

Investigation of Organic Matter Extraction from Moroccan Oil Shale

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Abstract

This study focuses on investigating the effect of various solvents on the supercritical extraction of organic matter from Moroccan oil shales, with the goal of determining the optimal operating conditions that result in a high yield of high-quality oil rich in aromatic compounds. The results of this study demonstrate that the extraction yield and quality of the extracted oil heavily depend on the chosen operating conditions for supercritical or subcritical extraction of organic matter from oil shale. Additionally, the study found that phenol can effectively degrade oil shale and enable extraction of nearly all the organic matter, even under mild conditions ($T = 390^{\circ}\text{C}$, $P = 1.2\text{ MPa}$, Time = 2.5 h). Furthermore, the oils obtained through this extraction process are of high quality, with a rich content of maltenes, and a higher concentration of aromatic compounds and lower levels of sulfur than those obtained using other solvents.

Keywords

Moroccan Oil Shale, Mineral Matter, Sub/Supercritical Extraction, Nature of Solvent, Phenol

1. Introduction

The constant growth in energy needs and the decline in fossil fuel reserves have changed the world's energy map in recent years, drawing the world's attention to unconventional hydrocarbons, a large part of which are found in oil shale. As a result, this natural resource has regained much interest in countries that have

large reserves of it, which can potentially provide them with energy independence from external energy suppliers.

Morocco has vast reserves of oil shale and clays. The valorization of these resources can provide a significant and highly interesting objective. In recent years, several research studies have focused on developing new materials for various applications using these resources [1] [2] [3] [4] [5].

While the oil shale industry is not as established as the traditional oil industry, it is rapidly gaining traction around the world as a means of industrializing and exploiting unconventional hydrocarbons. This alternative has become more widely accepted as the cost of producing a barrel of unconventional oil has become more competitive, thanks to the development of new extraction processes and their increased economic viability. As a result, the industry has become more profitable [6] [7] [8].

The extraction of organic matter from oil shale is accessible by different methods. The choice of extraction method and operating conditions directly affect the quality and quantity of extractable organic matter and oil produced.

Supercritical fluids have been of interest to researchers since the last century. Initially, there was a strong commercial interest in the use of supercritical toluene for petroleum and shale oil refining during the 1970s. Nowadays, supercritical water is being studied as a way of eliminating toxic wastes, as well as a unique medium for synthesis. For the last decade, the most significant interest has been in the applications of supercritical carbon dioxide. This is because it has a near ambient critical temperature of 31 °C, which allows for biological materials to be processed at temperatures around 35 °C. Supercritical fluids offer many advantages compared to other solvents, including low power consumption, easy separation of the solvent and the extracted fraction, high selectivity, and low resistance to mass transfer.

In a recent study, Torrente and Galan [9] discussed the extraction of kerogen from oil shale located in Puertollano, Spain, using supercritical toluene and methanol mixtures. They demonstrated that the extraction process had two effects: breaking of the kerogen's bonds, which resulted in hydrocarbons of lower molecular weight (bitumen), and chemical interaction between the solute and solvent. Out of the various solvents used for extraction, toluene is the most efficient while methanol is the least efficient. Furthermore, as the amount of toluene in the mixture increases, the quantity of extracted materials also increases.

Numerous studies and efforts [10] [11] [12] have been dedicated to developing methods for extracting organic matter from oil shale. Most of these studies focus on the extraction yield as well as the quality of the extracted oils. Supercritical extraction methods have been shown to yield significantly more organic matter from oil shale than conventional extraction methods, with the quality of the recovered oils depending on the operating conditions [13] [14] [15] [16].

Various studies have demonstrated that the extraction yield and quality of extracted oils depend on several parameters, such as the nature of the solvent,

modifier, temperature, pressure, duration of treatment, heating rate, and grain size. The impact of modifiers on the efficacy of supercritical extraction has been analyzed by several authors [17] [18] [19]. For instance, pentane was used as a solvent for extracting food products [20], while polycyclic aromatic hydrocarbons [21], acetone [22], and hexane [23] were utilized to extract pesticide residues. Some researchers [24] [25] have also employed reagents to break down the solute molecules.

Yang *et al.* [26] examined the impact of demineralization on the pyrolysis of Huadian Oil Shale in Northeastern China. They discovered that the oil yield from the pyrolysis of carbonate-free shales was higher than that from silicate-free shales.

Kök *et al.* [27] compared the effects of pyrolysis on eight Turkish oil shale and isolated kerogen. Their findings revealed that oil yields were higher when pyrolyzing oil shale as opposed to isolated kerogen. These results were confirmed by El Harfi [28], who conducted a comparative study on the pyrolysis of crude oil shales from Tarfaya and Timahdit and that of isolated kerogen.

The analysis of this work indicates that the extraction yield and quality of oil extracted from oil shale are dependent on various parameters. As a result, we conducted a study on the impact of solvents on the supercritical extraction of Moroccan oil shale. Our aim was to determine the optimal operating conditions that would result in high-quality oil and good recovery performance.

2. Experimental

2.1. Materials

The oil shale utilized in this study was sourced from the Tarfaya deposit situated in southern Morocco. The deposit comprises multiple layers, which are further subdivided into sub-layers, each with varying amounts of organic matter. Samples were extracted from the R3 sub-layer, which is distinguished by its high content of organic matter [29]. The chemical composition of the R3 sub-layer is presented in **Table 1** [30].

The carbonate-free oil shale (RH) was obtained by dissolving carbonates with HCl [31] [32]. To do this, 20 g of powdered R3 shale with a grain size of 0.063 - 0.08 mm was mixed with 80 mL of concentrated HCl (7 M) in an Erlenmeyer flask. The mixture was then stirred magnetically for 4 hours. The CO₂ that formed during the reaction was captured by bubbling the gas through a solution of barium hydroxide. After filtration, the solid residue (referred to as RH) was carefully washed with distilled water, dried at 100°C, and stored in a sealed plastic bag.

Table 1. Chemical composition of the R₃ sub-layer [30].

Composition	Carbonates	Kerogen	Silicates	Pyrite	Bitumen
Mass %	70.0	20.0	7.1	1.0	0.9

The carbonate-free shale (RH) was stirred with concentrated hydrofluoric acid (4 ml per gram of RH) for 4 hours. After filtration, the resulting residue (K3) was washed first with dilute hydrochloric acid solution, then with water, and finally dried at 100°C. The dried residue was then stored in a sealed plastic bag.

2.2. Apparatus

Preparation of the Asphaltenes

To extract the RH sample (10 g), a supercritical extraction was carried out using toluene as the solvent. The process took place in a 120 mL stainless steel autoclave equipped with a stirrer and heated in a tubular furnace. Both the temperature and heating rate of the furnace were carefully controlled, and the extraction temperature was set to 390°C for 2 hours 30 minutes with a heating rate of 16°C per minute. The choice of these conditions was made on the basis of our last work [33]. The maximum pressure reached during the 120-minute treatment was 8 MPa. Once the mixture was cooled down to room temperature, it was extracted using a Soxhlet apparatus and chloroform for 12 hours. After removing the solvent under reduced pressure, the organic material was dried for 12 hours at 40°C and weighed. The recovered oil was treated with *n*-hexane in a 1/10 oil-to-solvent mass ratio [34] in order to precipitate the high-molecular fraction (asphaltenes) that constitutes the pitch. After being stirred for 12 hours, the two fractions soluble (maltenes) and insoluble (asphaltenes) were separated through Whatman paper filtration. The maltenes and asphaltenes were then dried for 12 hours at 40°C and 80°C, respectively. The autoclave is illustrated in **Figure 1**.

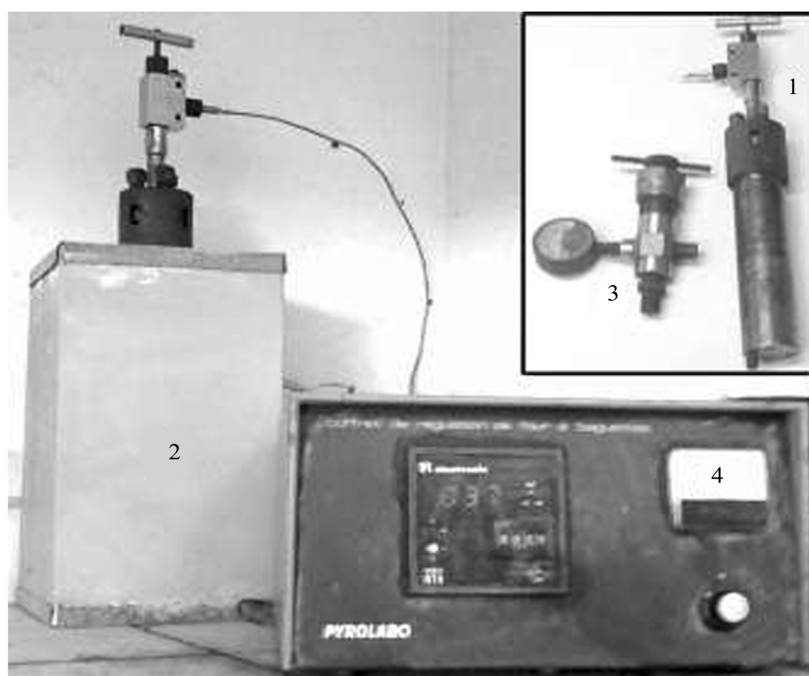


Figure 1. Schematic diagram of the apparatus used for supercritical extraction: (1) reactor; (2) furnace; (3) pressure gauge; (4) regulator.

2.3. Analyses

The X-ray photoelectron spectroscopy (ESCA-XPS) analyses were conducted using an Escalab VG220i-XL instrument.

For the thermogravimetric analyses (TGA), a TGS-2 Perkin-Elmer analyzer was utilized under a high-purity argon flow of 40 mL/min. Samples weighing approximately 12 mg were heated from 50°C to 950°C at a rate of 5°C/min.

Scanning electron microscopy (SEM) micrographs were captured using a Hitachi TM-1000 microscope. Fragments of approximately 0.5 cm² were cut from the corresponding samples and mounted on a carbon tab to ensure good conductivity. Prior to analysis, a thin layer of gold-palladium was sputtered onto the samples.

The size exclusion chromatography (SEC) was performed using a Waters analytical system composed of a pump 510, a refractometer 410, and a UV/ visible detector 486. The eluent used was THF at a flow rate of 1 mL/min, and the separation was carried out on a TSK GMHXL column with mixed porosity 1500 - 107 Å. The relative average molecular weights were calculated using a cubic, 12-point calibration curve obtained from monodisperse polystyrene standards.

¹H NMR spectra were recorded on a spectrometer Bruker AC 250 (250 MHz). The samples were placed in 5 mm-ID tubes with CDCl₃ as solvent. The chemical shifts are given in ppm relative to TMS $\delta = 0$ ppm.

3. Results and Discussion

To determine the most appropriate material for extracting organic matter from Moroccan oil shale, we conducted experiments on three different samples using the extraction protocol outlined in the experimental section.

Sample 1: sub-layer R₃;

Sample 2: sub-layer R₃ freed of carbonates RH;

Sample 3: sub-layer R₃ freed of carbonates and silicates K₃.

Prior to conducting supercritical extraction on the samples, we conducted analyses using various characterization methods. The goal was to better understand the structure of the sub-layer R₃ selected for this study and to track its evolution with respect to the demineralization stages.

3.1. Physicochemical and Mineralogical Characteristics of Raw Materials

3.1.1. Analyse Par Spectroscopie IR

Analysis of the IR spectrum of the sub-layer R₃ from the Tarfaya deposit, presented in **Figure 2(a)**, allows us to propose an allocation of absorption bands based on the work done by other authors (**Table 2**). [27] [35] [36] [37]

The major result of the IR analysis of the sub-layer R₃ is, as expected, the presence of a large amount of mineral material. Indeed, all the bands relating to this material are broad and very intense. In contrast, the organic material is present in the form of fine bands of low intensity.

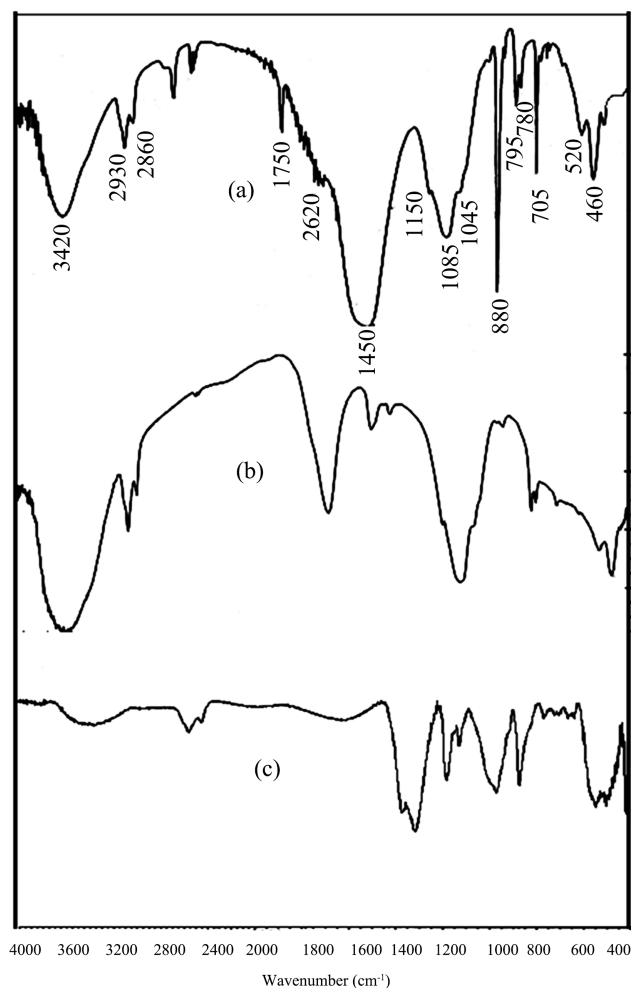


Figure 2. Infrared absorption spectrum of (a) sub-layer R₃, (b) sub-layer R₃ freed of carbonates RH and (c) sub-layer R₃ freed of carbonates and silicates K₃.

Table 2. Band allocation of the infrared absorption spectrum of the sub-layer R₃.

Wavenumber (cm ⁻¹)	Assignment
3420	O-H stretching
2970, 2930, 2860	C-H stretching (CH _{3as}), C-H stretching (CH _{2as}), C-H stretching (CH _{2s})
1750	C=O stretching
1622	C=C stretching (aromatic)
1450, 705, 880	Carbonates
1450	Asymmetric deformation of the C-H bond of -CH ₃ and -CH ₂
1045 - 1150	C-O stretching
1085	Vibration of Si-O-Al in clays
691, 795, 780	Quartz
460, 520	AlO ₆ and SiO ₄ in clays
350 - 425	Pyrite

In the spectrum of the sub-layer R₃ freed of carbonates RH, **Figure 2(b)**, we note the complete disappearance of the bands characterizing the carbonates and an increase in the intensity of the bands relating to the organic matter.

In addition to our previous observations, we have identified the appearance of bands at 1379 and 1457 cm⁻¹, which can be attributed to the symmetrical and asymmetrical deformation of C-H bonds found in the CH₂ and CH₃ groups. However, these bands are unfortunately masked by the presence of mineral matter in the raw shale.

Regarding the spectrum of sample K₃ (sub-layer R₃ freed of carbonates and silicates, **Figure 2(c)**), we note the absence of any band characteristic of mineral matter and the appearance of the following bands, relating to organic matter.

1050 cm⁻¹ and 1163 cm⁻¹: these bands may correspond to the Csp²-O or Csp³-O vibrations of the ether, ester or alcohol functions.

1705 cm⁻¹: groupe C=O.

880 cm⁻¹: pentasubstituted aromatic ring.

840 cm⁻¹: tetra-substituted aromatic ring with two adjacent hydrogens.

820 cm⁻¹: trisubstituted aromatic ring with three adjacent hydrogens.

3.1.2. X-Ray Diffraction Analysis

We conducted X-ray diffraction analysis on the samples from the Tarfaya deposit to identify the mineral elements present in the oil shale (**Figure 3**). The analysis of the X-ray diffraction patterns revealed that the sublayer R₃ primarily consists of carbonates such as calcite (CaCO₃) and dolomite (CaMg(CO₃)₂), as well as silica in the form of quartz (SiO₂) and hematite (Fe₂O₃).

The X-ray diffraction analysis of the RH sample (**Figure 3(b)**) indicates the presence of several phases, including quartz in the form of SiO₂, pyrite (FeS₂), and clay.

The X-ray diffraction pattern obtained for sample K₃, which consists mostly of organic matter, shows a significant reduction in the lines characteristic of the mineral phases present in the raw shale and carbonate-free shale (**Figure 3(c)**). However, the characteristic lines of pyrite are still observable, indicating that the treatment of the raw shale with hydrochloric and hydrofluoric acid does not affect the pyrite content. This result has already been reported by other authors [36] [38].

3.1.3. X-Ray Electron Spectroscopy Analysis (ESCA-XPS)

X-ray photoelectron spectroscopy, also known as XPS or ESCA, is a valuable technique used in research, development, and industrial manufacturing for surface characterization. This technique enables the identification of chemical elements present on a material's surface up to a depth of approximately 5 nm and provides information about its composition. Additionally, XPS provides valuable insight into the chemical bonds existing between these elements. We applied this technique to characterize the elements present in each sample. The results obtained are given in **Table 3** and **Figure 4**.

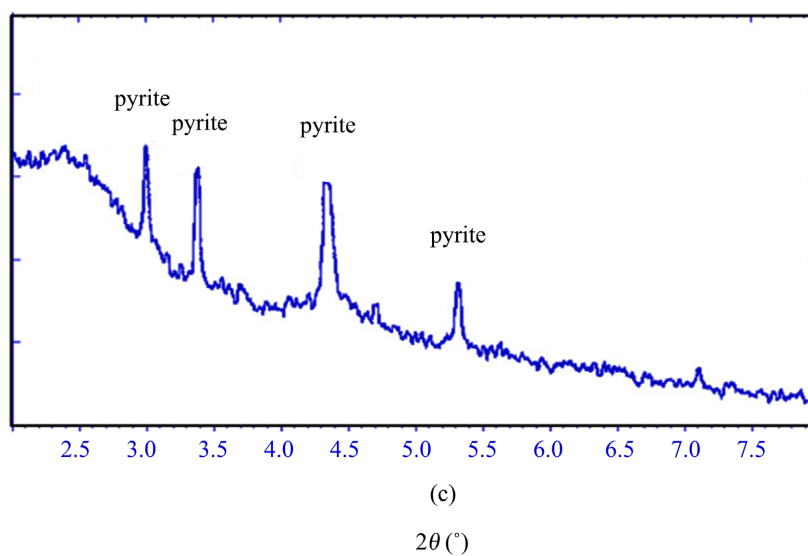
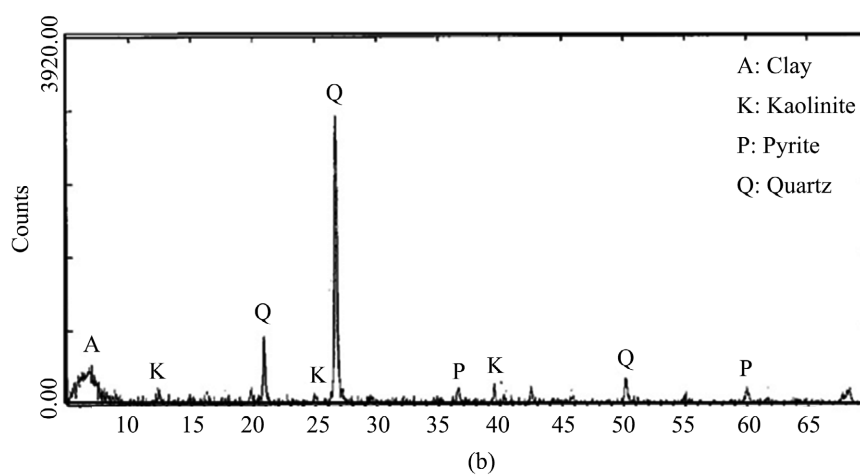
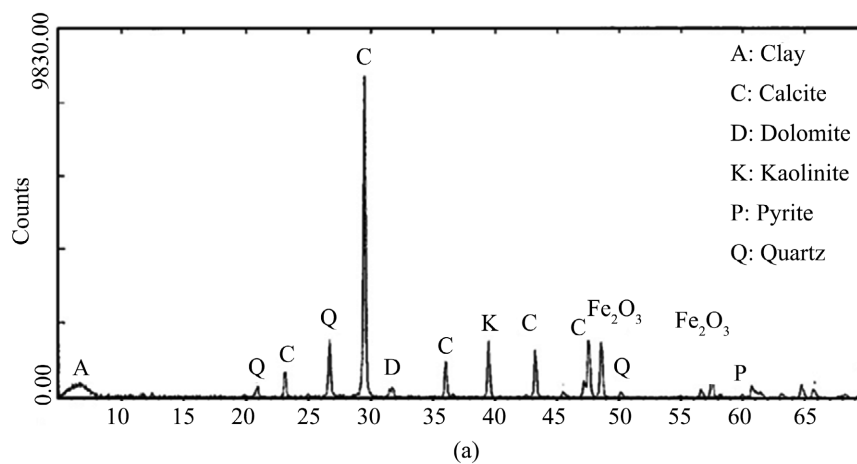
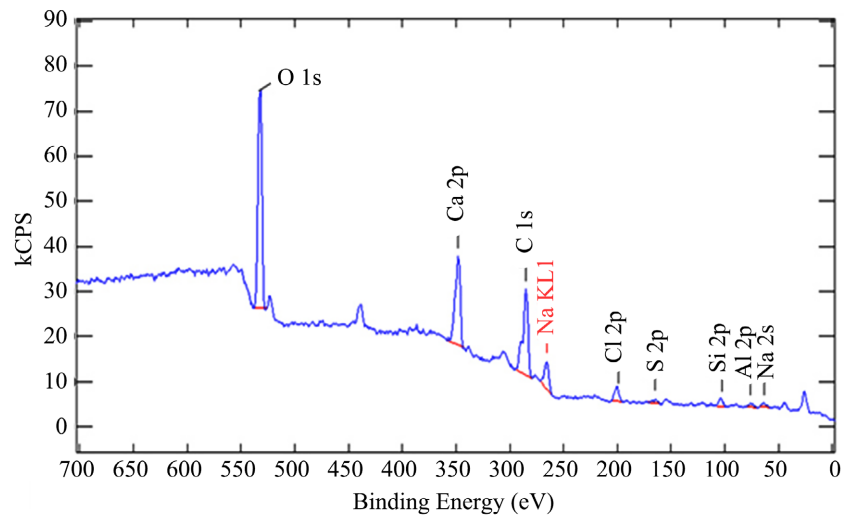
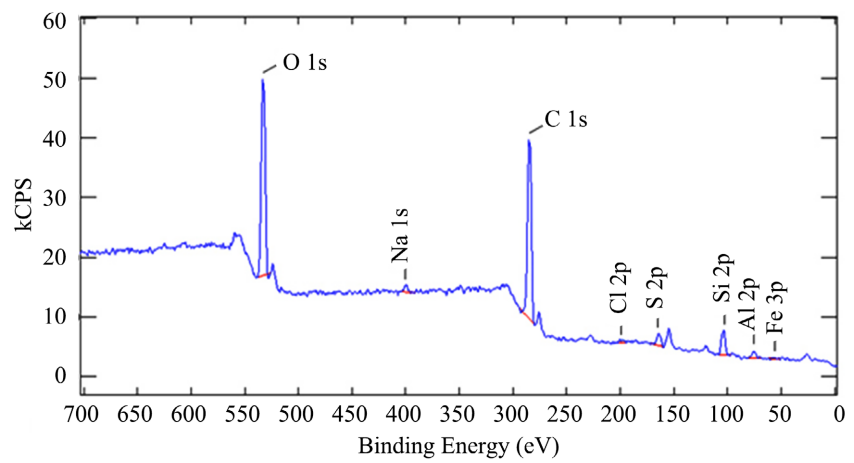


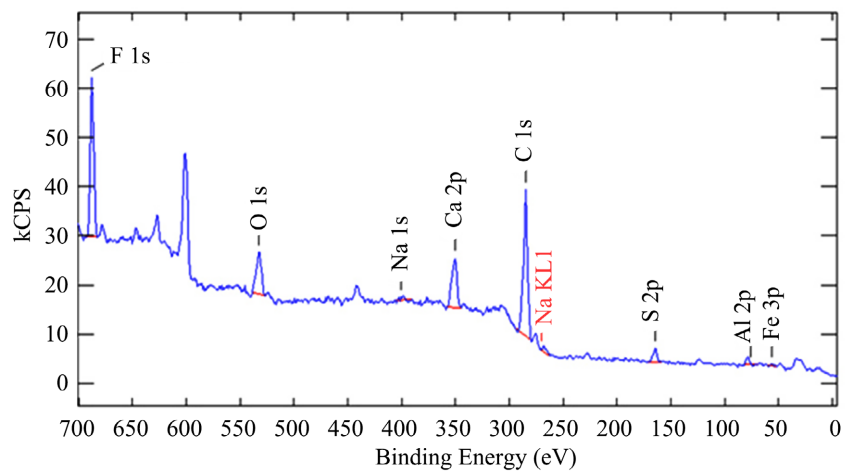
Figure 3. X-ray diffractograms of (a) sub-layer R_3 , (b) sub-layer R_3 freed of carbonates RH and (c) sub-layer R_3 freed of carbonates and silicates K_3 .



(a)



(b)



(c)

Figure 4. ESCA spectrum of (a) sub-layer R₃, (b) sub-layer R₃ freed of carbonates RH and (c) sub-layer R₃ freed of carbonates and silicates K₃.

Table 3. ESCA results of the different samples (atomic %).

Peak	Sample	R ₃	RH	K ₃
Fe 2p ³		-	0.172	0.075
O 1s		36.469	26.942	19.340
N 1s		0.395	1.294	1.035
C 1s		43.402	56.055	73.704
Cl 2p		2.570	0.458	-
S 2p		0.869	2.122	1.378
Al 2s		2.436	3.741	1.103
Si 2p		3.238	8.216	-
Ca 2p		9.399	-	-
Mg		Tracks	-	-
Na		0.222	-	-

Upon comparison of the results obtained from the three samples (**Table 3**), it can be observed that the RH sample is distinguished by the absence of calcium (Ca) and magnesium (Mg) elements, indicating that the rock was effectively treated with hydrochloric acid, leading to the complete dissolution of carbonates. Furthermore, the hydrofluoric acid treatment of silicates and clays in sample K₃ was also effective. These findings were corroborated by X-ray microprobe analysis (**Table 4** and **Figure 5**). In addition, the latter method revealed the presence of other elements that exist at greater depths.

It is worth noting that the presence of fluorine peaks in the ESCA spectrum of sample K₃ can be attributed entirely to the trace amounts of fluorine resulting from the hydrofluoric acid treatment of the RH sample. This fluorine was not removed during the washing process.

3.1.4. Electron Probe X-Ray Microanalysis (EPMA)

EPMA analysis results are given in **Table 4** and **Figure 5**. From these results, it can be seen that during the demineralization stages, the mineral elements present in the sample R₃, corresponding to carbonates, silicates and clays, such as Ca, Mg and Si, completely disappeared. We also note the appearance of other elements that could not be detected by XPS. This proves that the X-ray microprobe is a very sensitive technique compared to XPS, but the two methods remain indispensable and complementary for characterizing the surfaces of materials.

3.2. Solvent Extraction

Initially, we attempted to extract organic matter from oil shale under normal conditions of pressure and temperature by employing commonly used laboratory

extraction methods such as reflux assembly and Soxhlet apparatus. As previously reported in the literature, the oil yields obtained were lower compared to those obtained through pyrolysis or supercritical extraction. The lower oil yields obtained through gentle extraction methods can be attributed to the challenge of disrupting strong interactions between organic molecules and mineral matter under such conditions.

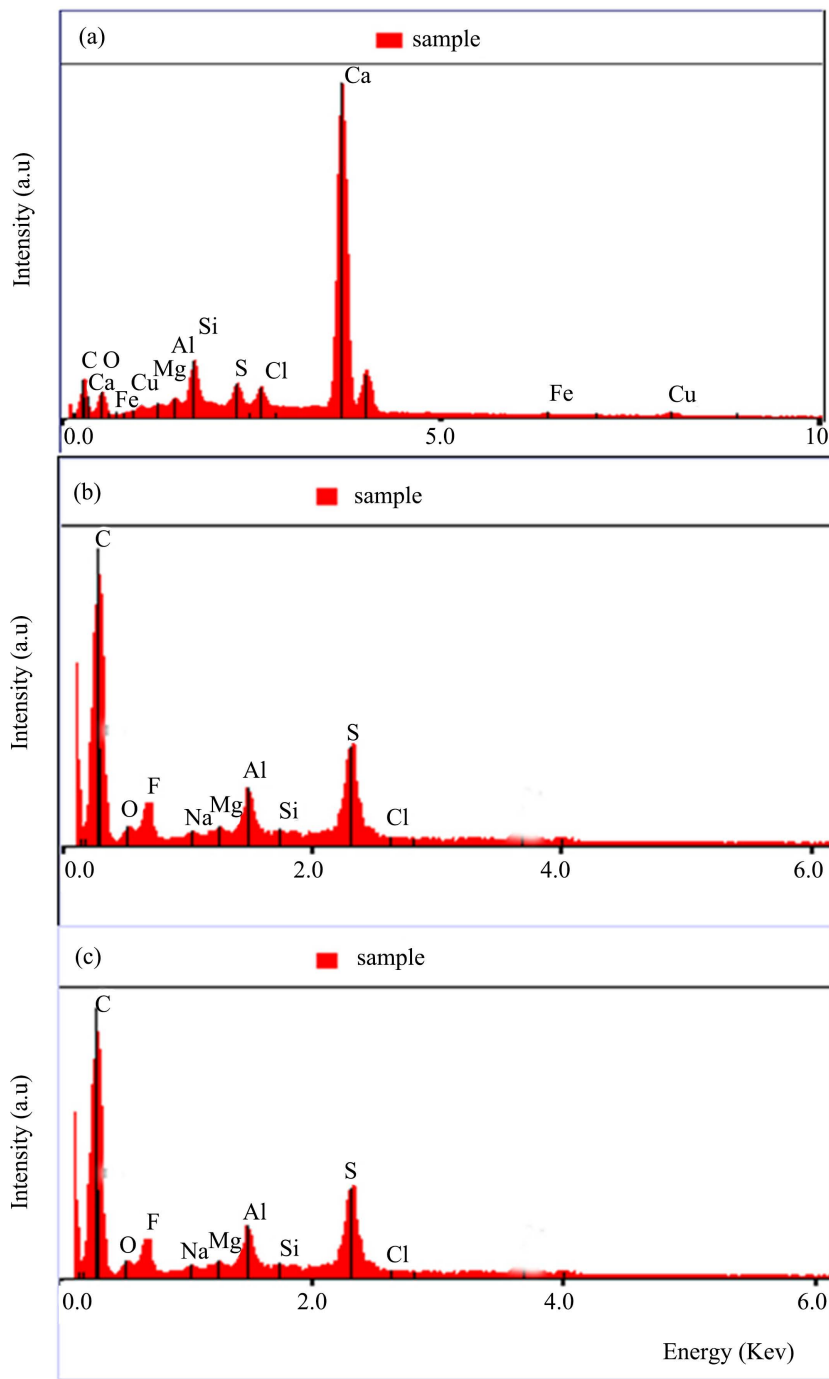


Figure 5. EDS spectrum of (a) sub-layer R₃, (b) sub-layer R₃ freed of carbonates RH and (c) sub-layer R₃ freed of carbonates and silicates K₃.

Table 4. EDS analysis of the different samples (atomic %).

Peak \ Sample	R ₃	RH	K ₃
Fe	0.37	0.78	-
O	21.02	7.63	6.13
Mg	0.75	-	Traces
C	14.57	55.95	89.36
Cl	2.12	1.22	-
S	2.47	9.31	3.29
Al	0.83	2.72	0.52
Si	5.10	20.39	0.09
Ca	49.68	-	-
Cu	3.07	1.37	-

3.3. Supercritical Extraction of Samples by Toluene

To investigate the impact of mineral matter on oil yield and composition, we carried out extractions on three distinct samples as outlined in the experimental procedures:

Sample 1: sub-layer R₃ → R₃;

Sample 2: sub-layer R₃ without carbonates → RH;

Sample 3: sub-layer R₃ without carbonates and silicates → K₃. The findings of our study on the influence of mineral matter on the recovery yield and composition of the extracted oils have been published recently [1].

The results demonstrated a considerable variation in the recovery yield among the different samples. Notably, the yields obtained for samples RH and K₃ were higher than that obtained for sample R₃, highlighting the impact of the mineral matter. The low yield obtained for sample R₃ can be attributed to the high porosity of carbonates, which allows organic matter to be trapped in the mineral matrix, thereby delaying its extraction. Previous research by Abourriche *et al.* [1] has indicated that the RH sample presents several advantages in terms of preparation (lower consumption of reagents) as well as the results obtained (higher recovery yield). Additionally, the presence of fluorine in the organic matter extracted from sample K₃ complicates its use. Considering these factors, we selected the RH sample as the starting material for our study.

The tables below (Table 5 and Table 6) present the findings of our study on the impact of mineral matter on the recovery efficiency of organic matter from oil shale. As shown in Table 5, the results indicate a considerable variation in the oil recovery efficiency among the different samples. Notably, the yields obtained for samples RH and K₃ were higher than that obtained for sample R₃.

The low yield obtained for sample R₃ can be attributed to the high porosity of the carbonates, which allows organic matter to be trapped in the mineral matrix, thereby delaying its extraction.

Table 5. Extraction of the treated shale by toluene.

Samples	R ₃	RH	K ₃
Mass of the sample (g)	10	10	10
Solvent (mL)	60	60	60
Heating rate (°C·min ⁻¹)	16	16	16
Temperature (°C)	390	390	390
Time (min)	150	150	150
Pressure (MPa)	4.5	4.5	4.5
Recovered oil (g)	0.5	3.0	4.3
Yield of recuperation (%)	18	43	56

Table 6. Elemental analyses of the oils (atomic %).

Oil	C %	H %	N %	S %	O %	H/C	O/C
Oil R ₃	41.34	55.11	0.55	0.73	2.26	1.33	0.055
Oil RH	40.81	53.33	0.55	1.04	4.04	1.31	0.099
Oil K ₃	42.25	54.10	0.72	1.06	1.87	1.28	0.044

O is determined by difference.

The Van Krevelen's diagram (**Figure 6**) illustrates the atomic ratios of H/C and O/C for the three oils obtained and highlights the impact of mineral matter on the degree of maturation of the extracted oils. As per the diagram, it is evident that the degree of maturation of the organic matter in the oil shale varies significantly depending on the samples used for supercritical fluid extraction. The results indicate that the oil obtained from sample K₃ exhibits a significantly higher degree of maturation compared to oils R₃ and RH. The oils obtained range from an immature organic matter of I-a type (oil R₃) to an immature organic matter of II-a type (oil RH) or a more mature organic matter, rich in carbon, which corresponds to standard catagenesis II-b (oil K₃). These findings were further confirmed by SEC analyses (**Table 7**).

The results of the SEC analysis (**Table 7**) show that the oil obtained with sample K₃ has the highest value of the average molecular weight (\bar{M}_w), compared to oils R₃ and RH. This suggests that, under these conditions, toluene is able to extract large molecules from kerogen.

It can be concluded from the above results that the sample RH presents several advantages, so much on the level of its preparation (less consumed products), that on the level of the results obtained (high yield of recuperation). Moreover, the presence of fluorine in the organic matter resulting from the sample K₃ makes difficult their use. Oumam [39] has previously reported that during the carbonization of the organic matter resulting from K₃, the walls of the silica tube were gradually attacked by carbonization gases rich in fluorine. These reasons led us to use RH as the starting material to carry on our study.

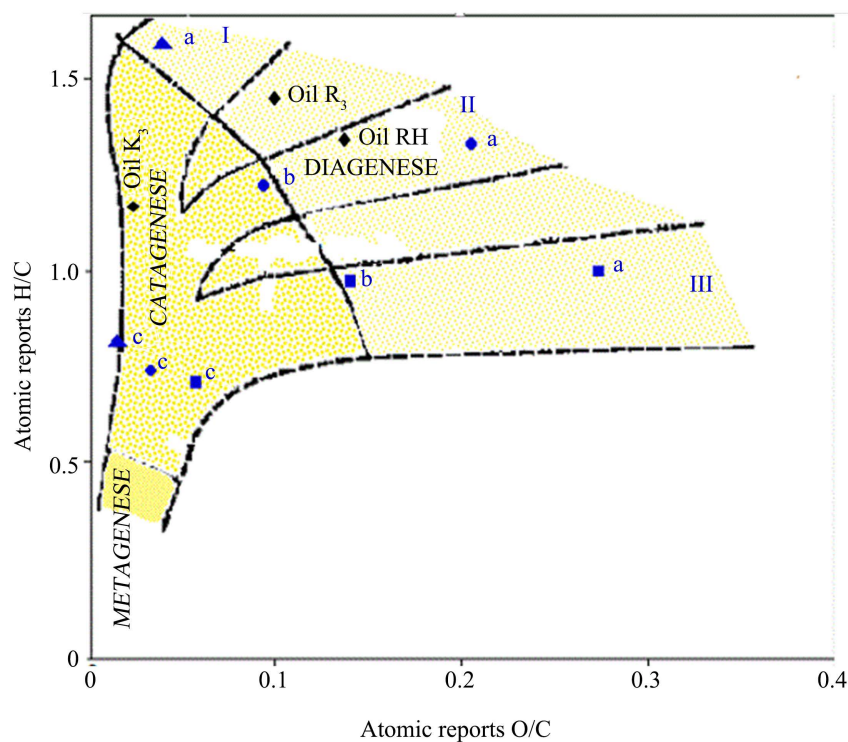


Figure 6. Classification of the oils extracted from the shale materials by the Van Krevelen diagram.

Table 7. Analysis of the oils by SEC.

Oil	\bar{M}_w ^a	\bar{M}_n ^b	I_p
Oil R ₃	1170	160	7.3
Oil RH	1340	200	6.8
Oil K ₃	1650	200	8.2

^aWeight average molecular weight; ^bNumber average molecular weight; I_p : polydispersity index = \bar{M}_w / \bar{M}_n .

3.3.1. Effect of the Solvent

This study was conducted using five distinct solvents (toluene, water, phenol, quinoline, and shale oil), all under the same conditions outlined in the experimental section. The yields and compositions of the resulting oils were recorded and are presented in **Table 8**. The data indicate that the oils extracted with quinoline and phenol solvents yielded significantly higher volumes compared to those produced by the other solvent.

The increased yield and maltene content found in the oil produced by phenol suggests that this solvent not only acts as an effective extraction agent, but also interacts with kerogen molecules. In fact, previous studies conducted by Abourriche *et al.* [40] have shown that phenol reacts with the double and triple bonds of the decomposition products, resulting in the production of alcohols and aldehydes.

Table 8. Yields and composition of the oils extracted from RH by different solvents.

Solvents	Without solvent	Toluene	Phenol	Quinoline	Water	Shale oil
Mass of the sample (g)	10	10	10	10	10	10
Amount of solvent	-	60 ml	15 g	60 ml	60 ml	60 ml
Heating rate ($^{\circ}\text{C}\cdot\text{min}^{-1}$)	16	16	16	16	16	16
Temperature ($^{\circ}\text{C}$)	390	390	390	390	390	390
Time (min)	150	150	150	150	150	150
Pressure (MPa)	0.3	4.5	1.2	1.3	28.5	20
Recovered oil (g)	4.21	3.2	5.71	7.1	4.8	3.7
Maltenes (w %)	59	47	62	65	33	34
Asphaltenes (w %)	41	53	38	35	57	65

3.3.2. Effect of Solvent Quantity

In order to investigate how the quantity of solvent impacts the recovery yield at 390°C , a series of experiments were conducted using a 10 g mass of RH and gradually increasing amounts of three distinct solvents (toluene, water, and phenol), with all other parameters held constant. The resulting data is presented in **Figure 7** and **Figure 8**.

Figure 7 displays the relationship between the amount of phenol used and the mass of chloroform insoluble. The observed decrease in mass of the insoluble substance with added phenol can be attributed to the fact that phenol tends to react with the kerogen molecules, resulting in the breakdown of larger molecules and the formation of smaller ones. It should be pointed out, as demonstrated by Leach [41], that transalkylation reactions can occur between 350°C - 550°C . Additionally, the transformation of phenol to phenolate in the presence of traces of water or bases gives it nucleophilic properties, making it capable of attacking various carbonyl groups. In a previous study conducted by Koel *et al.* [42] which explored the use of neoteric solvents in oil shale research, it was found that these solvents attack the kerogen, leading to chemical modification or degradation of the kerogen.

During the process of extracting organic matter from oil shales, the pressure measured is consistently below 1.2 MPa. This pressure is significantly lower than the critical point of phenol ($T = 419^{\circ}\text{C}$, $P = 6.1$ MPa) [43] [44] [45], indicating that the conditions for recovering organic matter from oil shales using phenol can be considered subcritical extraction. Furthermore, upon completion of each manipulation (*i.e.* once the autoclave was opened), a release of gas with a distinct sulfur odor was detected. This release was more pronounced with increased amounts of phenol. The elimination of sulfur through the action of phenol was confirmed by elemental analysis (as described in the following paragraph).

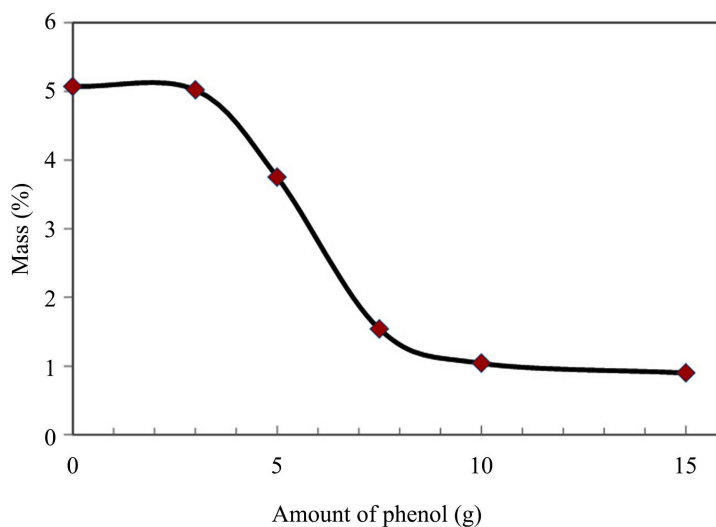
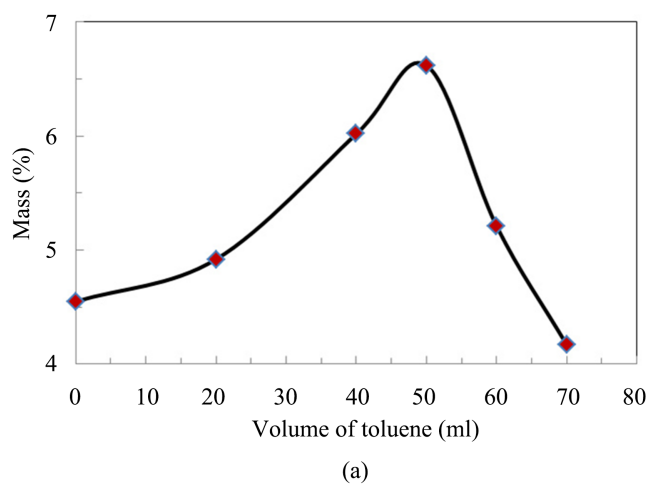
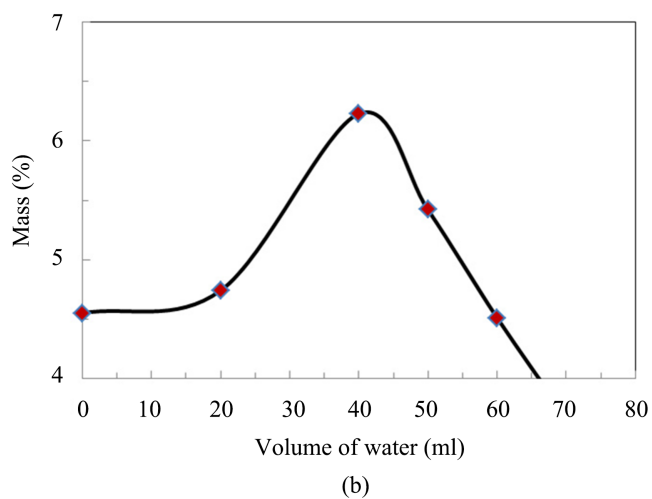


Figure 7. Variation of the mass of insoluble material in CHCl_3 as a function of the amount of phenol.



(a)



(b)

Figure 8. Variation of the mass of insoluble in CHCl_3 as a function of the volume of (a) toluene and (b) water.

In regards to the extraction process using either toluene or water (as depicted in **Figure 8**), two distinct extraction zones were observed. Within the first zone, the mass of insoluble matter increased as the volume of toluene or water was increased. Similar results were found in a study conducted by Zhuang [46], which investigated the supercritical extraction of petroleum pitch using toluene. This increase in the mass of insoluble matter can be explained by repulsion forces between the oil molecules present in solution. It's worth noting that the shape of the variation curve of the CHCl_3 insoluble material as the volume of toluene increases is similar to that observed with water. In the second extraction zone, we noticed that as the volume of toluene and water increased, the mass of CHCl_3 insoluble material decreased. At a temperature of 390°C , the pressure in the autoclave reached 4.5 MPa and 28.5 MPa for a volume of 60 ml of toluene and water, respectively. Interestingly, toluene and water exceeded their critical point in this scenario, which enhanced their solvent power. As a result, we observed a noticeable increase in extraction yield. Canel and Missal [47] conducted a study on the supercritical extraction of oil shale from Göynük (North-West Turkey) using water, and their findings were consistent with our own. Their research demonstrated that the extraction efficiency increased in tandem with the increase in pressure.

1) Analysis of the obtained oils

a) Elemental analysis of the obtained oils are presented in **Table 9**.

According to **Table 9**, the results of the elemental analysis indicate that the oil produced using phenol extraction has lower sulphur content and a greater aromaticity factor (H/C low) when compared to the other oils. Additionally, the ^{13}C and ^1H NMR analysis of the maltenes extracted from phenol-derived oil supports the increase in aromaticity factor mentioned previously (see next paragraph).

b) Analysis of the obtained oils by SEC

Table 10 groups the characteristics of oil shale extracts obtained by various solvents, analyzed using SEC. The results of the analysis (**Table 2**) reveal that water tends to cause kerogen degradation, resulting in a lower average molecular weight. Furthermore, the molecular distribution of the extract is relatively dispersed, albeit less significant than those of extracts obtained via maturation with toluene or without any solvent. When phenol is present as a solvent, the resulting oil shale extract exhibits different characteristics. Despite having a relatively

Table 9. Elemental analyses of the oils obtained from RH (atomic %).

Oil	C %	H %	N %	S %	O %	H/C	O/C
Oil (Without solvent)	42.56	53.67	0.63	1.2	1.94	1.26	0.04
Oil (water)	45.41	49.00	1.52	1.28	2.54	1.02	0.050
Oil (toluene)	40.81	53.33	0.55	1.04	4.04	1.31	0.099
Oil (phenol)	45.36	50.88	0.77	0.77	2.2	1.12	0.07

O is determined by difference.

high average molecular weight, the mixture dispersion is considerably low. The properties of this extract are more promising compared to those obtained using water as a solvent, which yields an extract with a very low average molecular weight upon extracting organic matter from oil shale.

c) Analysis of maltenes by ^1H and ^{13}C NMR spectroscopy

To demonstrate the effect of phenol on increasing the aromaticity factor of the produced oils, the maltenes were characterized through ^1H and ^{13}C NMR spectroscopy after the removal of phenol. **Figure 9** and **Figure 10** present the obtained spectra. As shown in **Figure 9**, it is evident that the maltene obtained using phenol as the solvent contains a higher concentration of aromatic compounds. The ratio of aromatic C-H to aliphatic C-H in the oil was found to be higher, as observed in the ^{13}C NMR spectrum of the maltenes (**Figure 10**). The spectrum shows that the maltene obtained from the oil using phenol as the solvent contains a greater number of aromatic carbons (located between 110 and 140 ppm). This further confirms that the presence of phenol plays a role in increasing the aromaticity of the extracted oils. Apart from the aromatic carbons, the ^{13}C NMR spectrum also displays signals between 0 and 50 ppm, corresponding to aliphatic carbons, and signals between 50 and 110 ppm, which can be attributed to C-O ethers and C=C double bonds.

Table 10. Analysis of the obtained oils by SEC.

Solvent	\bar{M}_w^a	\bar{M}_n^b	I_p
Without solvent	2804	494	5.7
Toluene	2916	570	5.1
Phenol	2313	1353	1.7
Oil (water)	1340	420	3.2

^aWeight average molecular weight; ^bNumber average molecular weight; I_p : polydispersity index = \bar{M}_w/\bar{M}_n .

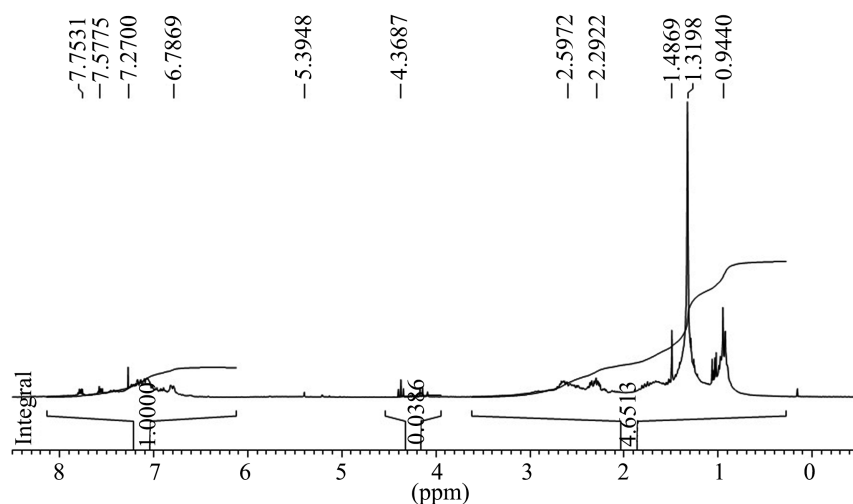


Figure 9. ^1H NMR spectrum of maltene obtained from oil extracted with phenol.

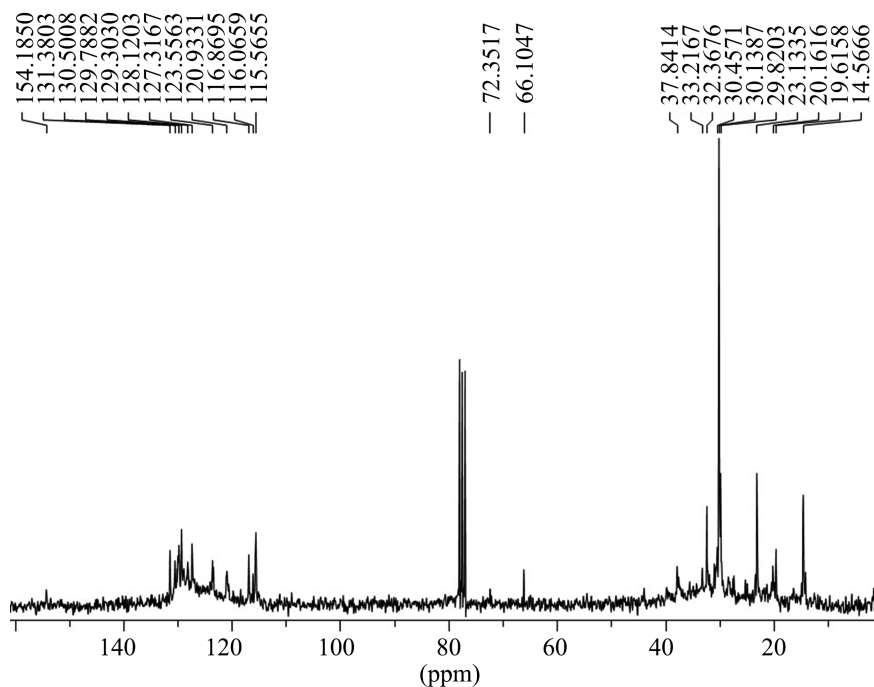


Figure 10. ^{13}C NMR spectrum of maltene obtained from oil extracted with phenol.

4. Conclusions

The results of this study demonstrate that:

- The presence of mineral matter affects the recovery yield and composition of the extracted oils from Moroccan oil shales.
- Oil shales that are free of carbonates sub-layers (RH) prove to be the best material for the extraction of organic matter.
- The organic matter contained in the R_3 layer of the Tarfaya oil shale deposit can be completely recovered using phenol under relatively mild conditions ($T = 390^\circ\text{C}$, $P = 1.2\text{ MPa}$, $t = 2.5\text{ hours}$).
- Phenol is a significant solvent in increasing the extraction yield and improving the quality of the produced oils compared to other solvents (toluene, water, phenol, quinoline, and shale oil) studied in this work. Phenol acts as a solvent capable of degrading the large molecules present in the oil shale, resulting in high-quality oil that is rich in maltenes and contains more aromatic compounds and less sulfur.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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