

Quantitative Determination of Petroleum Hydrocarbons in Oily Sludge Following Efficient N-Heptane Separation

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Accurate analysis of the main chemical components of oil-bearing sludge is an important prerequisite for effective soil remediation and resource reuse. However, precise analysis of the extract components is difficult to achieve because of the mutual interference of saturates, aromatics, and resins, collectively called SAR, and asphaltene that are introduced during chloroform extraction. In this study, SAR was efficiently extracted using n-heptane, while asphaltene components were retained in soil because of their insolubility in n-heptane. The maximum yield of SAR extraction was 27.0%, indicating an increase of 1.75% compared to chloroform extraction. The extracted SAR components were separated by chromatography and the main structural units and components were analyzed. The results show that saturates, aromatics, and resins have a single component, a high content of major components, and contain fewer impurities using n-heptane extraction. Moreover, the solubility of asphaltene was inhibited during the effective extraction of SAR components with n-heptane and did not influence the subsequent analysis of SAR component. Efficient SAR extraction, accurate SAR component analysis, and high efficiency asphaltene separation was achieved using n-heptane-extraction-assisted pyrolysis. This provides a new method for the component analysis of oily sludge and promotes its efficient separation.

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Keywords: Oily sludge; Extraction; Asphaltene; n-heptane; Separation

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INTRODUCTION

It is well-known that the advancements in fossil energy processing have significantly boosted the development of the modern industry (Feng *et al.* 2022; Liu *et al.* 2022b). During extraction, processing, transportation, and utilization of fossil fuels, an oily sludge containing toxic and carcinogenic organic pollutants is formed in high yields (Hu *et al.* 2013; Gong *et al.* 2017; Liu *et al.* 2021). Petroleum-containing sludge sometimes also contains lignocellulosic materials, which can raise further challenges related to environmental impacts (Peng *et al.* 2020). Proper treatment of this oily sludge is a major challenge with current soil pollution control practices. Currently, various treatment technologies are available including solvent extraction techniques (Zhang *et al.* 2021), elution (Ren *et al.* 2022), pyrolysis (Chu *et al.* 2021), biodegradation (Cerqueira *et al.* 2011; Chen *et al.* 2022), and oxidation (Mora *et al.* 2020). The elution method is suitable for oily sludge that is rich in light chemical components, whereas the pyrolysis method is appropriate for oily sludge with high oil content. Biodegradation is only suitable for

treating oily sludge with low or trace contamination (Su *et al.* 2021). Variation in the oily sludge components directly affects its different treatment technologies. Therefore, the identification of oily sludge components is important for its efficient separation technology.

Based on their polarity, petroleum hydrocarbons in oily sludge can be classified as saturates, aromatics, resins (SAR), and asphaltene (Mrayyan and Battikhi 2005). Extraction using organic solvents is a widely-used method for the extraction of petroleum hydrocarbons from oil-bearing sludge (Klemz *et al.* 2021). Organic solvents that are commonly employed for this purpose include naphtha, toluene, dimethyl ether, and chloroform. Wu *et al.* (2013) performed an extraction study using naphtha on tank bottom sludge and demonstrated the separation of 96% of extractable oil. Nezhdbahadori *et al.* (2018) used the response surface design to determine the optimal conditions of toluene extraction for the recovery of petroleum hydrocarbons from oily sludge and achieved 37.2% recovery. The effect of extraction and separation parameters of petroleum hydrocarbons from oily sludge using dimethyl ether was investigated by Zhang *et al.* (2021) and demonstrated that a 70.8% extraction yield was achieved using the optimum conditions (25 °C reaction temperature, 30 min extraction time, and 600 rpm stirring rate). Yasser *et al.* (2021) compared the effects of acetone, chloroform, dichloromethane, and n-hexane for hydrocarbon extraction from oily sludge in petroleum storage tanks. The results indicated that the highest extraction yield of 86% was achieved with chloroform as the extracting agent using a liquid-to-solid ratio of 10 and an extraction time of 30 min.

There are various factors affecting the extraction of hydrocarbons such as temperature, pressure, solvent-to-solute (*i.e.*, solvent to oily sludge) ratio, and the nature of solvent (Fisher *et al.* 1997; Zubaidy and Abouelnasr 2010; Hu *et al.* 2016), which make the effective extraction of petroleum hydrocarbons from oily sludge challenging. Moreover, qualitative and quantitative analyses of hydrocarbons in oily sludge are difficult to perform reliably. Among organic solvents, chloroform has been one of the best extractants for hydrocarbons; however, it shows poor selectivity for petroleum hydrocarbons over asphaltene, which is problematic because the subsequent qualitative analysis of the SAR is interfered by asphaltene residues. Asphaltenes are petroleum hydrocarbons that are insoluble in n-heptane, contain various heteroatoms, and have complex chemical structures (Pagán Pagán *et al.* 2022). Asphaltenes tend to flocculate and accumulate upon forming strong bonds with soil (León *et al.* 2002; Fakher *et al.* 2020), making them the most difficult component to extract. Therefore, it is crucial to inhibit the leaching of asphaltenes during the effective extraction of SAR components. The asphaltene content was determined using the pyrolysis method. This is a confirmed extraction strategy for the determination of petroleum hydrocarbon contents. n-Heptane can be effectively used for the selective extraction of SAR, and it does not affect the asphaltene extraction. Therefore, it is important to investigate the extraction of petroleum hydrocarbons from oily sludge using n-heptane and the subsequent asphaltene determination.

In this study, SAR of the oily sludge was extracted using n-heptane for analysis. The asphaltene that was retained in the oily sludge was pyrolyzed at a high temperature, followed by the analysis of asphaltene content. The effects of the solute ratio, extraction time, and number of extraction cycles on the SAR extraction by n-heptane were investigated. The SAR composition was analyzed after extraction. The results establish an n-heptane extraction-assisted high-temperature pyrolysis method, which will provide a new route for the quantitative and qualitative analysis of petroleum hydrocarbons in oily sludge.

EXPERIMENTAL

Materials

Oily sludge was obtained from Daqing Oil Field (Daqing, Heilongjiang, China). The oil sludge used in the laboratory is muddy, the proportion of the oil-water mixture is 50.06%, and the remaining solid mass after removing the oil-water mixture accounts for 49.96%, as shown in Table 1. N-Heptane and chloroform were purchased from Sigma-Aldrich (St. Louis, MO, USA). All other chemicals were of analytical grade and purchased from Aladdin Biochemical Technology Co. (Shanghai, China).

Table 1. The Oil Sludge Used for This Study

Water	Oil	Solid
13.76%	36.30%	49.94%

Methods

Moisture in the oily sludge was removed by freeze-drying using Lyovapor L-300 (BUCHI, Flawil, Switzerland). Absolutely dry oily sludge was obtained by drying at a temperature of -50 °C for 24 h. After drying, 1 g of the sample was mixed with n-heptane solvent. Upon thorough mixing, the petroleum hydrocarbon components were extracted using ultrasound at a frequency of 100 Hz. The effect of solute ratio, extraction time, and extraction cycle number on the extraction efficiency of petroleum hydrocarbons using n-heptane was studied. At the reaction temperature of 30 °C, the liquid–solid mixture was separated by centrifugation at 7000 rpm for 10 min, resulting in a solution phase that contained SAR and a solid consisted of retained asphaltene soil (RA). The SAR was concentrated to 5 mL at 50 °C at 100 Pa and then dried at 105 °C. The asphaltene content in RA was calculated using Eq. 1, after the standard curves of asphaltene pyrolysis were obtained using 0.1, 0.2, 0.3, 0.4, and 0.5 g oily sludge that were added to the ash meter (PrepASH 340, Precisa, Zurich, Switzerland) and heated at a rate of 20 °C min⁻¹ to 800 °C. The holding time was 30 min,

$$\text{Asphaltenes content: } M_{\text{Asph}} = (M - K_2 \times N) / (K_1 - K_2) \quad (1)$$

where M_{Asph} is the asphaltene content of the oily sludge (g), M is the mass of asphalt coke and coked soil (g), N is the weight of the original oily sludge (g), K_1 is the slope of the asphaltene pyrolysis standard curve, and K_2 is the slope of the calibration curve.

The separation of the oily sludge components with n-heptane was compared to that of chloroform extraction (Shen and Li 2008; Hamidi *et al.* 2021), for which a solute ratio of 1:40 (w:v), sonication frequency of 100 Hz, and extraction time of 8 h was used. Three replicate extractions were performed for every experiment. The solid–liquid separation and SAR content were the same for both chloroform and n-heptane. The chloroform in the extraction solution was evaporated and the residue SAR components were dissolved in n-heptane. Asphaltene precipitated because of their low solubility in n-heptane. The experimental process is shown in Fig. 1.

A sample of 0.01 g SAR was completely dissolved in 10 mL n-heptane. The individual saturates, aromatics and resin components were analyzed using Fourier transform infrared spectroscopy (FTIR; IRTracer-100, Shimadzu, Kyoto, Japan) (Liu *et al.* 2022a). The specific compound composition was analyzed using gas chromatography-mass spectrometry (GC-MS; 7890 B, Agilent, Palo Alto, CA, USA). The GC was equipped with an HP-5 capillary column and used 99.99% helium as the carrier gas. The partition

ratio was 80:1, the detector temperature was 250 °C, and the inlet temperature was 250 °C. Specific methods and procedures have been described in previous studies (Hao *et al.* 2022).

Soil samples with different SAR concentrations were prepared. The constituents of the extract were determined using extraction retention and asphaltene pyrolysis process. The results confirmed the accuracy of the newly developed method. Scanning electron microscopy (SEM; F16502, Phenom, Eindhoven, Netherlands) was used to examine the apparent morphology of the oily sludge before and after treatment (Zeng *et al.* 2022).

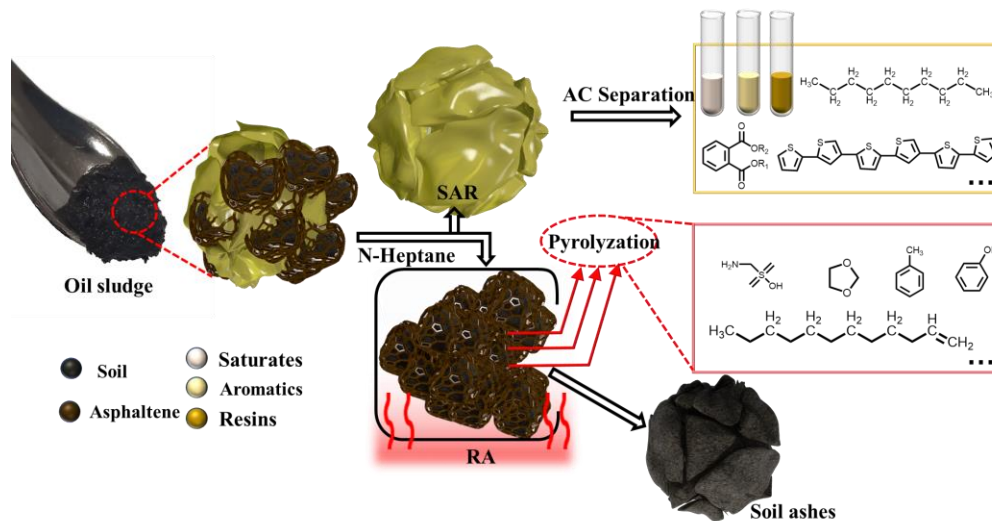


Fig. 1. Experimental flow chart

RESULTS AND DISCUSSION

Effect of Solute Ratio on Extraction of Oily Sludge SAR Component Using N-Heptane

Solubility, extraction time, solute ratio, and temperature are the main factors influencing the extraction efficiency of petroleum hydrocarbons from oily sludge (Fisher *et al.* 1997; Zubaidy and Abouelnasr 2010; Hu *et al.* 2016). It is well known that ineffective volatilization of organic solvents is promoted with increasing temperature. Therefore, it was not necessary to study the effect of temperature changes on SAR extraction. In this study, the extraction temperature was maintained at 30 °C. Increasing the solute ratio can maximize extraction efficiency at a certain temperature and time. However, the principles of sustainability and green chemistry require that the consumption of organic solvents is minimized (Yanagisawa *et al.* 2018). Therefore, the effect of the solute ratio on the SAR extraction was studied using 1:10, 1:20, 1:30, 1:40, and 1:50 ratios and a 6-hour extraction time. The variation in the SAR extraction yield with the solute ratio is shown in Fig. 2a. The extraction yield of SAR increased from 19.7% to 25.8% when the solute ratio was increased from 1:10 to 1:40, respectively. This was attributed to the low solubility of SAR in the solute at lower ratios. Moreover, the diffusivity of the solvent increases with increasing solute ratio (Zhou *et al.* 2011). Following the initial increase, the extraction yield of SAR tended to become independent of the solute ratio at ratios greater than 1:40, reaching a maximum value of 26.0% at the solute ratio of 1:50. Similar saturating effects were observed by Li *et al.* (2011), who used a composite extractant to extract oil sand. Nonetheless, the optimal solute ratio was 1:40 in n-heptane extraction.

Effect of Time on the Extraction of Oily Sludge SAR Component Using N-Heptane

It was found that SAR solubilization in the solvent is promoted by prolonging the extraction time (Sui *et al.* 2016). Therefore, the effect of time on the SAR extraction was studied using 2, 4, 6, 8, and 10 h extraction times and 1:40 solute ratio. Figure 2b shows the variation in SAR extraction yields with time. The results revealed two trends in the variation with time. Initially, the extraction yield increased from 18.3% to 26.9% with the extraction time ranging from 2 h to 8 h, respectively. However, the extended time hindered the extraction of the SAR, and a decrease in extraction yield to 23.2% was observed after 10 h. The maximum extraction yield of 26.9% was obtained after 8 h. This effect was attributed to the sorption limits of the soil. In longer extraction times, the equilibrium between the sorption and desorption of SAR is disrupted and the dissolved SAR will re-adsorb onto the surface of soil particles (Masakorala *et al.* 2014), resulting in a decrease in the extraction yield over time. Therefore, the optimal extraction time of 8 h was considered for the n-heptane extraction of SAR.

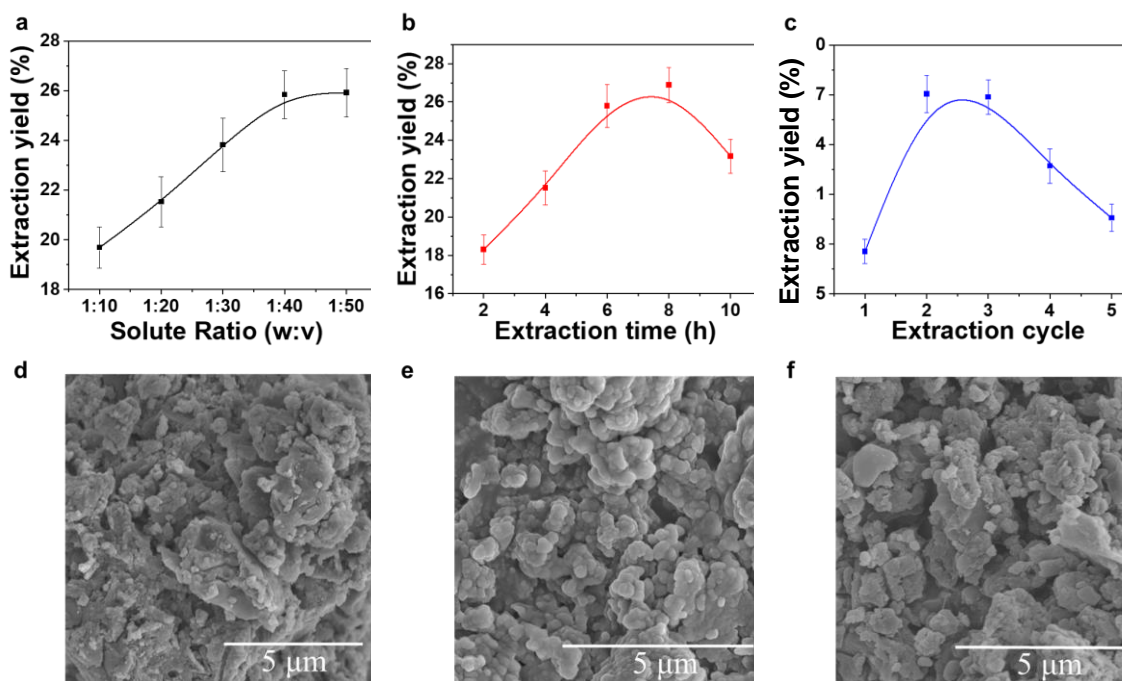


Fig. 2. Effect of n-heptane on SAR extraction from oily sludge and the surface morphology of oily sludge before and after extraction (a, b, and c: Effect of solute ratio, extraction time, and extraction cycle, respectively, on SAR extraction from oily sludge using n-heptane; d, e, and f: SEM of original oily sludge, oily sludge after n-heptane extraction, and oily sludge after chloroform extraction, respectively)

Effect of Number of Cycles on the Extraction of Oily Sludge SAR Component Using N-Heptane

Zhu *et al.* (2020) found that the recovery of the oil component decreased with the number of solvent recoveries, reaching a maximum (67%) after four cycles. Therefore, the effect of the number of extraction cycles on SAR extraction was studied. The selected cycle numbers were 1, 2, 3, 4, and 5 using the solute ratio of 1:40 and extraction time of 8 h. The variation in SAR extraction under different extraction cycles is shown in Fig. 2c. The

extraction yield increased from 17.6% to 27.0% from cycles 1 to 2, respectively, then remained unchanged at three extraction cycles. A negative effect of increasing the number of cycles on SAR extraction was seen after cycle 3 from 22.7% to 19.6% after cycle 4. This initial increase in the yield with the number of cycles was because of the adequate contact of n-heptane with the SAR components in the oily sludge, which led to the enhancement of the extraction efficiency. However, SAR agglomerates were dispersed by persistent cyclic extraction sonication (Su *et al.* 2017), and the resultant fine SAR components were dissolved in the aqueous solution. In addition, SAR was adsorbed onto the surface of soil particles. All these effects led to a decrease in the extraction efficiency. Therefore, the optimal number of extraction cycles for the n-heptane extraction of SAR was 2.

The optimal conditions for SAR extraction using n-heptane were 1:40 solute ratio, 8 h of extraction time at 100 Hz ultrasonic frequency, and using 2 extraction cycles. Under these conditions, an extraction yield of 27.0% was achieved for SAR from the oily sludge, which was 1.75% higher compared to that of the chloroform extraction method.

When n-heptane is mixed with petroleum hydrocarbons, asphaltene precipitates and fills in the soil voids (Hosseini *et al.* 2016), and the remaining SAR components have high fluidity and low viscosity (Peralta-Martinez *et al.* 2011), and they fill the gaps between the soil particles. The soil particles are encapsulated by asphaltene to form flocculent deposits. Figure 2e shows the morphological characteristics of the oily sludge before and after different treatments. Ovoid and spherical structures were present in the original oily sludge samples, indicating the encapsulation of soil particles by asphaltene. In addition, the soil particles were filled with the SAR components between them. After chloroform extraction, the filling between soil particles in the oily sludge was removed, and the agglomeration of soil particles was significantly reduced. Notably, samples with larger void fractions and larger soil particle agglomerations were observed after n-heptane extraction, indicating that asphaltene retention was effectively maintained during SAR extraction with n-heptane. This observation demonstrates that the low solubility of asphaltene affects the SAR compositions during the process of n-heptane extraction.

Analysis of Asphaltene Content in Oily Sludge

Petroleum hydrocarbons in oily sludge are not homogeneous and form a rather stable colloidal dispersion with the asphaltene being the colloidal nuclei. Because the solvated shell of the colloid in the dispersion medium is removed during n-heptane extraction (Zhao *et al.* 2018), the asphaltene content in oily sludge can impact the n-heptane extraction efficiency. The asphaltene content in the oily sludge was analyzed using hyperthermal pyrolysis method following the n-heptane extraction. In this experiment, the single asphaltene extracted from oil sludge is called standard asphaltene. Clean soil that is not contaminated by crude oil is called clean soil. The pyrolysis rate curve of standard asphaltene and clean soil is called standard pyrolysis curve. Prior to pyrolysis, asphaltene pyrolysis standard (Fig. 3a) and clean soil calibration curves (Fig. 3b) were constructed separately. The asphaltene content in the oily sludge was determined by high-temperature pyrolysis of the oily sludge after n-heptane extraction and was calculated using Eq. 1.

Within the temperature range of 400 to 800 °C, the pyrolysis rate was consistent with $y = 0.0648x$ for the asphaltene in oily sludge used for this study. The clean soil pyrolytic weight-loss rate curve at the same temperature range was $y = 0.8706x$. Based on these values, an asphaltene content of 16.2% was calculated for the oily sludge, which was considerably higher than the asphaltene content measured after chloroform extraction (7.4%). The higher asphaltene content indicated suppressed leaching of asphaltene during

n-heptane extraction, which remarkably reduced the mutual interference of different petroleum hydrocarbon components in the subsequent qualitative analysis.

In the next step, the analytical results of the different extraction methods and their subsequent treatments of the main components of the oily sludge were compared. The results are shown in Fig. 3c. The content of total petroleum hydrocarbons obtained using different methods showed a significant discrepancy. The total SAR content was measured as 26.3% after n-heptane extraction followed by high-temperature pyrolysis, which was almost double the 13.2% value measured after chloroform extraction and n-heptane precipitation. Similarly, a SAR content of 10.6% was measured after n-heptane extraction, whereas the SAR content in the oily sludge was reduced to 9.9% after chloroform extraction, reflecting the high efficiency of n-heptane for SAR extraction. The results indicated that more asphaltenes were retained using n-heptane compared to chloroform for the extraction. This effect was primarily attributed to the strong binding of asphaltene to the soil (Adams 2014) and the inability of the intermolecular forces of n-heptane to overcome and break the strong adhesion of asphaltene to between asphaltene and soil particles. Chloroform is more polar than n-heptane. Asphaltenes with more polar substances are more likely to dissolve in chloroform, while they precipitate in n-heptane and remain in the soil. Therefore, the leaching of asphaltene from oily sludge was reduced in n-heptane extraction.

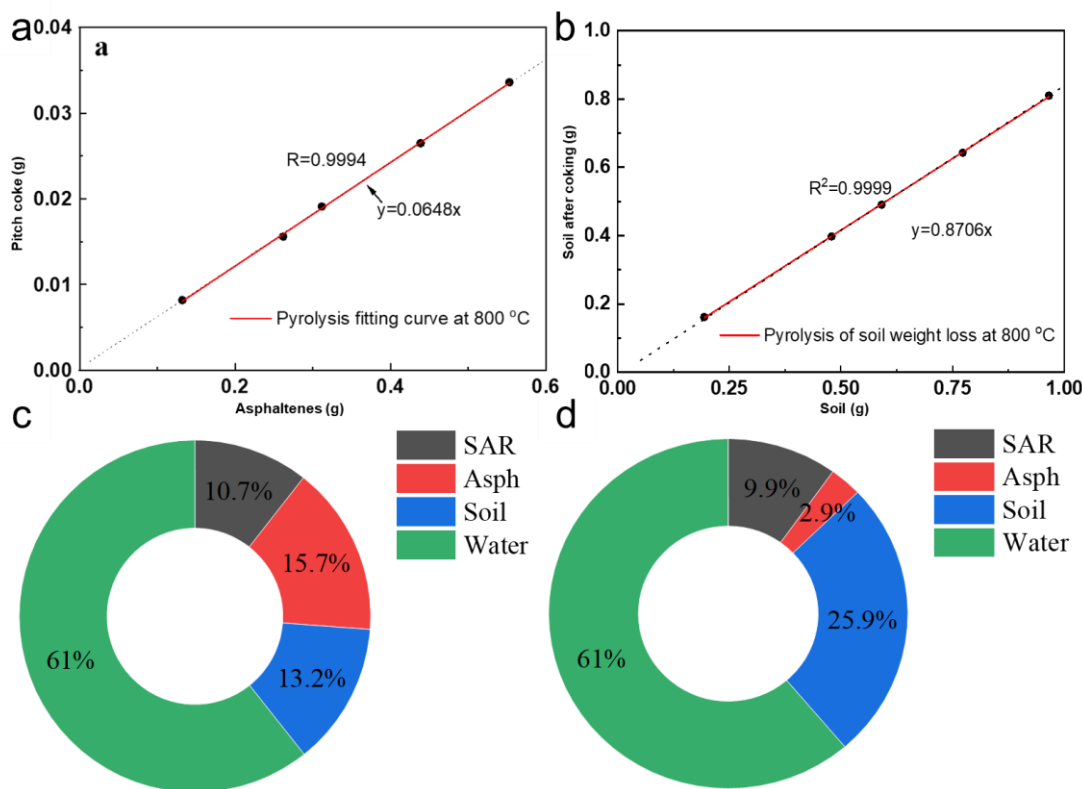


Fig. 3. Standard curve for calculation of asphaltene content and main composition of oily sludge obtained by different extraction methods (a: Asphaltene pyrolysis standard curve; b: Clean soil calibration curve; c: N-Heptane extraction followed by high-temperature pyrolysis; and d: Chloroform extraction followed by n-heptane precipitation)

Comparison of the Accuracy of Various Component Separation Techniques

Simulated oily sludge samples and clean soil samples with different added levels of SAR contents were prepared and used to investigate the effect of n-heptane extraction followed by high-temperature pyrolysis on the extraction efficiency and separation of oily sludge components. The SAR content in Fig. 3 was obtained by gravimetric method after n-heptane extraction, and the asphaltene content was calculated by pyrolysis method using the above Eq. 1. Figure 4a shows the different compositions obtained for the oily sludge samples with their respective separated soils and SAR. Despite the apparent variation in the extracted SAR with the amount added to the soil samples, it cannot be concluded that n-heptane extraction exhibits low efficiency. As shown in Fig. 4b, which depicts the different contents of SAR and asphaltene and the variation in their extraction efficiencies for various samples, the extraction efficiency of the SAR remained stable at 96%. This implied that the n-heptane extraction of the SAR was indeed highly stable.

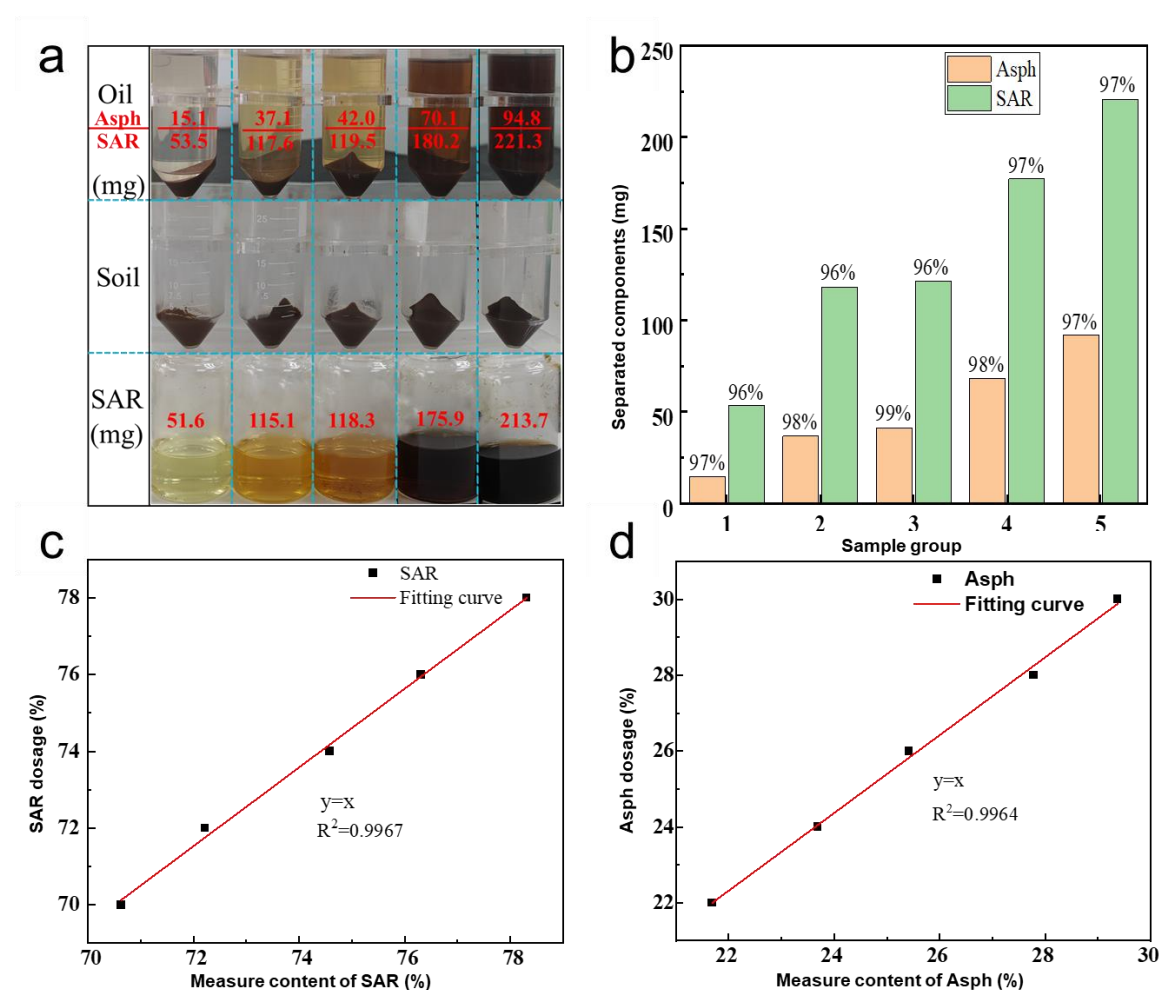


Fig. 4. Extraction and separation of different oily sludge using n-heptane extraction followed by high-temperature pyrolysis (a: different oily sludge samples, separated sludge, and extracted SAR components; b: Extraction content and separation effect on different components; c: Linear relationship between SAR dosage and measured content; and d: Linear relationship between asphaltene dosage and measured content)

The asphaltene content of the samples after extraction was analyzed and separation efficiency of 98% was obtained, suggesting that the remaining asphaltene content was too low to negatively impact the qualitative and quantitative analysis of SAR components. In addition, the measured values of the SAR and asphaltene contents, and the standard additions showed a linear correlation. Further, the effectiveness of the new oily sludge extraction/separation method was analyzed. Based on the results in Fig. 4c and 4d, a linear relationship between the added concentrations of SAR and asphaltene and their respective measured values was observed, with all the fits exhibiting R^2 values greater than 0.99. Therefore, efficient stability of n-heptane extraction followed by high-temperature pyrolysis for the extraction and separation of oily sludge is confirmed.

Chemical Components Analysis of SAR

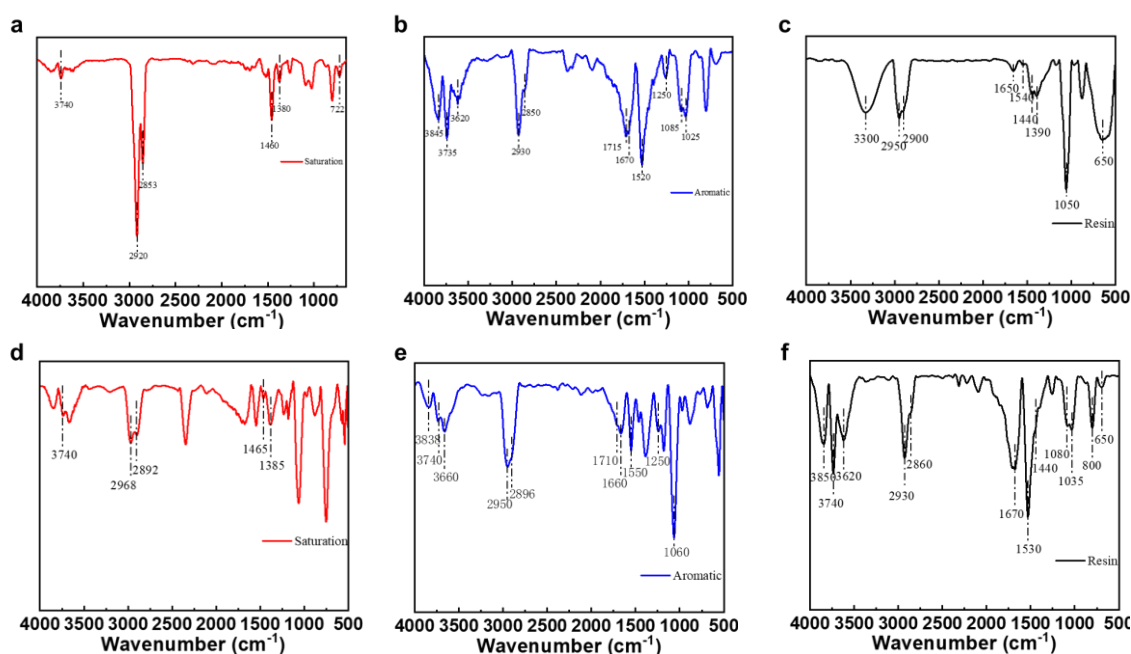


Fig. 5. Main functional group analysis of SAR components obtained by different extraction methods (a, b, and c are saturates, aromatics, and resins, respectively, as separated by n-heptane extraction; d, e, and f are saturates, aromatics, and resins, respectively, separated by chloroform extraction)

The extracted SAR mainly includes saturates, aromatics, and resins (Mrayyan and Battikhi 2005). The saturates were 4.57%, the aromatics were 2.72%, and the resins were 0.93% after chromatographic separation. The effect of n-heptane extraction on the SAR components was analyzed after separation using chromatography. The structural changes in the main functional groups of the SAR fractions obtained by the various extraction methods are shown in Fig. 5. The chromatographs of samples differed noticeably in terms of the band distribution and relative intensities. Figures 5a and 5d show the distributions of the main functional groups of saturates. The stretching vibrations found at 3740 cm⁻¹ were attributed to free OH groups, and the peaks at 2920 cm⁻¹ and 2853 cm⁻¹ were attributed to the stretching vibrations of -CH₂ groups (Bagheri Garmarudi *et al.* 2019). The peaks at 1460 cm⁻¹ and 1380 cm⁻¹ were related to in-plane and out-of-plane deformation vibrations of -CH₃ group, respectively. The in-plane deformation vibrations of -CH₂ appeared at 1465

cm^{-1} and 1460 cm^{-1} , and the in-plane deformation vibrations of skeletal $-\text{C}-\text{C}$ were observed at 1250 cm^{-1} . Finally, the out-of-plane deformation vibrations at 722 cm^{-1} were attributed to $-\text{CH}_2$. Based on this information, it was concluded that the saturates had a lower variety of characteristic absorption peaks and mainly contained long-chain structures. However, some of the peaks were more concentrated. In particular, the $-\text{CH}_2$ stretching and deformation vibrations that are the main structural feature of saturates, were stronger than those of the chloroform-extracted components, indicating that the n-heptane-extracted saturates were more concentrated and had less impurities.

Figures 5b and 5e show the distribution of the main functional groups of aromatics. The absorption peaks at 3845 cm^{-1} , 3735 cm^{-1} , and 3620 cm^{-1} are attributed to the absorption peaks of the oxygen heteroatoms. The characteristic peaks at 1715 cm^{-1} represent the $\text{C}=\text{O}$ double bond, and the peaks at 1670 cm^{-1} and 1520 cm^{-1} are due to the stretching vibrations of the aromatic backbone (Mohammadi *et al.* 2020). The absorption peak at 1250 cm^{-1} is attributed to the aromatic ether bond, suggesting that the aromatics contained carbonyl compounds. The same characteristic absorption peaks of aromatics were observed for both n-heptane and chloroform extraction methods; however, the vibration peaks in the benzene ring substitution region were stronger for samples after n-heptane extraction than those of chloroform extraction, implying that n-heptane is more effective for the extraction of aromatics. The $\text{C}-\text{H}$ off-plane bending vibration of the benzene ring at 880 to 680 cm^{-1} (Melendez *et al.* 2012) indicated the presence of more aromatic nuclear substitutions in the resins and that the resins separated by chloroform extraction contained more aromatic compounds. This was attributed to the strong interactions of aromatic hydrocarbons with the resins that contain asphaltene (Zhao *et al.* 2018) and was consistent with the previous finding that some asphaltene were entrapped during chloroform extraction of the resins.

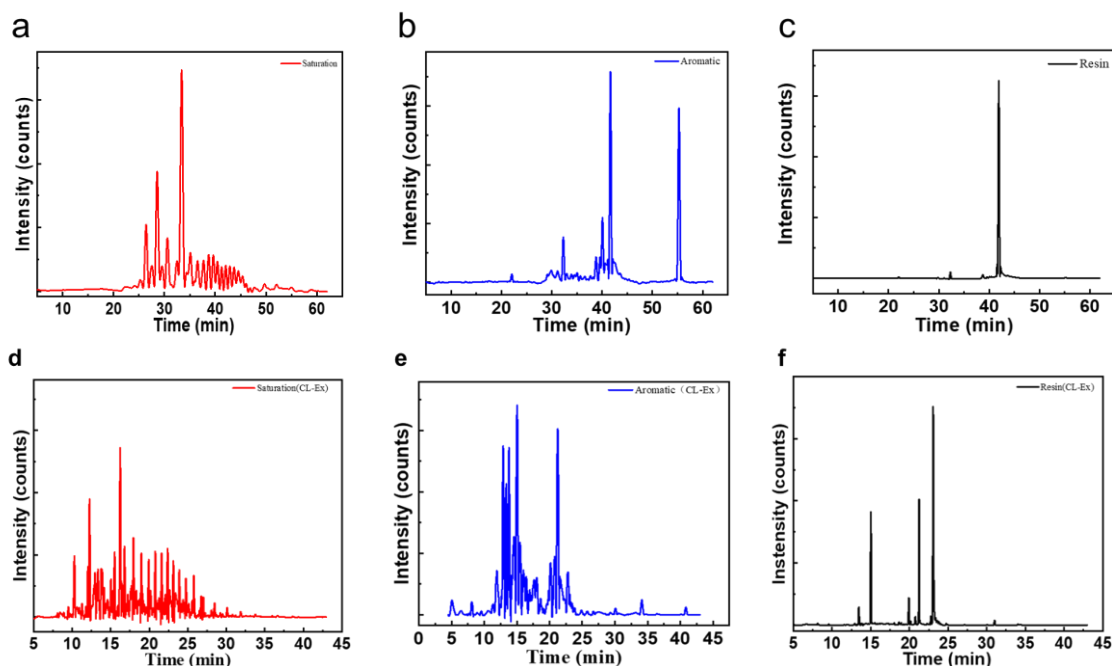


Fig. 6. Main functional group structures of SAR components obtained by different extraction methods (a, b, and c are saturates, aromatics, and resins, respectively, after n-heptane extraction; d, e, and f are saturates, aromatics, and resins, respectively, after chloroform extraction)

n-Heptane extraction showed a combined hydroxyl vibration peak, implying that n-heptane-extracted resins contained fewer asphaltene, which was in agreement with previous studies in which resins were demonstrated to contain benzene ring condensation structures (Li *et al.* 2018). Overall, the results indicated that saturates, aromatics, and resins were separated in the chloroform-extracted SAR with a large variety of major functional groups and a weak intensity of the major absorption peaks. In contrast, the n-heptane-extracted SAR exhibited a high concentration of functional groups and remarkably intense absorption peaks for the main components, suggesting that the dissolution of asphaltene was restricted in n-heptane extraction of the SAR components. It is difficult to influence the subsequent qualitative analysis of the SAR components.

Different types of saturates, aromatics, and resins in SAR exhibit different volatilities (Xiao *et al.* 2022), and hence specific product fractions were analyzed. Figures 6a and 6d show the ion chromatograms of saturates. In Fig. 6a, the absorbance peaks at 26.42 and 28.61 min were attributed to 2,6,10,14-tetramethyl hexadecane, and the peak at 30.66 min was attributed to 9-hexadecane. Peaks appearing at 36.52 and 36.54 min were related to hexadecane. Heptacosan was observed at 37.69 and 38.72 min, and the absorbance peak at 39.63 min was identified as tetradecane according to Sanches Filho *et al.* (2017). In Fig. 6d, the absorbance peaks at 17.98 and 18.99 min were attributed to docosan and heptadecane, respectively. The absorbance peaks at 19.93, 20.81, and 21.60 min were attributed to tetradecane, and the peak at 22.24 min was attributed to triacontane. The absorbance peak at 23.11 min was attributed to hexadecane. The absorbance peak at 25.76 min corresponds to 1-(2,6,6-trimethyl)-1-cyclohexene-1-penton-3-one, which is a ketone type compound identified by Guo *et al.* (2011). The saturates extracted with n-heptane were predominantly hexadecane, with small amounts of heptadecane, octadecane, heptacosan, and tetradecane. However, chloroform-extracted saturates dominantly contained docosanes, which are alkanes with longer molecular chains, and they also contained ketones. Nonetheless, n-heptane-extracted saturates had a single composition and did not contain ketone impurities.

Figures 6b and 6e show the ion chromatograms of aromatics. In Fig. 6b, the absorbance peaks at 32.28, 40.08, 41.17, and 56.1.1 min were attributed to dipentyl phthalate, diheptyl phthalate, 2,6,10,14-tetramethylpentadecane, and di(2-methylheptyl) phthalate, respectively. The absorbance peaks at 12.93, 13.73, 15.02, and 21.24 min in Fig. 6e corresponded to 3,4,6-trimethylcarbazole, 2,5-bis (1,1-dimethyl ethyl)-1,4-phenylene glycol, 2,6-di-tert-butyl-4-methoxyphenyl, and dioctyl phthalate, respectively. The results indicated that the aromatics extracted using different methods primarily included benzene rings with branched chains and their esters. The aromatics extracted using n-heptane mainly included phthalate esters, whereas the aromatics extracted using chloroform were a complex mixture containing 3,4,6-trimethylcarbazole, benzyl alcohol, and phenol and nonheterocyclic substances. Hence, the specific efficiency of n-heptane for aromatic extraction was confirmed. Figures 6c and 6f show ion chromatograms of the resins. The absorbance peak in Fig. 6c, mainly concentrated at 41.33 min was a hexathiophene compound previously identified in resins by Robson *et al.* (2017). The absorbance peak at 15.04 min in Fig. 6f was attributed to 1,7-dimethyl-9,10-phenanthrenedione. The absorbance peak at 18.03 min was attributed to octadecene. The absorbance peak at 21.35 min was attributed to eicosane, and the absorption peak at 23.08 min corresponded to docosaenamide. Therefore, chloroform-extracted resins contained complex fractions involving polycyclic structures and other components that were detected. This indicated that the chromatographic separation was disturbed. The main component of the n-heptane-

extracted resin included hexathiophene, and the saturated hydrocarbons, aromatic hydrocarbons, and resins were efficiently extracted using n-heptane.

CONCLUSIONS

1. A new method was developed for the analysis of oily sludge fractions based on efficient extraction of saturates, aromatics, and resin (SAR) components using n-heptane. Under the experimental conditions, the optimum time, solute ratio and extraction times required in the process of extracting SAR with n-heptane were explored. The new method enabled higher SAR extraction efficiency compared to chloroform extraction. Asphaltene components were mainly retained in the soil and were measured using a post-extraction high-temperature pyrolysis method. Higher levels of asphaltene were found using the n-heptane precipitation method than chloroform extraction.
2. The results indicated that in the new method, the asphaltene were protected from leaching during the selective extraction of SAR with n-heptane. The advantages of the new method included the higher efficiency of SAR extraction, in addition to achieving single species extracts with higher concentration and fewer impurities.

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