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Solvent extraction of oil from Haoud El Hamra storage tank sludge using MEK, cyclohexane, and their mixture: Characterization of extracted products

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Petroleum sludge that accumulates at the bottom of storage tanks presents both an environmental challenge and a potential source of valuable hydrocarbons. This study evaluated oil recovery from refinery petroleum sludge using cyclohexane (CHX), methyl ethyl ketone (MEK), and a relatively underexplored binary solvent system combining the two solvents. The effects of extraction temperature, stirring time, solvent volume, and solvent blend ratio were systematically investigated to determine the optimal extraction conditions. The complementary solvency characteristics of CHX, a non-polar solvent, and MEK, a relatively polar solvent, were evaluated to determine their effectiveness in enhancing oil recovery compared with the individual solvents. The maximum oil recoveries obtained using MEK and CHX individually were 34.67% and 45.26%, respectively. In contrast, the CHX/MEK binary mixture achieved the highest oil recovery of 51.47% under the optimal conditions of 40 °C, 2 h of stirring, a solvent volume of 40 mL, and a CHX:MEK volumetric ratio of 60:40. The recovered oil and residual solids were characterized using Fourier transform infrared spectroscopy (FTIR), gas chromatography–mass spectrometry (GC–MS), X-ray diffraction (XRD), and X-ray fluorescence (XRF). The improved extraction performance of the CHX/MEK binary mixture was likely associated with the complementary solvation behaviour of the two solvents, which may have facilitated the dissolution of different hydrocarbon fractions within the petroleum sludge matrix and enhanced mass transfer during extraction. These results demonstrated that the CHX/MEK binary solvent system provided a promising solvent-based approach for hydrocarbon recovery, with potential applications in resource recovery, waste valorization, and the sustainable management of refinery petroleum sludge.

Keywords: Binary mixture, Cyclohexane, Methyl ethyl ketone, Oil yield, Petroleum sludge, Solvent extraction

Introduction

Significant amounts of oily sludge are produced by the petroleum industry during various oil production processes such as exploration, transportation, storage, and downstream refining[1]. The quantity and characteristics of oily sludge are based on the type of the crude oil, storage conditions, refinery configuration, and downstream processing methods[2]. Most often, oil sludge is formed during storage when heavy hydrocarbons and solids precipitate gradually and eventually precipitate and accumulate to form oil sludg[3]. It consists of a complex mixture of water, petroleum hydrocarbons, and inorganic contaminants, such as clay, sand, and metal oxides[4,5]. The high concentrations of hydrocarbons and heavy metals in oily sludge make it an environmentally hazardous material, because they prevent it from decomposing[6,7]. Oily sludge seriously contaminates the nearby soil, groundwater, and atmosphere, which has an adverse effect on human health as well as the typical growth of plants and animals[2,8]. The treatment of oil sludge has become a global issue and has drawn a lot of attention from relevant experts and researchers because of its complicated composition and substantial environmental impact[9]. Recycling is a good substitute for other recovery techniques. It has been demonstrated to help lower environmental pollution and the amount of oil deposits[10,11]. There are various treatment methods available, such as solvent extraction[12], pyrolysis[13], oxidation[14], and biodegradation[15]. Solvent extraction is a simple and efficient method for separating oily sludge into valuable hydrocarbons and a reduced-volume solid or semi-solid residue[16]. It also offers the advantages of removing water from the process and enabling solvent recovery and reuse[10,11]. This method is based on the principle of "like dissolves like," whereby organic solvents with physicochemical properties compatible with those of the hydrocarbons in oily sludge can selectively dissolve and extract the hydrocarbon

fraction[17]. Therefore, the efficiency of hydrocarbon extraction depends largely on the affinity between the solvent and the hydrocarbon components of the sludge[18].

Numerous organic solvents have been investigated for the extraction of hydrocarbons from oily sludge. Yasser *et al.*[19] examined the effectiveness of dichloromethane, n-hexane, acetone, and chloroform for hydrocarbon extraction from oily sludge and reported a maximum recovery of 86% using chloroform. Nezhdbahadori *et al.*[7] compared toluene and methyl ethyl ketone (MEK) for oil recovery and reported recoveries of 30.41% and 37.24%, respectively. Similarly, El Naggar *et al.*[6] evaluated the extraction performance of various solvents and reported a maximum recovery of 75.94% using toluene. Zhang *et al.*[12] investigated the extraction of crude oil hydrocarbons from oily sludge using dimethyl ether and optimized the operating conditions, achieving a maximum extraction yield of 70.8%. Wu *et al.*[20] examined the use of naphtha for oil extraction from tank-bottom sludge and reported a recovery of 96%. In addition, Hu *et al.*[21] investigated the effects of solvent type, solvent volume, extraction time, and agitation speed and achieved an oil recovery of 68.8% under the optimum conditions. Other solvents reported for oily sludge extraction include turpentine, MEK, n-heptane, toluene, hexane, ethanol, acetone, dichloromethane, cyclohexane, and liquefied petroleum gas condensate (LPGC)[22,23,24,25]. In contrast, studies investigating the use of solvent mixtures for oil extraction from oily sludge remain relatively limited. Mohit *et al.*[3] investigated oil recovery using solvent blends, including a MEK–xylene mixture, and optimized the operating parameters affecting extraction performance. Taiwo and Otoloren[26] also investigated hydrocarbon extraction from oily sludge using both pure solvents and solvent mixtures, achieving an oil recovery of 66.25%.

This study investigates oil recovery from petroleum sludge collected from storage tanks at the SONATRACH oil refinery in Haoud El Hamra, Algeria, using methyl ethyl ketone (MEK), cyclohexane (CHX), and their binary mixture. MEK and CHX were selected because of their distinct polarities and complementary physicochemical properties, enabling an assessment of the potential benefits of combining polar and non-polar solvents for petroleum sludge extraction. Although previous studies have investigated solvent blending for hydrocarbon recovery from petroleum sludge, most have focused on solvent combinations with similar or different physicochemical characteristics, while the MEK–CHX binary system has received relatively limited attention. The novelty of this study lies in evaluating the combined use of MEK, a relatively polar solvent, and CHX, a non-polar solvent, for oil recovery from petroleum sludge. Their complementary polarity and solvent–hydrocarbon interactions may facilitate the dissolution of different hydrocarbon fractions within the complex sludge matrix, potentially improving extraction performance compared with the use of either solvent alone. This study specifically evaluates the effect of the MEK–CHX blending ratio on oil recovery and investigates whether combining these solvents enhances extraction performance under optimized operating conditions. The effects of key operating parameters, including agitation time, solvent volume, solvent blending ratio, and extraction temperature, were systematically investigated, with particular emphasis on identifying the optimum conditions for the binary solvent system. The extracted oil was characterized using Fourier transform infrared (FTIR) spectroscopy and gas chromatography–mass spectrometry (GC–MS), while the residual solid phase was characterized using X-ray fluorescence (XRF), X-ray diffraction (XRD), and FTIR spectroscopy. These analyses were conducted to determine the chemical composition of the recovered oil and the chemical and mineralogical characteristics of the residual solids, thereby providing further insight into the extraction behavior and performance of the MEK–CHX solvent system.

Experimental Section

Raw material and solvents

Petroleum sludge collected from the storage tank of the Algerian oil company SONATRACH at Haoud El Hamra was employed in this study and maintained at 25 °C until use in the experimental procedures. Oil extraction from this semi-solid sludge was conducted in two stages. In the first stage, pure solvents, methyl ethyl ketone (MEK, purity ≥ 98.0%) and cyclohexane (CHX, purity ≥ 99.5%), purchased from Biochem Chemopharma (France), were individually tested. In the second stage, a solvent mixture of MEK and cyclohexane was employed for oil extraction, with volume fractions of 0.2, 0.4, 0.6, and 0.8. The primary

Table 1 — Principal properties of the solvents used in this study

Property	Cyclohexane	Methyl ethyl ketone
Chemical formula	C_6H_{12}	C_4H_8O
Molecular weight (g/mol)	84.16	72.11
Density (g/mL)	0.7785	0.805-0.806
Fusion point (°C)	6.47	-86
Flash point (°C)	-20	-9
Boiling point	80.74	79.64
Viscosity (cP,20°C)	1.02	0.43
Polarity	Non-polar	Slightly polar

Table 2 — Composition of the sludge examined

Property	Sludge (%)
Water content	0.00
Light hydrocarbons and moisture	12
Non-volatile hydrocarbons	30.5
Solid content	57.5

physical and chemical properties of the two solvents employed in this research are presented in Table 1 [27].

Experimental methods

Proximate characteristic of petroleum sludge

For the proximate analysis of the oily sludge constituents, the contents of hydrocarbons (including light and heavy fractions), water, and solids were determined[6]. The composition of the examined sludge fractions is summarized in Table 2.

Water content (WC): To determine the water content of the petroleum sludge, the American Society for Testing and Materials (ASTM) standard technique D95 was employed[28]. The sludge sample collected from the storage tanks was treated with cyclohexane (boiling point: 40 °C), followed by centrifugation to facilitate phase separation into water, solvent, and oil. After centrifugation, the recovered sample consisted of two distinct phases (oil and solvent), and no separate water phase was detected.

Light hydrocarbon content (VHC): An 8 g sample of the sludge was dried at 105 °C for 24 h until a constant mass was achieved. The mass loss was attributed to moisture and light hydrocarbon components present in the sludge. The percentage of light hydrocarbons was calculated using Eq. (1) [25,29].

$$\text{Light hydrocarbon content} = \frac{\text{reduced mass (g)}}{\text{mass of tested sample (g)}} \text{ x } 100\% - \text{water content (wt\%)} \quad \ldots (1)$$

Solid content (wt%): Following the determination of the light hydrocarbon and moisture contents, the sample, previously dried at 105 °C, was heated in a muffle furnace at 600 °C for 30 min. After heating, the mass of the remaining solid residue was recorded, and the solid content of the sludge was determined gravimetrically using Eq. (2).

$$\text{Solid content} = \frac{\text{residue remaining after burning (g)}}{\text{mass of tested sample (g)}} \text{ x } 100\% \quad \ldots (2)$$

Non-volatile hydrocarbons content (wt %): After determining the solid content (SC), water content (WC), and volatile (light) hydrocarbon content (VHC), the non-volatile hydrocarbon (NVH) content (wt%) was calculated using Eq. (3) [30].

$$\text{NVH} = 100\% - \text{VH} + \text{SC} + \text{WC} \quad \ldots (3)$$

Recovery oil by pure solvents and solvent blend

Oil extraction from sludge collected from storage tanks was conducted in two distinct phases. The first phase involved evaluating pure solvents, specifically methyl ethyl ketone (MEK) and cyclohexane (CHX), individually. The second phase involved evaluating a binary mixture of these solvents (CHX/MEK). To optimize oil recovery, the effects of key operating parameters, including agitation time, solvent volume, temperatures, and solvent blending ratio, were systematically examined.

The following extraction procedure was applied to all experiments. Five grams of sludge were mixed with a specified volume of solvent and transferred to a centrifuge tube. The tube was placed on a mechanical shaker and agitated at a constant speed of 160 rpm[31]. After agitation, the solid residue was separated from the liquid phase, which consisted of the solvent and extracted oil, by centrifugation at 4000 rpm for approximately 15 min[32]. The oil was subsequently separated from the solvent by rotary evaporation to obtain the recovered oil. To optimize oil extraction from petroleum sludge various operating parameters were systematically investigated[23]. The effect of solvent volume was then investigated using different volumes (20, 30, and 40 mL) at 25 °C, while maintaining the optimum agitation time determined previously. Finally, the effect of temperature on oil recovery was examined using a water bath with agitation at 40 and 50 °C, with a solvent volume of 40 mL and an agitation time of 2 h, corresponding to the optimum conditions identified in preceding experiments[7].

The same extraction procedure was subsequently applied using a binary solvent mixture of cyclohexane

(CHX) and methyl ethyl ketone (MEK) to evaluate its extraction efficiency and potential to enhance oil recovery[3]. Experiments were conducted with a total solvent volume of 40 mL and an agitation time of 2 h. Different CHX/MEK volume fractions (0.2, 0.4, 0.6, and 0.8) were investigated[26]. The effect of temperature was also assessed at 30, 40, and 50 °C. Oil recovery efficiency for each experiment was calculated using Eq. (4), based on the ratio of the mass of recovered oil to the initial mass of sludge[29].

$$\text{Percentage oil recovery} = \frac{\text{reduced mass (g)}}{\text{mass of tested sample (g)}} \times 100\% \quad \ldots (4)$$

Analysis of the extracted phases

Solid residues obtained after extraction with methyl ethyl ketone and cyclohexane were dried at 105 °C for 24 h, while fresh oily sludge collected from storage tanks was calcined at 600 °C for 30 min. Various analytical techniques were employed to characterize the resulting materials and determine their physicochemical composition and structure. The crystalline phases and structures of the solid residues and calcined petroleum sludge were analyzed by X-ray diffraction (XRD) using a DeWitt Berker diffractometer, with a scanning step of 0.02° over a 2θ range of 5°–80° [33]. X-ray fluorescence (XRF) analysis was conducted using a SciAps X-200 portable instrument to identify and quantify the elemental composition of the samples. Fourier transform infrared (FTIR) spectroscopy was used to identify the functional groups present in the solid residues and recovered oil. The analyses were performed using the KBr pellet method with a Shimadzu IR Affinity spectrometer over a wavenumber range of 400–4000 cm^{-1} [34].

The oil recovered from the oily sludge was analyzed by gas chromatography–mass spectrometry (GC–MS) using a Shimadzu GCMS- QP-2030 instrument[35,36]. The GC–MS analysis was performed with an initial oven temperature of 60 °C, held for 2 min, followed by an increase to 200 °C at a rate of 10 °C/min and held for 7 min. The temperature was then increased to 250 °C at a rate of 5 °C/min and maintained for 30 min. A 1.0 µL aliquot of the hydrocarbon fraction diluted in cyclohexane was injected into the gas chromatograph in split mode at a split ratio of 80:1. Helium was used as the carrier gas at a flow rate of 0.60 mL/min. The solvent cut time was set at 3 min, and mass spectra were acquired in scan mode over an m/z range of 35–500.

Statistical analysis

All experiments were carried out in triplicate, and the results are expressed as mean ± standard deviation (SD). Depending on the experimental design, the effects of the investigated factors on oil recovery were evaluated using one-way or two-way analysis of variance (ANOVA). When significant differences were detected, Tukey's honestly significant difference (HSD) post hoc test was applied for multiple pair-wise comparisons. Statistical significance was considered at $p < 0.05$. All statistical analyses were performed using Python 3.12.13 with the Stats models 0.14.6 package in the Kaggle Notebook environment.

Result and Discussion

Effect of solvent type and process parameters on oil recovery

The efficiency of petroleum hydrocarbon extraction from oily sludge is influenced by the main factors of solubility, stirring time, solvent volume, and temperature[21,37]. The statistical significance of the investigated process parameters was evaluated using analysis of variance (ANOVA).

Effect of stirring time

The effect of stirring time on oil recovery is presented in Fig. 1. The results show that oil recovery varied with agitation time for both solvents at 25 °C. Under these conditions, the highest oil recovery was

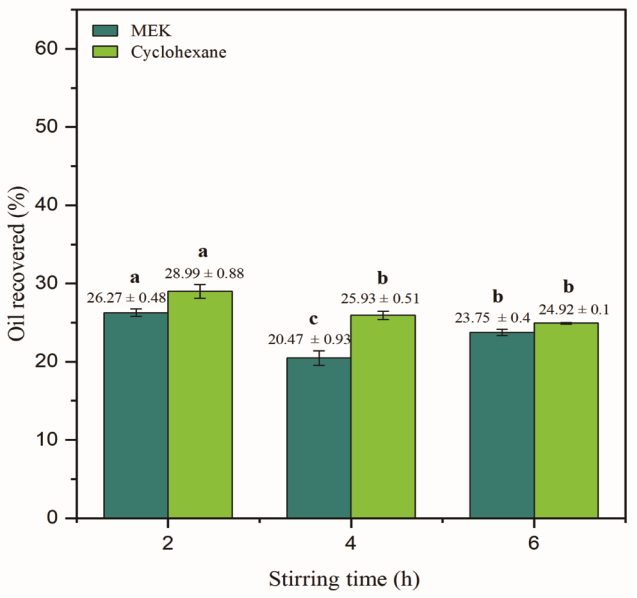

Fig. 1 — Effect of stirring time on oil recovery using MEK and cyclohexane (mean ± SD, n = 3) at 25 °C and a solvent volume of 20 mL. Different lowercase letters indicate significant differences among stirring times within each solvent according to Tukey's HSD test ($p < 0.05$)

obtained after 2 h of agitation, reaching 26.27 ± 0.48% for methyl ethyl ketone (MEK) and 28.99 ± 0.88% for cyclohexane. Further increasing the stirring time beyond 2 h did not improve oil recovery; instead, recovery gradually decreased with prolonged stirring. According to Hu *et al.*[2], increasing the stirring time can enhance oil recovery by improving mass transfer and increasing contact between the solvent and petroleum sludge, thereby facilitating the diffusion of oil into the solvent phase. However, once equilibrium is approached, prolonged agitation offers limited additional benefit. These results are consistent with previous studies. For instance, Al-Zubaidi and Abu Al-Nasr[38] evaluated several organic solvents, including methyl ethyl ketone (MEK) and liquefied petroleum gas condensate, and found that MEK achieved an oil recovery of 39% at a solvent-to-sludge ratio of 4:1 and a stirring time of 2 h. Other studies have also reported higher oil recoveries when MEK and other petroleum-derived solvents were used with stirring times of approximately 3 h[32]. Hu *et al.*[2] further noted that the optimum extraction time generally ranges from 60 to 180 min, depending on solvent characteristics and sludge properties.

The effects of solvent type and stirring time on oil recovery were further evaluated using two-way analysis of variance (ANOVA). The analysis revealed significant effects of solvent type ($F = 114.23$, $p < 0.001$) and stirring time ($F = 83.00$, $p < 0.001$). A significant solvent × stirring time interaction was also observed ($F = 18.53$, $p < 0.001$), indicating that the effect of stirring time depended on the solvent employed. For MEK, the highest recovery (26.27 ± 0.47%) was obtained after 2 h of agitation. Oil recovery decreased significantly to 20.47 ± 0.93% and 23.75 ± 0.40% after 4 and 6 h, respectively. Tukey's HSD test confirmed significant differences between all agitation times (2 h vs. 4 h, $p < 0.001$; 2 h vs. 6 h, $p = 0.003$; 4 h vs. 6 h, $p < 0.001$). For cyclohexane, the highest recovery (28.99 ± 0.88%) was also achieved after 2 h. Oil recovery decreased significantly to 25.93 ± 0.51% after 4 h and 24.92 ± 0.10% after 6 h compared with the 2 h treatment ($p < 0.001$ for both comparisons). However, no significant difference was observed between 4 and 6 h (mean difference = 1.01 percentage points, $p = 0.396$).

Overall, both solvent type and stirring time significantly influenced oil recovery, as demonstrated by the two-way ANOVA. Under the investigated conditions, a stirring time of 2 h resulted in the highest oil recovery for both solvents and was therefore selected as the optimum extraction time. This duration provided sufficient contact between the solvent and the sludge matrix, thereby promoting effective mass transfer and hydrocarbon diffusion into the solvent phase[2]. Extending the stirring time beyond 2 h did not improve oil recovery and may increase energy consumption without providing additional extraction benefits.

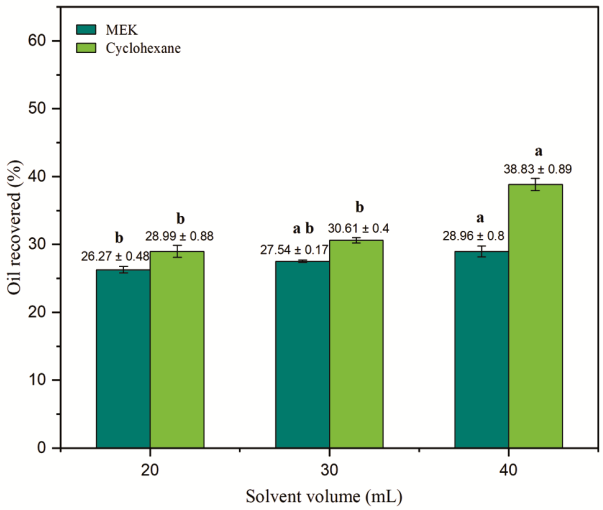

Fig. 2 — Effect of solvent volume on oil recovery using MEK and cyclohexane (mean ± SD, n = 3) at 25 °C and a stirring time of 2 h. Different lowercase letters indicate significant differences among solvent volumes within each solvent according to Tukey's HSD test ($p < 0.05$)

Effect of solvent volume

The influence of solvent volume on oil recovery is illustrated in Fig. 2. Increasing the solvent volume from 20 to 40 mL resulted in an overall increase in oil recovery for both solvents at 25 °C. For cyclohexane, oil recovery increased from 28.99 ± 0.88% at 20 mL to 38.83 ± 0.89% at 40 mL, whereas for MEK, it increased from 26.27 ± 0.48% to 28.96 ± 0.80%. Cyclohexane consistently achieved higher oil recovery than MEK at all solvent volumes tested. According to Al-Zahrani *et al.*[17] and Al-Doury[32], increasing the solvent volume enhances contact between the solvent and sludge, improves the solubility of hydrocarbons in the solvent, and increases molecular spacing in the liquid phase, thereby reducing the viscosity of the oil–sludge mixture. These findings are consistent with previous studies by Zubaidy and Abouelnasr[23], who reported that increasing the solvent-to-sludge ratio significantly, enhanced oil recovery. Similarly,

Hu *et al.*[39] reported that solvent extraction using cyclohexane and methyl ethyl ketone (MEK) achieved the highest oil recovery rates of 42.4% and 37.2%, respectively, after 30 min of extraction at a solvent-to-sludge ratio of 4:1.

A two-way analysis of variance (ANOVA) was performed to assess the influence of solvent type and stirring time on oil recovery. Significant effects were observed for both solvent type ($F = 281.35$, $p < 0.001$) and solvent volume ($F = 148.18$, $p < 0.001$). A significant solvent × volume interaction was also observed ($F = 55.95$, $p < 0.001$), indicating that the effect of solvent volume depended on the solvent employed. For MEK, oil recovery increased from 26.27 ± 0.48% at 20 mL to 27.54 ± 0.17% at 30 mL and 28.96 ± 0.80% at 40 mL. Tukey's HSD test showed that the differences between 20 and 30 mL ($p = 0.245$) and between 30 and 40 mL ($p = 0.162$) were not statistically significant, whereas the difference between 20 and 40 mL was significant ($p = 0.003$). For cyclohexane, oil recovery increased from 28.99 ± 0.88% at 20 mL to 30.61 ± 0.40% at 30 mL, although this increase was not statistically significant ($p = 0.090$). A marked increase was observed at 40 mL, where oil recovery reached 38.83 ± 0.89%. This value was significantly higher than those obtained at both 20 and 30 mL (adjusted $p < 0.001$ for both comparisons).

The findings demonstrate that both solvent type and solvent volume significantly influenced oil recovery. The significant solvent × volume interaction indicates that the effect of solvent volume depended on the solvent used. Under the investigated conditions, a solvent volume of 40 mL resulted in the highest oil recovery for both solvents and was therefore selected as the optimum solvent volume. This volume provided sufficient solvent–sludge contact, enhanced hydrocarbon dissolution, and promoted efficient mass transfer [17,32].

Effect of temperature

The effect of temperature on oil recovery was evaluated using 40 mL of solvent and a stirring time of 2 h, which were the optimal conditions determined in the preceding experiments. The results are shown in Fig. 3. An Increase the temperature from 25 to 40 °C increased oil recovery from 38.83 ± 0.89% to 45.26 ± 0.31% for cyclohexane and from 28.96 ± 0.80% to 34.67 ± 0.72% for methyl ethyl ketone (MEK). This increase can be attributed to the reduction in oil viscosity with increasing temperature,

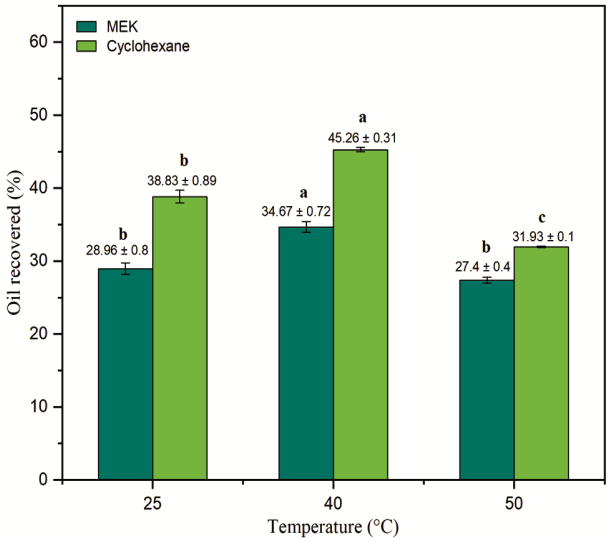

Fig. 3 — Effect of extraction temperature on oil recovery using MEK and cyclohexane (mean ± SD, n = 3) at a solvent volume of 40 mL and a stirring time of 2 h. Different lowercase letters indicate significant differences among extraction temperatures within each solvent according to Tukey's HSD test ($p < 0.05$)

which enhances contact between the sludge and the organic solvent. Increased molecular mobility at higher temperatures may facilitate the disruption of intermolecular interactions and improve the diffusion and distribution of dissolved organic compounds into the solvent phase, thereby promoting the dissolution of a greater amount of hydrocarbons[7,29,40]. However, increasing the temperature to 50 °C resulted in a marked decrease in oil recovery, from 45.26 ± 0.31% to 31.93 ± 0.10% for cyclohexane and from 34.67 ± 0.72% to 27.40 ± 0.40% for MEK. According to Zhang *et al.*[41], this decrease may be attributed to the increased volatility of organic solvents at elevated temperatures, which can reduce the effective solvent volume and consequently impair their ability to extract and dissolve hydrocarbons from the sludge.

The results of the two-way analysis of variance (ANOVA) demonstrated that both solvent type ($F = 843.67$, $p < 0.001$) and extraction temperature ($F = 434.67$, $p < 0.001$) had significant effects on oil recovery. A significant solvent × temperature interaction was also observed ($F = 44.41$, $p < 0.001$), indicating that the effect of temperature depended on the solvent employed. For MEK, oil recovery increased significantly from 25 to 40 °C ($p < 0.001$), whereas no significant difference was observed between 25 and 50 °C ($p = 0.072$). In contrast, oil recovery at 40 °C was significantly higher than that at 50 °C ($p < 0.001$), confirming 40 °C as the optimum

extraction temperature for MEK. For cyclohexane, the highest oil recovery (45.26 ± 0.31%) was also obtained at 40 °C. Oil recovery increased significantly from 25 to 40 °C and subsequently decreased markedly at 50 °C, with all pairwise comparisons being statistically significant ($p < 0.001$). These results demonstrate that both solvent type and extraction temperature significantly influenced oil recovery, while the significant solvent × temperature interaction highlights the importance of optimizing the extraction temperature according to the solvent employed. Under the investigated conditions, 40 °C was therefore selected as the optimum extraction temperature because it provided the highest oil recovery for both solvents. At this temperature, the reduction in oil viscosity and the enhancement of hydrocarbon diffusion and mass transfer outweighed the adverse effects associated with solvent volatility[29,40]. Further increasing the temperature to 50 °C did not improve extraction efficiency and instead reduced oil recovery, likely due to increased solvent evaporation and a consequent reduction in the effective solvent volume available for extraction[41].

According to the experimental findings of this study, the optimal conditions for extraction of oil from petroleum sludge were identified as follows: a solvent volume of 40 mL, a stirring time of 2 h, and a temperature of 40 °C, using pure cyclohexane and methyl ethyl ketone (MEK) as solvents for extraction. The maximum oil yield obtained under these conditions was 45.26 ± 0.31% and 34.67± 0.72% for the two solvents, respectively. These results closely align with the findings reported by Nezhdbahadori *et al.*[7], who obtained a similar yield of 30.41% using methyl ethyl ketone. This confirms the validity of MEK (polar solvent) as a moderately effective solvent for oil recovery from petroleum sludge. The oil recovery obtained with cyclohexane in this study was 45.26%, which agrees with the findings of Hu *et al.*[31], who achieved an oil recovery yield around 40% using cyclohexane. Some published results reported higher extraction efficiency when using non-polar solvents like cyclohexane at elevated temperatures. Hu *et al.*[21] carried out a study on ultrasound-assisted extraction using pure solvents, including cyclohexane, methyl ethyl ketone (MEK), and ethyl acetate, and found that cyclohexane achieved the highest oil recovery rate of 68.8%, whereas MEK yielded 34.8%. The variation in oil extraction yield observed in this study compared to some other published works may be attributed to several factors, including the properties of the oily sludge being examined, the lack of any pretreatment, operating conditions, and the non-utilization of advanced extraction techniques such as ultrasound or microwave treatment.

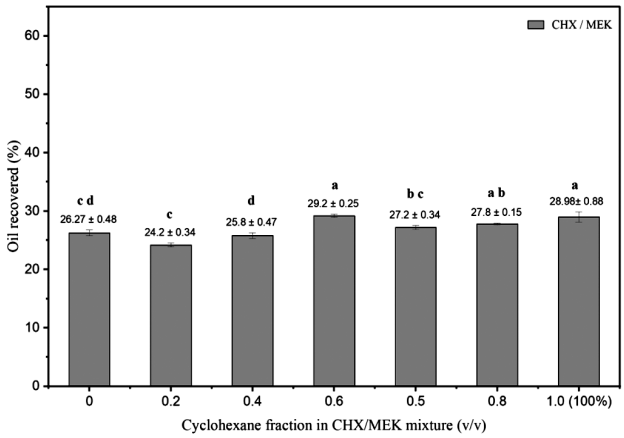

Fig. 4 — Effect of CHX/MEK volume ratio on oil recovery at 25°C, using a total solvent volume of 40 mL and a stirring time of 2 h. Different letters indicate statistically significant differences according to Tukey's HSD test ($p < 0.05$)

Optimization of the yield of extraction using solvent blend

Impact of solvent mixture proportion on oil extraction

A combination of cyclohexane (CHX), a non-polar solvent, and methyl ethyl ketone (MEK), a polar solvent, was used to investigate the effect of solvent blending on oil recovery from petroleum sludge at 25 °C. The results are illustrated in Fig. 4. As the solvent composition varied, oil recovery exhibited a nonlinear trend. The maximum oil recovery of 29.20 ± 0.25% was obtained at a CHX:MEK volumetric ratio of 60:40 (v/v). The relatively high recovery obtained with this blend suggests that an appropriate balance between the non-polar and polar solvents may enhance the dissolution of different hydrocarbon fractions present in the sludge. This behavior may be attributed to the complementary solvation properties of CHX and MEK and their ability to interact with both non-polar and relatively polar components of the sludge[3]. When the proportion of cyclohexane increased beyond 60%, oil recovery decreased to 27.80 ± 0.15% at a CHX:MEK volumetric ratio of 0.8:0.2 (v/v) and to 28.98 ± 0.88% with pure cyclohexane. This decrease may be attributed to the limited polarity of cyclohexane, which can restrict its ability to dissolve relatively polar components when used alone. As noted by Crossley[42], the low polarity of cyclohexane, reflected by its low dielectric constant, may limit the solubilization of polar compounds.

Table 3 — Summary of ANOVA results for the optimization experiments

Experiment	Statistical test	Source of variation	Degrees of Freedom	F-value	p-value
1. Solvent type × Stirring time	Two-way ANOVA	Solvent	1	114.23	<0.001
		Stirring time	2	83.00	<0.001
		Solvent × Stirring time	2	18.53	<0.001
2. Solvent type × extraction temperature	Two-way ANOVA	Solvent	1	843.67	<0.001
		Extraction temperature	2	434.67	<0.001
		Solvent × Temperature	2	44.41	<0.001
3. Solvent type × solvent volume	Two-way ANOVA	Solvent	1	281.35	<0.001
		Solvent volume	2	148.18	<0.001
		Solvent × Volume	2	55.95	<0.001
4. CHX/MEK volume ratio	One-way ANOVA	Volume ratio	6	43.63	<0.001
5. Extraction temperature using CHX/MEK (60:40)	One-way ANOVA	Extraction temperature	3	1045.86	<0.001

Statistical significance was considered at $p < 0.05$

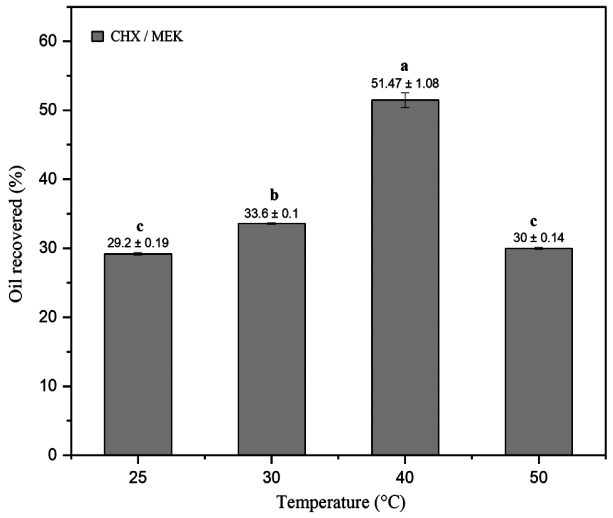

Fig. 5 — Effect of extraction temperature on oil recovery using the CHX/MEK (60:40, v/v) solvent blend at a stirring time of 2 h (mean ± SD, n = 3). Different lowercase letters indicate significant differences among extraction temperatures according to Tukey's HSD test ($p < 0.05$)

Similarly, Dongmu and Giacometti[43] reported that non-polar solvents generally exhibit low solubility toward polar substances, supporting this interpretation. In contrast, mixtures containing higher proportions of MEK generally showed lower oil recovery. The CHX:MEK volumetric ratio of 0.2:0.8 and 0.4:0.6 resulted in oil recoveries of 24.20 ± 0.34% and 25.80 ± 0.47%, respectively, whereas pure MEK yielded 26.27 ± 0.48%. The CHX/MEK blend with a volumetric ratio of 0.5:0.5 (v/v) resulted in a higher recovery of 27.20 ± 0.34%, indicating that an appropriate balance between solvent polarity and non-polarity may improve extraction efficiency compared with MEK alone. Similar observations have been reported in previous studies, which showed that solvent mixtures can improve oil extraction from petroleum sludge through complementary interactions between the chemical and physical properties of the solvents[41,29,32].

The effect of the CHX/MEK volume ratio on oil recovery was further evaluated using one-way ANOVA. As shown in Table 3, the solvent mixture composition significantly affected oil recovery ($F = 43.63$, $p < 0.001$). Tukey's HSD test showed that the 0.6/0.4 CHX/MEK mixture produced significantly higher oil recovery than the 0.2/0.8 ($p < 0.001$), 0.4/0.6 ($p < 0.001$), 0.5/0.5 ($p = 0.0019$), 0.8/0.2 ($p = 0.0328$), and 0/1 ($p < 0.001$), 0.4/0.6 ($p < 0.001$), 0.5/0.5 ($p = 0.0019$), 0.8/0.2 ($p = 0.0328$), and 0/1 ($p < 0.001$) mixtures. However, no significant difference was observed between the CHX:MEK (0.6:0.4, v/v) mixture and pure cyclohexane (1:0, v/v) ($p = 0.9972$).These results demonstrate that the CHX:MEK (0.6:0.4, v/v) mixture provided the highest oil recovery under the investigated conditions and performed statistically comparably to pure cyclohexane. The significantly higher recovery compared with the other tested mixtures indicates that the appropriate combination of non-polar and polar solvents can improve extraction efficiency. Therefore, the CHX: MEK (0.6:0.4, v/v) mixture was selected as the optimum solvent composition for the subsequent temperature optimization experiments.

Impact of temperature on oil extraction

To further optimize oil recovery, the effect of extraction temperature was investigated, as shown in Fig. 5. The temperature was varied from 25 to 30, 40, and 50 °C while maintaining a constant stirring time

of 2 h and a CHX/MEK volume ratio of 60:40 (v/v).Increasing the extraction temperature from 25 to 40 °C progressively enhanced oil recovery from petroleum sludge. This improvement may be attributed to the reduction in oil viscosity with increasing temperature, which facilitates mass transfer and improves contact between the sludge and the solvent phase[44]. Accordingly, oil recovery increased from 29.20 ± 0.19% at 25 °C to 33.60 ± 0.10% at 30 °C, reaching a maximum of 51.47 ± 1.08% at 40 °C. However, a further increase in temperature to 50 °C resulted in a marked decline in oil recovery to 30.00 ± 0.14%. This reduction may be attributed to the increased volatility of the organic solvents at elevated temperatures, leading to solvent losses and consequently reducing the effective solvent available for hydrocarbon dissolution and extraction[41,29].

One-way analysis of variance (ANOVA) was conducted to evaluate the effect of extraction temperature on oil recovery using the CHX/MEK (60:40, v/v) solvent blend, as summarized in Table 3. The analysis revealed that extraction temperature had a significant effect on oil recovery ($F = 1045.86$, $p < 0.001$). Tukey's HSD test showed that oil recovery increased significantly from 25 to 30 °C ($p < 0.001$) and reached its maximum at 40 °C, which was significantly higher than that obtained at all other temperatures ($p < 0.001$ for all comparisons). When the temperature was increased to 50 °C, oil recovery decreased significantly compared with both 30 and 40 °C ($p < 0.001$), whereas no significant difference was observed between 25 and 50 °C ($p = 0.360$). These findings demonstrate that extraction temperature significantly influenced oil recovery and identify 40 °C as the optimum extraction temperature under the investigated conditions.

The optimum temperature identified in the present study is generally consistent with the well-established influence of temperature on solvent extraction, although it differs from the optimum temperatures reported in previous studies. Mohit *et al.*[3] achieved a higher oil recovery of 64.04% using an MEK/xylene solvent blend at 50 °C with a stirring time of 20 min, whereas Nezhdbahadori *et al.*[7] reported that 30 °C was the optimum extraction temperature for MEK, yielding a maximum oil recovery of 30.41%, with extraction efficiency decreasing at higher temperatures. These differences are likely attributable to variations in sludge characteristics, solvent composition, extraction conditions, and experimental methodology. Under the operating conditions investigated in the present study, the CHX:MEK volumetric ratio of (60:40, v/v) solvent blend achieved a maximum oil recovery of 51.47 ± 1.08% at the moderate temperature of 40 °C, demonstrating that this solvent system is highly effective for oil recovery from petroleum sludge.

Synergistic effect of the solvent blend

After identifying the optimum extraction conditions, the synergistic effect of the CHX/MEK solvent blend was investigated to determine whether the enhanced oil recovery resulted from the combined action of the two solvents. Cyclohexane, a relatively non-polar solvent, exhibits a strong affinity for non-polar hydrocarbon constituents, whereas the higher polarity of methyl ethyl ketone (MEK) facilitates the dissolution of relatively polar organic compounds present in petroleum sludge. Previous studies have shown that cyclohexane generally provides higher oil recovery than MEK when the target compounds are predominantly non-polar, whereas MEK exhibits superior extraction performance for aromatic and relatively polar organic compounds[11,25]. Consequently, combining solvents with different polarities can broaden the range of compounds extracted from the heterogeneous sludge matrix. This interpretation is consistent with the principle of molecular compatibility, according to which extraction is favoured when the polarity and intermolecular interactions of the solvent are compatible with those of the target compounds[45]. Previous studies have also demonstrated that mixtures of polar and non-polar solvents can outperform individual solvents when extracting compounds spanning a wide polarity range[46]. Likewise, Nezhdbahadori *et al.*[7] reported that combining polar and non-polar solvents, particularly with a higher proportion of the non-polar component, enhanced oil recovery compared with the corresponding pure solvents. Similarly, Wang *et al.*[47] investigated MEK–cyclohexane mixtures for bitumen recovery from oil sands and observed that recovery increased with increasing MEK content up to an optimum composition, followed by a gradual decline at higher MEK fractions. Collectively, these studies indicate that extraction efficiency depends on achieving an appropriate balance between solvent properties and the characteristics of the target compounds rather than simply increasing solvent polarity.

In the present study, oil recovery increased from 45.26 ± 0.31% with pure cyclohexane and 34.67 ± 0.72% with pure MEK to 51.47 ± 1.08% when the CHX/MEK (60:40, v/v) solvent blend was used. To evaluate the potential synergistic effect of the solvent blend, the theoretical oil recovery of the 60:40 (v/v) mixture was calculated as the weighted average of the recoveries obtained with the two pure solvents, following the method described by Gordon and Scott[48]. The theoretical recovery was 41.02%, whereas the experimental recovery reached 51.47 ± 1.08%, corresponding to a positive deviation of 10.45 percentage points. This positive deviation suggests a potential synergistic interaction between cyclohexane and MEK at the 60:40 (v/v) ratio. The enhanced recovery may be attributed to the complementary roles of the two solvents, whereby cyclohexane preferentially dissolves non-polar hydrocarbons while MEK facilitates the extraction of relatively polar organic constituents. Consequently, the combined solvent system may improve the dissolution of a broader range of organic compounds present in the heterogeneous sludge matrix, thereby enhancing the overall oil recovery. However, this explanation is proposed as a plausible extraction mechanism based on the physicochemical properties of the solvents and should not be interpreted as direct experimental evidence of synergistic interactions. Nevertheless, one-way ANOVA followed by Tukey's HSD test showed that the difference in oil recovery between the CHX/MEK (60:40, v/v) solvent blend and pure cyclohexane was not statistically significant ($p > 0.05$). Therefore, although the blend exhibited a higher numerical oil recovery than pure cyclohexane, the positive deviation from the theoretical recovery should be interpreted as evidence of potential rather than statistically confirmed synergistic behavior. Similar observations have been reported in previous studies. Mohit *et al.*[3] demonstrated that combining solvents with different polarities facilitates the dissolution of a broader range of compounds in petroleum sludge and enhances hydrocarbon recovery. Using an MEK/xylene solvent mixture, they achieved a maximum petroleum hydrocarbon recovery of 61.44%. Likewise, Taiwo and Otolorin[26] reported maximum oil recoveries of 61.10% and 66.25% using xylene-cyclohexane and xylene–n-hexane solvent mixtures, respectively, for tank-bottom sludge at 29 °C. Collectively, these findings support the use of solvent mixtures with complementary physicochemical properties as an effective strategy for improving the extraction of heterogeneous organic constituents from petroleum sludge.

Comparison with previously reported oil recovery methods

Oil recovery in the present study reached 51.47% under the optimum conditions of 40 °C, 2 h of stirring, and a CHX ratio of 60:40. This value is comparable to the recovery obtained by conventional cyclohexane extraction (50.98%) as reported by Abdulqawi *et al.*[49]. However, previous studies have shown that combining solvent extraction with additional physical or chemical intensification steps can substantially improve oil recovery. For example, the recovery increased to 60.98% when cyclohexane extraction was followed by freeze–thaw treatment[49]. Cyclohexane extraction assisted by a dispersing agent achieved an even higher recovery (>98%) by promoting the disruption of solid aggregates and facilitating the release of entrapped hydrocarbons[50]. Similarly, a froth flotation-centrifugation process achieved an oil recovery of 93.7% at 33 °C [51], whereas ultrasound-assisted reached 68.8% recovery within 20s [21]. These findings demonstrate that process intensification can enhance oil recovery and, in some cases, substantially reduce processing time. Despite the higher recoveries achieved by some intensified approaches, the CHX–MEK system offers the advantage of a relatively simple process configuration without the need for freeze–thaw treatment, dispersant addition, ultrasound, flotation, or centrifugation. Its performance may be attributed to the complementary salvation properties of the two solvents. Cyclohexane, a non-polar solvent, is effective for dissolving non-polar hydrocarbon fractions, whereas MEK, with its relatively higher polarity, can enhance the solubilization of more polar organic constituents. Their combined use may therefore promote the dissolution of different components within the complex organic matrix of petroleum sludge, which could contribute to the synergistic effect observed with the binary solvent system.

Direct comparison of oil recovery values should nevertheless be made with caution because extraction performance is strongly influenced by factors such as sludge composition, solvent-to-sludge ratio, extraction time, temperature, and process configuration[52]. Therefore, recovery percentages should be interpreted in the context of differences in operating conditions and sludge characteristics among studies. In this regard, the CHX–MEK system represents a promising

approach when process simplicity and the use of conventional equipment are prioritized, although its recovery remains lower than that achieved by some intensified processes.

The proposed method offers several advantages, including a relatively simple process configuration, moderate operating temperature, and the use of conventional mechanical agitation. The use of a binary solvent system is also consistent with previous studies demonstrating the potential of solvent blends for hydrocarbon recovery from oily sludge[3]. In addition, unlike some intensified extraction approaches, the present method does not require dispersing agents or specialized separation equipment. Its limitations include a relatively longer extraction time compared with ultrasound-assisted extraction[21], lower recovery than that achieved by some intensified processes,[50,51] and the use of volatile organic solvents, which necessitates appropriate control of solvent losses, solvent recovery, and safety measures. Future research should therefore focus on economic and environmental assessment, and process scale-up. In addition, integrating the CHX–MEK system with mild process-intensification techniques could further improve oil recovery while maintaining the simplicity and synergistic behavior of the binary solvent system.

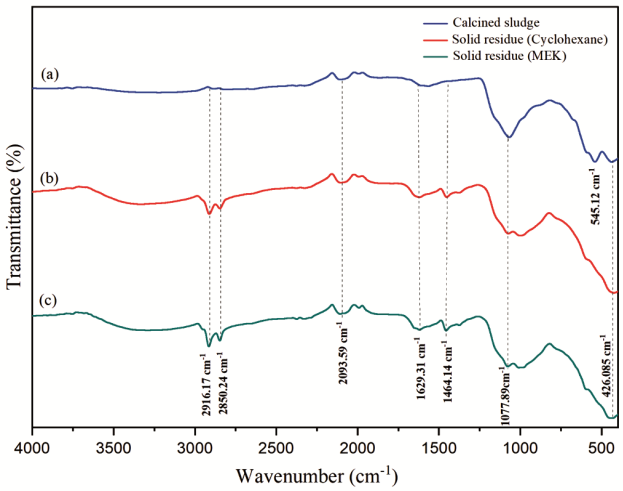

Fig. 6 — FTIR spectra of calcined sludge and residues after solvent extraction; (a) calcined sludge, (b) residue after cyclohexane extraction and (c) residue after methyl ethyl ketone (MEK) extraction

Characterization of the residual solids

The FTIR spectra shown in Fig. 6 reveal a strong similarity between the solid residues extracted with methyl ethyl ketone (MEK) and cyclohexane. In both samples, the absorption peak observed at 1464 cm^{-1} corresponds to the scissoring vibration of methyl groups, which is characteristic of paraffinic hydrocarbon structures, as reported by Boiko *et al.*[53] and He *et al.*[54]. According to Gulzat Aitkaliyeva *et al.*[34] and Onchoke *et al.*[33], the bands observed at 2916 and 2850 cm^{-1} correspond to the asymmetric and symmetric C–H stretching vibrations of aliphatic methylene groups, respectively. All samples exhibited absorption bands at 2093.59 and 1629 cm^{-1}, which may be attributed to the stretching vibrations of alkynyl (C≡C) and aromatic C=C groups, respectively[55,33,56]. The absorption band at 1077 cm^{-1} is assigned to the Si–O–Si stretching vibration, which is characteristic of silicate compounds[57,58]. This absorption band, together with the XRD results, confirms the presence of silicate minerals, particularly quartz, in the solid residues. The peak observed at 426 cm^{-1} is attributed to Si–O or Al–O bond vibrations, indicating the presence of residual inorganic mineral phases[56]. These observations are in good agreement with the XRD and XRF results (Fig. 7). A characteristic band at 545 cm^{-1} in the FTIR

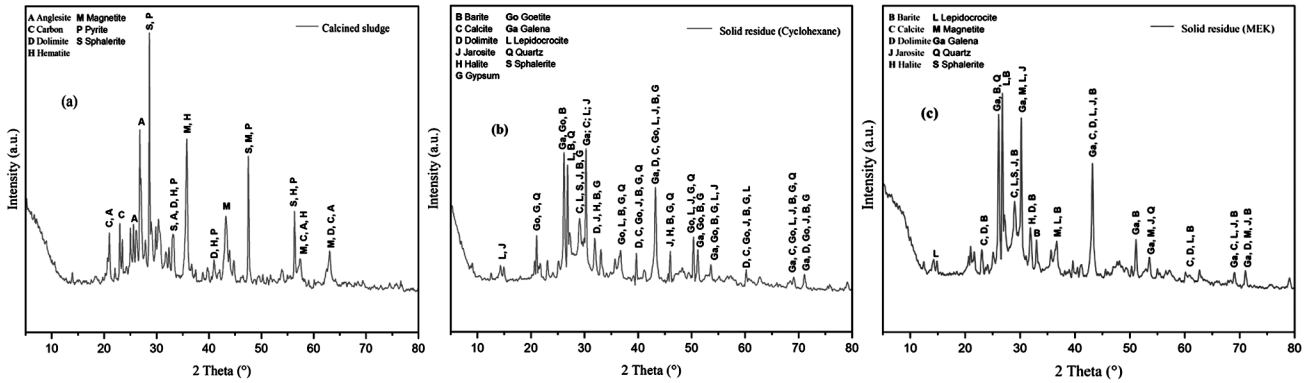

Fig. 7— X-ray diffraction patterns of calcined sludge and residues after solvent extraction; (a) calcined sludge, (b) cyclohexane residue and (c) methyl ethyl ketone (MEK) residue

spectrum of the calcined oily sludge (Fig. 6a) is attributed to metal-oxygen stretching vibrations, suggesting the formation of metal oxides during the calcination process[59].

The FTIR analysis provides valuable insight into the extraction behaviour of the investigated solvents. The persistence of the aliphatic C–H bands suggests that a fraction of hydrocarbons remained associated with the solid matrix and could not be completely extracted under the investigated conditions. This behavior may be attributed to the strong interactions between asphaltenes and silicate minerals. According to Zhao *et al.*[60], the inorganic phase of oily sludge is mainly composed of SiO_2, whereas asphaltene molecules contain oxygen-containing functional groups capable of forming hydrogen bonds with silicate surfaces. These interactions hinder the desorption of heavy organic compounds, thereby reducing their extractability. This interpretation is further supported by the recent review of Abbasi *et al.*[52]. In contrast, the pronounced Si–O–Si and Si–O/Al–O vibrations confirm that the inorganic mineral constituents remained largely unaffected by solvent extraction. These findings indicate that the extraction process was highly selective toward the organic phase while preserving the mineral framework of the oily sludge. This selective extraction behavior is consistent with the high oil recovery reported for solvent extraction processes under optimized operating conditions [21,61].

The X-ray diffraction (XRD) patterns shown in Fig. 7 demonstrate the crystalline structure and the different mineral phases present in the investigated samples. The identification of inorganic phases after extraction with cyclohexane and methyl ethyl ketone (MEK) revealed characteristic diffraction peaks corresponding to quartz (SiO_2), calcite ($CaCO_3$), and dolomite ($CaMg(CO_3)_2$). These results are consistent with previous studies reporting the presence of similar mineral phases in oily sludge residues[29]. Additional diffraction peaks indicated the presence of iron-containing corrosion products, including lepidocrocite (FeO(OH)), goethite (FeO(OH)), magnetite (Fe_3O_4)[35], and iron sulfate phases such as jarosite ($KFe_3(SO_4)_2(OH)_6$). Other mineral phases, including barite ($BaSO_4$)[62], galena (PbS), and sphalerite (ZnS), were detected in both extracted residues. However, halite (NaCl) was identified in the MEKextracted residue, whereas gypsum ($CaSO_4 \cdot 2H_2O$)[35] was detected in the cyclohexane extracted residue. These differences may be related to the selective retention or detectability of specific mineral phases after solvent extraction rather than a direct transformation of the mineral structure. For the calcined oily sludge sample, XRD analysis revealed the presence of residual carbon, confirmed by diffraction peaks observed at 2θ values of 20.98°, 22.97°, and 63.05°. This observation suggests that a fraction of the initial organic matter was not completely oxidized during calcination[63]. In addition, anglesite ($PbSO_4$) exhibited characteristic diffraction peaks at 20.98°, 25.61°, 26.77°, 32.38°, 33.10°, 57.37°, and 63.05°. Hematite (Fe_2O_3) was identified through peaks at 33.10°, 35.79°, 40.97°, 56.32°, and 57.37°, while pyrite (FeS_2) showed diffraction peaks at 28.62°, 33.11°, 40.97°, 47.50°, and 56.32°. Other mineral phases detected in the extracted residues, including dolomite ($CaMg(CO_3)_2$), magnetite (Fe_3O_4), and sphalerite (ZnS), were also identified in the calcined sample.

To validate these findings and determine the elemental composition of the samples, X-ray fluorescence (XRF) analysis was performed on the three samples. The analysis revealed similar elemental compositions among the three samples, with only minor variations in the relative percentages of the detected elements. Sodium oxide (Na_2O) was the most abundant component, ranging from 37% to 38%, followed by Fe_2O_3 (17.5–18.9%). The Al_2O_3 content ranged from 14.38% to 14.65%, while ZnO, MgO, and SO_3 ranged from 8.31 to 8.9%, 5.2 to 6.5%, and 5.4 to 6.4%, respectively. Other detected components included PbO (2.77–2.81%), Ba (2.14–2.42%), CaO (1.53–2.11%), and Cl (1.69–2.14%). The detected elemental composition is consistent with previous findings reported by Alexandrovich and Sergeevich[64]. At concentrations below 0.5%, other oxides, including SiO_2 (silicon dioxide), NiO (nickel oxide), V_2O_5 (vanadium oxide), CuO (copper oxide), and K_2O (potassium oxide), were also detected. These results are consistent with the XRD analysis, which identified several crystalline mineral phases containing these elements. The sodium detected by XRF is in agreement with the identification of halite (NaCl) by XRD. Similarly, the high iron content measured by XRF may be associated with iron-bearing mineral phases, including goethite (FeO(OH)), magnetite (Fe_3O_4), lepidocrocite (FeO(OH)), hematite (Fe_2O_3), and jarosite ($KFe_3(SO_4)_2(OH)_6$), which may originate from corrosion processes of storage tanks or oilpipelines[56,65]. Calcium detected by XRF may correspond to calcium-

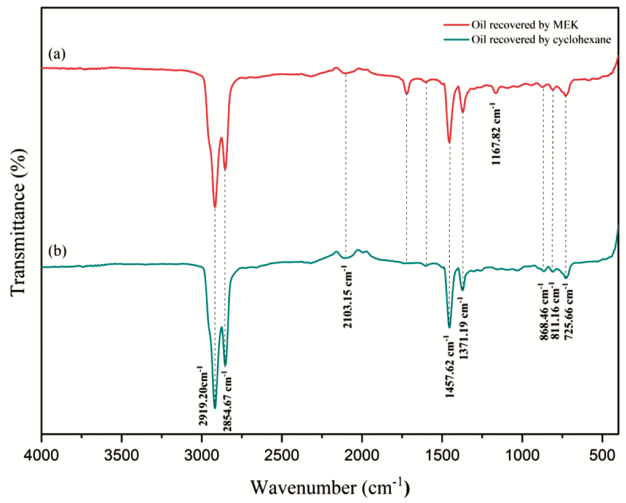

Fig. 8 — FTIR spectra of oil recovered from oily sludge using two solvents; (a) oil recovered using methyl ethyl ketone (MEK) and (b) Oil recovered using cyclohexane

containing mineral phases identified by XRD, such as gypsum ($CaSO_4 \cdot 2H_2O$), dolomite ($CaMg(CO_3)_2$), and calcite ($CaCO_3$). Similarly, zinc and sulfur containing elements may be associated with crystalline phases such as sphalerite (ZnS), galena (PbS), pyrite (FeS_2), and barite ($BaSO_4$), as confirmed by XRD analysis. Although Al_2O_3 was detected at a significant concentration by XRF, no aluminum-containing crystalline phases were observed in the XRD patterns. This discrepancy suggests that aluminum may be present mainly in amorphous or poorly crystalline phases that cannot be detected by XRD. Furthermore, the solid residues obtained after solvent extraction exhibited a very low silicon content (<0.5%) according to XRF analysis; however, several diffraction peaks corresponding to quartz were clearly observed by XRD. This apparent discrepancy can be attributed to the high crystallinity and strong diffraction response of quartz, which allows its detection by XRD even at relatively low concentrations.

The combined XRD and XRF results further confirm the selective nature of the solvent extraction process. The persistence of crystalline mineral phases, including quartz, calcite, dolomite, iron oxides, sulfates, and sulfides, together with the similar elemental compositions of the residues obtained after cyclohexane and methyl ethyl ketone (MEK) extraction, indicates that the solvents mainly removed the organic hydrocarbon fraction, while the inorganic mineral matrix remained concentrated in the solid phase. Similar behavior has been reported during solvent-based recovery of oil from petrochemical sludge, where the recovered products were mainly composed of organic compounds, whereas mineral constituents remained in the residual solid phase[23,29]. The good agreement between XRD-identified mineral phases and XRF-detected elements, such as Fe associated with iron-containing minerals, Ca with carbonate and sulfate phases, and Na with halite, confirms the stability of the inorganic fraction during solvent extraction. This selective separation minimizes the transfer of mineral impurities into the recovered oil, thereby improving its quality. However, the residual mineral components may influence the extraction mechanism by providing adsorption sites for heavy organic compounds and affecting their desorption from the sludge matrix[60]. Furthermore, the comparable mineralogical and elemental compositions of the residues after cyclohexane and MEK extraction suggest that differences in oil recovery are mainly governed by solvent–hydrocarbon interactions and the dissolution capacities of the solvents rather than by significant changes in the inorganic composition of the sludge[11,66]. Overall, these findings demonstrate that the optimized solvent extraction process efficiently recovers the organic fraction while maintaining the integrity of the inorganic mineral matrix, which contributes to the high extraction efficiencies achieved under optimized operating conditions.

Characterization of extracted oil

The FTIR spectra of the two oils extracted using MEK and cyclohexane, as shown in Fig. 8, indicated that both samples exhibited similar characteristic absorption bands. The absorption bands at 2919 cm^{-1} and 2854 cm^{-1} were assigned to the asymmetric and symmetric stretching vibrations of methylene groups ($–CH_2$), respectively, according to Pei and Fan[67]. The band observed at 2103 cm^{-1} was attributed to the stretching vibration of the C≡C bond[55]. The bending vibrations of $–CH_2$ and $–CH_3$ groups were represented by the bands at 1457 cm^{-1} and 1371 cm^{-1}, respectively, confirming the presence of aliphatic hydrocarbon chains[63]. A band at 1167 cm^{-1} was observed only in the oil extracted using MEK and was assigned to C–O stretching vibrations, indicating the presence of oxygen-containing compounds, as reported by Kowalski *et al.*[68]and Silverstein *et al.*[69]. This band was absent in the cyclohexane-extracted oil, suggesting that MEK, due to its higher polarity, may preferentially extract more polar organic compounds compared with cyclohexane. The

Table 4 — GC-MS identification of the principal organic components of oil recovered from the oily sludge

RT (min)	Compound	Chemical formula	Classe	Area (%)
13.362	Tetradecane (n-C14)	$C_{14}H_{30}$	n-alkane	2.39
14.644	Pentadecane (n-C15)	$C_{15}H_{32}$	n-alkane	6.30
15.222	3-Ethyl-2,6,10-trimethylundecane (pristane/phytane)	$C_{16}H_{34}$	Iso-alkane	1.65
15.305	3-(2-Methyl-propenyl)-1H-indene	$C_{13}H_{15}$	aromatic	1.57
15.512	Hexadecane, 2,6,10,14-tetramethyl- (phytane)	$C_{20}H_{42}$	Isoprenoid alkane	1
15.753	Dodecane, 3-methyl-	$C_{13}H_{28}$	isoparaffin	1.15
16.395	Heptadecane, 8-methyl-	$C_{18}H_{38}$	iso-alkane	1.02
16.441	Pentadecane, 2,6,10,14-tetramethyl-(pristane)	$C_{19}H_{40}$	Isoprenoid alkane	3.46
16.623	2-Methyltetracosane	$C_{25}H_{52}$	isoparaffin	1.43
17.107	Eicosane (n-C20)	$C_{20}H_{42}$	n-alkane	8.64
17.190	Pentadecane, 2,6,10,14-tetramethyl- (pristane)	$C_{19}H_{40}$	Isoprenoid alkane	3.52
17.736	Heneicosane (n-C21)	$C_{21}H_{44}$	n-alkane	2.06
17.858	Eicosane (n-C24)	$C_{20}H_{42}$	n-alkane	1.16
18.026	Heptadecane, 2-methyl-	$C_{18}H_{38}$	isoparaffin	1.04
18.630	Docosane (n-C24)	$C_{22}H_{46}$	n-alkane	7.07
18.804	Hexadecane, 2,6,10,14-tetramethyl- (pristane)	$C_{19}H_{40}$	isoprenoid	2.71
19.388	Tetracosane (n-C24)	$C_{24}H_{50}$	n-alkane	1.11
20.601	Heneicosane (n-C21)	$C_{21}H_{44}$	n-alkane	6.65
25.113	1,2,3,4,5,6,7,8-Octathiocane	C_8S_8	Cyclic polysulfide	2.48
26.027	Heneicosane(n-C21)	$C_{21}H_{44}$	n-alkane	3.62
28.492	Pentacosane (n-C15)	$C_{25}H_{52}$	n-alkane	2.39

absorption bands at 725 cm^{-1}, 811 cm^{-1}, and 868 cm^{-1} were attributed to the out-of-plane bending vibrations of aromatic C–H bonds, indicating the presence of substituted aromatic structures[54].

The FTIR results provide additional insight into the influence of solvent properties on oil recovery efficiency. The similar aliphatic hydrocarbon bands observed in both MEK- and cyclohexane-extracted oils indicate the presence of common non-polar hydrocarbon fractions, suggesting that both solvents were able to dissolve aliphatic organic compounds from oily sludge. This behavior is consistent with previous studies reporting the effectiveness of solvent extraction for hydrocarbon recovery from petroleum sludge and oil sands[25,45,47]. However, the presence of the C–O stretching band at 1167 cm^{-1} only in the MEK-extracted oil indicates the extraction of oxygen-containing and relatively polar organic compounds. This observation can be attributed to the higher polarity of MEK compared with cyclohexane, allowing the dissolution of a broader range of organic compounds, including fractions with intermediate polarity[58,59]. In contrast, the absence of this band in the cyclohexane-extracted oil suggests that cyclohexane mainly favors the extraction of non-polar hydrocarbon compounds. The difference in the chemical composition of the recovered oils may contribute to the improved extraction efficiency obtained with the MEK-containing solvent system. The complementary solvation behaviour of polar and non-polar solvents enhances the dissolution of complex organic mixtures by combining the ability of cyclohexane to dissolve non-polar hydrocarbons with the capacity of MEK to extract more polar compounds. Similar improvements in hydrocarbon recovery using solvent blends have been reported for petroleum sludge treatment [11,26,66]. Therefore, the FTIR findings support the synergistic effect observed in the cyclohexane/MEK mixture, where the complementary solvent properties contribute to the enhanced overall extraction efficiency.

The oil recovered from crude oil sludge was analyzed by gas chromatography-mass spectrometry (GC–MS) to determine its chemical composition. The major compounds identified in the recovered oil are listed in Table 4, including only those with a relative

peak area greater than 1%, based on comparison of the mass spectra with the National Institute of Standards and Technology (NIST) library. The chromatographic analysis revealed that the recovered oil was dominated by saturated hydrocarbons, primarily linear *n*-alkanes (C_{14}–C_{25}), including tetradecane, pentadecane, eicosane, tetracosane, and pentacosane. These compounds have also been reported in previous studies on petroleum sludge and recovered oils[70]. Branched paraffinic isoalkanes, including 2-methyldodecane, 3-methylheptadecane, 6-methylheptadecane, and 2-methyltetracosane, were also identified. In addition, the biomarker isoprenoids pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethylhexadecane) were detected. These biomarkers are widely recognized as indicators of petroleum origin and have previously been reported in refinery oily sludge by Gallego *et al.*[71] and Jasmine and Mukherji[65]. Because pristane and phytane are more resistant to biodegradation than the corresponding linear alkanes (n-C_{17} and n-C_{18}), the Pr/n-C_{17} and Ph/n-C_{18} ratios are commonly used as geochemical indicators of petroleum biodegradation[72,73]. Minor amounts of aromatic hydrocarbons, including 3-(2-methylpropenyl)-1H-indene, and a sulfur-containing compound (1,2,3,4,5,6,7,8-octathiocane) were also detected[63]. Overall, the GC–MS results indicate that the recovered oil consists predominantly of saturated hydrocarbons accompanied by petroleum biomarkers and only minor amounts of aromatic and sulfur-containing compounds, which is consistent with previous reports on refinery oily sludge[74,65].

Beyond compositional characterization, the GC–MS analysis also provides insight into the extraction mechanism of the cyclohexane–MEK solvent blend. The extraction performance of this solvent system is closely related to the complementary physicochemical properties of its components, which influence both the extraction efficiency and the composition of the recovered oil[23,26,54]. The predominance of saturated hydrocarbons, particularly linear n-alkanes (C_{14}–C_{25}) and isoprenoid biomarkers, confirms that the extraction process efficiently recovered the major petroleum-derived constituents contained within the oily sludge[65,70]. Since petroleum sludge is predominantly composed of non-polar hydrocarbons, the high abundance of these compounds reflects the strong solvating ability of the solvent blend to dissolve non-polar fractions[25,66], while the detection of minor aromatic and sulfur-containing compounds may be attributed to the contribution of MEK, whose relatively higher polarity is likely to facilitate the extraction of moderately polar compounds[66]. Consequently, this complementary solvation behavior broadened the spectrum of hydrocarbons recovered from the oily sludge, thereby enhancing the overall oil recovery efficiency, consistent with previous studies demonstrating the superior performance of solvent blends in petroleum sludge treatment[11,26]. Moreover, the presence of biomarkers such as pristane and phytane indicates that the recovered oil largely preserved its original geochemical characteristics, suggesting that the extraction process was sufficiently mild to maintain the chemical integrity of the recovered hydrocarbons[71]. Therefore, the GC–MS findings not only characterize the recovered oil but also provide mechanistic evidence supporting the enhanced extraction efficiency of the cyclohexane–MEK solvent system, thereby confirming its suitability for the recovery of valuable petroleum hydrocarbons from oily sludge.

Economic, environmental, and industrial perspectives of the proposed extraction process

Although the proposed process achieved high extraction efficiency under laboratory conditions, its practical implementation also depends on its economic feasibility, environmental sustainability, operational safety, and industrial applicability. The following sections provide a detailed discussion of these aspects.

Economic feasibility and solvent recovery

The economic feasibility of the proposed solvent extraction process is primarily determined by the efficiency of solvent recovery and reuse. The main objective of the recovery step is to recycle the cyclohexane–MEK solvent mixture directly, without separating its individual components. The cyclohexane–MEK system forms a minimum-boiling azeotrope at atmospheric pressure, with an azeotropic composition of approximately 52.3 mol% cyclohexane and a boiling temperature of 71.5 °C[75,76]. Because the recovered solvent is reused as a single extraction medium, this azeotropic behavior avoids the need for complete separation of the individual solvents when the recovered solvent mixture is intended for direct reuse. The solvent mixture can therefore be recovered by conventional distillation followed by condensation under atmospheric or

reduced-pressure conditions. Additionally, the similar boiling points of MEK (79.6 °C) and cyclohexane (80.7 °C), as reported in the NIST Chemistry WebBook[77], facilitate direct recovery and repeated reuse of the mixture. This approach aligns with green chemistry principles by minimizing fresh solvent consumption, reducing waste generation, and simplifying process operations[78,79,80]. Although solvent recovery efficiency was not experimentally evaluated in this study, solvent regeneration by distillation is a well-established industrial practice for recovering and recycling organic solvents[78,81]. Industrial data from Capello *et al.*[82], based on approximately 150 waste-solvent distillation processes, indicate an average solvent recovery efficiency of about 90%. Optimized industrial distillation systems may achieve even higher efficiencies, depending on solvent properties and process configuration. Based on these published data, a preliminary recovery scenario of approximately 95% was conservatively considered solely to illustrate the potential benefits of solvent recycling in the proposed process. In this scenario, only about 5% of fresh solvent would be required to compensate for losses during each extraction cycle, substantially reducing both fresh solvent consumption and associated purchasing costs compared to single-pass utilization. Since solvent replacement represents a major operating cost in solvent extraction processes, efficient recycling is expected to improve process economics while reducing solvent waste generation and volatile organic compound (VOC) emissions, thereby enhancing environmental performance and alignment with green chemistry and circular economy principles[78,79,82]. Implementing a closed-loop solvent recovery system with efficient condensers can further enhance both environmental and economic performance by minimizing solvent losses and enabling repeated reuse[79,81]. Selecting an appropriate recovery technology is essential for maintaining solvent quality during recycling, minimizing energy consumption, and optimizing operating costs [79,83]. However, this assessment relies on literature data and the thermodynamic properties of the cyclohexane–MEK system rather than experimentally determined recovery efficiencies. Consequently, pilot-scale investigations are necessary to quantify recovery efficiency, assess solvent quality after multiple recycling cycles, determine the energy requirements of the distillation process, and conduct a comprehensive techno-economic evaluation prior to industrial implementation. Overall, the favourable thermodynamic characteristics of the cyclohexane–MEK system, together with reported industrial solvent recovery efficiencies, suggest that direct recovery and reuse of the solvent mixture is technically feasible and has the potential to improve the sustainability and economic viability of petroleum sludge treatment by solvent extraction.

Environmental and safety considerations

The performance of solvent-intensive processes depends not only on extraction efficiency but also on solvent properties, including volatility, vapor pressure, flammability, and potential volatile organic compound (VOC) emissions. These characteristics require careful evaluation during solvent selection and process design[84,85,86]. Cyclohexane and MEK require particular attention because both solvents are volatile, highly flammable, and classified as VOCs. Their evaporation during processing may contribute to atmospheric emissions and increase occupational exposure if adequate engineering controls are not implemented[80]. Implementing closed extraction systems, adequate ventilation, explosion-proof equipment, and rigorous solvent handling procedures is essential to ensure operational safety and minimize environmental impacts. The use of personal protective equipment in accordance with industrial safety regulations is also necessary to reduce fire hazards and health risks. These engineering and operational measures are consistent with solvent selection frameworks that integrate environmental, health, and safety (EHS/SHE) criteria to minimize solvent losses, VOC emissions, and occupational risks throughout the process life cycle[85,86]. Efficient solvent recovery and recycling can further reduce solvent consumption, waste generation, and VOC emissions, thereby improving the overall sustainability of the extraction process[81]. Future research should incorporate comprehensive environmental and techno-economic assessments, such as life-cycle assessment (LCA) and quantitative risk analysis, to further evaluate the feasibility, safety, and industrial applicability of the proposed process[87].

Industrial applicability

The proposed extraction process demonstrates significant practical and industrial potential for treating and valorizing crude oil sludge. Solvent extraction is recognized as an effective recovery

technique because it enables the selective extraction of valuable hydrocarbons while reducing the amount of hazardous waste requiring disposal[1,2]. However, although conventional solvents are widely used for oily sludge treatment, their extraction efficiency may be limited when applied individually, often requiring higher solvent consumption or extended processing times[88]. Recent studies indicate that blending solvents with complementary physicochemical properties is an effective strategy for overcoming extraction limitations and enhancing extraction efficiency[26,52]. In line with this approach, the cyclohexane/MEK solvent blend evaluated in this study achieved the highest oil recovery among the tested solvent systems under the selected operating conditions. The superior extraction performance of the cyclohexane/MEK blend can be attributed to the complementary physicochemical properties of the two solvents, which facilitate the dissolution of various hydrocarbon fractions and enhance mass transfer during extraction[52]. Consequently, this improved extraction performance may result in higher hydrocarbon recovery while reducing solvent consumption per unit of recovered oil, thereby improving overall process efficiency and industrial applicability. This finding aligns with contemporary solvent selection strategies for industrial applications, where selection criteria consider not only extraction performance but also solvent recoverability, separation efficiency, safety, environmental impact, and overall process economics to support successful process scale-up and industrial implementation[80,86]. Additionally, the proposed process relies on conventional unit operations, including solvent mixing, solid-liquid separation, and solvent recovery by distillation, all of which are well established in the petroleum and chemical industries. This facilitates integration into existing industrial facilities with minimal process modifications and without requiring highly specialized equipment[1,2]. Compared with conventional oily sludge treatment technologies, solvent extraction offers several advantages, including potentially lower energy requirements, milder operating conditions, and improved preservation of valuable hydrocarbon fractions[16,17,50] . Furthermore, integrating efficient solvent recovery and recycling systems can enhance the economic feasibility and environmental performance of the process by reducing fresh solvent consumption, operating costs, waste management expenses, and overall waste generation. However, effective process design and robust solvent recovery systems are essential for minimizing solvent losses and ensuring safe industrial operation[10,11]. Although additional pilot-scale studies and comprehensive techno-economic evaluations are required before full-scale implementation, recent research demonstrates that thorough techno-economic assessments and appropriate selection of solvent recovery technologies are crucial for improving process efficiency, reducing operating costs, and facilitating the industrial adoption of solvent-intensive processes[83,89]. These findings indicate that the proposed extraction process has promising potential for future industrial application in crude oil sludge treatment, resource recovery, and sustainable waste management.

Conclusion

In conclusion, this study demonstrated that methyl ethyl ketone (MEK), cyclohexane (CHX), and their binary mixture exhibited different extraction efficiencies for oil recovery from petroleum sludge without pretreatment. The highest oil recovery (51.47%) was obtained with the CHX/MEK mixture under the optimized extraction conditions, highlighting the potential advantages of combining polar and non-polar solvents for petroleum sludge oil recovery. Characterization of the recovered oil and residual solids further confirmed the effective separation of paraffinic hydrocarbons (C_{14}–C_{25}), biomarkers (pristane and phytane), trace aromatic and sulfur-containing compounds, while the solid residues consisted mainly of inorganic oxides and amorphous carbonaceous materials. However, this study was limited to laboratory-scale experiments and did not investigate solvent recovery and long-term recycling performance or the techno-economic feasibility of large-scale implementation. Future work should therefore focus on pilot-scale validation, optimization of solvent recovery and recycling strategies, and comprehensive techno-economic and environmental assessments to facilitate industrial application of the proposed extraction process**.**

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Conflict of interest

The authors declare that there are no conflicts of interest associated with this work.

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