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ORIGINAL ARTICLE

Geochemistry and environmental impacts of retorted oil shale from Jordan

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Abstract Physical and chemical characterization of spent oil shale (OS) from El-Lajjun area has been carried out and compared with the original OS. The spent shale (SS) is subjected to leaching tests to detect the possibilities of heavy metals released from it into the environment. Standard column leaching experiments have revealed no detectable release of heavy metals to the percolating water. The effectiveness of the SS in removing Pb^{2+} from wastewater has been investigated. The SS is very efficient in removing most of Pb^{2+} where 1 m^3 of SS has an efficiency to remove from 64 to 94% of Pb^{2+} from about 1,300 m^3 wastewater sample containing 50 ppm Pb^{2+}. The efficiency decreases substantially with increasing Pb^{2+} concentration in the wastewater. In real situations, where Pb^{2+} concentration is very low (i.e., less than 5 ppm), the efficiency of the SS is expected to be 100%.

Keywords Jordan · Spent oil shale · Heavy metals leaching · Water treatment · Pb-removal

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Introduction

Oil shale (OS) is a compact sedimentary rock containing organic, high-molecular weight mineraloid called kerogen. Kerogen in OS yields petroleum hydrocarbons only upon destructive distillation by heat at about 500°C. At present, OS is being utilized on commercial basis in Astonia, China, Brazil, Canada, and Germany.

Oil shale in Jordan had been known since ancient times. The El-Lajjun OS deposits occurrence in central Jordan (about 130 km south of Amman) were discovered by the German Geological Mission in 1966 (Bender 1974). Later on, discoveries were recorded in several localities in Jordan with a total reserve of about 4.4 billion tons (Jaber and Probert 1997; Hamarneh 1998). Jordanian OS deposits are kerogen-rich bituminous argillaceous limestone of the Muwaqqar Chalk–Marl Formation that was deposited in a shallow marine, anoxic environment during the Maastrichtain and Paleocene times (Powell 1989). The origin of the kerogen is the organic matter of plants and animals remains that were accumulated in Tethys Ocean that covered most of Jordan during the Upper Cretaceous and Tertiary times (Abed and Amireh 1983). The OS deposits in the El-Lajjun area occur as elongate, flat to lenticular body occupying faulted basins (Abu-Ajamieh 1989). The organic content varies laterally and vertically (Hamarneh 1998). Proprieties of the El-Lajjun OS are summarized in Table 1.

Spent (retorted) shale containing organic matter and heavy metals stored in spent shale (SS) dumps is one of the main problems of OS industry (Jaber and Probert 1999). In 2005, the proposed charge of storing environmentally hazardous SS in Estonia, as an example,

Table 1 Specifications of El-Lajjun oil shale (Hamarneh 1998)

Average oil content (wt%)	10.5
Total organic matter (wt%)	22.1
Calorific value (kcal/kg)	1,590
$CaCO_3$ (wt%)	54.3
SO_3 (wt%)	4.8
Bulk density (g/cm^3)	1.81
Moisture (wt%)	2.43

was 4.5 times more than that of OS ash (Arro et al. 2002). This may make production oil from OS economically unprofitable.

The main objective of this work is to carry out physical and chemical characterization of the SS material from El-Lajjun OS in order to determine its environmental impact. Therefore, the mobility of the ionic constituent in the SS as a result of leaching by the action of infiltrated rainwater will be investigated and evaluated. The possible leaching of toxic ions from OS to surface and groundwater recourses has been already recorded in the literature (Meyer et al. 1985; Shirav and Robl 1993). Trace element mineral transformations associated with hydration and re-carbonation of SS was also studied (Essington 1989).

The possible utilization of the SS from El-Lajjun area in environmental application has been also evaluated in the present work. The efficiency of the OS and the SS to remove Pb, Cd, Cu, Zn, and Ni from aqueous solution has been investigated by Gharaibeh et al. (1999) and Al-Asheh and Banat (2001). Their experiments were batch experiments carried out using solution loaded with multi-heavy metals at very low concentrations (i.e., $Pb^{2+} < 10$ ppm). The current experiments are performed by passing 50, 150, 180, and 200 ppm Pb^{2+} influent solutions in a column loaded with a bed of SS at a constant flow rate.

Materials and methods

Five representative OS rock samples and one bulk sample from El-Lajjun area were collected. The samples were washed, crushed and sieved to collect the less than 4 mm fraction, and pyrolyzed at 500°C for 5 h to vaporize all solid kerogen. Four portions of each sample were collected based on the particle size distribution which are the size fraction >4, 2.0–2.83, 0.71–1.0, and <0.25 mm size fractions. X-ray diffraction (XRD) analysis and multi-elemental analysis using ICP-AES technique were performed to evaluate the mineralogical and chemical constituents. Mineral identification was carried out using X Pert MPD-Philips X-ray diffractometer by Co Kα radiation hosted in the Natural Resources Authority. The technical parameters of the SS from the bulk sample were verified. Packed-bed density and attrition resistances were determined following the recommendations of Mercer and Ames (1978). Surface area is estimated by methylene blue (MB) method using the amount of MB adsorbed by the SS sample from an aqueous solution. It is determined from the measured amount of MB remaining in solution, which occurred spectrophotometrically at a constant sample weight and different concentration of MB.

The size fractions 2.0–2.83 mm (sample 1) and size fraction 0.71–1.0 mm (sample 2) from the SS were selected in order to evaluate their impact on the environment by using column experiments. Therefore, 35 g of each sample was loaded in a column 22 mm in diameter and leached by 2 L distilled water at a slow flow rate. The column effluent was collected as volume. The first 100 mL were collected as ten samples, 10 mL each; then 20 samples were collected, 100 mL each. The heavy metals V, Pb, Zn, Cr, Ni, and Cu were measured using the AAS. The same procedure was repeated using (6, 5, 4.5, and 1) pH solutions ($2HNO_3/H_2SO_4$) instead of distilled water.

The chemical oxygen demand (COD) and total organic carbon (TOC) were also measured in the collected effluent to evaluate the possibilities of leaching of organic pollutants. The closed reflux, titrimetric method is used to determine the COD, whereas the TOC of the analyzed samples was measured by using Shematsu TOC-V_{CPN} instrument.

To examine the ability of SS to absorb toxic heavy elements from wastewater, Pb^{2+} solutions of different concentrations have been used as influent solutions. The experiments were performed by passing 50, 150, 180, and 200 ppm Pb^{2+} influent solutions in a column loaded with a bed of SS at a constant flow rate by using the same procedure of column preparation used earlier. The experiment was repeated several times using sample (2). The effluent solution from the column was collected at constant volumes every 200 mL and the concentration of Pb^{2+} was determined.

Results and discussion

Fisher assay

The results of the Fisher assay of selected size fractions of the bulk sample illustrated in Table 2 indicate that oil yield is from 14.0 to 14.6%. Water content in the samples is between 2.2 and 3.0% and their gas loss varies from 5.2 to 5.7%. The SS content is very high

Table 2 Fischer assay data sheet of El-Lajjun oil shale

Grain size	>4.0 mm	2.0–2.83 mm	0.71–1.0 mm
Oil yield (%)	14.6	14.0	14.4
Water content (%)	2.2	2.6	3.0
Gas loss (%)	5.2	5.7	5.3
Spent shale (%)	78.1	77.8	77.4
Total	100.0	100.0	100.0

making up to 78.1%. Such results are in full agreement with those reported in a previous paper for the same deposit (Jaber et al. 1999).

Mineralogical and chemical properties

The analysis reveals that mineralogical constituents of the original OS samples are calcite and quartz with traces of apatite, hematite, and clay. This is supported by the chemical analysis, which shows that the average CaO and SiO_2 content in the OS is 27.38 and 16.80%, respectively (Table 3). The other less important major oxides include Al_2O_3, P_2O_5, and Fe_2O_3 with average of 2.79, 2.17, and 1.41%, respectively.

The major and trace elements constituents of selected size fractions from the original bulk oil shale sample (BOS) compared with the SS sample reveal the differences in chemical composition in the size fractions from both samples (Table 4). In detail, the SiO_2 percent ranges from 25.37% in the fine-grained size fraction of the BOS to 16.41% in the coarse-grained size fraction and from 32.41 to 21.02% in the SS taking same trend. This clearly indicates that quartz content is more concentrated in the fine-grained size fraction, to the contrary of the CaO content, which is higher in the coarse-grained size fraction relative to the fine-grained fraction. Meanwhile, the trend for the P_2O_3 is similar to that for the SiO_2. Trace elements analyses shown in Table 4 indicate that both the BOS and SS are enriched with Cr, Cu, Zn Ni, Sr, and Pb compared with the pure limestone and sandy limestone facies. This indicates that these elements are associated with the hydrocarbons content of OS.

Table 3 Chemical composition of El-Lajjun original oil shale samples

wt%	OS1	OS2	OS3	OS4	OS5	Average
SiO_2	16.41	15.71	16.65	15.90	19.32	16.80
TiO_2	0.12	0.12	0.11	0.11	0.11	0.11
Al_2O_3	2.97	2.61	2.90	2.81	2.68	2.79
Fe_2O_3	1.40	1.40	1.45	1.42	1.37	1.41
MnO	0.03	0.03	0.03	0.03	0.03	0.03
MgO	1.00	0.91	1.02	1.04	1.07	1.01
CaO	28.22	26.95	26.96	26.94	27.83	27.38
Na_2O	0.00	0.00	0.31	3.63	0.30	0.85
K_2O	0.25	0.26	0.29	0.35	0.23	0.28
P_2O_5	2.26	2.17	2.17	2.07	2.20	2.17

Table 4 Major and selected trace elements constituents of the studied size fractions of the bulk oil shale and spent shale samples

	Bulk oil shale		Spent shale	
	Sample 2 (0.71–1.0)	Sample 1 (2–2.8)	Sample 2 (0.71–1.0)	Sample 1 (2–2.8)
Major oxides (wt%)				
SiO_2	25.37	16.41	32.41	21.02
TiO_2	0.13	0.11	0.12	0.14
Al_2O_3	2.72	2.59	3.46	3.54
Fe_2O_3	1.30	1.43	1.65	1.67
MnO	0.01	0.00	0.01	0.00
MgO	0.61	0.00	0.77	0.00
CaO	20.64	28.57	26.61	34.5
Na_2O	0.23	0.33	0.28	0.26
K_2O	0.54	0.24	0.68	0.40
P_2O_5	3.16	2.06	4.05	2.55
SO_3	2.12	2.01	1.10	0.92
LOI	41.21	45.93	28.76	36.27
Total	98.04	98.88	99.9	100.47
TOC (wt%)	27.77	11.29	5.65	5.02
V (ppm)	80	116	202	82
Cr	282	479	395	279
Ni	149	646	296	118
Cu	115	79	215	89
Zn	105	455	515	233
Sr	522	1,025	871	497
Pb	18	25	18	31

Recalculation of the chemical constituents of the bulk and spent OS samples on the basis of absence of organic carbon is plotted in Fig. 1, which shows comparison between the elements and percents of loss or gain after retorting. Figure 1 reveals that most of the chemical constituents do not exhibit any changes as a result of retorting. Major loss occurs to the loss on ignition (LOI), which is up to 50%. This is due to escaping of the water content and other gases from the shale due to retorting. The noticed loss of TiO_2, MnO, and some heavy elements (Sr, Ni, Cu, Pb, and Cd) is most probably related to adsorption of these constituents by organic matter.

The LOI in the BOS and the SS samples is high (Table 4). This value is related to the presence of several components, including the TOC, and CO_2 in carbonates and water content in the minerals. The LOI varies in the BOS between 41.21% in the (0.71–1 mm) size fraction and 45.93% in the (2–2.8 mm) size fraction; whereas, in the SS, it varies from 28.76 to 38.66% (Table 4).

The TOC analyses of the size fractions of the original OS samples indicate that TOC content increases

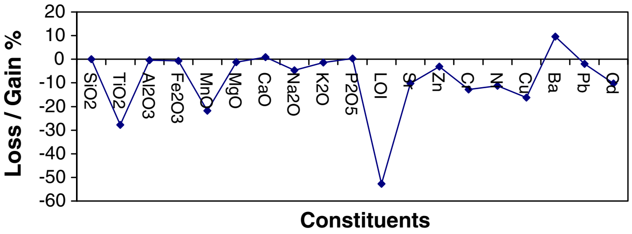

Fig. 1 Spider diagram showing chemical composition of the spent shale relative to chemical composition of original oil shale sample

toward the finer-size fraction. In details, the TOC content in the 0.71–1.0 mm size fraction is about 27.77% by weight, whereas in the 2–2.82 mm size fraction, it makes up only 11.29% (Table 4). A similar trend was also noted in the SS sample, i.e., the fine-grained fraction has a higher TOC content than that of the coarse-grained fraction. The SO_3 content in the bulk samples is 2.12 compared with 1.10 in the SS.

Technical parameters

The size fractions 2.0–2.83 mm (sample 1) and size fraction 0.71–1.0 mm (sample 2) have been selected to perform column experiments, and were subjected to detailed characterization. As can be noticed in Table 5, surface area is between 28.88 and 30.39 m^2/g in samples 1 and 2, respectively. The wet attrition resistance test is a technical parameter that measures the resistance of material to abrasion when it is used in column operation. Table 5 indicates that sample (2) is more resistant to aggressive environments because the wet attrition resistance is 1% compared with 1.98% in sample (1).

Leaching of heavy elements

Chemical analyses of the effluent solution collected from the column indicate that this effluent displays absence of leaching for all of the analyzed heavy elements (Cu, Pb^{2+}, Zn, Cd, Ni, and Cr) when distilled water, 6, 5, and 4.5 pH solutions were used as percolating solutions (Table 6). Whenever any traces of heavy metals are recorded, the values were below the detection limit of the instrument. In conclusion, trace elements in the SS are immobile and will not be leached to the groundwater by the action of water infiltration through the SS piles. When highly acidic solution (1 pH) percolated through the column, rigorous movement of SS particles was noticed due to the reaction with the carbonates present in the sample. The amount of Cu and Cd in the first 10 mL collected from the effluent column was 3.52 and 0.50 ppm, respectively, indicating slight leaching of these elements. It is important to mention that this acidic condition is extreme and rarely occurs in natural environments. Among the other results of this experiment, the SS slightly raises the pH of percolating solution from about 5.9 to 7.3. In some cases, traces of organic compound were detected in the effluent (TOC < 10 ppm).

Table 5 Technical parameters of spent shale from the bulk sample

	Sample 1	Sample 2
Surface area (m^2/g)	28.88	30.39
Packed-bed density (g/mL)		
Dry	0.74	0.75
Wet	0.77	0.78
Wet attrition resistances (%)	1.98	1.00
Grain size (mm)	2.0–2.83	0.71–1.0

Application of spent shale in wastewater treatment

The operation conditions of the experiments to remove Pb^{2+} from the wastewater are listed in Table 7. When the initial Pb^{2+} concentration is 50 ppm, it has been found that the SS bed is very efficient in removing most of Pb^{2+} from wastewater. It has been determined that the Pb^{2+} concentration in the first 200 mL was 4 ppm, and at 10,000 mL [equivalent to 1,300 bed volume (BV)] Pb^{2+} concentration was less than 19 ppm (Fig. 2). Consequently, 1 m^3 of SS from El-Lajjun area has an efficiency to remove from 94 to 64% of Pb^{2+} from about 1,300 m^3 of wastewater containing 50 ppm Pb^{2+} (Fig. 3). The results of treating solutions containing 150, 180, and 200 ppm of Pb^{2+} are summarized

Table 6 Column parameters and results of leaching tests

Parameters	Sample 1	Sample 2
Weight of sample (g)	35.0	35.0
Bed length before flow (cm)	16.5	14.5
pH of influent (distilled water)	5.9	5.85
Flow rate (mL/min)	0.6	0.8
Results		
pH of effluent	7.5	7.10
COD (mg O_2/L)	49.84	0
TOC (ppm)	9	
Pb, Cu, Zn, Cd (pH 6–4.5)	Not detected	Not detected
Pb, Zn, Ni, Cr (pH 6–1)	Not detected	Not detected
Cu (pH = 1) in the first 10 mL	3.52 ppm	
Cd (pH = 1) in the first 10 mL	0.50 ppm	
Other features	Oily odor	Oily odor

Table 7 Operation conditions and results of Pb removal from wastewater

	1	2	3	4
Pb^{2+} concentration in the initial solution (ppm)	**50**	**150**	**180**	**200**
Weight of sample (g)	10.0	10.0	10	5.0
Length of bed in column (cm)	3.9	4.1	4.0	2.0
Bed volume (mL)	7.7	7.7	7.7	3.85
Volume of Pb^{2+}-solution (L)	10.00	5.20	5.10	6.03
Volume of Pb^{2+}-solution (bed volume, BV)	1,300	675	662	1,566
Flow rate (mL/min)	15.0	15.0	15.0	15.0
Pb^{2+} concentration in the first 200 mL (ppm)	4	25	63	97
Pb^{2+} concentration in the final solution (ppm)	19	124	141	200
Removal efficiency (%)	94–64	87–17	65–22	52–0

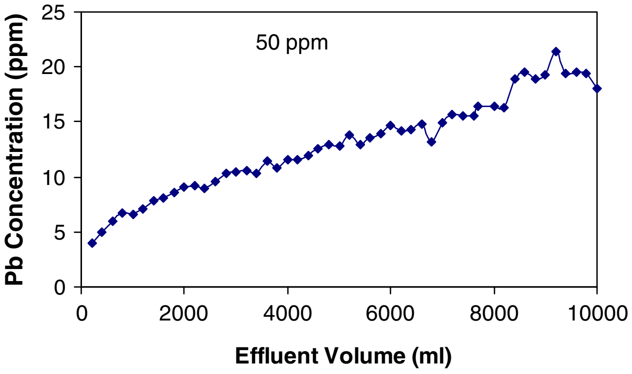

Fig. 2 Concentration of Pb effluent collected from experiment 1 at (Pb^{2+} = 50 ppm)

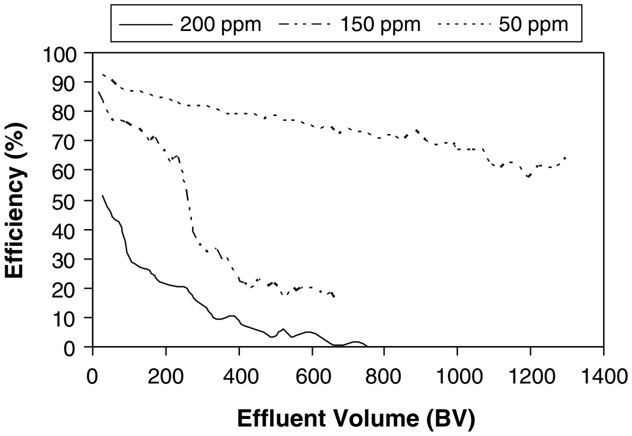

Fig. 3 Efficiency of the spent shale in removing Pb^{2+} from effluents at different concentrations

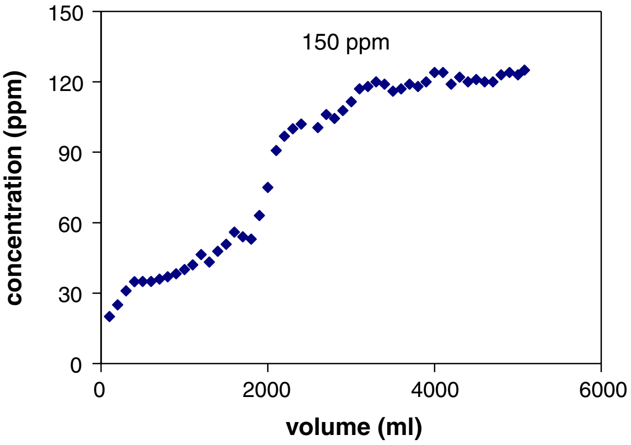

Fig. 4 Composition of Pb effluent collected from experiment 2 at (Pb^{2+} = 150 ppm)

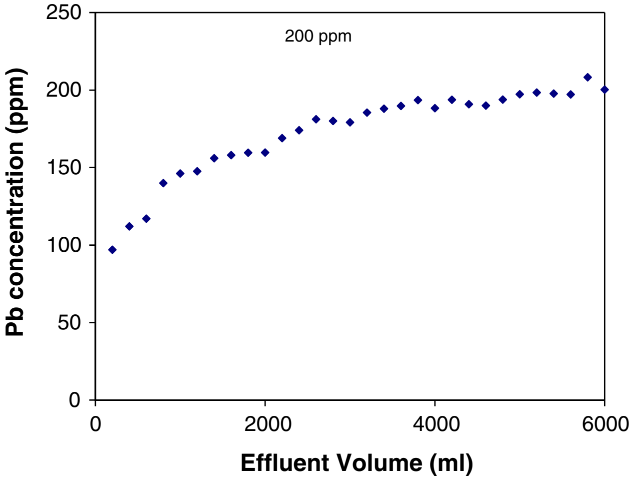

Fig. 5 Composition of Pb effluent from experiment 3 at (Pb^{2+} = 200 ppm)

in Table 7 and illustrated in Figs. 3, 4, 5. It is evident that the efficiency of the SS decreases with the increment of the ionic strength of Pb^{2+} in the effluent solutions. Whenever the Pb^{2+} concentration is 150 ppm, the efficiency of the SS to remove Pb^{2+} has been found to vary between 87 and 17%. The efficiency in the case of 200 ppm Pb^{2+} concentration is always less than 50%. It is important to say that Pb^{2+} concentration in real industrial wastewater is usually lower than 20 ppm (see Ibrahim and Akasha 2004).

This means that in real situations, the efficiency of the SS to remove Pb^{2+} from industrial wastewater will be higher than 94% and may reach 100%.

Conclusions

About 1.17 billion tons of OS deposits occur in El-Lajjun area of central Jordan that are characterized by having an acceptable production properties. Utilization of such deposits has not started as yet, awaiting international investment. The results of the Fisher assay of selected size fractions of the OS indicate that oil yield is from 14.0 to 14.6% and SS content is up to 78%. The mineralogical constituents are calcite and quartz with traces of apatite, hematite, and clay. The average CaO and SiO_2 content is 27.38 and 16.80%, respectively. The physical and chemical characterization of spent OS from the area was examined and compared with the original OS. The SS was subjected to leaching tests to detect the possibilities of its heavy metals release to the environment. This was carried out by percolating water at a very slow and constant flow rate using column experiments. Standard column leaching experiments reveal no detectable release of heavy metals to the percolating water, even at very low pH conditions. The effectiveness of the SS in removing Pb^{2+} from wastewater has been investigated under very high Pb^{2+} ionic strength conditions. The SS is very efficient in removing most of Pb^{2+} ions from influent solutions, where 1 m^3 of SS has the efficiency to remove from 64 to 94% of Pb^{2+} from about 1,300 m^3 wastewater containing 50 ppm Pb^{2+}. The efficiency of the SS decreases substantially with increasing Pb^{2+} concentration in the wastewater. In real situations, where Pb^{2+} concentration is very low, i.e., less than 5 ppm, the efficiency of the SS to remove Pb^{2+} is expected to be 100%.

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