Green Energy, Environment and Sustainable Development
C. Wang et al. (Eds.)

doi:10.3233/ATDE230400

Comparisons of Azeotropic Distillation, Infrared Spectrophotometry and Ultraviolet Spectrophotometry for Oil Content Measurement

Keqing LI, Yin WANG and Yimin ZHU[1]
Collaborative Innovation Center for Vessel Pollution Monitoring and Control, Dalian Maritime University, Dalian 116026, Liaoning, China

Abstract. At present, the huge output of oily sludge is seriously harmful to the environment, so it must be treated as resources and detoxification. Oil content is the key technical indicator in its treatment process. In this paper, azeotropic distillation, infrared spectrophotometry and ultraviolet spectrophotometry were used to determine the oil content of two kinds of oily sludge. The results show that the oil content of oil sludge OS-1 and OS-2 measured by azeotropic distillation method is 56.96(±2.65)% and 7.62(±0.63)%, respectively. Azeotropic distillation method is suitable for the three-phase determination of oil, water and residue in oily sludge, and provides basic parameters for the selection of oily sludge treatment method and oil content detection method. The oil content of OS-1 and OS-2 measured by ultraviolet spectrophotometry is only 14.78(±1.15)% and 3.16(±0.40)%, respectively. Ultraviolet spectrophotometry is suitable for the detection of oily sludge with unsaturated petroleum hydrocarbons as the main component. Infrared spectrophotometry can fully detect petroleum components, so infrared spectrophotometry is relatively reliable and can be widely used in experiments and production. This study provides theoretical basis and data support for the selection of oil content detection methods for different oily sludge.

Keywords. Oily sludge, oil content, azeotropic distillation, infrared spectrophotometry, ultraviolet spectrophotometry

1. Introduction

Oily sludge is a hazardous waste and its improper discharge can cause serious hazards [1-4], and the oil content is one of the important indicators to assess its pollution risk and whether it meets the discharge standards after treatment [5]. The results of oil content determination are affected by the type, composition and structure of the oily sludge, so it is important to choose different testing methods according to the characteristics of the oily sludge to determine its oil content accurately.

Methods and standards for the detection of oil content of oily sludge have not yet been introduced, and the methods that have been studied include azeotropic distillation, infrared spectrophotometry, and ultraviolet spectrophotometry, mainly with reference

[1] Corresponding Author, Yimin ZHU, Collaborative Innovation Center for Vessel Pollution Monitoring and Control, Dalian Maritime University, Dalian 116026, Liaoning, China; E-mail: ntp@dlmu.edu.cn.

to the determination of oil in water or soil [6-8]. The azeotropic distillation method involves azeotropic distillation of oily sludge mixed with toluene under heating conditions to form three phases: water, oil, and solid, and the oil content is represented by the oil phase content in the mixed system [9]. Infrared spectrophotometry estimates the oil content by detecting the absorbance of C-H bonds in saturated methylene, methylene and aromatic functional groups, which is a standard method for determining the petroleum content in water with the advantages of excellent accuracy, wide measurement range and data reference [10]. Our group optimized the influencing factors such as oscillation time, water bath temperature, and sonication time in the previous study, and accurately determined the oil content of oily sludge using infrared spectrophotometry [11]. Ultraviolet spectrophotometry is also a standard method for the determination of petroleum content in water [8], which utilizes the absorption of UV light in the range of 250-260 nm and 215-230 nm for benzene ring and conjugated double bond, respectively. For the rapid determination of aromatic compounds and conjugated double bond compounds, it is suitable for the detection of oily sludge containing less oil [12], with the advantages of simple operation, safe and economical extractant, and accurate detection results [13].

In this paper, the azeotropic distillation, infrared spectrophotometric and ultraviolet spectrophotometric methods were used to detect the oil content of two kinds of oily sludge, in order to clarify the application range of the three methods and provide theoretical basis and data support for the selection of different detection methods.

2. Materials and Methods

2.1. Source and Nature of Oily Sludge

Two types of oily sludge with different oil content were taken from different treatment processes in a northern oil field and named as OS-1 and OS-2, respectively. The ash and volatile solids contents in OS-1 were 40.17% and 59.83%, respectively, while those in OS-2 were 91.99% and 8.01%, respectively.

2.2. Determination of Oil Content

Azeotropic distillation method. According to "Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillaton" [6], 6-8 g of oily sludge and 200 mL of toluene (analytical purity, Tianjin Fuyu Fine Chemical Co.) were added into the round bottom flask and kept heating and eluting for 8-12 h until the color of toluene and water in the water separator is thorough and stratified. The water content of the sludge was calculated by reading the water content of the water separator and the sludge content was calculated by drying the residue phase to a constant weight and calculating the oil content of the sludge by the differential subtraction method. To ensure the accuracy of the experimental data, each sample was tested 6 times and the average value was taken.

Infrared spectrophotometry. According to the HJ1051-2019 [7], the oil phase components in the oily sludge were extracted by shaking, ultrasonication and water bath heating using carbon tetrachloride reagent (Tianjin Aoran Fine Chemical Research Institute), and the extract was fixed and diluted, and the oil content of the oily sludge was determined using an infrared oil measurement instrument (OIL460, Beijing, China). To ensure the accuracy of the experimental data, each sample was tested 6 times and the average value was taken.

Ultraviolet spectrophotometry. According to the HJ970-2018 [8], petroleum ether (analytical purity, Tianjin Fuyu Fine Chemical Co., Ltd.) reagent was used to extract the oil phase components in the oily sludge by shaking, and the extract was fixed and diluted, and the absorbance of the samples was measured at 190-300 nm using an ultraviolet spectrophotometer (UV-1900i, Shimadzu, Japan) to determine the oil content of the oily sludge. To ensure the accuracy of the experimental data, each sample was tested 6 times and the average value was taken.

2.3. Thermogravimetric and Infrared Spectral Characterization

Thermogravimetric analysis was performed on two types of oily sludge and its residue phase after extraction with toluene, carbon tetrachloride and petroleum ether, respectively, using a thermogravimetric analyzer (TG209F3, NETZSCH, Germany), which was ramped up from room temperature to 800°C at a temperature increase rate of 10°C/min.

The infrared spectra of the oily sludge and its residue after extraction with toluene, carbon tetrachloride and petroleum ether were analyzed by FTIR (EQUINOX55, Bruker, Germany) using a KBr press with a scanning range of 400-4000 cm^{-1} and a resolution of 1.0 cm^{-1}. The infrared spectra were obtained after 32 scans in transmission mode.

3. Results and Discussion

3.1. Changes in the Properties of Oily Sludge after Extraction

Thermogravimetric analysis presented the weight loss process of two oily sludge and its residue phase after extraction by toluene, carbon tetrachloride and petroleum ether, respectively. The thermogravimetric curves of oily sludge OS-1 are shown in Figure 1a, and the percent weight loss of OS-1 at three temperature stages of 0°C-120°C, 120°C-350°C, and 350°C-700°C were 1.25%, 29.42%, and 19.26%, respectively, indicating that it contained a large amount of light and heavy hydrocarbons [14-16]. The percentage weight loss of residue phase after toluene extraction at each temperature stage was 0.31%, 4.52% and 6.09%, respectively. After extraction by carbon tetrachloride, the percent weight loss of residue phase at each temperature stage was 0.13%, 11.26%, and 8.03%, respectively. After extraction by petroleum ether, the percent weight loss at each temperature stage of the residue phase was 1.39%, 6.29%, 8.95% respectively. The above results showed that the residue phase of OS-1 still contained some light hydrocarbons and heavy hydrocarbons after solvent extraction, and the extraction effect of toluene was better than that of petroleum ether and carbon tetrachloride. Comparing Figures 1A and 1B, it can be seen that the pyrolysis process of oil sludge OS-2 and OS-1 were basically the same, but the weight loss curves were significantly different. Comparing the thermogravimetric curves of each solvent before and after extraction, it was also confirmed that toluene extraction had the best effect.

The infrared spectral analysis reflected the changes of functional groups in the residue phase after extracted by toluene, carbon tetrachloride and petroleum ether. As shown in Figure 2, the functional groups of the oily sludge OS-1 and OS-2 were basically the same, both of them contained mineral oil. OS-1 had a strong characteristic peak at 1025 cm^{-1}-1678 cm^{-1}, which was the stretching vibration of the aromatic ring skeleton. Two peaks appeared in the range of 2843 cm^{-1}-2972 cm^{-1}, which were the antisymmetric stretching vibration and symmetric stretching vibration of $-CH_2$. They were long-chain alkyl peaks, indicating that both the sludge and the extracted residue phase contained mineral oil. A broader vibration peak at 3616 cm^{-1}-3656 cm^{-1} was the stretching vibration of crystallized water. The peak intensity of the residue phase was significantly weakened, and some of the IR characteristic peaks disappeared, indicating that the content of some compounds in the residue phase was reduced. The presence of anti-symmetric stretching vibration of $-CH_2$ and symmetric stretching vibration of $-CH_2$ on the IR spectra of both OS-2 and solvent-extracted residue phase indicated that both contained mineral oil, and the content of mineral oil in the residue phase after extraction was significantly reduced.

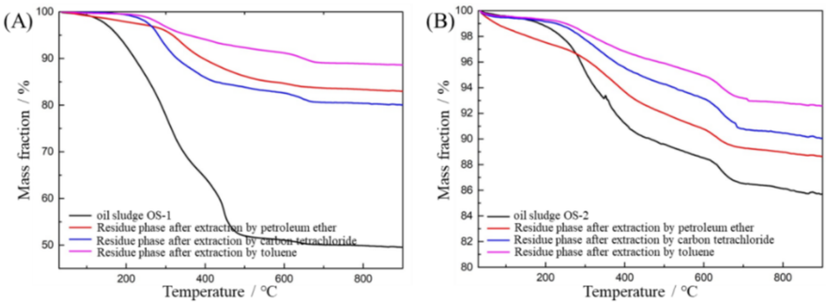

Figure 1. (a) Thermogravimetric curves of oily sludge OS-1 before and after extraction; (b) Thermogravimetric curves of oily sludge OS-2 before and after extraction.

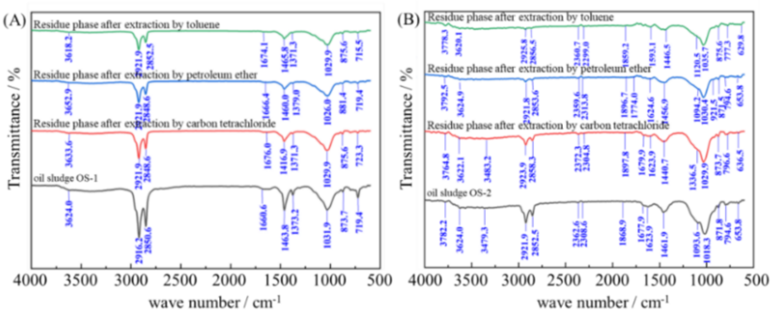

Figure 2. (a) Infrared spectra of oily sludge OS-1 before and after extraction; (b) Infrared spectra of oily sludge OS-2 before and after extraction.

3.2. Oil Content Test by Three Methods

The oily sludge OS-1 and OS-2 were extracted by carbon tetrachloride, and the solvent was removed by spin evaporation. As shown in Figure 3, the oil phase was weighed and the calculated oil content was 43.67(±1.33)% and 4.89(±0.07)%, respectively, which was close to the oil content of 42.07(±1.04)% and 4.57(±0.21)% measured by infrared spectrophotometer. The results indicated that all the components extracted by carbon tetrachloride were effectively detected, and the oil phase components obtained from the extraction were all petroleum. After OS-1 and OS-2 were extracted by petroleum ether, the solvent was removed by spin evaporation, and the oil phase was weighed and calculated to be 45.22(±2.92)% and 4.94(±0.14)%, which were much higher than the oil content measured by UV spectrophotometer at 14.78(±1.15)% and 3.13%(±0.40). The results indicated that petroleum ether can adequately extract petroleum hydrocarbons, but since the UV spectrophotometer can only detect aromatic compounds containing benzene rings and conjugated double bond compounds, but not saturated hydrocarbons, the oil content measured by UV spectrophotometry was low, and about 30% and 1.8% of saturated hydrocarbons in OS-1 and OS-2, respectively, were not detected.

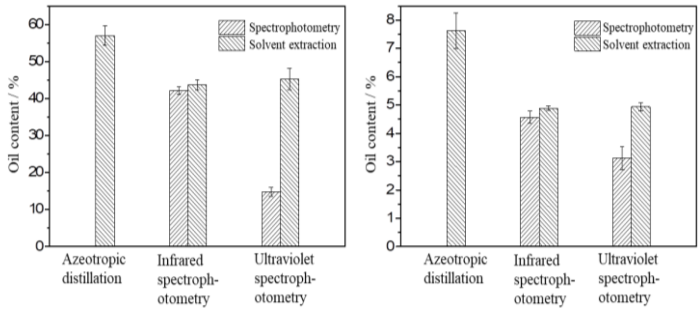

Figure 3. (a) Oil content of oily sludge OS-1 measured by three methods; (b) Oil content of oily sludge OS-2 measured by three methods.

The azeotropic distillation method uses the characteristics of crude oil being easily soluble in toluene and the formation of azeotropic compounds by toluene and water to separate and measure the oil, water and sludge phases in the oily sludge. By weighing the water and sludge phases, the oil content of the oily sludge was calculated by differential subtraction. So the organic components dissolved by toluene were all calculated in the oil content, and the oil content measured by azeotropic distillation was 56.96(±2.65)% and 7.62(±0.63)%, respectively, which was close to the volatile solids content of 59.83% and 8.01% of the oily sludge OS-1 and OS-2. The results indicated that the azeotropic distillation method accounted for most of the volatile organic components in the oil sludge, so the highest oil content was measured by azeotropic distillation. The azeotropic distillation method is essentially a weight method with a large systematic error, which leads to a large error in the detection of oil content. The infrared spectrophotometry extracts the petroleum substances with all or part of the spectral band at wave numbers of 2930 cm^{-1}, 2960 cm^{-1}, 2020 cm^{-1} in the oily sludge sample with carbon tetrachloride. And the UV spectrophotometry can effectively detect the aromatic compounds and compounds with conjugated double bonds in the oily sludge without saturated hydrocarbons. The measured oil content was 42.07(±1.04)% and 4.57(±0.21)%, respectively for OS-1 and OS-2 by infrared spectrophotometry, which were lower than the test results of the azeotropic distillation method, and the smallest oil content was measured by UV spectrophotometry, which was only 14.78(±1.15)% and 3.16(±0.40)%, respectively. The results showed that the IR and UV spectrophotometry were highly accurate and the error of the measured oil content was less.

4. Conclusion

In this study, we compared the results of oil content determination of two types of oily sludge OS-1 and OS-2 by azeotropic distillation, infrared spectrophotometry and UV spectrophotometry. The azeotropic distillation method measured the highest oil content, which was close to the volatile solids content of the oily sludge samples. The azeotropic distillation method was suitable for the determination of oil, water and residue phases of oily sludge, providing basic parameters for the selection of oily sludge treatment methods and oil content detection methods. Infrared spectrophotometry and UV spectrophotometry are highly accurate, and UV spectrophotometry is suitable for the detection of oily sludge with unsaturated petroleum hydrocarbons as the main components, while IR spectrophotometry can adequately detect petroleum components, so IR spectrophotometry is relatively reliable and can be promoted in the experimental and production processes.

Acknowledgements

This study was funded by the Liaoning Industrial Research and Industrialization Guidance Program (2019JH8/10100096).

References

[1] Liu JG, Jiang XM, Zhou LS, Wang H, Han XX. Co-firing of oil sludge with coal-water slurry in an industrial internal circulating fluidized bed boiler. Journal of Hazardous Materials. 2009;167(1-3):817-823.
[2] Shen L, Zhang DK. An experimental study of oil recovery from sewage sludge by low-temperature pyrolysis in a fluidised-bed. Fuel. 2003;82(4):465-472.
[3] Chen FE, Wang XM, Bai ZW, Zhang RF, Zhang LQ. Experiment on refinery sludge treatment by solvent extraction. Chemical Engineering (China). 2005;33(1):52-55.
[4] Zubaidy EAH, Abouelnasr DM. Fuel recovery from waste oily sludge using solvent extraction. Process Safety and Environmental Protection. 2010;88(5):318-326.
[5] Liu MZ. Research on the Development Status and Countermeasures of the Xinjiang Uygur Autonomous Region Rural and Urban Refined Oil Market. Urumqi: Xinjiang Agricultural University. Master's Thesis. 2016.
[6] ASTM D9-2013. Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation.
[7] HJ1051-2019. Soil-Determination of Petroleum Oil-Infrared Spectrophotometry.
[8] HJ970-2018. Water Quality-Determination of Petroleum-Ultraviolet Spectrophotometry Method.
[9] Jin YQ, Zheng XY, Chi Y, Ni MJ. Experimental study and assessment of different measurement methods of water in oil sludge. Drying Technology. 2014;32(3):251-257.
[10] Zhang B. Research on application of infrared oil meter laboratory. Applied Science and Technology. 2014;(08):294-295.
[11] Lv QW. Study on Reducing Mineral Oil Content in Petroleum Sludge by Soil Remediation Agent. Dalian: Dalian Maritime University. Master's Thesis. 2018
[12] Zhang J, Wang ZY, Sun JX, Wei L, Wang BS, Ma J, Chen ZX. Ultrasound-UV method detect oil content of oily sludge from Daqing oilfield. Environment Materials and Environment Management. 2010;(113-116):2292-2295.
[13] Mao LH, Han XM. Study of ultraviolet spectrophotometer for rapid analysis of oil content in the oil-contaminated soil. Environmental Engineering. 2013;(864-867):930-934.
[14] HJ168-2010. Environmental Monitoring-Technical Guideline on Drawing and Revising Analytical Method Standards.
[15] Lin BC. Study on Target-Oriented Catalytic Pyrolysis of Oil-Rich Sludge. Hangzhou: Zhejiang University. Master's Thesis. 2020.
[16] Guo XJ, Wang SR, Guo ZG, Liu QA, Luo ZY, Cen KF. Pyrolysis characteristics of bio-oil fractions separated by molecular distillation. Applied Energy. 2010;87(9):2892-2898.