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EXTRANEOUS DIFFUSION KINETICS OF AMMONIUM IONS ADSORPTION IN THE PRESENCE OF OTHER IONS

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Abtract. The article presents the results of the study of the kinetics of ions adsorption from multi-component mixtures. The isotherms of sorption of ammonium nitrogen in the presence of phosphates indicate a decrease in the exchange capacity of zeolite due to its competition for active absorption centres. This study was carried out with two ions of inorganic nature. In the presence of the third organic component in the solution (protein substance – albumin), the sorption capacity of zeolite decreases even more in comparison with ammonium ions. It was found that in the presence of phosphates, the equilibrium capacity of zeolite towards ammonium decreases by about 30 %; in the three-component system the reduction reaches about 70 %.

Keywords: adsorption, sorbents, wastewaters, ammonium ions, albumin, phosphates.

1. Introduction

The intensive development of industry, agriculture, energy, transport and utilities is accompanied by the consumption of considerable quantities of water, the quality of which must meet certain standards. Depending on the purpose of use, water quality indicators are divided into certain categories, depending on the signs of harmfulness (Wu et al., 2019). Before being discharged into natural waters, wastewater must meet certain criteria for the concentration of the chemical, mineral and organic compounds, biological pollutants and suspended solids. Discharge of polluted wastewater into natural waters has resulted in the fact that currently, all surface waters in Ukraine are close to the water quality class IV–V in terms of pollutant content, which is designated as polluted and very polluted (Muscarella et al., 2021; de Haro Martí et al., 2020). This leads to the catastrophic deterioration of ecosystems in water bodies. Agricultural livestock complexes and facilities for processing meat and dairy products are among the most important polluters. The processing of agricultural raw materials is accompanied by the consumption of a considerable amount of water, which, after its industrial use, is enriched with organic substances, as well as a number of biogenic elements, mainly nitrogen and phosphorus compounds (Lin et al., 2016; Bernal et al., 1993). The input of these elements into water bodies leads to eutrophication. Due to the rapid development of vegetation, the oxygen dissolved in water decreases sharply, the process of self-purification is disturbed, which leads to the death of aerobic flora and fauna (Sabadash et al., 2020). Especially dangerous for humans, animals and plants are nitrogen compounds, which can accumulate in surface and ground waters, as well as in the air (Soudejani et al., 2019; Wang, et al., 2018). The concentration of ammonium nitrogen in wastewater from meat processing plants varies in the range of 1.0–3.2 mg eq./dm^3 and exceeds their maximum permissible concentration (MPC(NH_4^+) < 1.1 mg eq./dm^3) (Wang, et al., 2018; Sabadash et al., 2018). Therefore, wastewater must be treated before it is discharged. In practice, wastewater is treated by coagulation, settling, and then filtration through sand filters to reduce the pollution of water bodies and especially to prevent the phenomenon of eutrophication of water bodies. However, after such

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treatment, the wastewater contains a significant amount of ammonium nitrogen, which cannot be removed from the water by the above methods. Removal of harmful contaminants from wastewater is possible in various ways (Sabadash et al., 2018). Considering the fact that significant amounts of wastewater need to be treated, the most economical way is to use a natural sorbent that can be used as fertilizer for agriculture after the treatment process is complete. This sorbent not only adds nutrients to the soil but also improves its structure. From this point of view, we used zeolite as a sorbent, whose main component is clinoptilolite in sodium form (Wang, et al., 2018). This work aimed to study the kinetic laws of sorption of ammonium ions by zeolite in the range of low concentrations typical of wastewater from meat processing plants, as well as the effects of the accompanying wastewater pollution on the absorption of NH_4^+.

2. Experimental researches

Statics of ammonium ions sorption on zeolite. To determine the adsorption capacity of ammonium ions, 200 ml of an ammonium nitrate solution prepared in distilled water of various initial concentrations (Cn 0.55–3.33 mg eq/dm^3) were measured in glass flasks and identically weighed amounts of clinoptilolite (~ 1 g) were added. The concentration range corresponded to the concentration of the ammonium group in real wastewater. The flasks were hermetically sealed and left at a temperature of (20 ± 0.5) °C for two days with regular stirring. The sorbent was separated from the solution and analyzed for the content of ammonium ions using a photoelectric colourimeter according to a known method (Sabadash, et al., 2020).

In the next steps, the adsorption capacity of zeolite was investigated concerning ammonium ions in the simultaneous presence of two and three contaminating components in the solution. These contaminants include phosphates and proteins in the wastewater, the concentration of which is also controlled. A model solution in which ammonium nitrogen and phosphates were present corresponded to the two-component system. Adsorption of ammonium nitrogen on clinoptilolite in the presence of phosphates with initial concentrations of ammonium nitrogen (Cn 0.55–3.33 mg eq./dm^3) and initial phosphate content (Cn 0.03–0.2 mg eq./dm^3) was carried out with regular stirring of aqueous solutions at a temperature of (20 ± 0.5) °C. Adsorption of ammonium nitrogen on clinoptilolite in the presence of phosphates with initial concentrations of ammonium nitrogen (CH 0.55–3.33 mg eq./dm^3) and initial phosphate content (CH 0.03–0.2 mg eq. /dm^3) was carried out. The ratio of adsorption solution was 200 ml to 1 g of clinoptilolite. The contact time was two days. Sorption of ammonium ions from a three-component system in which albumin was added as a third pollutant with initial concentrations (Cn 0.013–0.13 mg eq./dm^3) was carried out under similar conditions as in the previous studies with the ratio of solution 100 ml of adsorbent to1 g of clinoptilolite. The solutions were analyzed for the content of ammonium ions using a photoelectric colourimeter according to the method (Sabadash et al., 2020).

Kinetics of ammonium ions sorption on zeolite. To determine the kinetics of absorption of ammonium nitrogen from wastewater on clinoptilolite, 1 dm^3 of the previously prepared solutions was measured in three glass flasks. The first vessel contained a solution with ammonium nitrogen (Cn 2.19 mg eq./dm^3), the second – a model two-component solution with an ammonium ion (Cn 2.17 mg eq./dm^3) and phosphates with an initial concentration (Cn 0.207 mg eq./dm^3). The third solution was a three-component system with an initial concentration of ammonium nitrogen (Cn 2.17 mg eq./dm^3), phosphates (Cn 0.213 mg eq./dm^3) and albumin (Cn 0.077 mg eq. /dm^3). The pH of the three-component solution is 6.6. Note that the concentrations of the contaminating components in the model solutions correspond to the content of the same contaminants in real wastewater from meat processing plants. Equal weighed portions of sorbent (~10 g) were added to the solutions. The vials were capped and stirred with a mechanical stirrer. Samples were taken at specific intervals of contact between the solution and the adsorbent at a speed of n = 200 rpm. The experiments were performed at a temperature of (20 ± 5) °C. The taken samples of the solution were analyzed for the content of ammonium ions using a photoelectric colourimeter according to the method (Sabadash et al., 2020).

This sorbent was also used by us to study the kinetics of absorption of the above polluting components from real wastewater, followed by the content of initial concentrations – ammonium ions (CH 1.73 mg eq./dm^3), phosphates (Ch 0.15 mg eq./dm^3) and protein (Cn 0.071 mg eq./dm^3). The experimental procedure and the analysis of the content of ammonium ions are the same as in the model study. The pH of the wastewater is 7.68.

Methodology for determining the mass transfer coefficient. The mass transfer coefficient is determined based on the mass transfer equation for a short time interval Δτ, which allows the use of the concentration values averaged over a certain time interval.

$$\beta = \frac{\Delta M}{F(\overline{C} - \overline{C}_s)\Delta\tau}\,. \qquad (1)$$

The time interval Δτ is calculated from the beginning of the process when the concentration of the adsorbent in the solution is equal to the initial Cs and at the surface of the adsorbent Cs = 0. The concentration of the adsorbent at the surface should be considered as its amount in the first monomolecular layer of the liquid. Moreover, the value of adsorbate concentration in the pores of the sorbent Cn is in equilibrium with the value of adsorbate concentration on the surface of the adsorbent Ca. Therefore, the determination of the concentration causes certain difficulties in contrast to mass transfer processes with a solid phase, such as dissolution, crystallization, drying in the first period, where the concentration of the adsorbed substance on the surface of the solid phase does not change over time.

At the beginning of the adsorption process, an external diffusion process takes place and the adsorbate concentrates on the outer surface of the adsorbent grains (Hyvlud et al., 2019). Of course, diffusion into the adsorbent grains also occurs, but this process is much slower than external diffusion. An analogy is the drying process (desorption of moisture from solids). There is an initial phase of drying that occurs at a constant rate and is called external diffusion. Although in the initial time interval from 0 to τ_1 moisture can diffuse from the inner layers of the particle, the concentration of the adsorbent changes linearly (which is confirmed by the external diffusion process) from C_1 to C_n. The average value in this range is determined as an arithmetic mean, and the amount of the mass of the substance absorbed by the adsorbent is the same:

$$\Delta M = V(C_n - C_1)\,. \tag{2}$$

The concentration of the substance on the adsorbent at time τ_1 is determined by:

$$C_{a1} = \frac{\Delta M}{m}\,. \tag{3}$$

At low concentrations of the adsorbent, the isotherm is described by Henry's equation. Assuming that the near-surface layer of the liquid is in equilibrium with the surface of the solid (according to the theory of mass transfer processes), the concentration of the substance in the near-surface layer Cs is:

$$C_{s1} = \frac{C_{a1}}{\mathrm{H}}\,. \tag{4}$$

Using the obtained value of Cs_1 at time τ_1, we find the arithmetic mean value, which is inserted into equation (1).

3. Results and their interpretation

A peculiarity of zeolites is the fact that they act both as adsorbents and ion exchangers (Sabadash, et al., 2018). In the second case, the counterions are sodium ions, which have the ability to exchange with positively charged cations from the solution. The exchange reaction between the zeolite and the NH_4^+ ion can be described as follows:

$$\text{R-Na} + NH_4^+ \leftrightarrow \text{R-}NH_4 + Na^+;$$

where R are solid ions that form the framework of the ion exchanger and cannot transfer into a solution.

The dependences obtained by us between the concentration of NH_4^+ ion in the CNH_4^+ solution and the NH_4^+ concentration in the solid phase (the exchange capacity of zeolite) a* are shown in Fig. 1 (curve 1), from which it can be seen that for a certain range of CNH_4^+ concentrations, the dependence is linear and for a certain constant temperature + (20 ± 0.5) °C it is the isotherm of ion exchange sorption and corresponds to the first linear section of the Langmuir isotherm. This dependence is described by the linear Henry equation (Wu et al., 2019), which for the studied range (mg eq./dm^3) $0 < CNH_4^+ < 2$, has the form:

$$a^* = 0{,}271\ CNH_4^+ \tag{5}$$

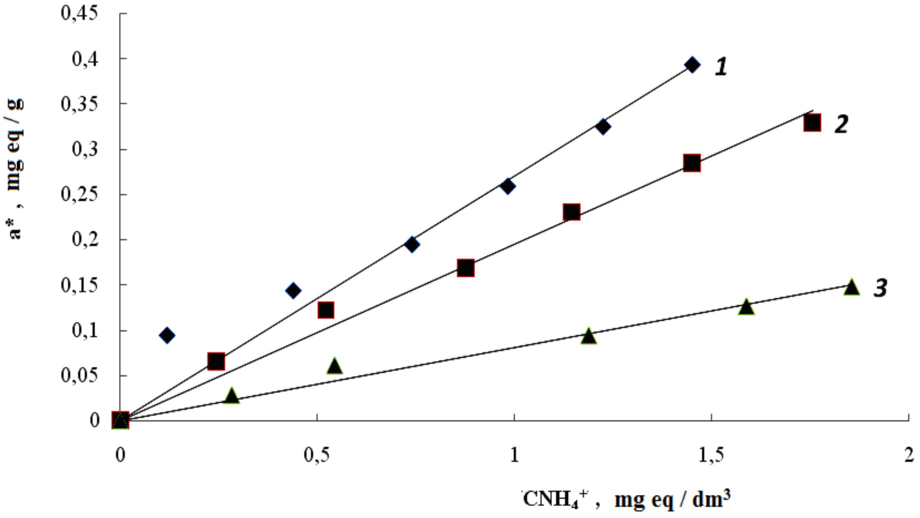

Fig. 1. Sorption isotherm of ammonium nitrogen on natural zeolite:
♦ – isotherm of sorption of ammonium nitrogen; ■ – isotherm of sorption of ammonium nitrogen in the presence of phosphates; ▲ – isotherm of sorption of ammonium nitrogen in the presence of phosphates and albumin

Curve 2 (Fig. 1) corresponds to the sorption isotherm of ammonium nitrogen in the presence of phosphates (standardized pollutant of wastewater from meat processing plants). These values indicate a decrease in the exchange capacity of zeolite due to its concentration for active absorption centres. In the presence of the third component in the solution (the protein substance albumin), an even greater decrease in the sorption capacity of zeolite for ammonium ions is observed (curve 3). Thus, if in the presence of phosphates the equilibrium capacity decreases by about 30 %, in a three-component system the decrease is about 70 %.

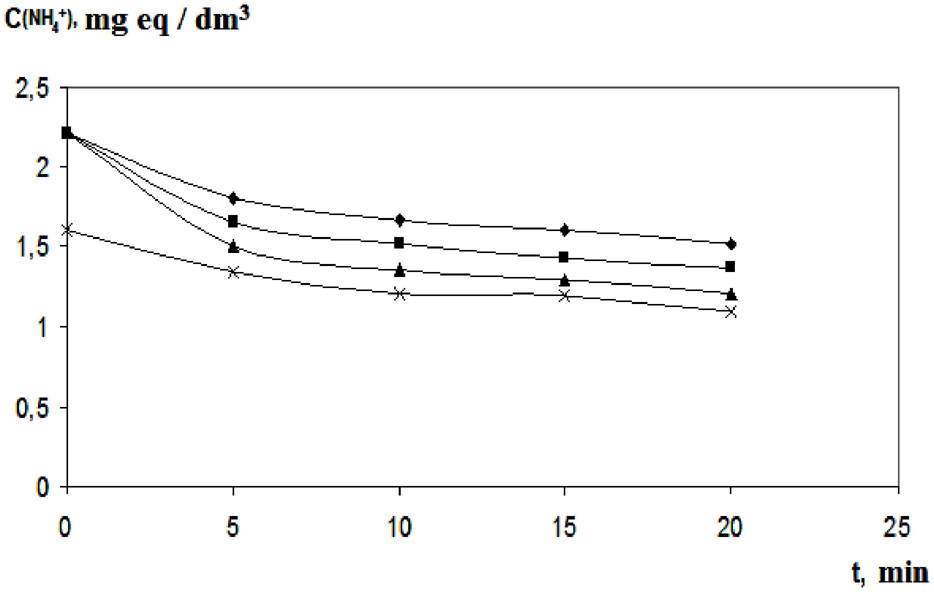

Fig. 2. Kinetics of ion-exchange sorption of ammonium nitrogen:
♦ – sorption of ammonium nitrogen; ■ – sorption of ammonium nitrogen in the presence of phosphates; ▲ – sorption of ammonium nitrogen in the presence of phosphates and albumin; x – sorption of ammonium nitrogen in wastewater

The justification of the kinetics of ion exchange and its mathematical description is based on the mechanism of sorption, which makes it possible to determine the limiting phases of the process. As a result of the experimental studies, we obtained the dependencies of the change in the concentration of ammonium nitrogen in the solution as a function of time t (Fig. 2).

Analyzing the kinetic curve of adsorption of ammonium nitrogen (Fig. 2, curve 1), the dynamics of a decrease in the content of ammonium ions in the solution as a function of the contact time of this solution with the sorbent is observed, with a significant amount of ammonium cation decreasing already in the first time interval (5 minutes) and its content gradually decreasing in the following periods. After 20 minutes of contact of the solution with the sorbent, the concentration of ammonium nitrogen has decreased by about two times compared to the initial concentration and has reached the maximum permissible standard, so that the wastewater can be discharged into the general sewage network ($MPCNH_4^+ < 1.1$ mg eq./dm^3). Fig. 2 also shows the kinetics of absorption of ammonium ions from the real wastewater of a meat processing plant. The coefficient of mass transfer of the process of ammonium adsorption by zeolite is equal to $\beta = 4,69 \cdot 10^{-5}\,\frac{\mathrm{m}}{\mathrm{s}}$, in the presence of phosphates $\beta = 6,62 \cdot 10^{-5}\,\frac{\mathrm{m}}{\mathrm{s}}$, in the presence of phosphates and albumin $\beta = 8,85 \cdot 10^{-5}\,\frac{\mathrm{m}}{\mathrm{s}}$, with sorption of ammonium nitrogen in wastewater $\beta = 3,97 \cdot 10^{-5}\,\frac{\mathrm{m}}{\mathrm{s}}$.

The presented data show that the absorption rate of NH_4^+ corresponds to curve 3, which corresponds to a model solution with the presence of a three-component system.

4. Conclusions

The article presents the laws of ammonium ions adsorption in the presence of phosphates and albumin. A mathematical model of adsorption for the external diffusion process was developed. The coefficients of mass transfer of the processes depending on the composition of the adsorbate are determined. It is found that the introduction of additional ions into the adsorbate reduces the adsorption capacity of the sorbent from 30 to

70 %. Limiting stages of the process were identified, and it was shown that the introduction of macromolecular compounds can lead to a shift of the process to the external diffusion stage.

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