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Removal of organosulfur from Jordanian Oil Shale

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ABSTRACT

Environmental worries have led the necessity to remove organosulfur-containing compounds from shale oil. The Jordanian oil shale have been retorted, to produce shale oil. The total organosulfur content in the produced shale oil was found to be 10.634%. Adsorption technique was tested to find out the effective in removing organosulfur from the produced shale oil to keep up with the environmental regulation if shale oil can be used in the future as an energy alternative. The adsorption technique depend mainly on varying parameters. Among the varying adsorption parameters were, the ratio of zeolite to shale oil, particle size, height of column and flow rate. The total organosulfur reduction by applying adsorption techniques was slightly influenced by low zeolite particle size (75 μm)followed by zeolite/shale oil ratio (4:1). The corresponding reduction values of total organoorganosulfur are 10.03% and 10.48% respectively. Meanwhile, the factors flow rate and column height were less significant. As a result, different removal techniques should be considered to ensure producing environmental friendly shale oil.

Keywords: *Adsorption, ,Jordanian , Oil shale, Organosulfur, Removal.*

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I. INTRODUCTION

The jordanian oil shale deposit which found in the sedimentary basins of Central Jordan; are argillaceous bituminous marls and limestones. Oils are derived from carbonate or carbonate-evaporite rock sequences have high-organosulfur content. Recently, awareness to the environmental issue increasing due to harmful effects of the high proportion of organosulfur compounds in oil, on health, environment and economy. Hydrodesulfurization (HDS) the best-known technology for removal organosulfur-containing hydrocarbons in liquid oils but still cannot efficiently remove thiophenic compounds [1]. Alternative method such as adsorptive are being developed in recent years for removing organosulfur compounds [2]. Adsorption processes are some of the most economically attractive methods because of the straightforward operating conditions and availability of inexpensive and regenerable adsorbents including zeolites [1]. Many studies have studied zeolites-based adsorbent as promising materials for removing the organosulfur compounds because of the channels present in the structure and the ease with which the properties are tuned [3], [4], [5], [6] and [7].

II. METHODS

Adsorption technique using zeolite was used to reach the objectives of this research. The Jordanian oil shale samples were retorted by Fischer Assay Analyses to produce shale oil. The organosulfur concentration in yielded shale oil was measured by using the SC-144DR Organosulfur and Carbon Analyzer.

The zeolite samples were collected from Aretin have been crushed then sieved for particle size (75, 150, 250, 1000 µm). Column and mixing methods will have been undertaken using columns and magnetic stirrer each method was controlled by several parameters. Mixing using magnetic stirrer depending on various parameters which are: The weight of zeolite is in g units, temperature in degree and particle size in micron, whereas the fixed parameters are oil volume (ml), time of mixing (hour) and stirring (rpm). This treatment takes place in two conditions; at room temperature and heat (50˚C) [8]. Column of zeolite experiments was controlled by several parameters which are weight of zeolite in g units, volume of oil (ml), height of column (cm), flow rate (ml/min) and particle size of zeolite (µm). To enhance zeolite acid activation of zeolite have been done by preparing 1.0 gram of zeolite mixing with a solution of 8.0 gram ammonium nitrate (NH_4 NO_3) dissolved in 50.0 ml of distilled water at 80 °C / 200 rpm for 24 hour .The mixture was then dried for 4 hour at 500 °C. The purpose of acid activation is to increase the positive charge by increase hydrogen ions H^+ on zeolite, this ion has the ability to make bonds with organosulfur and form H_2S and to improve the adsorption efficiency by increasing channels and pores in the structure. Using pure thiophene is meant to find out the efficiency of zeolite to adsorption thiophene without presence of any impurities which take place in the pore spaces of zeolite and prevent to adsorbed thiophene.

III. RESULTS

3.1 Organosulfur Concentration

The organosulfur concentration in yielded shale oil was measured by using the SC-144DR Organosulfur and Carbon Analyze the average amount of total organosulfur is 10.634 %. The analysis was repeated 15 times to account for results accuracy and precision the degree of uncertainty is very low < 5 %. The obtained results are compatible with [9]

3.2 Adsorption Treatments by Natural Zeolite

3.2.1 Mixing technique

Mixing technique using magnetic stirrer was carried out under various parameters as follows: The weight of zeolite in g unit, shale oil volume (ml), time of mixing (hour), stirring (rpm), temperature in degrees centigrade, and particle size in micron. The shale oil exposures to the treatment took place several times and each experiment used different parameters, one of the parameters was changed and others were kept constant. This treatment was repeated under different conditions. The obtained results in both mixing at 25˚C and 50 ˚C indicate that at particle size 75 µm better organosulfur reduction is achieved around, 10.322% and 10.408% respectively from initial organosulfur concentration 10.634%. The obtained results using zeolite as adsorbing material for deorganosulfurization are incompatible with results obtained by [10], [2], [7], [6] [11].

(i) Mixing 50 ˚C.

In this experiment the following parameters were fixed; weight of zeolite (2.0g), volume of shale oil (5ml), time of mixing (2 hour) and stirring (700rpm). The varying parameter was particle size. The first experiment used the particle size 75µm, after preparing the sample it has been mixed for two hours, and then kept to settle for 24 hours, after that the treated shale oil was analyzed using SC-144 DR Organosulfur and Carbon Analyzer to obtain the concentration of the organic organosulfur after treatment. Comparable procedure was repeated using different particle sizes 150µm, 250 µm, and 1000 µm. (Figure 1) describes the relationship between average organosulfur concentration in shale oil before treatment (%) and organosulfur reduction (%) in shale oil after treatment for the sizes 75µm, 150 µm, 250 µm and 1000 µm.

Table 1: Organosulfur Concentration (%) in shale oil after heat mixing treatment, using SC-144 DR Analyzer at 1200 ˚C.

Particle Size	2.0g + 5 ml + 2 hour + 700 rpm+ 50˚C						Average (%)
75 µm	Organosulfur %	10.48	10.40	10.40	10.38	10.36	10.408
	Carbon%	71.46	71.29	72.56	73.93	72.69	
150 µm	Organosulfur %	10.56	10.47	10.43	10.40	10.38	10.452
	Carbon%	71.74	72.18	73.97	72.81	72.46	
250 µm	Organosulfur %	10.58	10.53	10.51	10.48	10.44	10.510
	Carbon%	73.24	71.29	71.08	71.98	70.86	
1000 µm	Organosulfur %	10.63	10.62	10.58	10.53	10.51	10.575
	Carbon%	76.48	75.82	74.56	74.25	73.96	

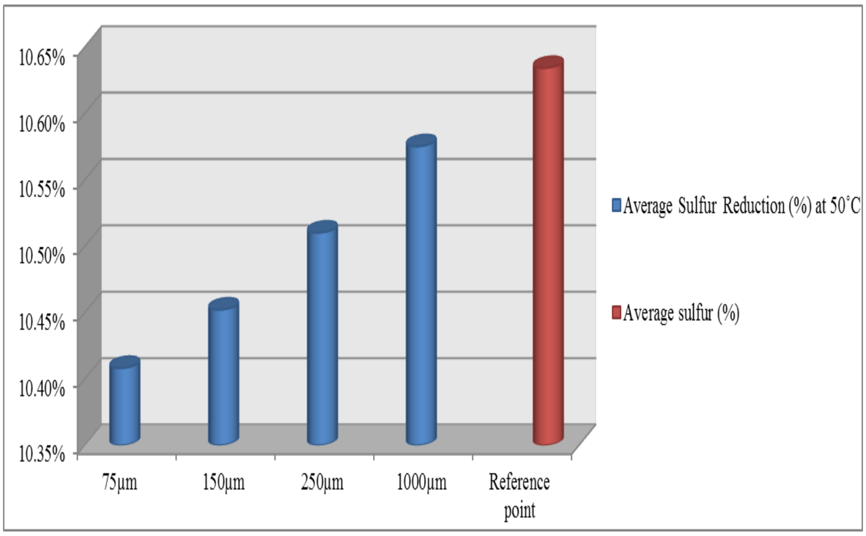

Figure 1: Relationship between average organosulfur (%) and treated shale oil (Organosulfur reduction %) of 75µm, 150 µm250 µm and 1000 µm.

(ii) Mixing at Room Temperature (RT).
In this experiment, the following parameters were fixed; weight of zeolite (5.0g), volume of shale oil (5ml), and others as mentioned, whereas the varying one was the particle size (µm). The first experiment used the particle size 75 µm, after preparation the sample has been mixed for two hours, and then kept to settle for 24 hours.
The same procedure was repeated for different particle sizes (150 µm and 250 µm). Figure 2 illustrates the relationship between average organosulfur in shale oil before treatment (%) and organosulfur reduction (%) in shale oil after treatment for 75µm, 150 µm and 250 µm sizes. As might be figured out from figure 2 the particle size 75 μm yielded the best deorganosulfurization results at room temperatures.

Table 2: Organosulfur Concentration in shale oil (in wt %) after (RT) mixing treatment using SC-144 DR Analyzer at 1200 ˚C.

Particle Size	5.0g + 5 ml + 2 hour + 700 rpm+ Room Temperature						Average (%)
75 µm	Organosulfur %	10.38	10.34	10.3	10.29	10.28	10.322
	Carbon%	73.93	72.89	72.1	71.62	70.56	
150 µm	Organosulfur %	10.52	10.51	10.42	10.39	10.33	10.438
	Carbon%	73.677	72.75	73.09	71.93	71.09	
250 µm	Organosulfur %	10.522	10.51	10.50	10.45	10.41	10.481
	Carbon%	72.40	71.69	71.08	71.20	70.86	

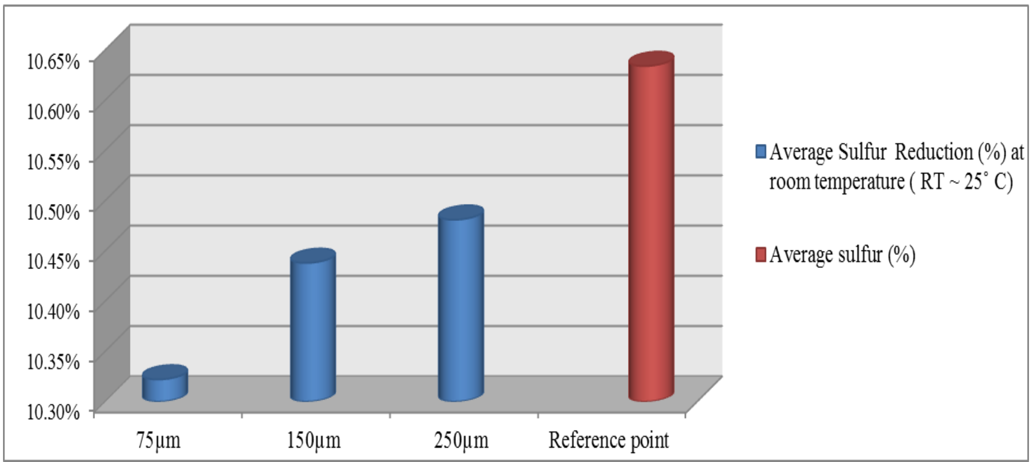

Figure 2: Relationship between average organosulfur (%) and treated shale oil (organosulfur reduction %) of 75µm, 150 µm and 250 µm.

3.2.2 Column Technique
Other experiments were carried out by changing the method using zeolite column. The important parameters have been used in these experiments were; weight of zeolite (g), volume of shale oil (ml), height of column (cm), flow rate (ml/min) and particle size of zeolite (µm), whereas the varying parameter was the particle size (µm). It has been found that the important parameters that affect the experiments are the column height and particles size. Firstly, the particles size was fixed at 75µm and the height was changed each time. The encountered organosulfur concentration after column techniques is shown in Figure 3. The obtained results at ratio 4:1and particle size 75 µm show better organosulfur reduction to 10.03 % from the initial organosulfur concentration 10.634%. The obtained results using zeolite as adsorbed material for deorganosulfurization are incompatible with results obtained by [12].

Table 3: Organosulfur concentration (%) in shale oil after treatment using column technique.

Particle size of Zeolite (75 µm) and Flow rate (0.1 ml/min)							
Ratio {(weight of zeolite, g) To volume of oil, ml)}	Ratio (4:1)	Ratio (3:1)			(Ratio 2:1)		
Height of column (cm)	2.0	8.0			10.0		
Carbon %	73.08	73.2	73.0	73.6	74.1	74.2	74.5
Organosulfur (%)	10.03	10.4	10.4	10.5	10.5	10.5	10.5
Average (%)	10.03	10.48			10.533		

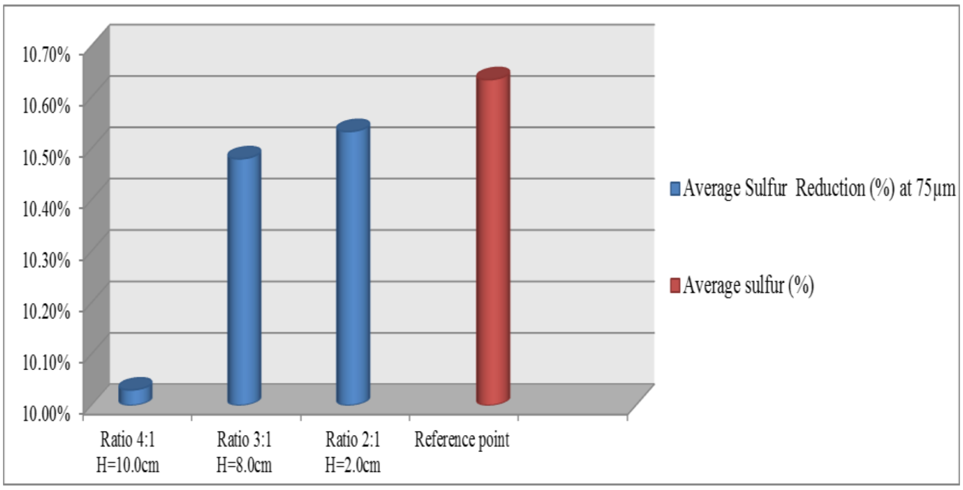

Figure 3: Relationship between average organosulfur (%) and treated shale oil of 75µm as column.

Furthermore, the particle size was fixed at 250µm and the height has been changed each time. The results of organosulfur concentration after adsorption technique are listed in table 4, and shown in Figure 4. The obtained results at ratio 2:1and particle size 250 µm with column higher of 5.0 cm show organosulfur reduction to 10.53 % from initial organosulfur concentration 10.634%, there is no significant reduction in this case The obtained results using zeolite as adsorbed material for deorganosulfurization are incompatible with results obtained by [18].

Table 4: Measured organosulfur concentration (%) using SC-144DR analyzer at 1200 ˚C after column techniques.

Particle size of zeolite (250 µm) and flow rate (0.1ml/min).				
Ratio weight of zeolite (g) to Volume of oil (ml)	1:1		2:1	
Height of column (cm)	2.0		5.0	
Carbon%	73.43	73.61	73.24	73.02
Organosulfur %	10.55	10.6	10.54	10.53
Average %	10.575		10.535	

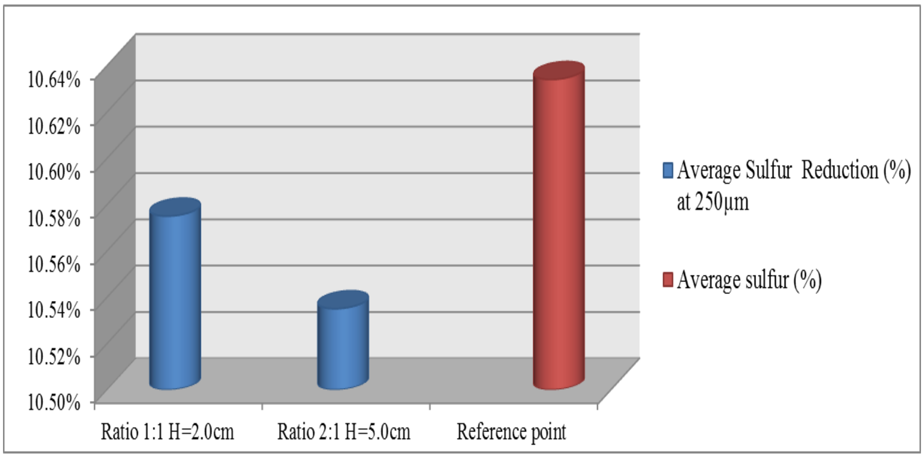

Figure 4: Relationship between average organosulfur (%) and treated shale oil of 250µm as column.

3.2.3 Treatment using acid activated zeolite (adsorption techniques).

A solution of 2.0 gram pure thiophene was treated using 1.0 gram activated zeolite by mixing techniques for one hour at room temperature. The results are listed in tables 5 and 6 below. This experiment was carried out to study the ability of zeolite to adsorb organic organosulfur and the results obtained results at 250 µm particle size show organosulfur reduction to 15.284 % from initial organosulfur concentration 26.136 %. This result cannot be considered as an acceptable percent for removing organic organosulfur. The results in Table (5) show that using activated zeolite to adsorbed organic organosulfur on shale oil is not effective at greater particle size.

Table 5: Measured organosulfur concentration (%) using SC-144DR analyzer at 1200 ˚C after mixing techniques.

Particle Size	1.0g + 2.0 g wt + 1 hour + 700 rpm+ RT						Average (%)
250 µm	Organosulfur %	15.44	16.12	15.29	14. 89	14.28	15.284
	Carbon%	26.23	27.76	25.98	25.12	14.65	
Thiophene	Organosulfur%	26.34	25.76	27.04	24.67	26.87	26.136
	Carbon%	40.12	38.56	40.88	33.98	43.01	

Table 6: Measured organosulfur concentration (%) using SC-144DR analyzer at 1200 ˚C after mixing techniques

Particle Size	1.0g + 2.0 ml + 1 hour + 700 rpm+ RT						Average (%)
250 µm	Organosulfur %	9.44	8.97	9.08	9. 32	8.78	9.067
	Carbon%	70.09	69.45	69.78	71.21	68.98	69.90

IV. DISCUSSIONS AND CONCLUSIONS

4.1 Discussions

The removal of organosulfur in shale oil is a serious concern for the whole world, together with Jordan. The Jordanian shale oil contains high percentage of organosulfur about 10.63%. Such a fraction needs a complicated process to minimize. This research critically discusses the non-hydrodeorganosulfurization processes of shale oil using adsorption technique. This process is briefly evaluated in this research, namely their impact and variances. The adsorption technique produced comparable results in the measured organosulfur reduction values in Jordanian shale oil.

4.1.1 Adsorption Technique

The removal of organosulfur compounds from shale oil by adsorption technique using natural and activated zeolite was investigated and implemented using different methods; fixed bed column and mixing, has shown several manifestations using zeolite under different experimental conditions.

Fixed bed column was conducted at ambient temperature was applied to study the effects of parameters such as flow rate, height of bed column, weight of zeolite to shale, oil volume ratio and particle size. The experimental bed column adsorption results show the effects of three parameters: Zeolite particle size, height of bed column, and ratio of zeolite in grams to shale oil in milliliter. The experimental mixing used a magnetic stirrer to study effects of parameters such as particle size of zeolite and temperature conditions.

4.1.1.1 Results of Using Pure Thiophene and Activated Zeolite

The reduction of organosulfur was approximately 42% from an initial amount of about 26.14 % to 15.28 % content, while the reduction of organosulfur using activated zeolite with shale oil was 15 % from an initial amount of 10.63 % to 9.06 %. These results indicate that the shale oil is full of impurities that have desirable charge and appropriate size competing organosulfur compounds in occupying the channels and pores structure of zeolite. Because of that, shale oil should be processed from impurities to make sure that oil will get rid of all the organosulfur compounds using activated zeolite. Furthermore, differences resulting from using natural or activated zeolite did not occur or cannot be noticed due to the fact that shale oil is not pure.

4.1.1.2 Effect of Particle Size

The change in particle size has a major influence on the organosulfur concentration output (Figure1-5). Decreasing particle size from 1000µm-75µm with mixing and fixed bed column adsorption caused lowering of initial organosulfur concentration output regardless of temperatures change. Particle size was found to be a decisive factor in the organosulfur reduction using both methods. It can be seen that the smallest particle size is causing the lowering of organosulfur output. This can be accounted for by the fact that smaller particle sizes have greater surface areas, accordingly will cause greater organosulfur reduction.

4.1.1.3 Effect of Zeolite Weight / Shale Oil Ratio

The difference in the ratio of zeolite in grams to shale oil in milliliter was investigated. The increase in ratio from 1:1 to 2:1 (g: ml) will ensure increase in organosulfur reduction due to the increase in weight of adsorbed material. This is due to the fact that the increase in the zeolite mass provides greater adsorption sites.

4.1.1.4 Effect of Bed Column Height

The height of the bed column influences the organosulfur concentration output significantly as expected. It was found that increasing the bed column causes the lowering of initial organosulfur concentration output (Figures

3-4). This is due to the fact that the height of the bed column will ensure an increase in organosulfur reduction because shale oil will pass through thicker zeolite beds for a longer period of time thus allowing for greater adsorption, due to the availability of more sorption sites [13].

4.1.1.5 Effect of Temperature

Temperature affects the removal of organosulfur from shale oil by mixing adsorption. This can be noticed from (Figures 1-2). The increase in temperature from 25 °C to 50 °C caused the decrease in organosulfur because high temperature will break any bonds between organosulfur bearing compound and the surfaces of zeolite particles. Accordingly, elevated temperatures do not play an important role in the adsorption process.

4.1.1.6 Effect of Flow Rate

Flow rate at 0.1ml / min and 0. 2ml / min did not show positive signs regarding the effectiveness of adsorption with changing flow rate. From the obtained results we can conclude that deorganosulfurization adsorption technique has minor promising results in organosulfur reduction.

4.2 Conclusions

1. The concentration of total organosulfur measured in Jordanian shale oil by pyrolysis at 520ºC is considered high (10.634%) this will cause negative impact on the environmental and human health when used as energy resources, therefore special procedures desulfurization it before refinery treatment.
2. Experimental results are required to show that decreasing the particle size and increasing the bed column, decreases organosulfur concentration. This can be accounted for as due to the fact that small particle sizes have greater surface areas, accordingly adsorption will be greater.
3. Decreasing temperature from 50 to 25 °C caused the lowering of organosulfur.
4. Adsorption using natural zeolite has been found to be an ineffectual approach for removal of organosulfur; the percentage of removed organosulfur is slightly small at ambient condition than at elevated temperatures.
5. Adsorption using activated zeolite gave better but not prominent results. Such results could be enhanced using purified shale oil.

4.3 Recommendations for Future Research

1. This study was carried out on 20 samples from certain outcrops at. Its results apply only to the investigated site and do not necessarily represent the entire oil shale occurrences in Jordan. Therefore is recommended to carry out similar studies on other oil shale occurrences in Jordan.
2. Additional studies should be conducted on the zeolite to improve its adsorption capacity.
3. Further studies and analysis should be carried out on the shale oil to obtain better knowledge about the organosulfur associated organic compounds present in shale oil.
4. Further studies on the use and disposal of shale oil distillates should be carried out to ensure environmental friendly treatment.
5. Complementary studies of removal organosulfur processes are necessary to finally accomplish 100% removal of organosulfur from shale oil.

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