KINETIC REGULARITIES OF COPPER IONS ADSORPTION BY NATURAL ZEOLITE

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Abstract. The kinetics of copper ions adsorption by natural zeolite has been investigated in the apparatus with mechanical stirrer. The presence of external diffusion and pore diffusion area was established. For the external diffusive area, the dependence of mass transfer coefficient on stirrer rotation speed was confirmed; the dependence was described using a criterial equation. For the pore diffusion area, the equation is adduced by means of which the effective coefficient of pore diffusion was calculated.

Keywords: adsorption, copper, zeolite, kinetics, stirring, external diffusion, pore diffusion.

1. Introduction

Adsorption processes are used for the industry and environment friendly technologies: improvement of water quality, waste water purification, and noxious gases adsorption. The synthetic adsorbents are expensive and therefore the natural ones like different zeolites, glues, silica, phosphates, *etc.* are of special interest. [1]. The adsorbent is selected according to its sorption and regeneration ability, accessibility and price. Natural zeolites, the resources of which are considerable in Ukraine, are most widely used.

The problem of copper ions adsorption is urgent for purification of waste water from the plants using copper compounds, primarily galvanic plants. Waste water with heavy metals, including copper compounds, contaminates environment and reduces reserves of fresh water. Environmental protection requires to increase the efficiency of waste water purification and its recycling.

Taking into account the toxicity of copper compounds, it is very important to purify waste water from them. Copper ions, like ions of other heavy metals, are absorbed by phytoplankton and passed to people by food chain. The demands for water quality are defined by boundary permissible concentration of contaminants in water. For potable water the copper permissible concentration is 1.0 mg/dm^3; for the ponds of fish farms – 0.001 mg/dm^3 [1].

Nowadays, natural zeolites are widely used to purify waste water. Zeolites are effective adsorbents for a series of raw metals, including copper [2, 3]. Their advantages are high selectivity, cation-exchange properties, relatively low cost, and accessibility.

The investigation of heavy metal adsorption by natural sorbents involves studying sorption ability, construction of adsorption isotherms and equation describing the process statics, studying kinetic regularities, sorption dynamics in the sorbent layer and sorbent recycling.

The statics of heavy metals adsorption over natural zeolites was investigated by several authors [4-6]. Zhao *et al*. [7] studied simultaneous sorption of copper and nickel ions over zeolites and determined their static activity.

Kinetic regularities of copper ions adsorption by natural zeolite are described in [8-10]. The experiments were carried out in the apparatus with a mechanical stirrer. Two adsorption areas were determined: external diffusion and pore diffusion areas. For external diffusion area the mass transfer coefficients were determined, as well as their increase with the increase in rotation speed of the stirrer. The simulation of adsorption process over natural zeolite is described in [11-12]. O. Sydorczuk [13] investigated the problem of zeolites with adsorbed heavy metals usage.

It is obvious from above-mentioned that adsorption kinetics, especially pore diffusion area, was investigated insufficiently; the pore diffusions coefficients were not determined. Therefore, this problem is the main task of the present investigation.

2. Experimental

We determined the kinetic regularities of Cu^{2+} ions absorption by clinoptylolite type zeolite. The experiments were carried out in the apparatus equipped with a stirrer.

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The zeolite composition determined by XRF is given in [14]. 0.5 dm^3 of CuSO$_4$ with the initial concentration of Cu^{2+} 0.9149 g/dm^3 and 30 g of clinoptylolite were placed in a vessel ($V = 1$ dm^3). The initial solution pH was 2.2. The paddle stirrer with $D = 0.05$ m and $h = 0.02$ m was used. The stirrer operation was provided by electric motor, number of revolutions was determined by tachometer. The experimental range of revolutions ($n = 150$–600 rpm) provides the contact of the solid particles with liquid. The experimental temperature was 293±0.5 K.

After the finishing of stirring the samples were analyzed for the content of copper ions using photometric method. The results were averaged relative to three samples.

3. Results and Discussion

3.1. Analysis of Adsorption Kinetics and Determination of Kinetic Coefficients

The results represented in Fig. 1 allow to determine peculiarities of copper ions adsorption by natural zeolite.
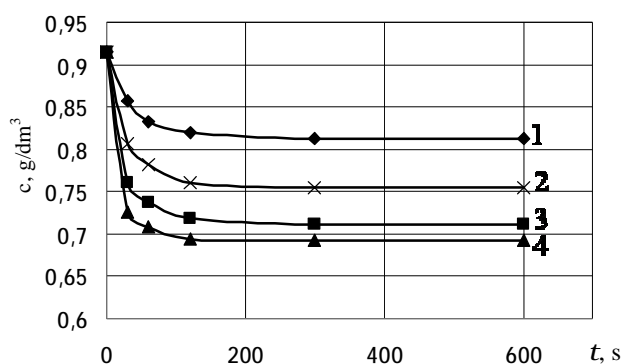

Fig. 1. Cu^{2+} concentration *vs*. adsorption time at different rpm: 150 (1); 250 (2); 350 (3) and 450 (4)

The presence of external diffusion area is confirmed by dependence of copper concentration change on mixer rpm. Maximal intensity of adsorption is achieved at $n = 450$ rpm. The increase in revolutions number to 600 rpm does not affect the copper concentration. The mechanical stirring allows to intensify only external diffusion, which takes place at the beginning of adsorption. One can see from Fig. 1 that at adsorption time of 30 s the copper concentration is sharply changed, that confirms the mechanism of external diffusion. Then the concentration curves become flat and parallel indicating concentration independence on stirring; it is typical of pore diffusion area.

External diffusion area is characterized by the mass transfer coefficient which is the weight of compound diffused to the zeolite surface per time unit at its different concentrations in the liquid and over adsorbent surface. It is defined from the main equation of mass transfer (1):

$$b = \frac{\Delta M}{F \cdot (\overline{c} - \overline{c}_s) \cdot \Delta t} \tag{1}$$

where ΔM – weight of copper ions adsorbed by external surface of zeolite, g; Δt – time of sampling, s; $\overline{c}$ – average concentration of copper ions in liquid, g/dm^3; $\overline{c}_s$ – average concentration of copper ions in a near-surface layer of liquid which is in equilibrium with adsorption layer over adsorbent surface, g/dm^3; F – external surface of the adsorbent, dm^3.

ΔM was determined according to the material balance for the first 30 s of the experiment.

$$\Delta M = V\left(c_{in} - c_{30}\right) \tag{2}$$

where V – liquid volume in the apparatus, $V = 0.5$ dm^3; c_{in} – initial concentration of copper ions in the solution, $c_{in} = 0.9149$ g/dm^3; c_{30} – concentration of copper ions in the solution for 30 s.

Dividing ΔM by adsorbent weight (30 g) we get copper ions concentration in adsorption phase, g/g$_{ads}$:

$$a = \frac{\Delta M}{30} \tag{3}$$

We assume that for the first 30 s the component is located over the external surface of the adsorbent which is in equilibrium with near-surface layer of liquid. The concentration of near-surface layer (c_l) is determined by equilibrium isotherm [6] for each separate experiment. The values of average concentration in Eq. (1) were determined as follows:

$$\overline{c} = \frac{c_{in} + c_{30}}{2}; \quad \overline{c}_s = \frac{0 + c_l}{2} \tag{4}$$

Mass transfer coefficients which were calculated according to Eq. (1) are presented in Table.

Calculated values of mass transfer coefficient

n, rpm	b, m/s
150	$2.6 \cdot 10^{-5}$
250	$6.05 \cdot 10^{-5}$
350	$9.55 \cdot 10^{-5}$
450	$1.14 \cdot 10^{-4}$

In the heat-and-mass transfer theory the experimental results are represented by generalized variables – similarity criteria. The mass transfer coefficient in dimensionless form is represented by Sherwood number (Sh), and hydrodynamics – by Reynolds number (Re). Their dependence is expressed by (4):

$$Sh = f(Re) \tag{4}$$

where $Sh = \dfrac{b \cdot d}{D}$; $Re = \dfrac{r \cdot n \cdot d_m^2}{m}$; r – liquid density, kg/m^3; m – coefficient of dynamic viscosity, Pa·s; D – coefficient of copper ions molecular diffusion in water, m^2/s.

The experimental results represented by dimensionless criteria (Fig. 2) are satisfactorily described by Eq. (5):

$$Sh = 0.017Re - 38.6 \qquad (5)$$

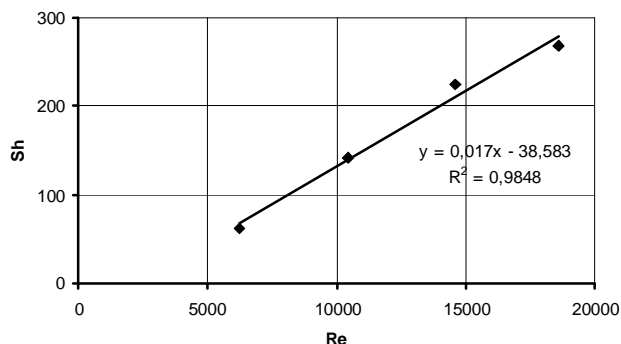which is correct within the range $6000 < Re < 20000$.

Fig. 2. Sherwood number *vs.* Reynolds number

The next step in kinetics research is studying pore diffusion of copper ions in adsorbent grains. The possible mechanism is only molecular diffusion, which occurs due to the gradient of copper ions concentration on the surface of adsorbent grain and inside it. The rate of external surface saturation by adsorbate is considerably higher compared with that of diffusion (Fig. 1). So, we may consider the concentration of copper ions to be constant. The experiments were carried out for low concentrations of copper ions in the liquid phase,s that is typical for waste water with low concentrations of contaminant. For the area of low concentrations, the adsorption isotherm may be approximated with linear dependence (6):

$$a^* = 0.0119c \qquad (6)$$

where a^* – concentration of copper ions in adsorbent grain (g/g$_{ads}$) which is in equilibrium with the concentration c (g/dm^3) in the liquid phase.

Pore diffusion process is described by differential equation of the molecular diffusion, which for the ball-shaped particles takes a form:

$$\frac{\partial c_A}{\partial t} = D^*\left(\frac{\partial^2 c_A}{\partial r^2} + \frac{2}{r}\frac{\partial c_A}{\partial r}\right) \qquad (7)$$

where c_A – concentration of copper ions in the adsorbent grain on running radius r, g/dm^3; t – time, s; D^* – effective coefficient of pore diffusion, m^2/s.

The differential equation (7) is supplemented with initial and boundary conditions:

$$c_A(r, t=0) = 0 \qquad (8)$$

$$c_A(r=R, t) = c_{AR} = const \qquad (9)$$

Boundary condition (9) means the constant concentration of copper ions on external surface of the adsorbent grain. This Dirichlet boundary condition simplifies the solution of Eq. (7). Average concentration of copper ions in zeolite grain $\bar{c}_A$ is related to running concentration c_A:

$$\bar{c}_A = \frac{3}{R}\int_0^R r^2 \cdot c_A \cdot dr \qquad (10)$$

The solution of Eq. (10) takes a form:

$$\frac{\bar{c}_A}{\bar{c}_{AE}} = 1 - \sum_{n=1}^{\infty}\frac{6}{p^2 n^2}\exp\left(-p^2 n^2 \frac{D^* t}{R^2}\right) \qquad (11)$$

where $\bar{c}_{AE}$ – volumetric concentration in the grain which is equilibrium with the concentration in liquid, kg/m$^3_{ads}$.

The relation between concentration in liquid c and volumetric concentration in the grain $\bar{c}_A$ is described by Eq. (12):

$$V(c_n - c) = \frac{m}{r_s}(\bar{c}_A - c) \qquad (12)$$

Defining $\bar{c}_A$ and $\bar{c}_{AE}$ from Eq. (12) the dependence (11) can be rewritten in the form that allows direct use of experimental results

$$\frac{c_n - c}{c_n - c_p} = 1 - \sum_{n=1}^{\infty}\frac{6}{p^2 n^2}\exp\left(-p^2 n^2 \frac{D^* t}{R^2}\right) \qquad (13)$$

Presenting Eq. (13) in the logarithmic form for the first member of the sum we obtain:

$$\ln\left(1 - \frac{c_n - c}{c_n - c_p}\right) = \ln\frac{6}{p^2} - p^2\frac{D^* t}{R^2} \qquad (14)$$

the construction of which in the co-ordinates $\ln\left(1 - \dfrac{c_n - c}{c_n - c_p}\right) = f(t)$ gives a straight line. The effective coefficient of pore diffusion D^* is defined from its slope angle.

The calculation of effective coefficient of pore diffusion for the experimental data ($n = 450$ rpm, Fig. 3), corresponding to the maximum intensification of external diffusion, allows to define the coefficient of pore diffusion. It was found to be $2.194 \cdot 10^{-10}$ m^2/s. For other values of n the logarithmic dependencies (Eq. (14)) are parallel indicating the identical values of slope angle and values of effective coefficients.

4. Conclusions

Copper ions adsorption by natural zeolite is characterized by two adsorption areas, namely external

and pore diffusion areas. Mechanical stirring accelerates the external diffusion. The increase in mass transfer coefficient with the increase in rpm value confirms this fact. The dependence was described by criterial equation. The mathematical model of pore diffusion adsorption was developed and coefficient of pore diffusion was defined. Low coefficients indicate low rates of adsorption during pore diffusion.
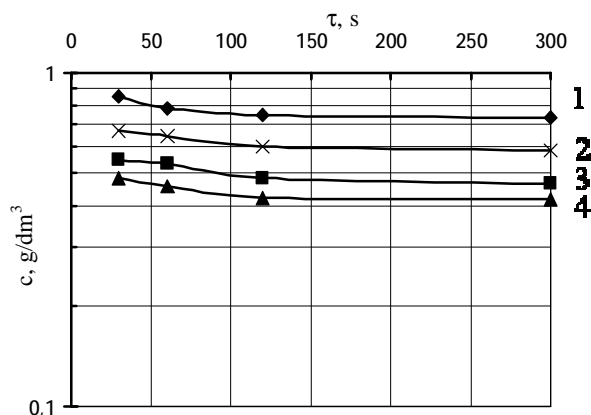

Fig. 3. Dependence $\ln\left(1 - \dfrac{c_n - c}{c_n - c_p}\right) = f(t)$ at different rpm:
150 (1); 250 (2); 350 (3) and 450 (4)

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КІНЕТИЧНІ ЗАКОНОМІРНОСТІ АДСОРБЦІЇ ЙОНІВ КУПРУМУ ПРИРОДНИМ ЦЕОЛІТОМ

Анотація. *Експериментально досліджено кінетику адсорбції йонів купруму природним цеолітом в апараті з механічним перемішуванням. Встановлено наявність двох областей поглинання: зовнішньодифузійної та внутрішньо-дифузійної. Для зовнішньодифузійної області підтверджено залежність коефіцієнта масовіддачі від числа обертів мішалки та описано цю залежність критеріальним рівнянням. Для внутрішньодифузійної області наведено рівняння, за допомогою якого визначено ефективний коефіцієнт внутрішньої дифузії.*

Ключові слова: адсорбція, купрум, цеоліт, кінетика, перемішування, зовнішня дифузія, внутрішня дифузія.