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Study on the Technology of Ultrasonic, Chemical and Mechanical Combined Treatment of Oilfield Aging Oil

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ABSTRACT

Aging oil is a common pollutant in petrochemical enterprises due to its severe emulsification and flocculation, poor settling performance, low oil recovery rate, and high difficulty in treatment. This article adopts the method of mechanical, ultrasonic, and chemical coupling demulsification to treat aging oil, with the water content and oil recovery rate of the treated aging oil as the inspection indicators. The experiment shows that when the oil-water ratio is 1:4, the heating temperature is 50℃, the stirring speed is 180rpm, the ultrasonic frequency is 25kHz, the power is 40W, the ultrasonic time is 25min, and the pH is adjusted to 3-4. The additional amount of $FeSO_4$ is 160mg/L, the additional amount of H_2O_2 is 0.11%, and the heating stirring reaction is 40min. When the dosage of cationic PAM with an ion degree of 50 is 35mg/L, the centrifugation speed is 3200rpm. The centrifugation time is 20 min, the crude oil recovery rate after aging oil treatment can reach over 94.6%, and the water content of the treated crude oil is less than 0.5%, meeting the standards for crude oil gathering and transportation in China. The oil content in the water generated after aging oil treatment is about 150 $mg.L^{-1}$, the suspended solids content is 200 $mg.L^{-1}$, the oil content in the residue is 6%, and the water content is 53%. By analyzing the appearance of aging oil before and after treatment, it was found that when using this process to treat aging oil, the original spatial cross-linking network structure of the aging oil was broken, allowing the water droplets wrapped in the oil to be released, thereby significantly reducing the water content in the recovered oil and improving the oil recovery rate.

INTRODUCTION

At present, with the extensive application of tertiary oil recovery technology in the mid to late stage of oilfield development, the crude oil recovery rate is constantly improving. At the same time, the emulsification and complexity of the produced liquid are greatly increased (Anisimov et al. 2018). In addition, under the combined action of transportation, standing, temperature, oilfield chemicals, and various mechanical impurities, aging oil with diverse structures and forms, which stably exists in the form of emulsion in all aspects of the entire treatment system, has emerged (Appazov et al. 2021). The source of aging oil is complex, and in the early stages of reservoir development, aged oil mainly comes from the leakage of wellbore, landing crude oil, drilling waste liquid, and emulsified crude oil with a large number of oilfield chemicals added during the oil testing and production process (Hamidi et al. 2021a).

In the process of crude oil production, the aging oil mainly comes from the waste liquid from the workover, the sewage treatment system of the joint station, the bottom oil of the settling tank, and other waste liquid tanks (Chang et al. 2023). The main sources are the following four aspects: (1) Gathering and transportation system: During the oil production process, a large amount of chemical agents, such as demulsifiers, need to be added to the produced liquid (Chen et al. 2022a). Due to the high complexity of the incoming liquid, the compatibility of the agents is not good, resulting in demulsified crude oil re-emulsification. Combined with the solid particles and polymer generated in the environment of the gathering and transportation system, the old oil and residue are formed (Chen et al. 2022b); (2) Waste liquid pool: During drilling and workover operations, most of the waste liquid will eventually accumulate in an open-air waste liquid pool (Coleman 2021). During storage, it will be exposed to sunlight. Under conditions of full contact with air, the light components will continue to evaporate, resulting in the formation of aged oil due to the floating of crude oil (Dalhat et al. 2022) (3) Ground crude oil: During the process of oil and gas field exploitation, especially during drilling and workover operations, it is inevitable to produce ground crude oil. During the process of recovering ground crude oil, the mixture of crude oil with clay, quartz sand, and other substances causes the stability of the crude oil properties to form aged oil (Deng et al. 2021a); (4) Tank bottom sludge: In the produced liquid treatment system, the settling tank is an important component (Deng et al. 2021b). During the treatment process, a large amount of oily sludge is generated at the tank bottom, and eventually, stable aging oil is produced in the oily sludge treatment plant (Dhote et al. 2018).

The diverse sources of aged oil result in its extremely complex composition, with different sources of aged oil being different (Duan M et al. 2019). The formation of aged oil is closely related to its composition. On the one hand, the extensive use of oilfield chemicals in tertiary oil recovery has led to the joint action of polymers, alkalis, surfactants, and natural surfactants such as resins and asphaltenes in aged oil, increasing the emulsification degree of aged oil (Envelope et al. 2022). On the other hand, aged oil also contains conventional substances such as clay, sediment, mechanical impurities, suspended solids, sulfides, and metal oxide micelles (Gao et al. 2018). Under the combined action of suspended solids and solid particles, metal oxides, and sulfide micelles, the stability of aged oil is further strengthened (Gong et al. 2018).

The hazards of aging oil in oil fields are specifically manifested in the following aspects:

(1) The properties of aged crude oil are stable, with a density between normal crude oil and water (Hamidi et al. 2021b). It always exists between the dehydrated crude oil and water phase under the action of gravity sedimentation, resulting in a decrease in dehydration efficiency and a significant delay in the separation progress of the oil phase and water phase, increasing sedimentation time and operating costs (Jerez et al. 2022).

(2) The aging oil emulsion contains a large amount of highly conductive mechanical impurities such as sand and clay, which can easily form short circuits and cause equipment tripping after entering the electric dehydrator, and even cause safety accidents, damaging the electric dehydrator equipment (Khazaal et al. 2021).

(3) The strong stability of aging oil requires the use of specific demulsifiers during demulsification and dehydration, and the increased dosage increases economic costs and equipment losses, resulting in a decline in overall economic benefits (Kurilkina et al. 2021).

(4) During the storage and transportation of aged oil in the dehydration system of the joint station, a large number of sulfate-reducing bacteria will proliferate, and the raw materials and energy for proliferation come from the sulfate in the crude oil (Lee & Jou 2022). During aerobic or anaerobic respiration, sulfate-reducing bacteria generate hydrogen sulfide, corroding metals, and forming ferrous sulfide micelles. The micelles and the flocculent structure of sulfate-reducing bacteria work together to further enhance the stability of aged crude oil (Linhares et al. 2022).

With the continuous development of crude oil extraction, environmental protection is increasingly valued, and the use of green and safe demulsification methods to reduce the harm of aging crude oil has become more significant (Martínez González et al. 2018). Emulsion demulsification is mainly based on two changes: one is to reduce the strength or change the nature of the interfacial facial mask, and the other is to increase the tendency of droplet aggregation and demulsification (Muratova et al. 2022).

At present, the treatment technologies for aged oil at home and abroad mainly include thermochemical dehydration, centrifugal electric dehydration, ultrasonic dehydration, microbial dehydration technology, etc. (Neto et al. 2023). To solve the problem of demulsification and dehydration of aged oil, the article conducted low-cost and rapid demulsification/dehydration technology research experiments on aged oil using a combination of ultrasound, chemistry, and mechanical dehydration methods based on the characteristics of aged oil. This solved the problems of low recovery rate and difficulty in demulsification of aged oil in oil fields.

MATERIALS AND METHODS

Materials

Thermostatic heating magnetic stirrer (MS7-H550-Pro), ultrasonic cleaning instrument (JP030), low-speed centrifuge (H2-16KR), pH meter (pHS-3C), Soxhlet extractor, water separator, electric heating sleeve (250 mL), electric blast drying oven (DHG-9140), infrared oil measuring instrument (HD-HC500) and vacuum circulation pump were used in this experiment.

Analytical grade concentrated sulfuric acid (H_2SO_4), ferrous sulfate ($FeSO_4$), and hydrogen peroxide solution (H_2O_2, 30%) were used in the experiment. Industrial-grade Cationic polyacrylamide (PAM, Ionization degree 50) was

Table 1: Analysis of Oil and Water Content of Aging Oil.

Project	Oil content [%]	Water content [%]	Solid content [%]
Aging Oil	43.82	52.64	3.54

used in this experiment.

Aging oil samples were taken from the Nanyang Oilfield Oil Mud Reduction Treatment Station of China Petroleum and Chemical Corporation. These samples were stored in a refrigerator at 4°C to minimize biological and chemical reactions as much as possible. The general characteristics of the aging oil samples from the workplace are shown in Table 1.

Experimental Procedure

Take a certain amount of aged oil from a 500 mL beaker, mix it with a certain proportion of water, and place it in a constant temperature heating magnetic stirrer. Start stirring and heating, and heat it to a certain temperature. Take out the beaker, place it in an ultrasonic cleaning device at the same temperature, and activate the ultrasonic function to break the oil-water interface for the first time through the ultrasonic function. After a certain time of ultrasonic treatment, take out the beaker and put it back into the constant temperature heating magnetic stirrer. The mixing and heating functions continue to be turned on. Then add H_2SO_4 solution to the aging oil to adjust the pH of the system to 4~4.5, and then add $FeSO_4$ and H_2O_2 into the beaker quickly in turn, and continue to stir for a certain time so that the agent can fully contact the aging oil, further break the oil-water interface, and improve the performance of the oil-water interface facial mask. After stirring, the aged oil is subjected to centrifugal dehydration treatment. After centrifugation, the water content in the separated upper oil phase is measured, and the volume of the separated upper oil is measured.

Analytical Methods

The pH of aged oil was measured using a pH meter (PHS-3C, Shanghai Youke Instrument Co., Ltd).

The determination method of water content in oil was in accordance with the method specified in the Determination of Water Content in Crude Oil Distillation Method (GB/T 8929-2006).

The oil recovery rate was calculated by using the following equation:

$$\text{Oil recovery rate:} \varphi = \frac{N}{M} \times 100\%$$

where φ is the oil recovery rate (%), N is the volume of recovered crude oil (mL), and M is the Volume of oil in aged oil (mL).

RESULTS AND DISCUSSION

Mechanical Demulsification Experiment

Oil-water ratio: Due to the high viscosity and poor water dispersibility of aged oil, the effect of directly adding water-soluble demulsifier additives is not ideal (Nezhdbahadori et al. 2018). Consider adding a certain proportion of water to the aging oil to mix it with water, allowing water-soluble demulsifiers to come into full contact with the aging oil to achieve a demulsification effect (Ramirez et al. 2019).

Mix aged oil and water in the proportions of 1:2, 1:3, 1:4, 1:5, and 1:6, respectively. Heat the experimental oil sample with the adjusted oil-water ratio in a 60 ℃ thermostatic magnetic stirrer, and adjust the stirring speed to 200 rpm for 30 min. After stirring, let it stand for another 30 min. Using the water content of the upper oil sample after standing as an indicator, investigate the effect of the oil-water ratio on

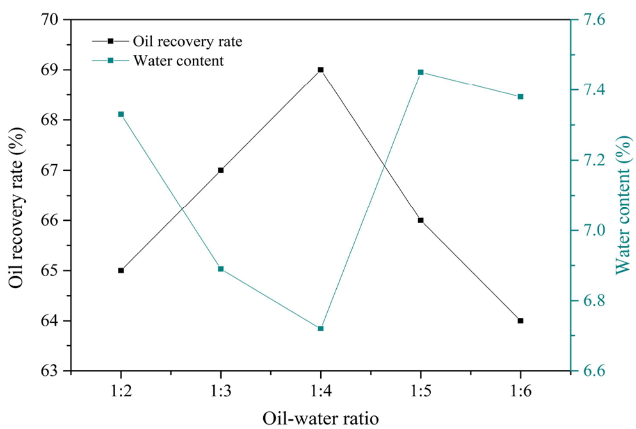


Fig. 1: The effect of the oil-water ratio on the demulsification effect of aged oil.

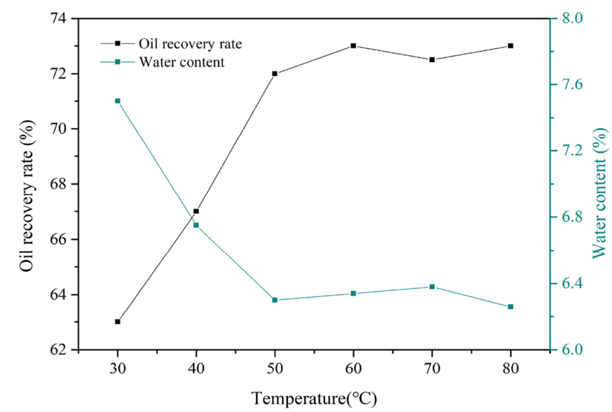


Fig. 2: The effect of heating temperature on the demulsification effect of aged oil.

the demulsification effect. The experimental results are shown in Fig. 1.

When other conditions are constant, as the amount of water added increases, the dispersion effect of the oil phase also increases, and the demulsification effect is obvious. The water content of the treated upper oil sample can be reduced to 7.5%, and the oil recovery rate also increases to 69%, as shown in Fig. 1. But when the water addition ratio exceeds 1:4, the water content of the treated upper oil sample increases with the increase of water content, and the oil recovery rate also decreases. Due to the high water content and unreasonable particle grading in the aging oil system, the demulsification effect of the aging oil will be seriously affected. Therefore, further increasing the water addition ratio will lead to a poor dehydration effect. Therefore, the optimal ratio of oil to water selected is 1:4.

Heating temperature: Due to the significant differences in the flowability of aged oil at different temperatures and the significant impact of temperature on the effectiveness of the agent, selecting the temperature with the best demulsification effect is one of the key influencing factors (Tessaro et al. 2021).

Mix the aged oil and water in a 1:4 ratio, and heat the experimental oil samples with the adjusted oil-water ratio in a thermostatic magnetic stirrer at 30°C, 40°C, 50°C, 60°C, 70°C, and 80°C, respectively. Adjust the stirring speed to 200 rpm, continue stirring for 30 min, and then let stand for 30min. Using the moisture content of the upper oil sample after standing as an indicator, investigate the influence of temperature on the demulsification effect. The experimental results are shown in Fig. 2.

As the temperature increases, the water content of the upper oil phase gradually decreases after treatment, as shown in Fig. 2. When the heating temperature of the oil sample exceeds 50°C, the water content change of the upper oil phase after treatment is no longer significant. Therefore, the optimal demulsification temperature selected is 50°C. At this time, the water content of the upper oil phase after treatment can be reduced to 6.3%, and the oil recovery rate can reach 73.5%.

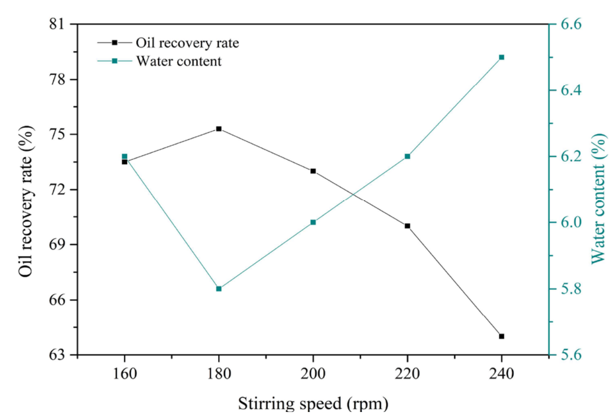


Fig. 3: The effect of stirring speed on the demulsification effect of aged oil.

Stirring speed: Mix aged oil and water in a 1:4 ratio, heat the experimental oil sample with the adjusted oil-water ratio in a 50°C thermostatic magnetic stirrer, and adjust the stirring speed to 160 rpm, 180 rpm, 200 rpm, 220 rpm, and 240 rpm, respectively. Continue stirring for 30min and let it stand for 30 min. Using the moisture content of the upper oil sample after standing as an indicator, investigate the effect of stirring speed on the demulsification effect. The experimental results are shown in Fig. 3.

Both too fast and too slow stirring speeds are not conducive to demulsification. When the stirring speed is below 180 rpm, as the stirring speed increases, the water content of the upper oil phase after treatment gradually decreases. When the speed is higher than 180 rpm, the water content of the upper oil phase shows a significant increase after treatment, as shown in Fig. 3. Due to the emulsification effect of too fast stirring speed, the optimal stirring speed selected is 180 rpm. At this time, the water content of the upper oil phase can be reduced to 5.8% after treatment, and the oil recovery rate can also reach 75.5%. Due to the rapid stirring speed, it will have a re-emulsification effect, which is not conducive to the demulsification of aged oil. Therefore, there will be an increase in water content and a decrease in the oil recovery rate in the treated aged oil.

Ultrasonic Demulsification Experiment

Ultrasound has good conductivity in both oil and water, so the use of ultrasound can improve the demulsification efficiency of aged oil (Wang et al. 2018). When ultrasound with a certain frequency and sound intensity acts on a solution, small bubble nuclei in the liquid are excited under the action of ultrasound, manifested as oscillation, growth, contraction, and collapse of bubble nuclei (Zhang et al. 2018). A series of extreme physical processes such as high temperature, high pressure, luminescence, discharge, shock wave, and jet are generated in the liquid. Under the action of the negative pressure phase of sound waves, cavitation bubbles are generated and then rapidly collapse under the action of the positive pressure phase of sound waves (Zhao et al. 2019). When cavitation bubbles collapse instantly, local high-temperature and high-pressure zones are generated within a very small space around them. By utilizing the locally generated high-temperature and high-pressure zones, the oil-water interface can be destroyed, leading to the demulsification of aged oil (Hamidi et al. 2021c, Wang et al. 2022).

Ultrasonic frequency and power: Mix aged oil and water in a 1:4 ratio and place them in a constant temperature magnetic stirrer. Stir at a speed of 180 rpm while heating to 50°C. Place the mixed sample in an ultrasonic cleaning device for ultrasonic treatment. This group of experiments studied the effect of ultrasonic frequency and power on the demulsification effect at the same ultrasonic time, using the water content of the upper oil sample after standing as the indicator. Examine the effect of Ultrasonic frequency and power on demulsification efficiency. The experimental results are shown in Fig. 4.

The frequency and power of ultrasound have a significant impact on the demulsification effect of aged oil. As the frequency and power of ultrasound gradually increase, they both exhibit excellent demulsification effects, as shown in Fig. 4. When the frequency reaches 25 kHz, the water content in the aged oil after treatment decreases to a minimum of 5.5%, and the oil recovery rate reaches over 78%. When the power reaches 60W, the water content in the aged oil after treatment decreases to the lowest of 4.8%, and the oil recovery rate reaches over 80%. However, from an energy-saving perspective, when the ultrasonic power increases from 40 W to 60 W, the water content and oil recovery rate in the aged oil after treatment do not change significantly. Therefore, 40 W is chosen as the optimal ultrasonic power.

Ultrasound time: The experimental conditions in this group are the same as those in 3.2.1, mainly studying the effect of

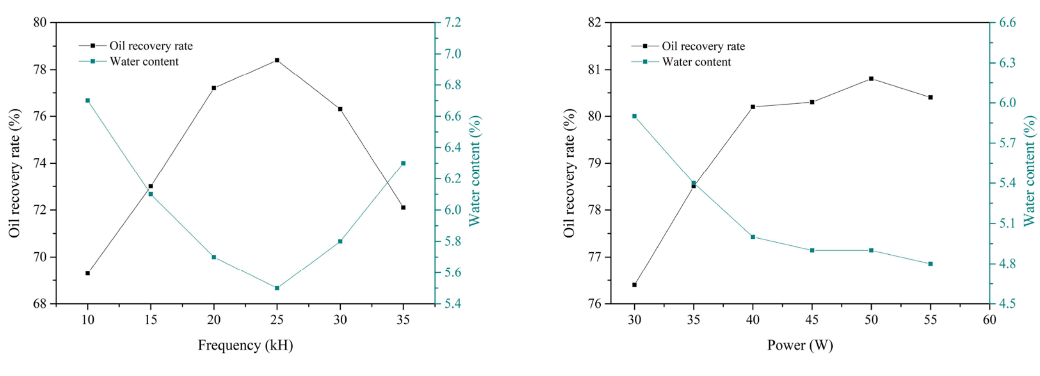


Fig. 4: The effect of ultrasonic frequency and power on the demulsification effect of aged oil.

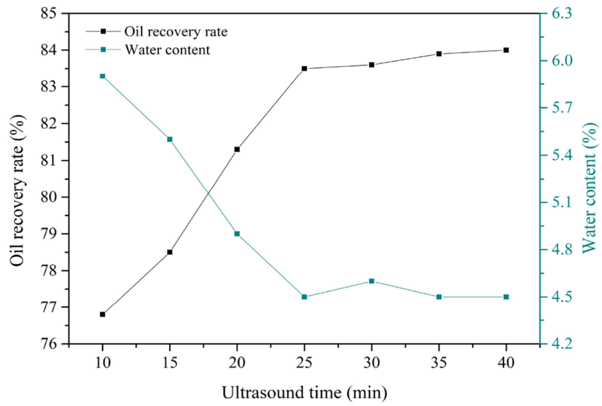


Fig. 5: The effect of ultrasound time on the demulsification effect of aged oil.

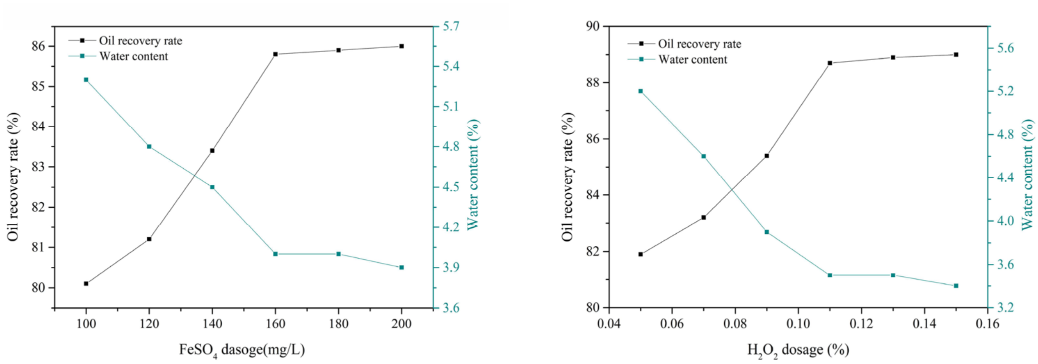


Fig. 6: The effect of reagent dosage on the demulsification effect of aged oil.

different ultrasonic times on the demulsification effect of aged oil at a frequency of 25 kHz and a power of 40W. The experimental results are shown in Fig. 5.

With the extension of ultrasound time, the demulsification effect of aged oil is more obvious, as shown in Fig. 5. When the ultrasound time is 25 min, the optimal demulsification effect has been achieved. At this time, the water content of the aged oil after treatment decreases to 4.5%, and the oil recovery rate reaches 83.5%. When the time exceeds 25 min, the demulsification effect no longer changes significantly. Because the oil-water interface that ultrasound can damage is limited, when the ultrasound time reaches a fixed value, no matter how long the time is extended, the effect of ultrasound no longer significantly increases. It has reached the limit of how ultrasound can handle aging oil.

Chemical Demulsification Experiment

After adding demulsifiers to aged oil, they penetrate the emulsified water droplet protective layer and damage the protective layer (Ramirez et al. 2021). After destroying the original oil-water interface, the tension of the oil-water interface is reduced. When the surface tension decreases, oil and water droplets continuously collide and coalesce. As the temperature gradually increases, the stability of the oil-water interface decreases, and the kinetic energy of oil-water molecules increases, accelerating the movement of oil and water droplets, ultimately leading to demulsification and precipitation of oil (Duan et al. 2018). This experiment uses the Fenton method for chemical demulsification experiments.

Reagent dosage: The experimental conditions in this group are the same as those in 3.2.2, and the ultrasound time of 25 min is selected. After ultrasonic treatment, the mixed sample is further subjected to chemical demulsification using the Fenton method. Firstly, the pH of the mixed sample is adjusted to 3-4 using a sulfuric acid solution, and then FeSO4 and H2O2 are sequentially added for oxidation treatment. After a certain period of reaction, the water content of the upper oil sample is used as an indicator to investigate the effect of the Fenton reagent on the demulsification effect of aged oil. The experimental results are shown in Fig. 6.

The effect of chemical demulsification is very good, as it can significantly reduce the water content in the aged oil

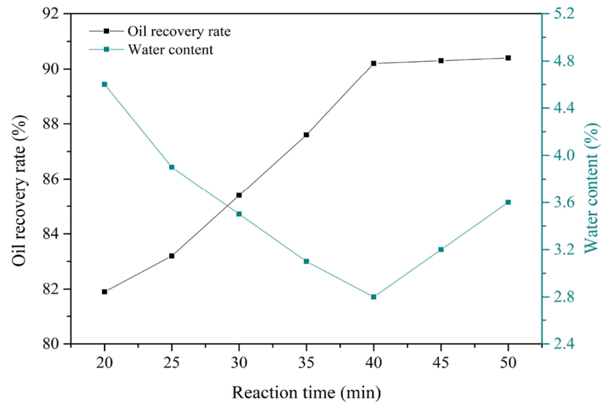


Fig. 7: The effect of chemical reaction time on the demulsification effect of aged oil.

after treatment, as shown in Fig. 6. The experimental results show that the best demulsification effect is achieved when the $FeSO_4$ dosage is 140 $mg.L^{-1}$, and the H_2O_2 dosage is 0.11%. At this time, the water content in the aged oil after treatment can be reduced to 3.5%, and the oil recovery rate can reach 89%. Fenton reagent can exert its strong oxidizing ability to disrupt the oil-water interface of aged oil, thereby releasing most of the water droplets encapsulated in the aged oil, further reducing the water content in the recovered oil.

Chemical reaction time: The experimental conditions of this group are the same as the optimal experimental conditions in 3.3.1. The main focus is to study the effect of chemical reaction time on the demulsification effect of aged oil. The water content of the upper oil sample after different reaction times is used as an indicator to investigate the effect of reaction time on the demulsification effect of aged oil. The experimental results are shown in Fig. 7.

As the reaction time prolongs, the demulsification of aged oil also exhibits good results, as shown in Fig. 7. When the reaction time is 40 min, the demulsification effect is the best. At this time, the water content of the aged oil after treatment decreases to 2.8%, and the oil recovery rate reaches 90.5%. When the reaction time exceeds 40 min, the water content and oil recovery rate of the aged oil after treatment no longer show significant changes as the reaction time prolongs. Because the oil-water interface that can be broken by chemical demulsification has been completely broken, even adding more chemical agents or longer reaction times cannot improve the effect. That is, when the reaction time is 40 min, all chemical reactions in the aging oil system have been completed.

Dehydration Experiment

Conduct experiments on aged oil under the optimal conditions selected in 3.1, 3.2, and 3.3, and dehydrate the sludge after the experiment. During the dehydration experiment, cationic PAM with an ion degree of 50 needs to be added and then centrifuged for dehydration.

Flocculant dosage: By adding different amounts of PAM for dehydration experiments, the optimal amount of PAM was selected. Using the water content of the upper layer oil

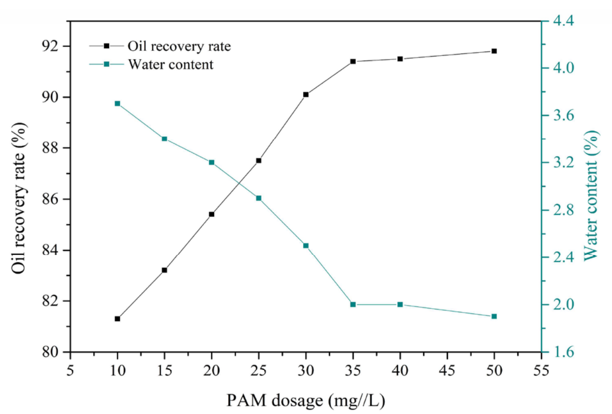


Fig. 8: The effect of flocculant dosage on the demulsification effect of aged oil.

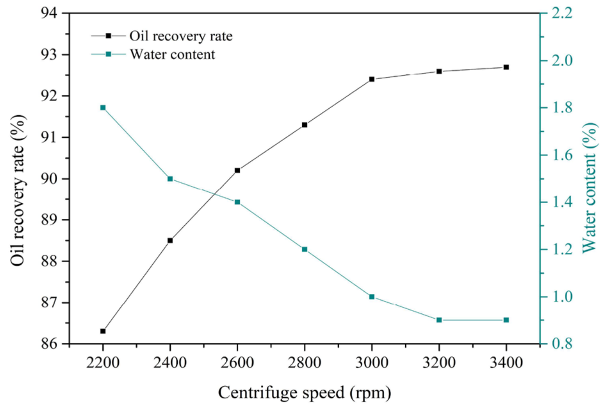


Fig. 9: The effect of centrifuge speed on the demulsification effect of aged oil.

sample after centrifugation as an indicator, investigate the effect of PAM dosage on the demulsification effect of aged oil. The experimental results are shown in Fig. 8.

With the increase in PAM dosage, the water content of the upper oil phase after centrifugal treatment showed a trend of first decreasing and then increasing, as shown in Fig. 8. When the dosage is increased to 35 mg.L^{-1}, the dehydration effect reaches its best. At this time, the water content of the aged oil after treatment can be reduced to 2%, and the oil recovery rate can reach 91.5%. However, further increasing the dosage will result in a worse effect, as excessive addition of PAM will make the aged oil system more dense, which is not conducive to centrifugal dehydration, resulting in a worse effect.

Centrifuge speed: The optimal experimental conditions in this group of experiments are the same as those in 3.4.1. The aged oil is centrifuged at different centrifuge speeds for 10 min, and the water content and oil recovery rate in the upper oil phase after centrifugation are used as indicators to investigate the effect of different centrifuge speeds on the dehydration effect of aged oil. The experimental results are shown in Fig. 9.

As the centrifuge speed continues to increase, the water content of the upper oil phase after centrifugal treatment shows a trend of first decreasing and then increasing, as shown in Fig. 9. When the speed reaches 3200 rpm, the dehydration effect reaches its best. At this time, the moisture

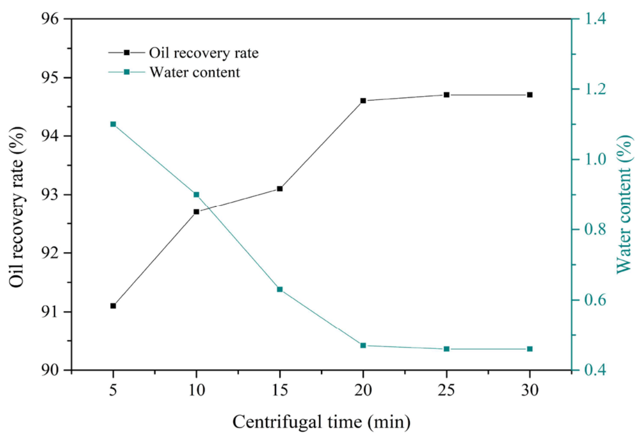
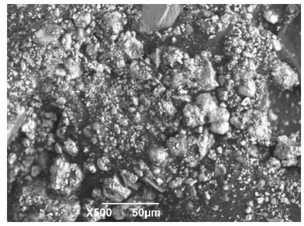
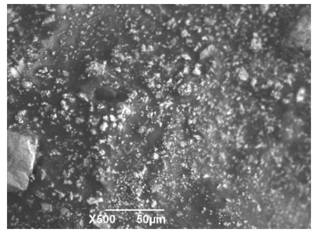
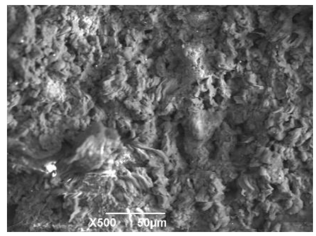
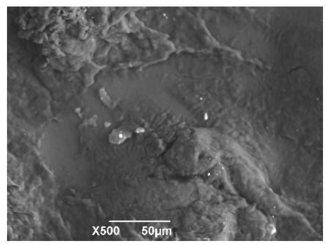
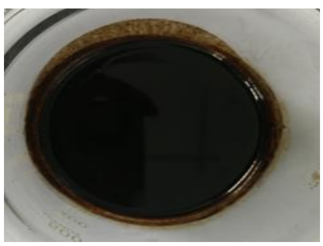
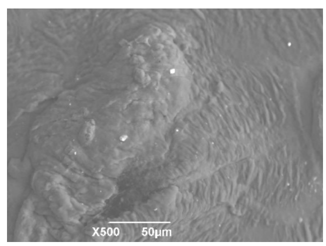
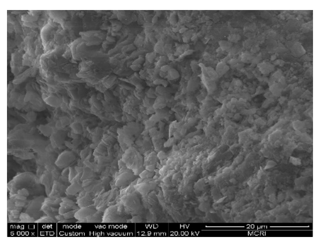


Fig. 10: The effect of centrifugal time on the demulsification effect of aged oil.

Table 2: Analysis of aged oil separation water and solid residue.

Project	Oil content [%]	Water content [%]	Solid content [%]	Oil content [mg.L^{-1}]	Suspend solid [mg.L^{-1}]
Water	-	-	-	150	200
Solid residue	6	53	41	-	-

Table 3: Aging oil characteristics at different stages of the experiment.

Aging oil at different stages	Experimental image	SEM image
Aging oil original sample		
Aging oil sample after mechanical demulsification		
Aging oil after ultrasonic demulsification		
Aging oil after chemical demulsification		
Aging oil after centrifugal dehydration		
Residue after centrifugation		

content of the aged oil after treatment can be reduced to 0.9%, and the oil recovery rate can reach 92.7%. But, as the rotational speed continues to increase, the water content and oil recovery rate of the aged oil after treatment no longer show significant changes. Because at a speed of 3200 rpm, all the free water in the aged oil system has been separated, further reduction of water content requires screening of centrifugation time.

Centrifugal time: The optimal experimental conditions in this group of experiments are the same as those in 3.4.2. The aged oil is centrifuged at a speed of 3200 rpm for different times, and the water content and oil recovery rate in the upper oil phase after centrifugation are used as indicators to investigate the effect of different centrifuge speeds on the dehydration effect of aged oil. The experimental results are shown in Fig. 10.

As the centrifugation time continues to extend, the water content of the upper oil phase after centrifugation treatment shows a trend of first decreasing and then stabilizing, as shown in Fig. 10. When the centrifugation time is 20 min, the water content of the aged oil after treatment can be reduced to 0.47%, and the oil recovery rate can reach 94.6%, fully meeting the requirement of 0.5% water content in China's crude oil gathering and transportation standard.

After screening various influencing factors, the final determined aging oil treatment process is as follows: when the oil-water ratio is 1:4, the heating temperature is 50°C, the stirring speed is 180 rpm, the ultrasonic frequency is 25 kHz, the power is 40W, the ultrasonic time is 25 min, the pH is adjusted to 3-4, the addition amount of $FeSO_4$ is 160 mg.L^{-1}, the addition amount of H_2O_2 is 0.11%, the heating stirring reaction is 40 min, the addition amount of cationic PAM with an ion degree of 50 is 35 mg.L^{-1}, the centrifugal speed is 3200 rpm, and the centrifugal time is 20 min, The crude oil recovery rate after aging oil treatment can reach over 94.6%, and the water content of the treated crude oil is less than 0.5%, meeting the standards for crude oil gathering and transportation in China.

Analysis of Aged Oil Separation Water and Solid Impurities

Under the optimal experimental conditions, the properties of the separated water and residue are shown in Table 2. From the table, it can be seen that the oil content in the effluent after centrifugation is about 150 mg.L^{-1}, the suspended solids content is 200mg/L, the oil content in the residue is 6%, and the water content is 53%. After centrifugation, the effluent can be reinjected or reused after simple treatment, and the treated residue is transported to a hazardous waste treatment station for harmless treatment.

Characteristics of Changes During Aging Oil Treatment

This article mainly conducted mechanical demulsification experiments, ultrasonic demulsification experiments, chemical demulsification experiments, and dehydration experiments on aged oil. To better understand the dehydration process of aged oil from a microscopic perspective, this section used scanning electron microscopy to analyze the apparent characteristics of the four stages of aged oil treatment, as shown in Table 3.

The aged oil exhibits a certain cross-linked network structure before treatment, containing a lot of mechanical impurities, and the surface is extremely uneven and irregular, as shown in Table 3. However, with the mechanical, ultrasonic, chemical, and centrifugal processes carried out on the aged oil, there were significant differences in the structure of the aged oil, whether from the experimental sample or the microscopic surface. The small dispersed substances disappeared, the spatial cross-linking network structure of the aged oil was broken, and the water droplets wrapped in the oil could be released, making the surface of the treated aged oil gradually become flat and smooth. Most of the mechanical impurities and encapsulated water in the aged oil have been removed, while the remaining majority are petroleum, with an appearance similar to that of a homogeneous system, exhibiting a flat and smooth surface.

CONCLUSIONS

(1) In response to the technical challenges of low oil recovery rate and high water content in recovered oil, a mechanical ultrasonic chemical coupling demulsification and dehydration treatment process for aged oil has been developed.

(2) The final determined aging oil treatment process is as follows: when the oil-water ratio is 1:4, the heating temperature is 50°C, the stirring speed is 180rpm, the ultrasonic frequency is 25kH, the power is 40W, the ultrasonic time is 25 min, the pH is adjusted to 3-4, the addition amount of $FeSO_4$ is 160 mg.L^{-1}, the addition amount of H_2O_2 is 0.11%, the heating stirring reaction is 40 min, the addition amount of cationic PAM with an ion degree of 50 is 35 mg.L^{-1}, the centrifugal speed is 3200 rpm, and the centrifugal time is 20 min, The crude oil recovery rate after aging oil treatment can reach over 94.6%, and the water content of the treated crude oil is less than 0.5%, meeting the standards for crude oil gathering and transportation in China.

(3) The oil content in the water generated after aging oil treatment is about 150 mg.L^{-1}, the suspended solids

content is 200 mg.L^{-1}, the oil content in the residue is 6%, and the water content is 53%. After centrifugation, the effluent can be reinjected or reused after simple treatment, and the treated residue is transported to a hazardous waste treatment station for harmless treatment.

(4) Through scanning electron microscopy analysis of aged oil at different stages of the treatment process, it was found that when using this process to treat aged oil, the original spatial cross-linking network structure of the aged oil was broken, allowing the water droplets wrapped in the oil to be released, thereby significantly reducing the water content in the recovered oil and improving the oil recovery rate.

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REFERENCES

Anisimov, A.V., Frolov, V.I., Ivanov, E.V., Karakhanov, E.A., Lesin, S.V. and Vinokurov, V.A. 2018. Complex Technology of Oil Sludge Processing.Springer International Publishing, Cham, pp. 617-623.

Appazov, N.O., Diyarova, B.M., Bazarbayev, B.M., Assylbekkyzy, T. and Dzhiembaev, B.Z. 2021. Rice straw and husk oil sludge for processing through the use of lignosulfonate as a binder with activated charcoal. Ser. Chem. Technol., 2(446): 65-71.

Chang, X., Li, X. and Ge, S. 2023. Insight into the oil removal mechanism of quaternary ammonium ionic liquid microemulsions for oily sludge treatment. Sustainable Energy & Fuels, 6(12): 567-569.

Chen, X., Zhang, Y., Xu, B. and Li, Y. 2022a. A simple model for estimation of the higher heating value of oily sludge. Energy, 9(20): 235-239.

Chen, Z., Zheng, Z., He, C., Liu, J., Zhang, R. and Chen, Q. 2022b. Oily sludge treatment in subcritical and supercritical water: A review. J. Hazard. Mater., (Jul.5): 433-435.

Coleman, N. 2021. North Sea newcomers Zennor and Pandion target green shoots in aging oil province. Platt's Oilgram News, 5(25): 99-102.

Dalhat, M.A., Osman, S.A., Mu'Azu, N.D. and Alagha, O. 2022. Utilization of oil sludge as a rejuvenator in hot-mix-asphalt containing reclaimed asphalt concrete. Constr. Build. Mater., (Jul. 4): 338-340.

Deng, J., Zhang, H., Yu, B. and Liu, H. 2021a. Research progress on oil sludge treatment in oilfield: A mini-review. Recent Innov. Chem. Eng., 6(5): 14-17.

Deng, S., Lu, X., Tan, H., Wan, X. and Xiong, X. 2021b. Effects of a combination of biomass addition and atmosphere on combustion characteristics and kinetics of oily sludge. Biomass Conv. Bioref., 6(2): 11-15.

Dhote, M., Kumar, A., Juwarkar, A. 2018. Petroleum Contaminated Oil Sludge Degradation by Defined Consortium: Influence of Biosurfactant Production. Proc. Natl. Acad. Sci. India Sect. B Biol. Sci., 88(2): 517-523.

Duan, M., Li, C., Wang, X., Fang, S., Xiong, Y. and Shi, P. 2019. Solid separation from the heavy oil sludge produced from Liaohe Oilfield. J. Pet. Sci. Eng., 172: 1112-1119.

Duan, M., Wang, X., Fang, S., Zhao, B., Li, C. and Xiong, Y. 2018. Treatment of Daqing oily sludge by the thermochemical cleaning method. Colloids Surf. A Physicochem. Eng. Asp., 554: 272-278.

Gao, Y., Ding, R., Chen, X., Gong, Z., Zhang, Y. and Yang, M. 2018. Ultrasonic washing for oily sludge treatment in pilot scale. Ultrasonics, 90: 1-4.

Gong, Z., Wang, Z., Wang, Z., Fang, P. and Meng, F. 2018. Study on pyrolysis characteristics of tank oil sludge and pyrolysis char combustion. Chem. Eng. Res. Des., 135: 30-36.

Hamidi, Y., Ataei, S.A. and Saraffi, A. 2021a. A simple, fast, and low-cost method for the efficient separation of hydrocarbons from oily sludge. J. Hazard. Mater., 4(23): 134-136.

Hamidi, Y., Ataei, S.A. and Sarrafi, A. 2021b. A highly efficient method with low energy and water consumption in biodegradation of total petroleum hydrocarbons of oily sludge. J. Environ. Manage., 293: 112911.

Hamidi, Y., Ataei, S.A. and Sarrafi, A. 2021c. Effect of Dissolution of Extracted Hydrocarbons of Oily Sludge on Petroleum Products. Chem. Eng. Technol., 44(8): 456-458.

Jerez, S., Ventura, M., Molina, R., Martinez, F., Pariente, M.I. and Melero, J.A. 2022. Application of a Fenton process for the pretreatment of an iron-containing oily sludge: A sustainable management for refinery wastes. J. Environ. Manage., 23(4): 304-307.

Khazaal, R.M. and Ismail, Z.Z. 2021. Bioremediation and detoxification of real refinery oily sludge using mixed bacterial cells. Petrol. Res., 10(12): 245-250.

Kurilkina, M.Y., Muslyumova, D.M., Zavyalov, O.A. and Miroshnikov, S.A. 2021. Experience in applying the technology of cavitation treatment of sunflower oil sludge for feeding ruminants. IOP Conf. Ser. Earth Environ. Sci., 624(1): 12110-12116.

Lee, C.L. and Jou, C.J.G. 2022. Producing Refuse Derived Fuel with Refining Industry Oily Sludge and Mushroom Substrates. Energies, 5(8): 15-19.

Linhares, V.D.N., De Araujo, L.G., Vicente, R. and Marumo, J.T. 2022. Enhanced removal of radium from radioactive oil sludge using microwave irradiation and non-ionic surfactant. J. Pet. Sci. Eng., 34(5): 211-217.

Martínez González, A., Silva Lora, E.E., Escobar Palacio, J.C. and Almazán Del Olmo, O.A. 2018. Hydrogen production from oil sludge gasification/biomass mixtures and potential use in hydrotreatment processes. Int. J. Hydro. Energy, 43(16): 7808-7822.

Muratova, A., Lyubun, Y., Sungurtseva, I., Turkovskaya, O. and Nurzhanova, A. 2022. Physiological and biochemical characteristics of Miscanthus×giganteus grown in heavy metal–oil sludge co-contaminated soil. J. Environ. Sci., 115: 114-125.

Neto, O.D.M.M., Silva, I.M., Lucena, L.C.D.F., Lucena, L.D.F.L., Mendonca, A.M.G.D. and Lima, R.K.B.D. 2023. Physical and rheological study of asphalt binders with soybean oil sludge and soybean oil sludge fatty acid. Waste Biomass Valor., 22(10): 657-659.

Nezhdbahadori, F., Abdoli, M.A., Baghdadi, M. and Ghazban, F. 2018. A comparative study on the efficiency of polar and non-polar solvents in oil sludge recovery using solvent extraction. Environ. Monit. Assess., 190(7): 389-392.

Ramirez, D., Kowalczyk, R.M. and Collins, C.D. 2019. Characterization of oil sludges from different sources before treatment: High-field nuclear magnetic resonance (NMR) in the determination of oil and water content. J. Pet. Sci. Eng., 174: 729-737.

Ramirez, D., Shaw, L.J. and Collins, C.D. 2021. Oil sludge washing with surfactants and co-solvents: oil recovery from different types of oil sludges. Springer Berlin Heidelberg, 6(5): 123-126.

Tessaro, A.P.G., Vicente, R., Marumo, J.T., Teixeira, A.C.S.C. and Araujo,

L.G.D. 2021. Preliminary studies on electron beam irradiation as a treatment method of radioactive oil sludge. Braz. J. Radiat. Sci., 56(8): 211-215.
Wang, J., Han, X., Huang, Q., Ma, Z., Chi, Y. and Yan, J. 2018. Characterization and migration of oil and solids in oily sludge during centrifugation. Environ. Technol., 39(10): 1350-1358.
Wang, Z.L., Shi, H., Wang, S.Y., Wang, Z.M., Hao, M.M. and Wang, J. 2022. Theoretical study on the pressurization characteristics of disc-seal single screw pump used in high viscosity oily sludge conveying field. Petroleum Science, 23(4): 623-627.
Zhang, Z.Y., Li, L.H., Zhang, J.S., Ma, C. and Wu, X. 2018. Solidification of oily sludge. Pet. Sci. Technol., 36(4): 273-279.
Zhao, Y., Yan, X., Zhou, J., Li, R., Yang, S., Wang, B. and Deng, R. 2019. Treatment of oily sludge by two-stage wet air oxidation. J. Energy Inst., 92(5): 1451-1457.