

Remediation of Contaminated Soil with Crude Oil Using Solvent Extraction Method

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Abstract. An innovation for removing crude oil from contaminated soil was studied. A mixture of hexane, acetone, and water was used to investigate the ability of solvent extraction techniques to clean soil under various extraction conditions. The study was conducted with initial processing stages using batch and ultrasonic methods, followed by GC-MS and FTIR analysis. The results showed that the soil was contaminated with saturated hydrocarbons, aromatic naphthene's, polar aromatics, and asphaltenes. The effect of solvent ratio and extraction time was studied, and the results showed that the best solvent ratio and extraction time were 1:6 (w/v) and 60 minutes, with a solvent efficiency of 70% and successfully extracting contaminants (saturated fractions of 97.25% and aromatics of 2.75%). Repeated extraction was better than a single extraction where the solvent efficiency was 63.8% and the contaminants were paraffin compounds of 71.96% and naphtha of 28.04%.

1 Introduction

Soil contaminated with crude oil contains organic compounds such as aromatic, aliphatic, and heterocyclic compounds, which impact the environment and living organisms [1]. Crude oil spills in soil occur through various stages, including processing, storage, and use. The impacts of crude oil spills not only pollute the soil but also water resources and aquatic ecosystems [2,3]. Crude oil spills also occurred at the oil refinery of the Oil and Gas Education and Training Centre in the Cepu area, Blora Regency, Central Java. The refinery has an average capacity of 200 barrels per day (bpd) with an average oil loss of 0.4%. Crude oil released into the environment can cause oil spills on land.

Crude oil is a highly complex mixture of hydrocarbons. It typically contains small amounts of heteroatoms such as nitrogen, oxygen, and sulphur, as well as metals such as vanadium and nickel. Oil pollutants are classified into four types: saturated, naphthene aromatic, polar aromatic, and nC7-asphaltenes based on polarity and solubility.

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Soil contaminated by oil spills can pollute the environment. Oil spills contaminate the soil surface and evaporate, potentially even seeping into the ground. As a result, various chemicals will mix with the soil and contaminate groundwater, which can harm human health and the environment. Although they are low or non-toxic, they have the capacity to absorb into the soil surface, changing the surface from water-wet to oil-wet, and pose potential risks to human health and the environment [4].

Several methods for treating soil contaminated by oil spills include physical, chemical, and biological methods. The most common method for treating soil contaminated with crude oil is remediation using bacterial consortia [5] phytoremediation [6] ozonation [7] bio washing and bio pile [8] biochar and biosurfactant [9] bioremediation [10] microbial and phytoremediation [11]. Bioremediation methods have several drawbacks, such as long processing times and the need for special handling. One highly effective chemical method is solvent extraction. Solvent extraction is a cleanup method that uses solvents to extract or remove hazardous chemicals from contaminated material. Therefore, this method is efficient in removing hydrophobic organic contaminants from soil. The solvent extraction method is expected to quickly and simply treat oil-contaminated soil. Solvent extraction can treat soil contaminated with heavy crude oil. The extraction method can also be used to treat sludge contaminated with crude oil [12].

A solvent mixture of hexane and acetone (25% by volume) is very effective in removing crude oil hydrocarbons from contaminated soil containing aromatic naphthene, polar aromatics, and n-asphaltenes. However, further research is needed regarding solvent mixtures, as the hexane-acetone mixture does not produce a stable emulsion phase in the soil, making oil removal less effective. Extraction with water solvents can recycle organic solvents used for the extraction of crude oil-contaminated soil. In addition, water is readily available and safe to use. Based on the above, researchers will conduct research on the treatment of crude oil-contaminated soil using the solvent extraction method using a mixture of n-hexane, acetone, and water. The parameters used are extraction time, solvent-to-soil ratio, solvent efficiency, and extraction method. The novelty of this research is the use of water as a polar solvent to dissolve soil containing many polar compounds. Water can facilitate the extraction process. Furthermore, the novelty of this research is the soil profile after extraction and the comparison of extraction processes using magnetic stirrers and ultrasonic.

2 Experimental Section

2.1 Materials and instrumentation

The research equipment used was Magnetic Stirrer, Rotary Evaporator Buchi, GC-MS (Gas Chromatography Mass Spectrometry) QP 2010, FTIR (Fourier Transform Infrared Spectroscopy) Perkin Elmer and Ney Ultrasonic 28H. The research materials were n-hexane pro analysis and acetone pro analysis from JT Baker. Crude oil contaminated soil samples were taken from the Sumur-Ldk 175 well of PT. Blora Patra Energi, Blora Regency, Central Java. Sampling was carried out using a simple random sampling system. Soil samples were taken using a shovel. Samples were taken from the topmost layer of soil. To avoid evaporation of the contained substances and contamination from other materials, soil samples were put into plastic and stored in an ice box. The sampling location is shown in Figure 1.

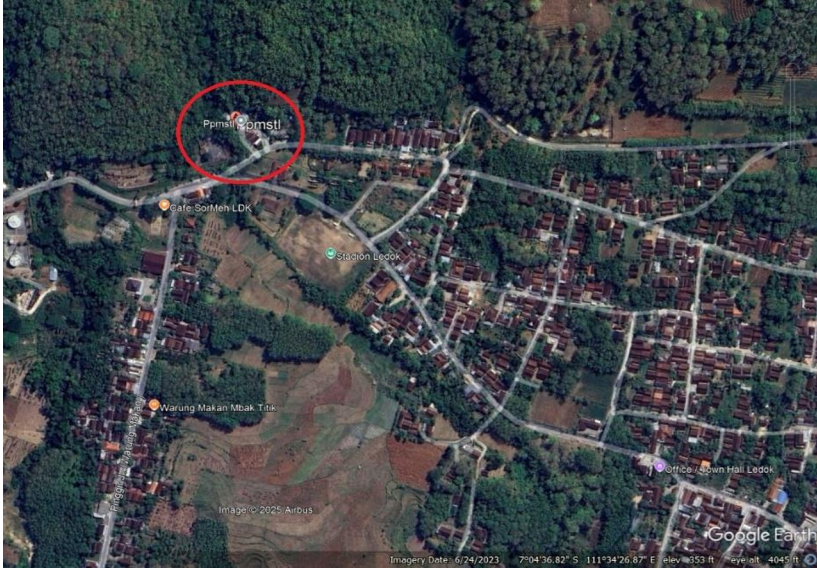


Fig. 1. Sampling area of the old oil well Ldk-175 in the Ledok Field, Ledok Village, Sambong District, Blora Regency, Central Java.

2.2 Solvent extraction of contaminated soil samples

A 50 g contaminated soil sample was placed in a 250 mL beaker glass. Then, n-hexane, acetone, and water were added to a ratio of 5:4:1. The beaker was then covered with aluminum foil. The extraction process was stirred using a magnetic stirrer for 20 minutes. The mixture was filtered using filter paper. The filtration was analyzed using FTIR. The volume of the filtration was determined using a measuring cylinder. The filtrate was transferred into a separating funnel to separate the organic compounds and water. The volume of the oil and organic solvent mixture was then determined. The solvent remaining in the filtrate was separated using a rotary evaporator at 69 °C. The volume of the crude oil obtained was determined and analyzed using GC-MS. This study also carried out three repeated soil sample extractions. The remediation process procedure is shown in Figure 2.

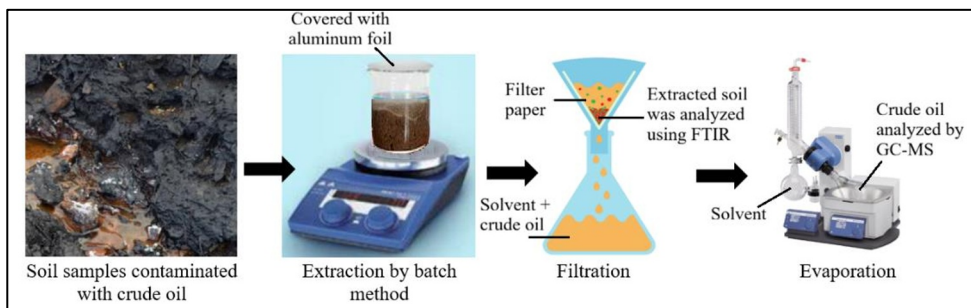


Fig. 2. Remediation process for crude oil-contaminated soil using the batch method

2.3 Ultrasonic oil extraction of soil samples

The extraction process was carried out with a sample-to-solvent ratio of 1:4 (w/v). A 50 g soil sample was placed in a 250 mL beaker. Then, n-hexane, acetone, and water were added, totaling 160 mL of solvent (100 mL n-hexane, 40 mL acetone, and 20 mL water). Water was added to the soil sample to form an emulsion to facilitate the extraction process. Next, a mixture of n-hexane and acetone was added. The beaker containing the soil sample and solvent was covered with aluminum foil. The beaker was placed in a Ney Ultrasonic 28 H reactor for 20 minutes at an operating temperature of 5-40 °C and a frequency of 28 Hz.

3 Result and Discussion

3.1 Extraction results with varying sample-to-solvent ratios

The solvent extraction process on crude oil-contaminated soil samples was carried out in three variations of soil sample-to-solvent ratios (1:2), (1:4) and (1:6) (w/v). Compound content analysis in the extracted results was performed using GC-MS (Gas Chromatography Mass Spectrometry) QP 2010 with the following operating conditions are injection temperature of 285 °C, column oven temperature of 50 °C, and a Flame Thermionic Detector (FTD). The GC-MS chromatogram of the extracted crude oil is shown in Figure 3.

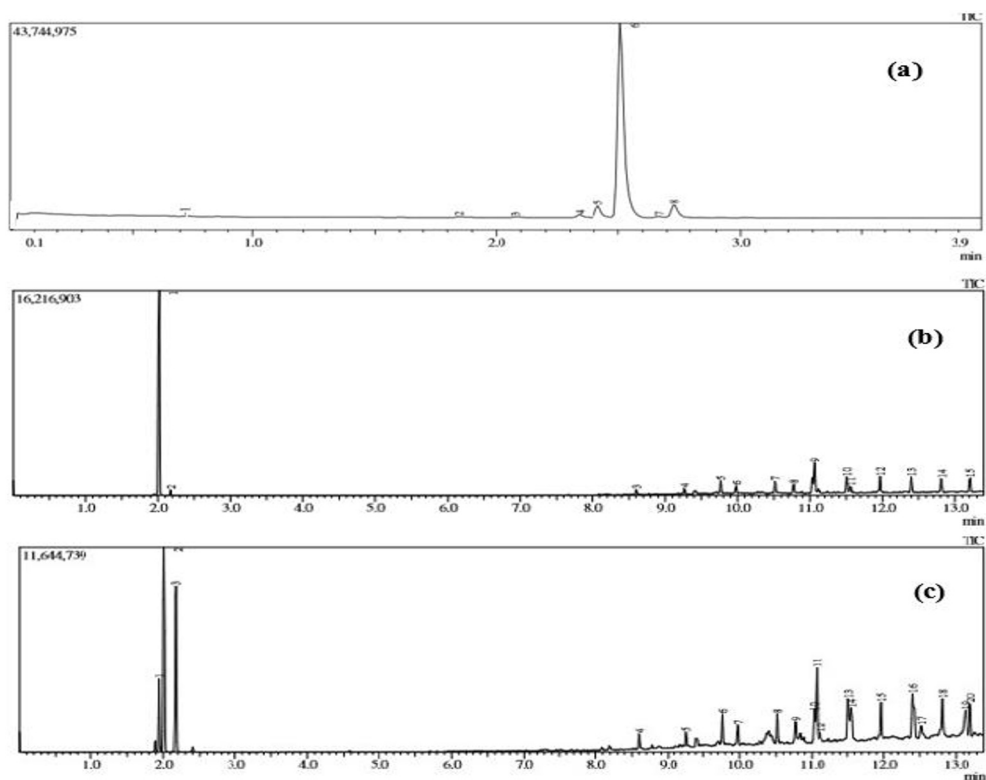


Fig. 3. Chromatograms of soil extract analysis results with soil sample: solvent ratios of (a) 1:2 (b) 1:4 (c) 1:6.

Chromatogram analysis was performed using mass spectra. The results are shown in Table 1. The three ratios (1:2), (1:4), and (1:6) were able to extract organic compounds from the contaminated soil samples. These compounds are saturated hydrocarbon fractions (saturates) and naphtha (aromatics). Based on the chromatograms and MS, it can be concluded that the best ratio was 1:6 (w/v). This conclusion is the extracted organic compounds contain paraffins (78%), naphthene (20.3%), and aromatics (1.2%).

Table 1. Content of the top five chemical compounds extracted with varying soil sample: solvent ratios

No.	Comparison of soil sample weight with solvent (w/v)					
	1:2		1:4		1:6	
	Compound name	(%)	Compound name	(%)	Compound name	(%)
1	Methylcyclopentane	38.58	2,6,10,14-tetramethylpentadecane	26.48	Methylcyclopentane	20.30
2	3-Methylpentane	31.49	Octadecane	8.40	Eicosane	10.20
3	1-propen-1-ol	14.68	Eicosane	8.27	2,6,10,14-tetramethylpentadecane	9.60
4	2-Methylpentan	8.46	Nonadecan	7.69	Octadecane	6.60
5	1-[8-(3-octyloxiranyl)-1-oxooctyl]Pyrolidine	3.45	2,6,10,15-Tetramethylheptadecane	6.82	Heptadecane	4.80

The more solvents used, the more organic compounds are extracted. The greater the liquid phase, the greater the mass transfer, increasing the contact area between the phases and the concentration gradient. The oil extraction process in crude oil-contaminated soil samples is significantly influenced by the amount of solvent. Based on variations in the sample-to-solvent ratio, the solvent efficiency is shown in Table 2.

Table 2. The results of extraction of soil contaminated with crude oil with variations in the sample and solvent ratios

No	Comparison	Initial solvent volume (mL)	Final solvent volume (mL)	Solvent recovery (%)	Crude oil volume extracted (mL)
1	1:2	90	47	52	2.1
2	1:4	180	113	62	4.4
3	1:6	270	200	74	5.6

Based on Table 2, the best solvent efficiency is at a ratio of 1:6 (w/v) with a crude oil extract yield of 5.6 mL. The correct ratio of solids to solvents will provide maximum extraction results [13]. The ratio of solvent used to solids must be in accordance with the solubility of the solute. The smaller the solubility of the solid to the solvent, the greater the ratio of solvent to solids. Water is essential in the extraction of organic compounds from soil samples. Extraction of soil contaminated with crude oil using organic solvents requires water. Extraction of soil contaminated with crude oil without water will cause clumping. Water is also easily separated because it is insoluble in n-hexane and acetone.

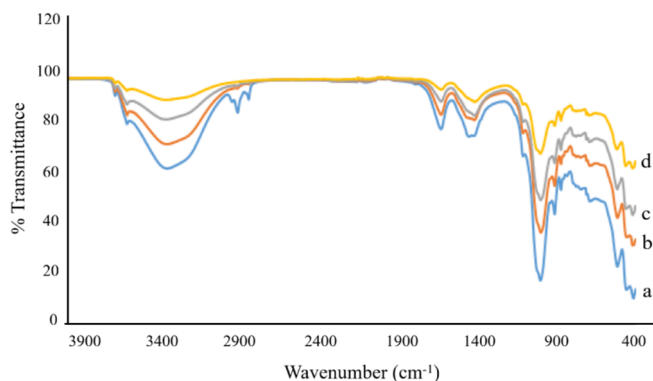


Fig. 4. FTIR spectra of (a) soil sample before extraction and soil sample after extraction with sample:solvent ratios of (b) 1:2 (c) 1:4 and (d) 1:6.

Figure 4 shows that the soil before extraction had an absorption peak around $2850.26\text{--}2955.40\text{ cm}^{-1}$, indicating C-H stretching vibrations (alkanes). After extraction, this absorption peak was not visible, indicating that the extraction process had occurred. Absorption at wavenumbers around 1455.27 cm^{-1} indicates C-H bending vibrations (cycloalkanes), which are classified as naphthene saturated hydrocarbons. However, in the spectra of the three sample ratios, the absorption peak shifted successively to 1420.33 , 1420.28 , and 1420.25 cm^{-1} . This indicates a reduction in the surface area of hydrocarbon compounds in the soil sample after extraction.

3.2 Extraction results with variations in extraction time

Extraction of crude oil-contaminated soil samples was carried out using varying extraction times of 20, 30, and 60 minutes. The sample-to-solvent ratio selected for the extraction time variation was 1:6 (w/v). Figure 5 shows that extraction times of 20, 30, and 60 minutes were effective in extracting organic compounds from crude oil. These compounds include the saturated hydrocarbon fraction (paraffin and naphthene) and the aromatic fraction. Longer extraction times increase solvent penetration into the material, increasing the number of extracted compounds [14]. This is demonstrated in the research results, where 60 minutes was the optimal extraction time. Based on GC-MS data, the extracted organic compounds included 82.53% of the paraffin fraction, 14.72% of the naphthene fraction, and 2.75% of the aromatic hydrocarbon fraction. Solvent efficiency is shown in Table 3. Table 3 shows that as extraction time increases, the volume of crude oil extracted decreases. The longer the extraction time, the more degradation and evaporation occur in crude oil. Components in the oil can degrade due to the influence of heat, light, and oxygen.

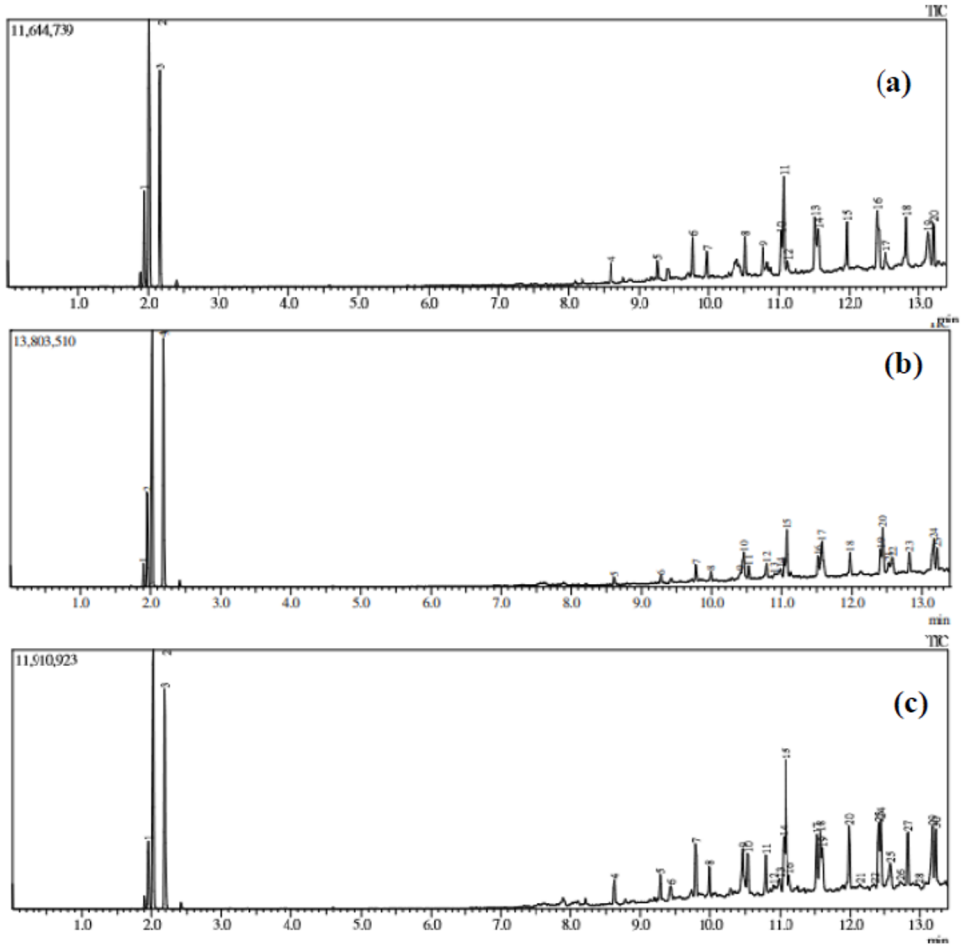


Fig. 5. Chromatogram of extract analysis results with varying extraction times (a) 20 (b) 30 (c) 60 minutes

Table 3. Data on the results of extraction of soil contaminated with crude oil with variations in extraction time

No	Extraction time (minutes)	Initial solvent volume (mL)	Final solvent volume (mL)	Solvent recovery (%)	Crude oil volume extracted (mL)
1	20	270	200	74.0	5.6
2	30	270	178	65.9	5.0
3	60	270	190	70.0	4.2

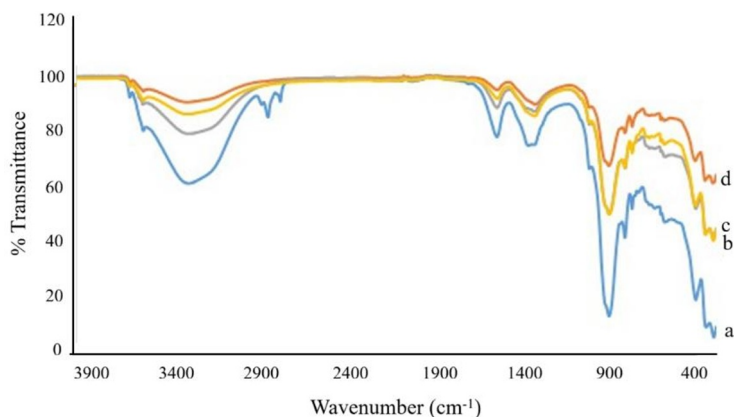


Fig. 6. Spectra of (a) soil samples before and after extraction with varying extraction times of (b) 20, (c) 30, and (d) 60 minutes.

Extraction of soil samples with a mixture of n-hexane, acetone, and water at extraction times of 20, 30, and 60 minutes reveals changes in absorption peaks indicating hydrocarbon compounds (Figure 6). Before extraction, the soil had an absorption peak around 2850.26-2955.40 cm^{-1} , indicating C-H stretching vibrations (alkanes). After extraction, absorption at this wavenumber disappeared. Absorption at a wavenumber around 1455.27 cm^{-1} indicates C-H bending vibrations (cycloalkanes) of naphthenes.

3.3 Extraction of soil samples using batch (stirring) and ultrasonic methods

Table 4 shows the differences in extraction results using the batch and ultrasound methods. The ultrasonic method has a faster extraction process than conventional methods. The mechanical effect caused by ultrasonic waves can increase the solvent penetration ability into the material cells, thereby increasing the number of components that diffuse into the solvent. The results of GC-MS analysis showed that paraffin compounds were 74.97%, naphthenes were 23.55%. The ultrasonic method produced a lower yield than the batch method (stirring). Sonication can significantly increase pollutant removal, and the increase depends on various factors such as sonication strength, flow rate, and soil type. Extraction with low power, ultrasonic frequency, and short time is not enough to produce high yields [15]. This study used a frequency of 28 kHz, while the ideal frequency for ultrasonic extraction is 37 kHz.

Table 4. Data on the results of extraction of soil contaminated with crude oil using the batch and ultrasonic methods

No	Method	Initial solvent volume (mL)	Final solvent volume (mL)	Solvent recovery (%)	Crude oil volume extracted (mL)
1	Batch (Stirring)	180	102	62.7	4.4
2	Ultrasound	180	112	62.2	2.0

Based on the FTIR results shown in Figure 7, it can be seen that the soil before extraction showed absorption in several peaks. The absorption of C-H (alkane) is shown by the appearance of three strong bands below 3000 cm^{-1} . The band with the strongest absorption intensity, namely at a wave number of 2923.9 cm^{-1} , is caused by absorption from the C-H group (alkane). This peak indicates a group of saturated hydrocarbon compounds. There is also a peak at a wave number around 1455.27 cm^{-1} indicating the bending vibration of C-H

(cycloalkane) which includes saturated hydrocarbon compounds of the naphthene fraction (naphthene aromatics).

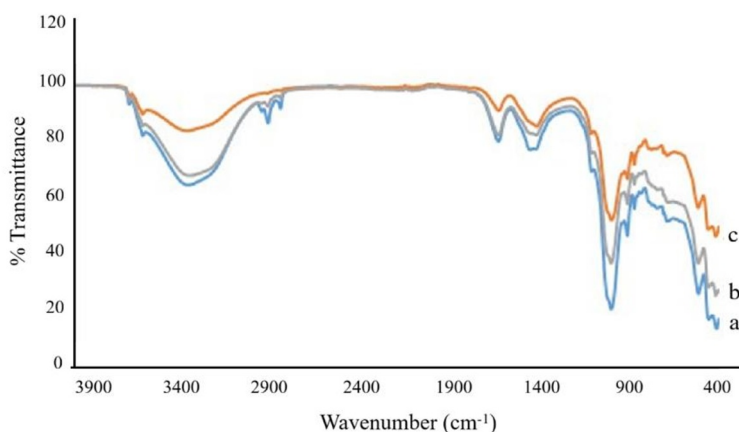


Fig. 7. FTIR spectra of soil samples before extraction (a), after extraction using the ultrasonic method (b), and in batch (c).

Extraction is more efficient when repeated with smaller amounts of solvent than when using a large amount of solvent but only extracted once. The extraction results of soil samples contaminated with crude oil with different extraction rates are shown in Table 5. Three extractions resulted in a solvent efficiency of 63.8% and a crude oil yield of 6.9 mL.

Table 5. Data on the results of extraction of soil contaminated with crude oil with the number of extractions one and three times

No	Number of extractions (times)	Initial solvent volume (mL)	Final solvent volume (mL)	Solvent recovery (%)	Crude oil volume extracted (mL)
1	1	180	113	62.7	4.4
2	3	360	230	63.8	6.9

4 Conclusions

Remediation of crude oil-contaminated soil was carried out by solvent extraction using a mixture of n-hexane, acetone, and water. This solvents mixture is very effective for extracting hydrocarbon compounds. The ratio of soil samples to solvent in extracting soil samples was 1:6 (w/v) with a solvent efficiency of 74% and the results of GC-MS analysis showed a paraffin saturated hydrocarbon content of 30.84% and a naphthene saturated hydrocarbon fraction of 69.19%. The best time to extract soil samples was 60 minutes. The extraction process using the ultrasonic method was better than the batch method. The repeated method had better results than a single extraction.

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