



COPPER REMOVAL FROM WASTEWATER VIA CLINOPTILOLITE: THE DIFFUSION KINETIC ANALYSIS

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Abstract

This study investigates the kinetic models of Cu²⁺ ion adsorption onto clinoptilolite-rich zeolite. The study highlights the importance of diffusion kinetic models in understanding the adsorption process. The initial phases are significantly influenced by the ion diffusion through the film to the particle surface, particularly within the first 30 minutes, which is crucial for the heterogeneous surfaces like zeolites. Following this, the surface adsorption (intraparticle diffusion) is described by the Weber-Morris model, effective primarily during the initial stage. As the process progresses beyond 20-30 minutes, the ion removal rates decrease sharply, and diffusion within the particle core becomes the dominant factor, influencing the overall reaction rate.

Keywords: copper, clinoptilolite, wastewater, diffusion model

1. INTRODUCTION

Understanding the kinetic models and their parameter effects helps to manage and mitigate changes in the process conditions. The diffusion kinetic models describe how diffusion rates impact the aqueous solution-adsorbent system. Depending on the approach, different diffusion kinetic models have been developed. The kinetic model of ion diffusion through the film to the particle surface significantly influences the overall mass transfer rate, especially during the initial 30 minutes of the process. It is important to note that this phase has a particularly pronounced impact when dealing with the heterogeneous surfaces, such as in the case of zeolites.

$$\ln\left(1 - \frac{q_t}{q_e}\right) = -t \frac{3Dc}{r\delta c_z} = -Dt$$

This is followed by the sorption on the adsorbent surface (intraparticle diffusion) well described by the Weber-Morris model:

$$\alpha_t = a + \left(\frac{D}{r^2}\right)^{1/2} t^{1/2}$$

a – dimensionless constant

This model accurately describes the reaction only during the initial stage of the process. After 20-30 minutes, the ion removal rate drops sharply, and diffusion within the particle core becomes the key factor affecting the overall reaction rate, as described by the following relation:

$$\alpha_t = \frac{1}{\rho} \ln t + C$$

2. EXPERIMENTAL

A clinoptilolite-rich zeolite tuff from the Zlatokop deposit in Vranjska Banja, Serbia contains ~80% clinoptilolite, with quartz, feldspar, and carbonate as the main impurities. Its total cation exchange capacity is 146 meq/100 g, measured with 1 M NH₄Cl.

For the adsorption experiments, zeolite (Cli) was ground and sieved to <0.043 mm. Cu uptake was tested by shaking 1 g of Cli with 50 mL of CuSO₄·5H₂O solution at various initial Cu concentrations. The experiments, conducted at room temperature for 120 minutes, used the batch technique. After equilibration, the suspensions were centrifuged, and Cu concentrations in the supernatants were measured by the AAS

3. RESULTS AND DISCUSSION

In the Cu(II) adsorption kinetics experiments on clinoptilolite, this paper focuses on the effect of initial solution concentration. Figure 1 shows the adsorption of Cu(II) ions per unit mass of adsorbent over time, where q_t is the Cu²⁺ concentration at time t (mg/g) and t is the contact time (minutes). All curves exhibit the same shape, regardless of the initial copper concentration.

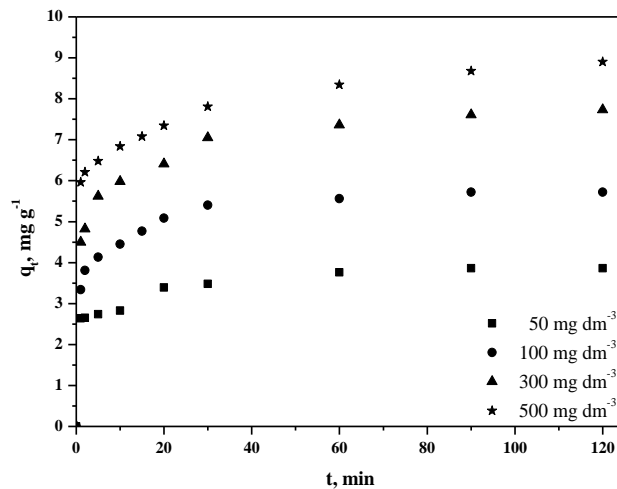


Figure 1. Effect of initial Cu²⁺ concentration on the clinoptilolite adsorption capacity over time

The results indicate that the copper adsorption process begins with a rapid reaction, during which the majority of adsorption occurs within the first 20 minutes.

During the experimental phase of this study, the obtained data were analyzed using the diffusion kinetic models. The film diffusion model (Figure 2) accurately describes the process for the examined time interval (120 min). The diffusion coefficient, obtained from the slope of the curve, is directly proportional to the Cu^{2+} ion content in solution and slightly decreases with increasing the initial copper ion concentration. It can be assumed that at higher copper concentrations, a thicker film forms on and around the surface of adsorbent particles due to the release of compensating cations.

Despite the high correlation between the experimental data and model, the lines describing the kinetics do not pass through the origin. This indicates that the diffusion of copper ions through a film on particle surface is not the only mechanism controlling the overall reaction rate.

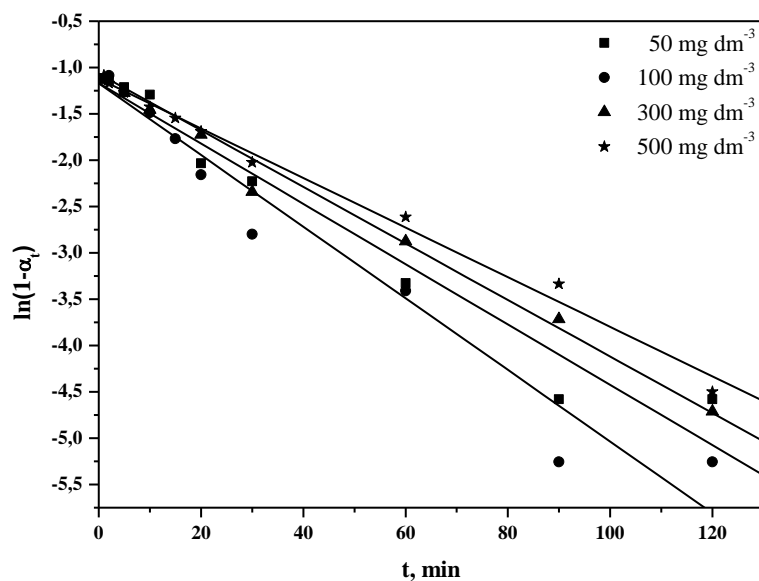


Figure 2. Diffusion of Cu^{2+} ions through the film at different initial concentrations

Following the diffusion of copper ions through the film, the intraparticle diffusion occurs, which is well described by the Weber-Morris model (Fig.3a).

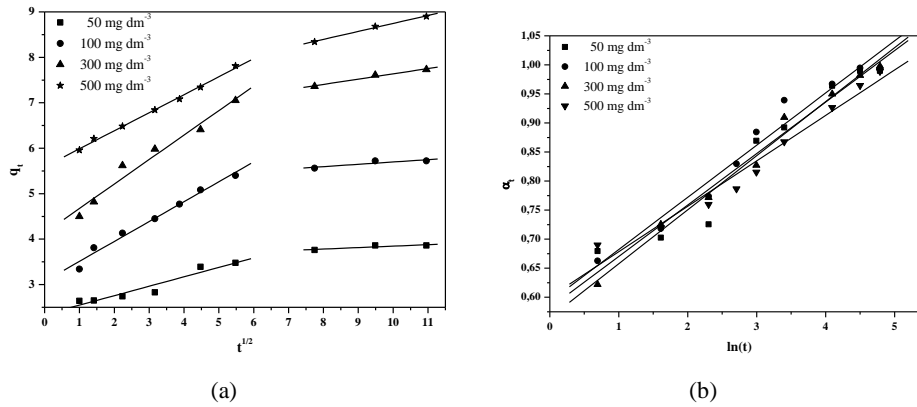


Figure 3. (a) Weber-Morris model, intraparticle diffusion of Cu²⁺ ions and (b) Internal heterogeneous diffusion of Cu²⁺ ions at different initial solution concentrations

In the experimental data analysis, the points from the first minute were excluded due to the significant deviations. It is assumed that during this time, Cu²⁺ ions diffuse through the film, and the intraparticle diffusion conditions are still forming. For the same initial copper ion concentration, the model shows two linear segments. The first, up to 30 minutes, corresponds to the surface diffusion, with a slope proportional to the initial adsorption rate, which increases slightly with concentration. As particles diffuse, the higher concentration difference between solution and adsorbate enhances the adsorption rate. The y-intercept, related to the boundary layer thickness, decreases with a higher initial concentration. After 30 minutes, the adsorption rate decreases, leading to the equilibrium. The second segment shows that more time is needed to reach equilibrium at higher concentrations.

After the initial phase, where Cu particles adsorb onto the zeolite surface, the internal diffusion (Figure 3b) occurs into adsorbent structure. Due to the zeolite channel-rich structure, the internal diffusion is slower and influenced by the channel size and Cu²⁺ ions. Displaced compensating cations also hinder the Cu²⁺ mobility, meaning both intraparticle and internal diffusion affect the overall adsorption rate. The analysis from the fifth minute to the equilibrium showed a strong linear relationship, while the initial data points deviated, indicating that the film and intraparticle diffusion occur early on, with the internal diffusion becoming significant after 3-4 minutes. The internal diffusion coefficient, and thus its rate, does not depend on the initial copper concentration.



Table 1. The main parameters, obtained applying the diffusion kinetic models for adsorption the Cu^{2+} ions on Cli, depending on the initial concentration of solution

Model	Parameter	$C_0, \text{mg dm}^{-3}$				
		50	100	300	500	
Film diffusion	R^2	0.980	0.977	0.992	0.996	
	D, min^{-1}	-	-	-	-	
	$n=0$	1.169	1.171	1.068	1.122	
Surface (intraparticle)diffusion (Weber-Morris)	0-30 min	R^2	0.961	0.991	0.983	0.998
		$k_{wb}, \text{mg g}^{-1} \text{min}^{-1/2}$	0.053	0.069	0.076	0.044
		$a, \text{mg g}^{-1}$	0.600	0.535	0.534	0.624
	60-120 min	R^2	0.999	0.999	0.999	0.999
		$k_{wb}, \text{mg g}^{-1} \text{min}^{-1/2}$	0.008	0.009	0.015	0.019
		$a, \text{mg g}^{-1}$	0.904	0.902	0.835	0.777
Internal (heterogeneous) diffusion	R^2	0.971	0.983	0.994	0.983	
	$1/\rho$	0.089	0.090	0.093	0.078	
	C	0.582	0.593	0.565	0.600	

4. CONCLUSION

Adsorption on zeolite, which belongs to the porous materials, can be analyzed applying the diffusion kinetic models. This study presents three kinetic models: film diffusion, intraparticle diffusion, and internal diffusion. The diffusion coefficient, obtained from the curve slope, is directly proportional to the content of Cu^{2+} ions in solution and slightly decreases with increase in the initial concentration of copper ions. The diffusion of copper ions through the film on the surface of particles is not the only mechanism controlling the overall reaction rate. It is followed by the intraparticle diffusion—it is observed that for the same initial concentration of copper ions in solution, two different linear segments can be observed when this model is applied. The first, steeper part up to 30 minutes relates to the surface diffusion on adsorbent. The line slope of is proportional to the initial adsorption rate and slightly increases with increase in the initial concentration. After the initial 30 minutes, the adsorption rate drastically decreases until equilibrium is established, as shown by the second linear segment. It is noted that with increase in the initial concentration of copper, the line slope slightly increases, indicating that at higher concentrations, more time is required to reach the equilibrium. The internal or heterogeneous diffusion starts only after 3-4 minutes of the process. Based on the previous analysis, it can be concluded that the internal diffusion



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coefficient, and therefore the rate of this part of process, does not depend on the initial concentration of copper in solution.

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REFERENCES

- [1] Robinson, S.M., Arnold, W.D., Bzers, C.H., AIChE J., 40, 1994, 2045-2054
- [2] Trgo, M., Perić, J., Vukojević Medvidović, N., J. Environ. Management, 79, 2006, 298-304
- [3] Helfferich F., Ion Exchange, Mc Graw-Hill, New Zork, 1962, 250-265
- [4] Guibal, E., Milot, C., Tobin, J.M., Ind. Eng. Chem. Res., 37 (4), 1998, 1454-1463
- [5] Trgo, M., Perić, J., J. Colloid Interf. Sci., 260 (1), 2003, 166-175