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Removal of Iron(III) from Model Solution Using Jordanian Natural Zeolite

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The possibility of using Jordanian natural zeolite (JNZ) as non-treated have been investigated for removing of Fe^{3+} from a model solution of (1000 ppm) at a correlation of liquid to solid phases, v:g = 50:1. It has been found out that the specific surface of zeolite takes leading part at the adsorption of Fe^{3+} from the aqua solution with different concentrations. The thermodynamics of adsorption has been described with the most appropriate isotherms uptake of Fe^{3+} using zeolite. The adsorption of Fe^{3+} equilibrium isotherm, which is constructed at 20, 30, 40, 50ºC is studied at a constant percentage of 1 % HNO_3 model solution and the ratio of sorbate to sorbent are identified. The methods of working are studied, along with their physical and chemical properties of the material towards magnetic properties of sorbate and electrical conductivity of the remaining sorbent solution.

Key Words: Jordanian natural zeolite, Fe^{3+}, Adsorption.

INTRODUCTION

Iron is classified as heavy metal that can cause serious environmental contamination if it presents at high level, which is more than recommended[1]. The main source of Fe^{3+} ions entry in aqua's stream include the large amount of Fe^{3+} present in the soil as well as corrosive water which will pick up iron Ions from pipes[2]. When water containing collarless dissolved Fe^{3+} is allowed to stand in a cooking container or comes in contact with a sink or bath tub, the Fe^{3+} combines with oxygen from the air to form reddish-brown particles (rust). These impurities can give a metallic taste to water or to food[3]. Fe^{3+} deposits can build up in pressure tanks, water heaters and pipelines, reducing the quantity and pressure of the water supply. Due to that, special attention should be paid to the problem. Therefore, purification is one of the widest spread technological processes[4,5]. For the up-take iron metals, different methods are employed, such as, physiochemical[6] and biological methods[7], in which the removal is usually achieved through ion exchange and/or adsorption. There are a number of inorganic adsorptive are used, for example, zeolite[8-11], feldspar[12].

A perspective method for purification of wastewater is adsorption-using zeolite[4,5,8-11]. Zeolites are highly selective scavengers of a variety of metal cations that can be removed from liquid effluents through the process of ion-exchange. These cations include lead, silver, cadmium, cobalt, zinc, copper, mercury, magnesium, iron, aluminum, chromium and others[13]. The big deposits of natural zeolite in the Jordan, their low self-value and their unique ion exchange and adsorption properties make them attractive for purification of Fe^{3+} from wastewater.

The objective in this study is to investigate the removal of Fe^{3+} from a model aqua solution of 1000 ppm by the Jordanian natural zeolite (JNZ). In particular, the adsorptions of Fe^{3+} inside the pores of the JNZ is carried out. A natural, non-treated zeolite and 1 % HNO_3 model solution and prepared Fe^{3+} concentration are used. The influence of zeolite after adsorption *via* pH and conductivity for the remaining metal solution is also investigated. Furthermore, the stimulation to the thermodynamic isotherm is carried out for the sample solution. The optimum conditions for the best Fe^{3+} removal will be examined. Finally, the magnetic studies of residue natural zeolite after the adsorption will be performed.

EXPERIMENTAL

All chemicals used were of reagent grades. The aqueous model solutions were prepared from $Fe(NO_3)_3{\cdot}6H_2O$. The starting pH was adjusted with 1 % HNO_3. Jordanian natural zeolite as non-treated was used as received from the Directorate of Laboratories in the Natural Resources Authority of Jordan. The grain size fractions were used as received from the Authorization of Natural Sources (Amman): 2.5-5.0 mm. Samples were filtered with a Millipore's filter and filter holders (25 mm dia, 1.2 µm) pore size. The zeolites are generally built from (AlO_4) and (SiO_4) tetrahedrons, which alternate in granularly three-dimensional structure.

Determination of residual metal concentration: Conductivity and pH was measured using hand held conductivity and hand held pH meters, respectively, combined electrode conductivity and pH meters, model with Cond. 315i/SET and pH 315i/SET, equipped with temperature probe. The residual metal concentration in the solution was measured using the atomic absorption spectrophotometer, Perkin Elmer Analyst 300. Determination of respective metal was done using it is specific lamp at specific wavelength.

Adsorption and the removal of iron(III) ions: A set of laboratory scale experiments was performed in which the JNZ material was contacted with acidic media 1 % HNO_3 model solution of $Fe(NO_3)_3{\cdot}6H_2O$ in constant doses (50 mL/1 g). The contact between the JNZ and the model solution is realized in static conditions with the help of magnetic stirrer in correlation liquid: solid, v:g = 50:1 for all experiments. Adsorption experiments were performed in stopper 100 cm^3 Pyrex volumetric flasks by mixing 50 cm^3 of $Fe(NO_3)_3 \cdot 6H_2O$ solution with 1 g of zeolite at constant pH of 1 % HNO_3. Variant temperatures are carried out.

For adsorption studies, some competitive methods will be carried out through using, *e.g.*, stirring, temperature, contact time, as well as reported one, the concentration of sorbent to sorbate[14]. The dipping of zeolite through water model solution involves over a period of 5 up to 150 min.

pH and conductivities method: The samples are poured into two separate clean beakers. The electrodes of the pH or conductivity indicator are then submerged into the beakers contains the samples and the readings are recorded, an average of three reading are taken.

RESULTS AND DISCUSSION

Adsorption method and the removal of Fe^{3+} from aqua solution

In general, the structure of JNZ contains intersecting channel systems of specific size and shape that restrict molecular diffusion into and through the framework. The porous material is therefore useful for adsorbing transition metals inside the porous material. The most of Fe^{3+} are sequestered very fast from a model solution within the first 0.5 h. After this time, almost no increases have been occurred in the level of bound metals, while the adsorption results are noisy during the first 5 min (Fig. 3).

The removal of iron(III) ions over zeolite through adsorption depends mainly on the thermodynamics parameters like temperature, concentration of adsorptive[14] and the environmental conditions of the adsorbent surface.

pH and conductivity for the residual Fe^{3+} solution

The first test conducted is the pH test, which test the acidity of the remaining solution. As seen from the results, the pH values of the samples increase from the value 0.92 (1 % HNO_3 initial solution) towards the pH = 2 after 2.5 h of the adsorption contact time. This shows that after the adsorption process, the samples become less acidity. This give high recommended materials, due to that, most of the industrial process which use the water, most likely to be less acidity to prevent the corrosion[15].

As shown in the Fig. 1, as increasing the adsorption contact time, the pH of the remaining water increases up to a maximum value of 2.0 at 2.5 h. We observe that the pH of the remaining water slightly increases over the time from 50 min to 2.5 h in various temperatures from 20 to 50°C. This is due to the adsorption and/or ion exchange equilibrium.

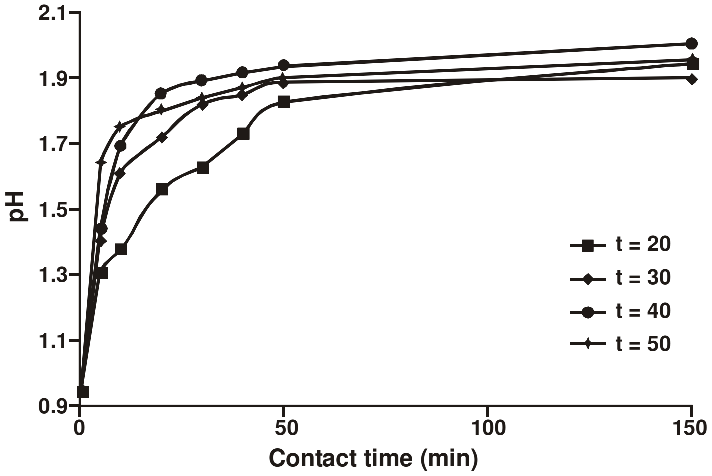

Fig. 1. Effect of adsorption contact time on the pH of the residual Fe^{3+} solution at different temperatures (20, 30, 40 and 50ºC)

The next test conducted is the conductivity, which indicates how a sample could conduct electricity. As shown in the Fig. 2, the conductivity of remaining water solution decreases as increases the contact time of adsorption over several temperature ranges.

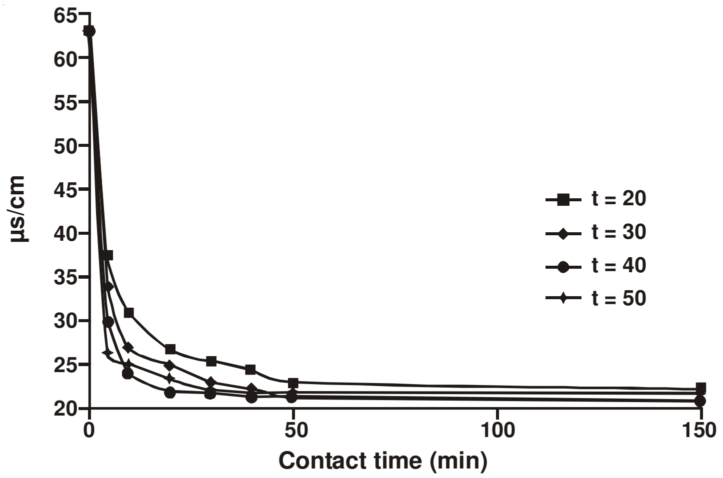

Fig. 2. Effect of adsorption contact time (min) on the conductivity of the residual Fe^{3+} solution at different adsorption temperatures (20, 30, 40 and 50ºC)

It can be seen from the results (Fig. 2), the conductivity of the model solution has decreased 40 µs/cm after going through the increasing of the adsorption contact time. This shows that the number of ions present are decreased after the adsorption process of Fe^{3+} of the model solution.

Contact time effect

Fig. 3 shows the removals of Fe^{3+} *vs.* the contact time at temperature 30°C and 300 rpm. The maximum removal of Fe^{3+} is found to be around 50% at the first 50 min of contact time. As the adsorption contact time increases, the concentration of Fe^{3+} in the model solution decreases. It can be seen that 70 % of Fe^{3+} is *ca.* adsorbed at the first 5 min while 15 % in the contact time interval of 5 min to 2.5 h.

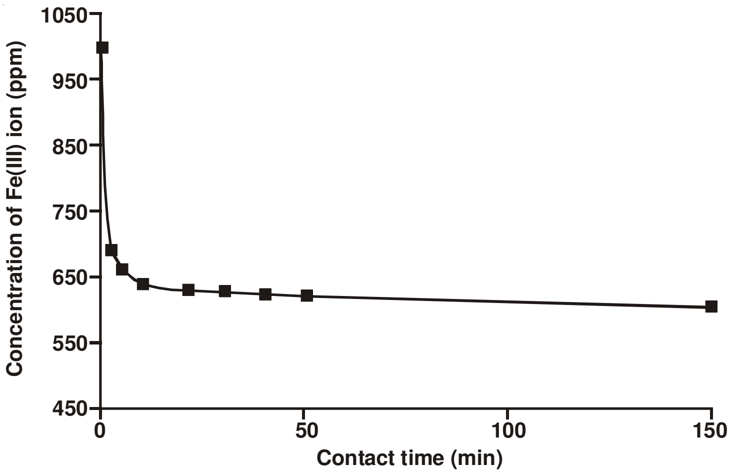

Fig. 3. Effect of contact time: The removal of Fe^{3+} from a model solution using JNZ at 30ºC, 1 % HNO_3 initial pH and 300 rpm

Temperature effect

The adsorption of Fe^{3+} on JNZ temperatures range from 30 to 60°C is studied as shown in Fig. 4. We observed that the equilibrium concentration reaches at time equals 50 min overall temperature ranges. The results show the removal of Fe^{3+} in the first of 5 min are 98, 316, 61 and 20 ppm at the adsorption temperature of 20, 30, 40 and 50°C, respectively. It can be seen that the removal efficiency increases in the range of temperatures 20 to 30°C and then declined in the range of 30 to 50ºC. It means that the best removal efficiency is occurred at 30°C (Fig. 4).

XRD and characterization of Jordanian natural zeolite

X-ray diffraction analysis indicated that their zeolite sample is rich in phillipsite with non zeolite materials such as calcite and clay[16]. XRD diffactogrames show the major phase of JNZ is sodium-aluminum-silicate-hydrate ($Na_{1.4}Al_2Si_{3.9}O_{11.5}\cdot 12H_2O$). From the XRD measurement for the sample of pure zeolite before the adsorption, the main element in the surface is Na^+; while after the adsorption we find the main elements in the surface are the Fe^{3+}.

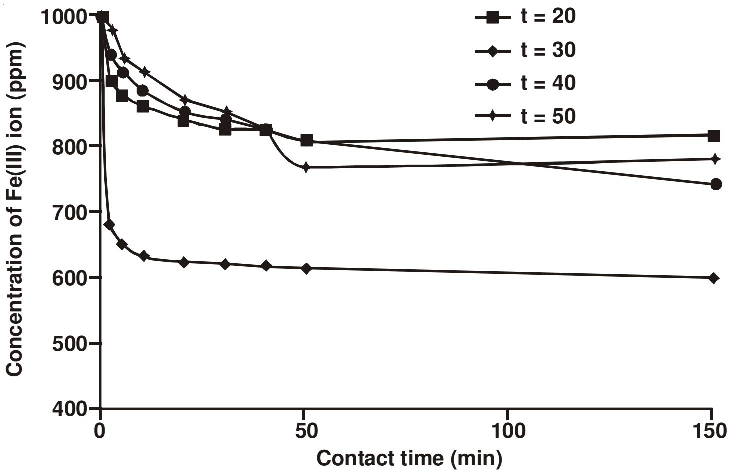

Fig. 4. The removal of Fe^{3+} concentration as a function of time and variant temperatures at the inital concentration of 1000 rpm

Magnetic susceptibility

The most commonly used method for measuring magnetic susceptibility is that introduced by Gouy method[17]. Fe^{3+} has five unpaired electrons (d^5) which caused magnetic properties. As it is expected that if the Fe^{3+} is entered the zeolite, the material will be improved and increased their magnetic properties. As increasing of contact time, the weight susceptibility (χ_g) will be increased, because the residual concentration of Fe^{3+} is decreased as shown in the Fig. 5. Jordanian natural zeolites have been successfully used for the removal of Fe^{3+} from a model solution at 30°C and 300 rpm agitation speed at the first 50 min of adsorption contact time. The magnetic properties of the residual zeolite increase as the contact time increase. This indicate of successfully increase of the Fe^{3+} from the solution toward the zeolite particles.

Adsorption isotherm

The equilibrium distribution of metal ions between the sorbent and the solution is important in determining the maximum sorption capacity. Several isotherm models are available to describe the equilibrium sorption distribution in which two models are used to fit the experimental data: Langmuir and Freundlich models.

The linear form of Langmuir model is given by

$$\frac{q_e}{a_L} = \frac{1}{k_L} + \frac{a_L}{k}$$

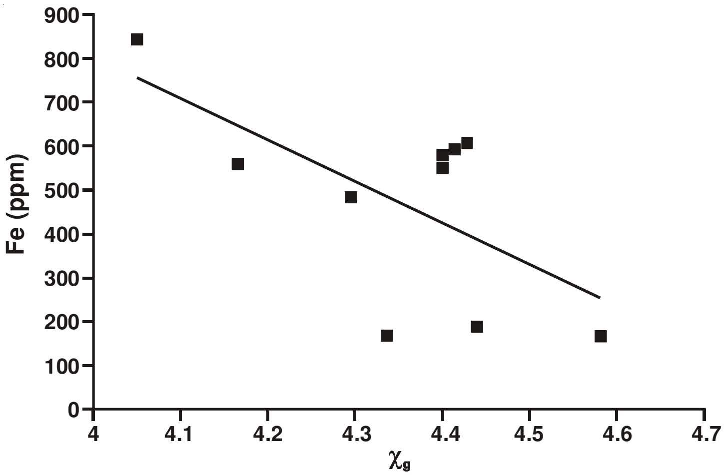

Fig. 5. Effect of the adsorption contact time (min) on the weight susceptibility of the JNZ after the Fe^{3+} adsorb from the model solution at 30°C, rpm = 300 and 1 % HNO_3 solution initial pH

k_L : the Langmuir equilibrium constant, which is related to the adsorption/desorption energy, the affinity of biding sites; a_L : The Langmuir constant q_e : Metal concentration on the zeolite at equilibrium (mg of metal ion/g of zeolite);

$$= \frac{(c_0 - c_e)}{S}$$

c_0 : Initial concentration of Fe^{3+} in solution (mg/L); c_e : The equilibrium concentration (final concentration) of Fe^{3+} in the solution (mg/L); S : Does or slurry concentration, g/L = m/v; v: Volume of initial Fe^{3+} solution used (L); m : Mass of zeloite used (g).

The constants k_L and a_L are determined ftom the slope and intercepts of the plot of c_e/q_e against c_e

The linear form of Freundlich model is also given by

$$\log q_e = \log K_F + \left(\frac{1}{n}\right)\log c_e$$

where K_F and n are Freundlich constants determined from the slope and intercept of plotting log q_e *vs.* log c_e.

The equilibrium results that are obtained at the 1 % HNO_3 model solution of $Fe(NO_3)_2 \cdot 6H_2O$. In this study, the results are well represented by the two models. The Langmuir isotherm model is applied to the experimental data as presented in Fig. 6. Our experimental results give R^2 equals to 0.984, which are a measure of goodness-of-fit and the general empirical formula of the Langmuir model by

$$\frac{c_e}{q_e} = 0.235c_e - 113.5$$

Fig. 7 represents the fitting data into the Freundlich model. The empirical formula of this model is found as log q_e = 7.83-2.34 log c_e with $R^2 = 0.994$.

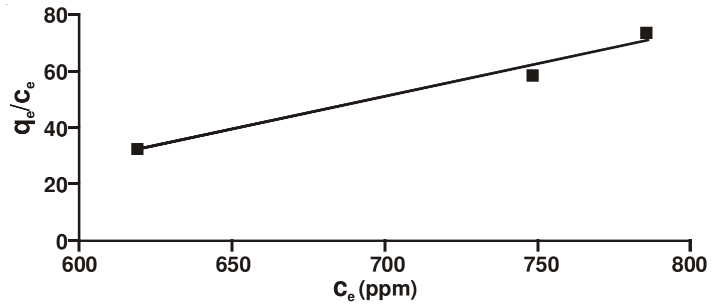

Fig. 6. Langmuir isotherm plot of q_e/c_e against the equilibrium concentration of Fe^{3+} c_e (ppm)

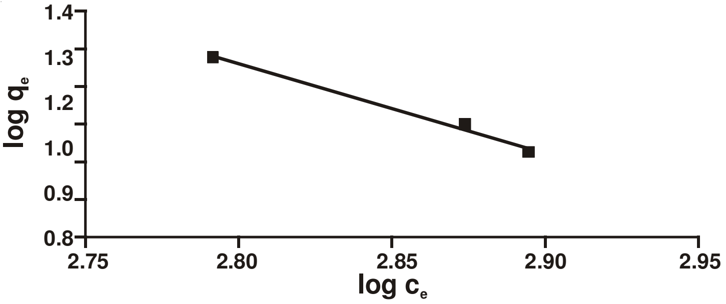

Fig. 7. Freundlich isotherm plot of log (q_e) against the equilibrium concentration of Fe^{3+} log(c_e)

Conclusion

In the present study, Jordanian natural zeolite have been successfully used for the removal of Fe^{3+} from a model solution of (1000 ppm, 1 % HNO_3) at a correlation of liquid to solid phases, v:g = 50:1. It has been found out, that the best adsorption environment 30ºC and 300 rpm agitation speed. The removal efficiency of Fe^{3+} is slightly constant at the contact time from 50 to 150 min. The conductivity of remaining solution is decreased as the contact time is increased, in which leads to increase of the pH. The weight susceptibility of Jordanian natural zeolite increases as the diffusion of the Fe^{3+} from the bulk solution to Jordanian natural zeolite increases. Equilibrium data are well plotted by both Langmuir and Freundlich models.

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