

Study of the adsorption of Cu(II) ions from aqueous solution using Zeolite NaA

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Study of the adsorption of Cu(II) ions from aqueous solution using Zeolite NaA: *In this study the adsorption of Cu (II) ions from aqueous solutions on synthetic Zeolite NaA was evaluated. The sorption kinetics Cu(II) ions by Zeolite NaA was studied using agitated batch laboratory apparatus at three temperature levels of 293, 313 and 329 K. Several kinetic models were used to test the experimental rate data and to examine the controlling mechanism of the sorption process. Lagergren pseudo-first order, the pseudo-second-order (Ho-McKay) and Weber-Morris model was analyzed using linear least squares method. The obtained results indicated that synthetic zeolite NaA could be used as an efficient material for the sorption of copper ions.*

Key words: *Kinetic models, Lagergren, Ho- McKay, Weber- Morris.*

INTRODUCTION

The presence of copper in wastewater of several industries has contributed in no small way to water pollution. The copper is an essential element, acute doses cause metabolic disorders.

Treatment of wastewater containing copper could be achieved by chemical precipitation, ultrafiltration and sorption [1-3]. Copper sorption is an attractive option because of the basic simplicity of the application.

Zeolite NaA is a synthetic porous product 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, manganese, cadmium, copper, chromium, cobalt), radionuclides as well as ammoniacal nitrogen (ammonia and ammonium) from municipal wastewaters, metal plating facilities, electroplating, mining operations, fertilizers, battery manufacture, dyestuff, chemical pharmaceutical, electronic device manufactures and many others [1-4]. Most of 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.

Using zeolites as sorbents is preferred due to their specific structure allowing selectivity of the processes involved (adsorption and ion-exchange), simple operation and effectiveness. This is achieved as a result of the main properties of synthetic zeolites like highly developed porous surface, phase purity and resistance to chemical reagents.

The present paper deals with issues referred to studies on the possibility to purify aqueous solutions containing copper ions using synthetic zeolite NaA with the methods of adsorption and ion-exchange.

For this purpose, the paper discusses the adsorption kinetics of synthetic zeolite NaA in model aqueous solutions containing Cu(II) ions, as well as the various factors affecting the process of adsorption. The results obtained are further adapted in kinetic models and an assessment of the adsorption processes is made.

EXPERIMENTAL

Adsorbent

The adsorbent used for the studies was synthetic zeolite NaA produced from kaolin of Bulgarian origin by a technology described earlier [4]. The Zeolite NaA was synthesized previously by dehydroxylation of low grade Bulgarian Kaolin at 650°C, receiving metakaolin granules using the fluidised bed method and hydrothermal reaction of metakaolinite with various aqueous alkali medium.

Figure 1 shows the X-ray diffraction pattern of the sample synthesized zeolite NaA. It is seen that the major crystalline phases are Zeolite A and small quantities of Quartz. Major phases: Zeol-A = Zeolite A ($\text{NaAlSi}_3\text{O}_8$); Q = Quartz (SiO_2). Minor phases: Hid = Hydroxycancrinite - ($\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{OH})_{2.04}(\text{H}_2\text{O})_{2.66}$); Par = Paragonite - ($\text{NaAl}_2(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2$); And = Andalusite ($\text{Al}_2(\text{SiO}_4)\text{O}$).

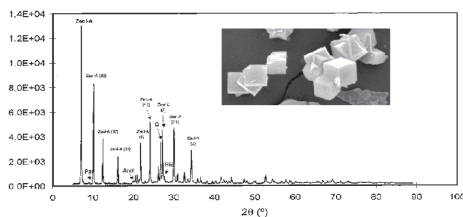


Figure 1. XRD end SEM for synthetic Zeolite NaA

Figure 1 is shows a photograph and a scanning electron microscope of the synthesized Zeolite NaA. Your photo clearly visible shapely crystal formations of synthesized zeolite.

Adsorbate

The heavy metal Cu, was used as adsorbate in the recent investigations. Synthetic single component solutions of Cu(II) prepared by dissolving a weighed mass of the analytical grade salt $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Merck) in 1000ml distilled water.

EXPERIMENTAL PROCEDURE

The adsorption kinetics was studied by the method of volt-ampometric, using volt-ampmeter ECOTEST-VA (ECONIX-EXSPERT). This method allows direct registration of the amount of Cu(II) in the adsorbate monitored at every moment of contact with the adsorbent (Zeolite NaA) [5].

The measuring system was specially designed for the experiments to allow constant homogenization (at varied propeller velocities) for better contact between adsorbent and adsorbate, as well as to provide possibilities for isothermal periods in thermostatic cell. The experiments were carried out at constant temperatures of 293, 313 and 328 K and constant initial Cu(II) concentrations in the model solution.

To study the kinetics of adsorption, 100 ml model solution of Cu(II) with initial concentration of 60 mg/L were placed in flat-bottomed flask (under continuous agitation and the constant temperature selected). By the mixing with the adsorbent, the decrease of the amount of the ions studied was monitored and recorded for a period of 60 min. Simultaneously, the change of pH in the adsorbate was also measured.

Based on material balance, the adsorption capacity was calculated by using the following expression [3]:

$$q_e = \frac{(C_o - C_e) \cdot V}{m} \quad (1)$$

Where: q_e is the mass of adsorbed metal ions per unit mass of adsorbent (mg/g), C_o and C_e are initial and final sample concentrations (mg/L) respectively, V (L) is volume of the sample solution and m (g) is the weight of adsorbent added.

RESULTS AND DISCUSSION

Effect of contact time and temperature

The experimental results of adsorption of Cu(II) onto the Zeolite NaA at various temperature 293–328K, (initial concentrations 60 mg/L) are shown in Figure 2.

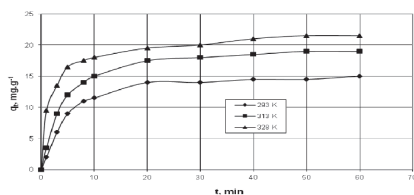


Fig. 2. The effect of contact time and temperature to adsorption of Cu(II) onto the Zeolite NaA (initial concentrations 60 mg/L)

Figure 2 illustrates that equilibrium time of sorption was obviously shortened with an increase of temperature from 293 to 328K. The equilibrium sorption was attained after about 60 min of solute-sorbent contact at temperature ranging from 293 to 328K, and there was not occur remarkable removal of Cu(II) for more contact time. The increase of Cu(II) adsorption capacity with increasing of temperature indicated that a higher temperature promoted Cu(II) adsorption onto the Zeolite NaA, and the adsorption was controlled by an endothermic process.

The preliminary studies showed that the aqueous solutions of Cu(II) are quite unstable due to the susceptibility of copper ions to hydrolyzation. This process depends in ion concentration in the solution and mainly on medium pH. Copper ions in aqueous solution are most stable at medium pH from 2 to 4.5. Studiees have shown that the probability for hydrolyzation is present at solution pH above 4.5–5.0. Thus, copper hydroxide precipitate was observed in the adsorbate at pH higher than 5.0 so the amount of copper ions sharply decreased and could not be registered by the ionometer (especially at low concentrations). Therefore, up to 25% buffer solution was added to the model aqueous solution for its stabilization.

Kinetic models

By studying the kinetics of adsorption process the rate was observed as well as the mechanism of reaction. According to [6-8], the adsorption kinetic models are grouped into two classes: adsorption reaction models (pseudo- first- order rate equation/ Lagergren model, pseudo- second- order rate equation/ Ho- McKay model, Elovich's equation, second- order rate equation) , and adsorption diffusion models (liquid film linear driving force rate equation, liquid film diffusion mass transfer rate equation, homogeneous solid diffusion model, Weber-Morris model, Dumwald- Wagner Model, double exponential model). Tree of these ten kinetic models are taken into consideration in this paper.

Pseudo-first-order kinetic model (Lagergren model) - Lagergren [6] published a first- order rate equation to describe the liquid solid phase adsorption of oxalic acid and of malonic acid onto charcoal. It is based on the adsorption capacity (q), not on the liquid phase concentration (C). Therefore, it was named "pseudo-first-order model". The integrated Lagergren equation (1) is confronted with our experimental data in the figure 2.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

where: - q_t ($\text{mol} \cdot \text{kg}^{-1}$) is the amount of metal ions adsorbed on the adsorbent at time t (min); - q_e ($\text{mol} \cdot \text{kg}^{-1}$) is the amount adsorbed at equilibrium; - k_1 (min^{-1}) is the rate constant of first-order adsorption.

After integration between boundary conditions ($t = 0$ to t and $q_t = 0$ to q_e), the equation becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

Pseudo-second-order model

The adsorption kinetic may be described by the pseudo-second-order model.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

The equation for linear form is:

$$\frac{t}{q_t} = \frac{1}{(K_2 q_e^2)} + \frac{t}{q_e} \quad (5)$$

Where q_e and q_t are ion of heavy metal per mass unit of adsorbent (mg/g) at

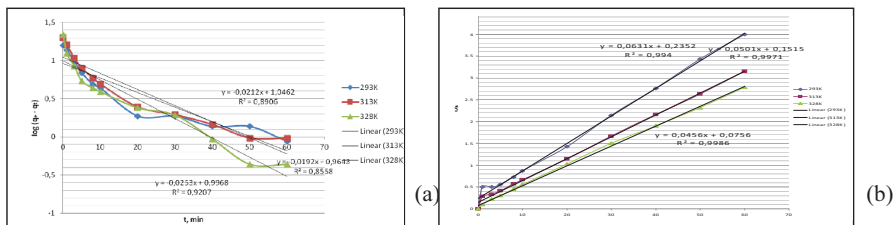


Fig. 3. Experimental validation of: a - the Lagergren equation (3); b - equation Ho-McKay (4) equilibrium and specific times, k_2 (g/mg min) are the rate constants of the second order kinetics.

The initial sorption rate, h , can be defined as

$$h = k^2 q_e^2 \quad (6)$$

so (6) can become:

$$q_t = \frac{t}{((1/h) + (t/q_e))} \quad (7)$$

The initial sorption rate, h ($\text{mmol g}^{-1} \text{min}^{-1}$), the equilibrium sorption capacity, q_e , and the pseudo-second-order rate constant, k_2 , can be determined experimentally from slope and intercept of plotting of t/q_t against t .

The activation energy for metal ions adsorption was calculated by the Arrhenius equation:

$$k = k_0 \exp\left[\frac{-E_a}{RT}\right] \quad (8)$$

where k_0 is the temperature independent factor in $\text{g mmol}^{-1} \text{min}^{-1}$, E_a is the activation energy of the reaction of adsorption in kJ mol^{-1} , R is the gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and T is the adsorption absolute temperature, K.

The linear form is:

$$\ln k = \frac{-E_a}{RT} + \ln k_0 \quad (9)$$

When $\ln k$ is plotted versus $1/T$, a straight line with slope $-E_a/R$ is obtained.

To calculate the thermodynamic activation parameters such as enthalpy of activation (ΔH^0), entropy of activation (ΔS^0), and free energy of activation (ΔG^0), the Eyring equation was applied :

$$\lg K_D = -\frac{\Delta H^0}{2.303RT} + \frac{\Delta S^0}{2.303R} \quad (10)$$

$$\Delta G^0 = \Delta H^0 - \Delta S^0 T \quad (11)$$

where $K_D = q_e/C_e$.

Intra-particle diffusion Weber-Morris model

The intra-particle diffusion model can be formulated using the Morris-Weber equation. A linear relationship between the amount adsorbed (qt) and the square root of the time describes this model, which can be expressed as:

$$q_t = k_p t^{1/2} + I_D \quad (12)$$

where k_p is the intraparticle diffusion rate constant ($\text{mmol g}^{-1} \text{min}^{-1/2}$), I_D is the constant (same units q_t).

The two parameters can be determined from the intercept of the plot of q_t versus $t^{0.5}$. The intercept (I_D) is used to examine the relative significance of the two transport mechanisms of the solute, namely: intraparticle diffusion and external mass transfer (film or surface diffusion through the film surrounding a zeolite particle). If $I = 0$, the intraparticle diffusion is considered as the rate-limiting step, while, if $I > 0$, both the external mass transfer and intraparticle diffusion are considered as the ratelimiting steps. An increase of I translates to a higher resistance to ions of the layer of liquid surrounding the particle of zeolite.

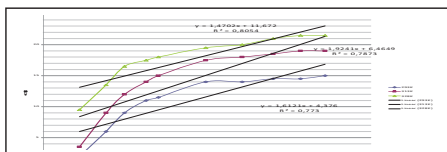


Fig. 4. Weber-Morris model checking

Table 1. Parameters of the adsorption kinetic models

Parameters	293K	313K	328K
1. Pseudo-first-order kinetic model			
$q_e, \text{mg} \cdot \text{g}^{-1}$	11.15	9.81	9.34
k_1, min^{-1}	0.0582	0.0488	0.0442
R	0.8906	0.8558	0.9207
2. Pseudo-second-order model			
$q_e, \text{mg} \cdot \text{g}^{-1}$	15.97	19.96	21.93
$k_2, \text{g/mg} \cdot \text{min}$	0.0168	0.0165	0.0275
R	0.9940	0.9971	0.9986
3. Intra-particle diffusion Weber-Morris model			
I_D	4.374	6.465	11.672
$k_p, \text{mmol g}^{-1} \text{min}^{-1/2}$	1.6121	1.19241	1.4702
R	0.7720	0.7873	0.8054

A plot of $\ln k_2$ against $1/T$ is shown in Figure 4. The activation energy (E_a) was determined according to the characteristics of the linear plot. The magnitude of activation energy may give an idea about the type of sorption. There are two main types of adsorption: physical and chemical. The activation energy for physical adsorption is usually no more than 4.2 kJ mol^{-1} , since the forces involved in physical adsorption are weak [8].

Chemical adsorption is specific and involves forces much stronger than in physical adsorption. There are two kinds of chemical adsorption including activated and nonactivated ones. Activated chemical adsorption means that the rate varies with temperature according to a finite activation energy ($8.4\text{--}83.7 \text{ kJ mol}^{-1}$) in the Arrhenius equation. In nonactivated chemical adsorption, the activation energy is near zero[7,8].

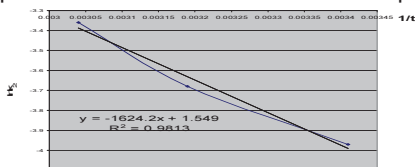


Fig. 5. The linear plot of $\ln K_2$ versus $1/T$

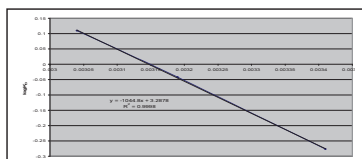


Fig. 6. The linear plot of $\log K_D$ versus $1/T$

The values of rate constant from the pseudo-second-order can be used to calculate the activation energy of sorption process. The energy of activation (E_a) was determined from the slope of the Arrhenius plot of $\ln k_2$ versus $1/T$ according to Eq. (10) and was found to be 13.5 kJ mol^{-1} for Cu(II) . This values are of the same magnitude as the activation

energy of activated chemical sorption. The positive values of E_a suggest that rise in temperature favours the adsorption and adsorption process is an endothermic.

To calculate the thermodynamic activation parameters such as ΔH^0 , ΔS^0 , and ΔG^0 , the Eyring equation Eq. (8,9) was applied [10] and the results are also listed in Table 2.

Table 2. The activation Energy and thermodynamic activation parametars of Cu(II) ADSORPTION ONTO Zeolite NaA

Thermodynamic Parameters	Value
1. Activation energy – E_a , kJ mol ⁻¹	13.5
2. Enthalpy of activation – ΔH^0 , kJ mol ⁻¹	20.0
3. Entropy of activation - ΔS^0 , kJ mol ⁻¹ K ⁻¹	0.062
4. Free energy of activation - ΔG^0 , kJ mol ⁻¹	
- for 293 K	1.84
- for 313 K	0.61
- for 328 K	-0.33

The positive ΔS^0 reflect that no significant change occurs in the internal structure of Zeolite NaA, during adsorption of copper ions. Positive values of ΔH^0 indicate the endothermic nature of the process. The negative ΔG^0 values of Cu(II) ions at temperature 328 K is due to the fact that the adsorption processes are spontaneous and the negative value of ΔG^0 decreased with an increase in temperature, indicating that the spontaneous nature of adsorption of Cu(II) are inversely proportional to the temperature. Obviously, it is shown from the results reported in Table 2 that the temperature affects the adsorption process of the metal ion adsorption onto in which the higher temperature provided more energy to enhance the adsorption rate.

CONCLUSIONS

In this study, the kinetic sorption of Cu(II) were investigated and the following conclusions can be obtained. The adsorption capacity of the sorbent (Zeolite NaA) strongly depends on pH and temperature on the sorbate.

The adsorption of Cu(II) are best in accordance with the pseudo-second order kinetic model at different physical and chemical conditions.

The measured E_a value (E_a , 13.5 kJ mol⁻¹) suggests that the adsorption may be a chemical reaction.

The values of thermodynamic parameters indicate that the adsorption is endothermic reaction in nature.

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This paper has been reviewed