

KINETIC MODELING OF COPPER REMOVAL FROM AQUEOUS SOLUTIONS USING NATURAL ZEOLITE

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ABSTRACT

In this work we have experimentally investigated sorption kinetics of Cu(II) ions from aqueous solutions at a concentration of 300 mg dm^{-3} at different temperatures (25, 35, 45 °C) using natural clinoptilolite from Serbia (Zlatokop mine) and then applied the Lagergren pseudo-second-order kinetic model. Although, apparently good overall agreements of model predictions with experimental data were obtained, discrepancies in the initial sorption period were noticed. The results indicated that the simple pseudo-second-order kinetic constant is actually a complex function and cannot be directly related to the ion exchange mechanism. Therefore, we have developed a novel kinetic model based on two reversible steps: 1) release of two Na^+ ions providing one free site for Cu^{2+} ion, and 2) bonding of Cu^{2+} ion to the site. The obtained results indicated potentials of the novel kinetic model to provide insights into the sorption mechanism of heavy metal ions in clinoptilolite.

Keywords: zeolite, heavy metal, kinetics model, ion-exchange.

INTRODUCTION

Sorption based on the use of low-cost, efficient sorbents is one of the most attractive methods for wastewater treatment providing in the same time, simple sorbent removal after the use. In this context, natural zeolites are advantageous due to their abundance, high sorption capacity and excellent selectivity for a number of toxic heavy metal cations. Design and scale up of ion exchange based wastewater treatment processes requires knowledge and understanding of sorption kinetics and mechanism. Lagergren's pseudo-first-order and pseudo-second-order model are usually used to describe sorption kinetics of heavy metal ions in zeolites [1-5], whereas, the latter model have shown better agreement with experimental data in most cases. However, the sorption mechanism is not fully elucidated yet while the physical meaning of the Lagergren's kinetic rate constant is not clear.

The aim of this work was to experimentally investigate sorption kinetics of Cu(II) ions from aqueous solutions at different temperatures using low-cost domestic natural clinoptilolite and then to develop an appropriate kinetic model.

EXPERIMENTAL

Natural clinoptilolite (Vranjska Banja, Serbia, particle size: 60 – 120 μm) was pretreated with NaCl (2.0 mol dm^{-3}) yielding Na-rich clinoptilolite (Na-CLI). Cu(II) solution at the concentration of 300 mg dm^{-3} was prepared by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water. Experiments were carried out in duplicates in closed erlenmeyer flasks of 250 cm^3 containing 1 g of Na-CLI in 0.1 dm^3 of the solution. Suspensions were shaken in a thermostated water bath (model WNB 22, Memmert, Germany) with the temperature control within $\pm 0.1^\circ\text{C}$ for up to 48 h. Liquid samples (1 ml) were taken at predetermined time intervals and immediately filtered using the $0.20\text{-}\mu\text{m}$ syringe filters (Roth, Germany). Concentrations of Cu(II) were determined to four-digit accuracy by an atomic absorption spectrophotometer (Varian SpectrAA 55B). At least five measurements were performed for each liquid sample.

RESULTS AND DISCUSSION

Natural clinoptilolite used in this work was shown to effectively remove Cu(II) ions from water solutions (Fig. 1). It can be noticed that the adsorbed amounts of Cu(II) ions increased with the increase in temperature and contact time (Fig. 1).

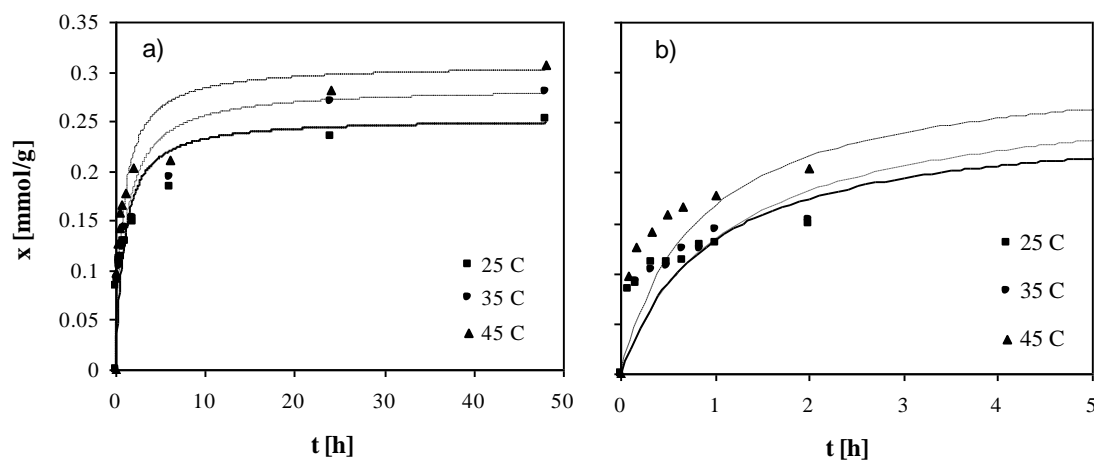


Figure 1. Experimental data (symbols) and predictions of the Lagregren pseudo-second order kinetic model (lines) of sorbed Cu(II) at different temperatures: a) overall period of 48 h to reach the equilibrium; b) initial sorption period of 5 h.

Experimental data were first modeled by the Lagergren pseudo-second-order kinetics as:

$$\frac{dx}{dt} = k(x_e - x)^2 \quad (1)$$

where x and x_e are the sorbed metal concentrations at time t and at equilibrium, respectively, and k is the rate constant. Experimental data were fitted with the integrated linear form of the Eq. (1):

$$\frac{t}{x} = \frac{1}{kx_e^2} + \frac{1}{x_e}t \quad (2)$$

The obtained values of rate constants and equilibrium concentrations of sorbed Cu(II) are summarized in Table 1.

Although apparently good overall agreements with the experimental data were obtained (Fig. 1a) with quite high values of the correlation coefficients ($R^2 \geq 0.996$), large discrepancies of the model predictions with experimental results could be noticed especially during the first several hours of adsorption (Fig 1b). In addition, kinetic rate constants did not exhibit any consistent trend with temperature (Table 1). Similar results have been reported in literature [1-5] indicating that the simple pseudo-second-order kinetic rate constant is actually a complex function and cannot be directly related to the sorption mechanism.

Table 1. Kinetic parameters of Lagergren pseudo-second-order model for Cu(II) ion sorption on Na-CLI at different temperatures.

Temperature (°C)	25	35	45
k_2 (g mmol ⁻¹ h ⁻¹)	4.4	3.1	3.9
x_e (mmol g ⁻¹)	0.25	0.28	0.31

In order to get an insight into the mechanism of Cu(II) ion sorption in zeolites, we have developed a novel kinetic model based on two consecutive, reversible steps:



where k represents the kinetic rate constant of each of the reactions and P is the free cation site in the zeolite lattice for binding of one metal (Cu^{2+}) ion. Index 0.5 in the Eq. (3) indicates that two sites occupied by Na^+ ions in the zeolite lattice are close to each other in order to provide one site (P) for the Cu^{2+} ion binding. It is assumed that the concentration of free sites is low and constant over time. Thus, the differential equations describing the rates of free sites generation and sorption of Cu^{2+} ions were coupled to derive the final expression for the Cu^{2+} sorption rate as:

$$\frac{dx}{dt} = k_1 \frac{(c_0 - x)(c_{BZ0} - 2x)^2 - 4K'x^3}{4k_2'x^2 + (c_0 - x)} \quad (5)$$

where c_0 and c_{BZ0} are the initial concentrations of Cu^{2+} in the solution and Na^+ ions in the zeolite lattice, respectively, and k_2' is the constant defined as:

$$k_2' = k_2/k_3 \quad (6)$$

The constant K' is determined from the equilibrium as:

$$K' = \frac{k_2 k_4}{k_1 k_3} = \frac{(c_0 - x_e)(c_{BZ0} - 2x_e)^2}{4x_e^3} \quad (7)$$

The Eq. (5) was solved numerically resulting in excellent agreements with the experimental data over the whole sorption period (Fig. 2). Kinetic parameters of the model are summarized in Table 2.

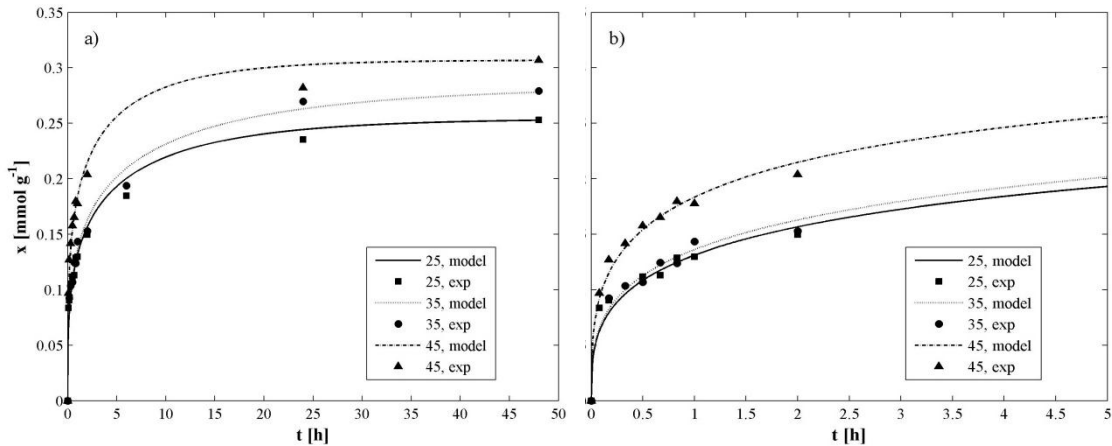


Figure 2. Experimental data (symbols) and predictions of the novel kinetic model (lines) of sorbed Cu(II) at different temperatures: a) overall period of 48 h to reach the equilibrium; b) initial sorption period of 5 h.

Table 2. Kinetic parameters of the novel kinetic model for Cu(II) ion sorption on Na-CLI at different temperatures.

Temperature (°C)	25	35	45
k_1 (g mmol ⁻¹ h ⁻¹)	18.6	17.9	17.1
$k_2' = k_2/k_3$ (g mmol ⁻¹)	2503	2086	626
k_4 (h ⁻¹)	1.4	0.9	1.7

Apparently, the strongest effect of temperature could be observed in the case of the Cu(II) ion bonding kinetic constant (k_3) that significantly increased with the increase in temperature. As a consequence, the constant k_2 decreased while the equilibrium constant increased as the temperature was increased (Table 2). These results imply that the rate controlling step in Cu(II) ion sorption in zeolites is bonding of the copper ion to the free site. However, further experimental and kinetic modeling studies are required to exactly determine all kinetic rate constants and fully clarify the sorption mechanism.

CONCLUSION

A novel kinetic model has been developed in order to get an insight into the mechanism of Cu(II) ion sorption on Na-rich natural clinoptilolite. The process was described as two consecutive, reversible steps: release of two neighboring Na^+ ions from the zeolite lattice followed by bonding of one Cu^{2+} ion to the free site. The model predictions were in excellent agreement with experimental data implying that the novel kinetic model could be extended to sorption of other heavy metal ions in zeolites.

REFERENCES

- [1] M. I. Panayotova, *Waste Manage.*, 2001, **21**, 671-676.
- [2] S. Kocaoba, Y. Orhan and T. Akyüz, *Desalination*, 2007, **214**, 1-10.
- [3] M. Panayotova and B. Velikov, *J. Environ. Sci. Heal. A*, 2002, **37**, 139-147.
- [4] M. V. Dinu and E. S. Dragan, *Chem. Eng. J.*, 2010, **160**, 157-163.
- [5] M. Sprynskyy, B. Buszewski, A. P. Terzyk and J. Namieśnik, *J. Colloid. Interf. Sci.*, 2006, **304**, 21-28.