A Kinetic Study on the Adsorption of Cd(II) and Zn(II) Ions from Aqueous Solutions on Zeolite NaA

Dimitar Georgiev, Bogdan Bogdanov, Irena Markovska, Yancho Hristov and Dencho Stanev

Abstract—The present paper reports the removal of Cd(II) and Zn(II) ions using synthetic Zeolit NaA. The adsorption capacity of the sorbent (Zeolite NaA) strongly depends on simultaneous or not simultaneous (concurrent) presence of Cd(II) and Zn(II) in the sorbate. When Cd(II) and Zn(II) are present simultaneously (concurrently) in the sorbate, Zn(II) ions were sorbed at higher rate. Equilibrium data fitted Langmuir, Freundlich and Tempkin isotherms well. The applicability of the isotherm equation to describe the adsorption process was judged by the correlation coefficients R^2. The Langmuir model yielded the best fit with R^2 values equal to or higher than 0.970, as compared to the Freundlich and Tempkin models. The fact that $1/n$ values range from 0.322 to 0.755 indicates that the adsorption of Cd(II) and Zn(II) ions from aqueous solutions also favored by the Freundlich model.

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

I. Introduction

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.

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 cadmium and zinc ions using synthetic zeolite NaA with the methods of adsorption and ion-exchange. Cadmium and zinc ions are hazardous components in drinking waters even at low concentrations (maximum allowable concentration of Cd(II) is 0.005 mg/dm^3) [1]-[4]. Higher levels of Cd(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 cadmium and zinc 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 cadmium and zinc solutions were prepared from deionized water and Cd(NO$_3$)$_2$.4H$_2$O and ZnSO$_4$ (Merck).

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].

C. Batch Adsorption Studies

The adsorption of Cd(II) and Zn(II) ions from model aqueous solutions by the zeolite NaA studied was performed with different initial concentrations and constangt temperature (20°C).

The adsorption kinetics was studied by the method of volt-ampermetric, using volt-ampermeter ECOTEST-VA (ECONIX-EXSPERT). This method allows direct regstration of the amount of Cd(II) and Zn(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 posibilities for isothermal periods in thermostatic cell.

First, certain amount of cadmium and zinc salts were added step-wise under continuous propelling to plot the concentation curve. Then the adsorbent was added (Zeolite NaA – 20mg) and, after a period of time, measurements of the residual amounts (non-adsorbed) of the ions studied were started. pH of the system was in the range 3-5 since the method requires addition of HCl and Hg(NO$_3$)$_2$.H$_2$O. Fig.1 shows the working

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voltage-current curves for the stridies of the adsorption in model solutions containing: (a) Cd(II) ions only, (b) Zn(II) ions only and (c) both Cd(II) and Zn(II)) ions.
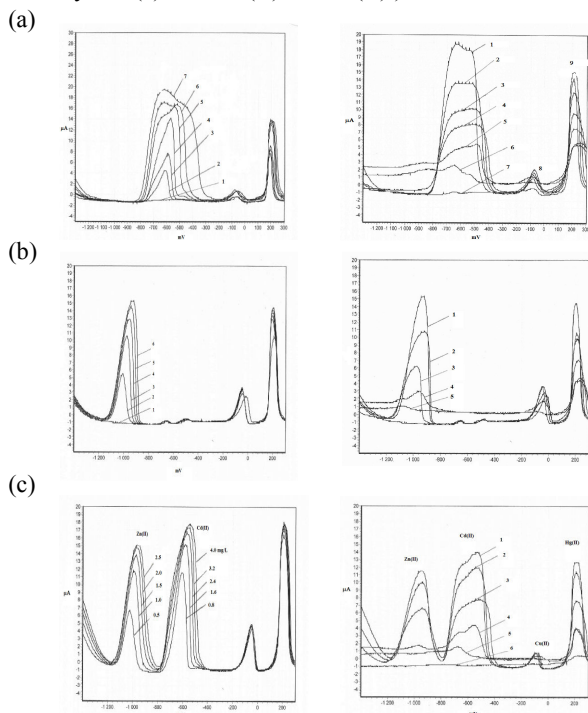
(a)

(b)

(c)

Fig. 1 Working voltage-current curves for the adsorption Zeolite NaA of model solutions containing: (a) Cd(II) ions only, (b) Zn(II) ions only and (c) both Cd(II) and Zn(II)) ions

As can be seen from the voltage-current plots, the Cd(II) ions were registered at voltages about -600 mV, Zn(II) ions at about -900-1000 mV, and certain amounts of Hg(II) ions were observed at about 200 mV. The amounts of these ions were calculated by the area of the peaks recorded. The method is quite sensitive because it allows registration of very small quantities of metal ions.

D. Adsorption Isotherms

To study the kinetics of adsorption, 100 ml model solution of Cd(II), Zn(II) and Cd(II)+Zn(II) (together) with initial concentration of 2 or 15 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 30 min.

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

$$q_e = (C_o - C_e)V/m \qquad (1)$$

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

III. RESULTS AND DISCUSSION

A. Isotherm Data Analysis

The parameters obtained from the different models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent. The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich models. The correlation with the amount of adsorption and the liquid-phase concentration was tested with the Langmuir, Freundlich and Tempkin isotherm equations. Linear regression is frequently used to determine the best-fitting isotherm, and the applicability of isotherm equations is compared by judging the correlation coefficients.

Fig.2 shows the adsorption kinetic isotherms from 100 ml model solution of Cd(II), Zn(II) and Cd(II)+Zn(II) (together).
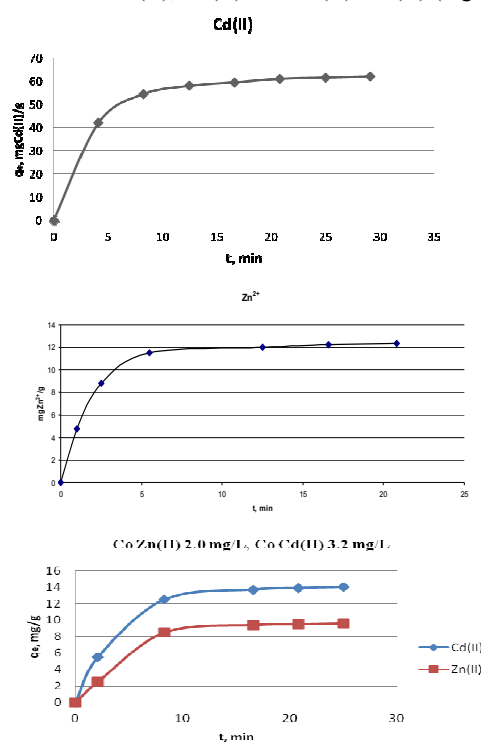

Fig. 2 Effect of contact time on the amount of Cd(II), Zn(II) and Cd(II)+Zn(II) (together) ions on Zeolite NaA (0.020 g; 100ml; temperature 20°C)

1. Langmuir Isotherm

The theoretical Langmuir isotherm is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface.

The Langmuir isotherm has an assumption that the adsorption occurs within adsorbent at specific homogeneous sites. The following equation (2) is the linear form of the Langmuir equation.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (2)$$

Where q_e is adsorption capacity at equilibrium (mg/g), q_m is the maximum adsorption capacity (mg/g), C_e (mg/l) is the solution concentration at equilibrium, and K_L is the Langmuir constant (l/mg) [10]-[14].

2. Freundlich Isotherm

The linear form equation of the Freundlich isotherm is listed as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (3)$$

Where q_e is adsorption capacity at equilibrium (mg/g), C_e is the concentration at equilibrium (mg/l), K_F and n are the Freundlich constants. The value of K_F can be taken as a relative indicator of adsorption capacity while $1/n$ is indicative of the energy or intensity of reaction. The values of q_m, K_L (2), K_F and n (3) are calculated from the intercepts and slopes of the equation plots.

3. Tempkin Isotherm

Temkin isotherm, which considers the effects of the heat of adsorption of all molecules in the layer would decrease linearly with coverage due to the adsorbate and adsorbent interactions and is given by:

$$q_t = \left(\frac{RT}{b}\right)\ln A + \left(\frac{RT}{b}\right)\ln C_e \qquad (4)$$

Here $RT/b = B$ (J mol^{-1}), which is Tempkin constant related to heat of sorption whereas a (L g^{-1}) is the equilibrium binding constant corresponding to the maximum binding energy. R (8.314, J mol^{-1} K^{-1}) is universal gas constant and Temperature (K) is absolute solution temperature.
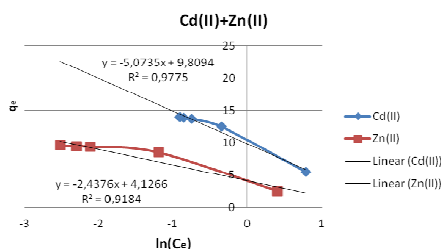
Fig. 3 Tempkin plot for Cd(II)+Zn(II) (together) ions adsorption onto Zeolite NaA

The linear model parameters of Langmuir, Freundlich and Tempkin Isotherm at 20°C temperature are listed in Table I.

B. Kinetic Models

Several steps can be used to examine the controlling mechanism of adsorption process such as chemical reaction, diffusion control and mass transfer. Kinetic models are used to test experimental data from the adsorption of Cd(II), Zn(II) and Cd(II)+Zn(II) (together) ions onto Zeolite NaA. The kinetics of adsorption ions onto Zeolite NaA is required for selecting optimum operating conditions for the full-scale batch process.

The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes.

TABLE I
ISOTHERM MODEL PARAMETERS AND CORRELATION COEFFICIENT AT 20°C TEMPERATURE

Isotherm model, parameters	Cd(II)	Zn(II)	Cd(II), (together)	Zn(II)
Langmuir				
q_m - maximum monolayer adsorption capacities, mg/g	2.347	4.587	4.830	7.735
K_L- Langmuir constant, L/mg	3.952	0.719	2.272	0.032
R^2 - Correlation coefficient	0.9733	0.9855	0.9995	0.9913
Freundlich				
$1/n$ - Freundlich exponent	0.322	0.554	0.588	0.755
K_F- Affinity Factor, mg/g	9.275	7.335	4.335	6.540
R^2- Correlation coefficient	0.8259	0.7723	0.8155	0.7922
Tempkin				
K_T, Tempkin constant, L/g			6.960	5.443
B, J/mol			5.050	2.437
R^2- Correlation coefficient			0.9775	0.9184

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:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (5)$$

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}).
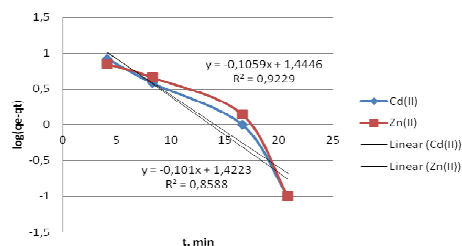
Fig. 4 Pseudo-first-order kinetics for Cd(II)+Zn(II) ions (together) adsorption onto Zeolite NaA. Conditions: adsorbent 0.02 g/100 ml, pH 3-5, temperature 20 ± 2 °C

2. Pseudo-second-order Model

The adsorption kinetic may be described by the pseudo-second-order model.
The equation for linear form is:

$$\frac{t}{q_t} = \frac{1}{(K_2 q_e^2)} + \frac{t}{q_e} \qquad (6)$$

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.

The initial sorption rate, h, can be defined as $h=K_2 q_e^2$ so (6) can become:

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

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 slop and intercept of plotting of t/q_t against t.
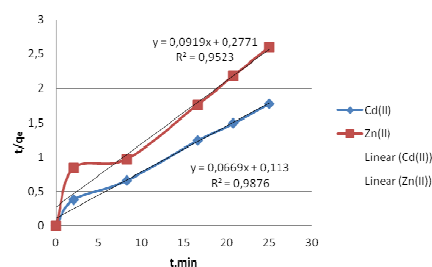

Fig. 5 Pseudo-second-order kinetics for Cd(II)+Zn(II) ions (together) adsorption onto Zeolite NaA. Conditions: adsorbent 0.02 g/100 ml, pH 3-5, temperature 20 ± 2 °C

The linear model parameters at 20°C temperature are listed in Table II.

TABLE II

COMPARISON OF THE FIRST- AND SECOND-ORDER ADSORPTION RATE CONSTANTS FOR ZEOLITE NaA (0.02g /100ml, pH 3-5)

Kinetic model, parameters	Cd(II)	Zn(II)	Cd(II), (together)	Zn(II)
First-order kinetic model				
K_1 - Constant of pseudo-first-order adsorption, L min^{-1}	0.4123	0.3135	0.2438	0.2326
R^2 - Correlation coefficient	0.8375	0.8235	0.8588	0.9229
Pseudo-second-order model				
K_2 - Pseudo-second-order rate constant, g/mg min	0.0154	0.0886	0.0397	0.0304
q_e - Equilibrium sorption capacity, mg/g	64.9	12.9	14.9	10.88
R^2 - Correlation coefficient	0.9974	0.9962	0.9876	0.9523

IV. CONCLUSION

In this study, the kinetic sorption of Cd(II), Zn(II) were investigated and the following conclusions can be obtained. The adsorption capacity of the sorbent (Zeolite NaA) strongly depends on simultaneous or not simultaneous (concurrent) presence of Cd(II) and Zn(II) in the sorbate. When Cd(II) and Zn(II) are present simultaneously (concurrently) in the sorbate, Zn(II) ions were sorbed at higher rate. The adsorption capacity of the metal ions were found to be strongly dependent on pH. Complete adsorption for Cd(II), Zn(II) ions was achieved at pH 3-5. The removal mechanism of the metal ions was mainly by adsorption and ion exchange processes. The Langmuir model have been proved as suitable model explaining the phenomena of adsorption isotherm.

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