

DYNAMICS OF ADSORPTION OF COPPER IONS IN FIXED-BED COLUMN AND MATHEMATICAL INTERPRETATION OF THE FIRST STAGE OF THE PROCESS

Jaroslav Gumnitsky¹, Vira Sabadash^{1,*}, Oksana Matsuska², Oksana Lyuta¹,
Anna Hyvlud¹, Lubov Venger¹

<https://doi.org/10.23939/chcht16.02.267>

Abstract. The dynamics of the adsorption process in the fixed-bed column was experimentally studied on the example of the system natural zeolite - water solution of copper salt with low concentrations, which are characteristic for wastewater treatment processes from toxic contaminants. The initial curves of the adsorption process for the height of the sorbent layer of 5 and 7 cm were constructed. The equilibrium of such processes can be described by Henry's linear equation. The adsorption process in the layer consists of two stages, which are examined in the study. The first stage is the formation of concentration front and the second one – its moving. The sum of the time of the first and second stages is the total adsorption time, which is determined before breakthrough time. The first stage of adsorption is mathematically formulated by the differential equation of molecular diffusion with a boundary condition of the first type. The second stage is supplemented by the balance equation, which takes into account not only the change of concentration in time, but also in the vertical coordinate and determines the time of movement of concentration front to breakthrough time. A mathematical model of the adsorption process in a fixed-bed column has been developed. Experimental data and theoretical calculations were compared. The results of statistical calculation of research results showed a satisfactory convergence of experimental and theoretical data.

Keywords: adsorption, fixed-bed column, dynamics, breakthrough time, adsorption stages, mathematical model.

1. Introduction

Adsorption processes are used in many industries.¹ They are most widely used in the chemical, oil refining, food industries, as well as in environmental technologies.^{2,3} In the latter case, the use of adsorption technologies refers to low concentrations of the component (adsorbent) in the liquid or gaseous phase before releasing into the environment.^{4,5} The concentration of harmful pollutants before release must suit the norms of concentrations that are not harmful for the environment.^{6,7} It is possible to ensure low concentrations after provided adsorption when the process is carried out in a fixed-bed column of granular adsorbent. Adsorption processes are widely described in the literature, but elements of chemical kinetics and empirical dependencies are often used, which do not fully reflect the peculiarities of the adsorption process in the fixed bed.⁸ The dynamics of adsorption in a fixed-bed column is theoretically complicated and the mathematical interpretation of the dynamics causes significant difficulties because the dynamics take into account the statics, kinetics and hydrodynamics of the process. In time space, the dynamics is divided into two periods. In the first period there is a formation of the concentration front.⁹ The formation of the front ends by the saturation of the upper layer of the adsorbent particles with the adsorbed component. The second period of adsorption means the movement of the concentration front to the appearance of the adsorbate at the outlet of the adsorbent layer. This effect is called the “breakthrough time”. Both periods are important and necessary when calculating

¹ Lviv National Polytechnic University,
12, S. Bandery Str., Lviv, 79013, Ukraine

² Gzhytskyi National University of Veterinary Medicine and
Biotechnologies,

50, Pekarska Str., Lviv, 79006, Ukraine

* virasabadash@gmail.com

© Gumnitsky, J.; Sabadash, V.; Matsuska, O.; Lyuta, O.; Hyvlud, A.;
Venger, L., 2022

the adsorption time in the fixed-bed column to the effect of breakthrough time.¹⁰

The dynamics of adsorption in a fixed-bed column is a complex mass transfer process and includes the need to study the equilibrium of the system, kinetic patterns in the system adsorbent - the medium from which the adsorption occurs, the movement of liquid or gaseous medium through the fixed-bed column.¹¹ This study presents the adsorption of copper ions on natural zeolite, which passes in a fixed-bed column. This problem is important for the purification of the water environment from a toxic substance that is harmful to water objects.¹² During the adsorption of a substance in a fixed-bed column, the individual particles of the adsorbent are saturated and the concentration of the substance in the grain (adsorbate) increases to saturation, which is determined by the adsorption isotherm. A number of studies that determines the adsorption capacity of natural raw materials against copper ions is devoted to the processes of studying equilibrium states on natural adsorbents. The influence of various physico-chemical factors on the adsorption capacity of zeolite after modification has been studied by Dignos *et al.*¹³ Sorption of copper ions by natural zeolite and mathematical determination of adsorption isotherms, verification of their reliability and determination of the dependence on the size of the dispersed phase are given.^{14,15}

A similar problem of the nonstationary process arises when considering the dissolution of the solid phase which is in an inert fixed-bed column of granular material.^{16,17} Two stages of dissolution are analyzed. At the first stage, the process of dissolving of the upper layer of particles is considered, when the depth of dissolving layer is equal to the diameter of the soluble particles. The second stage of dissolution begins after the dissolution of the upper layer. The movement rate of the dissolution zone and the time of the overall process are determined.^{10,18}

In previous studies the adsorption properties of zeolite from the Transcarpathian deposit, which is based on clinoptilolite, were studied with effect to Cu(II) and Cr(VI) ions.^{10,19} It was found that the adsorption isotherm has an s-shape and belongs to the type II isotherm. It was found that after the formation of the monomolecular adsorption bed, the adsorption continues.²⁰ This leads to the appearance of a bimolecular bed. The combined adsorption of copper(II) and chromium(VI) ions in the anionic form on natural zeolite has been studied and its adsorption capacity during their combined adsorption

has been determined.²¹ There is a significant difference in their sorption capacity, which is significantly higher for copper cations than for the anionic form of chromium.^{19,22} The elemental composition of the sorbent surface was investigated by X-ray fluorescence method after adsorption of heavy metals from a two-component system containing Cu²⁺ and Cr³⁺ ions.^{23,24} The mechanism of sorption extraction of copper and chromium from the solution was theoretically substantiated. It was established that the selectivity of metal extraction is influenced by the radius of the element and the solubility of its hydroxides. The deposition conditions of the corresponding metals hydroxides were calculated and the logarithmic diagram of the two-component system composition depending on pH was constructed.²⁴

The aim of this work was to study the dynamics of adsorption of copper ions by natural zeolite, to determine the nature of the breakthrough curves at different lengths of the zeolite layer and to describe mathematically the breakthrough curves using boundary conditions of the first type.

2. Experimental

The dynamics of the adsorption process of copper ions in the fixed-bed column was experimentally investigated in the laboratory setup shown in Fig. 1. The main part of the installation is a glass cylindrical tube with a diameter of 0.01 m with a sample of zeolite 4, which corresponded to the specified depth and was held in the column (3) by means of a lattice 5. The backfill of zeolite corresponded to a certain specified depth.

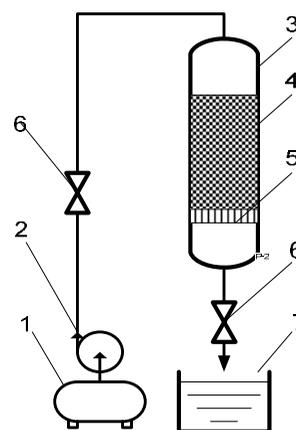
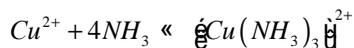


Fig. 1. Laboratory installation consisting of a container with a test solution of Cu(II) (1); pump (2); fixed-bed column (3); sorbent (4); lattice (5); tap (6) and collector for collecting eluate samples (7)

The pre-prepared solution of divalent copper salt was placed in tank 1. The solution from the tank to the column was given by pump 2. The rates of adsorbent flow and eluate flow were regulated by tap 6. The eluate was collected in the receiver 7. Liquid samples were taken to determine the concentration of copper ions. Eluate samples were taken over a period of time so that the volume of liquid was sufficient to determine the concentration of copper. The concentration time was taken as an average. Based on the results of the analysis, the breakthrough curves were constructed, which characterize the dynamics of processes in the fixed-bed column. These characteristics include the effect of "breakthrough time", *i.e.* the appearance of the adsorbent at the outlet of the fixed-bed column of granular material, as well as the curvature of the original curves. Note, that the work of the adsorption column stops when the concentration of copper in the eluate exceeds $0.05C_0$, where C_0 is the initial concentration of the component in the initial solution.

Determination of Cu(II) ions was performed by a spectrophotometric method using a SPECORD-75-IR spectrophotometer. The essence of the method was to determine the optical density of the ammonia complex of copper(II) according to the reaction:



To the 10 mL eluate samples obtained according to the procedure described above, 3 mL of 2N NH_4OH solution was added. The obtained samples were analyzed for the content of Cu(II) ions.

Statistical analysis was used to assess the significance of the obtained results. To establish the reproducibility of the experimental data, the values of statistical significance p and Pearson's criterion χ^2 , dispersion and standard deviation were calculated. The value of $p < 0.005$ was taken. The calculated value of the criterion χ^2 was compared with its critical value, which is in the range of $0 \leq \chi^2 \leq 1$.

3. Results and Discussion

Adsorption processes in the fixed-bed column allow to clean the liquid from harmful substances with high efficiency, so this method is widely used in industrial practice. Purification proceeds to the so-called "breakthrough time" phenomenon, which corresponds to the initial concentration curve equal to $0.05C_0$. The task at the design stage of the adsorber is to determine the

breakthrough time, after which the device is stopped for regeneration. In the adsorber shown in Fig. 1, the liquid with the adsorbed substance is filtered in the vertical direction according to the z axis. It is obvious that the concentration of the liquid decreases in depth from the initial value of C_0 to the final one, which at a certain depth is zero. The first stage of adsorption is established, during which the upper layer of the adsorbent grains increases its concentration (adsorption capacity) from $a = 0$ to the equilibrium value of a^* . At this time, the formation of the concentrations front of the adsorbent occurs, which ends with the saturation of the upper layer of the grains of the adsorbent. Denote the time of saturation of the upper layer of the adsorbent and the completion of the formation of the concentration front through τ_1 . The second stage of adsorption corresponds to the transfer of the concentration front from the top to the bottom and ends with the appearance of the adsorbed substance at the outlet of the adsorber, *i.e.* to the phenomenon of breakthrough time. The time of parallel transfer of the concentration front to the breakthrough time is denoted by τ_2 .

Continuation of adsorption after breakthrough time gives a characteristic breakthrough curve. The values of the breakthrough curves obtained during the adsorption of copper ions by natural zeolite on the installation (Fig. 1) are shown in Fig. 2. Two output curves for two lengths of the adsorbent layer were obtained. The total adsorption time to the breakthrough time τ consists of the time of formation of the concentration front τ_1 and the time of parallel movement of the concentration front to the breakthrough time τ_2 and will be:

$$\tau = \tau_1 + \tau_2 \quad (1)$$

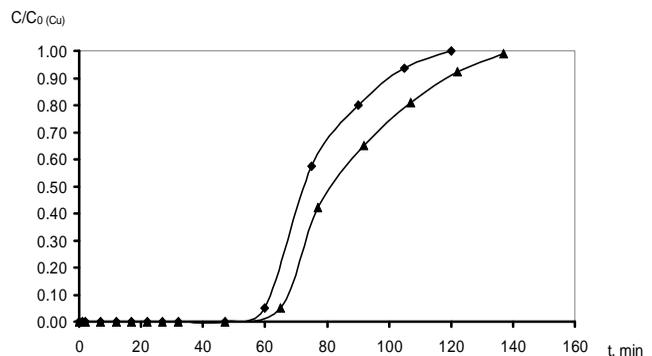


Fig. 2. Breakthrough curves of adsorption dynamics of copper ions on natural zeolite as a function of relative concentrations of C/C_0 from time t for different depth of the adsorbent layer

Let us consider the process of adsorption in the first upper layer of the adsorbent, the depth of which is equal to the diameter of the zeolite grain d . The first layer is always in contact with the fresh solution coming for purification with an initial concentration C_0 . Adsorption belongs to mass transfer processes and consists of two stages: external diffusion and intradiffusion. During the external diffusion stage, copper ions are transported by convective diffusion to the outer surface of the adsorbent grains, and the intensity of this process is determined by the mass transfer coefficient β , which depends on the hydrodynamics. The intradiffusion process is the movement of a component in the pores and channels of the adsorbent and its rate is characterized by an effective diffusion coefficient that takes into account the molecular diffusion in the pore volume of the adsorbent and along the pore walls. It is possible to determine the limiting stage of the adsorption process in the first row of adsorbent grains using the number Bi_0 ($Bi = \beta \cdot d / D^*$). Obviously, when the number $Bi \rightarrow \infty$, the mode will be intradiffusion.^{21,25} In fact, for numbers $Bi > 50$ the mode is considered to be intradiffusion. Using the data of our studies of the kinetics of adsorption of copper ions by natural zeolite, we found that under conditions of intensive hydrodynamics, the mass transfer coefficient $\beta = 1.14 \cdot 10^{-4}$ m/s.⁸ The study of the intradiffusion stage of adsorption of copper ions at a temperature of 293 K allowed to determine the effective internal diffusion coefficient $D^* = 2.5 \cdot 10^{-11}$ m²/s.^{8,10} For particles with the radius of $1 \cdot 10^{-3}$ m, the value of $Bi = 4560$, *i.e.* the value is large enough for the adsorption process in the first layer of adsorbent grains to be considered intradiffusion, which is described by the differential equation of molecular diffusion for spherical particles.

The slow stage of the intradiffusion adsorption process allows us to consider that the adsorbent concentrations on the grain surface of the adsorbent and in the volume of liquid are the same.^{24,25} For the first layer of adsorbent particles, you can take a concentration equal to the initial concentration of the adsorbent C_0 . This allows us to consider the conditions at the boundary of the adsorbent – liquid phase as the first type conditions:

$$\bar{a}^* = \Gamma \times C_0 \tag{2}$$

where \bar{a}^* is the average equilibrium adsorption capacity corresponding to the concentration of the adsorbent C_0 ; Γ is the tangent of the angle of inclination of the isotherm for the region of low concentrations.

For the first row of grains of the adsorbent mathematically, the adsorption problem for particles of spherical shape, taking into account equation (2) can be formulated as follows:

$$\begin{aligned} \frac{\partial C_a}{\partial t} &= D \cdot \frac{\partial^2 C_a}{\partial r^2} + \frac{2}{r} \frac{\partial C_a}{\partial r} & (0 < r < R) \\ C_a(r, 0) &= 0 \\ C_a(R, t) &= \Gamma \times C_0 \\ \frac{\partial C_a(0, t)}{\partial r} &= 0 \end{aligned} \tag{3}$$

We introduce dimensionless linear and temporal parameters:

$$\begin{aligned} j &= \frac{r}{R} - \text{dimensionless radius;} \\ Fo &= \frac{D^* \cdot t}{R^2} - \text{Fourier number.} \end{aligned}$$

Taking into account the dimensionless parameters, the system (3) will be written:

$$\begin{aligned} \frac{\partial C_a}{\partial Fo} &= \frac{\partial^2 C_a}{\partial j^2} + \frac{2}{j} \frac{\partial C_a}{\partial j} & (0 < j < 1) \\ C_a(j, 0) &= 0 \\ C_a^*(1, Fo) &= \Gamma \times C_0 \\ \frac{\partial C_a(0, Fo)}{\partial j} &= 0 \end{aligned} \tag{4}$$

The obtained solution of system (4) is given below:

$$\frac{C_a(j, Fo)}{C_a^*} = 1 - \sum_{n=1}^{\infty} (-1)^{n+1} \frac{2 \sin m_n j}{m_n j} e^{-m_n^2 Fo} \tag{5}$$

where $m_n = n \times \pi$ - roots of the characteristic equation.

In practical research, the use of solution (5) does not allow its experimental verification, because it is impossible to determine the concentration of the adsorbate at a certain relative radius φ . The average value of the concentration of the component in the particles of spherical shape during adsorption makes it possible to establish their saturation in time and the time of full saturation in the dimensionless form, which will approach to 1.^{24,25} This solution has the form:

$$\frac{\bar{C}_a}{C_a^*} = 1 - \sum_{n=1}^{\infty} \frac{6}{n^2 \pi^2} e^{-n^2 \pi^2 Fo} \tag{6}$$

In the right side of dependence (6), the variable is the Fourier number, which represents the dimensionless time. The calculation of the sum showed that it is enough to limit the first term. Giving the time τ , the values $\frac{\bar{C}_a}{C_a^*}$ were calculated and represented graphically as a function of time τ (Fig. 3).

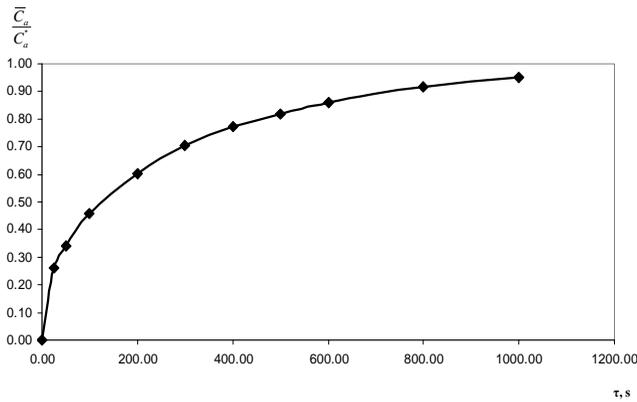


Fig. 3. The dependence of the relative degree of saturation of the first upper layer of the adsorbent $\frac{C_a}{C_{a^*}}$ on the time of adsorption τ

It is seen from Fig. 3 that the degree of saturation 0.95 is achieved in real time $\tau = 1000$ s. Obviously, this value is sufficient, because zeolite was a natural mineral in which the characteristics of the pores can be considered kinetically unequal. Thus, the saturation time of the first layer of adsorbent can be taken $\tau_1 = 1000$ s.

The first stage completes the formation of the concentration front and initiates its parallel movement in the z -axis direction. In the solid adsorbent medium, an adsorbate-filled zone is created in which adsorption takes place.

The recorded systems (3), (4) must be supplemented with a material balance of the interaction of the moving

$$\frac{\partial C_a}{\partial t} = C_{a^*} \sum_{n=1}^{n+1} a_n (-1)^{n+1} \times \frac{2 \sin \eta_n \cos \eta_n + \sin \eta_n}{\eta_n^2} \frac{\partial}{\partial z} \exp(-\eta_n^2 F_0) \quad (10)$$

Then we substituted the obtained value (10) into equation (8) and perform integration

$$\int_{C_0}^C dC = -3 C_{a^*} \sum_{n=1}^{n+1} a_n (-1)^{n+1} \times \frac{2 \sin \eta_n \cos \eta_n + \sin \eta_n}{\eta_n^2} \frac{\partial}{\partial z} \exp(-\eta_n^2 F_0) \int_0^w dw \quad (11)$$

Integration within these limits allows to determine the change in the concentration of the adsorbent in the liquid as a function of time τ at different lengths of the adsorbent bed z expressed in a dimensionless form w .

$$C = C_0 - 3w \times C_{a^*} \sum_{n=1}^{n+1} a_n (-1)^{n+1} \times \frac{2}{\eta_n^2} (\sin \eta_n \cos \eta_n + \sin \eta_n) \exp(-\eta_n^2 F_0) \quad (12)$$

We present the calculation of the exponent of the first and second terms of the sum in Eq. (12), for example, for time $\tau = 1000$ s.

$$\begin{aligned} n = 1 & \quad \exp(-\pi^2 \cdot 1^2 \cdot (2.51 \cdot 10^{-10} \cdot 10^3) / 1 \cdot 10^{-6}) = \\ & = 0.08397 \\ n = 2 & \quad \exp(-\pi^2 \cdot 2^2 \cdot (2.51 \cdot 10^{-10} \cdot 10^3) / 1 \cdot 10^{-6}) = \\ & = 0.00004972 \end{aligned}$$

fluid with the adsorbent and natural zeolite. Express the flow rate of filtration of the liquid through the bed of granular adsorbent as W (m^3/s), the current concentration of the adsorbent as C . So, the balance equation for the unit depth of the bed can be written:

$$W \frac{\partial C}{\partial z} = -D^* S \times (1 - \epsilon) \cdot \frac{1}{4/3(\rho R^3)} \frac{\partial C_a}{\partial t} \quad (7)$$

where ϵ is the porosity of the layer; S is the cross-sectional area of the apparatus; $W/S = w$ is a fictitious rate of the liquid, i.e. the rate is related to the cross-sectional area of the apparatus.

Entering the dimensionless linear parameter of particles φ and the dimensionless parameter of the grain bed of the adsorbent ω , we obtain:

$$\frac{\partial C}{\partial w} = -3 \frac{\partial C_a}{\partial t} \frac{\partial}{\partial z} \quad (8)$$

where $w = \frac{D^* (1 - \epsilon)}{w \times R^2} z$ - dimensionless parameter that characterizes the length of the bed.

Using solution (5), we differentiate it by $d\varphi$:

$$\frac{dC_a}{d\eta} = -C_{a^*} \sum_{n=1}^{n+1} a_n (-1)^{n+1} \cdot \frac{2 \sin \eta_n \cos \eta_n - \sin \eta_n}{\eta_n^2} \frac{\partial}{\partial z} \exp(-\eta_n^2 F_0) \quad (9)$$

For the value $\varphi = 1$

The integration of Eq. (11) sets the concentration of the adsorbent during the movement of the concentration front depending on the depth of the fixed-bed column z and time τ .

It is obvious that the second and subsequent terms of the sum in Eq. (12) can be neglected, especially since in the dynamics of the process time lasts quite a long time. We performed the calculation only for the first term of the sum according to Eq. (12). It is necessary to determine some parameters included in Eq. (12). The

concentration C_a^* has a dimension of kg/m^3 . In studies of equilibrium, this concentration is given in kg/kg of the adsorbent. The recalculation allowed obtaining the value C_a^* for the conditions of dynamic research equal to 23 kg/m^3 .

The dimensionless length of the fixed bed ω was determined. On average, the liquid filtration rate was estimated by us as the amount of collected liquid in the liquid receiver divided on the time and cross-sectional area of the apparatus.^{24,25} This value on average is $1.02 \cdot 10^{-5} \text{ m/s}$. The porosity of the fixed bed was $\varepsilon = 0.4$.²⁶ The value of the dimensionless layer length ω was equal to:

$$\omega = 15z \quad (13)$$

where z is the depth of the bed, which is variable.

The root of the characteristic equation $\mu_1 = \pi$.

The initial concentration of copper ions in the liquid was $C_0 = 0.2 \text{ kg/m}^3$.

Eq. (12) was used to determine the number Fo for only one case, when $C/C_0 = 0.05$, *i.e.* the value of breakthrough time at which the adsorption process must be completed. The real time of adsorption τ_2 was determined from the Fourier number for two values of the layer depth:

$$z = 7 \text{ cm} \quad \tau_2 = 2900 \text{ s};$$

$$z = 5 \text{ cm} \quad \tau_2 = 2700 \text{ s}.$$

The time to breakthrough consists of two values of time, which are determined from the sum of the formation time of the concentration front and its movement according to Eqs. (6) and (12).

$$z = 7 \text{ cm} \quad \tau_1 + \tau_2 = 3900 \text{ s}$$

$$z = 5 \text{ cm} \quad \tau_1 + \tau_2 = 3700 \text{ s}$$

The convergence of the results of the research presented in Fig. 2, and theoretical data were calculated using Statistica and MS Excell software. The statistical significance of parallel experiments was $p < 0.005$ for both depths of the zeolite bed. The value of the Pearson criterion for the bed depth of 5 cm was $c^2 = 0.91$, the standard deviation of experimental and theoretical data $\delta = 0.1$, the dispersion $D = 0.01$, and for the bed depth of 7 cm $c^2 = 0.85$, standard deviation $\delta = 0.12$, dispersion $D = 0.0144$. The results of statistical analysis of research results showed high reliability of the obtained data.

Comparison of values of adsorption time to breakthrough, determined by the ratio of the values of concentrations to the initial concentration $C/C_0 = 0.05$, calculated according to the presented mathematical model based on the differential equation of molecular diffusion with the boundary condition of the first type, and the real value of adsorption time in experimental

conditions showed their satisfactory coincidence. This allows us to recommend a method for estimating the adsorption time to breakthrough time during the design of adsorption equipment in real conditions.

4. Conclusions

The dynamics of adsorption of copper ions of low concentration on natural zeolite was investigated and the results of experimental research with breakthrough curves were presented. Mathematical models for two stages of adsorption were proposed, namely the formation of the concentration front in the fixed bed and its movement. The boundary conditions of the first type in the mathematical model were proved and used. The adsorption time to breakthrough time: for the bed depth of 5 cm $\tau = 3700 \text{ s}$, for the bed depth of 7 cm $\tau = 3900 \text{ s}$. Comparison of experimental and theoretical data showed the following results: statistical significance of the obtained results was $p < 0.005$, Pearson's criterion $\chi^2 = 0.91-0.85$, standard deviation $\delta = 0.1 \pm 0.097$, dispersion $D = 0.01 \pm 0.0044$. The results of statistical calculation of research results showed a satisfactory convergence of experimental and theoretical data.

References

- [1] Cheng, T.; Chen, C.; Tang, R.; Han, C.-H.; Tian, Y. Competitive Adsorption of Cu, Ni, Pb, and Cd from Aqueous Solution Onto Fly Ash-Based Linde F(K) Zeolite. *IJCCE* **2018**, *37*, 61-72. <https://doi.org/10.30492/IJCCE.2018.31971>.
- [2] Trokhymenko, G.; Gomelya, M. Development of Low Waste Technology of Water Purification from Copper Ions. *Chem. Chem. Technol.* **2017**, *11*, 372-377. <https://doi.org/10.23939/chcht11.03.372>
- [3] Ates, A.; Akgül, G. Modification of Natural Zeolite with NaOH for Removal of Manganese in Drinking Water. *Powder Technol.* **2016**, *287*, 285-291. <https://doi.org/10.1016/j.powtec.2015.10.021>
- [4] Symak, D.; Sabadash, V.; Gumnitsky, J.; Hnativ, Z. Kinetic Regularities and Mathematical Modelling of Potassium Chloride Dissolution. *Chem. Chem. Technol.* **2021**, *15*, 148-152. <https://doi.org/10.23939/chcht15.01.148>
- [5] Kithome, M.; Paul, J.W.; Lavkulich, L.M.; Bomke, A.A. Effect of pH on Ammonium Adsorption by Natural Zeolite Clinoptilolite. *Commun Soil Sci Plant Anal.* **1999**, *30*, 1417-1430.
- [6] Naidu, H.; Mathews, A.P. Linear Driving Force Analysis of Adsorption Dynamics in Stratified Fixed-Bed Adsorbers. *Sep. Purif. Technol.* **2021**, *257*, 117955. <https://doi.org/10.1016/j.seppur.2020.117955>
- [7] Lee, K.-Y.; Park, M.; Kim, J.; Oh, M.; Lee, E.-H. Equilibrium, Kinetic and Thermodynamic Study of Cesium Adsorption onto Nanocrystalline Mordenite from High-Salt Solution. *Chemosphere*

2016, 150, 765-771.

<https://doi.org/10.1016/j.chemosphere.2015.11.072>

- [8] Sabadash, V.; Gumnitsky, J.; Lyuta, O.; Pochapska, I. Thermodynamics of (NH₄⁺) Cation Adsorption under Static Conditions. *Chem. Chem. Technol.* **2018**, *12*, 143-146. <https://doi.org/10.23939/chcht12.02.143>
- [9] Wang, Z.; Tan, K.; Cai, J.; Hou, S.; Wang, Y.; Jiang, P.; Liang, M. Silica Oxide Encapsulated Natural Zeolite for High Efficiency Removal of Low Concentration Heavy Metals in Water. *Colloids Surf. A Physicochem. Eng. Asp.* **2019**, *561*, 388-394. <https://doi.org/10.1016/j.colsurfa.2018.10.065>
- [10] Gumnitsky, J.M.; Sabadash, V.V. Mathematical Model of Adsorption Dynamics in a Column-Type Apparatus. 6th International Scientific and Practical Conference "Computer Modeling in Chemistry, Technologies and Systems of Sustainable Development – ChTCTST-2018", Kyiv, Ukraine, 2018. (in Ukrainian).
- [11] Li, H.; Wang, F.; Li, J.; Deng, S.; Zhang, S. Adsorption of Three Pesticides on Polyethylene Microplastics in Aqueous Solutions: Kinetics, Isotherms, Thermodynamics, and Molecular Dynamics Simulation. *Chemosphere* **2021**, *264*, 128556. <https://doi.org/10.1016/j.chemosphere.2020.128556>
- [12] Salih, A.M.; Williams, C.; Khanaqa, P.A. Heavy Metal Removals from Industrial Wastewater Using Modified Zeolite: Study the Effect of Pre-Treatment. *Journal of Garmian University* **2019**, *6*, 406-416. <https://doi.org/10.24271/garmian.196233>
- [13] Dignos, E.C.G.; Gabejan, K.E.A.; Olegario-Sanchez, E.M.; Mendoza, H.D. The Comparison of the Alkali-Treated and Acid-Treated Naturally Mined Philippine Zeolite for Adsorption of Heavy Metals in Highly Polluted Waters. *IOP Conference Series: Materials Science and Engineering* **2019**, *478*, 012030.
- [14] Esmaeili, A.; Mobini, M.; Eslami, H. Removal of Heavy Metals from Acid Mine Drainage by Native Natural Clay Minerals, Batch and Continuous Studies. *Appl. Water Sci.* **2019**, *9*, 97. <https://doi.org/10.1007/s13201-019-0977-x>
- [15] Sabadash, V.; Mylanyk, O.; Matsuska, O.; Gumnitsky, J. Kinetic Regularities of Copper Ions Adsorption by Natural Zeolite. *Chem. Chem. Technol.* **2017**, *11*, 459-462. <https://doi.org/10.23939/chcht11.04.459>
- [16] Hyvlud, A.; Sabadash, V.; Gumnitsky, J.; Ripak, N. Statics and Kinetics of Albumin Adsorption by Natural Zeolite. *Chem. Chem. Technol.* **2019**, *13*, 95-100. <https://doi.org/10.23939/chcht13.01.095>
- [17] Mahmoodi, N.M.; Saffar-Dastgerdi, M.H. Zeolite Nanoparticle as a Superior Adsorbent with High Capacity: Synthesis, Surface Modification and Pollutant Adsorption Ability from Wastewater. *Microchem. J.* **2019**, *145*, 74-83. <https://doi.org/10.1016/j.microc.2018.10.018>
- [18] Symak, D.M.; Lyuta, O.V. Nestatsionarny process rozchynennya sharu zernystogo material. *Bulletin of Lviv Polytechnic National University: Chemistry, technology of substances and their application* **2015**, *812*, 308-312. (in Ukrainian).
- [19] Symak, D.M.; Sklabinsky, V.I. Extraction of Soluble Components from Porous Inert Parts. *Scientific Bulletin of UNFU* **2018**, *28*, 70-73. (in Ukrainian).
- [20] Zasadko, I.; Polutrenko, M.; Mandryk, O.; Stakhmych, Y.; Petroschchuk, N. Complex Technology of Sewage Purification from Heavy-Metal Ions by Natural Adsorbents and Utilization of Sewage Sludge. *J. Ecol. Eng.* **2019**, *20*, 209-216. <https://doi.org/10.12911/22998993/105576>

- [21] Bolisetty, S.; Peydayesh, M.; Mezzenga, R. Sustainable Technologies for Water Purification from Heavy Metals: Review and Analysis. *Chem. Soc. Rev.* **2019**, *48*, 463-487. <https://doi.org/10.1039/C8CS00493E>
- [22] Edebali, S.; Pehlivan, E. Evaluation of Chelate and Cation Exchange Resins to Remove Copper Ions. *Powder Technol.* **2016**, *301*, 520-525. <https://doi.org/10.1016/j.powtec.2016.06.011>
- [23] Sabadash, V.; Gumnitsky, J.; Mylianyk, O.; Romaniuk, L. Concurrent Sorption of Copper and Chromium Cations by Natural Zeolite. *Environmental problems* **2017**, *2*, 33-36. http://nbuv.gov.ua/UJRN/envpr_2017_2_1_9
- [24] Sabadash, V.; Gumnitsky, J.; Lyuta, O. Combined Adsorption of the Copper and Chromium Cations by Clinoptilolite of the Sokyrnytsya Deposit. *J. Ecol. Eng.* **2020**, *21*, 42-46. <https://doi.org/10.12911/22998993/122185>
- [25] Romankov, P.; Frolov, V.; Flisyuk, O. *Massoobmennyye protsessy khimicheskoy tekhnologii*; Khimizdat: Sankt-Peterburg, 2017.
- [26] Atamanyuk, V.; Huzova, I.; Gnativ, Z. Intensification of Drying Process During Activated Carbon Regeneration. *Chem. Chem. Technol.* **2018**, *12*, 263-271. <https://doi.org/10.23939/chcht12.02.26>

Received: March 1, 2021 / Revised: April 10, 2021 /

Accepted: April 24, 2021

ДИНАМІКА АДСОРБЦІЇ ЙОНІВ КУПРУМУ У НЕРУХОМОМУ ШАРІ АДСОРБЕНТА ТА МАТЕМАТИЧНА ІНТЕРПРЕТАЦІЯ ПЕРШОЇ СТАДІЇ ПРОЦЕСУ

Анотація. Експериментально досліджено динаміку процесу адсорбції у нерухомому шарі адсорбенту на прикладі системи природний цеоліт – водний розчин солі купруму низьких концентрацій, які характерні для процесів очищення стічних вод від токсичних забруднень. Побудовано вихідні криві процесу адсорбції для висоти шару сорбенту 5 та 7 см. Рівновагу таких процесів можна описати лінійним рівнянням Генрі. Процес адсорбції у шарі складається з двох стадій, які розглянуто у дослідженні. Перша стадія полягає у формуванні фронту концентрацій, друга – у переміщенні фронту. Сума часу першої та другої стадій становлять загальний час адсорбції, який визначається до проскоку. Перша стадія адсорбції математично сформульована диференціальним рівнянням молекулярної дифузії з граничною умовою першого роду. Друга стадія доповнена балансовим рівнянням, що враховує не лише зміну концентрації у часі, але і по вертикальній координаті та визначає час переміщення фронту концентрацій до проскоку. Розроблено математичну модель процесу адсорбції у нерухомому шарі сорбенту. Порівняно експериментальні дані та теоретичні розрахунки. Результати статистичного розрахунку результатів досліджень показали задовільну збіжність експериментальних та теоретичних даних.

Ключові слова: адсорбція, нерухомий шар, динаміка, проскок, стадії адсорбції, математична модель.