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ADSORPTION OF COPPER IONS FROM AQUEOUS SOLUTIONS ON NATURAL ZEOLITE

The adsorption of copper ions from synthetic aqueous solutions on natural zeolite (clinoptilolite) was examined. In order to determine the rate of adsorption and the copper uptake at equilibrium, a series of experiments were performed under batch conditions from single ion solutions. Equilibrium data were evaluated based on adsorption (Langmuir and Freundlich) isotherms. The adsorption kinetics is reasonably fast. In the first 20 min of the experiment, approximately 80% of Cu^{2+} ions is adsorbed from the solutions. Data obtained from the kinetic experiments have been described by the pseudo-second order kinetic model as well as by the Weber–Morris and Furusawa–Smith models.

1. INTRODUCTION

Heavy metals are common pollutants found in various industrial effluents. They are often encountered in metal plating facilities, electroplating, mining operations, acid mine drainage, fertilizers, battery manufacture, dyestuff, chemical pharmaceutical, electronic device manufactures and many others. Most heavy metals are highly toxic and are non-biodegradable, therefore they must be removed from the polluted streams in order to meet increasingly stringent environmental quality standards.

Their removal can be accomplished by a variety of techniques. Conventional methods typically involve such processes as coagulation, precipitation, ion-exchange, electrochemical methods, membrane processes, extraction, adsorption, etc. Among these, adsorption is currently considered to be very suitable for wastewater treatment because of its simplicity and cost effectiveness. Some widely used adsorbents for adsorption of

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heavy metals include activated carbon, clay minerals, biomaterials, industrial solid wastes and zeolites [1–3].

Zeolite is a natural porous mineral in which the partial substitution of Si^{4+} by Al^{3+} results in an excess of negative charge. This is compensated by alkali and alkaline earth cations (Na^+ , K^+ , Ca^{2+} or Mg^{2+}). Zeolites have been used as adsorbents, molecular sieves, membranes, ion-exchangers and catalysts, mainly because zeolite exchangeable ions are relatively innocuous. Thus, zeolites are particularly suitable for removing undesirable heavy metal ions (e.g. lead, nickel, zinc, cadmium, copper, chromium and/or cobalt), radionuclides as well as ammoniacal nitrogen from municipal wastewaters, electroplating effluents and agricultural wastewaters [4].

The aim of this work was to investigate the adsorption of copper ions onto a natural zeolite (clinoptilolite) in order to determine kinetic parameters and adsorption isotherms.

Summaries of some reported studies of adsorption of copper ions on various materials are presented in Table 1. Although these adsorption capacities refer to different experimental conditions, they represent the tendency for uptake of Cu^{2+} ions.

Table 1

Adsorption capacity of copper ions for various materials

Material	Cu uptake [mg/g]	Reference
Clinoptilolite from "Igras" Kopaonik, Serbia	5.25	[5]
Clinoptilolite from Gordes, Turkey	5.77	[6]
Clinoptilolite from Manisa-Gördes, Western Anatolia, Turkey	4.22	[7]

2. EXPERIMENTAL

Adsorbent. A natural zeolite – clinoptilolite – was used in the recent study as an adsorbent for adsorption of heavy metals such as copper. The range of particle size of the natural zeolite used in this study was 0.8–2.5 mm. The chemical composition and physicochemical characteristics of natural zeolite obtained from the supplier, AD Bentonite, Kardzhali, Bulgaria, are presented in Table 2.

X-Ray Diffractometer 6100, Shimadzu was used to investigate the mineralogical structure of the zeolite samples. This technique is based on observing the scattering intensity of an X-Ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. The diffraction data obtained are compared to the database maintained by the International Centre for Diffraction Data, in order to identify the material in the solid samples. The results (Fig. 1) showed that the natural zeolite contained clinoptilolite in the majority.

Table 2

Chemical composition and physicochemical characteristics of zeolite samples

Density, g/cm ³	hydrated	2.16 g/cm ³	
	dehydrated	1.88 g/cm ³	
Thermal dehydration		up to 500 °C	
Damp		maximal 10%	
Pore volume		0.34 cm ³ H ₂ O/cm ³ crystal	
Typical chemical composition [wt. %]			
SiO ₂	69.68	CaO	2.01
Al ₂ O ₃	11.40	Na ₂ O	0.62
TiO ₂	0.15	K ₂ O	2.90
Fe ₂ O ₃	0.93	H ₂ O	13.24
MgO	0.87	P ₂ O ₅	0.02
MnO	0.08	ratio Si/Al	4.0–5.2
Cation exchange per cation		Ion	Value [meq/100 g]
		K ⁺	41
		Na ⁺	16.10
		Ca ²⁺	67.14
		Mg ²⁺	3.88
Total cation exchange capacity		1.8–2.2 meq/g	

The surface morphology of natural zeolite was studied using a scanning electron microscope, VEGA3 LMU. This particular microscope is also fitted with an Inca 250 EDS (energy dispersive spectroscopy) system. It is an analytical technique used for the elemental analysis of a sample based on the emission of characteristic X-Rays by the sample when subjected to a high energy beam of charged particles such as electrons or protons.

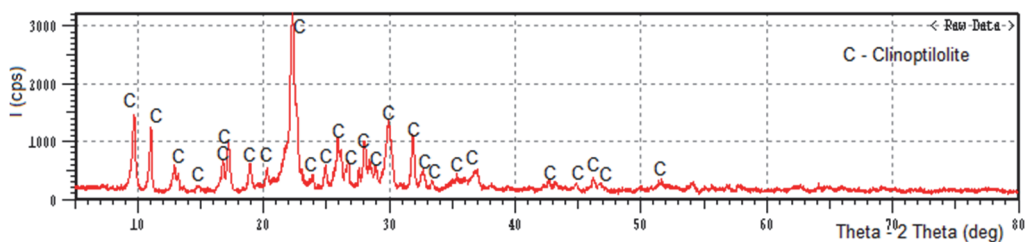


Fig. 1. Diffractogram of a sample of natural zeolite

Micrographs of samples of natural zeolite obtained from SEM analysis are given in Fig. 2. The micrographs clearly show a number of macro-pores in the zeolite structure. The micrographs also show well defined crystals of clinoptilolite.

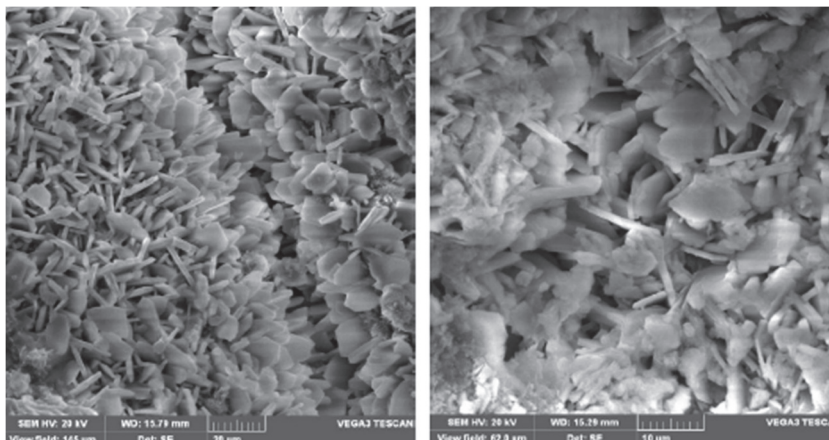


Fig. 2. Micrographs of samples of various parts of natural zeolite obtained from SEM analysis

An electron beam was directed onto various parts of the samples in order to get a more accurate analysis (Fig. 3) and the elemental composition of clinoptilolite is presented in Table 3.

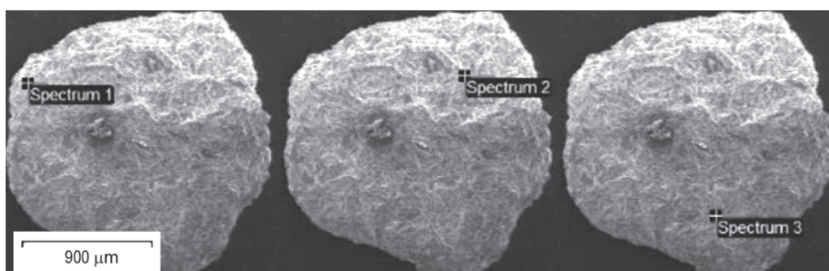


Fig. 3. EDS analysis showing the scanning method for natural zeolite

Table 3

EDS analysis showing the elemental composition for natural zeolite

Element	Spect 1	Spect 2	Spect 3	Average	Std. deviation
O	58.46	55.4	58.83	57.56	1.882
Na	0.27	0.15	0.3	0.24	0.079
Mg	0.72	0.66	0.77	0.72	0.055
Al	5.28	5.52	5.03	5.28	0.245
Si	29.55	31.36	29.47	30.13	1.068
K	2.73	2.96	2.44	2.71	0.26
Ca	1.9	2.42	1.66	1.99	0.388
Fe	1.1	1.53	1.5	1.38	0.24
Total	100	100	100	100	

Results of EDS analysis showed that the predominant exchangeable cations in natural zeolite (clinoptilolite) structure were K^+ and Ca^{2+} .

Adsorbate. The heavy metal, Cu, was used as an adsorbate in the recent investigations. Synthetic single component solutions of Cu^{2+} were prepared by dissolving a weighed mass of the analytical grade $CuSO_4 \cdot 5H_2O$ in distilled water. Single component solutions 400 cm^3 were mixed with 5 g natural zeolite and agitated for 120 min at $20 \pm 1\text{ }^\circ\text{C}$ and pH 3.5. The concentration of the single component solution was 5, 25, 50, 200 and $400\text{ Cu}^{2+}\text{ mg/dm}^3$.

Experimental procedure. Initial pH of prepared solutions was adjusted by adding 2% sulfuric acid and controlled by 210 Microprocessor pH Meter. Initial pH values of the tested solutions were 2.5, 3.5 and 4.5. The experiments were performed in a batch mode in a series of beakers equipped with magnetic stirrers by contacting zeolite (2, 5 and 10 g) with 400 cm^3 of solution of Cu^{2+} ions. Zeolite sample and aqueous phase were suspended with a magnetic stirrer at 400 rpm. The agitation time was up to 360 min. At the end of the predetermined time, the suspension was filtered and the filtrate was analysed. The final pH was also measured. All experiments were performed at room temperature on $20 \pm 1\text{ }^\circ\text{C}$. The initial and remaining concentrations of metal ions were determined by Liberty 110, ICP Emission Spectrometer, Varian. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is an analytical technique used for the detection of trace metals. It uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample.

Based on the material balance, the adsorption capacity was calculated by using the following expression [8]:

$$q_t = \frac{V(C_0 - C_t)}{m} \quad [\text{mg/g}] \quad (1)$$

where: q_t is the mass of adsorbed metal ions per unit mass of adsorbent (mg/g), C_0 and C_t are the initial and final metal ion concentrations (mg/dm^3), respectively, V is the volume of the aqueous phase (dm^3) and m is the mass of adsorbent used (g).

Degree of adsorption is calculated as:

$$AD = \left(1 - \frac{C_t}{C_0}\right) \times 100 \quad [\%] \quad (2)$$

Kinetic studies. Kinetic studies are the source of information about the process dynamics, that is, the adsorption rate, residence time and mass transfer parameters such as

external mass transfer coefficients and intraparticle diffusivity. These parameters are essential in the design and operation of any adsorption column in wastewater treatment plants. Therefore, kinetic studies enable one to evaluate the suitability of any material as a potential adsorbent in removing pollutants from solution [9].

The rate of adsorption is a complex function of several factors such that the overall reaction rate may be influenced by the separate or combined effect of these factors. Examples of such factors are adsorbent particle size, initial pH and concentration of the solution, temperature, agitation speed in the case of batch experiments and flow rate in columns. In our studies, some of these factors have been investigated with regard to their effect on the efficiency of natural zeolite in removing copper from solution.

A number of kinetic models were studied and recommended to describe the uptake process/mechanism. The models used in this investigation are the pseudo-second order kinetic model, Weber and Morris model and the film diffusion model as proposed by Furusawa and Smith.

The pseudo-second order kinetic model was used to investigate whether chemical reaction at the adsorption sites of zeolite was rate determining. The experimental data that fits to this model indicate that chemical reaction is involved in the removal of heavy metals from solution, that is, chemisorption [10, 11].

The pseudo second order kinetic model is given by:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where q_t and q_e are the amounts of metal adsorbed per unit weight of adsorbent (mg/g) at time t , and at equilibrium, respectively. k_2 (g/(mg·min)) is the adsorption rate constant.

Film transfer control was determined using a method proposed by Furusawa and Smith [2, 6, 12, 13]. The change in copper concentration with respect to time is related to the liquid–solid mass transfer coefficient, k_s (cm/s):

$$\frac{dC_t}{dt} = -k_s S_s (C_t - C_s) \quad (5)$$

where C_t is the adsorbate concentration in solution at a time t , C_s is the concentration in liquid at outer surface of particle; and S_s (1/cm) the specific surface area for mass transfer

$$S_s = \frac{6m_s}{d_p \rho_t (1 - \varepsilon_p)} \quad (6)$$

where m_s (g/cm³) is the mass of adsorbent in the solution, d_p is the diameter of zeolite particles (cm), ρ_t is the density of solid phase (g/cm³) and ε_p is the porosity of zeolite particles.

Weber and Morris [14] theorized that the rate of intraparticle diffusion varies proportionally with the half power of time and is expressed as:

$$q_t = k_t t^{1/2} + c \quad (7)$$

where q_t is the adsorbate uptake at time t (mg/g), k_t is the rate constant of intraparticle transport (mg/(g·min^{0.5})).

The values of interception c are related to the thickness of the boundary layer, i.e., the larger the value of the intercept is, the greater the boundary layer effect [10, 14].

Equilibrium studies. Equilibrium studies generally involve determination of the adsorption capacity of a given material. This determination is important in accessing the potential of the material as an economic and commercially viable adsorber.

Upon contacting an amount of adsorbent with solutions containing an adsorbate, adsorption will take place. Adsorption will continue until equilibrium will be established between the adsorbate in solution and in the adsorbed state [15].

Experimental data were fitted to conventional adsorption mathematical models, namely the Freundlich and Langmuir models. These were used to predict the adsorption performance of natural zeolite. The performance of natural zeolite was also assessed at various pH of the initial solution.

The Langmuir isotherm equation [16], based on monolayer coverage of adsorbent surfaces by the adsorbate at specific homogeneous sites within the adsorbent, is:

$$q_e = \frac{q_m K_l C_e}{1 + K_l C_e} \quad (8)$$

where q_e (mg/g) is the amount of solute adsorbed per unit mass of adsorbent at equilibrium, C_e (mg/dm³) is the residual adsorbate concentration in solution at equilibrium, q_m (mg/g) is the amount of solute adsorbed per unit mass of adsorbent corresponding to complete coverage of available sites, K_l (dm³/mg) is the Langmuir adsorption coefficient, this constant is related to the affinity between the adsorbent and solute, which is evaluated through linearization of Eq. (9):

$$\frac{1}{q_e} = \frac{1}{k_f q_m C_e} + \frac{1}{q_m} \quad (9)$$

The Freundlich isotherm equation, based on monolayer adsorption on heterogeneous surfaces with a non-uniform distribution of adsorption heat, is:

$$q_e = k_f C_e^{1/n} \quad (3)$$

where k_f and n are empirical constants dependent on experimental conditions, k_f (mg/g) is an indicator of adsorption capacity, n (g/dm^3) is related to the adsorption intensity or binding strength. Their values were determined from the linear form of the Freundlich equation:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (11)$$

$1/n$ is the heterogeneity factor; values of $1/n \ll 1$ indicate heterogeneous adsorbents, while values closer or even equal to 1 indicate a material with relatively homogeneous binding sites [17]. Natural zeolite should be a heterogeneous adsorbent due to its porous nature. Alvarez-Ayuso et al. [18], Avila [19] and Gunay et al. [20] successfully used the Freundlich adsorption isotherm to model their results from equilibrium experiments.

3. RESULTS AND DISCUSSION

3.1. KINETIC STUDIES

Effect of initial concentration of the solution. The results of the kinetic experiments to measure adsorption of cations from aqueous solutions onto natural zeolite in function of initial concentration of Cu in solution and time are shown in Fig. 4.

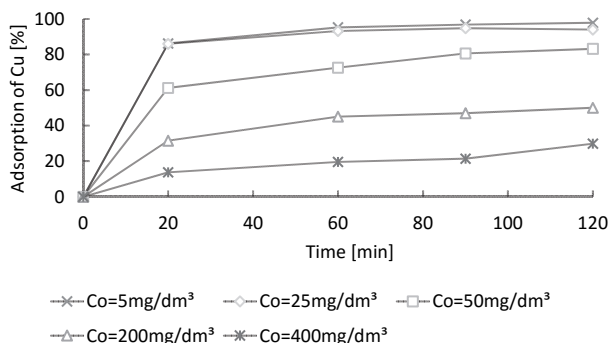


Fig. 4. Effect of initial Cu^{2+} concentration on the adsorption efficiency onto zeolite (5 g of zeolite, pH 3.5)

An increase in concentration generally results in an increase in the amount of copper adsorbed and the rate of adsorption. This may be a result of an increase in number of collisions between the reactants, leading to the observed increase in reaction rate and capacity according to the collision theory [9]. The adsorption capacity will increase with an increase in initial concentration until the system reaches a saturation point, at which further increase of the adsorbate concentration will not result in any significant change in the amount adsorbed, q_e . Table 4 presents the results of this investigation.

Table 4

Effect of initial concentration C_0 of solution
on the adsorption capacity of natural zeolite

Heavy metal	C_0 [mg/dm ³]	Amount adsorbed q_e	
		[mg/g]	[%]
Cu ²⁺	5	0.391	97.840
	25	1.880	94.000
	50	3.328	83.200
	200	8.008	50.050
	400	9.544	29.825

The above results indicate that the amount of copper adsorbed on natural zeolite at equilibrium is dependent on the initial copper concentration. The increase in the amount of copper adsorbed as initial concentration increases is a consequence of an increase in the concentration driving force. The concentration driving force is responsible for overcoming the mass transfer resistance associated with the adsorption of metals from solution by the zeolite [21]. Therefore, as initial concentration increases, the driving force also increases resulting in an increase in metals uptake by the zeolite.

Table 4 reveals also that an increase in initial concentration not only results in an increase in the amount adsorbed (q_e) but a decrease in the efficiency of natural zeolite for the removal of Cu from solution. This manifests itself by a general decrease in the percentage adsorption of Cu from ca. 97.8% to 29.8%, for an increase in initial concentration from 5 mg/dm³ to 400 mg/dm³. Motsi [6] also found a similar trend, that is, a decrease in efficiency, in his work on the adsorption of Cu, Mn, Zn and Fe from solution by clinoptilolite.

Effect of amount of the adsorbent. A series of kinetic experiments with various masses of the adsorbent (2, 5 and 10 g), were performed using fixed initial metal concentrations of Cu²⁺ (400 mg Cu²⁺/dm³) and other experimental conditions as described in Experimental.

Time dependences of the amount of metal adsorbed are shown in Fig. 5. An increase in adsorbent mass resulted in an increase in the adsorption of the copper (Table 5). This is due to the increase in number of adsorption sites available upon increasing amount of the adsorbent added.

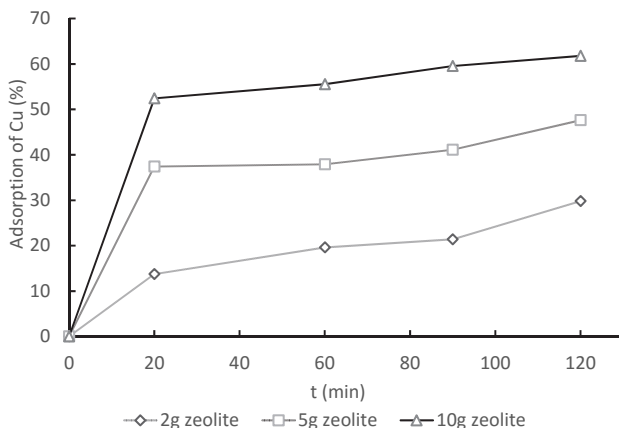


Fig. 5. Effect of mass of adsorbent on the adsorption efficiency onto zeolite ($400 \text{ mg Cu}^{2+}/\text{dm}^3$, pH 3.5)

Table 5

Effect of adsorbent weight on the efficiency of natural zeolite for the removal of copper from solution

Heavy metal	Adsorbent weight [g]	Copper adsorbed [%]
Cu	2	29.8
	5	47.6
	10	61.8

Effect of pH of initial solution. pH of the solution in contact with natural zeolite has an obvious impact on its ability to remove metals since the acidic solution can influence both the character of the exchanging ions and the character (structure) of the zeolite itself. Figure 6 shows that as solution pH decreases, copper removal efficiency also decreases.

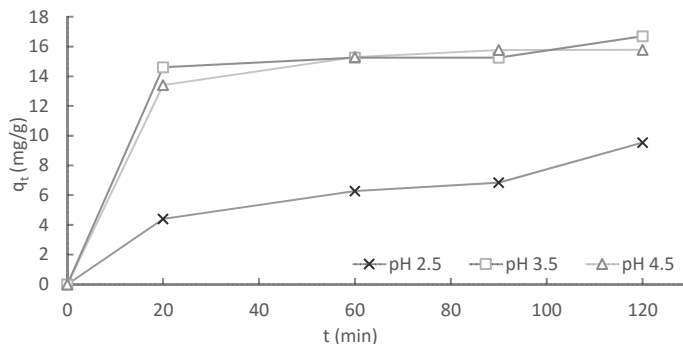


Fig. 6. Effect of initial pH of Cu^{2+} solution on adsorption capacity of zeolite ($400 \text{ mg Cu}^{2+}/\text{dm}^3$, 5 g of zeolite)

That is because H^+ ions compete with copper cations for the same exchange sites [18] and electrostatic repulsion between copper cations in solution and the protonated zeolite surface increases as more H^+ ions are adsorbed [22] Figure 6 shows how the adsorption capacity of natural zeolite is affected by pH of the solution.

3.2. KINETIC MODELING

Kinetic modelling was carried out to investigate the rate determining step in the removal of heavy metals from solution by using natural zeolite. The models used in this investigation are the pseudo-second order kinetic model for chemisorption, Weber and Morris model about intraparticle diffusion and the film diffusion model as proposed by Furusawa and Smith. To test whether the rate of removal of heavy metals from solution on natural zeolite is controlled by chemical reactions (i.e. chemisorption), a number of conditions must be met. These conditions are [6, 23]:

- The rate constant should be constant for all values of initial concentration of counterions,
- The rate constant should not change with the adsorbent particle size.
- The rate constant is sometimes independent of the degree of agitation (stirring rate).

If any of these conditions are not satisfied, chemical reaction kinetics is not rate determining even if rate data is successfully fitted to the pseudo second order kinetic model.

One of the above conditions was tested, that is, whether the rate constant remains constant with a change in initial concentration on Cu^{2+} ion in solution. The results obtained for the adsorption of Cu^{2+} onto natural zeolite were fitted to Eq. (4). This was achieved by plotting t/q vs. t , as shown in Fig. 7.

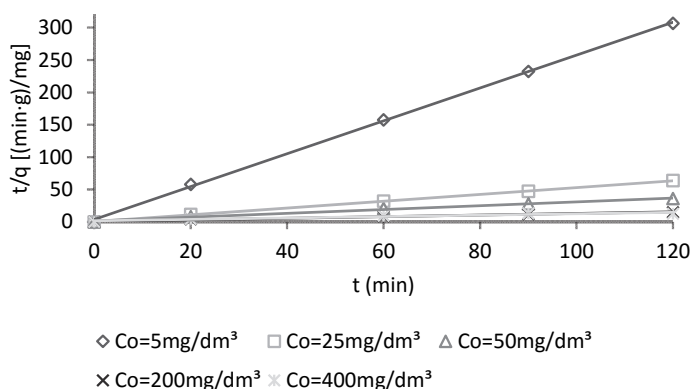


Fig. 7. Effect of initial Cu^{2+} concentration in solution on the reaction rate constant

The experimental data obtained for the effect of initial concentration of Cu^{2+} ions in solution gave a good fit to the pseudo-second order kinetic model as expected, indicating that chemisorption does take place in the removal of heavy metals from solution by natural zeolite [6]. But from Table 6, it is seen that the rate constant, k_2 , for the removal of cations from solution, was not constant for different initial concentration of Cu^{2+} in solution. This lack of constancy proves that even though the results gave a good fit to the kinetic model, the rate determining step is not chemisorption.

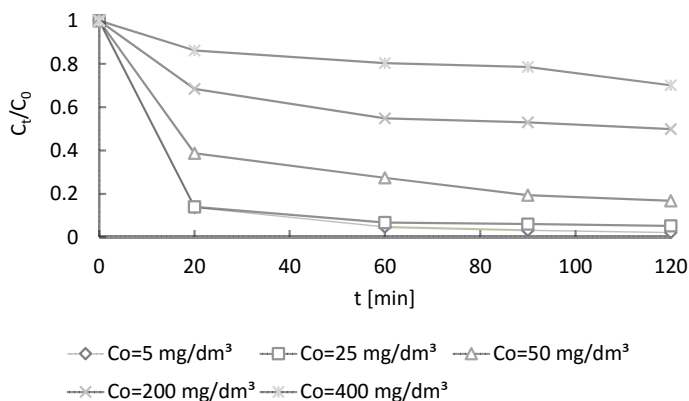
Table 6

Rate constants at various initial concentrations

C_0 , mg/dm ³	5	25	50	200	400
k_2 , g/(mg·min)	1.9772	0.573	0.0609	0.0188	0.0069
q_e , mg/g	0.3943	1.8997	3.3852	8.2169	9.2421
R^2	0.9996	0.9997	0.9932	0.99	0.8999

In a well-agitated batch system, the boundary layer surrounding the particle is much reduced, reducing the external mass transfer coefficient k_S , hence, intraparticle diffusion is more likely to be the rate determining step [2].

The results of the experiments were fitted to the model proposed by Furusawa and Smith (Figs. 8, 9 and Table 7). Plotting $\ln[(C_t/C_0) - (1/(1+m_S K_i))]$ vs. time, should give a straight line. The gradient of the straight line is $-[(1+m_S K_i)/(m_S K_i)]k_S S_S$ where K_i (dm³/mg) is the Langmuir adsorption coefficient. The external mass transfer coefficient between the bulk liquid and outer surface of the zeolite particle, k_S can then be evaluated.

Fig. 8. External mass transfer diffusion model; time dependence of C_t/C_0

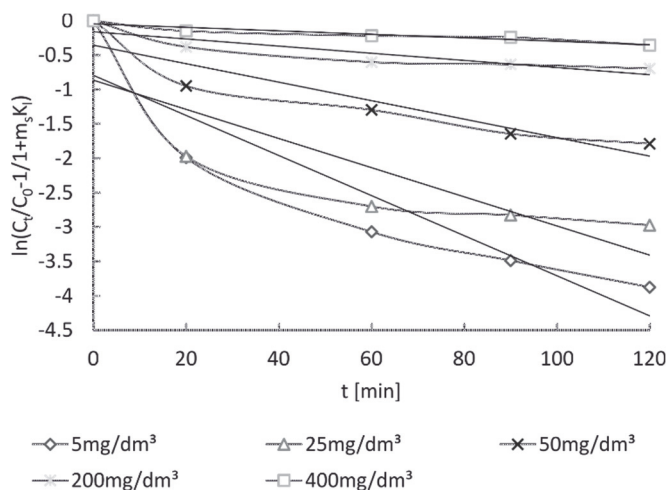


Fig. 9. Fitting external mass transfer diffusion

Table 7

Calculated film mass transfer coefficients

C_0 , mg/dm ³	5	25	50	200	400
k_s , cm/s	0.00118	0.00086	0.00054	0.00021	0.00010
R^2	0.8488	0.7161	0.8584	0.8041	0.9076

By increasing the concentration of copper ions in solution, film diffusion decreases. It can be seen from the external mass transfer coefficient k_s , which decreases as concentration of copper ions in solution is increasing. Thus the intraparticle diffusion is more likely the rate determining step. As R^2 points to poor fit, it seems that film diffusion cannot control the overall rate of adsorption.

According to Weber and Morris, if the rate determining step is intraparticle diffusion, the plot of solute adsorbed against the square root of the contact time should yield a straight line passing through the origin. Also, the rate constant for intraparticle diffusion is obtained from the slope of the curve.

According to this theory, C , the intercept gives an idea about the thickness of the boundary layer, i.e., the larger the intercept is, the greater the boundary layer effect. If intraparticle diffusion occurs, then the plot q_t vs. $t^{0.5}$ will be linear and if the plot passes through the origin, then the rate determining process is only due to the intraparticle diffusion. Otherwise, some other mechanism along with intraparticle diffusion is also involved [24, 25].

In this case, the intercept gives values different from zero. These values indicate that intraparticle diffusion does not control the overall rate of adsorption [24]. And as

can be seen from Fig. 10, the plot is linear but it does not pass through the origin and can be concluded that the intraparticle diffusion was not the only rate determining mechanism in the adsorption process.

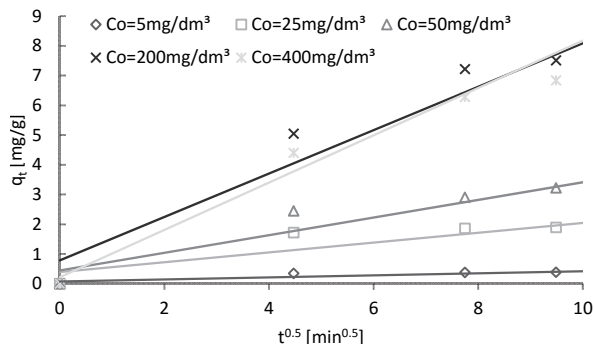


Fig. 10. Intraparticle diffusion control

In Table 8, the rate constants for intraparticle diffusion and the correlation coefficient R^2 are given. Due to R^2 value, upon increasing the concentration of copper ions in solution, intraparticle diffusion may be a rate determining step.

Table 8

Calculated rate constants of intraparticle transport

C_0 , mg/dm ³	5	25	50	200	400
k_p , mg/(g·min ^{0.5})	0.0343	0.1648	0.2964	0.7301	0.7954
R^2	0.7858	0.7635	0.8918	0.9347	0.9666

3.3. EQUILIBRIUM STUDIES

The main objective of the equilibrium studies was to determine the maximum capacity of natural zeolite towards copper removal under the studied conditions.

Table 9

Calculated equilibrium adsorption isotherm constants for the uptake of copper from solution using natural zeolite

pH	Experimental		Langmuir isotherm				Freundlich isotherm			
	q_e [mg/g]	C_e [mg/dm ³]	q_m [mg/g]	K_1 [dm ³ /mg]	R^2	R_L	K_f [dm ³ /mg]	$1/n$	n [g/dm ³]	R^2
2.5	3.712	214.4	3.992	0.0366	0.9645	0.0639	0.2221	0.5458	1.8322	0.9867
3.5	4.688	166.6	5.269	0.0404	0.9243	0.0583	0.3566	0.5247	1.9059	0.7135
4.5	4.406	179.7	5.184	0.0324	0.9288	0.0716	0.2867	0.5615	1.7809	0.6804

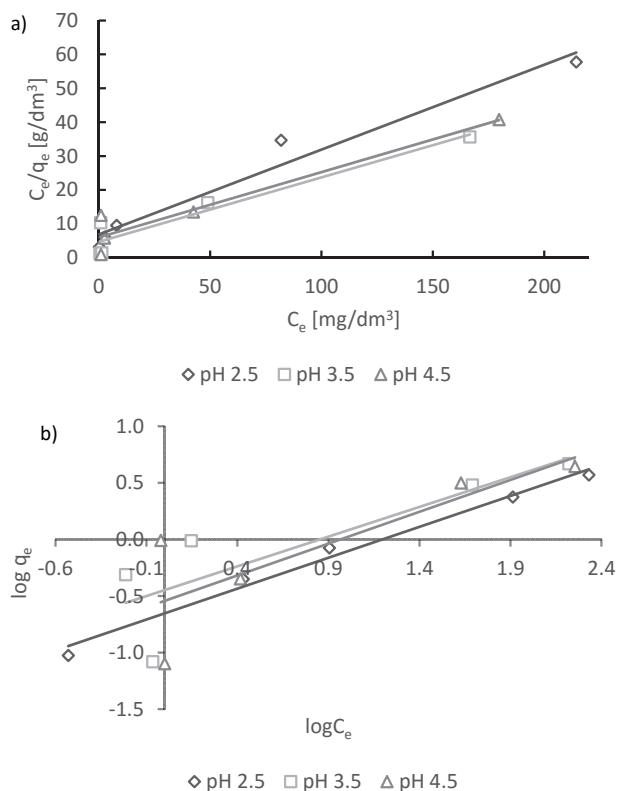


Fig. 11. Adsorption isotherms
a) Langmuir isotherms, b) Freundlich isotherms

5 g of natural zeolite was mixed with 100 cm³ of the copper solution at various initial pH values (2.5, 3.5 and 4.5) and concentrations (5, 25, 50, 200 and 400 mg/dm³), and agitated for 360 min. The results of equilibrium studies for copper cation are presented in Table 9 and Figs. 11–13. It is clear from Fig. 12 that as the initial concentration of copper cations increases, the amount of metal adsorbed per gram of natural zeolite (q_e) increases. This is mainly due to the fact that at high metal concentrations, there is a higher solute concentration gradient, and this provides the necessary driving force for metal ions to displace exchangeable cations on the surface and from the internal micropores of natural zeolite [6, 26]. However, this increasing trend is valid up to a point at which the maximum capacity of the natural zeolite samples for the respective heavy metal cation is achieved, that is, its saturation point.

Experimental data obtained from equilibrium experiments were fitted to the Langmuir and Freundlich adsorption isotherms. The values of the constants in the models and correlation coefficients obtained are summarized in Table 9 and the data calculated by theoretical models (lines) are shown in Figs. 11 and 12.

According to the Freundlich model, values of the heterogeneity factor $1/n$ indicate that natural zeolite is a heterogeneous adsorbent. Based on the correlation coefficients (R^2) shown in Table 9, the adsorption isotherms for various initial pH values of solutions can be best described by the Langmuir model. The applicability of the Langmuir isotherm suggests monolayer coverage of the Cu^{2+} at the surface of the natural zeolite or that a similar exchangeable ions with equivalent concentration was exchanged by Cu^{2+} .

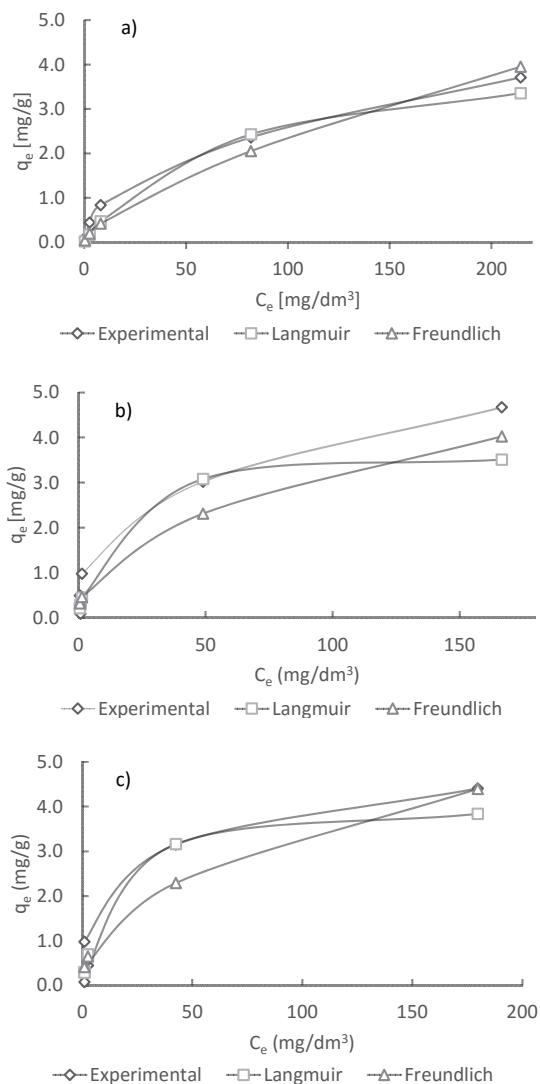


Fig. 12. Equilibrium isotherms for the removal of copper from solution
a) pH 2.5 b) pH 3.5 c) pH 4.5

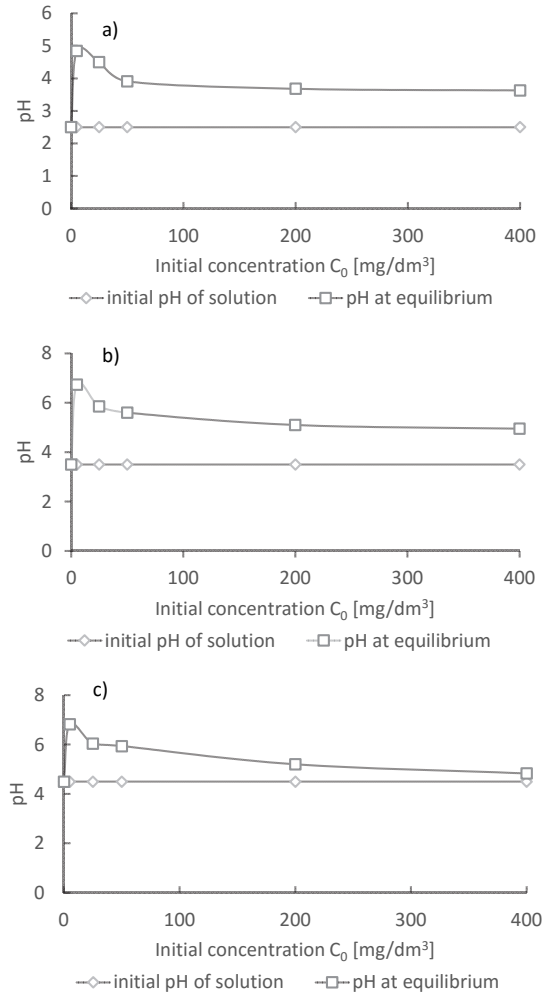


Fig. 13. Dependences of the equilibrium pH on the initial copper concentrations.
Error in pH reading is ± 0.2 ; initial pH a) 2.5, b) 3.5 c) 4.5

Basic parameter of the Langmuir theory is a dimensionless constant called equilibrium parameter, R_L , which is usually defined by:

$$R_L = \frac{1}{1 + K_L + C_0}$$

where C_0 is the highest initial Cu^{2+} concentration (mg/dm³) and K_L is the Langmuir constant that indicates the nature of adsorption. The value of R_L indicates the type of the

adsorption isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L values reported in Table 9 show that the Cu^{2+} adsorption for all pH values was efficient ($0 < R_L < 1$).

Figure 12 also shows the adsorption capacity of natural zeolite for copper at various pH values of the initial solution. There is a general increase in adsorption capacity as pH increases. This is mainly attributed to the decrease in concentration of H^+ ions as the initial pH increases from 2.5 to 4.5. H^+ ions act as competitors for available adsorption sites on the natural zeolite surface, and hence at low pH, they are more concentrated and thus because of the concentration driving force will be adsorbed in preference to copper ions, resulting in lower adsorption capacities for copper ions [18].

Figure 13 presents the dependences of the equilibrium pH values on the initial copper concentration. The equilibrium pH values are greater than the initially adjusted pH values and the difference between equilibrium pH and initial pH exhibits a descending trend upon increasing initial copper concentration. The increase in pH is a result of adsorption of H^+ ions from solution but upon increasing concentration of copper ions, the concentration driving force begins to favour the adsorption of Cu^{2+} ions in preference to H^+ ions, and thus the descending trend of the equilibrium pH at higher initial copper concentrations. The highest equilibrium pH was ca. 6.82 (Fig. 13c). The equilibrium pH values for the copper solutions were lower than the minimum pH value (7.2) needed for complete precipitation of copper as a hydroxide [27], thus no precipitate was observed during the experiment.

4. CONCLUSION

The adsorption of copper ions from diluted solutions on natural zeolite occurs efficiently. It is the most effective at lower concentration of copper ions, higher mass of zeolite and higher pH of the solution.

The adsorption kinetics is reasonably fast. This means that in the first 20 min approximately 80% of Cu^{2+} is adsorbed from single ion solutions.

The experimental data obtained for the effect of initial concentration on Cu^{2+} ion in solution gave a good fit to the pseudo-second order kinetic model. The rate constant k_2 , however, for the removal of cations from solution depended on the initial concentration of Cu^{2+} ions in solution, indicating that the rate determining step is not chemisorption.

According to Furusawa and Smith and by Weber and Morris it can be concluded that by increasing the concentration of copper ions in solution, intraparticle diffusion is more likely to be the rate determining step. At lower concentration of copper ions in solution, film diffusion may participate in the rate determining step.

Equilibrium studies show that adsorption of copper ions strongly depends on the initial concentration and pH of solutions. As the initial concentration of copper cations

increases, the amount of metal ions adsorbed per gram of natural zeolite (q_e) increases, and as the solution pH increases, there is a general increase in adsorption capacity.

Langmuir isotherms for the adsorption of copper from solution gave better fits of the experimental results than Freundlich isotherms. The applicability of the Langmuir isotherm suggests monolayer coverage of Cu^{2+} ions at the surface of the natural zeolite or that a similar exchangeable ions with equivalent concentration was exchanged by Cu^{2+} . As results from the R_L values, adsorption was efficient at the investigated pH range ($0 < R_L < 1$).

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