Zinc Removal From Aqueous Solutions By Turkish Clinoptilolite

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Abstract:- In this study, the removal of zinc ions from aqueous solution using natural Turkish zeolite, clinoptilolite, under different experimental conditions was investigated. Zeolite was used as a low cost adsorbent to remove zinc ions from water changing initial zinc concentration, pH and zeolite particle size. Langmiur and Freundlich isotherm models were tested to describe the adsorption data of Bigadic clinoptilolite about zinc ion uptake capacity. The results showed that the pretreatment with NaCl increased removal efficiency about 50 %. There were no significant effect changing pH`s and zeolite particle sizes. According to experimental data the Langmuir isotherm model has been fitted better than Freundlich.

Key Words: Zinc removal, Clinoptilolite, Adsorption, Ion Exchange

1. Introduction

High concentrations of heavy metals in the environment are mostly due to uncontrolled wastewater discharge. It is often the discharge of industrial wastewaters from plating, metal finishing and rinsing manufacturing processes. Some industries of organic compounds such as pesticides, pigments metal additives, petroleum refining and pulp industries produce large amounts of solid and liquid waste that contains different types and quantities of heavy metals.[1]

Zinc manufacturing and other industries release large quantities of metals, mainly Cadmium and Zinc, during production. The increasing demand for alkaline zinc manganese batteries, instead of mercury based ones, brings serious problems when those batteries are not disposed off properly. Zinc, one of the most preponderant pollutants, is difficult to remove from wastewater rather than other heavy metals (i.e. lead, copper and cadmium)[2]

Numerous processes exist for removing dissolved heavy metals, including ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis, and electrodialiysis. Nevertheless, many of these approaches can be marginally cost-effective or difficult to implement in developing countries.

Therefore, the need exists for a treatment strategy that is simple, robust, and that addresses local resources and constraints. In this regard, naturally occurring zeolites hold great potential for use as packing material in subsurface reactive barriers intercepting ground water plumes, and for fixed bed reactors designed to remove heavy metals from industrial wastewater [3].

Zeolites represent an appropriate material for removing heavy metal ions from wastewater because of their relatively low price coupled with the fact that their exchangeable ions (Na^+, Ca^{2+} and K^+) are relatively harmless. In addition, zeolite loaded with heavy metal ions can be easily regenerated[4].

Natural zeolites are volcanic minerals with unique characteristics. Their chemical structure classifies them as hydrated aluminum silicates, comprised of hydrogen, oxygen, aluminum, and silicon, arranged in an interconnecting lattice structure. The arrangement of these elements in a zeolite crystal gives rise to a honeycomb framework with consistent diameter connecting channels that vary in size depending on the type of zeolite mineral. Zeolite minerals with a cage-structure offers large internal and external surface areas for ion exchange (i.e., in the range of several hundred

square meters per gram). They posses a net negative structural charge due to isomorphic substitution of cations in the mineral lattice. Hence they have a strong affinity for transition metal cations, but only little affinity for anions and non-polar organic molecules [3,4,5].

In this study the aim is to search zinc removal capacity of Turkish cinoptilolite, zeolite, under different experimental conditions. Firstly, increasing in uptake of clinoptilolite by sodium homoionic form of natural zeolite was investigated then under different initial concentration and pH values. Equilibrium experiment results were tried to expressed with isotherm models.

2. Materials and Methods

2.1. Materials

The clinoptilolite zeolite was obtained from Bigadic locations, western part of Turkey. Mineral identification using X-ray diffraction (XRD) showed that the zeolite consisted mainly of clinoptilolite (% 85) with traces of quartz, silika, feldspat and clay. In addition the general chemical composition of the Bigadic zeolite is given in Table1.

Table1. Analysis of Bigadic clinoptilolite [8]

Oxide	% by weight
SiO_2	64.99
Al_2O_3	9.99
Fe_2O_3	3.99
Na_2O	0.18
K_2O	1.95
CaO	3.51
MgO	1.01
H_2O	14.47
Total	100

The zeolite sample was crushed and classified to a size range of 0.25–1.68 mm then washed with distilled water in order to remove undesirable materials and dust, then finally dried in at room temperature. It is well known from literature that chemical conditioning into homoionic form increases ion exchange capacity of the natural zeolite [9]. Therefore some part of sample has been modified with the 1M NaCl solution at a solid/liquid ratio 1g/25ml in Jar Test apparatus at 150 rpm and 48 hours then the samples were re-washed and

sieved to obtain particle sizes range from 0.25 to 1.68 mm at room temperature.

2.2. Methods

Experimental study was performed in two part as batch kinetic experiments and equilibrium experiment.

Stock zinc solutions were prepared from $ZnSO_4.7H_2O$ using deionized water. The solutions were stored in amber glass bottle with a 0.2 ml 1N HNO_3. Spectra A250Plus atomic absorption spectrometry (AAS) was used to determinate the concentrations of zinc in solutions.

2.1.1 Batch kinetic experiments

Stock zinc solutions were prepared from $ZnSO_4.7H_2O$ using deionized water. Examination of ion exchange kinetics of zinc ions was performed by means of the batch method in natural or Na modified clinoptilolite-Zinc aqueous solutions systems. The mixtures of 1 g of zeolite sample and 1L of zinc ion solutions were shaken at 150 rpm and room temperature in a beaker for different initial concentration (10, 30 and 50 mg/L) and zeolite particle size ranges (0.25–0.50, 0.50-1.0 and 1.0-1,68mm) and different pH`s (4, 5 and 7), the zinc uptake process has been observed during 300 minutes by taking samples. The samples were filtered then stored in amber glass bottle with a few drops of dilute HNO_3.

The interaction between the zinc ion and zeolite can be given by the equilibrium:

$$mZn^{2+}_{(s)}+2M^{m+}_{(z)}\rightarrow mZn^{2+}_{(z)} + 2M^{m+}_{(s)} \qquad (Eq.1)$$
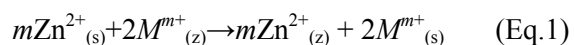
Where m is the valence of exchangeable cations M (Na, K, Ca, and Mg) and subscripts (s) and (z) denote solution and zeolite phases, respectively.

Effects of process parameter were determined by calculating zinc uptake by zeolite and changing that parameter and keeping other parameters constant. Clinoptilolite Zinc uptake was calculated using the equation:

$$\text{Uptake, \%}= (1-(C_i/C_0))x100 \qquad (Eq.2)$$

Where C_0 and C_i are the initial and after certain time concentration of zinc, mg/L.

2.1.2. Equilibrium Experiment

Batch adsorption isotherm studies are carried out 100 ml known initial zinc concentration of aqueous solution and known different zeolite mass (0.1-4.5 g). After addition of zeolite and solution to a bottle, the mixture was put on a shaker for 48 hours for equilibrium. All experiments are carried out 20 °C temperature.

Zinc concentration of samples were measured before shaking which was the initial concentration, C_0 and after 48 hours shaking which was the equilibrium concentration, C_e. Using initial concentration, C_0, equilibrium concentration, C_e, the solution concentration (V) and added zeolites mass (M), adsorption capacity of zeolite q_e, was calculated for all samples using Equation (3). The capacity of the clinoptilolite were evaluated in terms of grain size and pH.

$$q_e = (C_o - C_e)V/M \qquad (Eq\ 3)$$

Isotherms were drawn plotting the amount of zinc ion adsorbed on to the zeolite, q_e against the equilibrium concentration of zinc ion in the solution, C_e.

In this study the Langmiur and Freundlich isotherm were tested in terms of their ability to describe the adsorption data of Bigadic clinoptilolite about zinc ion uptake capacity. The Langmuir Model is expressed as;

$$q_e = (q_{max}\ b\ C_e) / (1 + b\ C_e) \qquad Eq\ (4)$$

Where; q_e(mg/g zeolite) is the adsorption capacity of the zeolite, q_{max}(mg/g zeolite) is the maximum adsorption capacity of the zeolite, C_e (mg/l) is the zinc ion concentration in solution at equilibrium and b express a measurement of (1/mg) is a constant.

Equation 4 can be modified a linearized form as given Equation (5).

$$C_e/q_e = (1/ q_{max}\ b) + (Ce/ q_{max}) \qquad Eq.\ (5)$$

The second isotherm model is Freundlich isotherm and its equation is as following:

$$q_e = K_f C_e^{1/n}$$
$$Eq\ (6)$$

Where K_f and n are the Freundlich constants.

Linearization form of Freunclich istherm is as Equation (7).

$$Log\ q_e = Log\ K_f + n\ Log\ C_e \qquad Eq.\ (7)$$

3. Results and Discussion

3.1 Effect of Na Modification of clinoptilolite on zinc uptake

In this experimental stage, aim is to determine zinc uptake of natural zeolite with chemical conditioning into Na-homoionic form how increases ion exchange capacity. Natural and Na-modified clinoptilolite were used at 0.25-0.5 mm particle size under 30 mg/L initial zinc concentration. Experimental results are given in Figure 1. Na homoionic form of Bigadic clinoptilolite zinc uptake capacity increases about 45-50 %. The equilibrium is established at approximately about 86 % part is completed during in 150 minutes. Uptake rate have not changed significantly after 150 minutes.
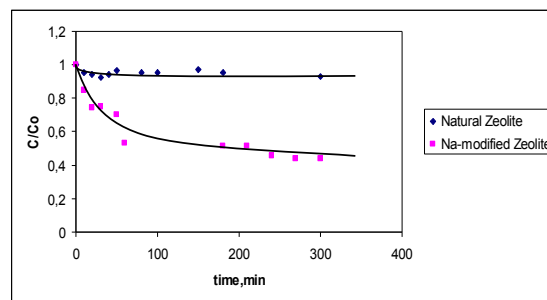

Fig.1. Na-modification effect to zinc uptake

3.2 Initial Zinc concentration Effect

Kinetics of zinc uptake by Na-modified zeolite are represented in Fig 2. Initial concentration of Zinc was changed 10 to 50 mg/L. Zinc uptakes efficienceis have approached over 96%, 53% and 15% at initial concenration respectively 10 mg/L, 30 mg/L and 50 mg/L during first 150 minutes. When the concentration was increased, uptake efficiency decreased.
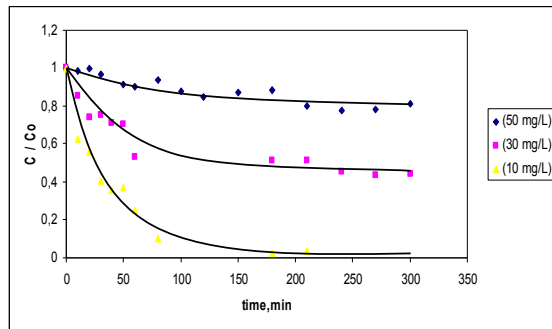
Fig.2. Relationship between initial concentration and zeolite uptake efficiency

3.3 Grain size effect

Grain size effect was observed as shown Figure 3 using three different Na modified zeolite size (0.25-0.5mm, 0.5-1.0mm and 1.0-1.68mm) at 10 mg/L initial zinc concentration at and room temperature. The finer zeolite particles leads to an increase in zinc uptake. Zeolite zinc uptake percentage increases from fine size (0.25-0.5mm) to coarse size (1.0-1.68) about 18 % during the first 150 minutes. Decreasing particle size as expected that is increasing surface area of zeolite. The smaller zeolite grain size gives larger surface areas and increasing effect zinc removal from the solution.
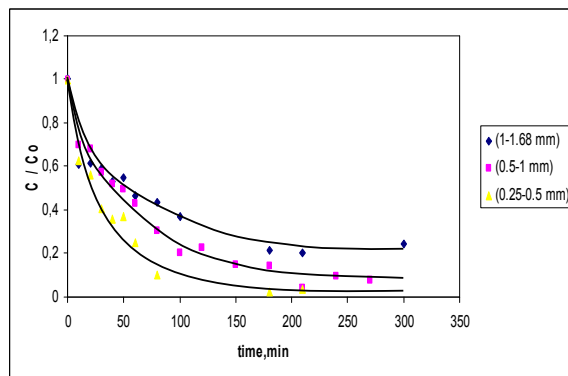

Fig.3. effect of grain size fractions on Zinc ion removal

3.4 pH effect

Figure 4 shows Zinc uptake experimental results at three different pH as 4, 5 and 7 at 0.25-0.5mm grain size and 50 mg/L initial concentration. The Zinc removal efficiency has not been changed significantly with observed pH`s.
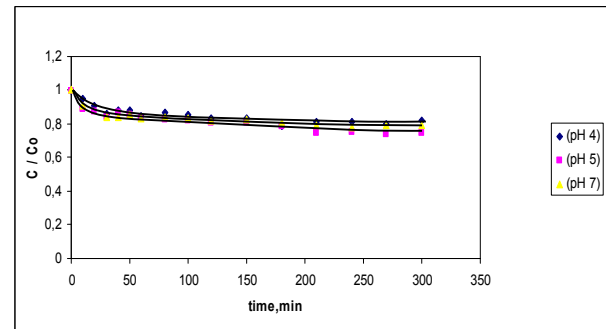

Fig.4. Zinc uptake efficiency in different pH`s

3.5 Isotherm and isotherm models

The equilibrium of zinc ion in solid, zeolite, phase with the concentration of the zinc ion in solution phase characterizes as isotherm and its graphical representation are given Figure 5 at 20 ºC. It represents the change in adsorption behaviour under different zinc ion concentrations. Increasing the zinc concentration led to increase in zinc ion uptake and reached maximum uptake capacity is about 12 mg/g zeolite.
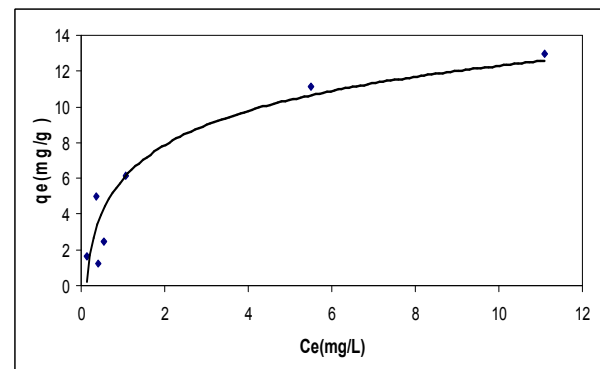

Fig.5. Zinc isotherm of Turkish clinoptilolite

Langmiur and Freundlich isotherm models were linearized as Equation (5) and (7) and drawn in Figure 6 and Figure 7 using equilibrium data.
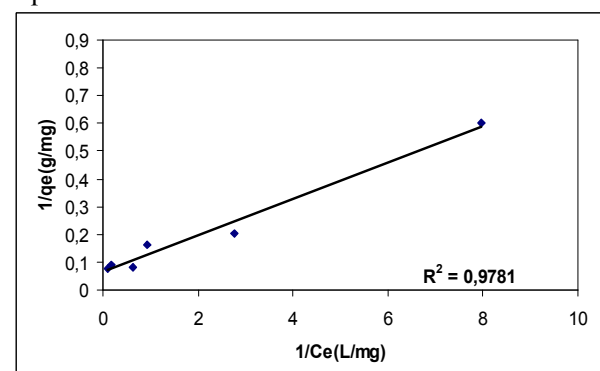
Fig.6. Linearized Langmuir isotherm for experimental data

Langmiur model were well fit with the experimental data rather than Freundlich isotherms.
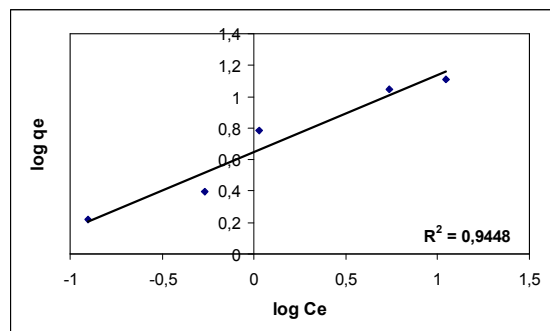

Fig.7. Linearized Freundlich isotherm for experimental data

4. Conclusions

Zinc ion removal capacity of Turkish clinoptilolte was observed at different grain size fractions, pH values, initial metal ion concentrations and also Na homoionic form of zeolite.   The obtained results can be summarized as follows:

- Clinoptilolite was converted to homoionic sodium form and therefore Zinc uptake capacity increased about 45-50 %.
- When initial concentration of zinc was increased, removal efficiency was decreased.
- The finer zeolite particles leads to an increase in zinc uptake about 18 % compairing coarse size.
- Changing of pH from 4 to 7 was not significantly effect on zinc removal.
- The uptake equilibrium experimental results were well described with the Langmuir than Freundlich isotherms.

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