

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

Dimitar Georgiev, Bogdan Bogdanov, Yanko Hristov and Irena Markovska

Abstract—In this study the adsorption of Cu (II) ions from aqueous solutions on synthetic zeolite NaA was evaluated. The effect of solution temperature and the determination of the kinetic parameters of adsorption of Cu(II) from aqueous solution on zeolite NaA is important in understanding the adsorption mechanism. Variables of the system include adsorption time, temperature (293–328K), initial solution concentration and pH for the system. The sorption kinetics of the copper ions were found to be strongly dependent on pH (the optimum pH 3–5), solute ion concentration and temperature (293 – 328 K). It was found, the pseudo-second-order model was the best choice among all the kinetic models to describe the adsorption behavior of Cu(II) onto zeolite NaA, suggesting that the adsorption mechanism might be a chemisorptions process. The activation energy of adsorption (E_a) was determined as Cu(II) 13.5 kJ mol⁻¹. The low value of E_a shows that Cu(II) adsorption process by zeolite NaA may be an activated chemical adsorption. The thermodynamic parameters (ΔG^0 , ΔH^0 , and ΔS^0) were also determined from the temperature dependence. The results show that the process of adsorption Cu(II) is spontaneous and endothermic process and rise in temperature favors the adsorption.

Keywords—Zeolite NaA, adsorption, adsorption capacity, kinetic sorption

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 represent an appropriate material for removing heavy metal ions from wastewater because of their relatively low price coupled with the fact that their exchangeable ions (Na⁺, Ca²⁺ and K⁺) 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 chemical compounds like nitrates, phosphates, heavy metals, etc. One method for removal of heavy metals from drinking water is treatment with synthetic zeolites [3],[4].

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.

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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. 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 for lowering 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 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.

II. MATERIALS AND METHODS

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(NO₃)₂·3H₂O (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 from kaolin of Bulgarian origin by a technology described earlier [7],[8]. The Zeolite NaA was synthesized previously by dehydroxylation of low grade Bulgarian Kaolin at 650°C, receiving metakaolin granules using the fluidized bed method and hydrothermal reaction of metakaolinite with various aqueous alkali medium.



Fig. 1 Granules synthetic Zeolite NaA prepared in fluid bed method

C. Batch Adsorption Experiments

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) [9]. 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 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 two 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 or 100 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.

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

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

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

III. RESULTS AND DISCUSSION

A. Theory

The models of adsorption kinetics were correlated with the solution uptake rate, hence these models are important in water treatment process design. In order to elucidate the adsorption mechanism and potential rate controlling step, four kinetic models including the pseudo-first-order equation [10], the pseudo-second-order equation [11], Elovich equation [12], and intraparticle diffusion model [13] are tested to fit experimental data obtained from batch metal ions removal experiments.

1. Pseudo-first-order Model

The adsorption kinetic data were described by the Lagergren pseudo-first-order model, which is the earliest known equation describing the adsorption rate based on the adsorption capacity. The equation for linear form is:

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

where q_e and q_t are the adsorption capacity at equilibrium and at time t , respectively (mg g⁻¹), k_1 is the rate constant of pseudo-first-order adsorption (L min⁻¹).

2. Pseudo-second-order Model

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

The equation for 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 ion of heavy metal per mass unit of adsorbent (mg/g) at equilibrium and specific times, K_2 (g/mg min) are the rate constants of the second order kinetics [14],[15].

The initial sorption rate, h , can be defined as

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

so (4) can become:

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

The initial sorption rate, h (mmol g⁻¹ 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 .

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 , α is the initial sorption rate of Elovich equation (mmol g⁻¹ min⁻¹), and the parameter β is related to the extent of surface coverage and activation energy for chemisorption (g mmol⁻¹). The constants can be obtained from the slope and intercept 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⁻¹ min^{-1/2}), C is the intercept.

The activation energy for metal ions adsorption was calculated by 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⁻¹ min⁻¹, E_a is the activation energy of the reaction of adsorption in kJ mol⁻¹, R is the gas constant, 8.314 J mol⁻¹ K⁻¹ 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 (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 $K_D = q_e/C_e$.

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.

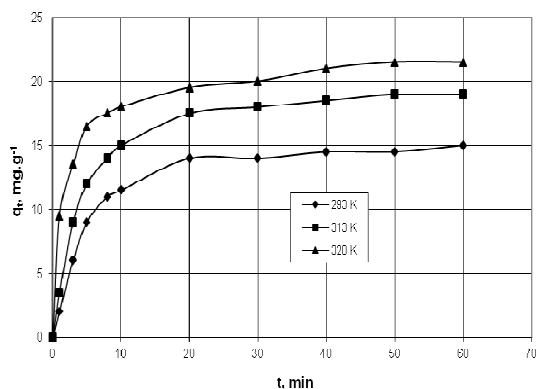


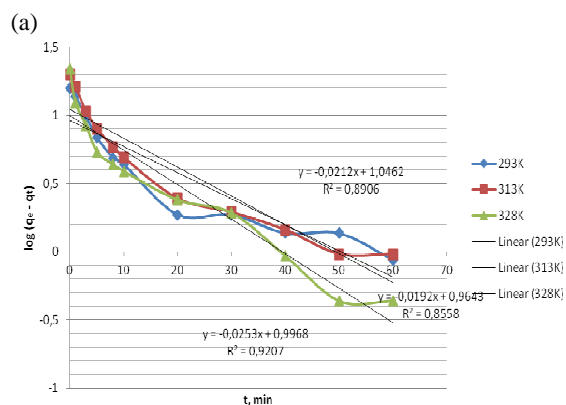
Fig. 2 The effect of contact time and temperature to adsorption of Cu(II) onto the Zeolite NaA (initial concentrations 60 mg/L)

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.

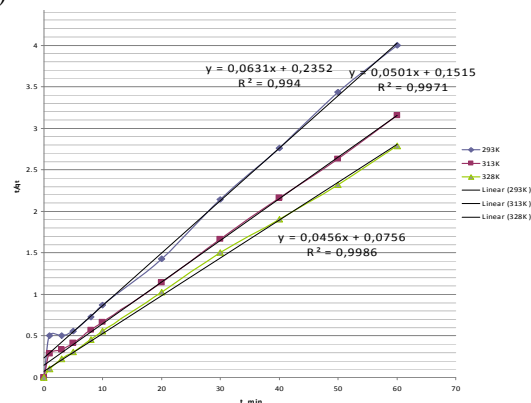
The preliminary studies showed that the aqueous solutions of Cu(II) are quite unstable due to the susceptibility of copper ions to hydrolyzation. This process depends in ion concentration in the solution and mainly on medium pH. Copper ions in aqueous solution are most stable at medium pH from 2 to 4.5. 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.

The different types of buffer solutions do not behave alike to the copper ions in aqueous solutions. For instance, it is irrelevant to use citrate buffers or such containing aminoacids because they contain functional groups which easily form copper compounds which settle down in the adsorbate. However, this concerns the chemical treatment of the solution.

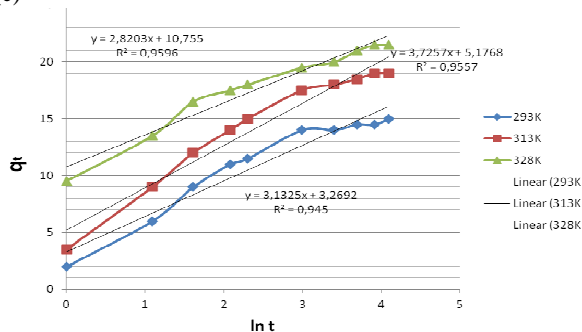
The selection of proper buffer solution and its amount is an important issue in the studies on the kinetics of sorption of copper ions from aqueous solutions since the process is accompanied by ion exchange with the zeolite. It should be taken into account also that, as a result from the ion exchange, sodium ions are released into the solution from the NaA zeolite which increase medium pH. This is registered directly by the pH measuring gauge. The theriotal cation exchange capacity (CEC) of synthetic zeolite A in Na⁺ form equals to 5.45 meq/g on the basis of the chemical formula [16],[17].



(b)



(c)



(d)

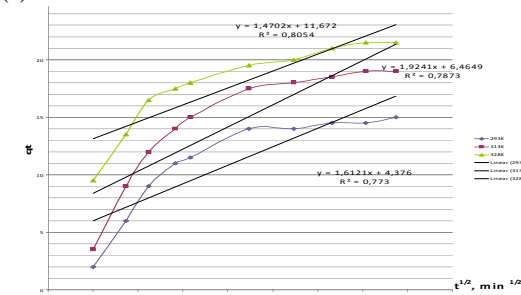


Fig. 3 The plots of the four kinetik models for Cu(II) adsorption onto Zeolite NaA at vareous temperature

The plots of the four kinetic models for Cu (II) adsorption onto the Zeolite NaA at various temperature were given in Figure 3. The kinetic parameters values of four kinetic models were calculated according to Figure 2. The kinetic parameter (k_2) measured from the pseudo-second order model showed very high correlation coefficients. The equilibrium adsorption capacity of Cu (II) measured from the pseudo-second order model showed a good agreement with experimental data. The values of kinetic parameter (k_2) increased from 0.00187 to 0.00345 kg/mg-min with an increase of temperature from 293 to 328K, respectively. The above features explained that the adsorption of Cu (II) onto the synthetic Zeolite NaA might be 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 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 [18],[19].

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 (8.4–83.7 kJ mol⁻¹) in the Arrhenius equation. In nonactivated chemical adsorption, the activation energy is near zero [20],[21].

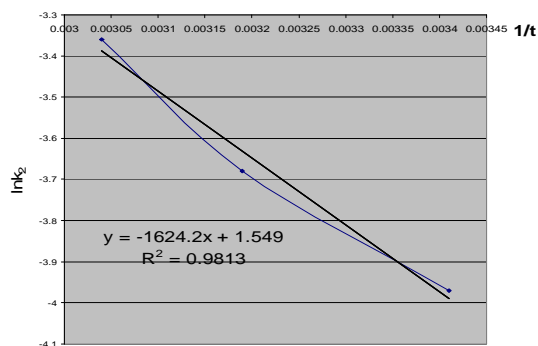


Fig. 4 The linear plot of $\ln k_2$ versus $1/T$

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 favors the adsorption and adsorption process is an endothermic.

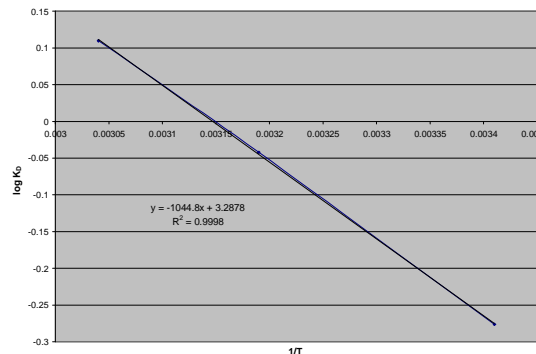


Fig. 5 The linear plot of $\log K_D$ versus $1/T$

To calculate the thermodynamic activation parameters such as ΔH^0 , ΔS^0 , and ΔG^0 , the Eyring equation Eq. (10,11) was applied [16] and the results are also 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 ⁻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 1 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.

IV. 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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