

A Composite Containing CR (III) Compounds and its Application to the Selective Sorption of Phosphate Ions

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ABSTRACT

The novelty of this research consist in the synthesis of metal compounds in the phase of polymers that do not contain in their matrix negatively charged or electron donors atoms and, theoretically, cannot interact with metal cations. The composite has property to selective sorption of phosphate from solutions. There was investigated the phosphate sorption by the obtained composite, containing polymer and ultra fine particles of chromium (III) compounds, (AV-17(Cr)), and by the commercial AV-17(Cl) polymer. Sorption on these sorbents, caused by ions and ligands exchange, can be used not only for water purification, but and for modeling of the processes occurring in soil at using of phosphorus fertilizers as well. Also it was investigated the sorption dependence on the solution pH and kinetics at 16 and 60 °C on AV-17(Cr) and at 20 and 54 °C on AV-17(Cl). The kinetics mechanism, which controls the sorption process is pseudo-second order model. It was determined the rate limiting step of sorption, depending on the sorbent nature and temperature. Isotherms were calculated with Langmuir, Freundlich, Sips, Dubinin-Radushkevich (AV-17(Cl) and BET (AV-17(Cr)) sorption models. To evaluate the influence of different factors (concentration of Na₃PO₄, KCl, NaNO₃ and Na₂SO₄, pH and temperature of solution, duration of the AV-17(Cr) contacting with solution) on phosphate sorption, the methods statistical mathematics (G.E.P.Box and K.B.Wilson) were used. Sorption optimizing was performed by the moving on the gradient method. Mathematical modeling and optimization allowed us not only a considerable increase in phosphate sorption (up to 102 mg P/g) on composite AV-17(Cr), but and show that sorption is a chemical selective process. Moreover, the conclusion is confirmed and by the studies carried out using the FTIR spectroscopy. Estimating the size and morphology of ultrafine particles of chromium (III) compounds in the phase of composite AV-17(Cr) were performed using the SEM.

Keywords: Composite, Selective Sorption, Phosphate, Isotherm, Optimizing

I. INTRODUCTION

Although phosphates in household use is prohibited in some countries, they are still widely used in other countries. But phosphorus compounds are used in many other areas of science and technology. The removing of phosphate excess from various categories of waters using sorption methods, requires obtaining of selective sorbents and investigation of sorbent-sorbate interactions.

It is known that intensive farming requires the use of different minerale fertilizers. A special role belongs to phosphate fertilizer. The application of phosphorus-containing fertilizers has lead to significant water

eutrophication problems that present a danger to human and ecological health. Unlike other types of fertilizers, fertilizers containing phosphate ions in soil form a different complex chemical equilibria. In soil a part of the phosphate ions is in solution, other part is labile bonded with soil and the third part of phosphate ions is non-labile bonded with soil:

P in solution ↔ P labile ↔ P non-labile. Even in solution there is a balance of various species of particles containing P(V): $H_3PO_4 \leftrightarrow H_2PO_4^- \leftrightarrow HPO_4^{2-} \leftrightarrow PO_4^{3-}$. These equilibria depend on many factors, but mostly they dependent on phosphate concentration, pH of the solution and nature of the soil (sorbent). There are many research papers dedicated to the interaction of the

phosphate ions with soil as a sorbent. Most of them take into account the particularities of soil in different geographical areas. Usually interaction of phosphate ions with the soil is investigated by means of sorption. Here are some works of this kind. Sorption and desorption of phosphate ions on different Philippines soil samples have been investigated [1]. It was shown that higher sorption capacity of phosphate ions had the soil with vermiculite and halloysite as the dominant clay minerals. In another article [2] it was shown that total sorbed and exchangeable P on Portuguese soils were described by modified Freundlich sorption model while those non-exchangeable P by Temkin model. The Langmuir sorption model is also provided to fit the data for non-exchangeable P. The amount of total sorbed P required to obtain 0.2 mg P/L in solution range from 5.3 to 819 mg P/kg. At this concentration exchangeable and non-exchangeable P values varied from 62.4 to 536.6 and from 0.4 to 322.1 mg P/kg respectively. As it was expected, phosphorus sorption isotherms varied from soils which varied in mineralogy, texture, and past history of phosphate fertilization [3]. Phosphate sorption isotherms were obtained for three acid highly weathered soils of Sierra Leone, by equilibrating air dry samples for 24 h with 0.01 M KH_2PO_4 solution at 25 °C [4]. The Langmuir and Temkin equations were used to evaluate the sorption capacities for phosphate. Phosphate sorption maxima of 2439, 2137 and 1429 mg/kg soil were calculated. It was investigated the effect of citrate and tartrate on phosphate adsorption by amorphous ferric hydroxide [5]. It appeared as though tartrate at 10^{-4} mol/L has no effect on P adsorption up to 750 mg P/g ferric hydroxide adsorbed.

It is important to realize that excessive use of phosphate fertilizers could lead to increased phosphorus concentrations in surface waters. And consequently - the increased abuse of flora in water. Many water sources are polluted with wastewater containing phosphorus compounds. An excess of phosphorus (P) is the most common cause of eutrophication of fresh water resources. Thus, it is very important to reduce the concentration of P to prevent harmful algal blooms. The development of technology of water purification from phosphate is an actual problem. The sorption methods of water purification from phosphate are quite promising.

There were investigated the effects of contact time of iron-zirconium sorbent, initial concentration of

phosphate solution, temperature, pH of solution, and ionic strength on the efficiency of phosphate removal [6]. It was shown that the adsorption data are fitted well to the Langmuir model with the maximum P adsorption capacity estimated to 24.9 mg P/g at pH 8.5 and 33.4 mg P/g at pH 5.5. The removal and recovery of phosphate from water using a hybrid nanocomposite containing aluminum nanoparticles (HPN) has been investigated [7]. The HPN-Pr removes 0.80 ± 0.01 mg P/g in a pH interval between 2.0 and 6.5. The sorption mechanism was described by the Freundlich sorption model. Three composite adsorbents, sulfate-coated zeolite, hydrotalcite, and activated alumina, were characterized and employed for the removal of phosphate from aqueous solution using equilibrium and kinetic batch experiments [8]. The SEM, FT-IR spectroscopy, and X-ray diffraction spectrum were used to study the surface characteristics of the coated layer. The adsorption of phosphate followed both Langmuir and Freundlich isotherms. The sulfate-coated zeolite was better for phosphate removal compared to hydrotalcite and activated alumina. The adsorption of phosphate was considered to take place mainly by ion exchange. The kinetic data followed a pseudo-second-order kinetic model.

In this paper we put in discussion the results of phosphate ions sorption investigation on Cr(III)-containing strongly basic cross-linked ionic commercial polymer AV-17. The choice of the Cr(III)-polymer composite as a sorbent is conditioned by the high stability of the metallic compounds in the polymer phase. For comparison, phosphate ions sorption has been studied on AV-17(Cl) as well.

These sorbents have a good hydrodynamic properties, possess selective sorption of phosphate ions, are able to be used cyclically after regeneration. On the other hand, the investigated systems may serve, to some extent, as a model of the behavior of the phosphate ions in different types of soil as sorbent.

II. METHODS AND MATERIAL

2.1. Materials

There was used AV-17(Cl), a commercial strongly basic cross-linked ionic polymer, containing $\text{N}(\text{CH}_3)_3\text{Cl}$

functional groups. The gel-type resin had a polystyrene-divinylbenzene matrix and full exchange capacity 3.5 – 4.2 mequiv./g [9]. Before sorption investigation the polymer was modified with Cr(III)-containing compounds according to reference [10] using $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. For investigation there was used AV-17 containing 35 mg Cr/g. The Cr^{3+} content in the composite was determined photocolorimetrically [11] after desorption [12]. There were prepared solutions of phosphate using $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$. Concentration of P(V) in the solution was determined photocolorimetrically [11] using NH_4VO_3 and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$. In order to adjust the pH of the solutions were used H_2SO_4 and NaOH. All the reagents were of analytical grade.

2.2. Methods

In all experiments 0.2 g of sorbent were contacted with 50 ml of phosphate solution. The amount of the phosphate ions sorbed at equilibrium was calculated with Eq. (1):

$$S_e = \frac{(C_o - C_e) \cdot V}{m} \quad (1)$$

where: S_e is the phosphate sorption at the equilibrium (mg P/g), C_o and C_e are the phosphate concentrations in solution respectively initial and at the sorption equilibrium (mg P/mL), V is the volume of the phosphate solution in contact with sorbent (mL), m is the mass of the air dried sorbent (g).

For the kinetic studies, the amount of the sorbed phosphate as a function of the contact time of the sorbent with the solution (S_t , mg P/g) was calculated by Eq (2):

$$S_t = \frac{(C_o - C_t) \cdot V}{m}, \quad (2)$$

where: C_o and C_t are the phosphate concentrations in solution respectively before and after contact with the sorbent (mg P/mL), V and m are the same as in Eq.(1).

To evaluate the influence of different factors (concentration of Na_3PO_4 , KCl, NaNO_3 and Na_2SO_4 , pH and temperature of solution, duration of the sorbent contacting with solution) on phosphate sorption, the methods statistical mathematics were used [13]. The experiences were carried out according to matrix of

Fractional Factorial Experiment Plane type FFE 2^{7-4} . There were measured and calculated the following responses of the system as a mean of two parallel experiences: Y_1 – sorption of phosphate (mg P/g) and Y_2 solution pH at sorption equilibrium.

The significance criterion, b_{sig} , was calculated at a level of significance of 5 % and number of freedom $f = 7$ [13]. A scanning electron microscope (Vega II ISH with accelerating voltage of 30 kV – Tescan Company) was used to examine the morphology of the metallic compounds on the surface and also within the bulk phase. The solid samples were attached to aluminium holders using a silver based adhesive. Samples conductivity was achieved by sputter coating with a 15 nm layer of gold.

The FTIR spectra of the sorbent samples were recorded at room temperature in the range of 400 – 4000 cm^{-1} on the Bruker Vertex 70 spectrometer.

III. RESULTS AND DISCUSSION

3.1. Solution pH impact on phosphate sorption

Sorption of anions as a result of anion exchange, practically, is not selective because is conditioned by Coulomb's electrostatic interactions and the modern technologies of purification of various categories of fluids and gases, concentration and separation of substances required new selective sorbents. One of the selective sorbents is composite AB-17(Cr). This composite is obtained by interaction of the polymer containing strongly basic functional groups (AV-17) with chromium sulphate or chromium alum solution in certain conditions [10]. As a result of these interactions, in the polymer phase, ultrafine particles (Fig.1) of the mineral jarosite type compounds are synthesized: $\text{R}_4\text{N}[\text{Cr}_3(\text{OH})_6(\text{SO}_4)_2]$, where R_4N^+ is a polymer functional group [14].

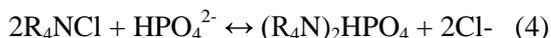
The selectivity of the composite is due to substitution of SO_4^{2-} ions by molecules or ions that are able to coordinate with metal cations. Choosing composite AV-17(Cr) for phosphate ions sorption research is conditioned by the formation of Cr(III)-containing compounds chemically less active, i.e. by forming kinetically stable complexes. Furthermore, composite

AB-17(Cr) is thermo stable at a wide range of temperatures [15].

As shown in Figure 2, the phosphate sorption on AV-17(Cl) depends much on the pH of the solution. In weak acid solutions the phosphate sorption on AV-17(Cl) takes place according to Eq.(3):



In a weakly alkaline solutions, the phosphate sorption on AV-17(Cl) is much lower and takes place specifically in accordance with Eq.(4):



Quite different looks the dependence on the pH the sorption of phosphate in the case of composite AV-17(Cr) (Fig.2).

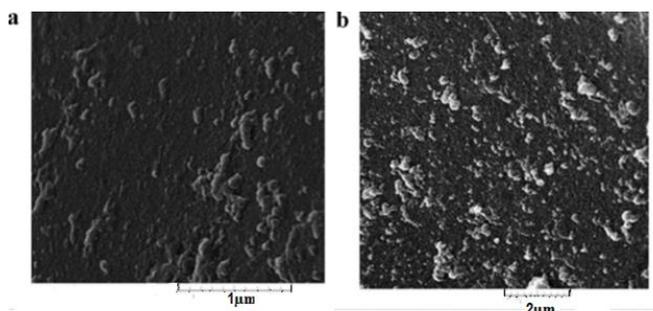


Figure 1: SEM images of the Cr (III)-containing particles on the surface (a) and in the volume (b) of AV-17(Cr) composite granule.

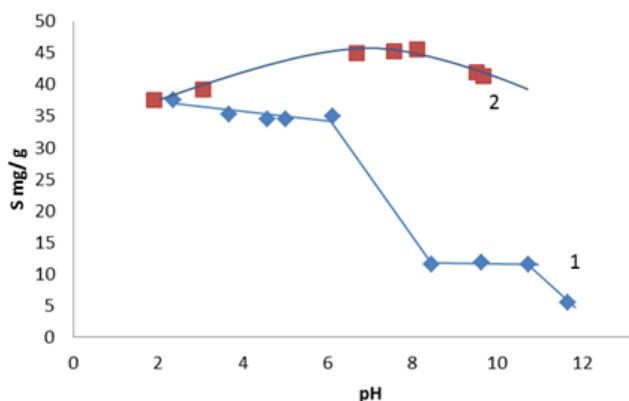


Figure 2: Phosphate sorption depending on pH solution on sorbent: 1 - AV-17(Cl), 2 - AV-17(Cr).

In the pH range 2-10 of solutions, phosphate sorption on composite AV-17(Cr) does not decrease, but on the contrary, increases slightly. This demonstrates that the

mechanism of phosphate sorption on the composite AV-17(Cr) differ from that on the AV-17(Cl).

Valuable information about the interaction of the phosphate ions with the sorbent AV-17(Cl) and the composite AV-17(Cr) gives FT-IR spectra (Figures 3 and 4). In the FTIR spectrum of the sorbent AV-17(Cl), which was in contact with the phosphate solution at pH 4.6, appear two close spectral lines at 1074 and 1067 cm^{-1} and a line at 1127 cm^{-1} (Fig.3). In the spectrum of the sorbent AV-17(Cl), which was in contact with the phosphate solution at pH 10, appear three close lines at 1074, 1067 and 1056 cm^{-1} and a line at 3675 cm^{-1} (Fig.3). In this spectrum also appears a line at 1259 cm^{-1} . According to the references [16, 17], the absorption spectral lines at 1074 and 1067 cm^{-1} in the FT-IR spectrum of the sorbent AV-17(Cl), which absorb phosphate from solution with pH 4.6, belong to $H_2PO_4^-$ but may correspond and to the HPO_4^{2-} ions. The state, at least, of a part of phosphate ions in the sorbent phase AV-17(Cl), which was in contact with the solution with pH 10, differs from that with pH 4.6. In the phase of AV-17(Cl), which was in contact with solution with pH 10, there are HPO_4^{2-} ions in which P=O group do not form H-bonds (line at 1250 cm^{-1}). Also, in this sorbent, the OH group of HPO_4^{2-} ion occupies a special position (line at 3675 cm^{-1}) unlike the OH groups of $H_2PO_4^-$ ions. It is possible to form in the sorbent phase not a too large amount of the phosphate oligomers.

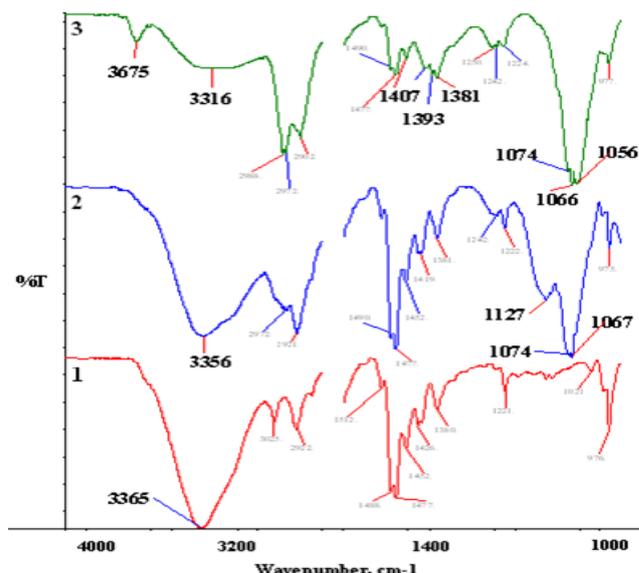


Figure 3: FTIR spectra of the sorbent: 1- AV-17(Cl), 2- AV-17(Cl) after phosphate sorption in solution with pH 4.6, 3- after phosphate sorption in solution with pH 10.

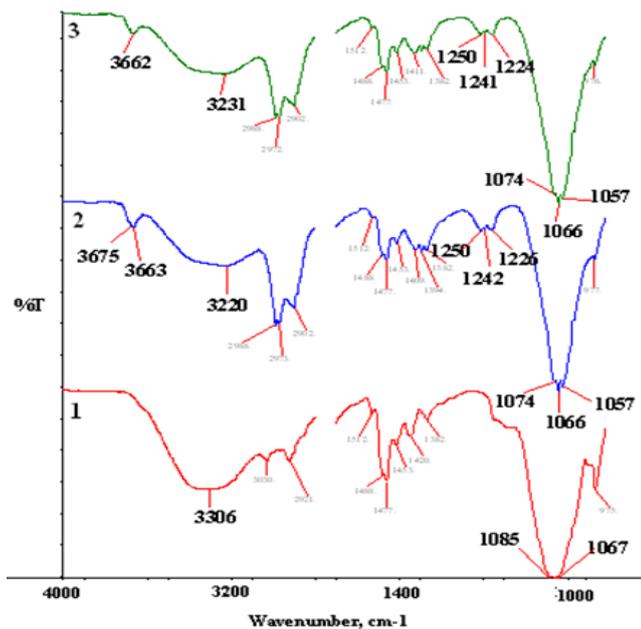
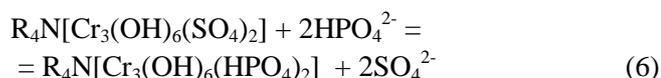
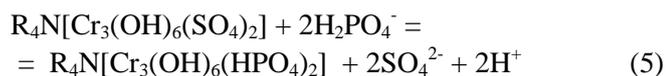


Figure 4: FTIR spectra of the composite: 1- AV-17(Cr), 2- AV-17(Cr) after phosphate sorption in solution with pH 4.7, 3- after phosphate sorption in solution with pH 8.5.

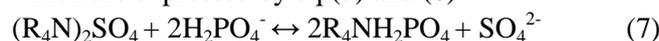
The FTIR spectra of the composite AV-17(Cr) which has been in contact with phosphate solutions with pH 4.7 and pH 8.5 (Figure 3), are similar to the spectrum of sorbent AV-17 (Cl), which contacted with the solution pH 10. Absorption bands around 1000 cm^{-1} of the composite AV-17(Cr), containing phosphate are similar to those of the composite that do not contain phosphate. However, as these bands are in the spectrum of the sorbent AV-17 (Cl), which retained the phosphate from the solution with pH 10, in which there are not SO_4^{2-} ions, it results that they belong to HPO_4^{2-} ions and, may be to phosphate oligomers. From data of FTIR spectra we can do the main conclusion that, whatever solution pH, the state of the phosphates in the AV-17(Cr) phase is similar. This explains the phosphate sorption on AV-17(Cr) depending on pH (Figure 2). Thus, processes of sorption of phosphates on the composite AV-17(Cr) occurs predominantly according to mechanism, expressed by eq. (5) and (6):



As it can be seen from eq.(5) and (6), in the phase of the composite, the dihydrophosphate ions are destroyed, and

solution becomes acidulated. Indeed, when the sorbent AV(Cr) was in contact with the phosphate solution, the pH decreased. In eq.(5) and (6) we can also see that regardless of the pH of the solution, the mechanism of interaction of the phosphate ions with the chromium compounds in the polymer phase is the same.

As not all groups R_4N^+ of the polymer are in the composition of the jarosite mineral type compounds, the remaining R_4NCl groups participate in the processes which are expressed by eq.(7) and (8):



This conditioned the passage of the phosphate sorption on composite AV-17(Cr) through a weak maximum in function of the solutions pH.

3.2. Sorption Kinetics

The integral kinetic curves of phosphate sorption on AV-17(Cl) at 20 and 54 °C and on composite AV-17(Cr) at 16 and 60 °C are shown in Fig.(5) and (6). After a visual analysis of the curves of Fig.(5) and (6), we can immediately make 2 conclusions:

1. Sorption of phosphate on composite AV-17(Cr) is much more dependent on temperature than on AV-17(Cl). This indicates that the sorption on AV-17(Cr) predominantly takes place due to the complex formation and not due to the ion exchange, a process that is little affected by temperature.

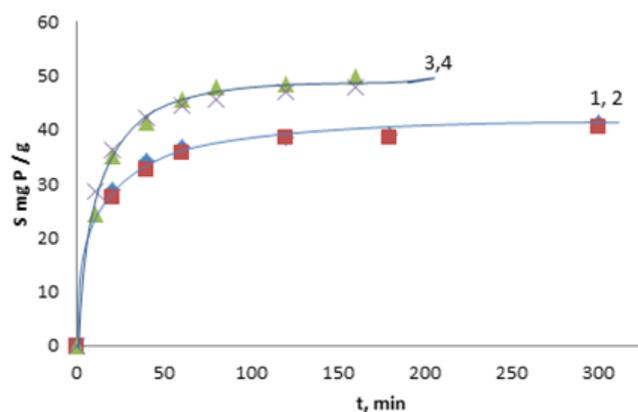


Figure 5 : Integral kinetic curves of phosphate sorption on AV-17(Cl) at 20 °C: 1 – experimentally obtained, 2 – calculated with PSO kinetic model; and at 54 °C: 3 – experimentally obtained, 4 - calculated with PSO kinetic model.

2. In 300 minutes of the sorbent contact with solution, the phosphate sorption on the composite AB-17 (Cr) does not reach the equilibrium. This proves again that

sorption on composite occurs, mainly, due to a chemical process. As it is known, the ligands exchange in the chromium (III) complexes is a slow process.

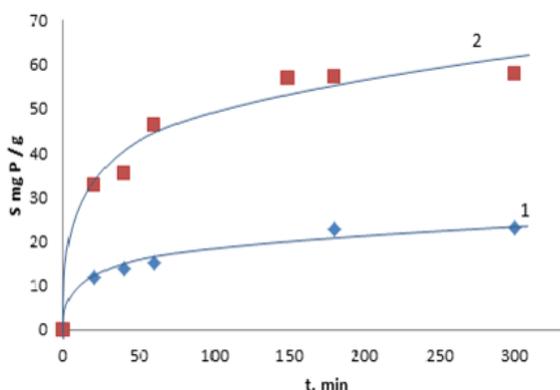


Figure 6 : Experimentally obtained integral kinetic curves of phosphate sorption on AV-17(Cr) obtained at 15 °C (1) and 60 °C (2).

In order to investigate the kinetics mechanism, which controls the sorption process of phosphate on AV-17(Cl) and composite AV-17(Cr), the nonlinear forms of the pseudo-first order (PFO) kinetic model and pseudo-second-order (PSO) kinetic model [18,19] were used to fit the experimental data. The nonlinear form of the integrated PFO kinetic model is described by Eq.(9):

$$St = Se(1 - e^{-k_1 t}), \quad (9)$$

where: St and Se are the amount of phosphate sorbed at a time t and at equilibrium (mg P/g), respectively; k_1 is the rate constant in the PFO kinetic model (min^{-1}).

The value of the k_1 was determined using the linear form of the PFO kinetic model which is expressed by Eq.(10):

$$\ln(Se - St) = \ln Se - k_1 t \quad (10)$$

The nonlinear form of the PSO kinetic model is expressed by Eq.(11):

$$St = \frac{k_2 Se^2 t}{1 + k_2 Se t}, \quad (11)$$

where: St and Se have the same meaning as in Eq.(9), and k_2 is the rate constant of PSO kinetic model ($\text{g mg}^{-1} \text{min}^{-1}$).

The value of the k_2 and Se were determined using the linear form of the PSO kinetic model which is expressed by Eq.(12):

$$\frac{t}{Se} = \frac{1}{k_2 Se^2} + \frac{1}{Se} t \quad (12)$$

To explain the diffusion mechanism of the sorption process, the intraparticle diffusion model [20], expressed by Eq.(13), was used:

$$St = k_{id} \cdot t^{0.5} + C_i \quad (13)$$

where: k_{id} is the intraparticle diffusion rate constant ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-0.5}$), C_i 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.(14) [21]:

$$(1 - F) = (t), \quad (14)$$

where: $F = St/Se$, t is time (min).

It is known [21], that, the dependency, expressed by Eq.(14) for the external diffusion processes, should be linear.

Besides the correlation coefficient of determination (R^2), the statistical analysis of errors was performed by the non-linear Chi-square test (χ^2) using Eq.(15)

$$S = \sum \frac{(S_{\text{exp}} - S_{\text{calc}})^2}{S_{\text{calc}}} \quad (15)$$

The experimental data, regardless of temperature, are well described by PSO kinetic model for phosphate sorption on AV-17(Cl) only: $k_2 = 0.00267 \text{ g} \cdot \text{mg}^{-1} \text{min}^{-1}$, $Se = 50 \text{ mg P/g}$, at 54 °C, and $k_2 = 0.00228 \text{ g} \cdot \text{mg}^{-1} \text{min}^{-1}$, $Se = 41.84 \text{ mg P/g}$, at 20 °C. The kinetics of the phosphate sorption on composite AV-17(Cr) at the temperature 16 and 60 °C, is not satisfactorily described neither by the PFO kinetic model, nor by the PSO model. 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 intraparticle 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 the rate-limiting step could be rate of chemical reaction.

For phosphate sorption at 20 and 54 °C on sorbent AV-17(Cl) the St dependency on $t^{0.5}$ is not a straight line which passes through the origin (Fig.7). This indicates that inter-particle diffusion is not the only rate-controlling step, the boundary layer diffusion having a contribution. Likewise, the dependence $-\ln(1-F) = f(t)$ confirms this. As shown in Figure 8, the dependence $-\ln(1-F) = f(t)$ for the sorption onto AV-17 (Cl) at 20 and 54 °C at the beginning is linear, then becomes non-linear. So, at the beginning, phosphate sorption rate is determined by external diffusion, and then by mixed diffusion.

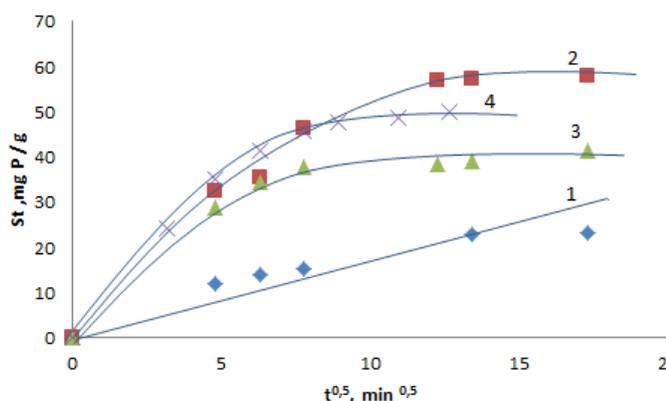


Figure 7: Dependence $S = f(t^{0.5})$ for the phosphate sorption on AV-17(Cr) at 16 °C (1), 60 °C (2) and on the AV-17(Cl) at 20 °C (3) and 54 °C (4).

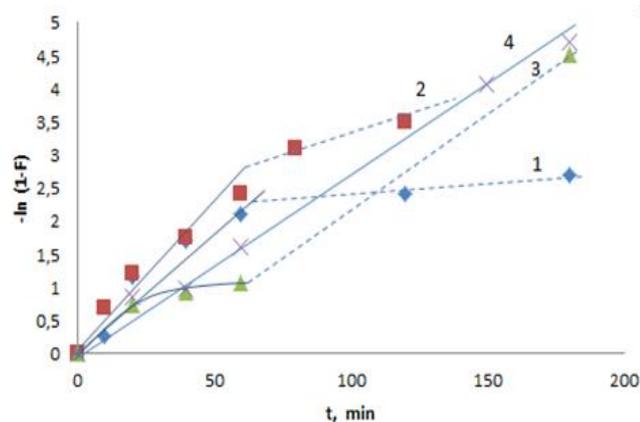


Figure 8: Dependence $-\ln(1-F) = f(t)$ for the phosphate sorption on AV-17(Cl) at 20 °C (1), 54 °C (2) and on the AV-17 (Cr) at 16 °C (3) and 60 °C (4).

The situation is completely different in the case of phosphate sorption on the composite AV-17(Cr). At a

temperature of 16 °C the St dependency on $t^{0.5}$ is a straight line (Fig.7) and is described by Equation $St = 0.9375 t^{0.5} + 8$. This indicates that inter-particle diffusion is the rate-controlling step. The dependence $-\ln(1-F) = f(t)$ also confirms this conclusion (Fig.8). It sounds strange, but at the temperature of 60 °C the situation is reversed. The St dependency on $t^{0.5}$ is not a straight line (Fig.7), but $-\ln(1-F) = f(t)$ is a straight line (Fig.8). The rate-controlling step of sorption is the boundary layer diffusion i.e. the external diffusion. This can be explained only if we admit that the phosphate sorption on composite AV - 17(Cr) is, mainly, a chemical process. At a temperature of 16 °C, the rate of the phosphate-sulfate ligands exchange in the jarosite mineral type compounds is less than the diffusion in the liquid layer surrounding the sorbent bead. With the increasing temperature, the reaction rate of exchange of the ligands grows faster than the rate of diffusion and at 60 °C it becomes larger as external diffusion rate.

3.3. Sorption isotherms

There were obtained sorption isotherms of phosphate from solutions on the composite AV-17(Cr) at 16 °C. For comparison the sorption isotherm of phosphate on the sorbent AV-17(Cl) at 20 °C has also been obtained. The isotherms were calculated according to different sorption models.

a) Langmuir Sorption Model

The nonlinear form of the Langmuir isotherm [22] is described by Eq.(16):

$$S = S_L \frac{K_L * C_e}{1 + K_L * C_e} \quad (16)$$

where: S is the phosphate sorption value at equilibrium (mg P/g); S_L is the monolayer capacity of the sorbent (mg P/g); K_L is the Langmuir isotherm constant (mg/mL), C_e is the phosphate concentration at sorption equilibrium (mg P/mL). The constants S_L and K_L were calculated by the graph of the linear Langmuir isotherm expressed by Eq.(17):

$$\frac{C_e}{S} = \frac{1}{S_L * K_L} + \frac{C_e}{S_L} \quad (17)$$

b) Freundlich Sorption Model

The nonlinear form of the Freundlich isotherm [23] is described by Eq.(18):

$$S = K_F * C_e^{1/n} \quad (18)$$

where: S is the same as in Equation (8), K_F is the Freundlich isotherm constant, which predicts the quantity of the phosphate 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 Eq.(19):

$$\ln S = \ln K_F + (1/n)\ln C_e \quad (19)$$

c) Sips Sorption Model.

The Sips isotherm is a combination of Langmuir and Freundlich sorption models [24,25]. 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.(20):

$$S = \frac{S_s * K_s * C_e^{1/n}}{1 + K_s * C_e^{1/n}} \quad (20)$$

where: S and C_e have the same meaning as in Equation (16) and (18), and K_s is the Sips constant related to the energy of sorption and S_s is the monolayer sorption capacity (mg P/g).

The constants S and K_s were calculated by the graph of the linear Sips isotherm, Eq. (21):

$$\frac{C_e^{1/n}}{S} = \frac{1}{S_s * K_s} + \frac{C_e^{1/n}}{S_s} \quad (21)$$

d) Dubinin-Radushkevich Sorption Model

The Dubinin-Radushkevich nonlinear isotherm[24,25] is expressed by Eq.(22):

$$S = S_{D-R} * \exp \left\{ -K_{D-R} \left[RT * \ln \left(1 + 1/C_e \right) \right]^2 \right\} \quad (22)$$

where S is the amount of adsorbed phosphate (mg P/g), S_{D-R} is the maximum adsorption capacity of the ions (mg/g), K_{D-R} is the Dubinin-Radushkevich isotherm constant (mol^2/kJ^2), C_e is the equilibrium concentration of phosphate (mg/mL), 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, E (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. (23):

$$E = \frac{1}{(2K_{D-R})^2} \quad (23)$$

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 graf of the linear Dubinin-Radushkevich isotherm, Eq.(24):

$$\ln S = \ln S_{D-R} - K_{D-R} \left[RT * \ln \left(1 + 1/C_e \right) \right]^2 \quad (24)$$

e) Brunauer, Emmett And Teller (BET) Sorption Model

The BET sorption model is based on the idea of multilayer adsorption theory [26]. Although BET sorption model, just like the Langmuir model, was developed for sorption in gas phase, it can be used for sorption in liquid phase [27,28]. Only in this case, in the equation of the isotherm, instead the saturated vapor pressure is used concentration of the saturated solution of sorbate (Eq.(25)):

$$S = \frac{S_{BET} * K_{BET} * C_e}{(C_s - C_e) * [C_s + (K_{BET} - 1)C_e]} \quad (25)$$

where: S is the amount of adsorbed phosphate (mg P/g), S_{BET} the capacity of monolayer (mg P/g), K_{BET} is the BET isotherm constant (g/mg), C_e and C_s is the equilibrium and, respectively, saturated concentration of phosphate (mg P/mL).

The constants S_{BET} and K_{BET} were calculated by the graf of the linear BET isotherm, Eq.(26):

$$\frac{C_e}{S(C_s - C_e)} = \frac{1}{S_{BET} \cdot K_{BET}} + \frac{(K_{BET} - 1) \cdot C_e}{S_{BET} \cdot K_{BET} \cdot C_s} \quad (26)$$

The experimental isotherm of phosphate sorption on AV-17(Cl), obtained at the contact of the sorbent with solution for 24 hours at 20 °C, is shown in Figure 9 (curve 1). The isotherm was constructed and calculated with the Langmuir, Freundlich, Sips and Dubinin-Radushkevich sorption models (Fig.9, curve 2-4).

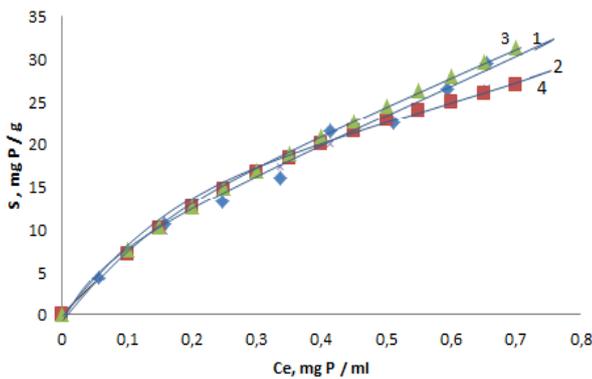


Figure 9: Equilibrium sorption isotherms of phosphate on AV-17(Cl): obtained experimentally (1) and calculated by Langmuir (2), Freundlich (3), and Dubinin-Radushkevich (4) sorption models.

The isotherms parameters and the value of R^2 and χ^2 are listed in Table 1. These parameters show that isotherm of phosphate sorption onto sorbent AV-17(Cl) is best described by the Langmuir sorption model. This was expected, since the active centers (R_4N^+) of the sorbent AV-17(Cl) energetically, practically, are equivalent. The Freundlich and Dubinin-Radushkevich sorption models satisfactorily describe the sorption isotherm of phosphate on AV-17(Cl), but Sips model can not describe the isotherm. The value of $E = 16.13$ kJ/mol (calculated with Eq.23), demonstrates that sorption of phosphate on AV-17(Cl) occurs, mainly, through the ion-exchange mechanism.

Table 1. Isotherm parameters of Langmuir, Freundlich, Dubinin –Radushkevich and BET sorption models for the sorption of phosphate.

Sorbent	t, °C	Sorption model	Isotherm parameters	R^2	X^2
Av-17(Cl)	20	Langmuir	$S_L = 50$ mg P/g $K_L = 1.667$ L/mg	0.9907	0.136
	20	Freudlich	$K_F = 40.447$ $1/n = 0.725$	0.9955	1.030
	20	Dubinin-Radushkevich	$S_{D-R} = 63.434$ mg/g $K_{D-R} = 0.00193$	0.9797	0.772
AV-17(Cr)	16	BET	$S_{BET} = 18.11$ mg P/g $K_{BET} = 4424.78$ g/mg	0.9440	0.848

As seen from Figure 10, the sorption isotherm of phosphate on the sorbent AV-17(Cr) differs from that of sorption on the sorbent AV-17(Cl). The shape of this isotherm is characteristic for the BET sorption model.

The isotherm parameters, calculated according to the BET model, are shown in Table 1.

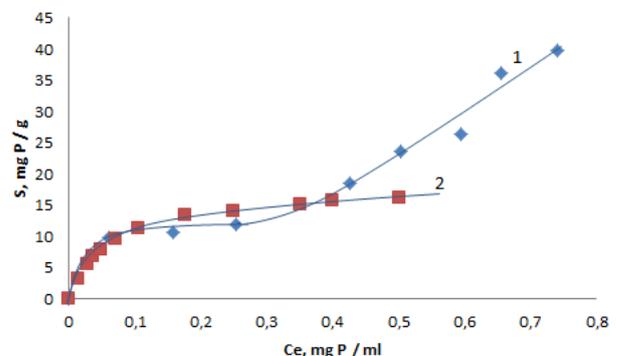


Figure 10: Equilibrium sorption isotherm of phosphate on AV-17(Cr): obtained experimentally (1) and calculated by BET (2) sorption model.

The BET adsorption model describes adequately only a part of the isotherm. This, and, also, the isotherm shape, again demonstrates that the phosphate sorption on the composite AV-17(Cr) is a complex process that includes, mainly, the exchange of ligands (Eq. (5) and (6)), and, to a minor extent, the polyphosphate formation and anions exchange.

3.4. Optimization of phosphate sorption

To perform optimization of the phosphate sorption on composite AV-17(Cr), first of all it is necessary to assess the degree of influence of various factors on the process.

To evaluate the influence of different factors (concentration of phosphate, Na₂SO₄, KCl, NaNO₃,

temperature and pH of solution and duration of the polymer contact with solution) the response surface methodology (G.E.P.Box and K.B.Wilson method) was used [13]. The investigated factors and their levels of variation are shown in Table 2. The experiments were carried out according to matrix of Fractional Factorial Experiment Plan. The influence degree of factors on the studied processes was expressed by the regression equations which were calculated according to [13].

The following responses of the systems, as results of the averages of two independent experiments, were measured and calculated:

$$Y_1 = 21.966 + 3.351 X_1 + 3.343 X_2 + 2.844 X_4, \quad b_{sig.} = 1.7542 \quad (27)$$

Table 2. The factors, their codes and variation levels.

Code	Factor	Low level (-)	Haigh level (+)
X ₁	Concentration of P, g/L	0.4	0.8
X ₂	Temperature, °C	20	40
X ₃	pH	7	8
X ₄ (X ₁ X ₂)	Contact duration of AV-17(Cr) with solution, h	1	2
X ₅ (X ₁ X ₃)	Concentration of KCl, mequiv./L	4	8
X ₆ (X ₂ X ₃)	Concentration of NaNO ₃ , mequiv./L	4	8
X ₇ (X ₁ X ₂ X ₃)	Concentration of Na ₂ SO ₄ , mequiv./L	4	8

Where: Y₁ is the sorption of phosphate, (mg P/g);
Y₂ = 7.275 - 0.270 X₂ + 0.440 X₃ - 0.109 X₆,

$$b_{sig.} = 0.0859 \quad (28)$$

where: Y₂ is the solution pH

Table 3. Phosphate sorption optimizing

Experiment no.and step.	X ₁	X ₂	X ₃	X ₄ , min	X ₅	X ₆	X ₇	Y ₁ , mg P/g
Step	+ 0.1	+ 5.0	0	+ 12	0	0	0	-
1	0.7	35	7.5	112	6	6	6	-
2	0.8	40	7.5	124	6	6	6	31.9
3	0.9	45	7.5	136	6	6	6	-
4	1.0	50	7.5	148	6	6	6	36.88
5	1.1	55	7.5	160	6	6	6	-
6	1.2	60	7.5	172	6	6	6	54.9
7	1.3	65	7.5	184	6	6	6	-
8	1.4	70	7.5	196	6	6	6	84.4
9	1.5	75	7.5	208	6	6	6	90.75
10	1.7	75	7.5	232	6	6	6	91.5
11.	1.8	75	7.5	244	6	6	6	97.75
12	1.8	75	7.5	256	6	6	6	102.38

From the data of Equation (27) it follows that only the phosphate concentration (X_1), temperature (X_2) and the duration of contacting of the composite AV-17(Cr) with phosphate solution (X_4), essentially and positively influences the sorption. In the indicated concentration range of Na_2SO_4 , NaNO_3 and KCl , the coefficients of X_1 , X_2 , X_5 in regression equation are insignificant. This shows that the phosphate sorption on composite AV-17(Cr) is a selective process, which is important for application of AV-17(Cr) in water purification. On the other hand, the insignificant influence of SO_4^{2-} , NO_3^- and Cl^- ions, the strong influence of temperature and low speed of sorption, toughly demonstrates that phosphate sorption on the composite AV-17(Cr) is, in fact, a chemical process. The insignificant influence of solution pH (X_3 , Eq.(27)) on phosphate sorption confirms the data in Figure 2.

The negative influence of temperature on solution pH (X_2 in Equation (28)), confirms that during of sorption, the dihydrogenphosphate ions are converted into hydrogenphosphate according to Equation (7). The Equations (27) and (28) enable planning the optimization of the parameters Y_1 and Y_2 . We optimized parameter Y_1 . The experiments were performed by the moving on the gradient method [13] in the conditions indicated in the Table 3. During the experiment the pH of solutions was set at 7.5 and the concentration of the anions SO_4^{2-} , NO_3^- and Cl^- was fixed at 6 mequiv./L. The increase levels of variables was reasonably stopped. The obtained results are presented in Table 3. These data show, that modifying the factors resulted in considerable increase of phosphate sorption (up to 102,38 mg P/g) by the composite AV-17(Cr). This confirms the validity of the designed experiment and interpretation of the results obtained previously.

IV. CONCLUSION

Composite AB-17(Cr) containing ultra fine Cr(III)-containing compounds particles can be used successfully as an effective sorbent for selective removal of phosphate from solutions. The regularities obtained in this research can serve as models of processes which take place in soil (as sorbent) using the phosphorus fertilizers. The phosphate sorption selectivity on the composite AB-17(Cr) is due to the chemical process of ligands exchange. The phosphate sorption on the composite AV-17(Cr) almost does not depend on pH of

the solution and increases with increasing the temperature. The sorption kinetics of phosphate on AV-17(Cr) at 16 °C is limited by the rate of ligands exchange process, and at 60 °C by the external diffusion. The kinetics of the phosphate sorption on composite AV-17(Cr) at the temperature 16 and 60 °C is described neither satisfactorily by the PFO kinetic model, nor by the PSO model. This demonstrates that phosphate sorption on AV-17(Cr) is a complex process that includes not only change of ligands, but on a less extent, also the anion exchange and polyphosphate formation. Sorption isotherm can be described by the BET sorption model. As a result of the mathematical modeling (regression equation which indicates the degree of influence of concentration of phosphate, Na_2SO_4 , KCl and KNO_3 , temperature, pH and time contact of composite with solution) and optimization, the sorption of phosphate on composite AV-17(Cr) has been increased considerably. The phosphate sorption on the sorbent AV-17(Cl) takes place through the anions exchange and decreases with the increasing pH of the solution. Sorption kinetics at 20 and 54 °C is determined by the external diffusion at the beginning and then by the mixed diffusion. The experimental data, regardless of temperature, are well described by pseudo-second order kinetic model for phosphate sorption on AV-17(Cl). The phosphate sorption isotherms on AV-17(Cl) are better described by Langmuir, satisfactorily by Freundlich and Dubinin-Radushkevich and unsatisfactorily by Sips sorption models. The composite AV-17(Cr) is an effective sorbent with a high capacity for selective purification of solutions from ions of phosphates.

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VI. REFERENCES

- [1]. A.C.Roy, S.K.Datta ,Phosphate sorption isotherms for evaluating phosphorus requirement of wetland rice soils. *Plant Soil*. 86 (1985) 185-196.
- [2]. M.L.V.Fernandes, G.P.Waren, Exchangeable and non-exchangeable phosphate sorption in Portuguese soils. *Fert. Res.* 37 (1994) 23-34.

- [3]. R. L. Fox, E. J. Kamprath, Phosphate sorption isotherms for evaluating the phosphate requirements of soil, *Soil Sci. Soc. Am. J.* 34 (1970) 911-916
- [4]. Edward R. Rhodes, Phosphate sorption isotherms for some Sierra Leone soils, *J. Sci. Food Agricult.* 26 (2006) 895-902.
- [5]. C.Dye, Effect of citrate and tartrate on phosphate adsorption by amorphous ferric hydroxide, *Fert. Res.* 40 (1995) 129-134.
- [6]. Zongmin Ren, Lina Shao, Gaosheng Zhang, Adsorption of phosphate from aqueous solution using an iron-zirconium binary oxide sorbent, *Water, Air, Soil Pollut.* 223 ((2012) 4221-4231.
- [7]. M. Oliveira, A. V. Machado, R. Nogueira, Phosphorus removal from eutrophic waters with an aluminum hybrid nanocomposite, *Water, Air, Soil Pollut.* 223 (2012) 4831- 4840
- [8]. Jae-Woo Choi, Seung-Yeon Lee, Sang-Hyup Lee, Ji-Eun Kim, Ki-Young Park, Dong-Ju Kim, Seok-Won Hong, Comparison of surface- modified adsorbents for phosphate removal, *Water, Air, Soil Pollut.* 223, (2012) 2881-2890.
- [9]. A.A Lurie, *Sorbents and Chromatographic Carriers*, Nauka, Moscow, 1972 (in Russian).
- [10]. V. Gutsanu, R. Drutsa, Patent MD 1027, BOPI. 9 (1998) 23.
- [11]. Z. Marchenco, *Photometrical Determination of Elements*, Mir, Moscow, 1971 (in Russian).
- [12]. V. Gutsanu, R. Drutsa, Patent MD 2234, BOPI. 8 (2003) 21.
- [13]. A. Bondar, *Mathematical Modeling in Chemical Technology*, Visha Shcola, Kiev, 1973 (in Russian).
- [14]. R. Drutsa, V. Gutsanu, V. Rusu, Sorption of Cr(III)-containing cations on strongly basic anion Exchangers, *J. App. Polym. Sci.* 102 (2006) 3978-3985.
- [15]. V. Gutsanu, N. Tudorachi, G. Lisa, The behavior of the AV-17(Cr) sorbent in various media, *Thermochim. Acta.* 574 (2013) 109-115.
- [16]. Evert J. Elzinga, Donald L. Sparks, Phosphate adsorption onto hematite: An in situ ATR-FTIR investigation of the effect of pH and loading level on the mode of phosphate surface complexation, *Colloid. Interf. Sci.* 308 (2007) 53-70.
- [17]. Zhongqi He, Wayne Honeycutt, Baoshan Xing, Richard W. McDowell, Perrz J. Pellechia, Tieguan Zhang, Solid-state fourier transform infrared and ³¹P nuclear magnetic resonance spectral features of phosphate compounds, *Soil Sci.* 172 (2007) 501-515.
- [18]. Y. S. Ho, J. C. Y. Ng, G. McKay, Kinetics of pollutant sorption by biosorbents: review, *Separ. Purif. Methods.* 29 (2000) 189-232.
- [19]. H.W. Cheung, J.C.Y. Ng, G. McKay, Kinetic analysis of the sorption of copper (II) ions on chitosan, *J. Chem. Technol. Biotechnol.* 78 (2003) 562-571.
- [20]. J.W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, *J. Sanit. Eng. Div. Am. Soc. Civil. Eng.* 89 (1963) 31-60.
- [21]. F. Helfferich, *Ion Exchangers*, Izd. In. Lit., Moscow, 1962 (in Russian).
- [22]. I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361-1403.
- [23]. H.M.F. Freundlich, Über die adsorption in lösungen, *Zeit. Phys. Chem.* 57(A) (1906), 385-470.
- [24]. C. Gerente, V. K. C. Lee, P. Le Cloirec, G. McKay, Application of chitosan for the removal of metals from wastewaters by adsorption-mechanisms and models review, *Crit. Rev. Environ. Sci. Technol.* 37 (2007) 41-127.
- [25]. K. Y. Foo, B. H. Hameed, Insights into the modeling adsorption isotherm systems,
- [26]. S. Brunauer, P. H. Emmett, Teller, Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* 60 (1938) 309-319.
- [27]. V. I. Zelentsov, T. Y. Datsko, Adsorption models to describe the equilibrium in the aluminum oxyhydroxide - fluoride system, *Surf. Eng. App. Electrochem.* 48 (2012) 65-73.
- [28]. V. Gutsanu, Iodine ions sorption on polymer AV-17(Cl) and sorbent AV-17(Bi), *Chem. J. Mold.* 9 (2014) 90-98.