

A STUDY OF THE REMOVAL OF COPPER IONS FROM AQUEOUS SOLUTION USING CLINOPTILOLITE FROM SERBIA

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Abstract—Toxic metal contamination of waste waters can be mitigated by metal adsorption to clay and zeolitic minerals, but in developing countries such environmental remediation can be cost prohibitive if these minerals are not readily available. Because of its abundance, low cost, and excellent selectivity for several toxic metal ions, clinoptilolite from the Zlatokop deposit in Serbia was investigated for its ability to remove copper ions from aqueous solutions and serve as an effective local resource for this purpose. The sorption capacity of the clinoptilolite at 298 K varied from 8.3 mg Cu g⁻¹ (for C₀ = 100 mg Cu dm⁻³) to 16.8 mg Cu g⁻¹ (for C₀ = 400 mg Cu dm⁻³). The sorption data were best described by the Freundlich isotherm and the sorption kinetics followed the pseudo-second-order model. Intra-particle diffusion of Cu²⁺ was present but it is not the rate-limiting step. The sorption of Cu²⁺ on the clinoptilolite occurred spontaneously, the free energy change decreasing with temperature. The sorption was endothermic and was accompanied by an increase in entropy. Dehydration of the Cu-loaded clinoptilolite at 540°C led to the formation of nanocrystalline Cu(I) oxide particles with an average size of ~2 nm, suggesting possible novel applications for the Cu-loaded clinoptilolite.

Key Words—Clinoptilolite, Copper Removal, Kinetics, Nano-cuprite, Thermodynamics.

INTRODUCTION

The release of toxic heavy metals into the environment can cause serious soil and water pollution. Industrial wastewaters may contain considerable amounts of heavy metals which must be removed before discharge. In Serbia, a Balkan country in economic transition, legislation for wastewater management has not yet been fully implemented even though numerous ecological ‘hot spots’ exist throughout the country. An example is the city of Bor where a copper mine which has been closed since 2002 is still having an impact on the quality of the surrounding groundwater (Georgievski *et al.*, 2009). Mine waters emanating from active or closed copper mines usually contain Cu²⁺ in very large concentrations (~1 g dm⁻³). For Serbia, as for many other developing countries, an effective, economic, and easily implemented set of wastewater-treatment protocols is necessary.

Various techniques have been employed for the removal of heavy-metal ions including adsorption, biotechnology, catalytic and membrane processes, and radiation- and magnetically-assisted processes (Ambashta *et al.*, 2010). Adsorption is the most studied technique because it is simple, effective and depends mostly on adsorbent efficiency. Natural zeolites have attracted much attention because of their abundance, low cost, and

excellent selectivity for a number of toxic heavy-metal cations (Wang and Peng, 2010).

Several regions in Serbia have abundant supplies of the natural zeolite, clinoptilolite. The clinoptilolite from different regions shows different degrees of efficiency in the removal of heavy-metal ions from aqueous media (caused mainly by differences in the Al/Si molar ratio and different types of exchangeable cations). A research program was commenced (Rajic *et al.*, 2010a, 2010b; Stojakovic *et al.*, 2011) to study in detail the natural zeolitic tuff from a large deposit (Zlatokop) in southern Serbia with a view to using the mineral as an adsorbent in the treatment of wastewater. The present study examines the effectiveness of Zlatokop clinoptilolite in the adsorption of Cu²⁺ ions from aqueous solutions.

MATERIALS AND METHODS

Sorption of Cu on clinoptilolite tuff

The natural zeolite material, clinoptilolite (CLI), was obtained from a large sedimentary deposit in Zlatokop, Vranjska Banja, Serbia. Material with a grain size in the range 0.063–0.1 mm was chosen for the experiments. A previous powder X-ray diffraction (XRD) analysis showed that the zeolitic tuff contains 72.6% clinoptilolite, 14.6% plagioclase, and 12.8% quartz (Cerjan Stefanović *et al.*, 2007). The chemical composition of the clinoptilolite phase, expressed in wt.% oxide, is: SiO₂ 65.63, Al₂O₃ 12.97, Fe₂O₃ 1.48, Na₂O 0.95, K₂O 1.33, CaO 3.08, MgO 1.41, and loss on ignition 12.96 (Cerjan Stefanović *et al.*, 2007).

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In order to improve the tuff's sorption capacity, the CLI was modified to Na-CLI as reported in detail by Rajic *et al.* (2010a) and Cerjan Stefanović *et al.* (2007). Elemental analysis showed that the amount of exchangeable cations in Na-CLI theoretically allows for an uptake (by cation exchange) of $\sim 45 \text{ mg Cu g}^{-1}$ Na-CLI.

The Cu^{2+} sorption isotherms were determined at 298, 308, 318, and 328 K using the batch method. The suspension of Na-CLI and the chosen Cu^{2+} solution ($50\text{--}400 \text{ mg Cu dm}^{-3}$) was shaken at $\sim 100 \text{ rpm}$ for 24 h in a thermostated water bath (Memmert WPE 45, Schwabach, Germany). The starting pH value in solution was 5, and increased slightly to 5.2 by the end of sorption reaction experiment. In all experiments the solution volume/solid weight ratio was $100 \text{ cm}^3/\text{g}$. Preliminary investigations showed that the Cu^{2+} -removal capacity of Na-CLI increased by $\sim 10\%$ when the solution pH was raised from 4 to 7. Subsequent experiments were conducted at $\sim \text{pH } 5$ in order to avoid any possible hydroxide precipitation [the solubility product of copper hydroxide is 1.6×10^{-19} (Whitten *et al.*, 2007)]. The pH value increased slightly at the end of sorption.

The rate of sorption of Cu^{2+} by Na-CLI was studied at temperatures of 298, 308, 318, and 328 K in solutions with initial Cu^{2+} concentrations of 100, 200, 300, and $400 \text{ mg Cu}^{2+} \text{ dm}^{-3}$. The suspension was shaken at a rate of $\sim 100 \text{ rpm}$ for periods of time from 20 min to 24 h. The solid was then separated by filtration.

All experiments were carried out under controlled conditions: the temperature of the thermostated bath was kept constant within $\pm 0.1^\circ\text{C}$, the solid samples were weighed to four-digit accuracy using a Shimadzu electronic balance AX200 (Kyoto, Japan), and the solution concentrations were also determined to four-digit accuracy by atomic absorption spectroscopy (Varian Spectra A55, Mulgrave Victoria, Australia).

Post-treatment of the Cu-loaded sample

A sample of Cu-CLI (containing 16 mg Cu g^{-1}) was treated thermally under air at 540°C at a heating rate of $10^\circ\text{C min}^{-1}$ (starting from 298 K). The product obtained was examined by transmission electron microscopy (TEM) as described by Rajic *et al.* (2010b). The crystal phase formed during the thermal treatment of Cu-CLI was identified using energy dispersive X-ray spectroscopy (EDX).

Analytical techniques

All chemicals used were of analytical grade. The Cu^{2+} solutions were prepared by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (obtained from Fluka, Buchs, Switzerland) in deionized water. The metal concentrations in solutions were determined by atomic absorption spectroscopy (AAS – Varian Spectra A55 atomic absorption spectrophotometer, Mulgrave, Victoria, Australia). At least five measurements were made for

each determination. The relative standard deviation was found to be $< 2\%$. Chemical analysis of the clinoptilolite samples was performed using a scanning electron microscope, JEOL JSM-6610LV (JEOL Ltd., Tokyo, Japan). The samples were prepared by embedding grains in an epoxy film by a procedure described by Stojakovic *et al.* (2011). An average elemental composition of the sample was obtained by data collection at five different mm^2 -sized windows on the sample surface. The accuracy of the method was $\pm 3\%$.

The TEM studies were performed using a 200 kV TEM (JEM-2100 UHR, JEOL, Inc., Tokyo, Japan) equipped with an ultrahigh-resolution, objective-lens pole piece having a point-to-point resolution of 0.19 nm. The sample was crushed in an agate mortar, dispersed in absolute ethanol, and applied to a Ni-hole carbon grid.

RESULTS AND DISCUSSION

Sorption isotherms

Sorption data (Figure 1) revealed that the sorption capacity of the clinoptilolite increased both with temperature and with the initial Cu^{2+} solution concentration.

The clinoptilolite was quite effective at removing the Cu^{2+} ions from aqueous solutions at ambient temperature: the sorption capacity at 298 K varied from 8.3 mg Cu g^{-1} (for $C_0 = 100 \text{ mg Cu dm}^{-3}$) to $16.8 \text{ mg Cu g}^{-1}$ (for $C_0 = 400 \text{ mg Cu dm}^{-3}$), which corresponds to 18.6–37.6% cation exchange (relative to the Na-exchange capacity). The sorption capacity increased with increase of the Cu^{2+} concentration in contrast to the results reported for the clinoptilolite from Anatolia for which a decreasing trend was found (Erdem *et al.*, 2004). A slight increase in the sorption capacity was found at 328 K: from 9.9 mg Cu g^{-1} (for $C_0 = 100 \text{ mg Cu dm}^{-3}$) to $22.7 \text{ mg Cu g}^{-1}$ (for $C_0 = 400 \text{ mg Cu dm}^{-3}$), corresponding to 22.2–50.1% cation exchange, respectively.

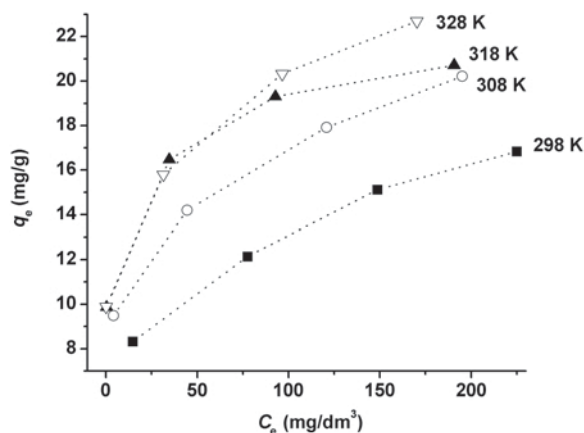


Figure 1. Sorption isotherms for Cu^{2+} on Na-CLI; q_e is the amount of the metal sorbed (mg/g Na-CLI) and C_e is the solution concentration at equilibrium.

The equilibrium data from Figure 1 were analyzed using several empirical isotherm models commonly employed in adsorption studies (Vijayaraghavan and Yun, 2008; Ho *et al.*, 2002). Satisfactory fits (*i.e.* those where the correlation coefficient (R^2) was >0.8) were only obtained with the Freundlich model and, therefore, only the results for this model are presented here. For a clinoptilolite from the Transcarpathian region (Ukraine), the Freundlich isotherm was also most suitable (Sprynskyy *et al.*, 2006), whereas for the Bulgarian natural zeolite (Panayotova, 2001) and the natural zeolites from Turkey (Kocaoba *et al.*, 2007; Çoruh *et al.*, 2009) the best fit was obtained using the Langmuir isotherm.

The Freundlich model was originally empirical, but can be interpreted (Vijayaraghavan *et al.*, 2006) as non-ideal sorption on heterogeneous surfaces or surfaces having sites of varied affinities. Such an interpretation is based on two assumptions: (1) the stronger binding sites are occupied first; and (2) the binding strength decreases as the degree of site occupation increases. The Freundlich isotherm is given by:

$$q_e = K_F C_e^n \quad (1)$$

where q_e (mg g^{-1}) is the equilibrium solute uptake, K_F ($\text{dm}^3 \text{g}^{-1}$) is the Freundlich model isotherm constant, C_e (mg dm^{-3}) is the equilibrium solution concentration, and n is the Freundlich model exponent. K_F and n are characteristics of the system and are indicators of the sorbent capacity (or affinity for the solute) and adsorption intensity, respectively.

The analysis of the isotherm data using equation 1 gave parameters listed in Table 1.

The Freundlich coefficient n can be regarded as a parameter which varies with the degree of system heterogeneity (Kinniburgh, 1986) and is a measure of the isotherm linearity (Weber *et al.*, 1992). The closer n is to 1, the more linear is the isotherm. The equilibrium distribution of a solute between the fluid and solid phases is often a linear relationship, particularly at low fluid-phase solute concentrations. Non-linear equilibrium distribution relationships are typically encountered if the concentrations span several orders of magnitude (Pedit and Miller, 1994). The results

(Table 1) show that, in the system studied, the distribution relationship was non-linear even though the fluid-phase solute concentrations lay in a rather narrow range. The degree of non-linearity increased with sorption capacity, K_F (which increases with temperature).

Kinetic analysis

The Cu^{2+} sorption dependence on time was investigated at 298, 308, 318, and 328 K for solutions with $C_0 = 100, 200, 300,$ and $400 \text{ mg Cu dm}^{-3}$. The time dependence was followed until the sorption equilibrium was reached, after ~ 24 h. The uptake values of Cu^{2+} from solution (Figure 2) showed that in the early stages of sorption (*i.e.* in the first ~ 150 – 200 min) the Cu^{2+} uptake increased sharply and thereafter proceeded more gradually. Similar behavior was reported for sorption of Cu^{2+} by clinoptilolite from other regions (Sprynskyy *et al.*, 2006; Panayotova, 2001; Kocaoba, 2007) and by some other sorbents (Svilović *et al.*, 2009; Božić *et al.*, 2009). The data from Figure 2 were analyzed using two reaction-based kinetics models and a diffusion-based model.

The first reaction-based model was described by the Ritchie second-order rate expression (Svilović *et al.*, 2009; Ho, 2006); its integrated form is given by equation 2:

$$q_t = q_e \left\{ 1 - \left[\frac{1}{1 + k_{2r}t} \right] \right\} \quad (2)$$

where q_e (mg g^{-1}) is the adsorption capacity at equilibrium and k_{2r} (min^{-1}) is the rate constant of the Ritchie second-order model. The plot of q_t vs. t can be analyzed by non-linear regression to estimate whether the experimental data agree with this model. The Ritchie model was originally designed for the adsorption of gases (Ritchie, 1977), but in recent years has also been applied to solution/solid systems (Svilović *et al.*, 2009; Cheung *et al.*, 2001).

The second reaction-based model is defined (Ho, 2006) by the pseudo-second-order rate equation which has the following integrated form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of the pseudo-second-order adsorption. The plot of t/q_t vs. t is a straight line if the experimental data correspond to this model; q_e and k_2 are obtained from the slope and intercept, respectively.

Application of the two models showed that the pseudo-second-order model gave a slightly better description of the Cu^{2+} sorption kinetics as judged by the R^2 values (Table 2).

The k_{2r} and k_2 rate constant values obtained for the two models changed irregularly with temperature for all

Table 1. Parameters obtained by the adsorption isotherm equation 1 for the sorption of Cu^{2+} on Na-CLI; R^2 is the correlation coefficient.

T (K)	Freundlich isotherm		R^2
	K_F ($\text{dm}^3 \text{g}^{-1}$)	n ($\text{dm}^3 \text{mg}^{-1}$)	
298	3.94	0.267	0.993
308	6.83	0.203	0.992
318	10.9	0.122	0.996
328	11.2	0.129	0.954

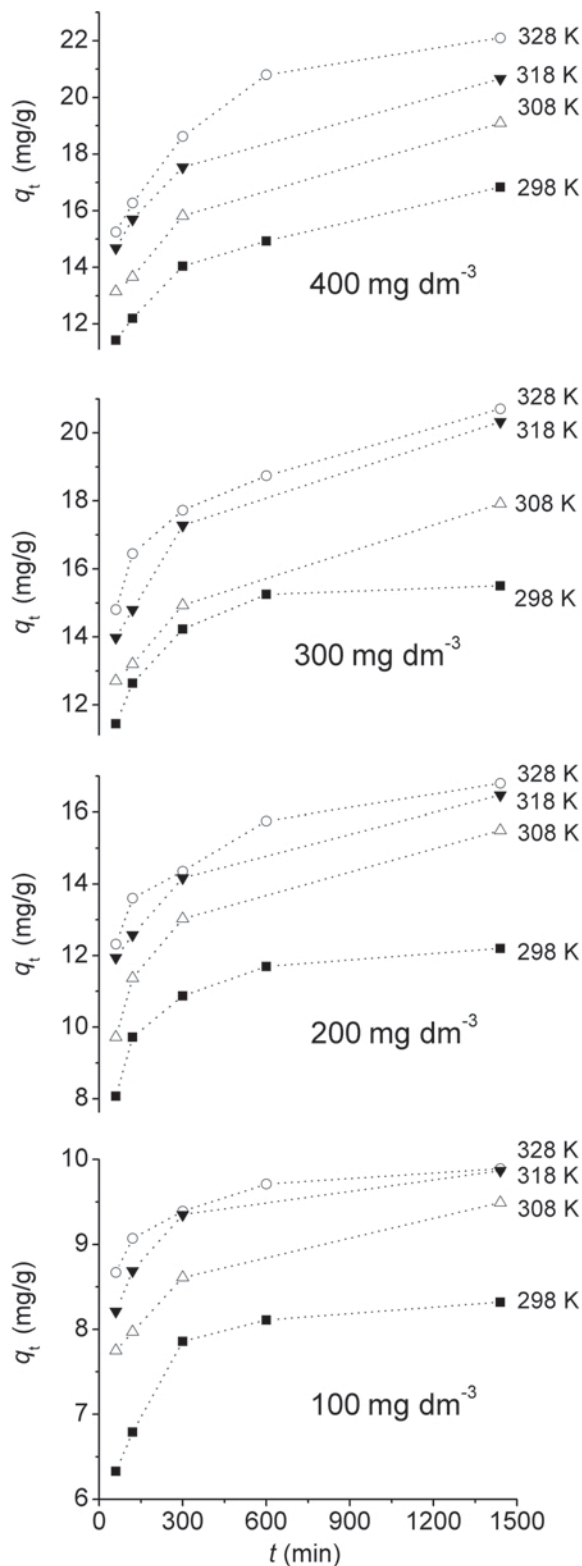


Figure 2. Sorption kinetics for Cu^{2+} on Na-CLI for different initial Cu^{2+} concentrations; q_t is the amount of the Cu^{2+} sorbed (mg/g Na-CLI) after time t .

initial Cu^{2+} concentrations (Table 2). Similar behavior was also found for Zn^{2+} sorption on clinoptilolite (Stojakovic *et al.*, 2011), confirming that the hydrolysis of transition-metal salts affected the sorption kinetics significantly. Cu^{2+} shows a propensity to form polynuclear hydroxido complexes: $\text{Cu}_2(\text{OH})_2^{2+}$ and, to a lesser extent, $\text{Cu}_2(\text{OH})_3^{3+}$ and $\text{Cu}_3(\text{OH})_4^{4+}$ (Powell *et al.*, 2007; Bryantsev *et al.*, 2009). Although in the present sorption study the Cu^{2+} species existed in solution predominantly as $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex ions (see below), at higher temperatures the formation of some polynuclear Cu^{2+} species due to the increased hydrolysis was likely. Because of their increased size, the bulky polynuclear hydrolysis products are less able to enter the pores of the clinoptilolite lattice, accounting for the observed irregularities in the change of the rate constant with temperature.

Diffusion effects. In order to examine the role of diffusion in the sorption process, the data were also analyzed using the Weber-Morris mass transfer model (Weber and Morris, 1963). This model is defined by the rate equation 4:

$$q_t = k_d t^{1/2} + I \quad (4)$$

where q_t (mg g^{-1}) is the adsorption capacity at time t (min), k_d ($\text{mg g}^{-1} \text{min}^{-1/2}$) is the diffusion rate constant, and I (mg g^{-1}) is the intercept at the ordinate.

The plots of q_t vs. $t^{1/2}$ for various temperatures and various initial Cu^{2+} concentrations appeared to be very similar to those shown in Figure 2 and are not presented here. The plots were straight lines consisting of two segments: the first segment, with a steeper slope, occurred in the $t^{1/2}$ region up to $\sim 20 \text{ min}^{1/2}$ while the second corresponded to larger $t^{1/2}$ values. The second segment can be attributed (Cheung *et al.*, 2007) to the intra-particle diffusion of Cu^{2+} into clinoptilolite channels and vacancies. Linear regression analysis revealed in all cases the intercept I (equation 4) to be >0 , indicating that in the present study intra-particle diffusion was not the rate-limiting step (Aravindhan *et al.*, 2009).

As the Cu^{2+} sorption experiments throughout the present work were conducted in relatively dilute solutions ($C < 10^{-2} \text{ mol dm}^3$), the Cu^{2+} species were present predominantly as $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex ions (Powell *et al.*, 2007; Skorik *et al.*, 2005). Note that $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ions have a radius of 0.73 nm (Greenwood and Earnshaw, 1984), which is significantly larger than the aperture of the largest 10-membered clinoptilolite ring channel ($0.44 \text{ nm} \times 0.72 \text{ nm}$) (Korkuna *et al.*, 2006). Rodriguez Iznaga *et al.* (2007) reported for the ion-exchange of NH_4^+ by Cu^{2+} inside the Cuba clinoptilolite that intracrystalline diffusion was the rate-limiting step, which suggests that a steric hindrance appeared in the ion-exchange reaction. This was confirmed indirectly by an extended X-ray absorption fine structure (EXAFS)

Table 2. Rate constants for the two kinetics models studied for the sorption of Cu^{2+} on Na-CLI (R^2 is the correlation coefficient of the regression).

C_0 (mg Cu dm ⁻³)	T (K)	Ritchie second-order rate parameters			Pseudo-second-order rate parameters		
		k_{2r} (min ⁻¹)	q_e (mg g ⁻¹)	R^2	k_2 (g mg ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	R^2
50	298	0.142	4.67	0.999	1.82×10^{-2}	4.74	0.999
	298	0.0460	8.38	0.997	4.83×10^{-3}	8.46	0.999
100	308	0.0715	9.26	0.994	4.23×10^{-3}	9.64	0.999
	318	0.0778	9.82	0.999	5.97×10^{-3}	9.98	0.999
	328	0.117	9.81	0.999	7.49×10^{-3}	9.97	0.999
	298	0.0310	12.3	0.999	2.12×10^{-3}	12.5	0.999
200	308	0.0255	15.4	0.994	1.22×10^{-3}	16.0	0.999
	318	0.0400	16.0	0.989	1.47×10^{-3}	16.9	0.999
	328	0.0456	16.3	0.992	1.47×10^{-3}	17.2	0.999
	298	0.0414	15.6	0.998	2.33×10^{-3}	15.8	0.999
300	308	0.0365	17.3	0.983	1.15×10^{-3}	18.5	0.999
	318	0.0319	19.9	0.988	1.02×10^{-3}	20.9	0.999
	328	0.0430	19.9	0.992	1.04×10^{-3}	21.1	0.999
	298	0.0331	16.1	0.986	1.01×10^{-3}	17.3	0.999
400	308	0.0320	18.5	0.982	0.993×10^{-3}	19.7	0.999
	318	0.0376	20.1	0.989	1.10×10^{-3}	21.2	0.999
	328	0.0323	21.7	0.988	0.907×10^{-3}	22.7	0.999
	298	0.0331	16.1	0.986	1.01×10^{-3}	17.3	0.999

study of the Cu-containing clinoptilolite (N. Zabukovec Logar, unpublished data, 2011) where Cu^{2+} was found inside the large clinoptilolite channel in a 4-fold coordination. The latter finding also indicates that the ion-exchange is probably accompanied by a change in coordination geometry of Cu^{2+} ions. The ion exchange of Cu^{2+} probably involves a decrease in the copper coordination number. This is not surprising because two of the coordinated water molecules in $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ are expected to be more weakly bound to the copper atom due to the Jahn-Teller effect (Cotton *et al.*, 1995).

Thermodynamic study

The data obtained by sorption experiments at 298, 308, 318, and 328 K and the initial Cu^{2+} concentrations of 100, 200, 300, and 400 mg Cu dm⁻³ were used to estimate some thermodynamic variables. The standard Gibbs free energy of sorption (ΔG°) was calculated by equation 5:

$$\Delta G^\circ = -RT \ln K \quad (5)$$

where R is the universal gas constant and K is the equilibrium constant at temperature T . The constant K was calculated as the ratio of the equilibrium Cu^{2+} concentrations on the sorbent and in solution after 24 h of exchange. The enthalpy and entropy of sorption were calculated from equation 6:

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

The plot of $\ln K$ vs. $1/T$ gave a straight line (Figure 3), and the values of ΔS° and ΔH° (Table 3) were evaluated from its intercept and slope, respectively.

The ΔG° values show that the sorption of Cu^{2+} on Na-CLI occurred spontaneously (negative change in ΔG°) in the 298–328 K range. The negative change in ΔG° decreased with temperature for all initial Cu^{2+} concentrations. The Cu^{2+} sorption was endothermic ($\Delta H^\circ > 0$) and occurred with an increase in entropy. The positive ΔS° values are in accord with the fact that two Na^+ ions are liberated when one Cu^{2+} ion is adsorbed. The negative change in ΔG° of the Cu^{2+} sorption, endothermic character of the sorption, and its occurrence with an increase in entropy were observed for a Bulgarian natural zeolite (Panayotova, 2001). The negative ΔG° values (at a given temperature) increased, while the ΔH° and ΔS° values decreased, as the initial Cu^{2+} concentration increased (Table 3). The same

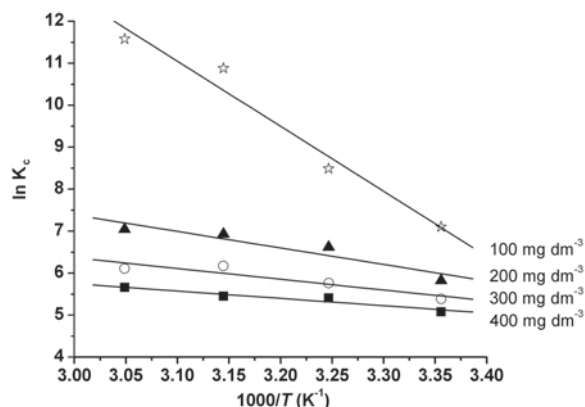


Figure 3. The plot of $\ln K$ (where K is the equilibrium constant) vs. $1/T$ for different initial Cu^{2+} concentrations.

Table 3. Thermodynamic variables for the sorption of Cu^{2+} on Na-CLI.

C_0 (mg Cu dm ⁻³)	T (K)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J K ⁻¹ mol ⁻¹)	R^2
100	298	-17.6	129	491	0.983
	308	-21.7			
	318	-28.7			
	328	-31.5			
200	298	-14.4	32.7	159	0.941
	308	-16.9			
	318	-18.3			
	328	-19.2			
300	298	-13.3	21.3	117	0.930
	308	-14.8			
	318	-16.3			
	328	-16.7			
400	298	-12.6	14.5	91.2	0.964
	308	-13.8			
	318	-14.4			
	328	-15.4			

behavior was found for Ni^{2+} and Zn^{2+} sorption (Rajic *et al.*, 2010b; Stojakovic *et al.*, 2011).

Post-treatment of the Cu-loaded sample

Full dehydration of the Ni- and Zn-loaded clinoptilolite (Rajic *et al.*, 2010b; Stojakovic *et al.*, 2011) led to the formation of nano-oxide particles spread over the

clinoptilolite surface (Rajic *et al.*, 2010b; Stojakovic *et al.*, 2011). A similar experiment was also performed with Cu-CLI at 540°C because thermal analysis (not presented) showed that at this temperature complete dehydration occurred. The TEM image of the surfaces of Cu-CLI (Figure 4a) and of the dehydrated Cu-CLI (Figure 4b) showed that the dehydration affected the

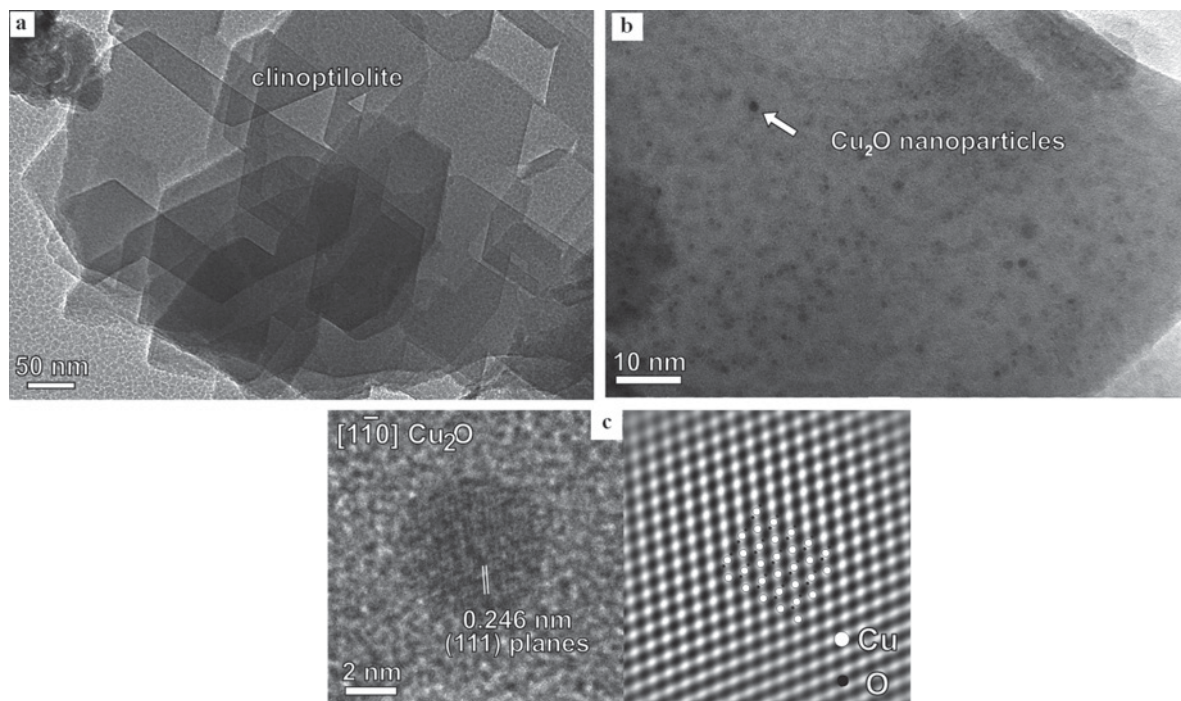


Figure 4. TEM images of Cu-loaded clinoptilolite (a) and the dehydrated Cu-clinoptilolite grain with multiple Cu_2O nanoparticles (b). A HRTEM image of the cuprite particle along the $\{1\bar{1}0\}$ orientation (c); the filtered image with the superimposed cuprite atomic model is also presented (on the right).

Table 4. The sorption capacity of Na-CLI (mmol g^{-1}) for Cu^{2+} , Mn^{2+} , Ni^{2+} , and Zn^{2+} obtained at the initial M^{2+} concentration of 400 mg dm^{-3} .

T (K)	Cu	Mn ^a	Ni ^b	Zn ^c
298	0.26	0.15	0.056	0.15
308	0.32	*	0.083	0.20
318	0.33	*	0.10	0.22
328	0.36	*	0.15	0.22

^a Rajic *et al.* (2010a); ^b Rajic *et al.* (2010b); ^c Stojakovic *et al.* (2011); * not studied at this temperature.

surfaces of the clinoptilolite crystal clusters. The surfaces were populated to various degrees with spherical nanocrystalline particles with an average size of $\sim 2 \text{ nm}$. The EDS analyses (not shown) indicated that the particles belong to a copper oxide phase. In the high-resolution TEM image (Figure 4c), the particle was oriented along the $(\bar{1}10)$ direction of cuprite so that the (111) planes were clearly distinguished. A filtered HRTEM image of the copper oxide nanoparticle with a superimposed cuprite structure model (*CrystalMaker*) showed that it fitted well with the experimentally obtained image (Figure 4c). Recent years have seen increased interest in synthesizing Cu_2O nanostructures due to their unique sensing, catalytic, electrical, and surface properties (Kuo and Huang, 2010). The present results indicated that the dehydration of Cu-loaded clinoptilolite yielded a composite material which could find application in the field of catalysis or optoelectronics. Recently, a composite prepared by impregnation of a natural zeolite with a synthetic Fe oxide-containing material was reported as a novel magnetic material (Gutierrez *et al.*, 2010).

Comparison of Cu^{2+} , Mn^{2+} , Ni^{2+} , and Zn^{2+} sorption by the Serbian clinoptilolite. The sorption capacity of the Serbian clinoptilolite for Cu^{2+} , Mn^{2+} , Ni^{2+} , and Zn^{2+} (Tables 4–6) revealed that it increased in the order $\text{Ni}^{2+} < \text{Mn}^{2+} \approx \text{Zn}^{2+} < \text{Cu}^{2+}$. The capacity also increased with temperature (Table 4). The pseudo-second-order rate model gave the best description for all four cations. The

Table 5. Pseudo-second-order rate constants for Cu^{2+} , Mn^{2+} , Ni^{2+} , and Zn^{2+} sorption on Na-CLI obtained at the initial M^{2+} concentration of 400 mg dm^{-3} .

T (K)	k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$)			
	Cu	Mn ^a	Ni ^b	Zn ^c
298	1.01×10^{-3}	3.75×10^{-5}	2.21×10^{-3}	2.37×10^{-4}
308	0.993×10^{-3}	5.94×10^{-4}	2.49×10^{-3}	4.11×10^{-4}
318	1.10×10^{-3}	2.12×10^{-3}	2.62×10^{-3}	3.77×10^{-4}
328	0.907×10^{-3}	4.58×10^{-3}	2.85×10^{-3}	11.1×10^{-4}

^a Rajic *et al.* (2010a); ^b Rajic *et al.* (2010b); ^c Stojakovic *et al.* (2011)

rate of sorption (Table 5) increased with temperature for Mn^{2+} and Ni^{2+} only, with the increase being significant in the case of Mn^{2+} . At 298 K the rate increased in the order: $\text{Mn}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+} < \text{Ni}^{2+}$, whereas at 328 K the rate of sorption was greatest for Mn^{2+} (*i.e.* the order was: $\text{Zn}^{2+} < \text{Cu}^{2+} < \text{Ni}^{2+} < \text{Mn}^{2+}$). The rate increase order of: $\text{Zn}^{2+} < \text{Cu}^{2+} < \text{Ni}^{2+}$ held for all temperatures in the study (Table 5).

The sorption occurred spontaneously for all four cations as the change in ΔG° was negative with temperature in all cases (Table 6). For all temperatures, the ΔG° values varied in a similar M^{2+} order as the sorption capacity. The sorption was endothermic, the ΔH° values of sorption increasing in the order: $\text{Mn}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+} < \text{Ni}^{2+}$. The same trend of increase was found for the ΔS° values of sorption (they were all positive).

CONCLUSIONS

Clinoptilolite from Zlatokop mine (Serbia) was quite effective at removing Cu^{2+} ions from aqueous solutions. The sorption capacity for Cu^{2+} was greater than for Ni^{2+} , Mn^{2+} , and Zn^{2+} ions, studied previously. For all of these cations the sorption kinetics was best described by the pseudo-second-order model. The sorption isotherm of Cu^{2+} was in accord with the Freundlich model only.

Dehydration of the Cu-exhausted clinoptilolite at 540°C in air led to the formation of spherical nanocrystalline Cu(I) oxide particles $\sim 2 \text{ nm}$ in diameter. The nano-

Table 6. Thermodynamic parameters for Cu^{2+} , Mn^{2+a} , Ni^{2+b} , and Zn^{2+c} sorption on Na-CLI obtained at the initial M^{2+} concentration of 400 mg dm^{-3} .

T (K)	ΔG° (kJ mol^{-1})				ΔH° (kJ mol^{-1})				ΔS° ($\text{J K}^{-1} \text{ mol}^{-1}$)			
	Cu	Mn	Ni	Zn	Cu	Mn	Ni	Zn	Cu	Mn	Ni	Zn
298	-12.6	-9.8	-7.3	-10.8								
308	-13.8	-10.3	-8.9	-12.1								
318	-14.4	-10.6	-9.7	-12.9	14.5	11.4	27.7	11.8	91.2	69.5	118	77.0
328	-15.4	-10.7	-11.2	-13.4								

^a Rajic *et al.* (2010a); ^b Rajic *et al.* (2010b); ^c Stojakovic *et al.* (2011)

oxide particles had the cuprite structure and were distributed uniformly over the clinoptilolite surface. The results obtained indicated that the exhausted clinoptilolite may be considered not only as a sludge but it may also have applications in catalysis and optoelectronics. Use of the exhausted clinoptilolite in this fashion would reduce the operating costs of wastewater treatment significantly, because sludge management would otherwise be a significant part of the total cost.

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