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Experimental Investigation of Adsorption of heavy metals (Copper (II)) from Industrial Wastewater With Synthetic Zeolite (4A)

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The contamination soils and aquatic bodies by industrial effluents rich in heavy metals have received much attention in the last decades. Although many heavy metals are essential in small amounts for the correct progress of biological cycles, most of the exert toxic effects at concentrations encountered in polluted environments. For these reasons, in recent years many researchers studied the behaviour of synthetic adsorbent materials having high adsorption capacity for the removal of heavy metals from various effluents. Since copper is an essential metal in a number of enzymes for all forms of life, problems arise when it is deficient or in excess. Excess copper accumulates in the liver, brain, skin, pancreas and myocardium.

The present study involves an investigation of synthetic zeolite adsorbent, 4A for the removal of copper from aqueous solutions. The effects of pH and temperature on the adsorption procces were examined. The optimum pH for adsorption was found to be 8. The rate of copper adsorption by synthetic zeolite was rapid in the first minute of the reaction time. Pseudo second order model best described the reaction rate. Batch adsorption experiments conducted at room temperature (25 °C) showed that the adsorption pattern followed the Langmiur and Freundlich isotherm models. The maximum removal of copper obtained from batch studies was 99.99 %. The concentration of metal ions were measured by atomic absorption spectroscopy (AAS). Overall, the results showed that synthetic zeolite could be considered as a potential adsorbent for copper removal from aqueous solutions.

1. Experimental

1.1 Materials

Zeolite 4A used in this study comes from Afrazand company (Iran). Zeolite 4A was ground and sieved to obtain aggregates less than 2500 mesh for use in our experiments. The chemical properties of the zeolite 4A are listed in table 1.

A stock solution of Cu^{2+} at a concentration of 1000 mgl^{-1} was prepared by desolving $Cu(NO_3)_2.3H_2O$ in distilled water. The pH was adjusted using 0.01 M $H(NO)_3$ and NaOH solutions.

Table 1 Chemical analysis of Zeolite 4A

	SiO_2	Al_2O_3	P_2O_3	Na_2O
Synthetic zeolite	51.69	41.09	0.2	6.03

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1.2 Instruments

The concentrations of metal ions were measured by atomic absorption spectroscopy (AAS), using a Varian Model spectrAA 200.

1.3 Batch adsorption studies

A series of experiments were performed to study the adsorption behaviour of zeolite 4A for Cu^{2+} ion. The initial copper concentrations in the solutions were 300, 500 and 700 $\mathrm{mg\,l}^{-1}$. For each experiment, 100 mL of the prepared Cu^{2+} solution was placed in 250 mL vessels. Then we added a certain amount of zeolite 4A (1 g). Suspensions were placed for specific time on the constant temperature magnetic force beater (200 rpm), until it remained static and was then filtered. The solution pH ranging from 2 to 8 was carefully adjusted by adding a small amount of $\mathrm{H(NO)_3}$ or NaOH solution and measured using a pH meter.

2. Results and discussion

2.1 adsorption kinetic

The time course variation in mineral suspensions and at different copper concentrations was described by following pseudo second-order kinetic model of Lagergern as Eq. (1).

$$\frac{t}{q_t} = \frac{1}{Kq_e^2} + \frac{t}{q_e} \qquad (1)$$

Where *K* is the rate constant of second-order biosorption (g/(mg.min)), q_t is the adsorbed cation quantity per gram of minerals at any time (mg.g^{-1}), q_e is the adsorbed cation quantity per gram of mineral at equilibrium (mg.g^{-1}) and *t* is the time (min).

The parameters q_e and *K* can be determined from the slope and intercept, respectively, of the *t*/q_t against t plots.

The amount of copper adsorbed onto the adsorbent, q_e (mg.g^{-1}), was calculated by a mass balance relationship presented in Eq. (2).

$$q_e = (C_0 - C_e)\frac{V}{W} \qquad (2)$$

Where C_0 (mg.l^{-1}) and C_e (mg.l^{-1}) are the initial and equilibrium liquid-phase concentrations. *V(L)* stands for the volume of the solution while*, W(g)* corresponds the dry weight of the adsorbent. The results are shown in Table 2.

Table 2 Kinetic parameters of pseudo second-order model for cover onto zeolite 4A (pH=8)

Cu	300 (mg.l^{-1})	500 (mg.l^{-1})	700 (mg.l^{-1})
K **(g/mg min)**	0.038	0.084	0.065
q_{pre} **(mg/g)**	6.99	25.57	34.39
q_{exp} **(mg/g)**	7.14	25.44	34.09
R^2	0.991	0.999	0.999

2.2 Adsorption isotherms

Adsorption isotherms of zeolite 4A for copper ion were expressed mathematically in terms of Langmuir and Freundlich models. The obtained experimental data are commonly well fitted with the Langmuir (3) and Freundlich (4) models.

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

$$q_e = K_F C_e^{1/n} \quad (4)$$

If these equations are rearranged to a linear form, we obtain:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a}{K_L} C_e \quad (5)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

where K_L , *a* are the constants for the Langmuir model and K_F , $\frac{1}{n}$ for the Freundlich model, $\frac{1}{n}$ ranging between *0* and *1* is a measured of adsorption intensity. The linearized forms of the Langmuir and Freundlich isotherms, using (5) and (6) on copper ion removal by zeolite 4A can be seen in Figure 2 and Figure 3 and the Langmuir and Freundlich parameters computed from Eq. (3)-(4) are listed in Table 3.

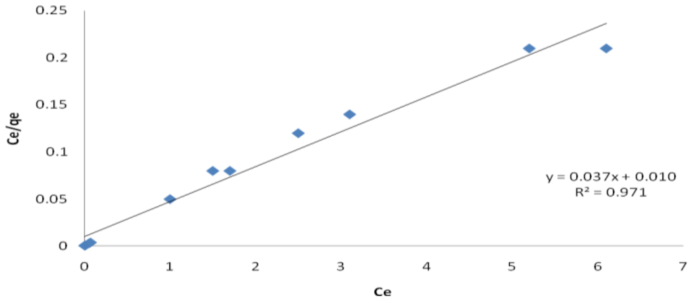

Figure 2 Linearized Langmuir isotherms for Cu^{2+} removal by zeolite 4A (shaking time 24 h, temperature 25 °C)

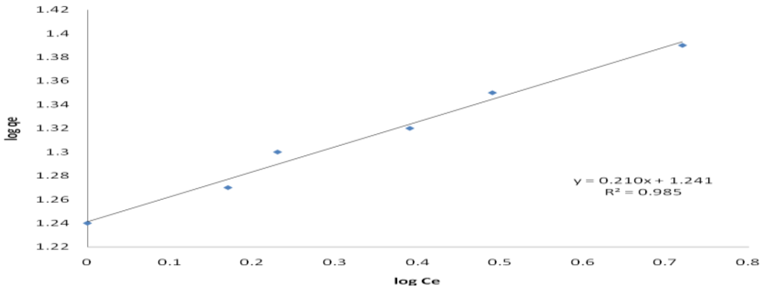

Figure 3: Linearized Freundlich isotherms for Cu^{2+} *removal by zeolite 4A (shaking time 24 h, temperature 25 °C)*

Table 3 Parameters of Langmuir and Freundlich isotherms for Cu(II) ion adsorbed on zeolite 4A (shaking time 24 h, temperature 25 °C)

Parameters	Zeolite 4A
K_L (Langmuir)	100
a (Langmuir)	3.7
K_F (Freundlich)	18.79
$\frac{1}{n}$ (Freundlich)	0.126

2.3 Effect of initial metal ion concentration

The time-dependent behaviour of copper adsorption was measured by varying the equilibrium time between the adsorbate and adsorbent in the range of 1-200 min. The percentage removal of copper from aqueous solution as a function of contact time (with agitation = 200 rpm, T = 25 °C) indicates that higher removal of copper was observed in the case of 700 ppm of copper (Figure 4).Figure 4 shows that the adsorption rates increased in higher ionic concentration.

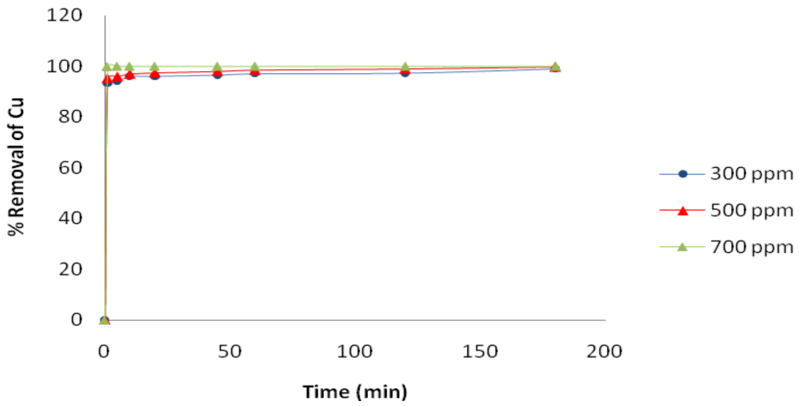

Figure 4 Percentage removal of copper as a function of contact time (T = 25 °C, agitation = 200 rpm)

2.4 Effects of pH

In the present work, adsorption of Cu^{2+} on the zeolite 4A adsorbent was studied over a pH range of 2.00-8.00 for a constant zeolite 4A (1 g) and Cu^{2+} concentration of 300 mg.l^{-1} at 25 °C. The pH of the solution was kept constant by the addition of 0.01 M HNO_3 or NaOH as needed. Figure 5 shows the change in Cu^{2+} uptake by zeolite 4A and different initial pH levels. It can be seen from Fig.5 that the pH of the aqueous solution is an important control parameter in the adsorption process. As seen from Fig.5, the removal rate (%) of zeolite 4A increased when initial pH of the solution was increased from 2.00 to 4.00 From pH 4.00 to 8.00, was noted and there were sharper increased in the adsorption of Cu^{2+} into the zeolite 4A within this range. The mechanisms that affect the adsorption characteristics of zeolite 4A can be explained by dissolution, ion exchange/adsorption and precipitation, which was recently confirmed (Altin 1999). From Figure 5, the lowest Cu^{2+} sorption rates were obtained at pH 2.00. This could be due to the increase in competition for adrsorption sites by H^+.

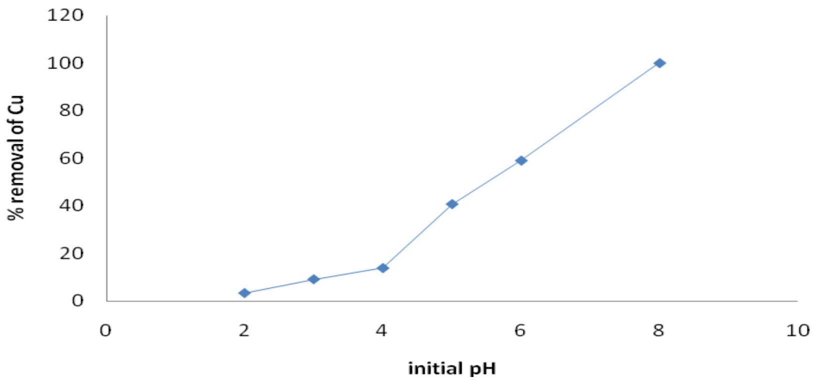

Figure 5 Effect of pH on Cu^{2+} sorption on zeolite at 25 °C

3. Conclusions

In this study, the equilibrium and kinetic parameters of copper(II) ions onto synthetic zeolite in aqueous solution was investigated. It may be concluded that zeolite 4A acts a respective adsorbent for the removal of copper(II) ions in aqueous solutions due to its high adsorption capacity. The maximum adsorption capacity was found to be 27.03 mg.g^{-1} at pH 8.00 and 25 °C.

The straight lines obtained for the Langmuir and Freundlich models obey to fit to the experimental equilibrium data.

The pseudo-second-order kinetic model agrees very well with the dynamic behavior for the adsorption of copper(II) ions onto zeolite 4A. The experimental data have also be applied to predict the rate constants of adsorption and adsorption capacities.

The adsorption characteristics of zeolite 4A was determined for Cu^{2+} at different pH levels. The pH of aqueous solution is an important controlling parameter in the adsorption process. The results indicate that synthetic zeolite 4A can easily adsorb copper(II) ions by a possible mechanism.

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