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COMPARISON OF RETORT WATER TREATMENT METHODS – A CASE STUDY IN JORDAN

Jämförelse av förbehandlingsmetoder av spillvatten från pyrolys av oljeskiffer – En fallstudie från Jordanien

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Abstract

In this work, physical and chemical characterization of El- Lajjoun retort water from oil shale pyrolysis process has been carried out. Comparison of different treatment methods (Air stripping, activated carbon, and oil shale ash) for the major components which could affect the design and operation of any set of wastewater treatment process were conducted. The removal of phenol and ammonia using activated carbon after 12 h resident time were 93 and 41 %, respectively. The activated carbon reduced the total organic carbon (TOC) and the chemical oxygen demand (COD) regardless of residence time. Using activated carbon as adsorbent proved to be effective for the treatment of high percentages of phenol and ammonia from retort water. On the other hand, air stripping was found to be a very effective method for removing ammonia from the retort water.

Key words – Retort water, oil shale, air stripping, activated carbon, oil shale ash, El- Lajjoun, Jordan

Sammanfattning

I denna studie har spillvatten från pyrolys av oljeskiffer i El- Lajjoun karaktäriserats kemiskt och fysikaliskt. Olika förbehandlingsmetoder (air stripping, aktivt kol samt en bädd av förbränningsaska) har jämförts med avseende på de viktigaste parametrarna som skulle kunna påverka drift och utformning av efterföljande vattenreningsprocesser. Vid behandling med aktivt kol har fenol och ammoniak god avskiljning efter 12 timmars uppehållstid, 93 % respektive 41 %. Även totalt organiskt kol (TOC) och kemisk syreförbrukning (COD) reduceras oavsett uppehållstid. Att använda aktivt kol som adsorbent visade sig vara en effektiv behandlingsmetod för processvatten med höga koncentrationer av fenol och ammoniak. Ammoniak avskiljdes även effektivt med air stripping.

1 Introduction

Jordan imports most of its energy needs which places a burden on the national economy due to the high cost of imported oil. The energy issue has posed numerous challenges for Jordan. Developing renewable and alternative energy resources has been prioritised during the last decade. Large quantities of oil shale exists in Jordan, it is considered to be the largest indigenous energy resource in the country (Jaber et al., 1999, Ibrahim and Jaber, 2007), it is estimated that 50 billion ton of oil shale can be mined by open pit mining (Shawabkeh et al., 2004). Jordan is ranked as 8th among 37 countries worldwide for their total oil shale reserve (Alali, 2006). Oil shale has been known in Jordan since ancient times. In 1966 the German Geological Mission discovered El-Lajjoun oil shale depots (Bender, 1974). Jordanian oil shale is a 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

Table 1. *Chemical and physical properties for Jordanian oil shale from 5 different locations.*

Parameters	Attarat Um El-Ghudran	Sultani	El- Lajjoun	Wadi Maghar	Jurf Ed Darawish
Average Oil Content (% by weight)	8.5	7.5	10.5	6.8	5.7
Total Organic matter (% by weight)	23.16	21.5	22.1	20.8	18
Calorific value (kcal/kg)	–	1210	1590	780–1270	864
$CaCO_3$ (% by weight)	52.2	46.96	54.3	48	69.1
SO_3 (% by weight)	4.9	4.4	4.8	4.2	4.3
Bulk density (g/cm^3)	–	1.96	1.81	–	2.1
Moisture (% by weight)	1.71	2.6	2.43	3.8	2.8

After (Alali, 2006)

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, Alali, 2006).

Jordanian oil shale contain about 2–5 % of moisture (Jaber, 2009, Yousef, 2006) see table 1. The production of shale oil however, also creates immense quantities of liquid and solid wastes. The volume of the produced wastewater, known as retorted water, to produce 1 m^3 of shale oil is 0.6 to 1 m^3 (Susie, 2002, Clarke, 2002). Retort water is produced when the shale is heated to 500–600 °C in the retorting process.

The quantity and nature of retort water is depending on the retorting process, in situ processes produced approximately equivalent quantities of retort water and shale oil, whereas above-ground retorting processes produce much less retort water.

In general retort water is not suitable for safe discharge into lakes and rivers or for use in the shale oil processes, because it contains a variety of suspended and dissolved pollutants, impurities and contaminants, such as raw, retorted and spent oil shale particulates, shale oil, grease, ammonia, phenols, sulfur, cyanide, lead, mercury and arsenic. In view of their nature, amounts, and fate, retort water poses environmental concerns if left untreated. However, to identify the nature of retort water, detailed chemical and physical analyses need to be conducted. The objective of this study is to compare three different simple in situ treatment methods for removing the major pollutants from El-Lajjoun oil shale retort water.

2 Method and materials

The retort water samples were obtained by retorting oil shale from the El- Lajjoun area in the southern region of Jordan, a pilot plant capable of retorting more than 10 kg oil shale per batch was established (see Figure 1) in the laboratory of Tafila technical university (TTU) in

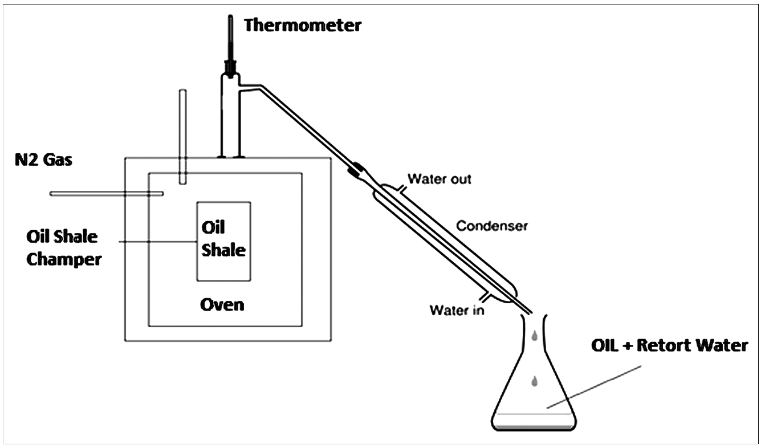

Figure 1. *The laboratory apparatus used for production oil from oil shale.*

2008. Oil shale samples were grinded in a ball mill, and sieved to a particle size of 0.5–2.1 mm. A sample of 1 kg of oil shale was electrically heated using furnace work in a temperature range from 200 to 1000 °C. The oil shale pyrolysis is conducted in the temperature range between 410–550 °C (Al-Ayed and Matouq, 2009). Nitrogen gas was used as sweeping gas inserted from the top of the furnace. The condensable liquids are collected using a condenser working on affixed rate to maintain the cooled temperature at 0–4 °C, while the light gases were vented out.

The final product will be shale oil and retort water, decantation and filtration is needed to separate the retort water. To collect the required volume of retort water for the analysis the experiment were repeated more than three times.

The produced retort water was analysed using the following instruments: Total Organic Carbon Analyzer, Atomic Absorption, Spectrophotometer, GC-Ms and PH meter. The analysis where conducted in Prince Faisal Center, Mutah University and Tafila Technical University. Four 50 ml samples of retort water were analysed.

Moreover, a set of laboratory experiments were conducted for different treatments methods for the possible reuses during the production process (e.g., cooling, washing) as well as, for reducing the pollutant in case of possible disposal, considering the cost of treatment and environmental impact.

2.1 Using oil shale ash for treatment of retort water

To prepare the ash 500 g oil shale from El- Lajjoun were crushed and burned using electrical furnace at 950 °C for two h. The residual ash was cooled, then milled and sieved to 250 and 355 µm diameters were obtained for analysis. A mass of 20 g was mixed with 100 ml of 0.2M HCl and heated to 50 °C with continuous stirring for 30 min. Acid treatment was necessary to activate the surface of the particles and to increase the surface area by dissolving part of the soluble portion of the ash. The ash was then filtered, washed with distilled water and finally dried. Two samples of 50 ml retort water were entered in the packed column with 20 g of pre-treated oil shale ash with deferent residence time.

2.2 Using activated carbon for treatment of retort water

The most widely used type of adsorbent materials is activated carbon, it is made from a substance having high carbon content, such as, coal and wood. Activated carbon has a very large surface area per unit volume allowing it to be used as adsorbents for a variety of substances. The experiment was carried out using simple batch technique at room temperature by contacting 0.5 g from commercial activated carbon (D.3016, 18002) with about 100 ml retort water with continues shaking using a water bath with shaker 150 cycles per min. The concentration of phenol in retort water was measured by using spectrophotometer at wavelength 269 nm.

2.3 Using air stripping for treatment of retort water

Air stripping is a physical mass transfer process and is generally considered as the best available technology for many volatile organic compounds (VOCs). It uses relatively clean air to remove contaminant dissolved in water and transfers the contaminants into the gaseous phase.

Air stripping works best on water containing chemicals that evaporate easily, since the ammonia is present as dissolved gas in retort water, some of the ammonia transfer from the water to the air. A simple apparatus was designed for this purpose; a glass vessel with air inlet allows the air to contact with retort water in fixed rate at room temperature and atmosphere pressure.

3 Results and Discussion

Table 2 shows the analysis of El- Lajjoun retort water. The analysed parameters represent the major components which could affect the design and operation of any set of wastewater treatment process and the most noticed pollutant which must be removed.

Table 2. *Retort Water Analysis.*

Parameters	Value
TSS(mg/l)	3616
TDS(mg/l)	3050
Total Carbon TC (ppm)	2646.7±0.283
TOC(mg/l)	3270.841
Ni(ppm)	0.82±0.00036
CU(ppm)	0.34±0.0033
Zn(ppm)	4.74±0.00072
Pb(ppm)	Not Detected
PH	6.54 at 25 C
Inorganic Carbon IC (ppm)	624.1±0.14
COD (mg/l)	13600
AS (ppm)	0.23
Phenols (mg/l)	29
NH_3 (mg/l)	2700

Table 3. *Retort Water after adsorption by oil shale ash.*

Parameter	Initial	After 1 h	% of removal	After 12 h	% of removal
TOC(mg/l)	3270	2630	20	2000	39
COD(mg/l)	13600	12800	5	10000	26
NH_3(mg/l)	2700	2220	18	1950	28
Phenol (mg/l)	29	13	60	9	70

Table 4. *Retort Water after adsorption by activated carbon.*

Parameter	Initial	After 1 h	% of removal	After 12 h	% of removal
TOC(mg/l)	3270	1610	51	1500	55
COD(mg/l)	13600	12100	11	10250	24
NH_3(mg/l)	2700	2150	21	1610	41
Phenol (mg/l)	29	3	89	2	93

3.1 Using oil shale ash for treatment of retort water

Table 3 shows the removal percentage using the ash treatment in different residence time. Ash treatment leads to a decrease in the TOC and COD of 39 and 26 %, respectively, during a residence time of 12 h. The phenols were reduced by 70 %. Moreover, the ammonia removal increased with time.

3.2 Using activated carbon for treatment of retort water

As shown in table 4. The removal of phenol and ammonia using activated carbon after 12 h resident time were 93 and 41 % respectively. Also it reduced TOC and COD regardless of residence time.

3.3 Using air stripping for treatment of retort water

As shown in table 5, the ammonia removal was very high; 94 % was removed from the retort water after 1 h and TOC and COD were reduced by 8.5 and 9 %, respectively. Determining the required air to water ratio in the stripping, the Henry law can be applied. The Henry law is usually expressed as:

$$Y^P = Hx \quad (1)$$

Where Y is the mole fraction in the gas phase, x is the mole fraction in the liquid phase, p is the total pressure and H is Henry's constant, when p is close to one atmosphere:

$$Y = Hx \quad (2)$$

The value of the H is set for most of the VOCs, so we can determine the air to water ratio which is best suitable for stripping.

Table 5. *Retort Water after air stripping.*

Parameter	Initial	After 1 h	% removal
TOC(mg/l)	3270	3000	8.5
COD(mg/l)	13600	12400	9
NH_3(mg/l)	2700	180	94
Phenol (mg/l)	29	26	10

3.4 Comparison of different treatment methods

Choosing a specific treatment method, or a combination of two or more, depends on the purpose of the treatment and which pollutants that must be removed.

Figure 2 shows a comparison between different treatment methods. It is recommended to use activated carbon followed by air stripping to decrease the TOC, COD, NH_3, and Phenols below allowable limits. When comparing our results with Jordanian allowable limit standards for the reuse of wastewater in irrigation, the phenol concentration should be less than 0.002 mg/l.

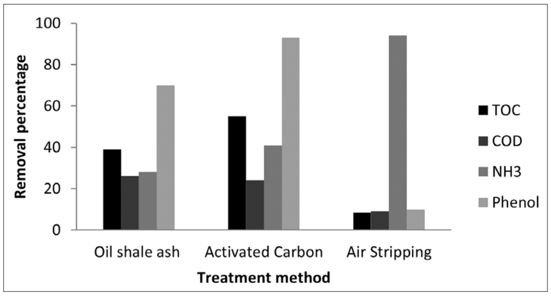

Figure 2. *Comparison of different treatment methods used.*

4 Conclusion

Wastewater recycling and reuse when properly implemented is cost effective, as well as environmentally sound if proper treatment is applied. The reuse of retort water from oil shale production can be a sufficient source of treated water for different activities especially in the agricultural sector. This research proved that reusing the retort water from oil shale production is economically visible, and environmentally safe. The removal of phenol and ammonia using activated carbon after 12 h resident time were 93 and 41 % respectively. Using activated carbon as adsorbent proved to be effective for the treatment of high percentages of phenol and ammonia form retort water. It reduced the TOC and COD regardless of residence time. However, air stripping is very effective method for removing ammonia from the retort water. Repeating the treatment methods could be used to achieve the maximum allowable limit. All suggested methods proved to be simple, applicable, and environmentally sound. Adsorbed phenol, active carbon and oil shale ash can be eluted and used as a raw material in different industries. More studies are needed to adapt new commercial treatment methods in order to enhance the removal considering the cost of treatment and environmental impact.

Many studies have been performed on the use of microbial degradation as a treatment method for the reduction and elimination of various contaminants in oil shale retort water that are of environmental concern. Biological waste treatment is normally one of the most economical means of removing organic contaminants from wastewaters.

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