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# Treatment of oil-based drilling cuttings by floatation-advanced oxidation two-step process

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In this paper, a floatation-advanced oxidation two-step process was proposed for deep oil removal of oil-based drilling cuttings (OBDC). In the first stage, a novel and simple degreasing solution was prepared and most of the base oil contained by OBDC was removed by flotation; in the second stage, the oil content of OBDC was further reduced by combined ultrasound + ozone (US + $O_3$) advanced oxidation. The recommended degreasing solution was a mixture of methanol, ammonium chloride, and water with a mass ratio of 1.48.1 : 0.25. The best flotation process was as follows: a mass ratio of OBDC to degreasing solution of 1 : 10, stirring speed of 400 rpm and $N_2$ flotation with a flow rate of 400 mL min$^{-1}$ for 60 min. The oil content of OBDC can be reduced from 14.57% to 1.42% after flotation treatment and the degreasing solution can be reused more than five times. The optimal process of US + $O_3$ advanced oxidation was as follows: a mass ratio of OBDC to water of 1 : 10, ultrasonic power of 1000 W, and an ozone flow rate of 4.0 L min$^{-1}$ for 100 min. The oil content of OBDC can be reduced from 1.42% to 0.14% after US + $O_3$ treatment at room temperature. The results of this paper provide a new method and idea for OBDC treatment.

## 1. Introduction

During the drilling stage of shale gas exploration, the high clay content of shale layers is easily able to cause drilling accidents when swelling with water occurs[1–3]. Therefore, oil-based drilling mud is widely used to protect the well wall when drilling in shale layers, and large amounts of oil-based drilling cuttings (OBDC) are inevitably generated. The composition of OBDC is complex; it contains petroleum hydrocarbons (the base oil in oil-based drilling mud), heavy metals, and soluble salts.[4] Discharge of untreated OBDC will result in severe environmental pollution. It has been included in the "Direction of National Hazardous Wastes (Version, 2021)" in the HW08 category in China.[5] Therefore, the oil content of OBDC must be effectively reduced before discharge or resource utilization. At present, the commonly used technologies for OBDC treatment mainly include thermal desorption, solvent extraction and chemical cleaning.[6] Thermal desorption refers to remove the base oil from OBDC by heating. It has been widely used because of its short treatment time, high oil removal efficiency, and recovery of base oil.[7,8] Solvent extraction refers to remove the base oil from OBDC by using strong solubility of base oil in organic solvent. It is simple and efficient. At present, the most used solvents are traditional organic solvents, such as toluene, petroleum ether, *n*-hexane, ethylene glycol, ethyl acetate, and ethyl lactate.[9,10] Thermal desorption and solvent extraction require large and complex equipment for heating and distillation, respectively. They are suitable for the centralized treatment of large amounts of OBDC and are not suitable for the treatment of OBDC at well sites.

However, there are many shale gas in Sichuan Basin (China), and the gas well sites are usually placed in the mountain area. It is not cost-effective for OBDC to be transport from the gas well site to the central treatment station. Usually, chemical cleaning refers to use chemical agents to reduce base oil adsorption on the cuttings surface.[11,12] Chemical cleaning has the advantages of high efficiency and simple cleaning equipment. It has attracted more and more attention because it has the possibility to be used at the well site. Surfactant cleaning and micro-emulsion cleaning are the most studied chemical cleaning methods.[13,14] Although they have good cleaning performance for OBDC treatment, they have a high possibility of surfactant contamination.[15] In addition, advanced oxidation also belongs to the chemical cleaning method. Advanced oxidation refers to the oxidation or mineralization of refractory organics by activation to produce reactive oxygen species (ROS), such as $SO_4^{-\bullet}$ and $^{\bullet}OH$.[16–19] Usually, it includes ozone oxidation,[20] Fenton oxidation,[21] and persulfate oxidation.[22] Ozone oxidation has the

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advantage of enabling *in situ* remediation because of its easy transfer between drilling cuttings particles.[23] But it also has the disadvantage of low efficiency.[11] Ultrasound can greatly improve the efficiency of ozone oxidation. At present, US + $O_3$ combined oxidation has been applied in the treatment of dyeing wastewater, cosmetics wastewater, pharmaceutical industry wastewater, *etc.*[24,25]

In our previous study,[26] a surfactant-free degreasing solution was proposed, which consisted of hydrophilic deep eutectic solvent (DES, mixture of choline chloride, methanol, and water) and mineral oil. The DES had low surface tension and could weaken the base oil adsorption on the surface of cuttings, and mineral oil dissolved the base oil. The oil content of OBDC can be reduced from 14.57% to 1.34% by using this degreasing solution. However, there are still two problems: (1) the cost of degreasing solution still needs to be reduced because the high cost of choline chloride and mineral oil; (2) the oil content of treated OBDC cannot meet the current local standard of Sichuan Province (oil content less than 0.3%). Therefore, the objective of this paper is to find a more economical degreasing solution having no choline chloride and mineral oil and to explore a combined process that can deeply reduce the oil content of OBDC. In this work, a cheap inorganic salt was used to replace the choline chloride in our pervious degreasing solution and a floatation-advanced oxidation two-step process was proposed to realize our objective. The new degreasing solution still had good interfacial activity. In the flotation stage, the base oil was stripped from the drilling cuttings by degreasing solution. The base oil can adhere to bubbles and be carried to the surface of degreasing solution. Most of the base oil was removed in this stage. In the advanced oxidation stage, the oil content was further reduced to be less than 0.3 wt% by using combined ultrasound (US) + ozone ($O_3$) treatment. The research idea and method of this paper are expected to provide a new reference for the OBDC treatment.

# 2. Experimental section

### 2.1 Materials

OBDC were taken from a shale gas production platform (water content of OBDC was 7.26%, oil content was 14.57%, and the others were cuttings). Ammonium chloride, sodium chloride, potassium chloride, sodium sulfate, methanol, hydrochloric acid and ammonia were purchased from Chengdu Cologne Chemicals Company Limited. 5# mineral oil was provided by Xiyou Huawei Technology Company, China.

### 2.2 Preparation of degreasing solution

The degreasing solution was prepared as follows: water, salt and methanol were added into the beaker, and stirred at room temperature until a uniform liquid was formed. Take an example as follows: 54.95 g water, 13.74 g ammonium chloride and 81.32 g methanol were added into the beaker and stirred for 10 min to get the degreasing solution.

### 2.3 Flotation experiment

Firstly, OBDC and degreasing solution were added into the beaker and stirred at 400 rpm. Then, the gas was introduced into the beaker through flowmeter and aeration header, successively (as shown in Fig. 1). The gas flow rate and bubble size were controlled by the flowmeter and the aeration header, respectively. After the floatation, there were three layers in the breaker including drilling cuttings, degreasing solution and base oil. After drying, the drilling cuttings were treated by the Soxhlet extraction method with tetrachloroethylene as a solvent and the oil content in tetrachloroethylene was measured by a JC-OIL-6 infrared spectrophotometer (Juchuang Environmental Protection Group Co., Ltd, China). At last, the oil content of drilling cuttings was calculated according to ref. 26. The degreasing solution was reused and base oil was recovered for preparing oil-based mud.

### 2.4 US + $O_3$ treatment

Firstly, the OBDC after flotation treatment and water were added into the beaker. Then, as shown in Fig. 2, the beaker was placed into an ultrasonic dispersion device (Shunma Tech Co., Ltd, China) and the $O_3$ was introduced into the beaker. The $O_3$ was produced by an ozone generator (Shanmei Shuimei Environmental Protection Hi-Tech Co., Ltd, China). After treatment, the clean drilling cuttings were obtained by filtration and its oil content was measured by the same method as described in Section 2.3. The water was reused.

### 2.5 Determination method of interface tension, contact angle and adhesion work

(1) Interfacial tension. The interfacial tension between base oil and degreasing solution was measured at 25 °C using a TX-500C rotating drop interfacial tension meter (CNG Company, USA).

(2) Contact angle. The contact angle between base oil and drilling cuttings in the degreasing solution environment was determined by the DSA30 drop shape analysis system (KRÜSS

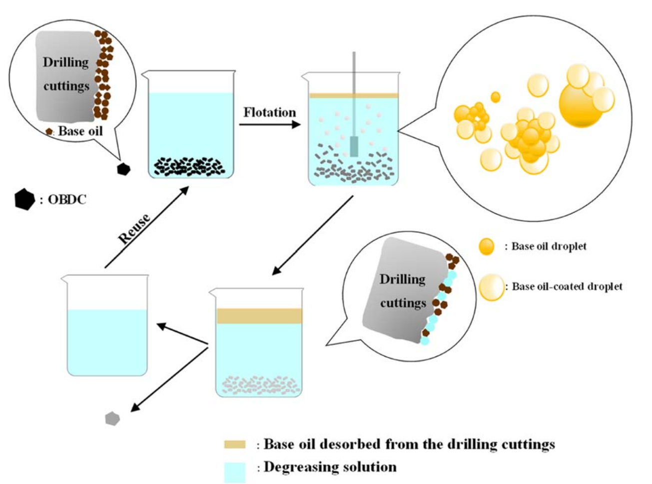


Fig. 1 Diagram of flotation treatment of OBDC.

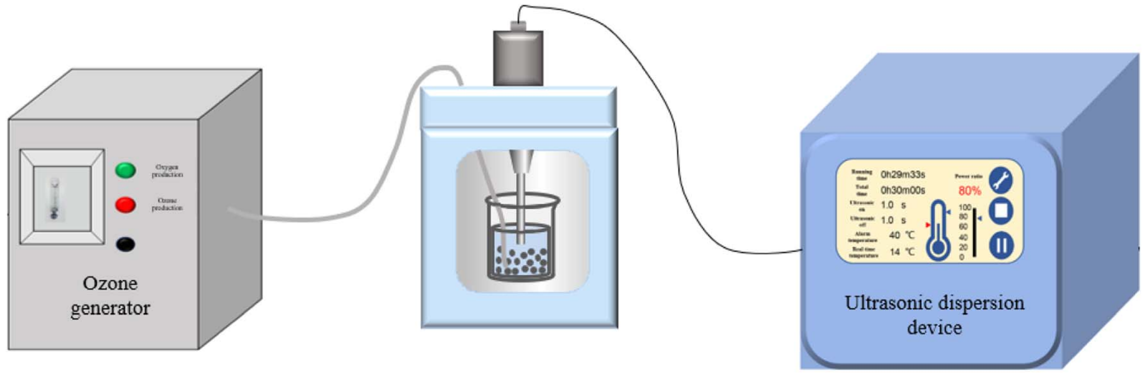


Fig. 2 Schematic diagram of US + $O_3$ treatment.

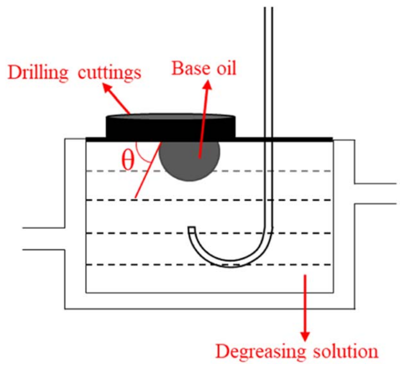


Fig. 3 The schematic diagram of contact angle measurement.

Company, Germany). The schematic diagram of contact angle measurement is shown in Fig. 3.

(3) Adhesive work: Adhesive work was defined as a work required to separate two phases from each other. In this paper, the adhesive work of the base oil on the surface of drilling cuttings ($W_{sl}$) was calculated according to eqn (1).

$$W_{sl} = r_l\,(1 + \cos\theta) \tag{1}$$

where $r_l$ is the interface tension and $\theta$ is the contact angle.

### 2.6 Determination of heavy metal and polycyclic aromatic hydrocarbon (PAH) concentration

The determination of heavy metal content was conducted according to ref. 27. Pb, Cr, Zn, Cu, Cd, and Ni were detected by flame atomic absorption spectrometry. Polycyclic aromatic hydrocarbon (PAH) concentration was determined according to ref. 28. Seven organic PAHs were identified and quantified by a gas chromatography/mass spectrometry (GC/MS, ISQ7K-VPI, ThermoFisher Company, USA).

## 3. Results and discussion

### 3.1 The degreasing solution composition

In this part, the floatation conditions were as follows: the mass ratio of OBDC to degreasing solution was 1 : 10, the aperture of aeration header was 0.5 μm, $N_2$ flow rate was 400 mL min$^{-1}$, and flotation time was 60 min.

Four cheap salts including NaCl, KCl, $Na_2SO_4$ and $NH_4Cl$ were mixed with water and methanol to prepare the degreasing solution, the salt concentration in water was 20%, and the mass ratio of methanol to water was 1.48 : 1. The effect of salt type on floatation treatment was investigated and the results are also shown in Fig. 4(a). In addition, Fig. 4(a) also shows the interfacial tension between degreasing solution and mineral oil and Fig. 4(b) shows the contact angle and adhesive work. When $NH_4Cl$ was used, the oil content of OBDC after flotation treatment had the smallest value of 1.54%. The degreasing solution prepared by $NH_4Cl$ has the lowest interfacial tension, the largest contact angle and the smallest adhesive work, which is good for the base oil stripping from drilling cuttings. Therefore, $NH_4Cl$ was selected for the next experiment.

When the mass ratio of methanol to water was 1.48 : 1, Fig. 4(c) shows the effect of $NH_4Cl$ concentration on the mineral oil and floatation treatment and on the interfacial tension, while Fig. 4(d) shows the contact angle and adhesive work. The oil content of drilling cuttings decreased with the increasing $NH_4Cl$ concentration, and it had the lowest value of 1.54% when the $NH_4Cl$ concentration in water was 20%. The reason also was relative with the adhesive work. We can see the adhesive work had the smallest value. However, when the $NH_4Cl$ concentration was larger than 20%, $NH_4Cl$ could not dissolve in the degreasing solution. Therefore, the recommended $NH_4Cl$ concentration was 20% in water.

When the $NH_4Cl$ concentration in water was 20%, Fig. 4(e) shows the effect of mass ratio of methanol to water on the floatation treatment and interfacial tension, while Fig. 4(f) shows the contact angle and adhesive work. Both the oil content of drilling cuttings and adhesive work decreased with the increasing methanol content in the degreasing solution. When the mass ratio of methanol to water was more than 1.48 : 1, the oil content had no obvious change. Therefore, the recommended mass ratio of methanol to water was 1.48 : 1.

Based on the above experimental results, it was recommended that the degreasing solution was a mixture of methanol, water and ammonium chloride with a mass ratio of 1.48 : 1 : 0.25. In addition, according to the results of interfacial

 

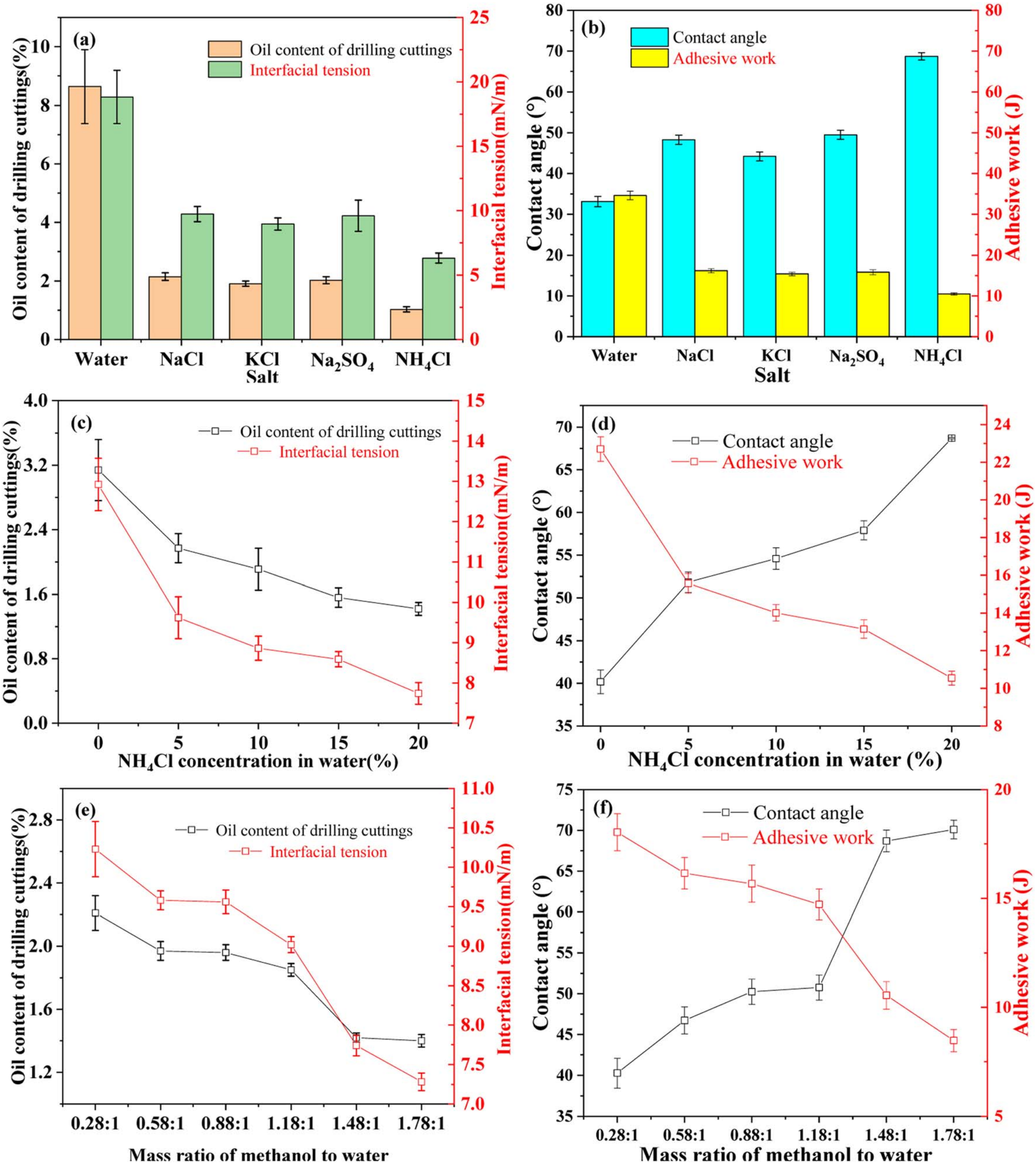


Fig. 4 Salt types (a and b), $NH_4Cl$ concentration in water (c and d), and mass ratio of methanol to water (e and f) on the flotation treatment, interfacial tension, contact angle and adhesive work.

tension, contact angle and adhesive work, the action process of the degreasing solution was proposed. When the OBDC was mixed with the degreasing solution, the low interface tension between the degreasing solution and base oil weakened the base oil adsorption on the surface of drilling cuttings. At the same time, the degreasing solution increased the contact angle between the base oil and the surface of drilling cuttings. Then, in the environment of the degreasing solution, the adhesive work between the base oil and the surface of drilling cuttings decreased, making it easy for the base oil to be removed from the surface of drilling cuttings. Meanwhile, because the surface of drilling cuttings was hydrophilic (the water contact angle on clean drilling cuttings was 65.16°), the hydrophilic degreasing solution can easily absorb onto the surface of drilling cuttings, which can hinder the adsorption of base oil onto the drilling cuttings again and further improve the treatment result. After the desorption from the drilling cuttings, the base oil was captured by $N_2$ bubble because they have a similar polarity and no longer adhere to the drilling cuttings.

### 3.2 Optimization of flotation process

When the mass ratio of OBDC to degreasing solution was 1 : 10, aperture of aeration header was 0.5 μm, gas flow rate was 400

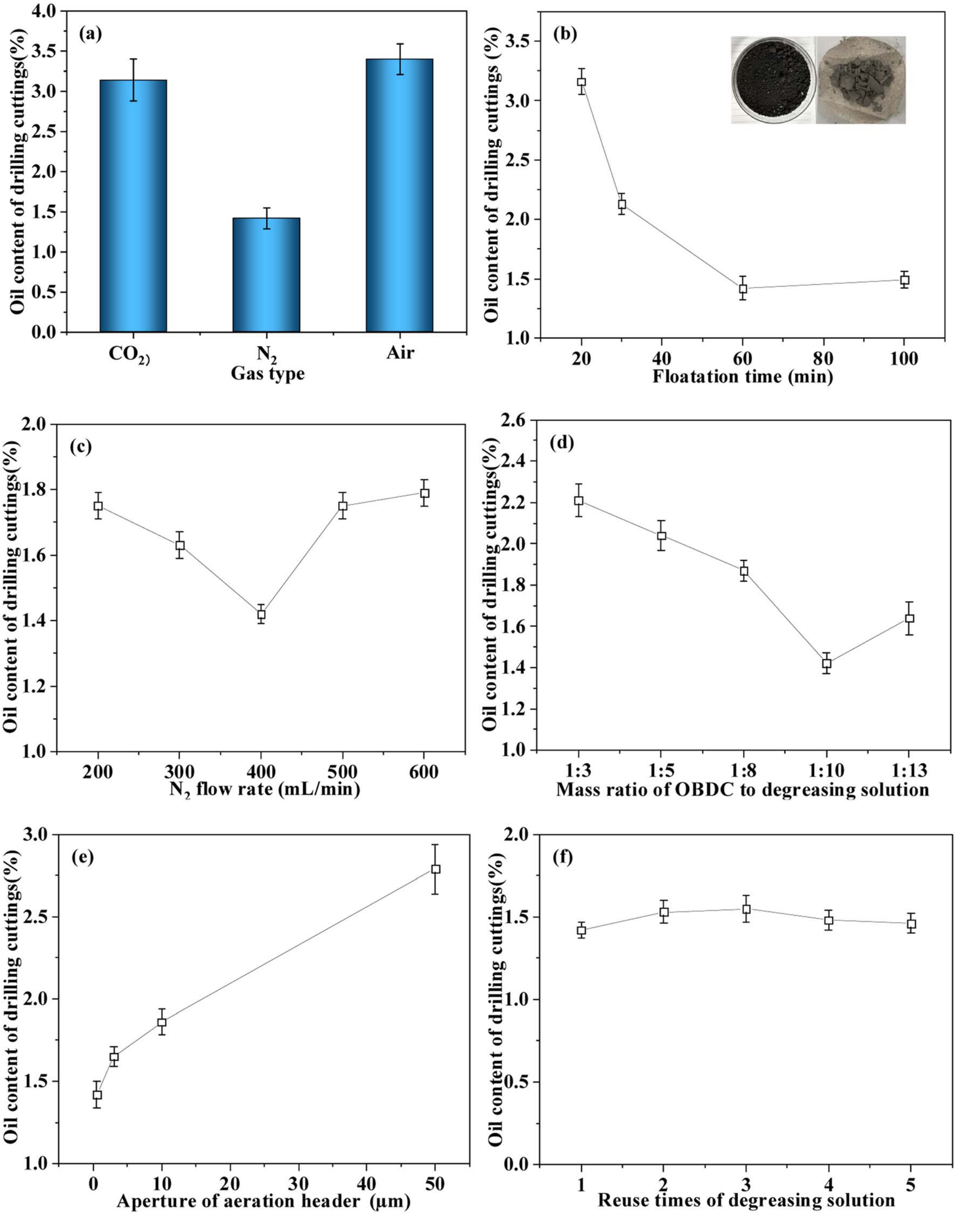


Fig. 5 Gas type (a), floatation time (b), $N_2$ flow rate (c), mass ratio of OBDC to degreasing solution (d), aperture of aeration header (e) and reuse times of degreasing solution (f) on the flotation treatment.

mL min$^{-1}$ and flotation time was 60 min, the influence of gas type on flotation treatment was investigated. The results are shown in Fig. 5(a). It was found that the oil content had the lowest value when the gas was $N_2$. The polarity of $N_2$ was smaller than that of $CO_2$ and air, the interaction between $N_2$ bubble and base oil may be the strongest. Therefore, the suitable gas was $N_2$.

When the mass ratio of OBDC to degreasing solution was 1 : 10, aperture of aeration header was 0.5 μm, $N_2$ flow rate was 400 mL min$^{-1}$, the influence of flotation time on flotation treatment was investigated and the results are shown in Fig. 5(b). The oil content decreased rapidly with the increasing time and was stable after 60 min. Both the base oil desorption from drilling

 

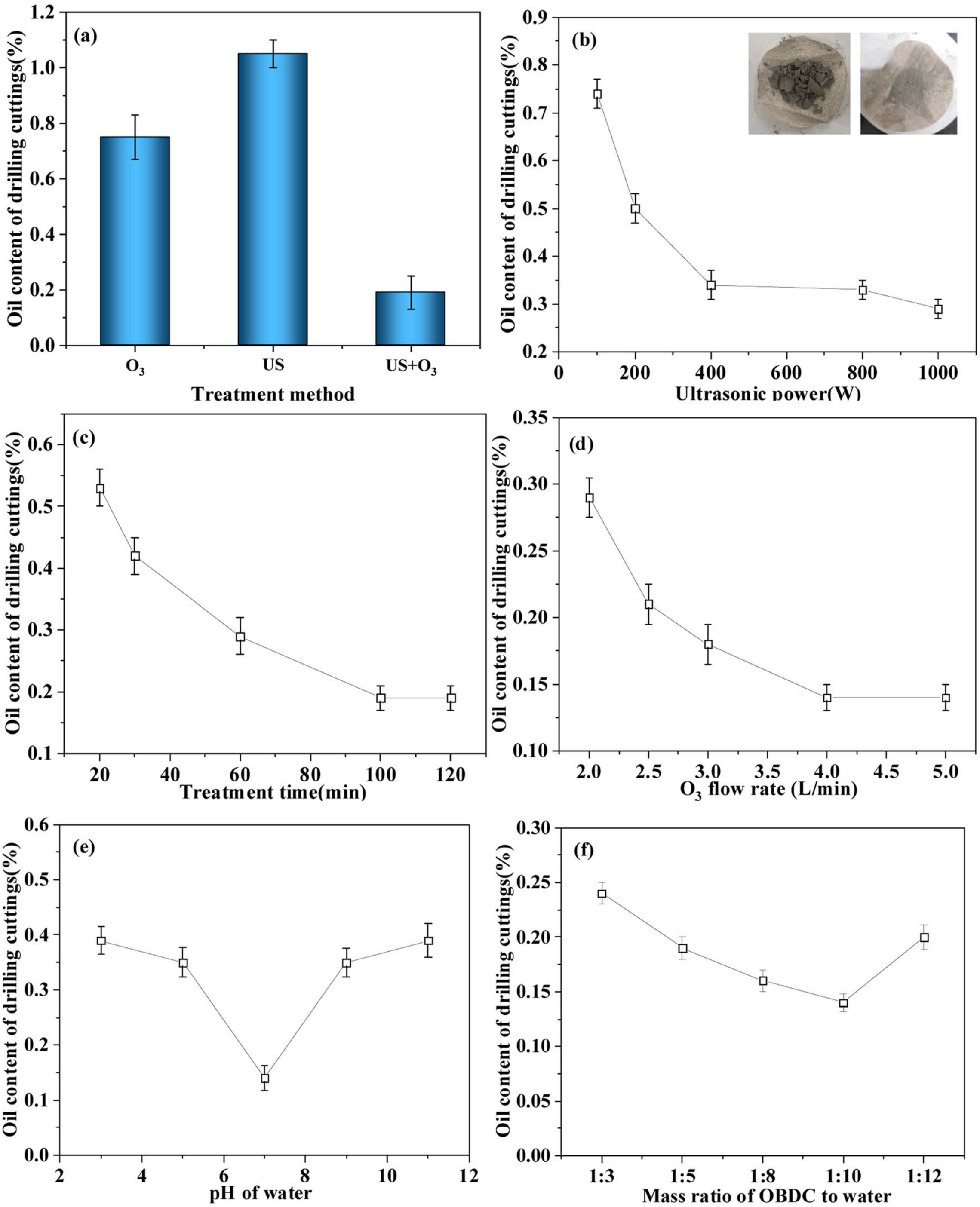

Fig. 6 Treatment method (a), ultrasonic power (b), treatment time (c), $O_3$ flow rate (d), pH of water (e), mass ratio of OBDC to water (f) on treatment results.

cuttings and the base oil adhesion onto $N_2$ bubble needed a long time. Thus, the recommended flotation time was 60 min.

When the mass ratio of OBDC to degreasing solution was 1 : 10, aperture of aeration header was 0.5 μm and flotation time was 60 min, the influence of $N_2$ flow rate on flotation treatment was investigated and the results are shown in Fig. 5(c). The oil content decreased with the increasing flow rate firstly and then increased. When the flow rate was 400 mL min$^{-1}$, the oil content had the lowest value of 1.42%. The collision frequency between base oil and $N_2$ bubbles increased with the increasing flow rate, which was helpful for the base oil desorption from drilling cuttings and base oil adhesion onto $N_2$ bubble, and the oil content decreased. However, when the gas flow rate was too large, the contact time between base oil and $N_2$ bubbles decreased and flotation result was affected. Therefore, the optimal $N_2$ flow rate was 400 mL min$^{-1}$.

Table 1 Comparison of oil removal rates of different chemical treatment methods

| Ref | Cleaning method | Initial oil content of OBDC | Oil removal rate |
|---|---|---|---|
| This work | Floatation-advanced oxidation | 14.57% | 99.03% |
| 10 | Solvent-based washing | 3% | 87.10% |
| 14 | Nanoemulsion washing | 25.80% | 95.70% |
| 16 | $Fe^{2+}$-based Fenton-like advanced oxidation | 15.24% | 45.04% |
| 22 | Heat activation persulfate-based oxidation | 15.24% | 51.84% |

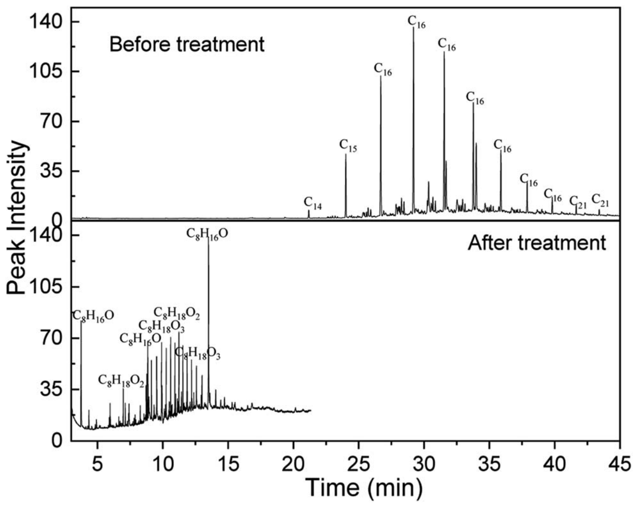

Fig. 7 The GC-MS results of base oil on the surface of drilling cuttings before and after treatment.

When the aperture of aeration header was 0.5 μm, $N_2$ flow rate was 400 mL $min^{-1}$, and flotation time was 60 min, the effect of mass ratio of OBDC to degreasing solution on flotation treatment was investigated and the results are shown in Fig. 5(d). The oil content decreased with the increasing mass ratio of OBDC to degreasing solution firstly and then increased. The oil content had the lowest value when the mass ratio of OBDC to degreasing solution was 1 : 10. The contact between OBDC and degreasing solution increased with the increasing mass ratio of OBDC to degreasing solution and the oil content decreased. When the degreasing solution was too much, the $N_2$ bubble concentration in the degreasing solution was too small, the collision frequency between base oil and $N_2$ bubbles decreased and the oil content increased. Thus, the recommended mass ratio of OBDC to degreasing solution was 1 : 10.

When the mass ratio of OBDC to degreasing solution was 1 : 10, $N_2$ flow rate was 400 mL $min^{-1}$ and flotation time was 60 min, the influence of aperture of aeration header (bubble size) on flotation treatment was investigated and the results are shown in Fig. 5(e). The oil content increased with the increasing aperture of aeration header. The bubble size increased with the increasing aperture of aeration header. The collision frequency base oil and $N_2$ bubbles decreased with the increasing bubble size, which was not good for the base oil desorption from drilling cuttings and base oil adhesion onto $N_2$ bubble and the oil content increased. Therefore, the recommended aperture of aeration header was 0.5 μm.

According to the above results, the flotation process was recommended as follows: the mass ratio of OBDC to degreasing solution was 1 : 10, aperture of aeration header was 0.5 μm, $N_2$ flow rate was 400 mL $min^{-1}$ and flotation time was 60 min. Especially, the process was conducted at room temperature, which is more energy-saving than thermal desorption and solvent extraction. The oil content can be reduced from 14.57% to 1.42%.

After the flotation, the degreasing solution was reused. The effect of reuse times of degreasing solution on the flotation treatment was studied and the results are shown in Fig. 5(f). We can find that the reuse times had little effect on the flotation treatment and the degreasing solution can be reused more than five times.

### 3.3 Optimization of US + $O_3$ treatment

After the floatation treatment, the OBDC (oil content was 1.42%) was further treated by US + $O_3$ treatment. When the treatment time was 100 min, the treatment results of $O_3$, US and US + $O_3$ were compared. The results are shown in Fig. 6(a). We

Table 2 Concentration of PAH in the treated OBDC and limit values

| PAHs | CAS no. | Concentration (μg $kg^{-1}$) | Concentration limit values for soil contamination of development land (μg $kg^{-1}$) |
|---|---|---|---|
| Naphthalene | 91-20-3 | 0.066 | 255 |
| Chrysene | 218-01-9 | 0.0088 | 4900 |
| Benz(*a*)anthracene | 56-55-3 | 2.169 | 55 |
| Benzo(*k*)fluoranthene | 207-08-9 | 0.0489 | 550 |
| Benzo(*a*)pyrene | 50-32-8 | 0.0228 | 5.5 |
| Benzo(*k*)tetraphene | 53-70-3 | 0.0193 | 5.5 |
| Benzo(*b*)fluoranthene | 205-99-2 | 0.01 | 55 |

 

Table 3 Concentration of heavy metal in the treated OBDC and limit values

| Heavy metal | Concentration (mg kg$^{-1}$) | Comprehensive utilization of pollution control indicators (mg kg$^{-1}$) | Concentration limit values of grade B sludge products (mg kg$^{-1}$) |
|---|---|---|---|
| Cd | 0.715 | 3 | 15 |
| Cr | 50.8 | — | 1000 |
| Cu | 26.6 | 150 | 1500 |
| Ni | 25.4 | 150 | 200 |
| Pb | 112 | 375 | 1000 |
| Zn | 272 | 600 | 3000 |

can find the oil content of US + $O_3$ was much lower than that of $O_3$ and US. There may be two main reasons why the US can enhance $O_3$ oxidation and reduce oil content:[26] (1) the division effect of ultrasonic wave promoted $O_3$ bubbles to be crushed into microbubbles, which can greatly improve the $O_3$ dissolution rate in water and increased the $O_3$ concentration. Base oil can be rapidly oxidized and degraded by high-concentration ozone. (2) The ultrasonic cavitation effect produced local high temperature and high-pressure conditions and promoted the rapid decomposition of $O_3$ in the ozone cavitation bubble to generate the hydroxyl radical in water, which was helpful for the oxidative degradation of base oil.

When the mass ratio of OBDC to water (pH = 7) was 1 : 10, $O_3$ flow rate was 2.0 L min$^{-1}$, and treatment time was 100 min, the influence of ultrasonic power on US + $O_3$ treatment was studied and the results are shown in Fig. 6(b). The oil content decreased with the increasing ultrasonic power and had no great change when the ultrasonic power was more than 400 W. The division effect and ultrasonic cavitation effect of US increased with the increasing ultrasonic power and the oil content decreased. From the perspective of energy conservation, the 400 W of ultrasonic power was recommended.

When the mass ratio of OBDC to water (pH = 7) was 1 : 10, ultrasonic power was 400 W and $O_3$ flow rate was 2.0 L min$^{-1}$, the effect of treatment time on US + $O_3$ treatment was studied and the results are shown in Fig. 6(c). The oil content decreased with the increasing treatment time and had no change when the treatment time was more than 100 min. The oxidative degradation of base oil by US + $O_3$ in water was a heterogeneous reaction, which needed a long time to finish. The suitable treatment time was 100 min.

When the mass ratio of OBDC to water (pH = 7) was 1 : 10, ultrasonic power was 400 W and treatment time was 100 min, the effect of $O_3$ flow rate on US + $O_3$ treatment was studied and the results are shown in Fig. 6(d). The oil content decreased with the increasing $O_3$ flow rate and had no change when the flow rate was more than 4 L min$^{-1}$. The oxidative degradation of base oil increased with the increasing $O_3$ concentration, and the oil content decreased. Therefore, the recommended $O_3$ flow rate was 4 L min$^{-1}$ and the oil content of the treated OBDC was 0.14%.

When the mass ratio of OBDC to water was 1 : 10, $O_3$ flow rate was 4 L min$^{-1}$, ultrasonic power was 400 W and the treatment time was 100 min, the effect of pH on US + $O_3$ treatment was studied and the results are shown in Fig. 6(e). The oil content decreased with the increasing pH firstly and then increased. $OH^-$ can cause $O_3$ decomposition to produce $^{\bullet}OH$. When the pH is small, ozone oxidation mainly depends on the oxidation capacity of $O_3$. With the increase in pH, the concentration of $^{\bullet}OH$ produced by $O_3$ decomposition increased. The oxidation capacity of $^{\bullet}OH$ is stronger than that of $O_3$, and the oil content decreased when the pH was smaller than 7. However, two $^{\bullet}OH$ are easy to quench each other when the pH continued to increase and cannot effectively oxidize the base oil on the drilling cuttings surface, and the treatment effect became poor. Thus, the suitable pH was 7.

When the pH was 7, $O_3$ flow rate was 4 L min$^{-1}$, ultrasonic power was 400 W and the treatment time was 100 min, the effect of mass ratio of OBDC to water on US + $O_3$ treatment was studied and the results are shown in Fig. 6(f). The oil content decreased with the increasing mass ratio firstly and then decreased. When the mass ratio was 1 : 10, the oil content had the lowest value of 0.14%. The dissolved $O_3$ increased with the water mass, which was good for the oxidative degradation of base oil and the oil content decreased. However, when the water volume was too large, the dissolved $O_3$ concentration was too small and the oil content increased. Therefore, the suitable mass ratio of OBDC to water was 1 : 10.

In conclusion, the US + $O_3$ treatment conditions were recommended as follows: the mass ratio of OBDC to water (pH = 7) was 1 : 10, ultrasonic power was 400 W, $O_3$ flow rate was 4.0 L min$^{-1}$, and treatment time was 100 min. At this condition, the oil content of treated OBDC was 0.14%.

Table 1 shows the oil removal rates of different chemical cleaning methods. We can see that the floatation-advanced oxidation two step process have much higher oil removal rate than the others.

The GC-MS results of base oil on the surface of drilling cuttings before and after treatment are shown in Fig. 7. Before the treatment, the organic compounds were mainly straight-chain alkanes. After the floatation-advanced oxidation treatment, the abundance of alkanes was significantly reduced, and the main remaining organic compounds was alcohol and ether organic matter.

The PAH and heavy metal concentration in treated OBDC were determined and compared with the disposal and utilization limits specified in relevant standards. The results are listed in Tables 2 and 3. Seven PAHs did not exceed the limit value of

"Soil environmental quality risk control standard for soil contamination of development land (GB36600-2018, China)". Six heavy metals also did not exceed the limit values of "Pollution control standard for comprehensive utilization of oilfield oily sludge (DB 23/T 1413-2010, China)" and "Control standards of pollutants in sludge for agricultural use (GB 4284-2018, China)".

# 4. Conclusion

In this paper, a new sample degreasing solution was developed, which was a mixture of methanol, water and ammonium chloride with a mass ratio of 1.48 : 1 : 0.25. By using this degreasing solution, a floatation-combined US + $O_3$ oxidation two-step process was proposed for deep oil removal of OBDC. In the floatation stage, the oil content of OBDC was reduced from 14.57% to 1.42% and the degreasing solution can be reused more than five times. Then in the US + $O_3$ oxidation stage, the oil content was further reduced to 0.14%.

# Conflicts of interest

There are no conflicts of interest to declare.

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