

Cr (III)-Containing Composite for Selective Sorption of Ammonium Ions from Solutions

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ABSTRACT: It was investigated the sorption of NH_4^+ (NH_3) on the sorbent AV-17(Cr) which is a composite, based on commercial ionic cross-linked polymer containing strongly basic groups and Cr(III)-containing compounds. The dependence of ammonium sorption on the pH of solution is complicated and passes through a maximum at about pH 5. The experimental data for ammonium sorption on sorbent AV-17(Cr) at 22 °C and pH 2; 5 and 10 are well described by the pseudo-first order kinetic model. The isotherms obtained at 22 and 40 °C were calculated using Freundlich, Langmuir, Sips and Dubinin-Radushkevich sorption models. The isotherms are better described by the Langmuir sorption model. The thermodynamic functions ΔG , ΔH and ΔS of the sorption process have been calculated.

KEYWORDS: Cr(III)-containing composite, Strongly basic cross-linked polymer, Chemisorption, Ion exchange, Ammonium ions, Sorption kinetics, Isotherms, Sorption models.

I. INTRODUCTION

A prevalent form of pollution of the surface waters with nitrogen compounds is the content of ammonium ions in them. An increased content of ammonium ions in the drinking water indicates the presence of bacterial contamination and gives the water an unpleasant odor and taste. The constant use of water containing excess ammonium ions leads to disturbance of acid-base balance in the body. For this reason the content of ammonium ions in drinking water is strictly regulated by the hygienic-sanitary state organs. The sources of contamination of surface waters are well known: the intensive farming with excessive use of nitrogenous fertilizers, waste from maintenance of animals, sewage, waters and waste from the meat and marine products processing industry and the decomposition of organic materials that contain nitrogen compounds and waste from chemical industry.

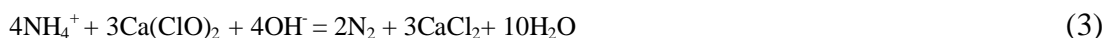
Ammonium ions in aqueous solutions are in equilibrium with ammonia:



Depending on concentration, pH and temperature, the balance (1) may move to the right until the emission of ammonia into the atmosphere will take place [1]. And as we know, the ammonia is very toxic.

The ammonium ions are hazardous to fish and other creatures of the lakes and rivers, for the ecosystems. Discharges of insufficiently treated by nitrogen compounds wastewater is the cause of eutrophication. Considering the above, it is clear that is necessary the removal of ammonium from municipal and industrial wastewater prior their discharge.

Various methods for removal of ammonium ions in water are known. One of such method is the chemical oxidation of ammonium nitrogen. The chemistry of oxidation by hypochlorite can be expressed by the following equations (2) and (3) [2,3]:



Anaerobic ammonium oxidation (anammox bacterium named *Candidatus Brocadia Anammoxidans*), is an effective ammonium removal process. Anammox oxidize ammonium to nitrogen gas [4,5]. There are many investigations in anaerobic oxidation of ammonium ions in water with nitrite ions to form molecular nitrogen by the following overall equation (4):

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Here are some of them [6-9]. The most of the investigations devoted to eliminating ammonium ions from various categories of water are those that use sorption methods. Methods of eliminating ammonium ions from water using natural and synthetic inorganic sorbents are proposed. It was shown that maximum sorption capacity of the Transcarpathian clinoptilolite toward ammonium evaluated under dynamic conditions varies in the interval 13.56–21.52 mg/g, being significantly higher than determined under static conditions [10]. In another paper [11], it is shown that Transcarpathian clinoptilolite for the removal of ions from aqueous solution attained at an initial ion concentration of 1000 mg/L was 11.6 mg/g. The effectiveness of ion sorption by the clinoptilolite samples decreased somewhat as the fraction size of the solid particles increased from 0.1–0.16 to 1.0–2.0 mm. The Langmuir isotherm gave a more adequate value for the correlation coefficient compared to that for the Freundlich isotherm. The ammonium ions sorption on the natural zeolite, clinoptilolite from Croatia, decreases with increasing particle size in range of 1–10 mm [12]. Kinetic studies suggest that ammonium sorption on zeolite could be described more favorably by the pseudo-second order kinetic model than by pseudo-first order. The Langmuir sorption model fitted well the experimental data. The sorption isotherms of the ammonium ions on natural sorbents as zeolite, glauconite and palygorskite (Ukraine) are best of all described by Langmuir sorption model [13]. But sorption isotherm of ammonium on Chinese natural zeolite is better described by Freundlich sorption model [14]. In the work [15] was performed the optimizing of absorption of ammonium ions from wastewater on natural zeolites. Many articles devoted to the ammonium ions sorption on natural and synthetic inorganic sorbents are reviewed in the Ref. [16]. The sorption of ammonium ions from solutions by natural or synthetic inorganic sorbents is conditioned mainly by the ion exchange process according to equation (5):



The advantages of methods to eliminate ammonium ions from solutions using inorganic sorbent are that many of them are not expensive and equilibrium sorption process can be established relative quickly. Disadvantages of these methods are that the ion exchange is a less selective process, usually sorbents are not stable in alkaline medium, phase's separation is often difficult and the sorbent is not rational to be regenerated.

This article explores the regularities of ammonium ions sorption from solution on a new sorbent, obtained by us.

II. MATERIALS AND METHODS

Materials: The commercial strongly basic cross-linked ionic polymers AV-17 in Cl⁻ form (AV-17(Cl)) have been used. The AV-17, containing R₄N⁺ functional groups, is a gel-type polymer, has a polystyrene-divinylbenzene matrix and full exchange capacity 3.5–4.0 meq./g [17]. Salts KCr(SO₄)₂·12H₂O, NH₄Cl, NaKC₄H₄O₆·4H₂O, Trilon B (complexon III), acid H₂SO₄, hydroxide NaOH, hydroxylamine NH₂OH·HCl, Nessler reactive have been used.

Analysis: The content of Cr³⁺ ions was determined photocolometrically using Trilon B, NH₂OH·HCl and NH₄OH [18]. The content of NH₄⁺ ions was also determined photocolometrically using Nessler reactive and NaKC₄H₄O₆·4H₂O [18], after contacting of 0.2 g of the sorbent with 100 mL of solution.

Obtaining of sorbent AV-17(Cr): A 5 g sample of the dried AV-17(Cl) was put in contact with 0.5 L of solution of KCr(SO₄)₂·12H₂O, containing 2 g Cr/L at 55 °C for 10 h. The system "polymer-solution of Cr(III) salt" pH value was adjusted periodically to 4.2 using NaOH solution. The Cr³⁺ content in the AV-17(Cr) was 32 mg/g.

FT-IR spectroscopy: The FT-IR spectra of the composites samples were recorded at 300 K in the range of 400–4000 cm⁻¹ on the Bruker Vertex 70 spectrometer. The composites samples were in the Vaseline-oil medium.

Scanning Electron Microscopy (SEM): For SEM analysis a Vega II ISH Tescan Company with acceleration voltage of 30 kV was used to examine the morphology of the compounds on the surface and in the volume of polymer granules. The solid samples were attached to aluminum holders using a silver based adhesive. Samples conductivity was achieved by sputter coating with a 15 nm layer of gold.

III. RESULTS AND DISCUSSION

The composite AV-17(Cr) consists of polymer AV-17 in the phase of which, the jarosite mineral type compound was synthesized: $R_4N[Cr_3(OH)_6(SO_4)_2]$, where R_4N^+ is functional group of the polymer. As it is shown in Fig.1, the metal compounds in the phase of sorbent are in the form of ultra-dispersed particles with a very low crystallinity that was confirmed and by X-ray diffraction analysis as well.

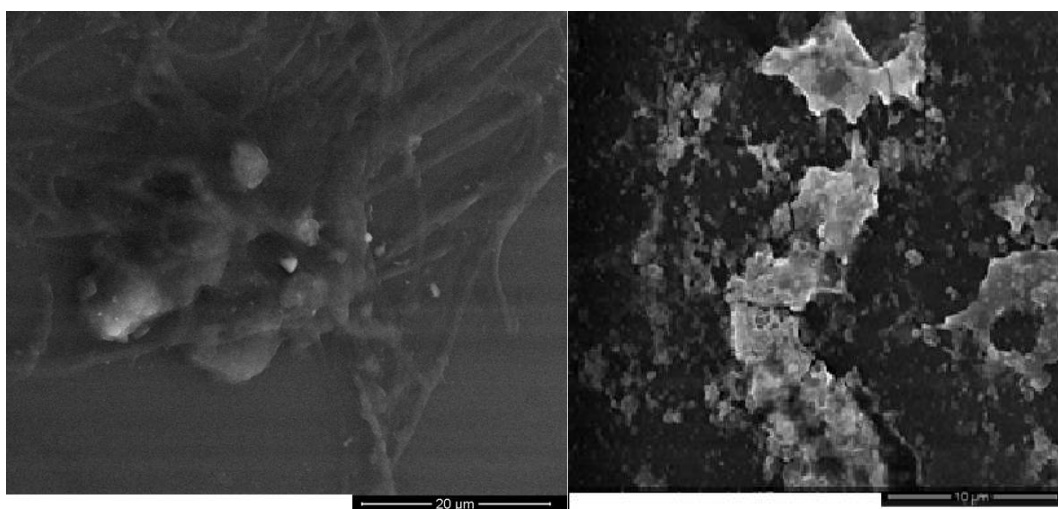
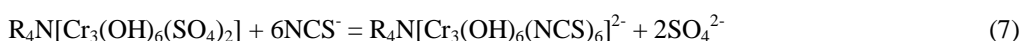
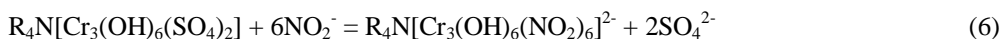


Fig.1. SEM images of the Cr(III) –containing sorbent AV-17(Cr).

The jarosite mineral type compounds are formed as layers of 3 or 6 octahedral cycles [19]. The OH⁻ groups are located in the equatorial plane, forming a bridge between metal ions, but SO₄²⁻ groups are located in axial position, each coordinate with 3 metal cations of 3 octahedra. Between the jarosite polymer layers there are mobile R_4N^+ and other cations (K⁺ and some H₃O⁺ for example) retained by electrostatic interactions. In fact, the R_4N^+ groups are linked by the organic polymer chains and their mobility is limited by the chains flexibility. This, together with the different degree of hydration of mobile ions, perhaps causes the formation in the polymer phase of jarosite type compounds with almost the absence of crystallinity. The natural jarosites have a high degree of crystallinity.

The absorbent AV-17(Cr) possesses selective sorption properties towards some anions [20-22] and molecules due to the coordination process (6-8):



We propose that sorbent AV-17(Cr) may retain NH₄⁺ ions as a result of exchange with R_4N^+ and coordination of Cr³⁺ with NH₃ molecules, destroying NH₄⁺ cations.

Solution pH impact on ammonium sorption. Since the composition of solution containing an ammonium salt is changing depending on pH, it is obviously that pH will significantly influence the ammonium sorption. Indeed, as shown in Fig.2, the sorption of ammonium ions by sorbent AV-17(Cr) depends considerably on the pH of the solution, passing through a maximum and a minimum.

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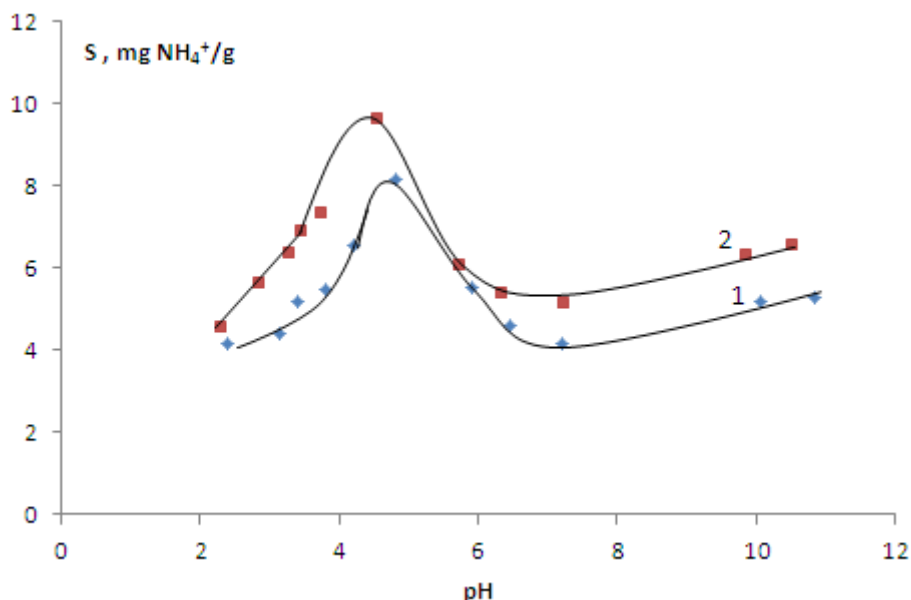


Fig. 2. Ammonium ions sorption on AV-17(Cr) as a function of the solution pH at 22 (1) and 50 °C (2)

In the work [15] is mentioned that ammonium ions adsorption on zeolites depends pointedly on the pH of the solution. The sorption of ammonium ions on Egyptian kaolinites depending on the pH passes through the pronounced maximum at pH 7 [23]. But in another article [24] it seems that sorption of ammonium ions on zeolites passes through two maximums (one of maximum is at pH 8 and a minimum at pH 7) depending on the pH of the solution. In several papers, it is deemed that the sorption of ammonium ions on mineral sorbents (Z-Na⁺) takes place according to the mechanism of ion exchange (9):



And the effect of pH on the ammonium ions sorption is conditioned by the processes (10) and (11):



Probably the absorption of ammonium ions on mineral sorbents is a more complicated process, although the ion exchange is predominant. According to the processes (9) - (11), sorption of ammonium ions should decrease monotonically with increasing pH of the solution. The changing of solution pH (by adding an acid or hydroxide solution, as NaOH for example) does not exclude the effect of process (10), but only lead to the displacement of it in one side or another.

In our systems we believe that the ammonium ions retention takes place according some processes. In the polymer phase we have a part of R₄N[Cr₃(OH)₆(SO₄)₂] and a part of H₃O[Cr₃(OH)₆(SO₄)₂] compounds. These compounds may participate in the process (12):



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Adding NaOH solution to change the pH of the system, OH⁻ ions penetrate faster than Na⁺ ions the polymer phase, because the polymer matrix contains positive charges (R₄N⁺). The OH⁻ ions combining with the H₃O⁺, favors the retention of the ammonium by the sorbent AV-17Cr). In solution, depending on pH, the balance (13) exists:



So with increasing pH the ammonium ions sorption on the sorbent AV-17(Cr) increases. But at pH at which takes place the formation of NH₃:H₂O, ammonium (NH₄⁺) sorption begins to decrease. From this moment begins the NH₃ complex forming with Cr³⁺ ions of jarosite type compounds (14):



Since the exchange of ligands in Cr³⁺ compounds is quite slow, the NH₃ sorption rate is also slow. As a result, ammonium NH₄⁺ (NH₃) sorption passes through a minimum in a function of the solution pH.

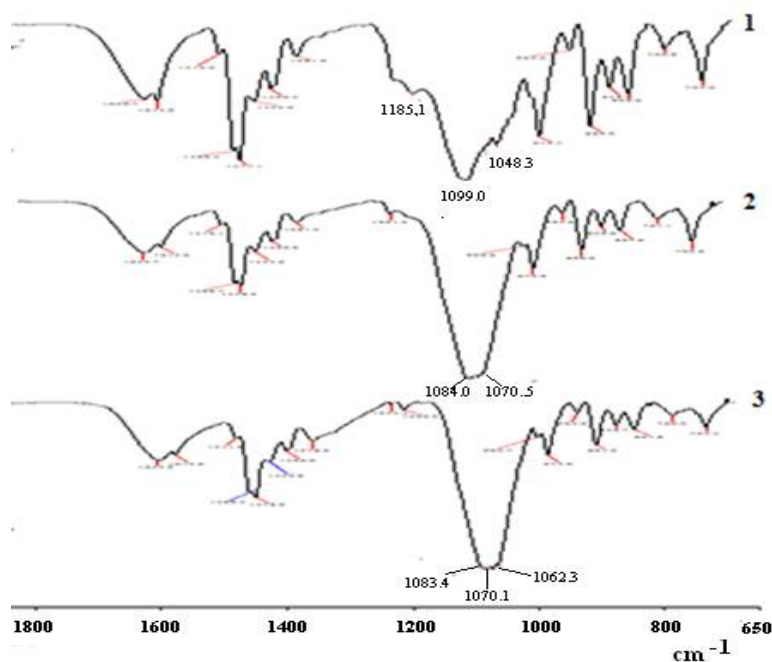


Fig.3. FTIR spectra of the AV-17(Cr) after sorption ammonium ions from solution with pH 2,0 (1), pH 5,0 (2) and pH 10,0 (3).

From Figure 3(1) it is seen that a part of SO₄²⁻ ions are tridentate bound with Cr³⁺ ions from sorbent (1185, 1099, 1048 cm⁻¹) [25, 26]. But not all R₄N⁺ groups of the polymer are part of the composition of the jarosite type compounds. The majority of the sulfate ions are related with the groups forming (R₄N)₂SO₄, (Fig.3, band at about 1100 cm⁻¹). In the FT-IR spectra of the sorbent samples, which retained ammonium from solutions with pH 5-10, adsorption band 1185 cm⁻¹ disappeared and band 1048 cm⁻¹ is shifted to 1070 cm⁻¹. This indicates that a part of ammonium is absorbed in the result of the process (14).

Sorption kinetics. The integral kinetic curves of ammonium sorption on sorbent AV-17(Cr) at 22°C are shown in Fig.(4). After a visual analysis of the curves of Fig.(4), we can make 2 conclusions: 1. Regardless of pH of the solution, sorption of ammonium on the sorbent AV-17(Cr) is a fairly slow process and equilibrium is not achieved even after

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20 hours. 2. Kinetic curves confirm that maximum of ammonia sorption is at the solution pH near 5. FT-IR spectra show that in the solution of pH 5 to 10 some of the sulphate ions in the phase of the composite are substituted by molecules of ammonia. So at least some of ammonium ions are retained in the composite because of NH_3 coordination with Cr^{3+} ions.

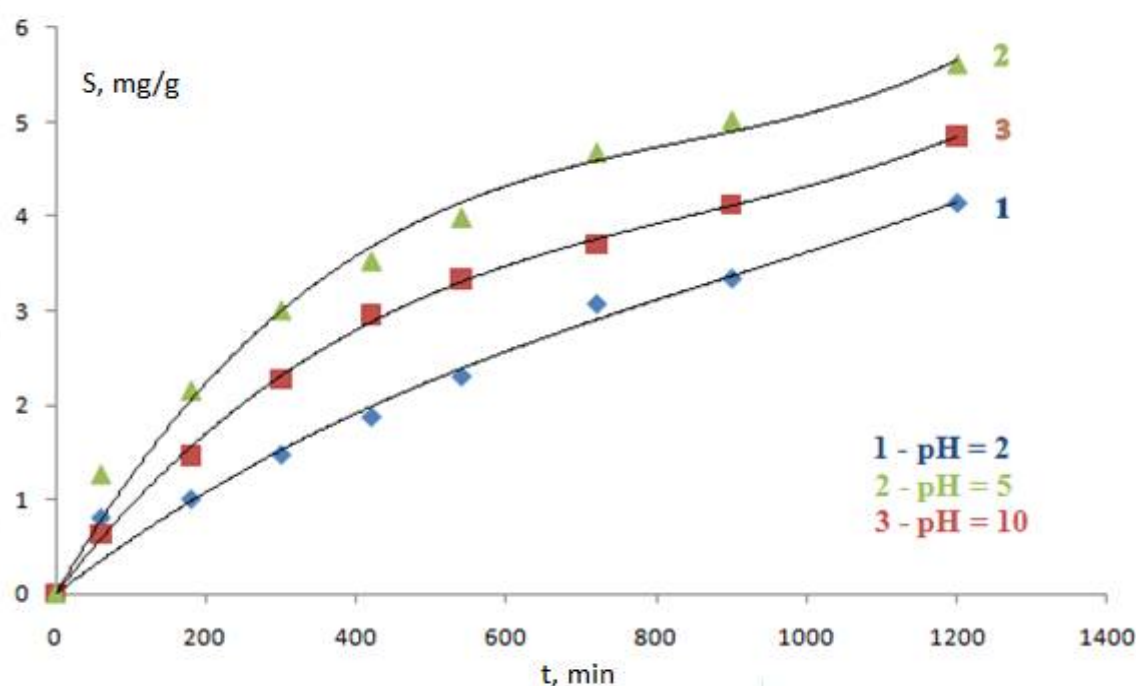


Fig.4. Integral kinetic curves of ammonium sorption at 22°C on AV-17(Cr) from solution with different pH values.

The ammonium sorption balance on mineral sorbents is achieved in different time intervals of the contact of sorbent with solution - from 2 hours to 1-2 days [23, 24]. And to be sure of reaching equilibrium, the sorbent was contacted with the solution even eight days [13]. Although ion exchange is a quick process, and we assume that in the acidic solution sorption NH_4^+ on sorbent AV-17(Cr) occurs as a result of cation exchange, as it is shown in Figure 4, sorption from solution with pH 2 is slow. This is explained by the fact that the matrix of the organic polymer contains groups with positive charges (R_4N^+).

In order to investigate the kinetics mechanism, which controls the sorption process of ammonium on sorbent AV-17(Cr), the nonlinear forms of the pseudo-first order (PFO) kinetic model and pseudo-second order (PSO) kinetic model [27,28] were used to fit the experimental data. The nonlinear form of the integrated PFO kinetic model is described by Eq.(15) and linear (to calculate the rate constant k_1) form by Eq.(16):

$$S_t = S_e(1 - e^{-k_1 t}) \quad (15) \quad \ln(S_e - k_1 t) \quad (16)$$

where: S_t Stand Seare the amount of ammonium sorbed at a time t and at equilibrium (mgNH_4^+/g), respectively; k_1 is the rate constant in the PFO kinetic model (min^{-1}).

The nonlinear form of the PSO kinetic model is expressed by Eq.(17) and linear form by Eq.(18):

$$S_t = \frac{k_2 S_e^2 t}{1 + k_2 S_e t} \quad (17) \quad \frac{t}{S_e} = \frac{1}{k_2 S_e^2} + \frac{1}{S_e} t \quad (18)$$

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where: Stand Sehave the same meaning as in Eq.(15), and k_2 is the rate constant of PSO kinetic model ($\text{g mg}^{-1} \text{min}^{-1}$).The calculated data of the kinetic parameters are shown in Table 1.

Table 1. Kinetic parameters of the sorption of ammonium on the sorbent AV-17(Cr)

| pH | PFO kinetic model | | | PSO kinetic model | |
|----|----------------------------------|------------------------|--------|----------------------------------|------------------------|
| | $S_e, \text{mg NH}_4^+/\text{g}$ | k_1, min^{-1} | R^2 | $S_e, \text{mg NH}_4^+/\text{g}$ | k_2, min^{-1} |
| 2 | 5.4 | 0.0011 | 0.9765 | 8.5 | $8.01 \cdot 10^{-4}$ |
| 5 | 5.4 | 0.0028 | 0.9445 | 9.35 | $1.57 \cdot 10^{-3}$ |
| 10 | 5.4 | 0.0015 | 0.9476 | 6.98 | $1.63 \cdot 10^{-3}$ |

The data in Table 1 demonstrates that sorption kinetics of ammonium ions by composite AV-17 (Cr) is described much better by the PFO kinetic model than PSO. This is well seen in Figures (5) - (7).

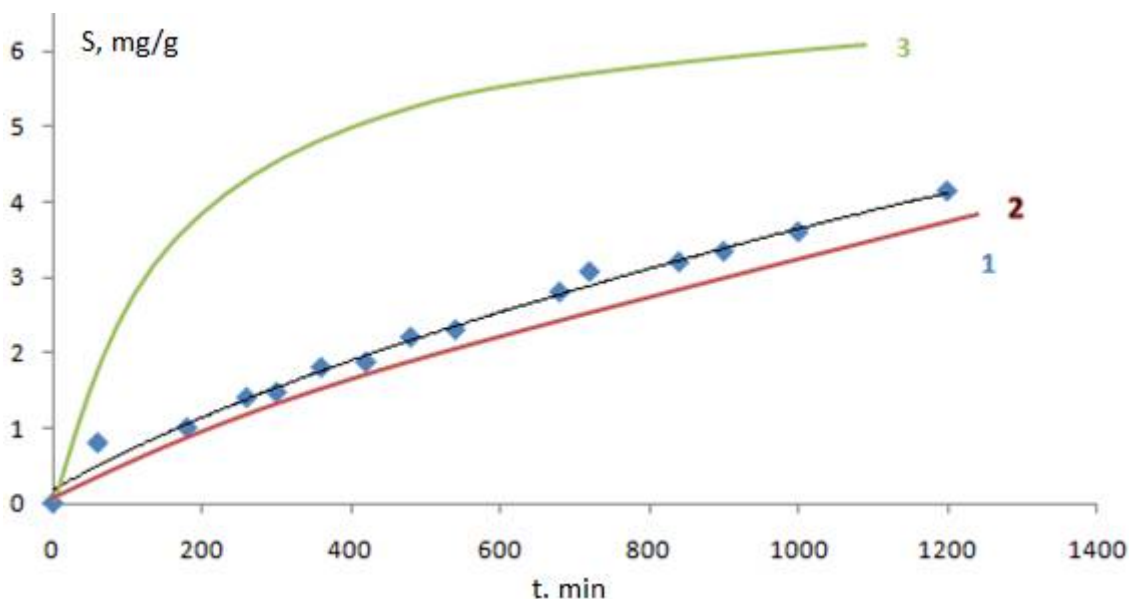


Fig.5. Kinetic curves of the ammonium sorption by AV-17(Cr) from solutions with pH 2: obtained experimentally (1), calculated with kinetic model PFO (2) and kinetic model PSO (3)

It is known that the sorption of a solute, involves three main stages: (i) film diffusion, which is the diffusion of the sorbate particles through the liquid layer to the sorbent surface; (ii) transport of the sorbate particles from the surface to the interior of the sorbent granules, called intra particle diffusion, or inner diffusion; (iii) sorption onto the active centers of the sorbent. Usually, the absorption rate is mainly controlled by the first two steps, the last one being very fast, in case of physical sorption. In case of chemisorption (ligands exchange) the rate-limiting step could be rate of chemical reaction. To explain the diffusion mechanism of the sorption process, the intra-particle diffusion model [29], expressed by Eq.(19), was used:

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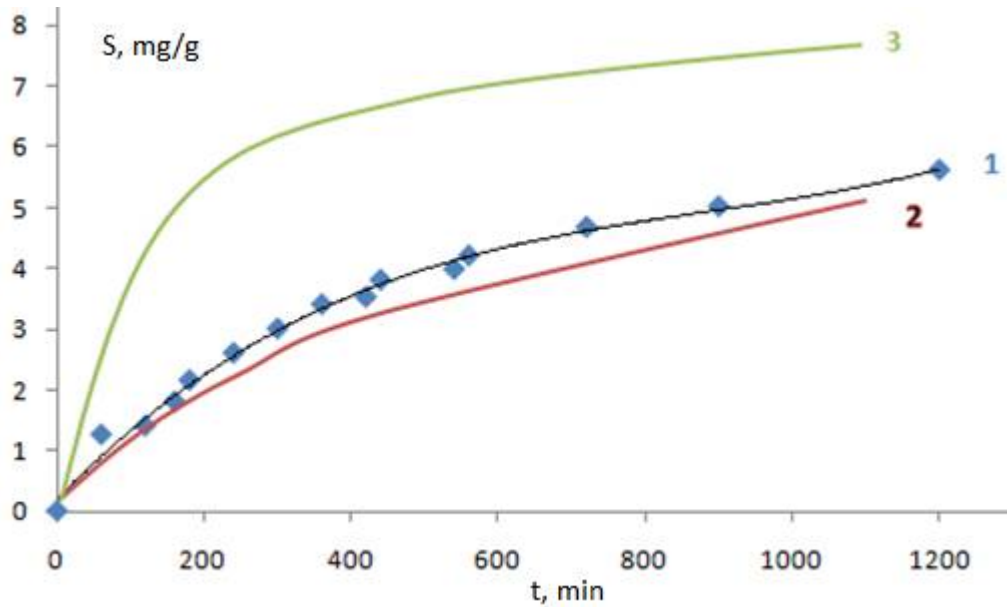


Fig.6. Kinetic curves of the ammonium sorption by AV-17(Cr) from solutions with pH 5: obtained experimentally (1), calculated with kinetic model PFO (2) and kinetic model PSO (3)

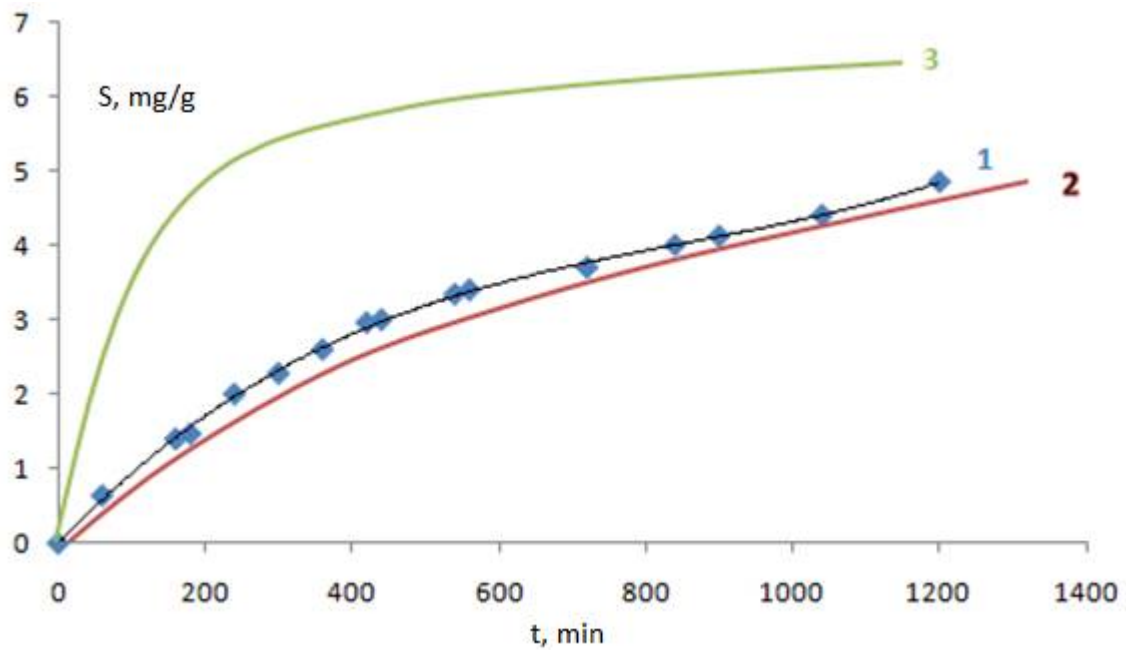


Fig.7. Kinetic curves of the ammonium sorption by AV-17(Cr) from solutions with pH 10: obtained experimentally (1), calculated with kinetic model PFO (2) and kinetic model PSO (3)

$$S_t = k_{id} t^{1/2} + C \quad (19)$$

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where: k_{id} is the intra-particle diffusion rate constant ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-0.5}$), C is a constant that gives an idea about the effect of boundary layer thickness, which means the larger the intercept, the greater the contribution of the film diffusion in the rate limiting step.

On the other hand, in order to determine the sorption limiting step, we have the graph Eq.(20) [30]:

$$-\ln(1 - F) = kt \quad (20)$$

where: $F = S_t/S$, t is time (min). It is known [30], that, the dependency, expressed by Eq.(20) for the external diffusion processes, should be linear.

The S dependency on for ammonium sorption in solution with pH 2 is a straight line (Fig.8).

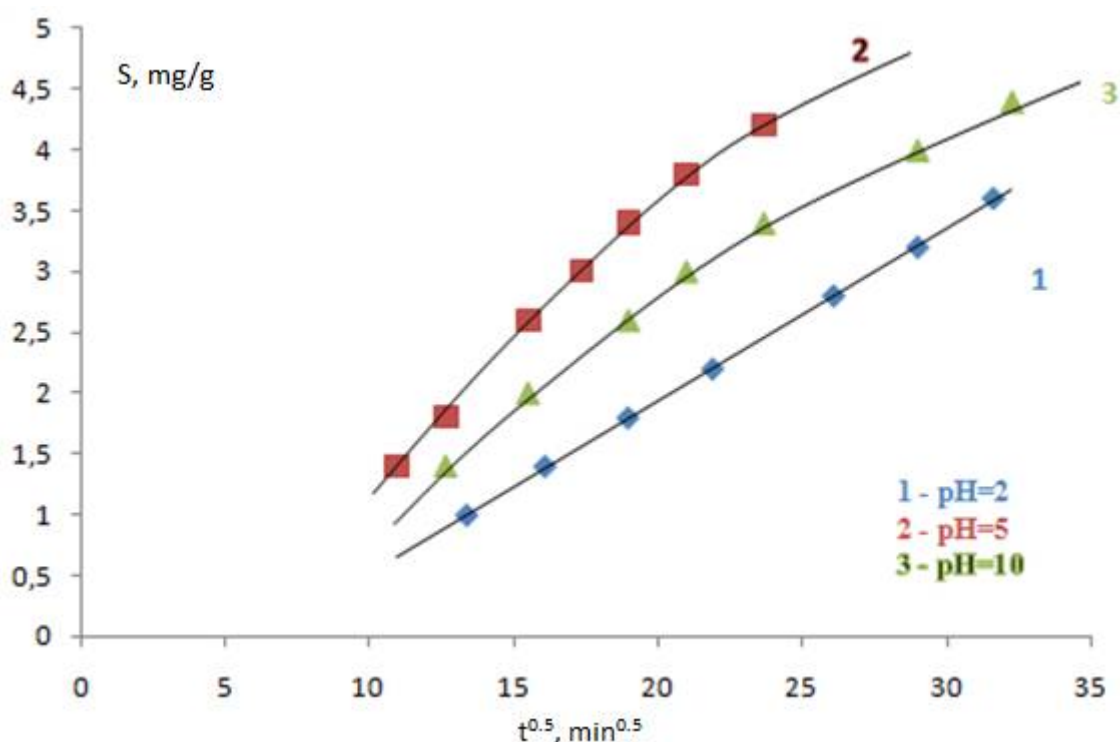


Fig.8. Dependence $S = f(t^{0.5})$ for the ammonium sorption on AV-17(Cr) from solution with different pH.

For ammonium sorption in solution with pH 2 dependence $-\ln(1-F) = f(t)$ also is linearly (Fig.9).

This indicates that intra-particle diffusion is the rate-controlling step. For sorption from solution with pH 5 and 10 the $S_t = f(t^{0.5})$ and $-\ln(1-F) = f(t)$ are not straight lines. This indicates that inter-particles diffusion is not the only rate-controlling step, the boundary layer diffusion having a contribution. The calculated diffusion mechanism data for the sorption process are shown in Table 2. The data in Table 2 confirm that the limiting step of the kinetic process (diffusion intra- and inter-particles) of ammonium sorption of composite AV-17 (Cr) depends on the pH of the solution. The dependency of diffusion mechanism on the pH of the solution can be explained by the fact that the report $\text{NH}_4^+/\text{NH}_3$ changes with pH. The NH_3 particles more easily penetrate the polymer phase than NH_4^+ , because the polymer matrix contains atoms with positive charges.

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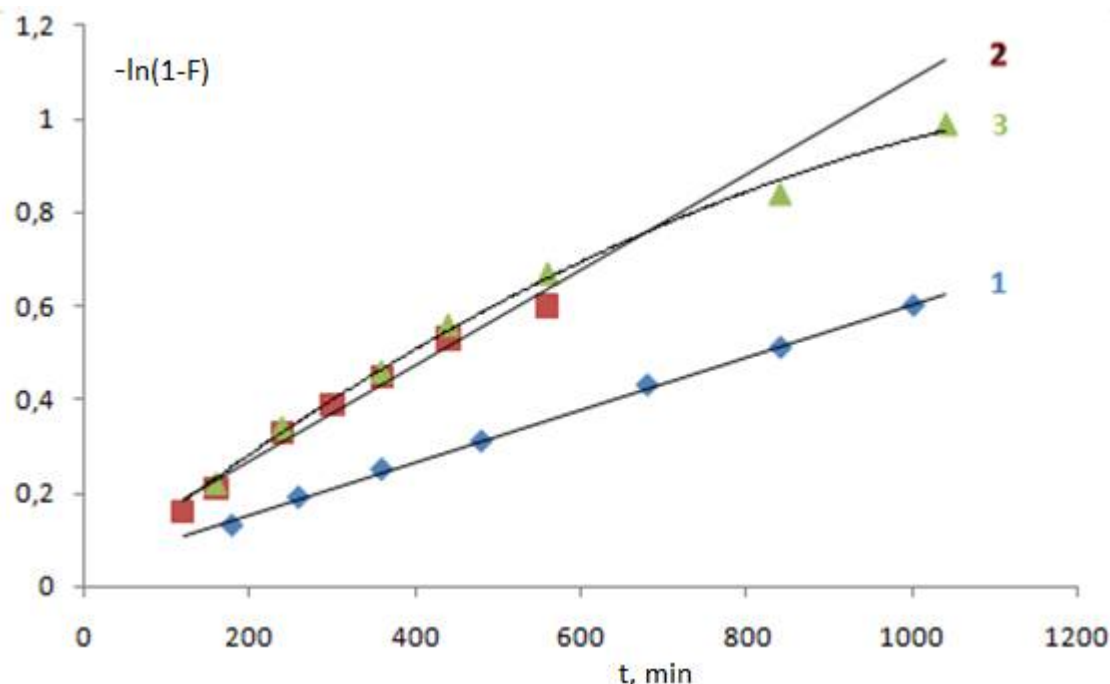


Fig.9. Dependence $-\ln(1-F) = f(t)$ for the ammonium sorption on AV-17(Cr) from solution with different pH.

Table 2. Diffusion data for the ammonium sorption process

| pH | External diffusion | | Internal diffusion | | |
|----|----------------------|----------------|-------------------------------------------------------------|------|----------------|
| | k. min ⁻¹ | R ² | k _{id} , mg. g ⁻¹ . min ^{-0.5} | C | R ² |
| 2 | 6 · 10 ⁻⁴ | 0.9985 | 0.1417 | -1 | 0.9999 |
| 5 | 1 · 10 ⁻³ | 0.9760 | 0.2264 | -1 | 0.9900 |
| 10 | 8 · 10 ⁻⁴ | 0.9783 | 0.1507 | -0.3 | 0.9840 |

Sorption isotherms. There were obtained sorption isotherms of ammonium from solutions on the composite AV-17(Cr) at 22 and 40 °C. The isotherms were calculated according to different sorption models.

a) Langmuir Sorption Model. The nonlinear form of the Langmuir sorption isotherms [31] are described by Eq.(21):

$$S = \frac{S_L K_L C_e}{1 + K_L C_e} \quad (21)$$

where: S is the ammonium sorption value at equilibrium (mg NH₄⁺/g); S_L is the monolayer capacity of the sorbent (mg NH₄⁺/g); K_L is the Langmuir isotherm constant (mg/L), C_e is the ammonium concentration at sorption equilibrium (mg NH₄⁺/L).

The constants S_L and K_L were calculated by the graph of the linear Langmuir isotherm expressed by Equation(22):

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$$\frac{C_e}{S} = \frac{1}{S_L K_L} + \frac{C_e}{S_L} \quad (22)$$

b) Freundlich Sorption Model. The Freundlich nonlinear isotherm [32] is described by Eq.(23) and the linear isotherm is described by Eq.(24):

$$S = K_F C_e^{1/n} \quad (23), \quad \ln S = \ln K_F + \frac{1}{n} \ln C_e \quad (24)$$

where: S is the same as in Equation (21), K_F is the Freundlich isotherm constant, which predicts the quantity of the ammonium per gram of sorbent at the equilibrium concentration (mg/g), $1/n$ is a measure of the nature and strength of the adsorption process and of the distribution of active sites. If $1/n > 1$, bond energies increase with the surface density; if $1/n < 1$, bond energies decrease with the surface density; and when $1/n = 1$, all surface sites are equivalent. The constants $1/n$ and K_F were calculated by the graph of the linear Freundlich isotherm, Equation (24).

c) Sips Sorption Model. The Sips isotherm is a combination of Langmuir and Freundlich sorption models [33,34]. At low concentration of sorbate, it reduces to a Freundlich sorption model, while at high of sorbate concentration; it predicts a monolayer adsorption capacity characteristic to the Langmuir sorption model. The nonlinear form of the Sips isotherm is expressed by Eq.(25) and the linear isotherm is expressed by Eq.(26):

$$S = \frac{S_s * K_s * C_e^{1/n}}{1 + K_s * C_e^{1/n}} \quad (25) \quad \frac{C_e^{1/n}}{S} = \frac{1}{S_s * K_s} + \frac{C_e^{1/n}}{S_s} \quad (26)$$

where: S and C_e have the same meaning as in Equation (21) and K_s is the Sips constant related to the energy of sorption and S_s is the monolayer sorption capacity.

d) Dubinin-Radushkevich (D-R) Sorption Model: The Dubinin-Radushkevich nonlinear isotherm [33,34] is expressed by Equation (25):

$$S = S_{D-R} * \exp\{-K_{D-R} [RT * \ln(1 + \frac{1}{C_e})]^2\} \quad (25)$$

where S is the amount of adsorbed ammonium (mg NH_4^+ /g), S_{D-R} is the maximum adsorption capacity of the ammonium (mg NH_4^+ /g), K_{D-R} is the Dubinin-Radushkevich isotherm constant (mol^2/kJ^2), C_e is the equilibrium concentration of ions (mg NH_4^+ /L), R is the constant (8.314 J/mol.K), T is the absolute temperature (K). The Dubinin-Radushkevich isotherm constant, K_{D-R} , is related to the mean free energy of adsorption, (kJ/mol), defined as the free energy when one mol of cations is transferred from infinity in solution to the surface of solid sorbent and computed using the Eq.(26):

$$S = \frac{1}{(2K_{D-R})^2} \quad (26)$$

The value of E is used to estimate the type of adsorption. When E is 1-8 kJ/mol, the sorption is determined by physical forces. The values of E between 9 and 16 kJ/mol are characteristic for ion exchange processes, and the E more than 16 kJ/mol - for chemisorption. The constants S_{D-R} and K_{D-R} were calculated by the graph of the linear Dubinin-Radushkevich isotherm, Eq.(27):

$$\ln S = \ln S_{D-R} - K_{D-R} [RT * \ln(1 + 1/C_e)]^2 \quad (27)$$

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Beside the correlation coefficient of determination (R^2), the statistical analysis of errors was performed by the nonlinear Chi-square test (χ^2) using Eq.(28) [35]:

$$\chi^2 = \sum \frac{(S_{exp.} - S_{calc.})^2}{S_{calc.}} \quad (28)$$

The experimental isotherms of ammonium sorption on composite AV-17(Cr), obtained at the contact of the sorbent with solution for 24 hours at 22 °C and 40 °C, are shown in Figures (10, 11, curve 1). The isotherms were constructed and calculated with the Langmuir, Freundlich, Sips and Dubinin-Radushkevich sorption models (Fig.10,11, curves 2-5).

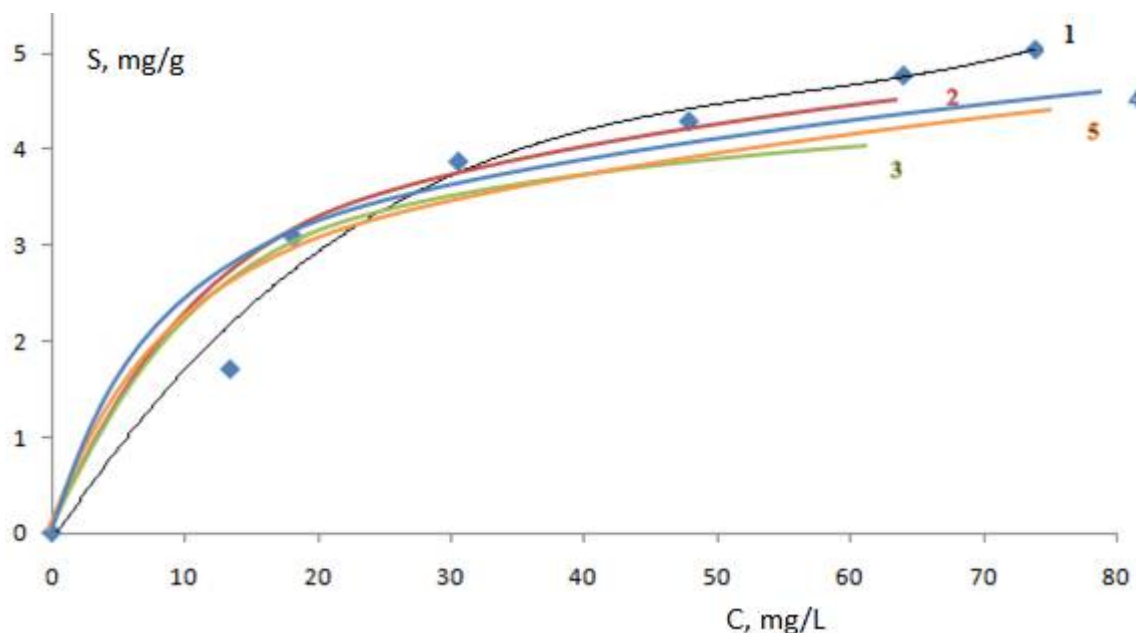


Fig. 10. Equilibrium sorption isotherms of ammonium ions on AV-17(Cr) at 22 °C, obtained experimentally (1) and calculated by Langmuir (2), Freundlich (3), Sips (4) and Dubinin-Radushkevich (5) sorption models.

The isotherms parameters and the value of R^2 and χ^2 are listed in Tables 3 and 4. These parameters show that isotherms of ammonium sorption onto sorbent AV-17(Cr) are best described by the Langmuir sorption model both at 22 and 40 °C. The data in Table 3 shows that 3 sorption models (Langmuir, Sips and Dubinin-Radushkevich) describe well enough the experimental sorption isotherm obtained at 22°C. However Langmuir sorption model more adequately describes the experimental isotherm. The obtained isotherm at 22 °C is the worst of all described by the Freundlich sorption model. This is seen and in Figure 10. The experimental isotherm, obtained at 40 °C may be described sufficiently well by almost all sorption models, but only at concentrations up to 40 mg NH_4^+ /L. This is clearly seen in Figure 11. The data in Table 4 shows, that we can consider the Langmuir and Sips models most appropriate.

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Table 3. Parameters of adsorption isotherm at $t = 22^\circ\text{C}$, calculated by Langmuir, Freundlich, Sips and Dubinin-Radushkevich sorption models

| Langmuir model | $S_L, \text{mg/g}$ | $K_L, \text{L/mg}$ | | R^2 | χ^2 |
|----------------------------|--------------------|---------------------|--------------------|--------|----------|
| | 5,4 | 0,077 | | 0,8258 | 0.024 |
| Freundlich model | K_F | $1/n$ | | R^2 | χ^2 |
| | 1,27 | 0,301 | | 0,8295 | 0.093 |
| Sips model | S_S | K_S | $1/n$ | R^2 | χ^2 |
| | 175,44 | $7,6 \cdot 10^{-3}$ | 0,301 | 0,8253 | 0.051 |
| Dubinin-Radushkevich model | S_{D-R} | K_{D-R} | $E, \text{kJ/mol}$ | R^2 | χ^2 |
| | 4,22 | $2 \cdot 10^{-5}$ | 15,81 | 0,8059 | 0.034 |

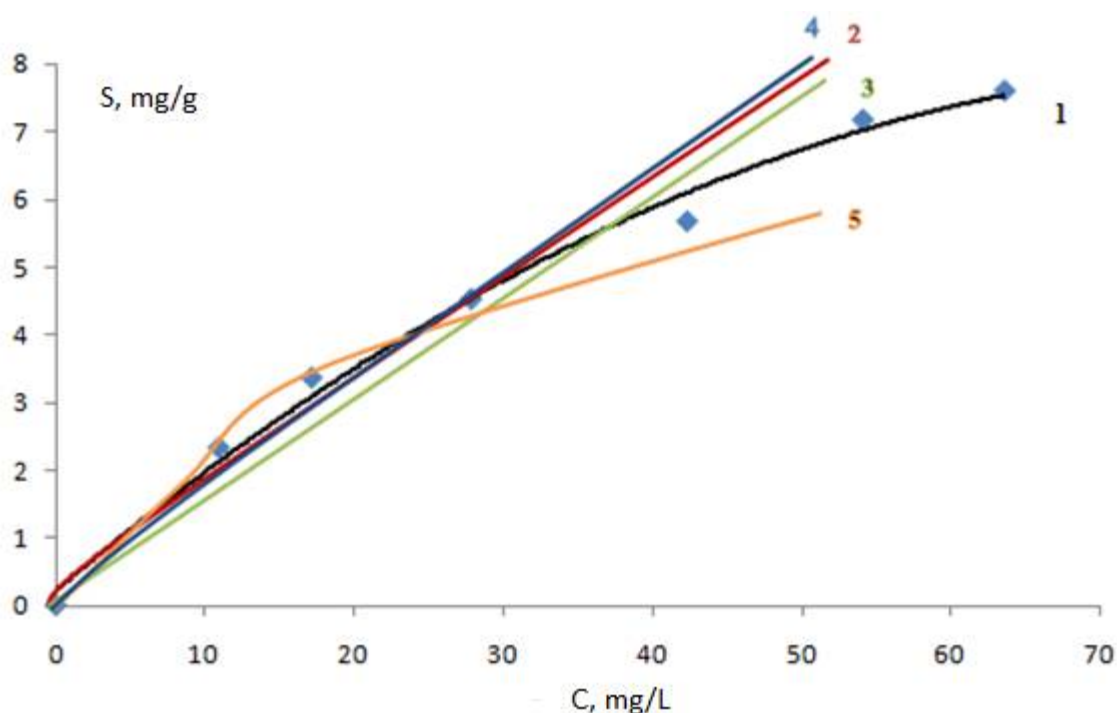


Fig.11. Equilibrium sorption isotherms of ammonium ions on AV-17(Cr) at 40°C , obtained experimentally (1) and calculated by Langmuir (2), Freundlich (3), Sips (4) and Dubinin-Radushkevich (5) sorption models.

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Table 4. Parameters of sorption isotherm obtained at $t = 40^{\circ}\text{C}$ and calculated by Langmuir, Freundlich, Sips and Dubinin-Radushkevich sorption models

| Langmuir model | $S_L, \text{mg/g}$ | $K_L, \text{L/mg}$ | | R^2 | χ^2 |
|----------------------------|--------------------|--------------------|----------------------|--------|----------|
| | | 18,25 | 0,012 | | 0.9779 |
| Ferundlich model | K_F | $1/n$ | | R^2 | χ^2 |
| | | 0,27 | 0,8354 | | 0.9459 |
| Sips model | S_s | K_s | $1/n$ | R^2 | χ^2 |
| | | 10000 | $2,86 \cdot 10^{-5}$ | 0,8354 | 0.9479 |
| Dubinin-Radushkevich model | S_{D-R} | K_{D-R} | $E, \text{kJ/mol}$ | R^2 | χ^2 |
| | | 4,39 | $1 \cdot 10^{-5}$ | 22,36 | 0.8259 |

Thermodynamic functions. The fact that the experimental isotherms of ammonia absorption are described well with Langmuir model, allows us to calculate the thermodynamic functions of sorption. There were calculated the thermodynamic functions ΔG , ΔH and ΔS of the sorption process using the Langmuir isotherm constant K_L . Since the thermodynamic functions are relative to one mole, the K_L constants at 22 and 40 °C were calculated based on the data S_L and C_e (Eq.21) respectively expressed by mol/g and mol/L

The ΔG value, equals to -20.52 kJ/mol at 22°C and -16.8 kJ/mol at 40°C was calculated by the Eq.(29):

$$\Delta G = - RT \ln K_L \quad (29)$$

The value of ΔH , equal to -81.52 kJ/mol, in the assumption that in the range of temperature 22-40 °C is constant, was calculated with Equation (30), were K_1 is K_L at 22 °C and K_2 is K_L at 40 °C :

$$\Delta H = \frac{T_1 T_2 (\ln K_2 / K_1)}{T_2 - T_1} \quad (30)$$

For calculation of the ΔS , the Equation (31) has been used:

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (31)$$

At 22°C the $\Delta S = - 221.2 \text{ J/mol}\cdot\text{K}$ and at 40°C the $\Delta S = - 206.8 \text{ J/mol}\cdot\text{K}$

The values of the thermodynamic functions confirm that ammonium absorption by the composite AV-17 (Cr) is a complex and exothermic process which occurs spontaneously.

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IV. CONCLUSION

We have reported the results of investigation of the ammonium $\text{NH}_4^+(\text{NH}_3)$ sorption on composite AV-17(Cr). The composite is a commercial cross-linked polymer (produced in Ukraine), containing strongly basic groups and jarosite mineral type compounds of chromium (III). It was shown, that ammonium ions sorption at 22 and 50 °C depends significantly on the pH of the solution, passing through the maximum at pH about 5. FTIR spectra show that in the solution of pH 5 to 10 some of the sulphate ions in the phase of the composite are substituted by molecules of ammonia. So at least some of ammonium ions is retained in the composite because of NH_3 coordination with Cr^{3+} ions. The coordination of ammonia molecules with the metal is confirmed by kinetic curves which demonstrate that equilibrium sorption is not established during 20 hours of the composite contact with the solution. The kinetics mechanism, which controls the sorption process of ammonium on sorbent AV-17(Cr), is described by pseudo-first order kinetic model. The intra-particle diffusion is the rate-controlling step of sorption in solution with pH 2. For sorption from solution with pH 5 and 10 inter-particle diffusion is not the only rate-controlling step, the boundary layer diffusion also having a contribution. The obtained at 22 and 40 °C isotherms were calculated with Langmuir, Freundlich, Sips and Dubinin-Radushkevich sorption models. The best model describing isotherms is the Langmuir sorption model. The constants of this model allowed calculation of the thermodynamic functions of sorption ΔG , ΔH and ΔS . To elucidate the chemistry of the adsorption process of $\text{NH}_4^+(\text{NH}_3)$ on the composite AV-17(Cr), it is necessary to make further investigation.

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