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RESEARCH AND MODELLING KINETICS ION EXCHANGE INTERACTIONS

Vira Sabadash, **Jaroslaw Gumnitsky**, **Oleh Konovalov**

Lviv Polytechnic National University,
12, S. Bandery Str., Lviv, 79013,Ukraine
viras.v.sabadash@lpnu.ua

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Abstract. In detail, this study analysed the kinetics of ammonium ion adsorption under dynamic conditions in the “clinoptilolite -ammonium ion system. The work includes constructing a mathematical model of this process, which allows us to estimate and predict its essential characteristics. Calculations of mass transfer coefficients revealed their dependence on the intensity of medium mixing. A significant result is that ion exchange occurs in externally diffusion and intradiffusion regions. Ion exchange rate constants were calculated for the regions of external and internal diffusion, contributing to a deeper understanding of the mechanisms of this complex process. The research results will expand our knowledge about ion exchange interactions in the “clinoptilolite -ammonium ion” system. In addition, they can be used to optimise the conditions of ammonium adsorption in similar systems, which is essential for practical applications related to water purification and other media from ammonium ions.

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

1. Introduction

In modern conditions, where environmental pollution problems are becoming increasingly urgent, removing ammonium ions from wastewater is becoming necessary in many countries. Nitrogenous compounds are critical pollutants of water resources and can hurt the ecosystems of water bodies and the quality of drinking water. Various technologies are used to remove ammonium ions effectively; ion exchange methods are widely used (Wu et al., 2019). Synthetic ion exchange resins and various zeolites are considered practical materials. Special attention is paid to the possibility of using the ion exchange method for nitrogen recovery, which is essential to working with wastewater. This article is devoted to studies that reveal the potential of natural zeolites, particularly clinoptilolite, in removing ammonium ions (Muscarella et al., 2021). Considering the natural properties of these materials, their possible cost and their ecological nature, it is essential to consider them an effective and affordable resource for combating water pollution. The results of these studies can contribute to improving ammonium ion removal technologies and provide new approaches to solving water pollution problems. The main goal of this work is an in-depth study and determination of the theoretical laws governing the process of ion exchange adsorption of ammonium ions by natural zeolite. Special attention is paid to the conditions of mechanical mixing since this aspect can significantly affect the efficiency of ion exchange between zeolite and ammonium ions (de Haro Martí et al., 2020). The research aims to identify the interaction between natural zeolite and ammonium ions under the conditions of mechanical mixing, as well as reveal and formulate theoretical dependencies that determine the kinetics and efficiency of this process. Since mechanical mixing can vary in intensity, the work also aims to study these parameters' influence on the zeolite material's ion exchange properties (Lin et al., 2016).

These studies aim not only to improve our understanding of the physicochemical processes occurring during the ion-exchange absorption of ammonium by natural zeolite but also to determine the optimal conditions of mechanical mixing for the maximum efficiency of this process (Bernal, et

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al., 1993). The work results can be necessary to develop technologies for further removing ammonium ions from water environments.

2. Materials and Methods

A polyethene container with a volume of 1 dm³ was used to study the kinetics of zeolite adsorption concerning ammonium ions. We used 0.2 dm³ of a solution containing ammonium ions was introduced into this container. The studied solution was prepared in distilled water, with an initial ammonium concentration of 0.5 mg/dm³, after which 5 g of zeolite was added. An installation consisting of an apparatus with a propeller-type stirrer was used to study the kinetics of ammonium adsorption. In the research process, the rotation frequency of the stirrer was adjusted in the range of 100 to 500 revolutions per minute (rpm).

The adsorption process was carried out in dynamic conditions in a stirrer. A particular rotation frequency of the stirrer was set, ensuring optimal system mixing. Samples of the solution after adsorption were analysed for the content of ammonium ions (NH_4^+) by the photometric method, using known methods (Wu et al., 2019).

It is important to note that the adsorption efficiency was determined as the change in the concentration of ammonium ions in the solution after interaction with the zeolite for a specific time. This approach allows us to establish the kinetic laws of the process and evaluate the effectiveness of zeolite as an adsorbent for removing ammonium ions under dynamic conditions.

3. Results and Discussion

The performed scientific experiments revealed that the adsorption process takes place mainly within the intradiffusion region. Type of the process was determined by finding the equilibrium of the process before reaching a constant value of the adsorption concentration of ammonium ($a\infty$)(Sabadash et al., 2020). The presentation of experimental data is illustrated in Fig. 1.

An important conclusion is that the adsorption rate reaches stability after a certain period, which indicates the completion of the intradiffusion stage of the process. The equilibrium value of ammonium adsorption concentration ($a\infty$), which was established as a result of research, can serve as a critical indicator for further analysis of adsorption efficiency based on this material.

Note that the scientific results presented in Fig. 1 determine not only the nature of the adsorption process but also indicate the possibility of optimising the experimental conditions to maximise the adsorption capacity of zeolite. Optimising the adsorption process can increase its efficiency in removing ammonium ions from solutions.

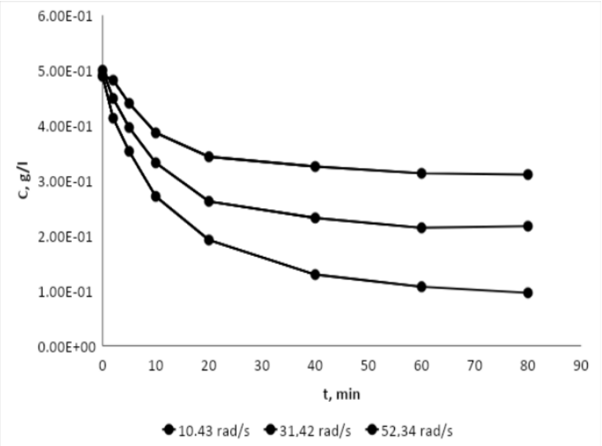

Fig. 1. Kinetics of adsorption of ammonium ions of model solutions

Modelling of the adsorption process of an active component by a granular sorbent includes the analysis of non-stationary diffusion-kinetic phenomena in complex multicomponent systems. In our case, we considered the mechanisms of liquid adsorption, determining a number of stages of this process (Soudejani et al., 2019):

- Diffusion of ammonium ions to the surface of the sorbent.
- Diffusion of ammonium ions from the surface of the ion exchanger to the point of reaction.
- Ion exchange, which is accompanied by chemisorption.
- Diffusion of the exchangeable zeolite ion from the site of the reaction to the surface of the ion exchanger.
- Diffusion of the exchangeable cation of the sorbent into the solution.
- For the quantitative description of the reaction system, we use the material balance equation for ammonium ions, allowing us to consider their concentration changes at each process stage.

These stages of interaction with the sorbent can be carefully studied and optimised to increase the efficiency of ammonium adsorption and determine the optimal conditions for this process (Wang et al., 2018). The presented material balance equations are a crucial tool for quantifying the effectiveness of the studied adsorption mechanisms.

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

The equation of the material balance of the ion exchange process:

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

where C_0 is the initial concentration of the corresponding cation; $\overline{C}$ is the average concentration of adsorbate in the sorbent volume; *V* is the volume of the adsorption medium; ε is the porosity of the zeolite; ρ is the density of the solid phase; *r* is the radius (Sabadash et al., 2018a), *t* is time.

The considered equation defines various parameters affecting the system's diffusion process of exchangeable cations. The initial concentration of the pollutant is denoted as C_0, which is the initial amount of the substance in the solution. The average concentration of the cation in the grain reflects the concentration changes internally in the adsorbent itself. The volume of the liquid phase is denoted by *V*, and the porosity is ε, which indicates the percentage ratio of the volume of pores in the adsorbent to its total volume. The density of the sorbent is considered as ρ, and the adsorbent grain's running radius is *r*. The time of the study is denoted as t.

The process of diffusion of exchangeable cations from the solution to the ionite surface is described by the mass transfer mechanism, where the equation $j_{NH_4^+} = -D\frac{dC_{NH_4^+}}{dn}$ can determine the mass flow:

$$\frac{dM_{NH_4^+}}{dt} = -\beta F \; C_{NH_4^+} - C^0{}_{NH_4^+} \; , \quad (3)$$

where β is the mass transfer coefficient from the solution to the surface of the adsorbent, m/s; *F* is the area, m²; C_0 is the initial concentration of the corresponding cation in the solution; *C* is the average concentration of the corresponding cation in the grain (Sabadash et al., 2018b).

Table 1 shows that the value of the mass transfer coefficient β increases with an increase in the number of revolutions of the stirrer. For example, at 100 rpm, β equals $8.06 \cdot 10^{-5}$ m/s, and at 500 rpm, it is already $1.19 \cdot 10^{-4}$ m/s. This indicates that the mixing intensity affects the rate of diffusion of exchangeable cations in the system and may be one of the critical factors determining the mass transfer coefficient.

The mechanism of transport of the component from the solution to the site of the reaction can be determined by the equation (Sabadash et al., 2020):

$$\frac{dM_{NH_4^+}}{dt} = -\frac{D}{r} F \; \overline{C}_{NH_4^+} - C_{NH_4^+} \; , \quad (4)$$

where *C* is the concentration of ammonium in the zeolite grain; *D* is the diffusion coefficient inside the adsorbent, m²/s; *F* is the zeolite surface area, m; *r* is the running radius of adsorbent grain, m; *t* is the time, p.

Table 1

Dependence of mass transfer coefficients β on the speed of rotation of the stirrer

Rotation speed, rad/s.	Mass transfer coefficient β, $м / с$
10.43	$8.063 \cdot 10^{-5}$
31.42	$1.041 \cdot 10^{-4}$
52.34	$1.21 \cdot 10^{-4}$

The average concentration in a zeolite grain can be determined as:

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

where *V* is the pore volume of the zeolite is equal $\frac{3}{4}\pi r^3 \varepsilon$; *n* is the relative number of zeolite particles; *C* is the molar concentration (Hyvlud et al., 2019).

$$\frac{4}{3}\frac{V}{\pi r^3 \varepsilon n} = k .$$

After substituting (5) into (4), we obtain the following expression:

$$\frac{dM_{NH_4^+}}{dt} = -\frac{D}{r} F \left(k \frac{C_{NH_4^+} - C^0{}_{NH_4^+}}{2} - C_{NH_4^+} \right) =$$

$$= -D \cdot 4\pi d_{nop} \varepsilon \;\; k \;\; C_{NH_4^+} - C^0{}_{NH_4^+} \;\; - 2C_{NH_4^+} \;\; = \cdot \quad (6)$$

$$-D \cdot 4\pi d_{nop} \varepsilon \;\; C_{NH_4^+} \;\; k - 2 \;\; - kC^0{}_{NH_4^+}$$

Under the conditions of the experiment, the amount of adsorption medium significantly exceeded the amount of adsorbent. Therefore, we denote (*k*−2) as *k*, and then (6) will take the form:

$$\frac{dM_{NH_4^+}}{dt} = -4D\pi d_{nop} \varepsilon k \;\; C_{NH_4^+} - C^0{}_{NH_4^+} \;\; . \quad (7)$$

The resulting equation allows us to calculate the dynamics of the decrease in the concentration of the reaction mixture, taking into account the total amount of absorbed substance due to adsorption and ion exchange.

The stage of diffusion of wastewater components in the pores of the sorbent is critical in the process of adsorption of ammonium ions. During this stage, ammonium ions move deep into the sorbent, penetrating its pores, where further ion exchange and adsorption occur.

Limiting factors and parameters affecting this stage:

Porosity of the sorbent (ε): Porosity determines the volume of pores of a portion of the sorbent to its total volume. Higher porosity contributes to a larger volume of available pores for diffusion, positively affecting the diffusion rate.

Sorbent pore diameter (d): The diameter also affects the diffusion rate. Larger pores allow larger particles to penetrate deeper into the sorbent, reducing diffusion resistance.

The diffusion coefficient within the adsorbent (D) determines how fast ions can move within the sorbent material. A significant diffusion coefficient indicates a rapid diffusion process.

Sorbent grain size (r): Larger grain sizes can reduce diffusion resistance, facilitating faster penetration of ions into the sorbent.

Contact time (t): The time that wastewater components spend in contact with the sorbent affects the efficiency of diffusion and adsorption.

Positively affect the process:

High porosity and large pore diameter of the sorbent: Provide more space for the movement of ions in the pores, promoting rapid diffusion.

Large sorbent grain sizes: Reduce diffusion resistance, improving the access of ions deep into the sorbent.

High diffusion coefficient inside the adsorbent: Indicates the rapid movement of ions inside the material.

Negatively affect the process:

Low porosity and small sorbent pore diameter may limit diffusion space and reduce pore availability.

Small sorbent grain size may lead to increased diffusion resistance.

Low diffusion coefficient inside the adsorbent: Indicates the slow movement of ions inside the material.

Short contact time may limit the interaction between ammonium ions and the sorbent.

The third stage of ammonium adsorption by the ion exchange mechanism includes the actual exchange of ions between the surface of the sorbent, such as clinoptilolite, and the wastewater solution. This process of ion exchange is the crucial mechanism that leads to the retention of ammonium ions on the surface of the sorbent, replacing them with other ions that were previously on the surface of the sorbent.

The main aspects of the third stage of ammonium adsorption by the ion exchange mechanism:

Ion exchange: A sorbent like a clinoptilolite has sodium (Na^+) ions on its surface. During contact with wastewater, ammonium ions (NH_4^+) exchange with sodium ions on the surface of the sorbent. Places obtained by ammonium on the surface of the sorbent ensure its effective retention.

Selectivity: The ion exchange mechanism can be selective because different ions have different degrees of affinity for the active sites on the sorbent surface. In the case of ammonium ion exchange, the sorbent is aimed at the selective exchange of ammonium ions for sodium or other ions on its surface.

Exchange equilibrium: The ion exchange process achieves equilibrium between the amount of ammonium ions that leave the solution and the amount of other ions that join the sorbent. Various factors, such as the concentration of ions in the solution and the properties of the sorbent itself, can determine the exchange equilibrium.

Influence of parameters: Parameters such as pH of the medium, temperature and concentration of ions in the solution can affect the efficiency of ion exchange. Optimisation of these parameters allows for an increase in the efficiency of the adsorption process.

Physico-chemical properties: Properties of the sorbent itself, such as its surface charge and chemical structure, determine the possibilities of interaction with ammonium and other ions.

In general, the ion exchange mechanism is an essential step in removing ammonium ions from wastewater using sorbents, and it is represented by equation (8).

The ion exchange mechanism can be evaluated by studying the amount of exchangeable cations Kat + that leave the solution from the zeolite volume. Since we are dealing with a second-order reaction, the rate of ion exchange can be described by the following equation:

$$NH_4{}^+ + Kat(zeolite) \rightarrow Kat^+ + NH_4(zeolite), \quad (8)$$

where Kat^+ represents exchangeable cations on the zeolite's surface.

The speed of this reaction depends on the concentration of exchange cations Kat^+ and the speed of the exchange reaction. In the case of a second-order reaction, the rate (*v*) can be determined by the equation:

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

where *k* is the reaction rate coefficient.

However, for a more accurate assessment of the mechanism of ion exchange, experiments should be conducted. The influence of other factors, such as temperature, pH of the medium, and other parameters that may affect the nature of ion exchange in the system, should be taken into account.

During the ion exchange process lasting t, x moles reacted NH_4^+ and x moles of exchangeable cations Kat^+ were desorbed.

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

optimising the experimental conditions; →

$$\frac{dx}{dt}=k\ \ m^0{}_{NH_4^+}-x\ \cdot\ m^0{}_{z-Kat^+}-x$$

$$kdt=\frac{dx}{m^0{}_{z-Kat^+}-x\ \ m^0{}_{NH_4^+}-x}\,. \qquad (10)$$

The solution of this problem is represented by equation (11):

$$k=\frac{1}{t\ \ m^0{}_{NH_4^+}-x\ \cdot\ m^0{}_{z-Kat^+}-x}\times$$

$$\times\ln\frac{m^0{}_{z-Kat^+}\ \ m^0{}_{NH_4^+}-x\ \cdot}{m^0{}_{NH_4^+}\ \ m^0{}_{z-Kat^+}-x}\,. \qquad (11)$$

The result of logarithmic solving of (11) is represented by equation (12):

$$\ln\frac{m^0{}_{z-Kat^+}\ \ m^0{}_{NH_4^+}-x\ \cdot}{m^0{}_{NH_4^+}\ \ m^0{}_{z-Kat^+}-x}\times$$

$$\times\ m^0{}_{NH_4^+}-x\ \cdot\ m^0{}_{z-Kat^+}-x\ =kt\,, \qquad (12)$$

where $x\equiv m_{Kat^+}\equiv a^*_{NH_4^+ обм}\cdot m_{ads}-\ a^*_{NH_4^+ обм}\cdot m_{ads}$ is the amount of ammonium that entered the reaction as a result of ion exchange, mg- equiv / g.ads m_{ads} is the mass of adsorbent.

Let us enter the notation:

$$\ln\frac{m^0{}_{z-Kat^+}\ \ m^0{}_{NH_4^+}-x\ \cdot}{m^0{}_{NH_4^+}\ \ m^0{}_{z-Kat^+}-x}\times$$

$$\times\ m^0{}_{NH_4^+}-x\ \cdot\ m^0{}_{z-Kat^+}-x\ =A_{обм}\,.$$

We get the reaction rate equation in the classical form:

$$A_{обм==}=kt. \qquad (13)$$

However, the objective process of adsorption of ammonium ions in dynamic conditions is more complicated since it includes ion exchange and can also occur in external and internal diffusion regions. This equation indicates that the interaction between ammonium ions and the sorbent has various mechanisms and can be determined by various factors affecting the adsorption process in different system parts. Suppose the concentration of ammonium (*a**) is expressed in terms of the mass of the absorbed ammonium ion at the moment (*t*). In that case, the calculated dependence will not pass through 0 because part of the ammonium can be absorbed due to physical adsorption. Therefore, we introduce into equation (13) a correction factor that takes into account the contribution of physical adsorption to the process:

$$a^*=M/m\cdot(1+b_0),$$

where *m* is the mass of the absorbed ammonium ion; *M* is the mass of the sorbent, and b_0 is the correction factor that considers physical adsorption.

This correction factor considers the contribution of physical adsorption and allows us to model the adsorption process correctly in dynamic conditions, avoiding systematic calculation errors.

$$A_{обм==}=kt+b_0\,. \qquad (14)$$

Coefficient b_0 considers the adsorbate mass absorbed by the physical adsorption mechanism. Relative to the line plotted for adsorption in the intradiffusive region, this value reflects the amount of adsorbate and exchangeable cations involved in the first stage of the process.

After constructing equation (14) as a graph, we obtained a graphical interpretation of the experimental adsorption data, presented in Fig. 2. This graph shows the dependence of adsorbate concentration on time. It determines the influence of various physical adsorption and adsorption mechanisms in the intradiffusion region.

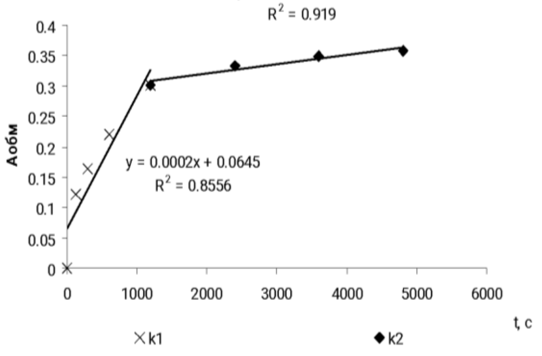

Fig. 2. Interpretation of the I and II stages of ammonium adsorption under stirring conditions for n=52.34 rad/s

Graphical interpretation is an essential tool for determining the dynamics of adsorption processes and confirming theoretical models. It provides an opportunity to evaluate the role of various mechanisms and make adjustments to optimise the parameters of the adsorption system.

In Fig. 2, the external and internal diffusion areas were graphically highlighted. The rate constants for these processes were calculated. The angular coefficient of the obtained curves corresponded to the reaction rate constant. However, none of the lines passed through the starting point (0,0) because the amount of the component that was already adsorbed from the solution at the time of the measurements was not considered. For the first stage of the process, which characterises adsorption on the outer surface of the sorbent, the rate constant was $k_1 = 2.4 \cdot 10^{-4}\ M^{-1} \cdot s^{-1}$. At the second (intradiffusion) stage of the process, the ion exchange rate constant was equal to $k_2 = 2.1 \times \times 10^{-5}\ M^{-1} \cdot s^{-1}$

4. Conclusions

In this study, we presented the results of an experiment that studied the kinetics of adsorption of ammonium ions by natural zeolite under mechanical stirring conditions using an apparatus with a stirrer. Based on the analysis of the obtained data, it was found that the adsorption process can be divided into two main stages: external and internal diffusion regions. A detailed examination of the experimental results allows us to establish that the interaction of ammonium ions with zeolite takes place in two different areas. The calculations of the rate constants of chemical reactions indicate that in the internal diffusion region, the ion exchange rate decreases by an order of magnitude compared to the external diffusion region. Thus, an important conclusion is that implementing the adsorption process in dynamic conditions is appropriate for external diffusion. In addition, it is determined that the adsorption process should be at most 20 minutes to ensure the practical nature of the ion exchange and provide optimal conditions for the reaction to proceed. These results are of practical importance for developing optimal conditions and regulating ammonium ion adsorption processes from wastewater.

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