



Adsorption Equilibrium of Zinc Ions from Aqueous Solution by Using Modified Clinoptilolite

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ABSTRACT

Adsorption of Zn(II) ions from aqueous solution onto clinoptilolite has been investigated to evaluate the effects of initial concentration, initial pH and contact time on the removal of Zn^{2+} . Experimental data obtained from batch equilibrium tests have been analyzed by four two-parameter (Freundlich, Langmuir, Temkin and Dubinin-Radushkevich) isotherm models. It was found that the optimum concentration of solution is about 500 ppm and the optimum pH value of water to be treated for adsorption was found to be 7. In adsorption studies, residual heavy metal ion concentration reached equilibrium in short duration of 2.0 h for initial Zn^{2+} concentration of 300 ppm. Maximum adsorption capacity, 9.43 mg Zn^{2+} /g zeolite, showed that this adsorbent was suitable for zinc removal from aqueous media. The process of metal ions uptake by natural zeolite is best described by the equation for adsorption and can be easily carried out with a satisfactory rate. The correlation found between the Zn^{2+} uptake and the amount of Na^+ , Ca^{2+} and K^+ released into solution by zeolite showed that the ion exchange sorption plays the basic role in metal ions uptake by natural zeolite. Adsorption phenomena appeared to follow two-parameter isotherms. The results showed that there is a good fit between the experimental data and empirical isotherms.

Keywords: Clinoptilolite, Zinc, Removal, Ion Exchange, Adsorption.

1. INTRODUCTION

Zinc manufacturing and other industries release large quantities of metals, mainly Cd and Zn, 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. Yet, another source of contamination can be due to the flooding of ore mines into the environment. Since heavy metals have toxic effects on the environment and public life, many researchers

suggest a cost-effective process, such as ion exchange, for removing dissolved heavy metals from wastewaters by using naturally occurring materials [1].

In the later years, utilization of natural zeolites to control the pollution due to the effluents polluted with heavy metal ions has increased. Natural zeolites have ion exchange capability to remove unwanted metal ions and this property makes zeolites favorable for wastewater treatment. Beside this, price

of zeolites is considered very cheap. Basically, zeolites are a naturally occurring crystalline aluminosilicates consisting of a framework of tetrahedral molecules, linked with each other by shared oxygen atoms and containing exchangeable alkaline and alkaline earth metal cations (normally Na^+ , K^+ , Ca^{2+} and Mg^{2+}) as well as water in their structural framework. The physical structure is porous, enclosing interconnected cavities in which the metal ions and water molecules are contained. The fundamental building block of the zeolites is a tetrahedron of four oxygen atoms surrounding a relatively small silicon or aluminum atom. Because aluminum has one less positive charge than silicon, the framework has a net negative charge of one at the site of each aluminum atom and is balanced by the exchangeable cation. Clinoptilolite is most abundant in nature and has a typical chemical formula of $\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_{30}]\cdot 24\text{H}_2\text{O}$. The chemical, surface, and ion exchange properties of clinoptilolite have been concerned in many studies [2].

Although the large number of different studies on the removal of Zn(II) ion from aqueous solutions using zeolite, every special zeolite material requires individual research.

The present work describes the batch adsorption characteristic of Zn(II) on clinoptilolite concentrating on various operational parameters; such as initial concentration, initial pH and contact time on adsorption capacity. Experimental data have been analyzed by adsorption isotherms.

2. MATERIALS AND METHODS

2.1 Materials Preparation

The natural zeolite used was obtained by Pesticide Free Agriculture Association, in Thailand. Clinoptilolite 38-75 mm was treated with 0.5 M NaCl solution for 24 h under slow stirring. It was dried for 24 h at 60 °C in an oven before starting the experiments.

All chemicals used were analytical grade reagents (Merck, >99% purity). A stock solution of metals was prepared in a concentration of 2,000 ppm using nitrate salts dissolved in deionized water. The chemical used in the batch experiments was nitrate solutions of $\text{Zn}(\text{NO}_3)_2$.

2.2 General Procedures

Batch mode adsorption isotherm was carried out at 30°C. An amount of 2.0 g clinoptilolite was introduced into conical flasks with 100 ml of zinc solution. The flasks were placed in a thermostatic shaker and agitated for 0.5-3.5 h at a fixed agitation speed of 700 rpm. Preliminary tests confirmed that 2-3 h contact time were enough to reach a steady state Zn(II) concentration. Samples were taken periodically for measurement of aqueous phase of zinc concentrations. The pH of metal solutions was appropriately adjusted by using HNO_3 or NaOH. Since, above pH 7 precipitations may occur. Adsorption isotherms were performed for initial Zn(II) concentrations of 50-1,000 ppm. The Zn(II) concentration of the samples was determined by using a Varian Liberty 220 inductive coupled plasma emission spectrometer (ICP-ES).

2.3 Determining the Amount of Metal Ion Removal

The amount of adsorbed Zn^{2+} ions (mg metal ions/g zeolite) was calculated from the decrease in the concentration of metal ions in the medium by considering the adsorption volume and used amount of the zeolite:

$$q_e = \frac{(C_o - C_e)}{m/V} = \frac{(C_o - C_e)}{S} \quad \dots(1)$$

Here q_e is the amount of metal ions adsorbed into unit mass of the zeolite (mg/g) at equilibrium, C_o is the concentration of the metal ions in the initial solution (ppm), C_e is the concentration of the metal ions in the

final solution (ppm), m is the amount of zeolite used (g), V is the volume of metal solution (L) and S is the slurry concentration (g/l).

2.4 Adsorption Isotherms

Adsorption isotherms for zinc ions removal by zeolite in terms of two-parameter isotherm models were expressed mathematically. The obtained experimental data here are expectedly well fitted with the linearized form of Freundlich, Langmuir, Temkin and Dubinin-Radushkevich models.

Freundlich isotherm assumes heterogeneous surface with a nonuniform distribution of heat of adsorption. Freundlich isotherm [3] is given as:

$$q_e = K_f C_e^{1/n} \quad \dots(2)$$

where K_f and n are indicative isotherm parameters of adsorption capacity and intensity, respectively.

Basic assumption of Langmuir isotherm is that adsorption takes place at specific homogeneous sites within the adsorbent. Langmuir isotherm [4] can be represented as:

$$q_e = \frac{K_L a_L C_e}{1 + a_L C_e} \quad \dots(3)$$

where K_L and a_L are the Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The theoretical maximum monolayer adsorption capacity, q_m (mg/g), is given by K_L/a_L .

Temkin isotherm assumes that decrease in the heat of adsorption is linear and the adsorption is characterized by a uniform distribution of binding energies. Temkin isotherm [5] is expressed by the following equation:

$$q_e = \frac{RT}{b} \ln (K_{Te} C_e) \quad \dots(4)$$

where K_{Te} is equilibrium binding constant

(l/g), b is related to heat of adsorption (J/mol), R is the gas constant (8.314×10^{-3} kJ/K mol) and T is the absolute temperature (K).

Dubinin-Radushkevich isotherm is applied to find out the adsorption mechanism based on the potential theory assuming heterogeneous surface [6]. Dubinin-Radushkevich isotherm [7,8] is expressed as follows:

$$q_e = q_m \exp \left(\frac{(RT \ln (1+1/C_e))^2}{-2E^2} \right) \quad \dots(5)$$

where q_m is the maximum adsorption capacity (mg/g) and E is energy of adsorption (kJ/mol).

3. RESULTS AND DISCUSSION

3.1 Effect of Initial Concentration

Figure 1 illustrates the adsorption of Zn^{2+} ions by zeolite as a function of initial metal ion concentration. The amounts of metal ions adsorbed were calculated using Eq. (1). This increase continues up to 500 ppm and beyond this value, there is not a significant change at the amount of adsorbed metal ions [1,2,9]. This plateau represents saturation of the active sites available on the zeolite samples for interaction with metal ions. It can be concluded that the amount of metal ions adsorbed into unit mass of the zeolite at equilibrium (the adsorption capacity) rapidly increases at the low initial metal ions concentration and then it begins to a slight increase with increasing metal concentration in aqueous solutions in the length between 500 and 800 ppm. These results indicate that energetically less favorable sites become involved with increasing metal concentrations in the aqueous solution.

3.2 Effect of Initial Solution pH

The pH dependence of Zn^{2+} adsorption onto zeolite is shown in Figure 2. As it is seen in figure, q_e is low at low pH values. The value and reaches a plateau at a pH value of 5 for

zinc. It is apparent that using solutions at pH values between 5 and 7 gives the highest q_e values due to the precipitation (precipitate of metal hydroxide) occurs during ion exchange experiments by NaOH. It revealed that the

adsorption capacity is low at pH values below 5 because of the dissolution of crystal structure and the competition between the protons (H^+) and metal ions (Zn^{2+}) for the exchange sites on the zeolite particle [1,2].

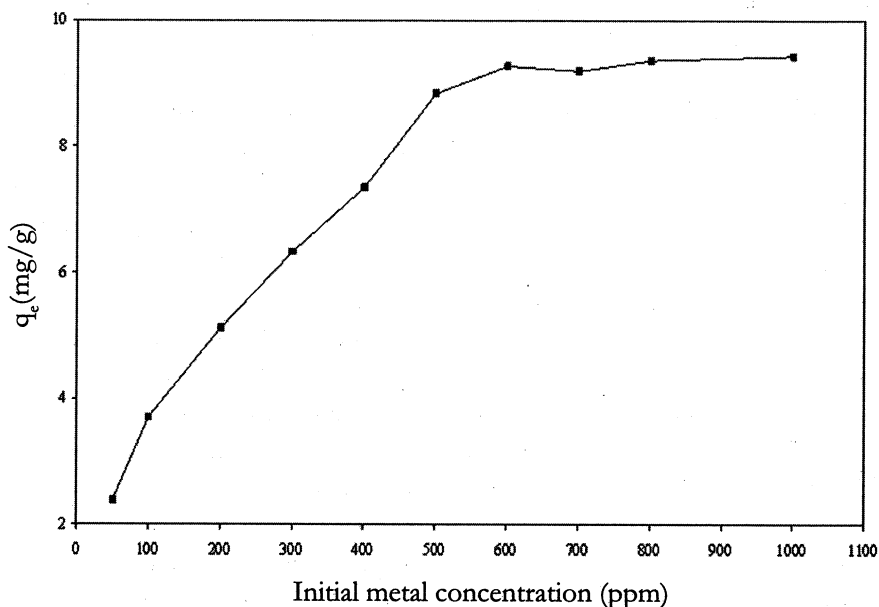


Figure 1. Variation of the adsorbed amount Zn^{2+} ions as a function of initial concentration (initial pH = 6.08, contact time = 2.0 h and temperature = 30 °C).

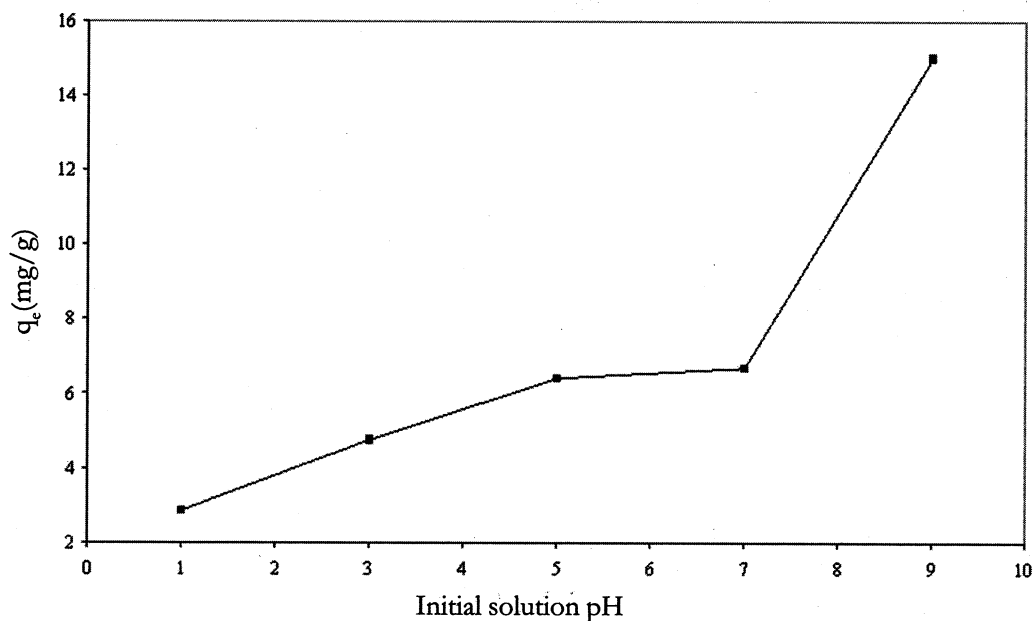


Figure 2. Variation of the adsorbed amount Zn^{2+} ions as a function of initial pH (initial concentration = 300 ppm, contact time = 2.0 h and temperature = 30 °C).

3.3 Effect of Contact Time

Experiments conducted with different contact times show that the amount of Zn^{2+} ions adsorbed per unit mass of zeolite increased with the contact time of metal ions (Figure 3). The slopes of the lines joining the data points in the figure reflect the adsorption rates. As it is seen, high adsorption rates were observed at the beginning and then plateau values were reached within 2.0 h for Zn^{2+} . In a previous study, several adsorbents were used for zinc(II) removal and several times are reported as equilibrium adsorption time [1,2]. The adsorption rate obtained with the zeolite seemed to be very satisfactory. Due to the preference of short adsorption times for the minimum energy consumption, clinoptilolite can be accepted as an efficient adsorbent for zinc removal when its short contact time is considered.

3.4 Comparison of Adsorption Isotherms

In addition to the experimental data, the linearized forms of Freundlich, Langmuir, Temkin and Dubinin-Radushkevich isotherms using Eqs. (2), (3), (4) and (5), are compared.

The relationship between the adsorbed and the aqueous concentrations at equilibrium has been described by four two-parameter isotherm models. The comparison of the experimental values with the values of q_e obtained by four two-parameter models is shown in Figure 4. As seen from this figure, the fitness between the experimental values and the predicted values using the models were generally very good for all two-parameter isotherm models. However, the Langmuir isotherm provided the best correlation for modified clinoptilolite. The applicability of all isotherm models to the Zn(II)-clinoptilolite system implies that both monolayer adsorption and heterogeneous surface conditions exist under the experimental conditions studied. The adsorption of Zn(II) ions on the clinoptilolite is thus complex, involving more than one mechanism [10]. Maximum experimental adsorption capacity of Zn(II) for the pretreated clinoptilolite was 9.43 mg Zn^{2+} /g zeolite, showed that this adsorbent was suitable for zinc removal from aqueous media.

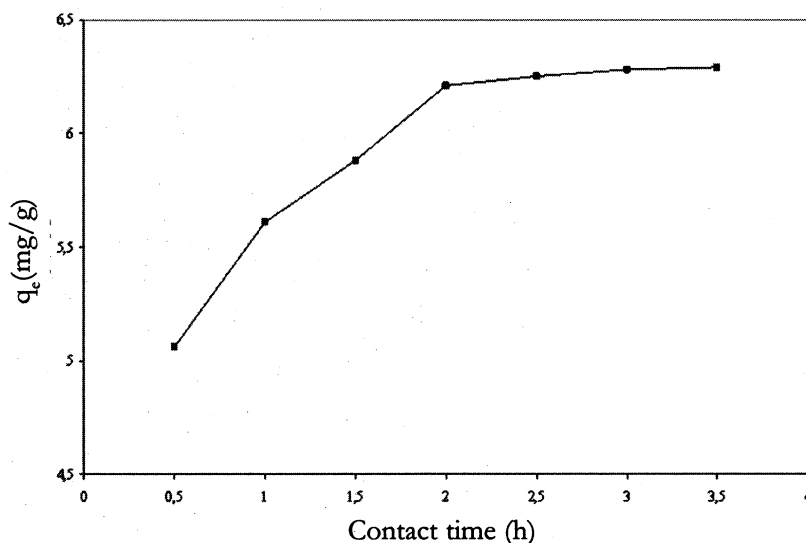


Figure 3. Variation of the adsorbed amount Zn^{2+} ions as a function of contact time (initial concentration = 300 ppm, initial pH = 6.08 and temperature = 30 °C).

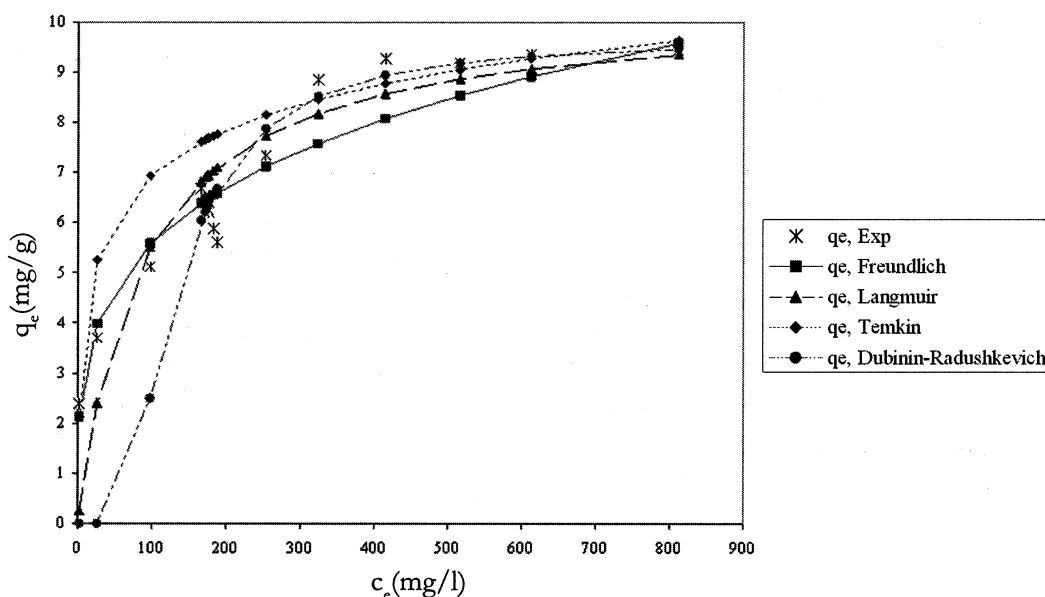


Figure 4. Comparison of the experimental results with the q_e values obtained by four two-parameter isotherm models for Zn^{2+} removal by zeolites.

4. CONCLUSIONS

In this study, the interaction between heavy metal ions (Zn^{2+}) and zeolite have been investigated. The results indicated that several factors such as metal ion concentration, adsorption time, pH and temperature affect the adsorption process. The physico-chemical characteristics of wastewaters from varying sources can be much more complex compared to the aqueous metal solution used in this study. Because of this, the effects of other components of wastewaters on commercial metal adsorption process should be determined. However, this work can be considered a preliminary study to conclude that clinoptilolite is suitable and efficient material for the adsorption of Zn^{2+} from aqueous solution.

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