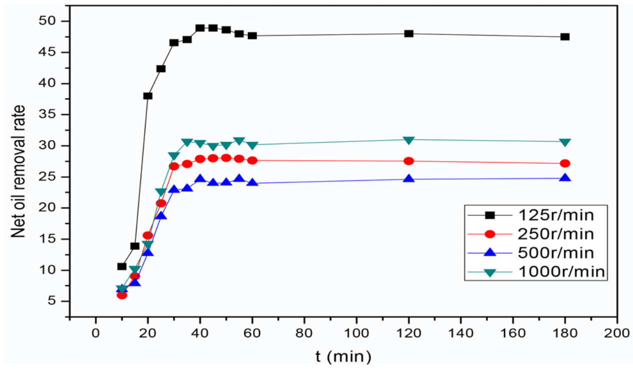

Fig. 6 Effects of different stirring rates on the removal rate of sludge.

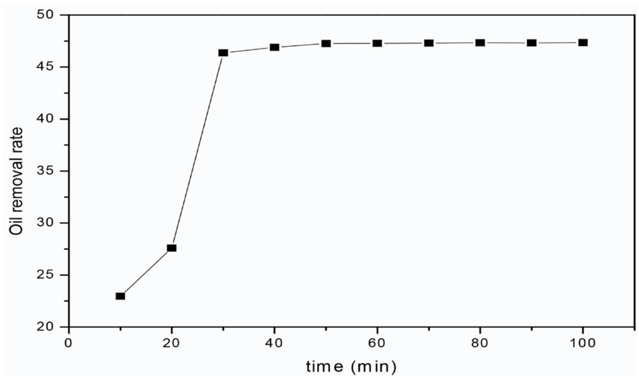

Fig. 7 Effect of stirring time on sludge removal rate.

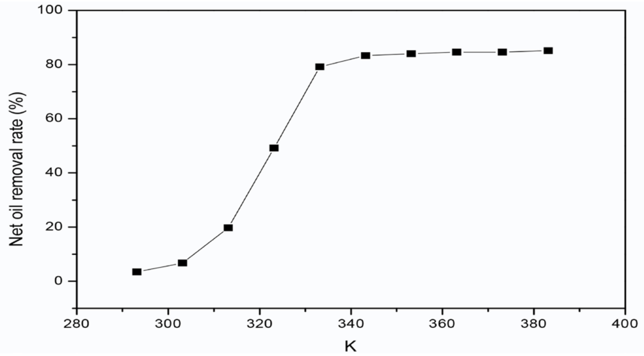

Fig. 8 Influence of temperature on the oil removal rate of sludge.

Influence of Demulsifier DW1 on Oil Removal Rate of Sludge

According to the Fig. 9, the oil removal rate was gradually increased to a state of equilibrium; with the increase in mass fraction DW1 to a fixed value, the system interface meet minimum film strength, interfacial film instability, so as to achieve demulsification DW1 doses at 1.0 g oil removal rate can reach 98.22% of sewage sludge from 2.5.1 track to rule 2.5.3 can know without DW1, under the action of the oil removal rate up to 82%, oil removal rate of sewage sludge are greatly influenced by temperature, after joining DW1, sewage sludge oil removal rate can reach 99% from 1.2 g for sewage sludge oil removal rate can reach 99.06%, after joining quantity is greater than 1.2 g are showing a slightly downward trend because of demulsifier concentration reaches a certain degree of convergence after integration micelle, cause formed between oil mud - water emulsion phenomenon, namely the formation of secondary emulsion, the effect of demulsification can cause certain negative influence on the processing results from cost so, for the processing of sewage sludge, DW1 the best choice is 1.0 g.

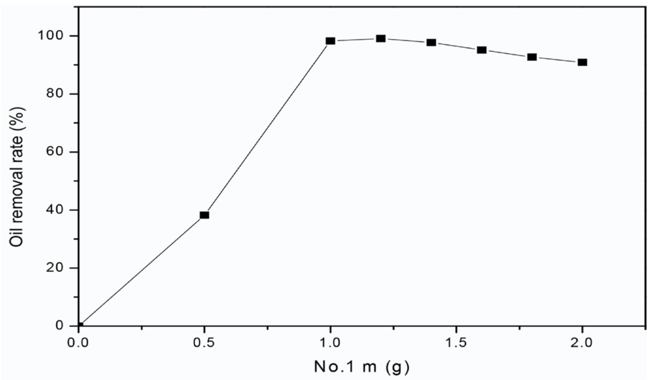

Fig. 9 Influence of demulsifier DW1 on oil removal rate.

Influence of Settling Time on Oil Removal Rate of Sludge

Under the conditions of temperature 353.15 K, stirring time 30 min, stirring rate 125 rpm/min and DW1 dosage 1g, the influence of static time on demulsification is investigated as shown in Fig. 10. It can be seen from the figure that with the increase of static time, oil removal first increases rapidly, then increases slowly, and finally shows negative growth, because when DW1 molecules enter the interface of oil-water-mud, the concentration of DW1 molecules in oil-water will become more and more stable with the increase of time. The time with the original sewage sludge in a competitive relation with the natural surface active agent, in the interface and the competitive adsorption of natural surface active agent, [18-23], DW1 molecules in oil - water - mud interface demulsification when with the increase in incubation time of 1 sewage sludge oil removal rate also gradually increased--incubation time is at most 180 min.

At the time of min (the effect is shown in Fig. 11), the oil-water-mud interface is stratified clearly, and the oil removal rate of no. 1 sludge reaches the highest, up to 99.55 %. However, the difference between the oil removal rate of Xinjiang sludge and that of 180 min is 0.57 % when the settling time is 150 min.

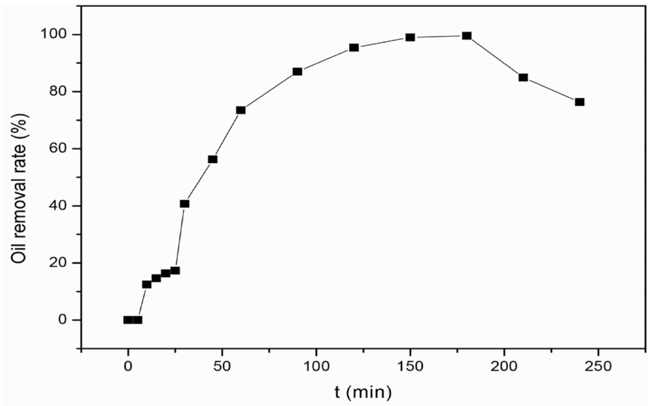

Fig. 10 Influence of settling time on oil removal rate.

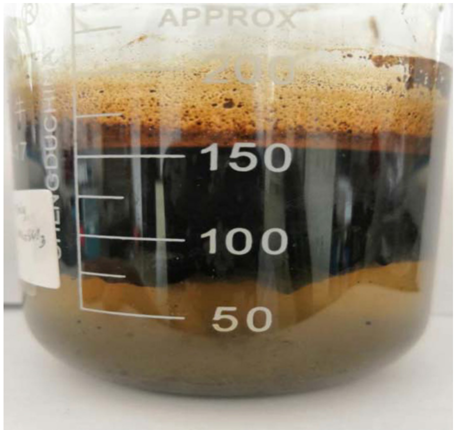

Fig. 11 The extent of Oil Sludge Settling after 180 min.

Scanning Electron Microscopy (SEM) Analysis Before and After Sludge Treatment in an Oil Field in Xinjiang

According to Fig. 12 a for the treatment of sewage sludge before 1.00 k times magnified, b for the treatment of sewage sludge before 10.0 k times magnified, c for after demulsification treatment of sewage sludge for the 1.00 k times magnified, and d after demulsification treatment of sewage sludge for 10.0 k times magnified image, it can be seen from the above a b c d before handling the micro structure of sewage sludge which it has no rules, and the larger gap between particles and particles, especially the rough surface.

The microstructure of the treated sludge has changed, because there are heating, stirring and DW1 adsorption treatment in the demulsification process, which makes the particles of the whole sludge more compact, the small particles of the sludge gather together as much as possible, and the properties of the sludge have also changed.

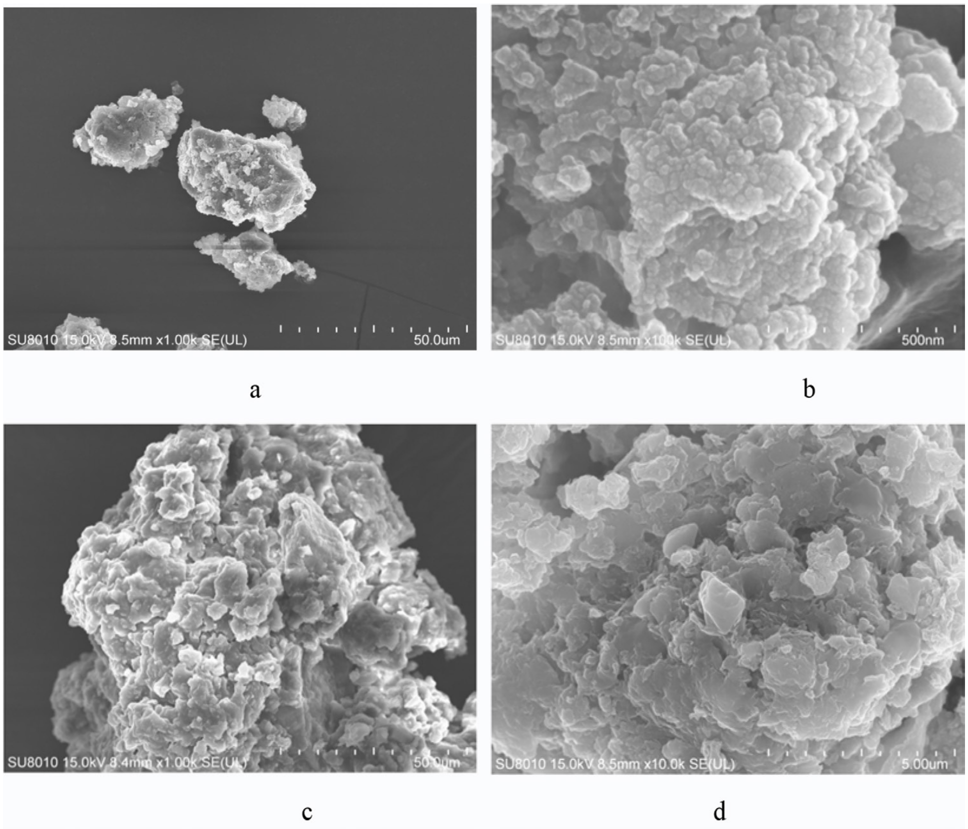

Fig. 12 SEM of Contaminated Sludge Before and After Treatment.

The demulsification treatment reduces the viscosity of the sludge and makes the oil phase easier to separate, which shows that the method of demulsification treatment is beneficial to reduce the oil content of the sludge [25-27]..

Conclusions

A novel emulsion breaking agent DW1 was prepared by emulsion polymerization. The Mw,GPC (weight average molecular weight) range of DW1 was 454319~3098678, Mn,GPC (number average molecular weight) was 801880, and the molecular weight distribution index was 1.73104. The median particle size (D50) of DW1 is 26.00 μm, and the average particle size is 25.00 μm. The particle size distribution is uneven, and the stability of DW1 is good within a certain range, the oil removal rate increased first and then decreased with the increase in stirring time, stirring rate and temperature. With the addition of demulsifier, the oil removal rate increased rapidly in the early stage and then grew slowly, and finally showed a trend of slow decline. The optimal demulsification process for Xinjiang sludge was: for 30 minutes, at a temperature of 353.15 K, the stirring rate was 125 rpm/min," instead of " stirring at a temperature of 353.15 K for 30 min, the stirring rate was 125 rpm/min the amount of DW1 added was 1 g, and the standing time was 2.5 h. Under the condition of this treatment process, the oil removal rate of the sludge can reach 99.55%.

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