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SIMULATION OF ION EXCHANGE INTERACTION KINETICS IN THE CLINOPTYLOLITE – AMMONIUM ION SYSTEM

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Abstract. The kinetics of adsorption of ammonium ions under dynamic conditions has been studied. A mathematical model of the process was built. The mass transfer coefficient was calculated depending on the intensity of the change of location. It was established that ion exchange occurs in external and internal diffusion regions. The rate constants of ion exchange for the region of external and internal diffusion were calculated.

Keywords: adsorption, ion exchange, kinetics, ammonium, zeolite.

1. Introduction

Nowadays, in most countries, the removal of ammonium ions from effluents has become almost a necessity. Ion exchange technologies are widely used to extract ammonium ions from wastewater (Wijesinghe et al., 2018). For this purpose, synthetic ion-exchange resins and various types of zeolites are used (Stelwagen et al., 2020). Possibilities of application of the ion-exchange method for nitrogen reduction are indicated (de Haro Martí et al., 2020). Particularly dangerous to humans, animals and plants are Nitrogen compounds, which can accumulate in surface and groundwater, as well as in the air. The literature states that the concentration of ammonium nitrogen in the effluents of meat processing plants significantly exceeds their maximum allowable concentration (MPCNH_4^+ <1.1 mg * eq / l) (Lin í et al., 2016), so, before discharge from the plant, wastewater requires mandatory treatment (Stelwagen et al., 2020). There are many methods of industrial wastewater treatment to reduce the load on natural waters (Bernal et al., 1993). Considering that large volumes of wastewater are subject to treatment, the use of natural sorbents is most economically feasible (Karamanlis et al., 2008). Therefore, zeolite, the main component of which was clinoptilolite in the Na - form, was used in the research. The statics and kinetics of ammonium ions of sorption on this sorbent in the range of low concentrations as well as the influence of concomitant effluent contaminants on the absorption processes of NH_4^+ ions were studied. Properties of the model solutions were identical to the wastewater from meat plants (Soudejani et al., 2019).

The results of studies of ammonium ions sorption equilibrium from solutions simulating the wastewater of meat processing plants have shown that clinoptilolite effectively removes this contaminant component from the solutions. The study of the adsorption capacity of clinoptilolite to ammonium ions in the presence of other components of the solution, namely phosphates and protein fractions, indicates a decrease in the exchange capacity of zeolite due to its competition for active absorption centres (Sabadash et al., 2018). Previous studies have shown that natural zeolites, especially clinoptilolite, can be effectively used to remove ammonium ions (Sabadash et al., 2018; Sabadash et al., 2020).

The work aims to establish the theoretical regularities of the process of ion exchange absorption of ammonium by natural zeolite under conditions of mechanical mixing.

2. Experimental researches

To study the adsorption kinetics of zeolite concerning phosphates, 0.2 dm^3 of a solution containing

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ammonium ions was added to a 1 dm^3 polyethylene container. The test solution was prepared in distilled water with an initial concentration of 0.5 mg/l, and 5 g of zeolite were added. The kinetics of ammonium adsorption was investigated on an installation that included an apparatus with a propeller-type stirrer. To carry out adsorption under dynamic conditions the stirrer was set to a given speed n = 100…500 rpm. Samples were analyzed for NH_4^+ content by a photometric method according to known methods (Sabadash et al., 2020). Studies have shown that the adsorption process takes place in the intra-diffusion region as evidenced by the establishment of the equilibrium of the process to reach the equilibrium value of $a\infty$. we present experimental data in Fig. 1.

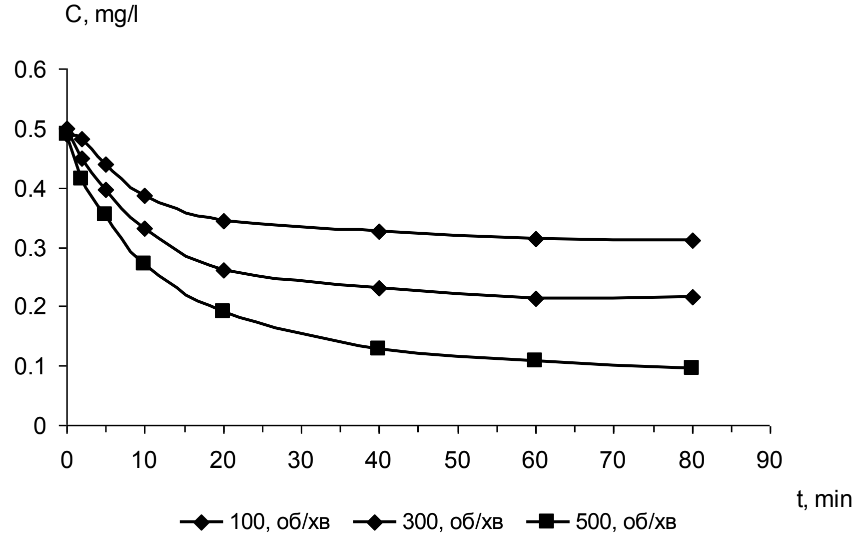

Fig. 1. Kinetics of $NH_4{}^+$ adsorption from model solutions

3. Results and their interpretation

Simulations of the process of absorption of the active component by a granular sorbent describe non-stationary diffusion-kinetic processes in multi-component distributed systems (Hyvlud et al., 2019).

To describe the mechanisms of absorption of ammonium from solutions, the following stages of the process were considered:

– diffusion of ammonium ion from the solution to the surface of the ion exchanger;

– diffusion of ammonium ion from the surface of the resin to the point of the reaction;

– ion exchange accompanied by a chemical reaction;

– diffusion of the exchange ion of the zeolite from the reaction site to the surface of the ion exchanger;

– diffusion of zeolite exchange ion from the surface of clinoptilolite into solution.

The quantitative ratio of the reaction system is described by the equations:

Material balance of ammonium ion:

$$V_{p(NH_4^+)} \cdot C_{0(NH_4^+)} = \frac{4}{3}\pi r_0^3 \varepsilon \rho_z \overline{C}_{NH_4^+} + V_{p(NH_4^+)} \cdot C_{(NH_4^+)}, \quad (1)$$

material balance of exchangeable cations:

$$V_{p(Kat^+)} \cdot C_{0(K^+)} = \frac{4}{3}\pi r_0^3 \varepsilon \rho_z \overline{C}_{Kat^+} + V_{p(Kat^+)} \cdot C_{(Kat^+)}, \quad (2)$$

where: C_0 is the initial concentration of the corresponding cation, mg / l; $\overline{C}$ is the average concentration of the corresponding cation in the zeolite grain, mg / l; V is the volume of the liquid phase, m^3: ε is clinoptilolite porosity, m^3/m^3; ρ is sorbent density; r is running radius of the adsorbent grain; τ is time, s;

Diffusion of exchangeable cations from solution to the surface of the zeolite takes place by the mechanism of mass transfer.

Mass flow: $j_{NH_4^+} = -D\frac{dC_{NH_4^+}}{dn}$, that is:

$$\frac{dM_{NH_4^+}}{d\tau} = -\beta F\left(C_{NH_4^+} - C^0{}_{NH_4^+}\right), \quad (3)$$

where β is the mass transfer coefficient from the solution to the surface of the adsorbent, m/s; F is the area, m^2

The values of the mass transfer coefficients according to Fig. 1 are given in Table. 1

Table 1

Dependence of mass transfer coefficients β on the number of revolutions n

Number of revolutions, n, rpm.	Mass transfer coefficient $\beta,\ m/s$
100	$8.06 \cdot 10^{-5}$
300	$1.04 \cdot 10^{-4}$
500	$1.19 \cdot 10^{-4}$

The mechanism of the component diffusion from the solution to the reaction site was described by the equation:

$$\frac{dM_{NH_4^+}}{d\tau} = -\frac{D}{r}F\left(\overline{C}_{NH_4^+} - C_{NH_4^+}\right), \qquad (4)$$

where $F = 2\pi d_p r\varepsilon$; *D is* diffusion coefficient inside the adsorbent, m^2/s; d_p is pore diameter, м; *r* is running radius of the adsorbent grain, m; τ is time, s;

The average concentration in the zeolite grain:

$$\overline{C}_{NH_4^+} = \frac{4}{3}\frac{C_{NH_4^+} - C^0{}_{NH_4^+}}{2}\frac{V}{\pi r^3 \varepsilon n}, \qquad (5)$$

where $\frac{3}{4}\pi r^3\varepsilon$ is zeolite pore volume; *n* is the number of sorbent grains per unit volume; $\frac{4}{3}\frac{V}{\pi r^3\varepsilon n} = k$.

Substituting (5) into (4) we obtain:

$$\frac{dM_{NH_4^+}}{d\tau} = -\frac{D}{r}F\left(k\frac{C_{NH_4^+} - C^0{}_{NH_4^+}}{2} - C_{NH_4^+}\right) = -D\cdot 4\pi d_p\varepsilon\left(k\left(C_{NH_4^+} - C^0{}_{NH_4^+}\right) - 2C_{NH_4^+}\right) =$$
$$= -D\cdot 4\pi d_p\varepsilon\left(C_{NH_4^+}\left(k-2\right) - kC^0{}_{NH_4^+}\right) \qquad (6)$$

Since the volume of the liquid phase significantly exceeds the pore volume of the zeolite, replace (k-2) with k, then (6) will take the form:

$$\frac{dM_{NH_4^+}}{d\tau} = -4D\pi d_p\varepsilon k\left(C_{NH_4^+} - C^0{}_{NH_4^+}\right) \qquad \mathbf{(7)}$$

The resulting equation makes it possible to estimate the change in the concentration of ammonium over time in the volume of the reaction mixture. Thus, the total amount of absorbed substance due to adsorption and ion exchange will be taken into account.

The third stage of ammonium uptake is described by the mechanism of ion exchange:

$$Z - Kat^+ + NH_4^+ \rightarrow Z - NH_4^+ + Kat^+ \qquad (8)$$

The actual ion exchange mechanism will be estimated by the number of Kat + exchange cations entering the solution from the volume of zeolite.

Since the reaction is of the second order, the rate of ion exchange is described by the following equation:

$$-\frac{dC}{d\tau} = kC_{NH_4^+}C_{Kat^+} \qquad (9)$$

After a period of time τ, x moles of NH_4^+ reacted and x moles of Kat $^+$ were released.

$$C_{NH_4^+} = \frac{m^0{}_{NH_4^+} - x}{V};\ C_{K^+} = \frac{m^0{}_{z-Kat^+} - x}{V}$$

$$-\frac{dC}{d\tau} = \frac{1}{V}\frac{dx}{d\tau};\rightarrow \frac{dx}{d\tau} = k\left(m^0{}_{NH_4^+} - x\right)\cdot\left(m^0{}_{z-Kat^+} - x\right)$$

$$kd\tau = \frac{dx}{\left(m^0{}_{z-Kat^+} - x\right)\left(m^0{}_{NH_4^+} - x\right)} \qquad (10)$$

Integrating this equation we obtain:

$$k = \frac{1}{\tau\left(m^0{}_{NH_4^+} - x\right)\cdot\left(m^0{}_{z-Kat^+} - x\right)}\ln\frac{m^0{}_{z-Kat^+}\left(m^0{}_{NH_4^+} - x\right)\cdot}{m^0{}_{NH_4^+}\left(m^0{}_{z-Kat^+} - x\right)} \qquad (11)$$

Rewrite the equation as:

$$\ln\frac{m^0{}_{z-Kat^+}\left(m^0{}_{NH_4^+} - x\right)\cdot}{m^0{}_{NH_4^+}\left(m^0{}_{z-Kat^+} - x\right)}\left(m^0{}_{NH_4^+} - x\right)\cdot\left(m^0{}_{z-Kat^+} - x\right) = k\tau \qquad (12)$$

Let’s rewrite the equation as follows $x \equiv m_{Kat^+} \equiv a^*_{NH_4^+ ex}\cdot m_{ads}$

where $a^*_{NH_4^+ ex}\cdot m_{ads}$ – the amount of ammonium reacted as a result of ion exchange, mg-eq / g.ads; m_{ads} – mass of adsorbent, g.

Let’s mark:

$$\ln\frac{m^0{}_{z-Kat^+}\left(m^0{}_{NH_4^+} - x\right)\cdot}{m^0{}_{NH_4^+}\left(m^0{}_{z-Kat^+} - x\right)}\left(m^0{}_{NH_4^+} - x\right)\cdot\left(m^0{}_{z-Kat^+} - x\right) = A_{\text{ex}},$$

we will receive:

$$A_{ex} = k\tau \qquad (13)$$

However, the real process of adsorption of ammonium ions under dynamic conditions includes not only ion exchange, but can also take place in the external and internal diffusion regions. If x is expressed in terms of the mass of absorbed ammonium ion at time τ, then the calculated dependence will not pass through 0 due to the fact that part of the ammonium can be absorbed due to physical adsorption. Therefore, we introduce the correction factor b_0 into equation (13).

$$A_{ex} = k\tau + b_0 \qquad (14)$$

b_0 is a factor that takes into account the mass of the adsorbate absorbed by the mechanism of physical adsorption. And for a line constructed for internal diffusion adsorption, this value will correspond to the amount of adsorbate and exchange cations that participated in the first stage of the process.

Representing (14) in the form of a graph $A_{ex=} = f\left(\tau\right)$, we obtain:

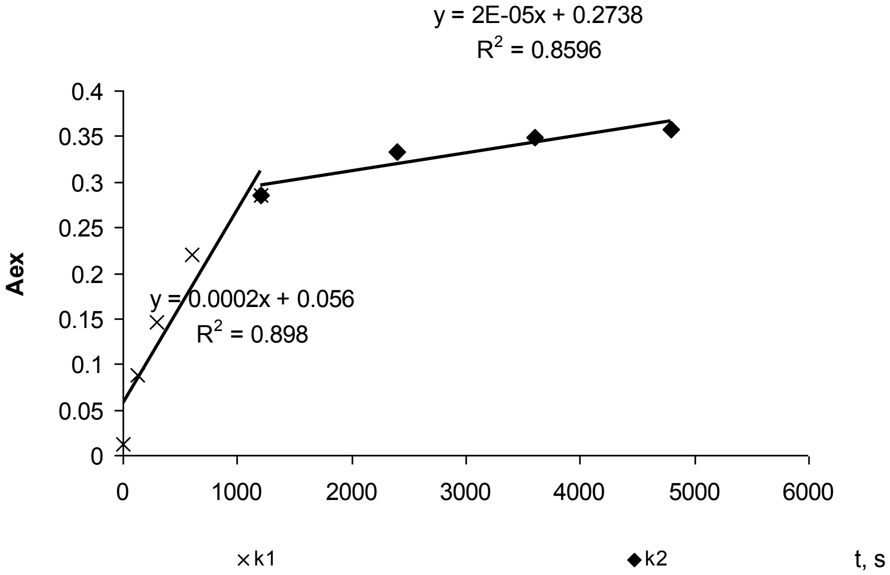

Fig. 2. Calculation of the rate constant of the reaction of ion exchange adsorption of ammonium ions by natural zeolite in the apparatus with a stirrer for n = 500 rpm

Fig. 2 presents a graphical interpretation of the experimental adsorption data to equation 12.

Since in Fig. 2 the areas of external and internal diffusion were selected, the rate constants for these two areas were calculated separately.

The angular coefficient of the obtained curves corresponded to the rate constant of reactions. However, none of the lines passed through 0 because we did not subtract the amount of the component that had already been adsorbed from the solution. Thus, at the first stage of external diffusion adsorption, the rate constant was $k_1 = 2 \cdot 10^{-4}$ $[m^{-1} \cdot s^{-1}]$. In the second stage of intradiffusion adsorption, the rate constant was $k_2=2 \cdot 10^{-5}$ $[m^{-1} \cdot s^{-1}]$.

4. Conclusions

The paper presents experimental data on the kinetics of adsorption of ammonium ions by natural zeolite under conditions of mechanical stirring in an apparatus with a stirrer. It is established that the process proceeds in two stages. The results of the calculation of the rate constants of chemical reactions showed that in the intrafusion region the rate of ion exchange decreases by an order of magnitude. Thus, the implementation of the process in dynamic conditions is appropriate in the field of external diffusion. The duration of the process should not exceed 20 minutes.

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