REMOVAL OF COPPER FROM AQUEOUS SOLUTIONS BY USING NATURAL AND Fe-MODIFIED CLINOPTILOLITE

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Abstract

Removal of copper from aqueous solution on the natural and modified clinoptilolite was studied under static conditions. Batch adsorptions of copper were performed to investigate the effects of contact time and initial metal ion concentration. The Freundlich and Langmuir adsorption isotherms were used to analyse the experimental data. The kinetic analyses of the adsorption processes were performed using the pseudo-first-order and pseudo-second-order kinetic models.

Key words

sorption, copper, natural clinoptilolite, Fe-modified clinoptilolite, isotherm, kinetic

INTRODUCTION

Pollution of water resources due to the indiscriminate disposal of metal ions has been causing worldwide concern. Wastewater from many industries such as metallurgical, tannery, chemical manufacturing, mining, battery manufacturing industries, etc. contains one or more toxic metal ions. It is necessary to remove these metal ions from the wastewaters before releasing them into the environment, because there is possibility of entry of toxic metal ions into food chain through waste discharges into water bodies. There are many conventional methods that are being used to remove the metal ions, including oxidation, reduction, precipitation, membrane filtration, ion exchange and adsorption. From the above-mentioned methods, the promising process for the removal of metal ions from water and wastewater is adsorption, because the employed adsorbent can be regenerated by suitable desorption process and it is highly effective and economical. Several adsorbents studied for adsorption of metal ions such as activated carbon, fly ash, peat, sewage sludge ash, zeolite, biomaterials, recycled alum sludge, manganese oxides, peanut hulls, kaolinite and resins (1).

Zeolites are microporous crystalline hydrated aluminosilicates which can structurally be considered as inorganic polymers built from an infinitely extending three-dimensional network

of tetrahedral TO_4 units, where T is Si or Al. Each aluminium ion that is present in the zeolite framework yields a net negative charge, which is balanced by an extra framework cation, usually from group IA or IIA. The zeolite framework structure contains channels or interconnected voids of discrete size (in the range of 3 - 20 Å) occupied by the charge balancing ions and water molecules. Owing to their unique physical and chemical properties (crystallinity, thermal stability, well-defined cage structure of molecular size, ion-exchange, etc.), zeolites have been used as heavy metals adsorbents, as chemical sieves and as water softeners (2). For sorption applications, zeolites were often reported to exhibit high sorption capacity for divalent sorbates. -Erdem et al. reported that natural zeolites hold great potential for the sorption of several divalent metal cations and can be used as alternative for activated carbon (3).

The presence of copper in wastewater of several industries has contributed in no small way to water pollution. Although copper is an essential element, acute doses cause metabolic disorders. Copper sorption is an attractive option because of the basic simplicity of application (3).

MATERIAL AND METHODS

Clinoptilolite

Clinoptilolite $(NaK)_6(Al_6Si_{30}O_{72})\cdot20H_2O$ (Table 1) is one of the most frequently used natural zeolites (5). The clinoptilolite used for the synthesis of the Fe-clinoptilolite system comes from a layer situated in Nižný Hrabovec (Slovakia) (2). This material has been used for metal adsorption experiments by many researchers, and therefore its physicochemical properties are well-known (5, 6, 7). The basic properties of clinoptilolite are shown in Table 2.

CHEMICAL ANALYSIS OF THE CLINOPTILOLITE FROM THE DEPOSIT
AT NIŽNÝ HRABOVEC (5)   Table 1

Compound	Content	Compound	Content
SiO_2	66.40 %	MgO	0.56 %
Al_2O_3	12.20 %	Na_2O	0.29 %
K_2O	3.33 %	MnO	0.02 %
CaO	3.04 %	TiO_2	0.15 %
Fe_2O_3	1.45 %	P_2O_5	0.02 %

BASIC PROPERTIES OF CLINOPTILOLITE (5)   Table 2

Clinoptilolite			
Colour	grey - green	Effective diameter of pores	0.4 nm
Compressive strength	33 MPa	Absorbability	34 - 36 %
Specific gravity	2200 - 2440 kg m^{-3}	Thermal stability	to 450 °C
Apparent density	800 - 900 kg m^{-3}	Stability against acids	79.50 %

Synthesis of the Fe-clinoptilolite system

The Fe-clinoptilolite system was synthesized by the method for pure goethite preparation, as described by Schwertmann and Cornell. The change made in this study concerns the presence of clinoptilolite, which was added in experimental flasks (2, 4).

The system was prepared by mixing 20.0 g of clinoptilolite, 100 mL of freshly prepared 1 M $Fe(NO_3)_3$ solution, and 180 mL of 5 M KOH solution in a 2 L polyethylene flask. The addition of KOH solution was rapid and accompanied by stirring. The suspension was diluted to 2 L with twice-distilled water and was held in a closed polyethylene flask at 70 °C for 60 hrs. After the appropriate period, the reaction vessel was removed from the oven, and the precipitate was centrifuged, washed and finally dried (2).

Batch experiment

For all batch studies, 1.000 g sample and 5 mL Cu(II) solution were combined in tube. For the isotherm study, the initial Cu(II) solution concentrations varied from 2, 5, 10, 20, 40, 60, 80 to 100 mg L^{-1}. The mixtures were shaken at room temperature (20 °C) and 150 rpm from 72 hrs. At the end of the shaking period, the mixtures were centrifuged at 4000 rpm for 2 min.

The kinetic study of Cu(II) removal was conducted at an initial concentrations of 100 mg L^{-1}, too. The mixtures were shaken at room temperature and 150 rpm from 15, 30, 60, 180 to 360 min. At the end of the shaking period, the mixtures were centrifuged at 4000 rpm for 2 min (10). The equilibrium concentration was analysed by UV-VIS spectrophotometry (16).

The amount of adsorbed Cu(II) ions by adsorbents was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{m},$$
[1]

where V is the volume of solution treated in mL, C_0 is the initial concentration of metal ion in the solution mg L^{-1}, C_e is the equilibrium metal ion concentration in mg L^{-1}, and m is the amount of the added adsorbent on the dry basic in g (10).

ATTAINED RESULTS AND DISCUSSION

Adsorption isotherm

An adsorption isotherm equation is an expression of the relation between the amount of solute adsorbed and the concentration of the solute in the fluid phase, since the adsorption isotherms are important to describe how adsorbates will interact with the adsorbents, and so are critical for design purposes; therefore, the correlation of equilibrium data using an equation is essential for the practical adsorption operation. Two isotherm equations were adopted in this study, as follows (9).

Freundlich isotherm equation

The Freundlich sorption isotherm, one of the most widely used mathematical descriptions, gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The Freundlich isotherm is defined as (9):

$$q_{\mathrm{e}} = k C_{\mathrm{e}}^{1/n} \tag{2}$$

and in linearized form it is:
$$\log q_{\mathrm{e}} = \log k + (1/n) \log C_{\mathrm{e}}, \tag{3}$$

where C_{e} is the equilibrium concentration in mg L^{-1}, q_{e} is amount of the adsorbate adsorbed per unit weight of adsorbent (mg g^{-1}). k is a parameter related to the temperature and n is a characteristic constant for the adsorption system under study. The plot of log q_{e} against log C_{e} is shown in Figure 1; the adsorption of copper ions onto the different adsorbents gave a straight line; values of n between 1 and 10 show good adsorption (9, 12). Larger value of n (smaller value of $1/n$) implies strong interaction between sorbent and metal ions while $1/n$ equal to 1 indicates linear adsorption leading to identical adsorption energies for all the sites. Freundlich equation fits in nearly all experimental adsorption-desorption data and is especially useful for the data from highly heterogeneous sorbent systems (12).

Langmuir isotherm equation

This quantitatively describes formation of a monolayer adsorbate on the outer surface of the adsorbent; after that no further adsorption takes place. Thereby, the Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Based upon these assumptions, Langmuir represented the following equation. The Langmuir isotherm is defined as (11):

$$q_{\mathrm{e}} = \frac{b Q_{\mathrm{m}} C_{\mathrm{e}}}{1 + b C_{\mathrm{e}}} \tag{4}$$

and in linearized form it is:

$$1/q_{\mathrm{e}} = 1/C_{\mathrm{e}} + 1/(C_{\mathrm{e}}\, b\, Q_{\mathrm{m}}), \tag{5}$$

where Q_{m} and b are Langmuir constants related to the sorption capacity, and sorption energy, respectively, C_{e} is the equilibrium concentration in mg L^{-1}, and q_{e} is the amount of adsorbate adsorbed per unit weight of adsorbent (mg g^{-1}). The plot of $1/q_{\mathrm{e}}$ against $1/C_{\mathrm{e}}$ is shown in Figure 2; the adsorption of copper on different adsorbents gives a straight line (9, 11).
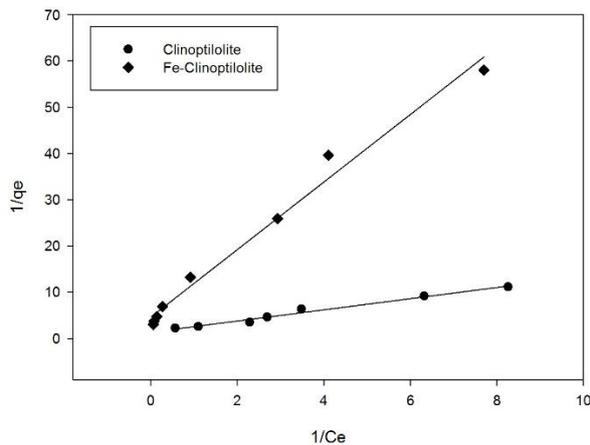
Evaluation of Adsorption Isotherms

Fig. 1 *Linearized Langmuir isotherms for the adsorption of copper onto natural clinoptilolite and Fe-clinoptilolite*
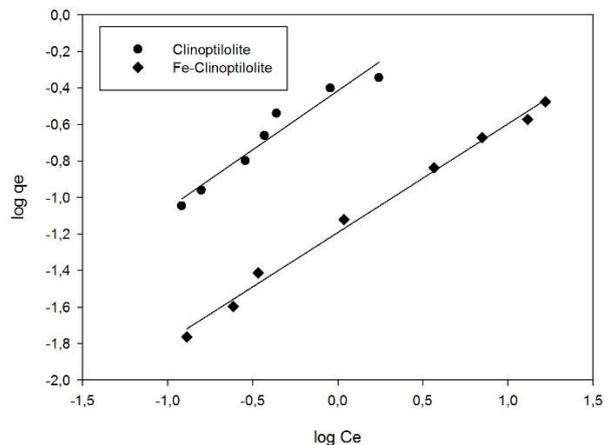
Fig. 2 *Linearized Freundlich isotherms for the adsorption of copper onto natural clinoptilolite and Fe-clinoptilolite*

Clinoptilolite

As seen in Table 3, the Langmuir isotherm fits correctly to the experimental data (R^2 = 0.9845), whereas the low correlation coefficient (R^2 = 0.9425) shows poor agreement of the Freundlich isotherm with the experimental data. Also, the fitness of the data to the Langmuir isotherm is an indicator of mono layer coverage of copper on the natural clinoptilolite surface and chemisorption.

Fe-clinoptilolite

Value of R^2 (0.9847) of Langmuir isotherm is lower than correlation coefficients (R^2 = 0.9931) of the Freundlich isotherm. This indicates that the adsorption data of the Freundlich isotherm are more accurate than the Langmuir's isotherm data, what in turn indicates that adsorption process is basically heterogeneous.

FREUNDLICH AND LANGMUIR CONSTANTS FOR THE SORPTION
OF COPPER ONTO ADSORBENTS   Table 3

Adsorbent	Langmuir model			Freundlich model		
	Q_m	b	R^2	k	n	R^2
Clinoptilolite	0.7447	1.108	0.9845	0.383	1.55	0.9425
Fe-clinoptilolite	0.21819	0.627	0.9847	0.064	1.68	0.9931

Sorption kinetics

There are essentially three stages in the adsorption process by porous adsorbents: [1] solute transfer from the bulk solution to the external surface of the sorbent through a liquid boundary layer (film resistance); solute transfer from the sorbent surface to the intraparticle active sites (intraparticle resistance); and [6] interactions of the solute with the available sites on both the external and internal surfaces of the sorbent (reaction resistance). One or more of the above mentioned stages may control the rate at which the solute is adsorbed and the amount of solute that is adsorbed onto the sorbent. In this study, the kinetics of sorption that defines the efficiency

of sorption of mixed metal ions was checked by the pseudo-first-order and pseudo-second-order equations (13).

Pseudo-first-order kinetics model

In 1898, Lagergren (14) suggested a pseudo-first-order equation for the sorption of liquid/solid system based on solid capacity. It assumes that the rate of change of sorbate uptake with time is directly proportional to the difference in the saturation concentration and the amount of solid uptake with time. The Lagergren equation is the most widely used rate equation in liquid phase sorption. The general equation is expressed as:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \ , \qquad [6]$$

where q_e and q_t are the amounts of metal ions adsorbed onto the adsorbents (mg g^{-1}) at equilibrium and at time t, respectively. k_1 is the rate constant of first order (min^{-1}). By plotting $\log(q_e-q_t)$ versus t, the first-order constant k_1 and the equilibrium capacity q_e can be obtained from the slope and intercept, respectively.

Pseudo-second-order kinetic model

Ho and Mckay (15) developed a pseudo-second-order equation based on the amount of sorbed sorbate on the sorbent. If the rate of sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetics rate equation is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2. \qquad [7]$$

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Eq. [8] becomes:

$$\frac{1}{(q_e-q_t)} = \frac{1}{q_e} + k_2 t \ , \qquad [8]$$

which is the integrated rate law for a pseudo-second-order reaction. Eq. [9] can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \ . \qquad [9]$$

The constants can be determined by plotting t/q_t versus t. The second-order sorption rate constant k_2 (g mg^{-1} min^{-1}) and q_e (mg g^{-1}) can be determined from the intercept and the slope of the plot. This model is based on the assumption that the rate limiting step may be a chemical sorption involving valence forces through sharing or exchange of electrons between the adsorbent and the adsorbate (13).

Evaluation of sorption kinetics

PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER KINETICS RATE
CONSTANTS FOR COPPER ONTO NATURAL CLINOPTILOLITE
AND Fe-CLINOPTILOLITE   Table 4

Adsorbent	q_e exp. [mg g⁻¹]	Pseudo-first-order kinetics model			Pseudo-second-order kinetics model		
		$q_{e\ cal.}$ [mg g⁻¹]	k_1 [min]	R^2	$q_{e\ cal.}$ [mg g⁻¹]	k_2 g mg⁻¹ min⁻¹	R^2
Clinoptilolite	0.3715	0.2303	0.0517	0.9983	0.3861	0.4491	0.999
Fe-clinoptilolite	0.3901	0.2589	0.0763	0.9908	0.3953	0.9645	1.000

Clinoptilolite

As can be seen from Table 4, the precisely calculated correlation coefficient ($R^2 = 0.999$), for the natural clinoptilolite indicates the validity of the pseudo-second-order model for copper sorption by this sorbent.

Fe-clinoptilolite

The correlation coefficient reached a maximum value ($R^2 = 1.000$) and its calculated equilibrium q_e was consistent according to the experimental data. Among these kinetic models the experimental data showed more accurate fitting with pseudo-second-order model.

CONCLUSION

This article presents the results of equilibrium study and kinetics of the sorption process for removing copper ions from aqueous solution using a common naturally occurring natural clinoptilolite and Fe-clinoptilolite. Fe-clinoptilolite system was synthesized by adding natural clinoptilolite to an iron nitrate solution under strongly basic condition. The Langmuir and Freundlich isotherm models were used to represent the experimental data and the models fitted precisely. The adsorption of copper onto natural clinoptilolite was adequately described by the Langmuir isotherm. The experimental data for Fe-clinoptilolite fitted well with the Freundlich model. In terms of materials adsorption of copper onto Fe-clinoptilolite is faster than adsorption onto natural clinoptilolite. Kinetics of copper sorption on both samples followed pseudo-second-order model. The results of this study indicate that, considering its low cost, natural and modified clinoptilolite has the potential to be used as an alternative adsorbent for the removal of copper from aqueous solutions.

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