

Experimental Investigation of Adsorption of heavy metals (Copper (II)) from Industrial Wastewater with Clinoptilolite

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Environmental pollution as a consequence of the industrialization process, is one of the major problems that have to be solved and controlled. Heavy metals have become an ecotoxicological hazard of prime interest and increasing significance owing to their harmful effect on human physiology. Copper has been reported as one of the most widely used heavy metal in electrical industries. A number of technologies for the removal of heavy metal ions from aqueous solutions have been developed over the years. The most important of these techniques include chemical precipitation and filtration. However, all these techniques have their inherent advantages and limitations in application. The process of adsorption has become one of the preferred methods for removal of toxic contaminants from water as it has been found to be very effective, economical and simple.

The ability of natural zeolite (Clinoptilolite) to remove copper from aqueous solutions was studied in batch reactors. The effect of solution pH (1.00-6.00) on the removal of heavy metals was studied. The removal of Cu(II) using clinoptilolite reached 89.7 % , at ambient temperature, initial pH (5.5) and at the agitation speed of 300 rpm, while it was approximately 11.2 % at pH=1. The concentration of metal ions were measured by atomic absorption spectroscopy (AAS). Clinoptilolite was found to be effective for the removal of copper in batch reactors under all the tested conditions. The acidity of the aqueous solution influences the removal of copper by minerals. Isotherms for the adsorption of Cu(II) on clinoptilolite were developed and the equilibrium data fitted well to the Langmuir and Freundlich models.

1. Introduction

Human intake of large doses of copper ions leads to severe mucosal irritation and corrosion, hepatic and renal damage, central nervous system irritation, liver and kidney damage and anemia, which was recently confirmed (ajmal et al,2005).

A number of technologies for the removal of heavy metal ions from aqueous solutions have been developed over the years, which was recently confirmed (shaker,2005). The most important of these techniques include chemical precipitation, filtration and reverse osmosis. Adsorption has the additional advantages of applicability at very low concentrations, suitability for using batch processes, ease of operation, little sludge generation and low capital cost .

Zeolites are naturally occurring hydrated aluminosilicate minerals. They belong to the class of minerals known as "tectosilicates". The structure of zeolites consists of the three-dimensional frameworks of SiO_4 and AlO_4 tetrahedra. The aluminium ion is small enough to occupy the position in the centre of the tetrahedron of four oxygen atoms, while the isomorphous replacement of by produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cations (Na, K or Ca). These cations are exchangeable with certain cations in solutions, such as lead, cadmium and zinc.

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The present paper continues the work of a previous study on the ability of clinoptilolite to reduce the copper concentration from aqueous solution. The aim of our work was to study the effects of pH, temperature and copper concentration on the adsorption capacity of clinoptilolite.

2. Experimental

2.1 Materials

The minerals used were a natural clay, type clinoptilolite (Afrazand company, Iran). Clinoptilolite was used in dust form having a size 2500 mesh. Clinoptilolite was used without any chemical pre-treatment. All the chemicals used in the study were of analytical grade. A stock solution of a concentration of 1000 mg·L⁻¹ was prepared by desolving [Cu(NO₃)₂·3H₂O] in distilled water. Further working solutions were made by appropriate dilution. The pH was adjusted using 0.01 M HNO₃ and NaOH solutions.

2.2 Instruments

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

3. Results and discussion

3.1 Adsorption kinetic.

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

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

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).

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

Where C_0 (mg·L⁻¹) and C_e (mg·L⁻¹) are the initial and equilibrium liquid-phase concentrations, respectively. $V(L)$ 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 Clinoptilolite (pH=5.5)

Cu	100 (mg·L ⁻¹)	200 (mg·L ⁻¹)	300 (mg·L ⁻¹)
K (g/mg min)	0.104	0.0155	0.042
q _{pre} (mg/g)	3.597	6.88	8.067
q _{exp} (mg/g)	3.59	6.91	8.064
R ²	0.999	0.995	0.999

3.2 adsorption isotherms

For the purpose of adsorption system design, adsorption isotherms, depicting how adsorbed molecule interacts with adsorbent, are commonly used to analyze equilibrium data. The analysis of the isotherm data is of great importance by fitting them to different isotherm models to optimize the adsorption system. The most widely used isotherm equations are Langmuir and Freundlich equations.

Langmuir isotherm is based on the assumption that an active point on the surface of the adsorbent is able to adsorb one molecule, indicating the adsorbed layer is one molecule thick. It is expressed as the following Eq. (3):

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

where, C_e ($mg.l^{-1}$) is the equilibrium concentration, q_e ($mg.g^{-1}$) is the amount adsorbed, K_L and a are the Langmuir constants.

Freundlich isotherm is valid for non-ideal adsorption on heterogeneous surfaces, suggesting multilayer adsorption on adsorbent surfaces. The empirical equation is presented as following Eq. (4):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where K_F is the Freundlich adsorption constant and the slope of the Freundlich equation ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, which may become more heterogeneous when gets close to zero.

The linearized forms of the Langmuir and Freundlich isotherms, using (5) and (6) on copper ion removal by clinoptilolite can be seen in Figure 1, and the Langmuir and Freundlich parameters computed from Eq. (3)-(4) are listed in Table 2.

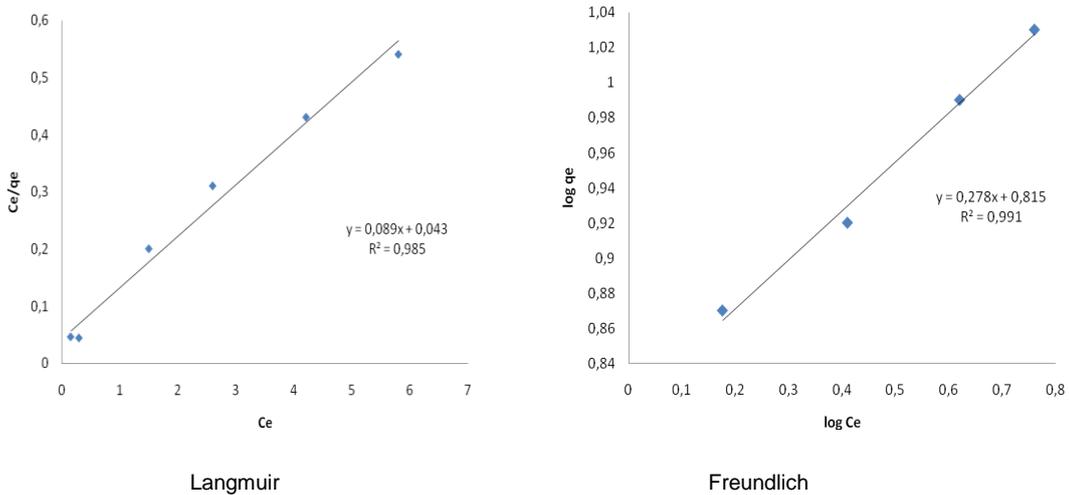


Figure 1: Langmuir and Freundlich isotherms of Cu(II) ion adsorption by clinoptilolite (shaking time 24 h, temperature 25 °C)

Table 2 Parameters of Langmuir and Freundlich isotherms for Cu(II) ion adsorbed on clinoptilolite (shaking time 24 h, temperature 25 °C)

Parameters	Clinoptilolite
K_L (Langmuir)	23.25
a (Langmuir)	2.07
K_F (Freundlich)	6.17
$\frac{1}{n}$ (Freundlich)	0.325

3.3 Effect of initial metal ion concentration

Batch kinetic experiments were studied by agitation 100 mL of three different concentration of Cu(II) (100, 200 and 300 mg L⁻¹) with 3 gr clinoptilolite at pH 5.5. The stirring rate was 200 rpm during the experiments. Samples were collected at 20, 45, 60, 70, 120, 180 minutes.

The percentage removal of copper from aqueous solution as a function of contact time indicates that higher removal of copper was observed in the case of 300 ppm of copper (Figure 2). Figure 2 shows that the adsorption rates increased in higher ionic concentration.

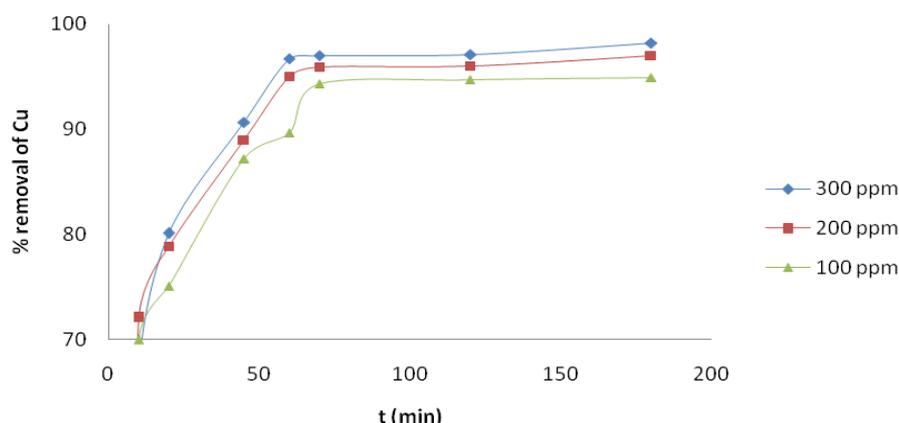


Figure 2: Percentage removal of copper as a function of contact time ($T=25\text{ }^{\circ}\text{C}$, agitation=200 rpm)

3.4 Effects of pH

The pH of the aqueous solution is an important variable, which controls the adsorption of the metal at the solid-water interfaces as well as the ion exchange of cations. The influence of pH on the adsorption of Cu(II) on clinoptilolite was examined in the pH range of 1.00-5.5. It is observed that acidity influences the removal of Cu^{2+} by the clinoptilolite (Figure 4). The increase of the pH of the solution from 1.00 to 5.5 increase the removal of copper. H^+ cations should be considered as competitive ones in ion exchange process and, consequently, ion exchange of metal is favored by high pH values, which should, however, be lower than the minimum pH of precipitation. However, low pH values may also have a beneficial effect as they influence the hydrolysis of the metals. Hydration is followed by hydrolysis, according to the following two-ray reversible reaction, giving acidic properties to heavy metal solutions. Consequently, at decreasing pH the above equilibrium is shifted to the left and more highly charged metal complexes are formed, a fact which is beneficial for the exchange.

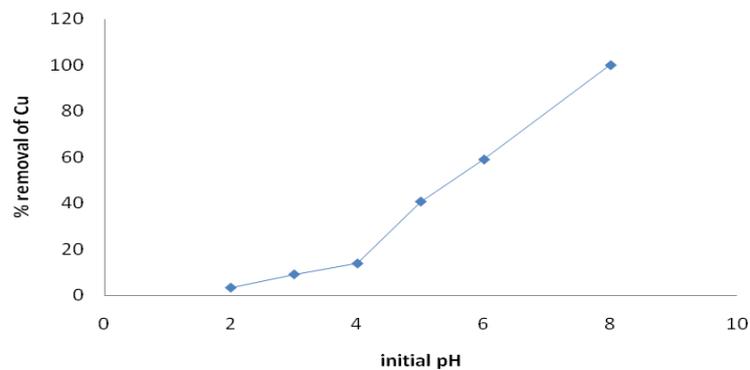
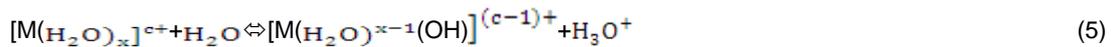


Figure 4 Effect of pH on Cu^{2+} sorption on zeolite at 25 °C

4. Conclusions

Based on the present investigation it can be concluded that clinoptilolite exhibits good adsorption properties for copper(II) ions in aqueous solution.

The adsorption capacity was found to be 11.24 mg.g^{-1} at pH 5.5 and 25 °C and 200 rpm agitation.

The adsorption of Cu^{2+} was strongly pH dependent. The pH value of 5.5 seems to give better results than lower pH values.

The equilibrium isotherm analysis of the experimental data showed that the adsorption Cu^{2+} ions onto the clinoptilolite follows Langmuir and Freundlich isotherms.

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

The result indicates that clinoptilolite preferentially sorbed Cu^{2+} . Therefore it is possible to conclude that clinoptilolite has good potentialities in cost-effective treatments of metal-contaminated wastewaters.

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