

## Efficiency of using mineral sorbents for purifying natural waters from ammonium ions

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### ABSTRACT

The work establishes the physicochemical regularities of  $\text{NH}_4^+$  ion sorption on the surface of natural mineral sorbents of various chemical nature. The relationship between the nature of the sorbents, the acid-base properties of the active centres of the hydroxyl-hydrate surface layer and the efficiency of  $\text{NH}_4^+$  ion extraction from aqueous solutions is established. Modern methods were used to study the properties of the sorbents: X-ray phase analysis, potentiometric analysis of aqueous suspensions, spectrophotometric analysis. Studies of the sorption capacity of sorbents in relation to  $\text{NH}_4^+$  ions were carried out under static conditions. A comparative characteristic of the efficiency of using sorbents of various chemical nature for the extraction of  $\text{NH}_4^+$  ions from aqueous solutions is provided. It is established that the sorption capacity of sorbents decreases in the order diabase flour > quartzite > kaolin clay > bentonite clay. It has been established that the main mechanism of sorption of  $\text{NH}_4^+$  ions on the surface of kaolin clay is ion exchange, and on the surface of diabase flour and quartzite – physical adsorption. In aqueous suspensions of bentonite clay, a mixed mechanism is implemented: physical adsorption and ion exchange. The established patterns will allow for more effective use of cheap and environmentally friendly natural mineral sorbents in water treatment technologies. Patterns and mechanisms of sorption of ammonium ions  $\text{NH}_4^+$  on the surface of natural mineral sorbents depending on the number and acid-base properties of surface-active centers is an important scientific and practical task. In addition, a comparative characteristic of some of the most common natural sorbents of various chemical and mineral nature is necessary regarding the possibility of their use for water purification from ammonium ions.

**Keywords:** mineral sorbent, natural water treatment, environmental and civil safety, environment.

### INTRODUCTION

Natural mineral dispersed sorbents are effectively used in technologies for purifying water environments from various polluting components. In most cases, mineral sorbents are used to remove inorganic ions of pollutants (cations and anions), since, firstly, the surface of minerals is characterized by a certain charge, and secondly, it can participate in ion-exchange reactions (Arean et al., 2014; Danchenko, 2021; Danchenko et al.,

2017; Danchenko et al., 2023; Rehman et al., 2022). Therefore, when removing charged particles (ions) of pollutants from water environments by mineral sorbents, two mechanisms are implemented simultaneously - physical and chemical. In general, such a purification mechanism can be called physico-chemical, or mixed. In this case, mineral sorbents can replace expensive coal and graphite sorbents, which work according to the physical mechanism, and ion-exchange resins, which implement chemical purification. Among

natural mineral sorbents in purification technologies, aluminosilicates (zeolites), palygorskites, glauconites, clinoptilolites, bentonites are the leaders. The use of mineral sorbents for water purification meets the requirements of energy saving, environmentally friendly production technologies, the principles of sustainable development and “green chemistry”. The advantages of using mineral dispersed sorbents are low cost, which makes it possible to exclude the regeneration link from the technological process. Spent sorbents can be used to improve the quality of soils with the simultaneous introduction of some ions, which is useful for plants or as secondary materials.

Ammonium ions are one of the standardized indicators of drinking water quality, the content of which is also standardized in wastewater, groundwater and surface waters. In the world, this indicator is strictly limited by relevant regulatory documents. In some countries of the European Union, the maximum permissible concentration of ammonium ions in drinking water and water for household needs should not exceed 2 mg/dm<sup>3</sup>. Ukraine, Poland, Germany, France and Hungary adhere to the norm recommended by the World Health Organization (WHO), namely, 0.5 mg/dm<sup>3</sup>. Pollution of groundwater and surface natural waters with ammonium ions, which enter from household and fecal wastewater, mineral fertilizers, and landfill effluents, is often a deterrent to the use of these waters for drinking and household use. One way to solve this problem is to use natural mineral sorbents for wastewater treatment, the reserves of which are found in large quantities in the bowels of Ukraine. The advantages of such a strategy are the relatively low cost of natural sorbents and significant deposits of deposits of the corresponding minerals. High adsorption, ion-exchange, filtration properties, ease of regeneration and utilization, the possibility of reuse, cheapness, environmental friendliness and wide distribution of natural minerals make their use promising for water treatment, including from ammonium ions (NH<sub>4</sub><sup>+</sup>).

Recent scientific studies have determined the adsorption capacity of various natural mineral sorbents with respect to ammonium ions-basalt tuff, zeolites, palygorskite, glauconite, bentonite, clinoptilolite, kaolinite, diabase, montmorillonite etc (Danchenko et al., 2018; Delgado et al., 2018; Demir et al., 2002; Gianni et al., 2021; Humnytskyi et al., 2011; Langwaldt, 2008; Malyovanyy et al., 2013; Malyovanyy et al., 2011a;

Malyovanyy et al., 2011b; Nair et al., 2024; Tsimabaljuk et al., 2009). It has been established that zeolites exhibit the best sorption properties.

Many researchers have established that to increase the sorption properties of natural sorbents, it is effective to use chemical or physical methods of surface activation. In (Andronov et al., 2018) it is noted that the nature of surface-active centers and, accordingly, the sorption properties of natural aluminosilicates (basalt tuff) are determined by the chemical composition and conditions of preliminary thermal treatment.

In studies (Demir et al., 2002; Gianni et al., 2021), a method of purifying drinking water from ammonium ions is proposed, which involves the use of natural dispersed sorbents - palygorskite, zeolite and glauconite. The study of the sorption capacity under static conditions at a ratio of sorbent to solution S:L=1:100 and an initial solution concentration of 14 mg NH<sub>4</sub><sup>+</sup>/dm<sup>3</sup> showed the efficiency of ammonium ion extraction for zeolite ~ 75%, for palygorskite ~ 29%, for glauconite ~ 14%. Based on the results of an experimental study of the adsorption of ammonium ions on different types of sorbents, it was shown that temperature (20 and 35 °C) has practically no effect on the adsorption process. As the authors themselves note, an important disadvantage of this method is the inability to easily and quickly separate the adsorbent from the purified water, because after the purification process the water becomes cloudy and requires filtration. Complete phase separation requires settling for at least 8 days or centrifugation, which requires additional equipment and energy.

The authors' studies (Malyovanyy et al., 2011a) have shown that irradiation of bentonite with ultrahigh electromagnetic radiation in combination with washing with purified water can be a promising method for increasing the efficiency of sorption purification of water from biogenic ions. The study of the sorption capacity under static conditions at a ratio of sorbent to solution S:L=1:100 and an initial solution concentration of 1.4 mg NH<sub>4</sub><sup>+</sup>/dm<sup>3</sup> showed a low efficiency of ammonium ion removal of ~ 5%. The highest efficiency of the sorbent is observed for a ratio of sorbent to solution S:L=1:400 and is ~ 17%. Therefore, the disadvantages of this method are, firstly, low purification efficiency even at sufficiently low initial concentrations of NH<sub>4</sub><sup>+</sup> ions; secondly, as the authors note, bentonites in aqueous solutions form stable colloidal solutions, which complicates the process of separating the

adsorbent from purified water and requires filtration or centrifugation, additional equipment and energy; Thirdly, when using bentonite for drinking water purification, pre-treatment is necessary, namely, significant pre-cleaning (2 or 3-fold washing with water to remove  $\text{NH}_4^+$  ions, which are by default on the surface) and surface activation by ultra-high-frequency electromagnetic radiation, which is associated with additional costs.

In (Papaevangelou et al., 2023) it was established that the adsorption capacity (capacity, diffusion coefficient, equilibrium constant) of natural aluminosilicates (montmorillonite and clinoptilolite) increases as a result of acid activation (surface treatment with sulfuric acid).

Some studies provide a probable mechanism of ammonium ion adsorption on the surface of inorganic adsorbents (Delgado et al., 2018; Malyovanyy et al., 2013; Malyovanyy et al., 2011a; Petrova et al., 2014). The authors (Delgado et al., 2018) established that the absorption of ammonium ions by clinoptilolite occurs simultaneously by two mechanisms. First, by ion exchange of  $\text{NH}_4^+$  for  $\text{Ca}^{2+}$  and  $\text{Na}^+$  ions and second, by the mechanism of physical adsorption of  $\text{NH}_4^+$  on Lewis basic surface centers and by replacing water molecules in the zeolite framework. According to (Lazaratou et al., 2024), the adsorption of  $\text{NH}_4^+$  on the surface of bentonite clay has a physical nature. The interaction of  $\text{NH}_4^+$  with the surface is weak and capillary condensation occurs in micropores. In addition, it was shown (Malyovanyy et al., 2011a) that the mechanism of sorption on the surface of bentonite depends on the purity of the initial sorbent, in particular, the content of its own mobile  $\text{NH}_4^+$  ions. Studies (Petrova et al., 2014), as a result of comparing the process of sorption of  $\text{NH}_4^+$  ions on the surface of natural and acid-activated aluminosilicate sorbents, established the following.  $\text{NH}_4^+$  ions from the solution are exchanged for  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions present on the surface of the sorbents. After treatment of the sorbents with sulfuric acid (2.33 mole/dm<sup>3</sup>), the processes of decationization, dealumination and cleavage of Si–O–Al bonds occur on the surface, resulting in the formation of silanol groups (Brønsted centers) and tricoordinate aluminum atoms (Lewis centers). The newly formed surface centers are able to additionally participate in the sorption of  $\text{NH}_4^+$ .

Therefore, taking into account the studies conducted by other authors, it can be stated that in the processes of sorption of  $\text{NH}_4^+$  ions on the

surface of natural sorbents, surface active Brønsted and Lewis centers of different acidity are of significant importance. The set of active centers is combined into a hydroxyl-hydrate layer of Brønsted and Lewis centers, which is the result of chemical and physical adsorption of water molecules on the surface (Danchenko et al., 2021; Rehman et al., 2022; Taneva et al., 2010; Tsimabaljuk et al., 2009; Widiastuti et al., 2011; Yusof et al., 2010). It is obvious that an increase in the number of active sorption centers on the surface will contribute to more effective sorption of  $\text{NH}_4^+$  ions, and the intensity of the interaction is determined by the acid-base characteristics of the above-mentioned centers.

## MATERIALS AND METHODS

Natural mineral sorbents of various chemical and mineral composition from deposits of Ukraine were selected as materials for the study: bentonite clay, kaolin clay, diabase flour and quartzite. Experimental studies were conducted for the selected sorbents to determine the mineral composition, dispersion, surface morphology and specific surface area of particles (Taneva et al., 2010; Widiastuti et al., 2011). The specific surface area was determined by the BET method (Brunauer, Emmet, Teller). X-ray phase analysis was performed to study the mineral composition. Studies of surface morphology and dispersion were carried out using a scanning electron microscope.

pK<sub>a</sub>-metric experimental method for determining the number of surface-active centers by adsorption of Gammet color indicators from aqueous solutions and photo colorimetric measurement of optical density. As a result, the indicators of the total number of acidic active centers  $\sum q_A$  with  $\text{pK}_a < 7$ , alkaline active centers  $\sum q_B$  with  $\text{pK}_a > 7$ , the total number of surface centers  $\sum q = \sum q_A + \sum q_B$  and the acid-base index  $Q = \sum q_A / \sum q_B$  were calculated. The obtained indicator makes it possible to assess the surface as a whole as neutral ( $Q \approx 1$ ), acidic ( $Q > 1$ ) or alkaline ( $Q < 1$ ). It is believed that the larger the value of  $Q$ , the more acidic the surface is characterized by its properties (has a positive charge). Accordingly, the smaller this value is from 1, the more alkaline the sorbent surface is (has a negative charge). The indicator of the integral acidity of the surface  $Q$  has certain advantages and disadvantages. The main disadvantage is that the  $Q$  value does not

allow to evaluate the acid-base properties of the surface separately according to Lewis and Brønsted and for these additional experimental studies are required. The advantages are the possibility of a more complete understanding of the acid-base nature of the surface of any sorbents within the framework of a small number of experimental and calculation operations.

pH-metric experimental method with potentiometric measurement of  $\text{pH}_{\text{eq}}$  of aqueous suspensions of sorbents in the process of establishing an equilibrium state. Taking into account the pH of pure water ( $\text{pH}_0$ ) and the pH of suspensions in the equilibrium state ( $\text{pH}_{\text{eq}}$ ), the  $\text{pH}_{\text{IIP}}$  values of aqueous suspensions were calculated, which correspond to the arithmetic mean  $\text{pK}_a$  of surface-active centers:  $\text{pH}_{\text{IIP}} = 1/n \sum_{i=1}^n (\text{pKa1} + \text{pKa2} \dots + \text{pKai})$ ;  $\text{pH}_{\text{IIP}} = \text{pH}_0 + (\text{pH}_{\text{eq}} - \text{pH}_0) \cdot (\text{pH}_0 - 6)$ . For an approximate estimate of the spectrum of active surface centers, the value  $\Delta\text{pH} = \text{pH}_{\text{IIP}} - \text{pH}_{\text{eq}}$  was calculated, which indicates the width of the  $\text{pK}_a$  range of centers on the surface. An increase in the value of  $\Delta\text{pH}$  shows an expansion of the spectrum of active centers in terms of  $\text{pK}_a$  on the surface. For an approximate quantitative estimate of the active surface centers, the duration of the time for establishing an equilibrium state in the suspension was established according to potentiometric studies. This value can characterize the total number of acid-base surface-active centers that participate in interactions with water molecules.

Studies of the sorption of  $\text{NH}_4^+$  ions by mineral sorbents under static conditions were carried out at a ratio of sorbent ( $S$ ) to aqueous solution ( $L$ )  $S:L = 1:100$  (Malyovanyy et al., 2011b). For this purpose,  $V = 0.05 \text{ dm}^3$  of aqueous solutions of ammonium chloride  $\text{NH}_4\text{Cl}$  with different initial concentrations of  $\text{NH}_4^+$  ions ( $C_0 = 0.011 - 0.099 \text{ mg-eq NH}_4^+/\text{dm}^3$ ) were poured into beakers and sorbent samples with a mass of  $m = 0.5 \text{ g}$  was added. The duration of contact of the sorbents with the solution was 2 hours with continuous stirring using a magnetic stirrer. The value of the duration of contact is due to the studies of work (Danchenko et al., 2019), where it was established that in 2 hours the processes of adsorption and ion exchange on the surface of the sorbents with the participation of  $\text{NH}_4^+$  occur completely. After separation of the solid phase in the mother liquor, the residual concentration of  $\text{NH}_4^+$  ( $C$ ) was determined by the photo colorimetric method with Nessler's reagent (Malyovanyy et al., 2011b). According to the results of the studies,

the adsorption  $A$  of  $\text{NH}_4^+$  ions in  $\text{mg-eq NH}_4^+/\text{m}^2$  was calculated according to the formula:  $A = (C_0 - C) V/1000 \text{ m S}$ .

The specific surface area of the sorbent  $S$  is included in the adsorption formula in order to establish relationships between the adsorption of  $\text{NH}_4^+$  ions, the number and acid-base properties of the surface-active centres of the sorbents. According to the results of the calculations, sorption isotherms were constructed under static conditions - graphs of the dependence  $A = f(C_0)$ . The pH of the mother liquor before and after adsorption was measured by the potentiometric method.

## RESULTS AND DISCUSSION

### Acid-base properties of the surface of the studied sorbents

The acidity of the surface of clay sorbents significantly depends on the mineral composition. The mineral composition of bentonite clay and kaolinite clay is almost homogeneous and is represented by the dominant mineral's montmorillonite and kaolinite, respectively. It is obvious that the presence of these minerals gives an almost neutral character to the surface of bentonite clay ( $Q \approx 0.9$ ) and a weakly alkaline one to kaolinite clay ( $Q \approx 0.7$ ). The composition of diabase flour includes several minerals: leucite, orthoclase, montmorillonite and quartz with impurities of limonite. The character of the surface of diabase flour occupies an intermediate value and is close to neutral ( $Q \approx 0.8$ ). The increase in the alkalinity of the surface of diabase flour compared to bentonite clay is associated with the presence of leucite and orthoclase minerals, which include potassium oxide. Additionally, alkalinity can be provided by impurities of limonite, which includes iron oxide. The surface of quartzite is characterized by the smallest number of active centers and the highest alkalinity ( $Q \approx 0.6$ ). This is apparently due to a more homogeneous mineral and chemical composition, since it consists almost entirely of silicon oxide ( $\beta$ -quartz). The results of the study of sorbents by the pK-metric method are presented in Table 1.

Regarding the acid-base nature of the surface, the results of the pH-metric study are fully confirmed by the data of the pK-metric analysis. Thus, from the data presented in Table 3, it follows that the surfaces of kaolin clay ( $\text{pH} = 9.1$ ) and quartzite ( $\text{pH} = 8.9$ ) are characterized by the



**Table 1.** Results of the study of the acid-base properties of the surface of sorbents by the pK-metric method

| Sorbent        | $\Sigma qA \cdot 10^{-12} (1/\text{cm}^2)$ | $\Sigma qB \cdot 10^{-12} (1/\text{cm}^2)$ | $\Sigma q \cdot 10^{-12} (1/\text{cm}^2)$ | Q   |
|----------------|--------------------------------------------|--------------------------------------------|-------------------------------------------|-----|
| Bentonite clay | 108                                        | 119                                        | 227                                       | 0.9 |
| Kaolin clay    | 78                                         | 120                                        | 198                                       | 0.7 |
| Diabase flour  | 148                                        | 185                                        | 333                                       | 0.8 |
| Quartzite      | 48                                         | 80                                         | 128                                       | 0.6 |

greatest alkalinity. This fully coincides with the data of the pK-metric analysis. Therefore, according to the results of the two methods, it can be concluded that the determining factor in the formation of the acid-base properties of sorbents is the mineral and chemical composition. From the data of Table 2, it is clear that the surface of diabase flour is characterized by the greatest number of active centers. This correlates with the greatest duration of the equilibrium state establishment time in aqueous suspensions of diabase flour (360 s). It should also be noted that for bentonite clay and kaolin clay sorbents, these indicators also agree:

the greater the total number of surface-active centers, the longer the duration of the equilibrium state in aqueous suspensions. There is an exception to this pattern: the quartzite surface has the smallest number of active centers, but the term for establishing equilibrium in quartzite suspension is quite long. Obviously, this is due to the fact that on the quartzite surface, active centers are characterized by a wide range of  $pK_a$  values. This is evidenced by the non-zero  $\Delta pH$  value. According to the results of Table 3, the spectrum of active surface centers of other sorbents is not wide. This conclusion follows from the fact that the values

**Table 2.** Results of the study of the acid-base properties of the surface of sorbents by the pH-metric method

| Sorbent        | $pH_0$ | $pH_{eq}$ | $pH_{IIP}$ | $\Delta pH$ | Duration of establishing equilibrium (s) |
|----------------|--------|-----------|------------|-------------|------------------------------------------|
| Bentonite clay | 7      | 7.4       | 7.5        | 0           | 300                                      |
| Kaolin clay    | 7      | 9.1       | 9.1        | 0           | 240                                      |
| Diabase flour  | 7      | 8.5       | 8.5        | 0           | 360                                      |
| Quartzite      | 7      | 8.5       | 8.9        | 0.5         | 360                                      |

**Table 3.** Mineral and chemical composition, dispersion, specific surface area of the studied sorbents

| Sorbent        | Mineral composition                                                                                                                                                                                                                                                                                                                                                      | Chemical composition (%)                                                                                                                                                                                                                                                     | Dispersion (microns) | Specific surface area ( $\text{m}^2/\text{g}$ ) |
|----------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------|-------------------------------------------------|
| Bentonite clay | Montmorillonite $(\text{Al,Mg})_2(\text{OH})_2[\text{Si}_4\text{O}_{10}]\text{nH}_2\text{O}^+$<br>$\beta$ -quartz $\text{SiO}_2^+$<br>Kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4^+$                                                                                                                                                                        | $\text{SiO}_2 - 30\text{--}70$ $\text{Al}_2\text{O}_3 - 10\text{--}40$ $\text{Fe}_2\text{O}_3 - 4\text{--}5$<br>$\text{TiO}_2 - 0.4$<br>$\text{MgO} - 3\text{--}3.5$<br>$\text{CaO} - 2.1$<br>$\text{Na}_2\text{O} - 1.9\text{--}2.3$ $\text{K}_2\text{O} - 0.9\text{--}1.2$ | 10–20                | 15.6                                            |
| Kaolin clay    | Kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4^+$<br>$\beta$ -quartz $\text{SiO}_2^+$<br>Biotite $(\text{Fe,Mg})_3[\text{OH}]_2(\text{Al,Fe})\text{Si}_3\text{O}_{10}^+$<br>Hydrous micas (K,Na) $\text{Al}_2(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2\text{nH}_2\text{O}^+$                                                                                  | $\text{SiO}_2 - 46\text{--}70$ $\text{Al}_2\text{O}_3 - 22\text{--}24$ $\text{Fe}_2\text{O}_3 - 0.2\text{--}0.4$<br>$\text{TiO}_2 - 0.2\text{--}1.1$<br>$\text{MgO}+\text{CaO} - 0.4\text{--}1.2$<br>$\text{Na}_2\text{O}+\text{K}_2\text{O} - 0.2\text{--}0.8$              | 4–5                  | 8.8                                             |
| Diabase flour  | $\beta$ -quartz $\text{SiO}_2^+$<br>Montmorillonite $(\text{Al,Mg})_2(\text{OH})_2[\text{Si}_4\text{O}_{10}]\text{nH}_2\text{O}^+$<br>Orthoclase $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2^+$<br>Leucite $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2^+$<br>Limonite $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}^+$ | $\text{SiO}_2 - 45\text{--}76$ $\text{Al}_2\text{O}_3 - 7\text{--}14$ $\text{Fe}_2\text{O}_3 - 4\text{--}15$<br>$\text{MgO} - 2\text{--}17$<br>$\text{CaO} - 4\text{--}6$                                                                                                    | 2–4                  | 1.9                                             |
| Quartzite      | $\beta$ -quartz $\text{SiO}_2^+$<br>Montmorillonite $(\text{Al,Mg})_2(\text{OH})_2[\text{Si}_4\text{O}_{10}]\text{nH}_2\text{O}^+$<br>Kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4^+$<br>Albite $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2^+$<br>Orthoclase $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2^+$ | $\text{SiO}_2 - 97\text{--}99$ $\text{Al}_2\text{O}_3 - 0.7\text{--}1.2$ $\text{Fe}_2\text{O}_3 - 0.1\text{--}0.4$<br>$\text{TiO}_2 - 0.03\text{--}0.2$<br>$\text{MgO}+\text{CaO} - \text{traces}$<br>$\text{Na}_2\text{O}+\text{K}_2\text{O} - 0.13$                        | 10–20                | 3                                               |

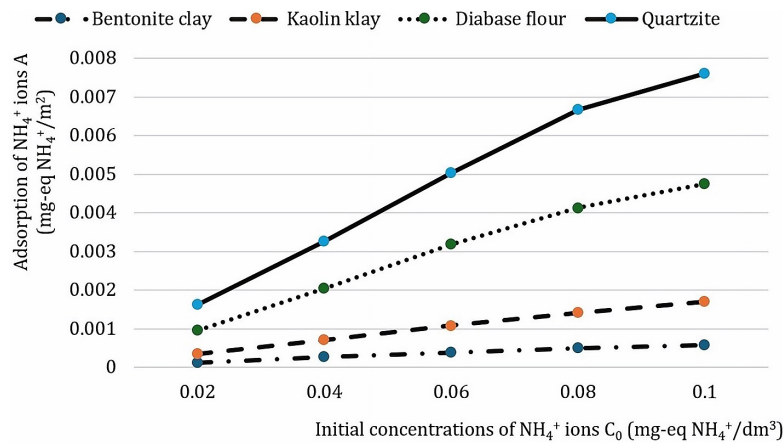
**Note:** • – basic mineral phase; + - side mineral phase; \* - traces.

of  $\Delta pH$  are equal to zero. Therefore, most of the surface-active centers of kaolin clay, bentonite clay and diabase flour, apparently, have close  $pK_a$  values. The results of the study of sorbents by the pH-metric method are presented in Table 2.

### Research into the mechanism of sorption of ammonium ions on the surface of natural mineral sorbents

The results obtained are shown in Figure 1, Table 3, Table 4 and Table 5. As can be seen from the presented results, the dependences  $A = f(C_0)$  for all sorbents in the studied concentration range are directly proportional. This fact is confirmed by the results of experiments by other authors (Delgado

et al., 2018; Malyovanyy et al., 2013; Petrova et al., 2014). As follows from the results of Figure 1, the efficiency of  $NH_4^+$  ion extraction decreases in the following order: Diabase flour > Quartzite > Kaolin clay > Bentonite clay. The complexity of the comparative analysis of the obtained data is due to the fact that the used mineral sorbents have a different morphological structure (Rehman et al., 2022; Taneva et al., 2010; Tsimabaljuk et al., 2009; Widiastuti et al., 2011), with which, probably, the mechanisms of  $NH_4^+$  ion extraction are associated. As was established (Delgado et al., 2018; Malyovanyy et al., 2013), the extraction of  $NH_4^+$  ions by bentonite clay occurs by two mechanisms: physical adsorption and ion exchange. In addition,



**Figure 1.** Isotherms of sorption on the surface of sorbents from aqueous solutions  $NH_4Cl$  in static conditions

**Table 4.** Acidity of the mother liquor bentonite clay and quartzite before and after sorption

| Initial concentrations of $NH_4^+$ ions $C_0$ (mg-eq $NH_4^+/dm^3$ ) | Bentonite clay     |                   | Quartzite          |                   |
|----------------------------------------------------------------------|--------------------|-------------------|--------------------|-------------------|
|                                                                      | pH before sorption | pH after sorption | pH before sorption | pH after sorption |
| 0.02                                                                 | 6.5                | 6.9               | 6.5                | 6.6               |
| 0.04                                                                 | 6.6                | 6.7               | 6.6                | 6.7               |
| 0.06                                                                 | 6.7                | 6.8               | 6.7                | 6.7               |
| 0.08                                                                 | 6.8                | 7.2               | 6.6                | 6.8               |
| 0.1                                                                  | 6.8                | 7.2               | 6.7                | 6.7               |

**Table 5.** Acidity of the mother liquor kaolin clay and diabase flour before and after sorption

| Initial concentrations of $NH_4^+$ ions $C_0$ (mg-eq $NH_4^+/dm^3$ ) | Kaolin clay        |                   | Diabase flour      |                   |
|----------------------------------------------------------------------|--------------------|-------------------|--------------------|-------------------|
|                                                                      | pH before sorption | pH after sorption | pH before sorption | pH after sorption |
| 0.02                                                                 | 6.2                | 6.1               | 6.2                | 7.1               |
| 0.04                                                                 | 6.8                | 6                 | 6.4                | 7.1               |
| 0.06                                                                 | 6.8                | 6.0               | 6.7                | 7.1               |
| 0.08                                                                 | 6.9                | 6.1               | 6.8                | 7.1               |
| 0.1                                                                  | 7                  | 6                 | 6.8                | 7.3               |

it was established that  $\text{NH}_4^+$  ions diffuse into the interlayer space of lamellar bentonite particles, where water molecules are replaced. Despite this, the obtained data (Figure 1) indicate that bentonite clay, in comparison with others, is the worst sorbent for  $\text{NH}_4^+$  ions. The most logical is to compare the sorption properties of diabase flour and kaolin clay. If we assume that both mechanisms are also implemented on the surface of these sorbents, the following conclusions can be drawn. Physical adsorption of positively charged  $\text{NH}_4^+$  ions can occur on Lewis alkaline centers  $-\text{MeO}^-$  and on ionized acidic and weakly acidic Brønsted centers  $-\text{Me}(\text{OH})_2^-$ . In this case, the pH of the mother liquors obviously increases due to the release of  $\text{OH}^-$  ions (Table 5). Ion exchange on the surface of the sorbents can be carried out due to the exchange of  $\text{NH}_4^+$  ions for  $\text{H}^+$  ions with the participation of Brønsted acidic centers. In this case, the pH of the mother liquors decreases due to an increase in the concentration of  $\text{H}^+$  ions.

Given the above assumptions and conclusions, as well as the results of experimental studies, the following can be formulated. Obviously, the removal of  $\text{NH}_4^+$  ions on the surface of kaolin clay occurs mainly by the mechanism of ion exchange. This is confirmed by the presence of a large number of acidic active centres, which are able to replace the  $\text{H}^+$  ion, as well as by a decrease in the pH of mother liquors after adsorption. The removal of  $\text{NH}_4^+$  ions by the surface of diabase flour, apparently, occurs mainly by the mechanism of physical adsorption.  $\text{NH}_4^+$  ions are adsorbed on ionized acidic and weakly acidic active centres, as well as on the alkaline centres of Brønsted and Lewis. At the same time, the pH of mother liquors after adsorption increases. It is obvious that the mechanism of physical adsorption is also implemented in quartzite suspensions. This is evidenced by the fact that the pH of the suspensions after sorption almost does not change. Considering the fact that the number of active centres on the quartzite surface is the smallest, and the sorption of  $\text{NH}_4^+$  ions is quite high, it can be argued that not only the electrostatic mechanism is implemented, but also Van der Waals interactions on the quartzite surface. In bentonite clay suspensions, a mixed mechanism may be implemented to extract  $\text{NH}_4^+$  ions. Interpretation of the results of the sorption of ammonium ions by the surface of bentonite clay is complicated by the fact that natural clay already contains  $\text{NH}_4^+$  ions, which can also migrate into the solution during the experiment.

## CONCLUSIONS

As a result of the conducted research, the mechanisms and patterns of  $\text{NH}_4^+$  ion extraction from aqueous solutions on the surface of natural mineral sorbents: bentonite clay, kaolin clay, diabase flour and quartzite were established. The relationships between the mineral composition and structure of the hydroxyl-hydrate surface layer and the acid-base characteristics of the surface-active centers of the sorbents were established. It was shown that the mechanism of  $\text{NH}_4^+$  ion extraction is determined by the number and acid-base properties of the surface-active centers of the hydroxyl-hydrate layer. It was established that the main mechanism of sorption of  $\text{NH}_4^+$  ions on the surface of kaolin clay is ion exchange, physical adsorption occurs on the surface of diabase flour and quartzite, and a mixed mechanism is implemented on the surface of bentonite clay.

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