Beneficiation and upgrading of Jordanian oil shale

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Abstract: Evaluation possibility of a low-quality Jordanian oil shale from Sultani, central Jordan as an alternative clean fuel by flotation technique was investigated. Oil shale sample was characterized with mineralogical and chemical analysis. X-ray fluorescence spectrometer, X-ray diffraction and Fourier transform infrared spectroscopy showed that calcite is the dominant mineral followed by quartz mineral. Other minerals such as apatite and gypsum were detected. Thermogravimetric analysis revealed that mass loss is due to organic matter decomposition at 280–600°C and carbonate decomposition at 650–850°C Fourier transform infrared analysis showed the main organic groups. The effects of collector and frother doses, pulp concentration and pulp pH on the flotation performance were investigated. The kerosene and MIBC were used as collecting and frothing agents, respectively. The optimal flotation performance occurred for a collector dosage of 1000g/t, a frother dosage of 600g/t, a pulp concentration of 20g/L, a pulp pH of 4.

Keywords: Sultani oil shale, flotation, collector, frother

1. Introduction

Oil shale is considered one of the world's largest energy resources. It is estimated that the equivalent of oil shale around the world is about 30 times crude oil reserves (Dyni, 2006).

According to geological investigations carried out by the Natural Resources Authority (NRA), Jordan has large oil shale reserves exceeding 70 billion tons (Sahawneh, 2015).

Oil shale is generally defined as a sedimentary rock that contain organic material in its inorganic matrix. the inorganic material is mainly composed of dolomite and limestone (Altun et al., 2006).

Geologically, the Jordanian Oil Shale is rich in kerogen,, bituminous, argillaceous limestone that was deposited in shallow marine during the upper Cretaceous and lower Tertiary period (Maestrichtian-Danian periods) (Abed et al., 2009). The origin of the kerogen is the dead plants and animals formed during sediment deposition that had been transformed into a hydrocarbon-carrying rock under the influence of time, pressure, and temperature (Hruljova et al., 2013).

Flotation has been widely used in mineral separation. Previous studies indicate that flotation is inexpensive, it reduces the amount of mineral ash, and it enriches the material in useful minerals (Cheng et al., 2017). However, so far, only a few articles have concentrated on oil-shale flotation. Altun et al., (2006a) examined the effects of the conditioning time, flotation time, pulp density, particle size, and the frother dose on the flotation performance to upgrade of Turkish low grade oil shale by employing amine-type collectors. Their investigated experiments showed that pulp density was the most important parameter affecting flotation performance. The FTIR spectrum confirmed the organic-rich and highly humic character of oil shale. Li et al., (2012) studied the effect of doses of an oleic acid collector, the kerosene collector, and the frother on the floatability of Fushun oil shale. Their results reveal that oleic acid and kerosene collectors affect the enrichment of organic matter in the oil shale. Liu et al., (2019) believe that forth flotation is an effective method of enhancing the grade of the oil shale.

In Jordan, the Sultani OS deposit is one of the most important central Jordan OS deposits (Fig. 1), the proved reserves of Sultani oil shale deposit are about 1.1 billion tons and covering an area of 24 km² (Alali, 2015). There are no detailed works dealing with the enrichment of organic matter of Jordanian oil shale by flotation method. The present study aims to evaluate the processing of Jordanian oil shale

obtained from Sultani using froth flotation technique for obtaining concentrate rich in kerogen, which can be used in a retorting process as an energy source. In addition, the parameters affecting the flotation performance such as reagents dosages, pH, and pulp concentration (solid-liquid ratio) were investigated.

2. Materials and methods

2.1. Raw material

Oil shale composite sample used in the present investigation was obtained from Oil shale Sultani deposit that is region of the central part of the Jordan (Fig. 1). The Sultani deposit is located about 115 km south of Amman, adjacent to the desert highway. Field inspection by author identified the OS type as gray, grey brown and calcareous bituminous marl. The sample was crushed and spilt, after proper mixing into 250 g samples.
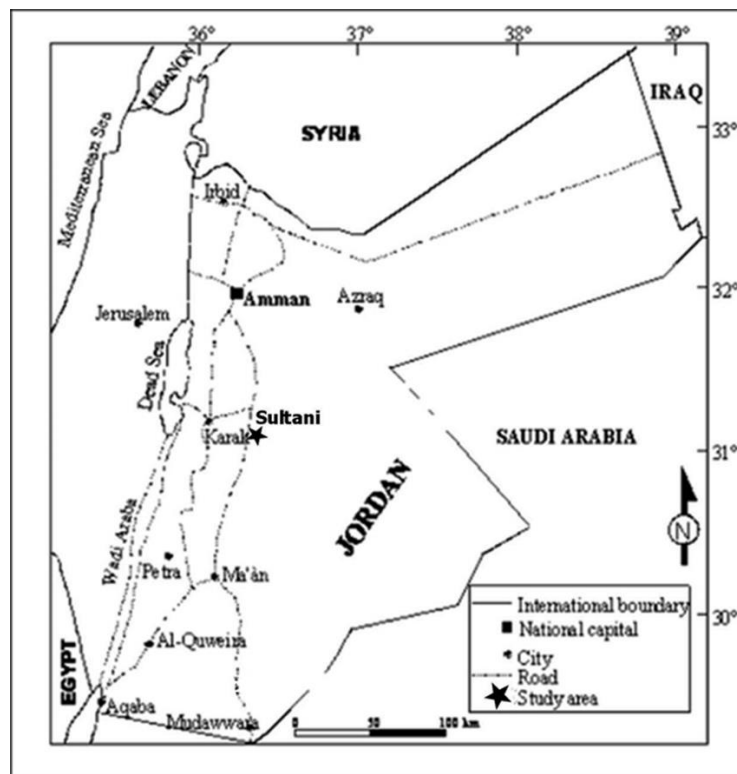

Fig. 1. Location of Sultani oil shale deposit, central Jordan

2.2. Methods

2.2.1. Chemical analysis

The oil shale sample was calcined at 1000°C, fused with lithium metaborate and cast into discs. The discs were analyzed by X-ray fluorescence (XRF) spectrometry using a Philips PW1400 Wavelength Dispersive Sequential X-ray fluorescence (XRF) Spectrometer and *SuperQ* software, and the results expressed as a percentages of the major oxides in each sample.

2.2.2. Mineralogical analysis

The Mineralogical, chemical, physical, and mechanical analyses of the oil shale sample were carried out at the Institute of Mineralogy and Institute of building materials, Leibniz University Hannover, Germany. Flotation studies of the oil shale sample were carried out at the faculty of Georesources and Material Engineering, RWTH-Aachen University, Aachen, Germany.

The mineralogical study was conducted through X-ray powder diffraction (XRD). The samples were dried at 105 °C for 24 h in an oven dryer. The analysis for mineral identification was performed with a

Bruker AXS D4 ENDEAVOR X-ray diffractometer using Ni-filtered Cu-Kα radiation and with the generator operating at 40 kV and 40 mA. The goniometer velocity was 0.02° (2θ) per 1 s in the interval between 4 and 80° (2θ). The powder data was analyzed with the Stoe WinXPOW software package. The FTIR analysis was obtained using a Bruker IFS66v FTIR spectrometer in the range of 400-4000 cm^{-1} using KBr pellets technique (analytical grade KBr from Merck) with the same weight as the dried oil shale samples (110°C). The sample (about 10-12 mg) was accurately weighed on a single pan electronic balance and thoroughly mixed with the spectroscopic grade KBr powder (about 200 mg) in an agate mortar. The FTIR spectra are processed using the Bruker OPUS software package at 2 cm^{-1} resolution in an absorbance mode.

The thermogravimetric analysis (TGA) of the oil shale sample was carried out in a Thermal Analyzer (Model: Setaram Setsys EV 1750). The TGA analysis was performed by taking approximately 25 mg of each sample in the alumina crucible, which was heated from ambient temperatures to 1200°C with the corundum (Al_2O_3) as an inert standard to 1200°C at a heating rate of 10°C/min in the nitrogen environment. The experiments were conducted at least three times for each sample. The error of mass loss and temperature was less than ±0.04μg and ±1°C, respectively.

The scanning electron microscopy (SEM) using a JEOL JSM-6390A system together with the EDAX energy-dispersive. X-ray analyzer was used to study the morphology of the mineral. The oil shale samples were carbon coated used an Edwards SCANCOAT SIX sputtering coater. Samples were mounted on a standard aluminum SEM stub using sticky electron-conductive carbon tabs. SEM investigations were carried out into the 20 kV acceleration voltages.

2.2.3. Flotation test

A representative oil shale sample "20 Kg" of Sultani was crushed using laboratory scale jaw crusher and then ground using and attrition mill under wet conditions to obtain feeds passing <100 μm size. For the flotation experiments, firstly the oil shale sample and water were agitated until complete wetting of the sample was assured. The pH of the pulp was then adjusted using HCL and/or NaOH solutions. Next, the collector was added and the pulp was conditioned. The frother was added during the last minute of the conditioning period and the air was introduced to the pulp at the end of conditioning. The froth product, collecting as the top layer, was removed in to a tray. The concentrate and the residue products were filtered, washed and dried in an oven at 105°C. The Effectiveness of cleaning was assessed in terms of the contents of kerogen concentrate and combustible recoveries of the concentrates. Therefore, the products were analyzed for the content of kerogen and combustible recovery values. Flotation of Jordanian oil shale was investigated as a function of frother and collector types, doses and pulp pH. Collectors are specific reagents used to modify the surface behavior of certain minerals in to hydrophobic, i.e. water repellent form. Kerosene as a common collector in oil shale.

3. Results and discussion

3.1. Characteristic analysis

The major chemical constituents of the oil shale sample were analyzed by XRF and expressed as the relevant oxides are listed in Table 1. The main oxides are CaO (32.03%), SiO_2 (20.51%), SO_3 (3.45%), Al_2O_3 (2.66%), P_2O_5 (3.32%), Fe_2O_3 (0.95%), MgO (0.76%), TiO_2 (0.11%). Na_2O (0.13%) and K_2O (0.23%). The results (Table 1) indicate that the loss on ignition (LOI) of the investigated oil shale sample was 35.35%. This is due to organic carbon and carbonate presence. Silica oxide is associated to quartz which is a primary silicate mineral, whereas calcium oxide is associated to calcite. The presence of SO_3 suggests that the CaO may be responsible for retention of sulphur in the oil shale as $CaSO_4$.

Table 1. Chemical analysis of Sultani oil shale deposit

SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	P_2O_5	LOI*
20.51	2.66	0.11	0.95	32.03	0.76	0.13	0.23	3.45	3.32	35.35

*LOI: loss on ignition

The mineral composition of the sample was analyzed using X-ray diffraction (XRD). Fig. 2 shows the XRD spectrum of raw Jordanian oil shale. It is clear from Fig. 2 that calcite is the dominant phase in the minerals of the oil shale followed by quartz. The minor phase was phosphate as apatite with traces gypsum. The results show the most that most characteristic peaks of calcite mineral are located at 3.36 Å, 3.04 Å, 2.49 Å, 2.29 Å, 2.10 Å, 1.91 Å, 1.88 Å, and 1.60 Å. The most characteristic peaks of quartz mineral are represented at 4.26 Å and 3.35 Å (Gougazeh and Buhl, 2010), while those at 2.8 Å and 2.70 Å are the characteristic peaks of apatite.

The FTIR spectra of raw oil shale is shown in Fig. 3. Table 2 also gives the characteristic bands of kerogen and inorganic minerals. The FTIR spectrum shows that the sample is rich in carbon and oxygen. The bands in the range 4000–2800 cm^{-1} in Fig. 3 correspond to the stretching vibrations of OH, NH and NH_2 groups of phenol and alcohol. The relatively high intensity of the broad OH band is found at 3420 cm^{-1} is attributed to the presence phenolic hydroxyls and carboxylic OH groups. The sharp bands at 2924 cm^{-1} and 2850 cm^{-1} are belong to aliphatic C-H stretching vibrations of CH_3 and CH_2 (Boukir et al., 1998). Additional aliphatic C-H peak is seen at 1106 cm^{-1}. The band at 1792 cm^{-1} is due to the C=O stretching vibration of carboxyl and carbonyl groups. The strong C–OH band at 1035 cm^{-1}, C–H band at 872 cm^{-1} and C–C band at 675 cm^{-1} show an intense aromatic matrix in the oil shale (Boukir et al., 1998). Several distinct and strong aliphatic C-H bands (2928, 2856, 1106 cm^{-1}) of CH_3 and CH_2, the broad aromatic of band of C-H and C-C (875 and 675 cm^{-1}) are due to high organic matter content of the
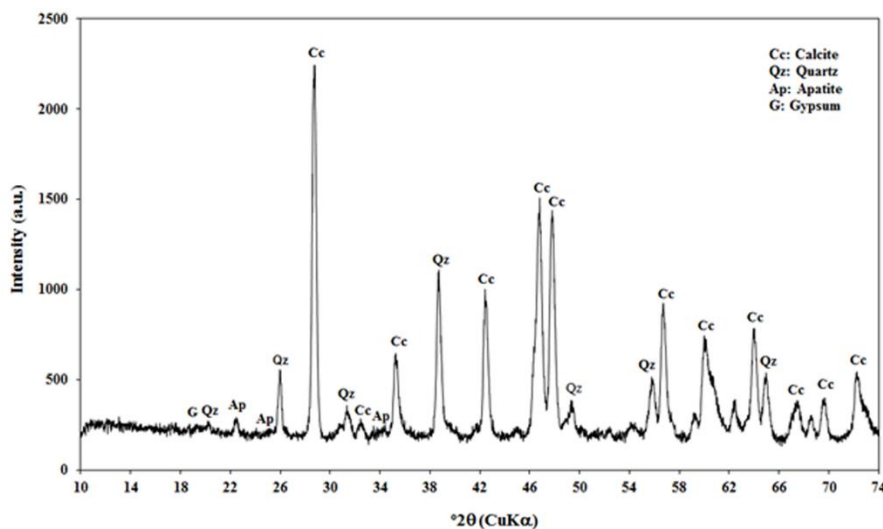

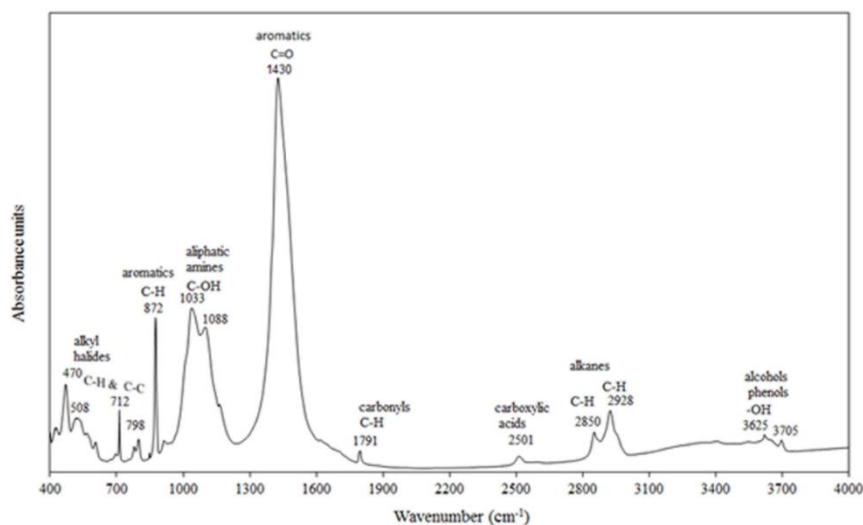Fig. 2. XRD pattern of raw Sultani oil shale, central Jordan

Fig. 3. FTIR spectrum of raw Sultani oil shale, central Jordan

Table 2. Major characteristic bands in FTIR spectra of the main components of Sultani oil shale

Wavenumber (cm^{-1})	Component
2518, 1430, 872, 742, 716, 697, 694	Calcite
1088, 798, 780, 778	Quartz
2924, 2928, 2850, 2852, 1750, 1625, 1460, 1000-1030	Kerogen (OM)
3710, 3655	Kaolinite
1164, 430, 420	Pyrite
1440, 530, 470	Silicate

sample. The relatively strong and broad form of the hydroxyl (3420 cm^{-1}) and carbonyl bands (1627 cm^{-1}) reveal the humic character of oil shale. Different organic functional groups were detected as indicated by each absorption band. The obtained results are agreeing with the fact that oil shale contains organic matter usually as kerogen, which will be the source of oil (Wright et al., 2015).

The thermogravimetric curve (TGA) obtained for the raw Sultani oil shale shale sample are shown in Fig. 4. Mass change of a substance is measured as a temperature function whilst the substance temperature is subjected to a controlled temperature program. The thermogravimetric curve shows that there are three main temperature stages. Fig. 4 illustrates that the first phase of low temperature stage occurs up to 280 °C where water loss is expected, the small mass loss (~1 %) is characterized by the loss of moisture in the structure. The second stage occurring in the temperature range of 280-600°C (approximately 21%), which the significant region of oil and gas production and results in the breaking down of the organic matter in the oil shale. Finally, the loss of the major mass between 600ºC and 850ºC which is equivalent to 20 % represents the decomposition of the mineral matter containing carbonate (calcite) minerals.
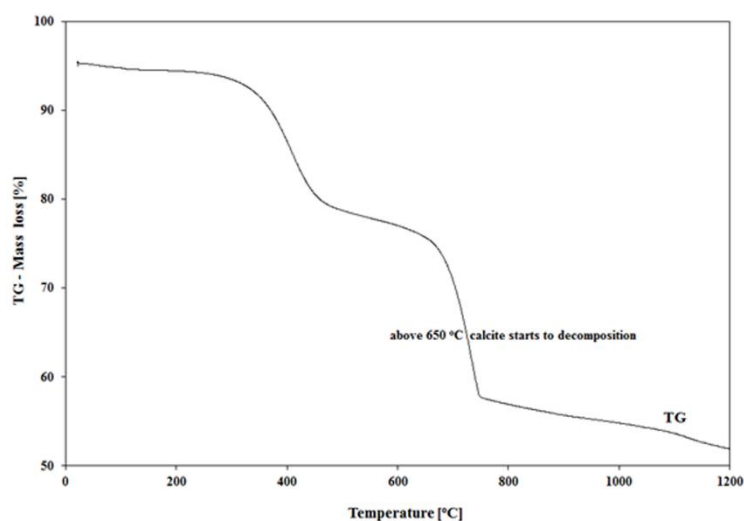

Fig. 4. TGA pattern of the raw Sultani oil shale sample

3.2. Flotation Results

The flotation of Jordanian oil shale was started using frothers and collectors which proved to be very efficient for the flotation of oil shale. Froth flotation experiments were conducted to study the separation of organic (kerogen) matter from inorganic minerals. The flotation is a well-known physico-chemical method and commonly applied to enrich solid fossil fuels. The flotation of oil shale (kerogen) depends on its natural floatability due to the hydrophobic nature as hydrocarbons. The main working conditions affecting the flotation of oil shale were investigated, pulp concentration (S/L ratio), reagent dosages (frother and collectors), pH of conditioning stage of oil shale. Flotation experiments with kerosene were conducted as a collector in conjunction with frother. It seems that the addition of kerosene increases the weight percent of the float but the kerogen grade was lower than that when using frother alone. This may be due to the entrapment of gangue mineral with the concentrate in the float fraction. The flotation

experiments were carried out in a standard laboratory type Denver D-12 flotation cell. Kerosene and MIBC (Methyl isobutyl carbinol) were used as collector and frother, respectively. The optimum of the flotation conditions are given in Table 3.

Table 3. Experimental conditions for flotation tests

Parameters	Components
Particle size	<100 μm
Cell Volume	1 Liter
Pulp density	20 % solid by weight
Pulp pH	4
Type of frother	MIBC
Type of collector	Kerosene
Flotation speed	900 rpm
Conditioning speed	1800 rpm
Conditioning time	15 min
Flotation time	4 min

3.2.1. Effects of pulp concentration

The effect of pulp concentration on oil shale recovery was investigated. The experimental parameters of pulp concentration used for the raw oil shale are as follows: a conditioning speed of 1800 rpm (revolutions per minute); a collector dosage of 1000 g/t; and a frother dosage of 600 g/t at pH 4. Solid-to-liquid ratio may have a significant effect on the recovery of kerogen [organic matter (OM)] by flotation. The pulp concentrations ranging from 50 to 400 g/L (Fig. 6).

Fig. 6 shows the influence of pulp concentration on the flotation performance of Sultani oil shale investigated at pH 4 and all the obtained results are represented in Fig. 6 at all levels of float recovery. As can be seen from Fig. 6, as the concentration increases, the concentrate recovery initially increases, and then, it slowly decreases. Fig. 6 indicated that the highest recovery (94.6 %) and kerogen content (53.8 %) were achieved at the solid-liquid ratio 1:4 (20 % of solid) and at pH 4. It is clear that the pulp concentration (S/L ratio) may have a significant effect on the recovery of organic matter (kerogen) by flotation. Therefore, 20 % was selected as the optimal S/L ratio.

3.2.2. Effects of conditioning speed

The speed of conditioning (agitation) is clearly affecting the performance of flotation process (the mixing strength of the pulp, temperature of the pulp, aeration rate, bubble size, etc.) So, it is necessary to check the speed of agitation. The pulp concentration was kept at 20 g/L.
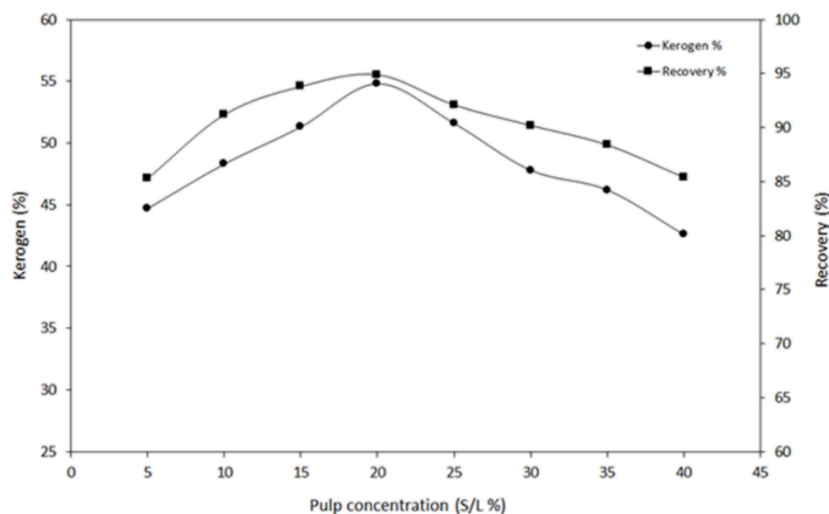

Fig. 6. Influence of pulp concentration on the flotation performance of Sultani oil shale

3.2.3. Effects of collector and frother quantities

The effect of concentration of reagents (collector and frother quantities) on the efficiency of kerogen (OM) flotation was investigated. The experimental conditions used as follows: a pulp concentration of 200 g/L (20 % of solid), a conditioning speed of 1800 rpm (revolutions per minute), 15 conditioning time min, flotation time 4 min and a frother concentration of 600 g/t at pH 4. The kerosene dosages range from 200 to 1400 g/t, which are shown in Fig. 7.

Figs. 7 and 8 illustrate the effect of kerosene and MIBC addition on the flotation performance of Sultani oil shale, respectively. The results obtained show that the recovery of float and percentage of kerogen (OM) improves with an increase in the collector and frother quantities, but continuing increase in reagent concentration reduces OM content in concentrate (Figs. 7 and 8). The recovery % of the float decreases with increasing the collector dosage up to about 90.8 % at 1200 g/t ore with kerogen of 46.1 %. Fig. 7 indicated that the maximum recovery was 94.5 % at a kerosene dosage of 1000 g/t ore with kerogen of 50.2 % at pH 4. Therefore, 1000 g/t was selected as the optimal kerosene dosage. It is suggested that kerosene molecules more attached to organic grains via hydrophobic bonding, which increases their hydrophobicity, than negatively charged silicate particles.

Kerosene dosages were maintained at 1000 g/t, while the different dosages of frother (MIBC) were tested. MIBC dosages tested were ranging from 200 to 1000 g/t at pH 4 and the experimental results are illustrated in Fig. 8. Fig. 8 reveals that the highest recovery and kerogen content (OM) of the froth concentrate were achieved at the dosage of 600 g/t with 94.8 % and 45.8%, respectively. Therefore, 600 g/t was selected as the optimal MIBC dosage.
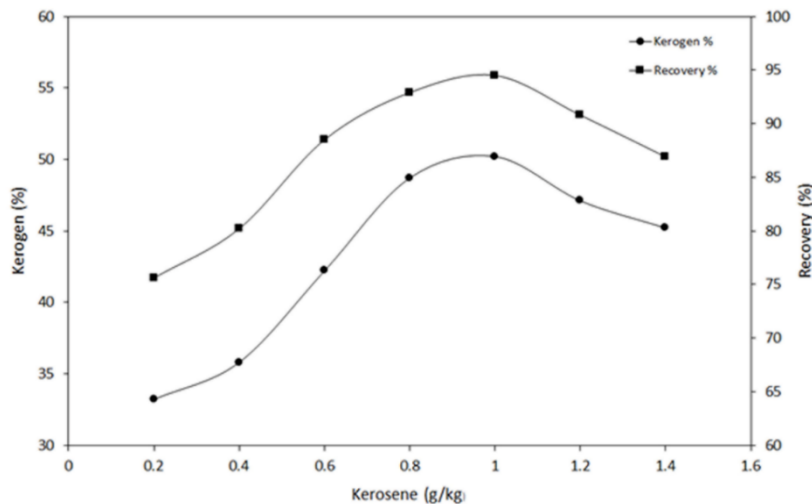

Fig. 7. Influence of the effect of kerosene addition on the flotation performance of Sultani oil shale
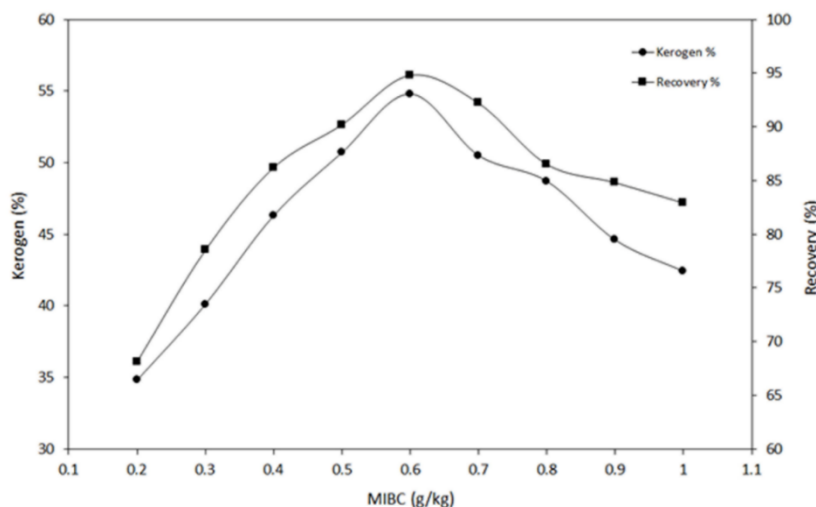

Fig. 8. Influence of MIBC addition on the flotation performance of Sultani oil shale

As the float recovery increases, the percentage kerogen (OM) increases. Float recovery of these magnitudes can be achieved by changing the collector and frother quantities (Figs. 7 and 8). In summary, the optimal reagent dosages were 1000 g/t and 600 g/t for the collector and frother, respectively.

3.2.4. Effects of pulp pH

Fig. 9 shows the effect of pulp pH on the recovery of kerogen (OM). The results obtained indicate that the significant effects on the flotation efficiency were achieved in the acidic pH medium. The recovery of float and thus the percentage of kerogen recovery (OM) significantly decreases as the pH value increases from acidic to basic pH ranges. It is clear that the best results were achieved at pH 4. The results indicate that at pH 4, the recovery of the concentrate was 95.5 % with kerogen of 53.6 % (Fig. 9). In the basic and neutral pH ranges, pH more than 7, the rate of flotation was slow due to the dissolution of carbonate minerals as well as the disintegration of oil shale particles.
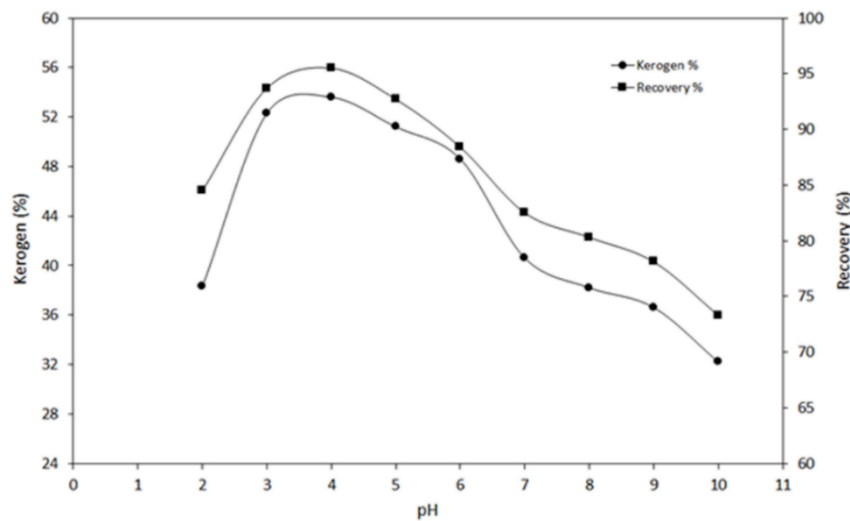

Fig. 9. Effect of the pulp pH on the recovery of kerogen (OM) of Sultani oil shale

4. Conclusions

Oil shale is a potential alternative energy resource. Thus, methods of improving the recovery and grade of oil shale are of great benefit. In this study, the flotation process was adopted and the flotation performance of the oil shale was also investigated. In addition, the effect of different parameters such as concentration of chemical reagents, pulp pH and solid-to-liquid ratio was tested and the conditions that provide the most favorable concentrate were determined.

Mineralogical and chemical analyses showed that the Jordanian Sultani oil shale is a calcareous organic-rich sedimentary rock. The mineral constituents of the oil shale is calcite as detected from XRD and XRF analysis. Minor amount of silica as quartz, and small amounts of apatite and gypsum. Major oxides presents are of CaO and SiO_2 which are equal to 32.03 and 20.51, respectively). Thermogravimetric analysis curve was obtained from TGA analysis. The decomposition process of Sultani oil shale involves three stages. The second mass loss can be observed between 280 and 600ºC, a stage governed by the thermal decomposition of the hydrocarbonaceous material (organic matter), which was about 21%. Thermal analysis revealed that mass loss is due to carbonate decomposition at 600–850°C. FTIR analysis exhibited the main organic groups present in the Sultani oil shale.

The obtained results of flotation process indicate that the effective kerosene dosage as a collector is 1 g/kg at the recovery of about 95% with kerogen of about 50%. The frother and pulp pH were playing a role in enhancing the selective recovery of kerogen. Also, higher solid content reduces both recovery and grade. By using a collector concentration 1000 g/t kerosene as a collector and 600 g/t of MIBC as a frother concentration at pulp concentration of 20 g/L and pH 4, kerogen of 50.2% with recovery of 94.5% was obtained from oil shale sample of 18%. The significant value of kerogen (OM) of the concentrate product of flotation experiments indicates that it would be possible to evaluate Sultani oil shale as a relevant source of oil.

Acknowledgments

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