

PRODUCTION OF ZEOLITE FROM JORDANIAN OIL SHALE ASH AND APPLICATION FOR ZINC REMOVAL FROM WASTEWATER

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Fly ash – a by-product of oil shale processing – was converted into zeolite by alkali hydrothermal activation using sodium hydroxide. Activation was performed at different temperatures using 1, 3 and 8 M sodium hydroxide. The cation-exchange capacity of zeolite obtained showed that the best conditions for synthesis in a closed reactor are: 8 M NaOH solution, 160 °C and reaction time 24 h. The produced zeolite was used as ion exchanger for cleaning wastewater from metal ions. Zinc was chosen as the test metal. The adsorption capacity measured was 89 mg zinc per g zeolite. The results were correlated using Langmuir, Freundlich, and Brunauer–Emmett–Teller isotherm equations, the latter showing a multilayer adsorption. Kinetics of adsorption proved that the rate of adsorption increases with increasing solution pH, temperature, agitation speed and zeolite mass, and decreasing particle size and solution initial concentration.

Introduction

Jordan possesses large quantities of oil shale. It is estimated that 50 billion tons of oil shale can be mined by open-pit mining, while about 25–40% of this quantity can be extracted as oil [1]. A by-product of oil shale processing – ash – is known to cause serious environmental problems. Therefore, there is a need for a proper strategy for ash handling, disposal and utilization. Usually the ash produced in central-heating furnaces and power plants worldwide is used for producing cement, concrete, asphalt shingle, and quarry fill, for stabilizing sludge, and treating soil for agricultural purpose, while large portions are dumped as landfills [2–6].

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An alternative manner is to convert this ash into a high-grade zeolite, which is considered an environmentally friendly product. Several researchers have 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 [7], the effect of alkali treatment on zeolite synthesis [8], and the possibilities of its application to metal removal from solutions and toxic gases from gas streams [9–11]. The cation-exchange capacity (CEC) of zeolite has also been studied and reported [12, 13].

In the present work, synthesis of zeolite from oil shale ash, is investigated.

Experimental

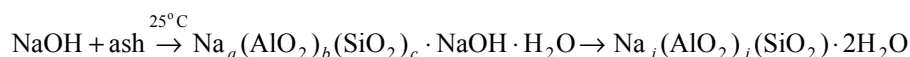
Zeolite Preparation

Oil shale samples taken from EL-Lajjun deposit in the southern part of Jordan were crushed to obtain different-size particles (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 hydrocarbons. The remaining ash was ground and stored.

Chemical composition of oil shale mineral part was determined in the laboratory of Jordan Royal Scientific Society [1], wt.%: SiO₂ 32.5; Al₂O₃ 6.5; Fe₂O₃ 3; P₂O₅ 4; CaO 50; MgO 3.3; TiO₂ 0.2; Na₂O 0.5. The content of lime, silica and alumina altogether accounts for 89% of the total weight of the average samples.

Zeolite synthesis was carried out by mixing 50 g ash with 100 ml sodium hydroxide solution. Concentration of sodium hydroxide solution was varied from 1.0 to 8.0 mole/L. The slurry placed in the reaction vessels was put into the oven and kept there for different periods of time (1–24 h). The temperature was varied from 25 to 180 °C. The reaction vessels used in this study were firmly sealed with rubber to maintain constant pressure and prevent any losses of the reactants during the heating process. The oven was equipped with photoionization detector temperature controller.

The reactions occurring in oven involved the formation of hydrous aluminosilicate gel. This gel was carefully cured to obtain maximum growth of zeolite crystals. The reaction between ash and sodium hydroxide solution is expected to complete [15] when alumina and silica are dissolved during the stages of zeolitisation:



At the end of the activation period the product was taken out, washed several times by distilled water, filtered, dried at 100 °C, and stored in a closed container for analysis.

The mineralogical composition of the ash and the synthesized zeolite were determined by X-ray diffraction spectrometer studies using a Rikant UY 10392 diffractometer operated at 40 kV and 40 mA. All chemicals were of analytical grade (*Scharlau*, Spain), and all the glasses were *Pyrex*, rinsed and washed several times with diluted nitric acid and distilled water to remove any adhered impurity from the glass surface.

Cation-Exchange Capacity

The fine-grained (<125 μm) samples, 4 g each, were mixed with 33 ml 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 ammonium acetate. The supernatant of acetate solution was collected and diluted to 100 ml with sodium acetate, and the sodium concentration was determined by 5000 Perkin-Elmer atomic absorption spectrophotometer.

Adsorption Isotherms

Aqueous solutions of zinc were prepared varying initial concentrations from 50 to 250 mg/L. Batch adsorption tests were performed with zeolite particles of fixed size. Equal weights of zeolite (0.1 g each) were placed into each of ten Erlenmeyer flasks where 100 ml of zinc solution of different initial concentration was added. The flasks were placed into an isothermal shaker ($20 \pm 1^\circ\text{C}$) for a fixed period of time to allow complete equilibration. A similar procedure was performed on blank samples with zeolite only. All solutions were buffered to pH 7. Equilibrated solutions were filtered and analyzed using a S4 thermoelement atomic absorption spectrophotometer.

Adsorption Kinetics

Adsorption kinetics was measured in a 2-L beaker where 1.0 g zeolite was added to 1.5 L zinc solution and agitated for one hour. Two-ml samples were drawn every minute in the first ten minutes and every ten minutes thereafter. The effect of zinc initial concentration, solution acidity, solution temperature, mass and particle size of zeolite, and stirring speed were considered to determine the rate of zinc adsorption onto the produced zeolite. All samples were analyzed using thermoelement atomic absorption spectrophotometer.

Theoretical

In order to study the metal uptake by the surface of the produced zeolite, several dynamic adsorption equilibrium equations were used in order to fit experimental findings. Langmuir, Freundlich, and Brunauer–Emmett–Teller (BET) equations were considered. Langmuir equation is valid for single-layer adsorption and assumes maximum adsorption corresponding to a

saturated monolayer of adsorbate molecules on the surface of the adsorbents where the energy of adsorption is considered to be constant.

Mathematical expression for Langmuir equation in terms of solute concentration in solution, C_e (mg/L), in equilibrium with that on the solid surface, q_e (mg/g), is

$$q_e = \frac{QbC_e}{1+bC_e} \quad (1)$$

where Q is the maximum amount of adsorbate per zeolite mass unit required to form a complete monolayer, mg/g;

b is the Langmuir constant related to the affinity of binding sites, L/mg.

On the other hand, BET equation assumes that a number of layers of adsorbate molecules form on the surface of adsorbent, and that the Langmuir equation is applied to each layer of adsorption, thus

$$q_e = \frac{Qk_1C_e}{(1-k_mC_e)[1+(k_1-k_m)C_e]} \quad (2)$$

where k_1 and k_m are the equilibrium constants for the first and subsequent layers, respectively.

Finally, the Freundlich equation was used to incorporate the effect of heterogeneous surface energy in which the energy term, b , in the Langmuir equation varies as a function of surface coverage due to the heat of adsorption [14].

The Freundlich equation takes the form

$$q_e = K_F C_e^{1/n} \quad (3)$$

where K_F and n are constants;

index $1/n$ is adsorption intensity;

coefficient K_F can be related to the surface energy by the proportionality relation

$$K_F \propto RTnbe^{\Delta H/RT} \quad (4)$$

Results and Discussion

The CEC of the produced zeolite is illustrated by Fig. 1. It appears that the increase in curing time from 1 to 24 h at fixed temperature (85 °C) and NaOH concentration (5 M) will increase the CEC of the produced zeolite from 68 to 89 meq/100 g. Increasing the curing time from 5 to 24 h has a slight effect on the increase in CEC (see Fig. 1a).

However, changing the curing temperature (see Fig. 1b) shows a noticeable effect on CEC, whereas its maximum value – 166 meq/100 g – was obtained under conditions 160 °C, 8 M NaOH and 24 h.

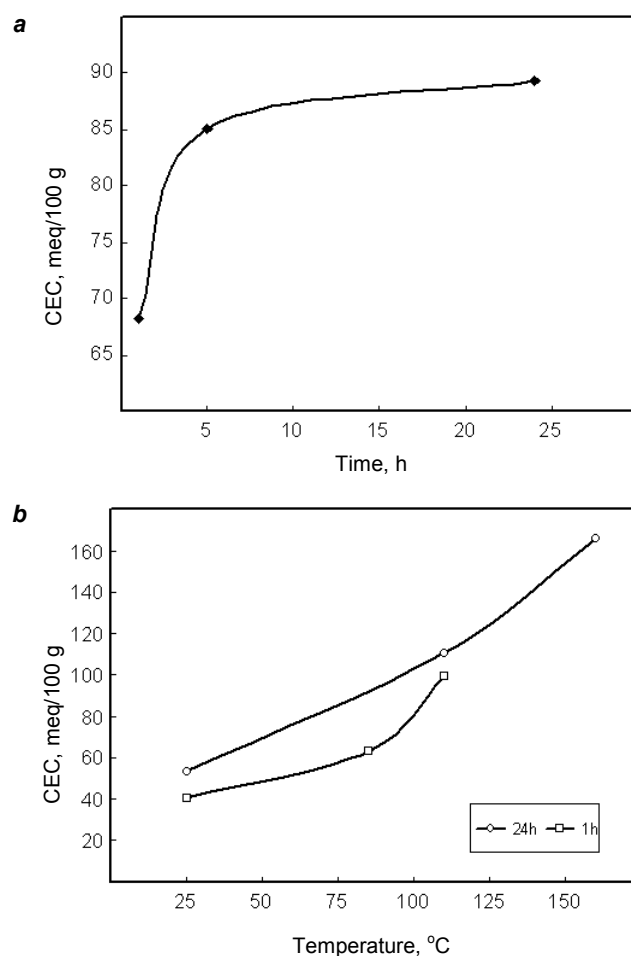


Fig. 1. Effect of time (a), and temperature and curing time (b) on CEC of the produced zeolite

Figure 2 shows the X-ray diffraction pattern of this product and that of the untreated ash. It is shown that the diminishing of quartz and feldspar peaks in the chart for cured ash is attributed to the reaction with 8 M sodium hydroxide. At this concentration the degree of zeolitization was expressed as the decrease in the intensity of quartz and feldspar peaks between 30 and 35° [16]. The hydroxide acts as a strong mineralizing agent forcing the reactants into solution. The greater the OH⁻ concentration, the greater the concentration of reactants in solution and thus the greater the rate of crystal growth [17].

Isotherms of zinc adsorption on the surface of the produced zeolite are shown in Fig. 3. The corresponding adsorption equilibrium equations are presented in the Table. Equilibrium data for zinc indicates a multilayer adsorption, which can be best fitted using the BET equation (correlation coefficient $R^2 = 0.986$).

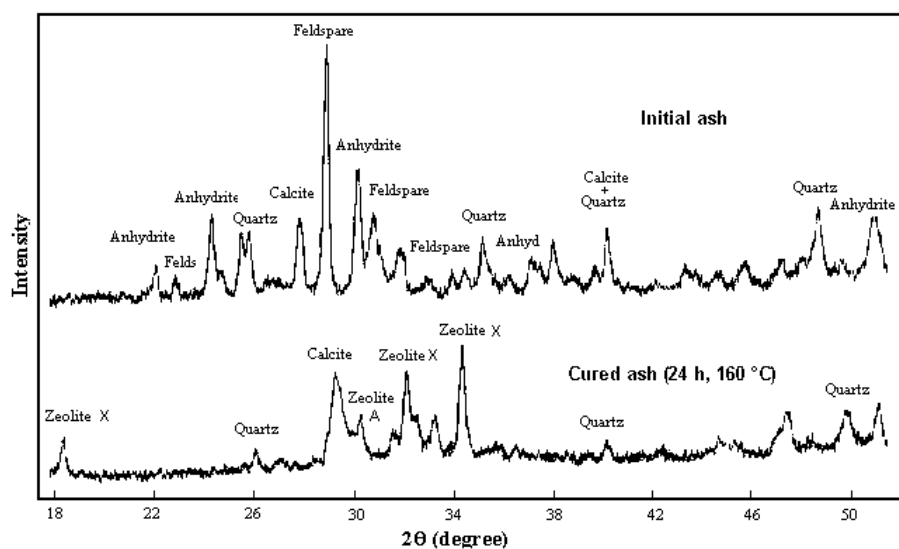


Fig. 2. X-ray diffraction pattern of the initial ash and ash cured with 8 M NaOH

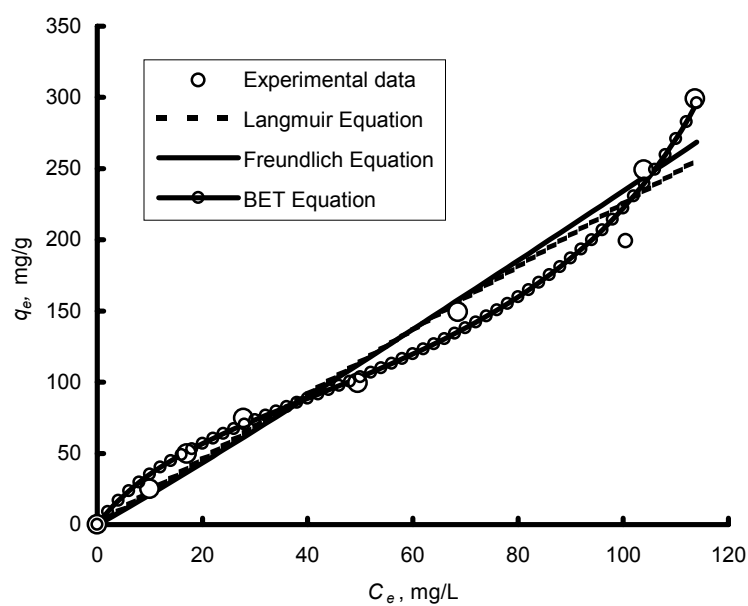


Fig. 3. Adsorption isotherm equations applied for zinc adsorption on the zeolite produced from oil shale ash

Isotherm Equations Applied to Determine Zinc Adsorption by Zeolite Synthesized from Oil Shale Ash

Equation		R ²
Langmuir	$q_e = \frac{2.308C_e}{1 + 0.00026C_e}$	0.959
Freundlich	$q_e = 1.877C_e^{1.048}$	0.963
BET	$q_e = \frac{4.918C_e}{(1 - 0.00625C_e)[1 + 0.0490C_e]}$	0.986

The corresponding values of k_1 and k_m were $k_1 = 0.05525$ L/mg and $k_m = 0.00625$ L/mg. The maximum adsorption capacity obtained is $Q = 89$ mg zinc per g zeolite. Langmuir and Freundlich equations can also be applied but with some deviation from the experimental data. Kinetic measurements show that the rate of zinc ion transport from the solution toward the zeolite particle surface is the controlling step (Figs 4–6).

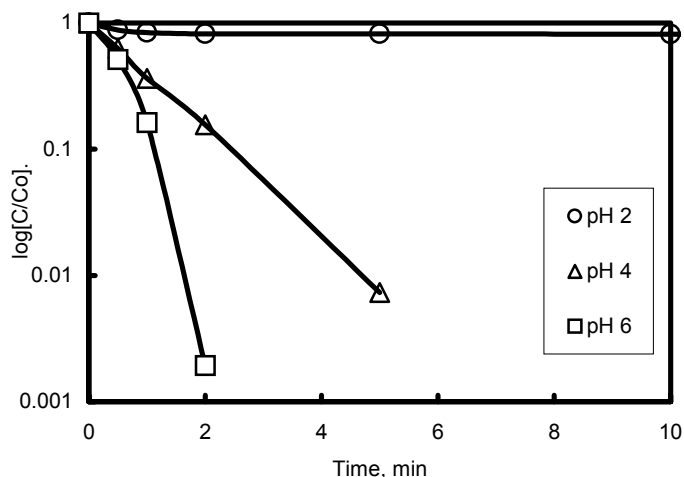
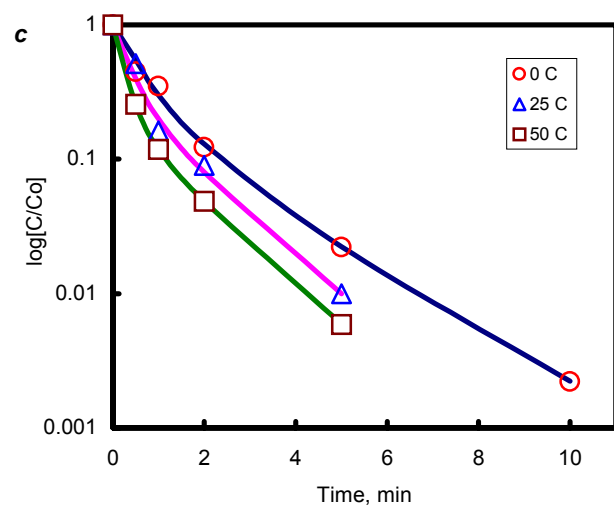
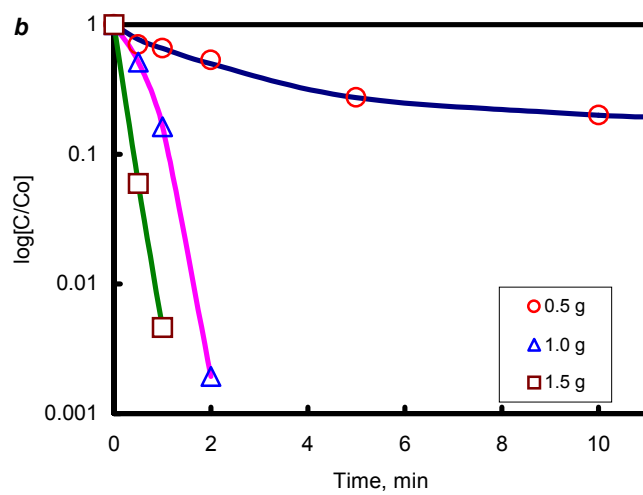
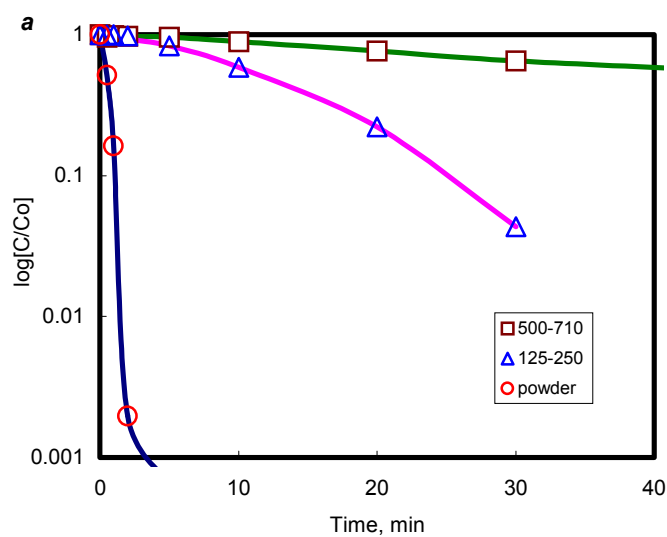
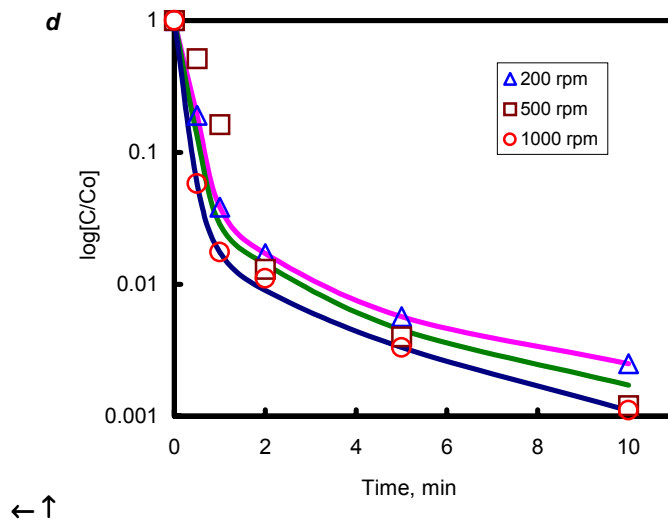


Fig. 4. Effect of pH on the kinetics of zinc adsorption on synthesized zeolite

Figure 4 illustrates the effect of solution acidity on the adsorption rate. As the solution pH increases from 2 to 6, the time required to attain a specific solution concentration decreases as well. Moreover, at pH 2 the diffusion of the zinc ions through the micropores of the zeolite particle controls the adsorption rate, while at pH 6 the rate of mass transfer of zinc ions in the solution is the controlling step. This behavior became clear when the zeolite particle size was decreased from the particle form to the powdered one (Fig. 5a).





← ↑
 Fig. 5. Effect of zeolite particle size (a), zeolite mass (b), solution temperature (c), and stirring speed (d) on the kinetics of zinc adsorption

Figure 5b illustrates the effect of zeolite mass on the zinc adsorption rate. As the sample mass increases, there will be more surface area available for adsorption, and hence the equilibrium is attained during a shorter period of time. On the other hand, as the solution temperature decreases, the rate of adsorption will decrease as well (Fig. 5c), indicating endothermic adsorption of zinc ions on the surface of zeolite.

Figure 5d shows the effect of agitation on the adsorption rate. Enhanced rate of adsorption is attributed to increasing kinetic energy of zinc ions and decreasing diffusion resistance of these ions throughout the micropores.

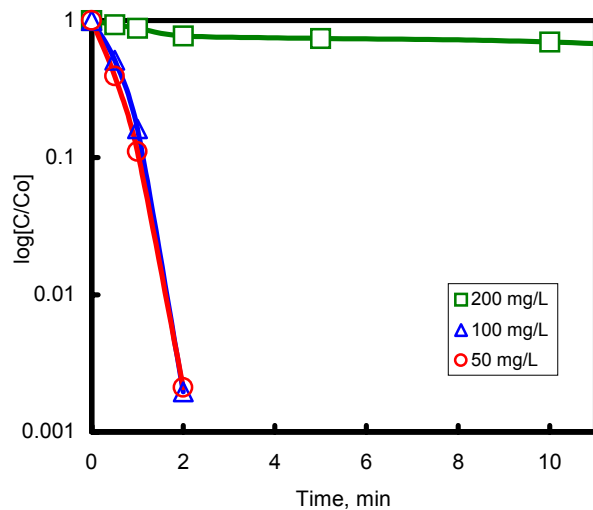


Fig. 6. Effect of solution concentration on the kinetics of zinc adsorption

Figure 6 displays the effect of initial concentration on the adsorption rate. The higher solution concentration, the lower adsorption rate expected. This is due to the intermolecular competition on the limited active surface that resists the movement of these ions toward the surface.

The process layout is shown in Fig. 7.

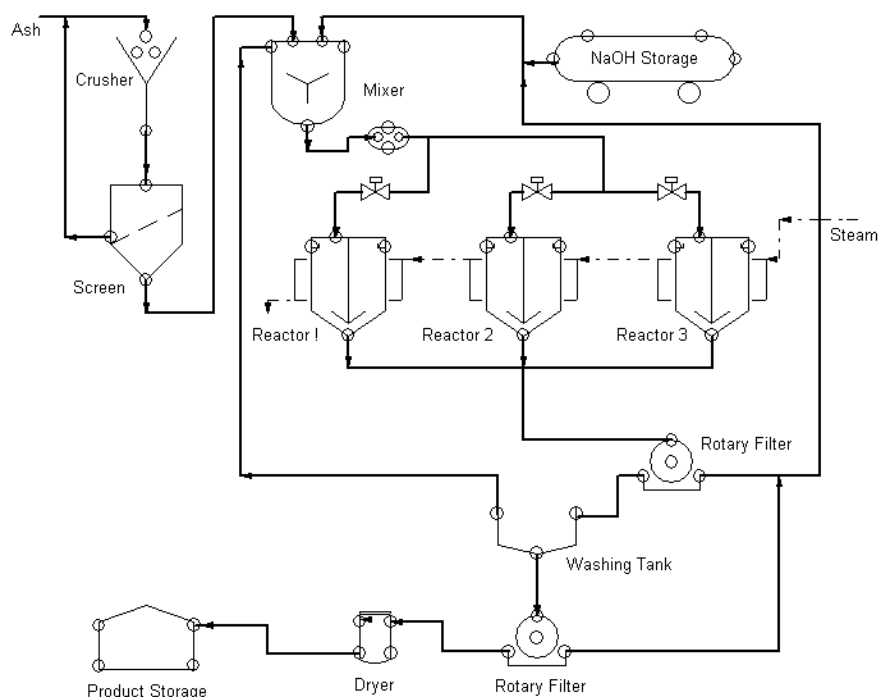


Fig. 7. Process flow diagram for the production of zeolite from ash

This unit is proposed to treat 300 kg ash per day. Solid ash from oil shale processing plant and sodium hydroxide solution (8 M) with a flowrate of $2 \text{ m}^3/\text{day}$ enter conical mixer and are agitated there for 1 h. The slurry of ash is pumped by a gear pump to the reaction vessels. These vessels are designed to work in series; one works while the others either stand by or are under washing.

The reactors designed will work under three bars and $160 \text{ }^\circ\text{C}$. Two control valves are located at the entrance and discharge of each reactor to maintain closed opening during the synthesis process. The reactors are jacketed and low-pressure steam will pass through these jackets to provide reaction solution with heat.

The product from each reactor is transferred by a screw conveyor to the filter drum. The supernatant solution from the filter is recycled to mixing tank while the solid is transferred by rubber belt to the washing tank to remove excess sodium hydroxide. After drying in a rotary dryer the solid is transported to the storage.

Conclusions

The process of oil shale ash zeolitization was studied at the experimental conditions: 8 M sodium hydroxide solution, 160 °C and reaction time 1–24 h.

Adsorption capability of the produced zeolite was tested using zinc.

The following conclusions can be drawn:

- Zeolite formation was observed in all samples studied.
- Adsorption of zinc on the surface of the produced zeolite could be described adequately with the BET equation.
- The process conditions significantly affect the adsorption rate.

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