

# The removal of Cu(II) Ions from Aqueous Solutions on Synthetic Zeolite NaA

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**Abstract** – In this study the adsorption of Cu (II) ions from aqueous solutions on synthetic zeolite NaA was evaluated. Determination of the effects of the temperature of the solution and the kinetic parameters of adsorption of Cu(II) from aqueous solution on zeolite NaA is important for the understanding of the mechanism of the adsorption. Variables of the system include the adsorption time, the temperature (293-328K), the initial concentration of the solution and pH of the system. The kinetic model of sorption of the copper ions was found to be strongly dependent on pH (the optimum pH 3-5), the concentration of ions in the solution and the temperature (293 – 328 K). It was found that the pseudo-second-order model was the best choice among all the kinetic models to describe the adsorption behaviour of Cu(II) onto zeolite NaA, suggesting that the adsorption mechanism might be a process of chemisorption. The activation energy of adsorption ( $E_a$ ) of Cu(II) was determined as 13.5 kJ mol<sup>-1</sup>. The low value of  $E_a$  shows that the process of adsorption of Cu(II) process on zeolite NaA may be an activated chemical adsorption. The thermodynamic parameters ( $\Delta G^0$ ,  $\Delta H^0$ , and  $\Delta S^0$ ) were also determined from the temperature dependence. The results show that the process of adsorption of Cu(II) is spontaneous and endothermic process and higher temperature favours the adsorption.

**Keywords** – Zeolite NaA, adsorption, adsorption capacity, kinetic sorption.

chemical compounds like nitrates, phosphates, heavy metals, etc. One method for removal of heavy metals from drinking water is the treatment with synthetic zeolites [3,4].

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

The present paper deals with issues referring to the studies on the opportunity of purifying aqueous solutions containing copper ions using synthetic zeolite NaA together with the methods of adsorption and ion-exchange. Higher levels of Cu(II), as well as other heavy metals, in water facilities poses great risk to human health. Therefore, it is of major importance to find ways of lowering the concentration or removing such contaminants from basins used for drinking water [5,6].

For this purpose, the paper discusses the adsorption kinetics of synthetic zeolite L 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 the kinetic models and an assessment of the adsorption processes is made.

## I. INTRODUCTION

Zeolites are aluminosilicate minerals containing exchangeable alkaline and alkaline earth metal cations (normally Na, K, Ca and Mg) as well as water in their structural framework. The physical structure is porous, enclosing interconnected cavities in which the metal ions and water molecules are contained [1,2]. Zeolites are appropriate material for the removing heavy metal ions from wastewater because of their relatively low price, together with the fact that their exchangeable ions (Na<sup>+</sup>, Ca<sup>2+</sup> and K<sup>+</sup>) are relatively harmless.

The properties of drinking waters and these used in food industry, as well as waters packed for retail selling should conform to certain requirements regarding their contents of

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## II. EXPERIMENTALS

### A. Adsorbate

All the compounds used to prepare the reagent solutions were of analytic reagent grade. The initial copper solutions were prepared from deionized water and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (Merck). To maintain certain values of pH during the process of adsorption, various buffer solutions were added to the total model solution studied in quantities up to 25%.

### B. Adsorbent

The adsorbent used for the studies was synthetic zeolite NaA produced through a technology described earlier [7,8].

### C. Batch Adsorption Experiments

The adsorption kinetics was studied through the method of volt-ampometric, a volt-ammeter ECOTEST-VA (ECONIX-EXSPERT) was used. 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) [9].

The measuring system was specially designed for the experiments to allow constant homogenization (through

varied velocities of a propeller) for better contact between the adsorbent and the adsorbate, as well as to provide the possibility of isothermal periods in thermostatic cell. The experiments were carried out at constant temperatures of 293, 313 and 328 K and two initial Cu(II) concentrations of the model solution.

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

The adsorption capacity of the sorbent ( $q_e$ , mg/g) was calculated by an equation (1).

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

Where  $C_o$  and  $C_e$  are respectively the initial and the final sample concentrations (mg/L),  $V$ (L) – the volume of the sample solution and  $m$  (g) is the weight of the added adsorbent.

### III. RESULTS AND DISCUSSION

#### A. Theory

The models of kinetics of the adsorption were correlated to the solution uptake rate, hence these models are important in the design of the water treatment process. In order to elucidate the adsorption mechanism and the potential rate controlling step, four kinetic models including the pseudo-first-order equation [10], the pseudo-second-order equation, the Elovich equation, and the intraparticle diffusion model were tested to fit the experimental data obtained from the batch of experiments on the removal of metal ions.

##### 1. Pseudo-first-order Model

The adsorption kinetic data was described by the Lagergren pseudo-first-order model, which is the first known equation that describes the adsorption rate based on the adsorption capacity. The equation in its linear form looks this way:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

where  $q_e$  and  $q_t$  are, respectively, the adsorption capacity at equilibrium and at time  $t$  (mg g<sup>-1</sup>),  $k_1$  is the rate constant in the pseudo-first-order adsorption (L min<sup>-1</sup>).

##### 2. Pseudo-second-order Model

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

The equation in its linear form is:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

Where  $q_e$  and  $q_t$  are the ions of heavy metals per mass unit of the adsorbent (mg/g) at equilibrium and at specific time,  $K_2$  (g/mg min) is the rate constant in the second order kinetics.

The initial sorption rate,  $h$ , can be defined as

$$h = K_2 q_e^2 \quad (4)$$

so (4) can be represented in the following way:

$$q_t = \frac{t}{((1/h) + (t/q_e))} \quad (5)$$

The initial sorption rate,  $h$  (mmol g<sup>-1</sup> min<sup>-1</sup>), the equilibrium sorption capacity,  $q_e$ , and the pseudo-second-order rate constant,  $K_2$ , can be determined experimentally through slope-intercept plotting of  $t/q_t$  against  $t$ .

##### 3. The Elovich equation

The Elovich equation is given as follows:

$$q_t = \frac{\ln(\alpha\beta)}{\beta} + \frac{\ln t}{\beta} \quad (6)$$

where  $q_t$  is the sorption capacity at time  $t$ ,  $\alpha$  is the initial sorption rate of the Elovich equation (mmol g<sup>-1</sup> min<sup>-1</sup>), and the parameter  $\beta$  is related to the extent of surface coverage and the activation energy for chemisorption (g mmol<sup>-1</sup>). The constants can be obtained from the slope and intercept equation form of a straight line of  $q_t$  versus  $\ln t$ .

##### 4. Intraparticle diffusion model

The intraparticle diffusion model is:

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

where  $k_p$  is the intraparticle diffusion rate constant (mmol g<sup>-1</sup> min<sup>-1/2</sup>),  $C$  is the intercept.

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

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

where  $k_o$  is the temperature independent factor in g mmol<sup>-1</sup> min<sup>-1</sup>,  $E_a$  is the activation energy of the reaction of adsorption in kJ mol<sup>-1</sup>,  $R$  is the gas constant, 8.314 J mol<sup>-1</sup> K<sup>-1</sup> and  $T$  is the adsorption absolute temperature, K.

The linear form is:

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

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 ( $\Delta H^0$ ), entropy of activation ( $\Delta S^0$ ), and free energy of activation ( $\Delta G^0$ ), 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  $K_D = q_e/C_e$ .

## B. Parameters of adsorption

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 1.

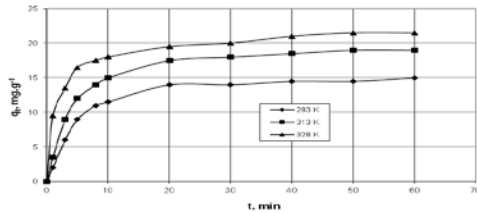


Fig. 1. The effect of contact time and temperature to adsorption of Cu(II) onto the Zeolite NaA (initial concentrations 60 mg/L)

Figure 1 illustrates that the equilibrium time of sorption was obviously shortened with the increase of the 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 wasn't any remarkable removal of Cu(II) in case of elongated contact time. The increase of Cu(II) adsorption capacity with the increase of the temperature indicates that higher temperature promotes Cu(II) adsorption onto the Zeolite NaA, and the adsorption is controlled by an endothermic process.

The preliminary studies show that the aqueous solutions of Cu(II) are quite unstable due to the susceptibility of the copper ions to hydrolyzation. This process depends on the ion concentration in the solution and mainly on the medium pH. Copper ions in aqueous solution are most stable at medium pH from 2 to 4.5. Studies have shown that there is probability for hydrolyzation at pH of the solution above 4.5–5.0. Thus, copper hydroxide precipitate was observed in the adsorbate at pH higher than 5.0, 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.

The selection of proper buffer solution and its amount is an important issue in the studies on the kinetics of sorption of copper ions from aqueous solutions since the process is accompanied by ion exchange with the zeolite. It should also be taken into account that, as a result from the ion exchange, sodium ions are released into the solution from the zeolite NaA which increases the medium pH. This is registered directly by the pH measuring gauge.

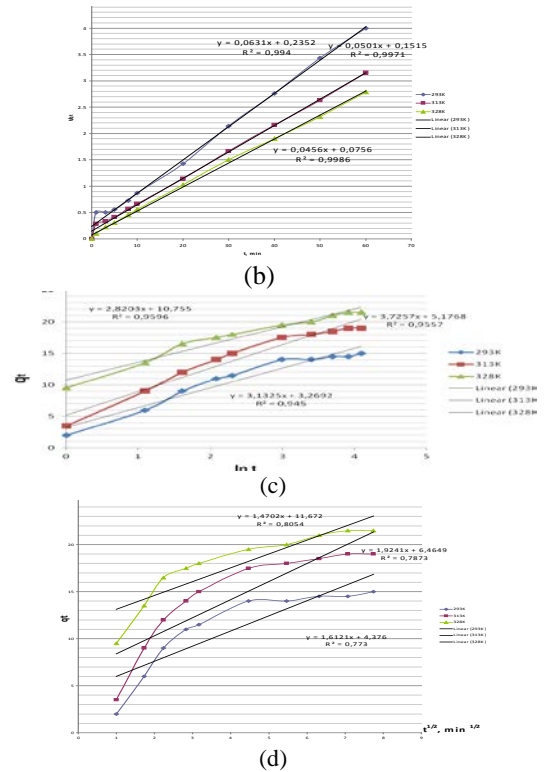
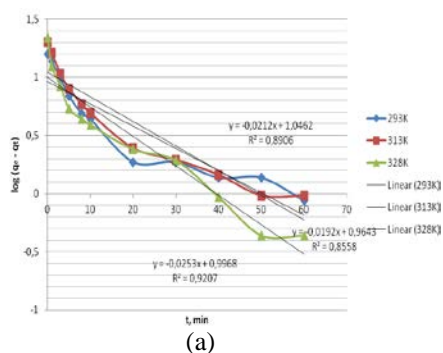


Fig.2. Plots of the four kinetic models for Cu(II) adsorption onto Zeolite NaA at various temperature

The plots of the four kinetic models for Cu (II) adsorption onto the Zeolite NaA at various temperature were given in Figure 2. The values of the kinetic parameters of the four kinetic models were calculated according to Figure 1. The kinetic parameter ( $k_2$ ) measured from the pseudo-second order model shows very high correlation coefficient. The equilibrium adsorption capacity of Cu (II) measured from the pseudo-second order model agrees with the experimental data. The value of the kinetic parameter ( $k_2$ ) increases from 0.00187 to 0.00345 kg/mg-min with the increase of the temperature from 293 to 328K. The above features explain why the adsorption of Cu (II) onto the synthetic Zeolite NaA might be a chemical reaction, and can be expressed by the pseudo-second order model.

## C. Thermodynamic parameters of adsorption

A plot of  $\ln k_2$  against  $1/T$  is shown in Figure 3. The activation energy ( $E_a$ ) was determined according to the characteristics of the linear plot. The magnitude of the 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 the physical adsorption is usually no more than  $4.2 \text{ kJ mol}^{-1}$ , since the forces involved in the physical adsorption are weak.

The chemical adsorption is specific and involves forces much stronger than those in the physical adsorption. There are two kinds of chemical adsorption which include activated and nonactivated chemical adsorption. The term activated chemical adsorption means that the rate varies with the

temperature according to the finite activation energy (8.4–83.7 kJ mol<sup>-1</sup>) in the Arrhenius equation. In nonactivated chemical adsorption, the activation energy is close to zero.

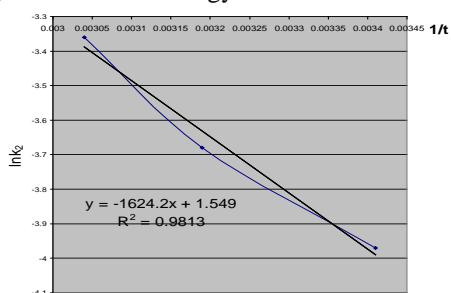


Fig. 3. Linear plot of  $\ln k_2$  versus  $1/T$

The values of the rate constant from the pseudo-second-order can be used in the calculation of the activation energy of the 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<sup>-1</sup> for Cu(II). This value is of the same magnitude as the activation energy of the activated chemical sorption. The positive values of  $E_a$  suggest that the rise in temperature favors the adsorption and that the adsorption process is an endothermic.

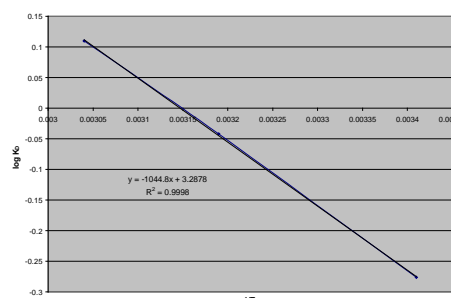


Fig. 4. The linear plot of  $\log K_D$  versus  $1/T$

To calculate the thermodynamic activation parameters such as  $\Delta H^0$ ,  $\Delta S^0$ , and  $\Delta G^0$ , the Eyring equation Eq (10,11) was applied and the results are listed in Table 1.

TABLE I  
THE ACTIVATION ENERGY AND THERMODYNAMIC ACTIVATION PARAMETERS OF Cu(II) ADSORPTION ONTO ZEOLITE NaA

THERMODYNAMIC PARAMETERS	VALUE
1. Activation energy – $E_a$ , kJ mol <sup>-1</sup>	13.5
2. Enthalpy of activation – $\Delta H^0$ , kJ mol <sup>-1</sup>	20.0
3. Entropy of activation - $\Delta S^0$ , kJ mol <sup>-1</sup> K <sup>-1</sup>	0.062
4. Free energy of activation - $\Delta G^0$ , kJ mol <sup>-1</sup>	
- for 293 K	1.84
- for 313 K	0.61
- for 328 K	-0.33

The positive  $\Delta S^0$  indicates that no significant change occurs in the internal structure of the Zeolite NaA, during the

adsorption of copper ions. The positive values of  $\Delta H^0$  indicate the endothermic nature of the process. The negative  $\Delta G^0$  values of Cu(II) ions at temperature 328 K are due to the fact that the adsorption processes are spontaneous and the negative value of  $\Delta G^0$  decrease with the increase of temperature, indicating that the spontaneous nature of adsorption of Cu(II) is inversely proportional to the temperature. It is obvious from the results reported in Table 1 that temperature affects the adsorption process of the metal ion adsorption, as the higher the temperature the more the energy to enhance the adsorption rate.

#### IV. CONCLUSION

In this study was investigated the kinetic sorption of Cu(II) and can be obtained the following conclusions:

The adsorption capacity of the sorbent (Zeolite NaA) strongly depends on the pH and the temperature of the sorbate.

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

The measured  $E_a$  value ( $E_a$ , 13.5 kJ mol<sup>-1</sup>) suggests that the adsorption may be a chemical reaction.

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

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