



Conversion of oil shale ash into zeolite for cadmium and lead removal from wastewater

Reyad Shawabkeh*, Adnan Al-Harahsheh, Malik Hami, Abdelaziz Khlaifat

Department of Chemical Engineering, Mutah University, AL-Karak 61710, Jordan

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Abstract

A by-product fly ash from oil shale processing was converted into zeolite by alkali hydrothermal activation using sodium hydroxide. The activation was performed at different activation temperatures using 8 M sodium hydroxide. The obtained cation exchange capacity (CEC) showed that the best condition for synthesis of zeolite performed in a closed reactor at 160 °C for 24 h. Powder patterns of X-ray diffraction analysis have shown that zeolite of type Na-PI was successfully synthesized at 29.5, 32.2 and 34.4°. The produced zeolite was used as an ion exchanger for the treatment of wastewater for metal ions. Lead and cadmium were chosen as target metal ions. The adsorption capacity was estimated to be 70.58 mg lead/g-zeolite and 95.6 mg cadmium/g-zeolite when the initial concentration for both ions was 100 mg/l. The results were correlated using Redlich–Peterson and Sips models. For cadmium the best fit was obtained with the Sips model while, for lead the Sips models fits the experimental data adequately. Based on such results, it is concluded that the treated ash may possess strong potentials for zeolite production used in wastewater treatment.

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1. Introduction

Oil shale exists in Jordan with large quantity. It is estimated that 50 billion ton of oil shale can be mined by open pit mining; while about 25% of this quantity can be extracted as oil [1]. A by-product of oil shale processing is ash, which is considered a serious environmental problem related to this ash. Therefore, there is a need for a proper strategy for ash handling, disposal and utilization. Usually ash produced from municipal incinerators and power plants worldwide is used for production of cement and concrete, asphalt shingle, quarry-fill and sludge stabilization, soil treatment for agricultural purpose, while the large portion is dumped in landfills [2–5]. An alternative manner is the conversion of this ash into a high-grade zeolite product, which is considered an environmental friendly product. Several researchers have applied this theme and synthesized different types of zeolite from fly ash. However, most of the research work reported in the literature has been

oriented towards establishing the experimental conditions for optimum zeolite production [6], the effect of alkali treatment on zeolite synthesis [7], and application to metal removal from solutions and toxic gases from gas streams [8–10]. The cation exchange capacity (CEC) has also been studied and reported [11,12]. In the present work, synthesis of zeolite from oil shale ash, which is a new type of ash, is investigated. The results relevant to the present work are going to be presented in a series of papers that will cover major areas in zeolite production from oil shale ash.

2. Experimental

2.1. Zeolite preparation

Oil shale samples were collected from EL-Lajjun area in the southern part of Jordan. These samples were crushed to different particle sizes ranging from 3 mm to 63 µm. The samples that passed the 1 mm mesh were collected and burned in a Muffle furnace at 950 °C to remove all

* Corresponding author. Tel.: +6-461-7860; fax: +6-465-4061.
E-mail address: rshawabk@mutah.edu.jo (R. Shawabkeh).

incorporated hydrocarbons. The remaining ash was grinded and stored.

Three reaction vessels were used in this study, which were custom-made by the engineering workshop. Each vessel was firmly sealed with rubber to maintain constant pressure and prevent any losses of the reactants during the heating process. Controlled temperature oven with PID temperature controller was used. Zeolite synthesis was carried out by mixing 50 g of ash with 100 ml of 8 M sodium hydroxide solution. Then the slurry was placed in the reaction vessels and transferred to the oven and kept for different periods of time (1–24 h). The reaction temperature was also varied from 25 to 160 °C. At the end of the activation period the product was collected, washed several times by distilled water, filtered, dried at 105 °C, and stored in a closed container for analysis.

The mineralogical compositions of the ash and the synthesized zeolite were determined by conducting X-ray diffraction (XRD) spectrometer studies using a Riyankn UY 10392 diffractometer operated at 40 kV and 40 mA.

All chemicals were analytical grade from Scharlau-Spain, and all the glasses were Pyrex rinsed and washed several times with diluted nitric acid and then with distilled water to remove any adhered impurity on the surface of the glass.

2.2. Cation exchange capacity

Samples of 4 g each of fine particle size (<125 µm) were mixed with 33 ml of 1.0 N sodium acetate solution. The procedure was repeated three times. Then the samples were washed three times with 33 ml isopropyl alcohol, followed by washing three times with 33 ml of ammonium acetate. The supernatant of acetate solution was collected and diluted to 100 ml with sodium acetate and the sodium concentration was determined by S4 ThermoElemental atomic absorption spectrophotometer.

2.3. Adsorption isotherms

Aqueous solutions of cadmium and lead of initial concentrations ranging from 50 to 250 mg/l were prepared. Batch adsorption tests were performed for fixed particle size of the produced zeolite. Using two sets of stopper bottles, equal weights of zeolite of 0.1 g were added to 100 ml of cadmium and lead solutions with different initial concentrations for each metal of interest. Both solutions were placed in an isothermal shaker (20 ± 1 °C) for a fixed period of time to allow complete equilibration. Similar procedure was performed on blank samples by the addition of zeolite into deionized water for the purpose of comparison. The pH was buffered at a value of 7 for all solutions. Samples of the equilibrated solutions were filtered and

analyzed using S4 ThermoElemental atomic absorption spectrophotometer.

3. Theoretical

In order to study the metal uptake by the surface of the produced zeolite, several dynamic adsorption equilibrium models were entitled in order to fit experimental findings. Accordingly, Redlich–Peterson and Sips models were considered. Redlich–Peterson model combined Langmuir and Freundlich adsorption isotherms to obtain the maximum adsorption corresponding to a saturated monolayer of adsorbate molecules on the surface of the heterogeneous adsorbents where the energy of adsorption is varied [13]. Mathematical expression for the Redlich–Peterson model in terms of solute concentration in solution, C_e (mg/l) in equilibrium with that on the solid surface, q_e (mg/g) is given by:

$$q_e = \frac{aC_e}{1 + bC_e^n}$$

Another empirical correlation that combines the Langmuir and Freundlich isotherms is the Sips model, which has the form [14]:

$$q_e = \frac{q_0(bC_e)^{1/n}}{1 + (bC_e)^{1/n}}$$

Where q_0 , b and n are constants.

4. Results and discussion

Samples of oil shale were tested in the Royal Scientific Society–Jordan for their chemical composition (Table 1) [1]. These samples were then burned at 950 °C for 8 h to evaporate the water content and the organic matters. The remaining represents class C fly ash with a high content of lime (50%) and reasonable percentages of silica (32.5%) and alumina (6.5%).

Synthesis of zeolite was carried out by mixing ash with sodium hydroxide solution at different solution temperatures

Table 1
Chemical composition of untreated oil shale ash from ALLAJOON area

Component	Wt (%)
SiO ₂	32.5
Al ₂ O ₃	6.5
Fe ₂ O ₃	3
P ₂ O ₅	4
CaO	50
MgO	3.3
TiO ₂	0.2
Na ₂ O	0.5

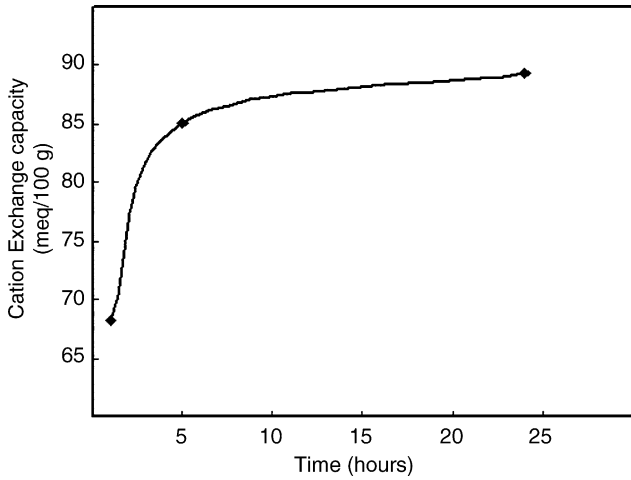


Fig. 1. Effect of reaction time on the cation exchange capacity for the produced zeolite.

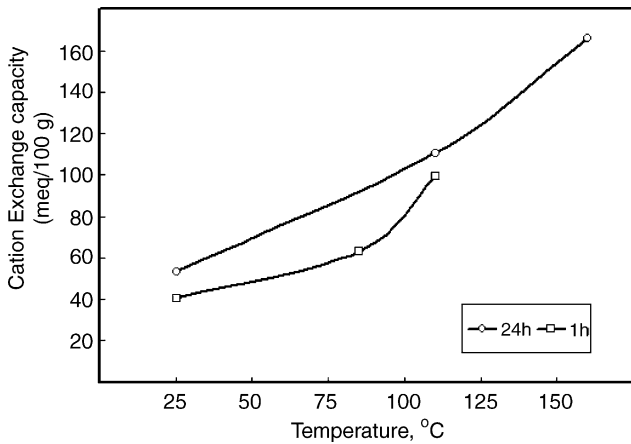
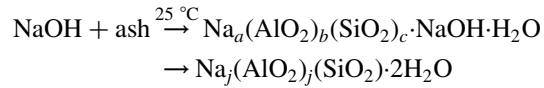


Fig. 2. Effect of temperature on the cation exchange capacity for the produced zeolite at different curing time.

for several periods of times. The sequence of reactions involved the formation of a hydrous aluminosilicate gel. This gel is then carefully cured at different temperatures to obtain maximum crystal growth of zeolite. The temperature

ranged from 25 to 160 °C. The reaction between the ash and sodium hydroxide solution is expected to be carried out accordingly [15]:



This product contains a three-dimensional network of alumina and silica, which plays an important role for adsorption, and exchange of metal ions. This is because of the generation of the electrical imbalance between the aluminum atoms and the four oxygen atoms in the silica [16]. Hence, the CEC is an important indicator to the removal efficiency of the produced zeolite toward metal ions. This CEC was tested for the produced zeolite obtained at different curing time and reaction temperature. The sodium hydroxide was kept constant during all the experiment at an optimum value of 8 M as reported by several researchers [11,17–19]. Effect of reaction time on the quality of the produced zeolite is shown in Fig. 1. It appears that the increase in curing time from 1 to 5 h will increase the CEC of the produced zeolite from 68 to 85 meq/100 g. However, increasing the curing time from 5 to 24 h has raised the CEC to only 89 meq/100 g. As a result, the 5 h reaction is considered an optimal time from economical point of view.

On the other hand, changing the curing temperature shows a noticeable effect on the CEC, Fig. 2, whereas a maximum value of 166 meq/100 g was obtained at 160 °C cured for 24 h. It is noticed that a proportional relation between the CEC and the reaction temperature. However, it is not advised to treat this ash at high temperature to obtain zeolite with high CEC values. This is because of higher curing temperature consumes considerable amount of energy and affect the reactor life [16].

Fig. 3 shows the XRD pattern for the synthesized zeolite obtained at 160 °C for a 24 h period compared with that of untreated ash. It appears that treatment of the ash with sodium hydroxide helped in the appearance of zeolite and calcite. As a result, the degree of zeolitisation was cleared

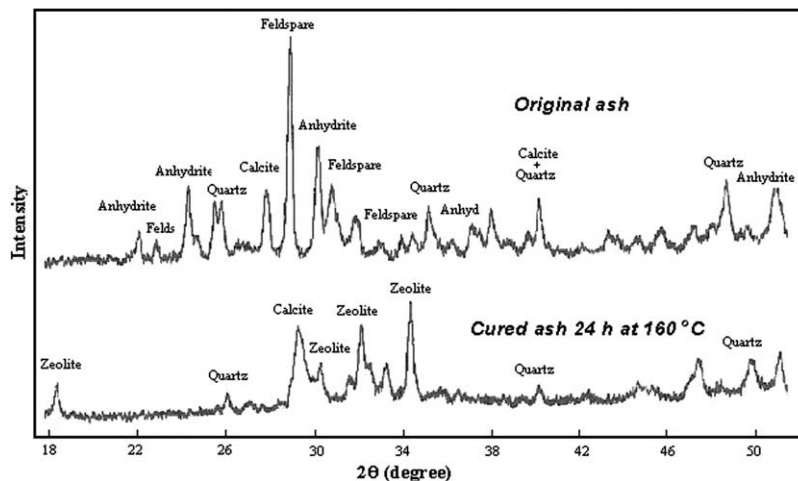


Fig. 3. X-ray diffraction pattern original ash and cured ash with 8 M NaOH.

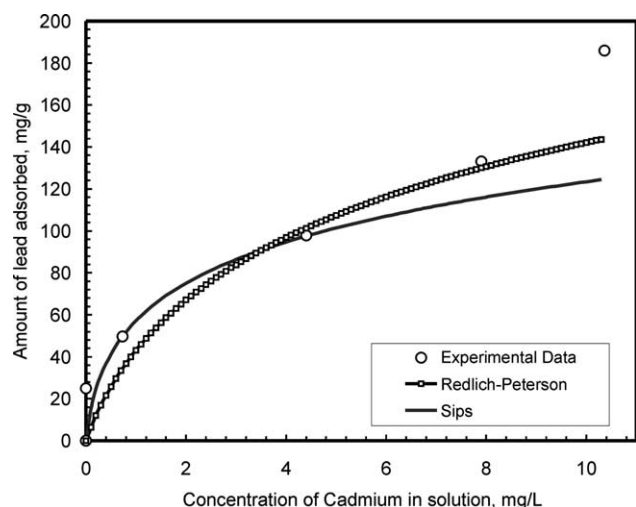


Fig. 4. Adsorption isotherm models for cadmium on zeolite from oil shale ash.

for the quartz and feldspar peaks at 30–35° [20,21]. The hydroxide acts as a strong mineralizing agent, which forces the reactants into solution.

Results of adsorption isotherms for Cd^{2+} and Pb^{2+} onto the surface of the produced zeolite are shown in Figs. 4 and 5, respectively. It is cleared that zeolite adsorb cadmium more efficiently than lead. A maximum uptake of 95.6 mg Cd^{2+} /g solid is obtained from a solution containing initially 100 mg/l to leave 4.4 mg/l in the solution, which shows a sharp increase in the amount to be adsorbed at low concentration before reach the plateau [22]. On the contrary, lead removal can reach only 70.58 mg/g base on the same condition for that of cadmium, which leaves 29.42 mg/l in solution. Therefore, the removal efficiency of this zeolite toward cadmium is greater than that of lead. This could be attributed to the fact that cadmium has lower ionic radius than that of lead. While their charge is equal, the charge to volume ratio for cadmium is higher than for that of lead. This difference leads cadmium to be attracted to the surface

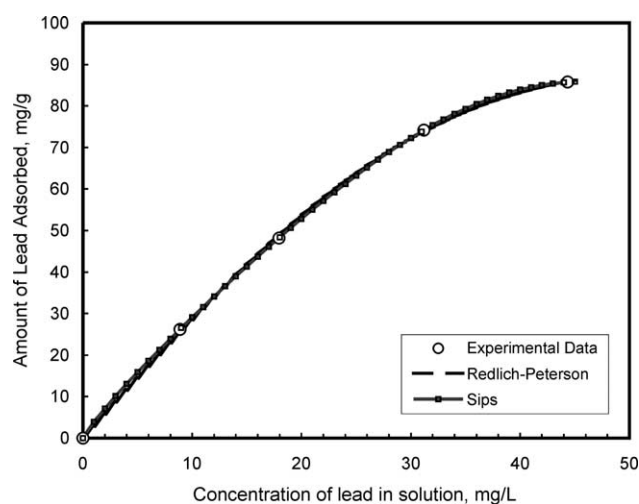


Fig. 5. Adsorption isotherm models for lead on zeolite from oil shale ash.

of zeolite more strongly than lead. In addition, the adsorption of transition metals in general can be explained by Lewis hard–soft acid base principle [23]. In this principle the cation that has high electronegativity and small ionic size obey a strong Lewis acid. Accordingly, this cation prefers to react or form complexes with hard Lewis base [24]. Lead has higher electronegativity (pauling electronegativity = 2.33) than cadmium (pauling electronegativity = 1.69), which yields a harder Lewis acid than cadmium. For this reason, it is expected that the prepared zeolite have mainly hydroxyl groups on its surface, which classify it as soft Lewis base. Therefore, its adsorption preference is directed towards soft Lewis acid as in cadmium.

The equilibrium curve for lead is of type I for which the isotherm is convex, while for the case of cadmium a sigmoid shape of type ii is presented. This sigmoid shape could be verified by a chemical reaction may take place between the cadmium ions and the zeolite surface. Indeed, the sharp jumping of the amount of cadmium adsorbed to 25 mg/g in the first region, Fig. 4, while leaving no cadmium ions in the solution is explained by an irreversible chemisorption behavior. Cadmium is a closed-shell cation where its d^{10} orbital valance is full. This favors coulombic-type reaction at the zeolite surface as opposed to inner-sphere surface reaction [25,26]. This chemisorption is favored for cadmium more than that for lead when the solution ph is fare away from the zero point of charge (zpc) of the zeolite. Experimentally the zpc for the produced zeolite was found to be 4.7 while all isotherm experiments were performed at buffered solution ph of 7. Higher than this ph value the cadmium and lead will precipitate as $\text{Ca}(\text{OH})_2$ and $\text{Pb}(\text{OH})_2$ on the surface of zeolite, respectively. More basic solution could lead the cadmium ion to hydrolyze to form $\text{Cd}(\text{OH})^+$ and $\text{Cd}(\text{OH})_4^-$. However, $\text{Cd}(\text{OH})^+$ is not an important species in relation to equilibrium with zeolite surface in the ph range of 4–7 [22]. The corresponding parameters for the isotherm models for both metals are presented in Tables 2 and 3. The redlich–peterson and sips models were chosen to combine the trend followed by Langmuir and Freundlich models. A close look to the parameters obtained by the two models for lead reveals that redlich–peterson's best fit the experimental data with correlation coefficient of 0.999 and sum of square errors of 1.267. Also a close fitting was obtained using sips model ($R^2 = 0.998$, $\sum(\text{error})^2 = 5.29$). One the other hand, sips

Table 2
Isotherm models for adsorption of Cd^{2+} by zeolite from oil shale ash

Model	Parameters	$\sum(\text{error})^2$	R^2
Redlich–Peterson	$a = 70$ $b = 0.627$ $n = 0.797$	907	0.937
Sips	$q_0 = 238.04$ $b = 0.1146$ $n = 1.862$	626	0.952

Table 3
Isotherm models for adsorption of Pb²⁺ by zeolite from oil shale ash

Model	Parameters	$\sum(\text{error})^2$	R ²
Redlich–Peterson	$a = 2.911$ $b = 1.08 \times 10^{-4}$ $n = 2.227$	1.267	0.999
Sips	$q_0 = 127.261$ $b = 0.0397$ $n = 0.7556$	5.290	0.998

model best-fitted cadmium isotherm with regression coefficient, $R^2 = 0.952$ and $\sum(\text{error})^2 = 626$.

5. Conclusions

The zeolitization process of oil shale ash was optimally synthesized at the experimental conditions of: 8 M sodium hydroxide solution, 160 °C and 1–24 h reaction times. The produced zeolite was tested by XRD and proved that several feldspars, anhydrites and quarts have been converted into zeolite. Then, this zeolite was tested for cadmium and lead removal from water. A better removal efficiency was observed for cadmium than lead. Three isotherm models were applied to each isotherm, which show that Redlich–Peterson model was best-fitted lead isotherms while cadmium isotherm could follow Sips model adequately.

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