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SYNTHESIS OF A PHOSPHORUS-CONTAINING POLYMERIC SORBENT AND STUDY OF THE KINETICS OF ZINC AND IRON IONS SORPTION

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Abstract. This paper presents the results of studies of the sorption properties of the synthesized phosphorus-containing sorbent based on butadiene styrene rubber. Modifications carried out by oxidative chlor-fosforilation conducted. It was proved the presence of phosphorus- and oxygen-containing functional groups in the resulting modifiers. Phosphorus-containing polymeric sorbent was used to remove zinc and iron from water. The research was carried out to study the sorption characteristics by determining the effects of various parameters, such as the pH of the solution, the initial concentration of metal ions, the sorbent mass, the phase contact time, and temperature. The ultraviolet spectra of the sorbent before and after adsorption were obtained. TG and DTG curves typical for the polymer, synthesized sorbent and sorbent after sorption of Zn(II) and Fe(III) ions. The regularities of the kinetics of the sorption of zinc and iron ions on the phosphorus-containing sorbent were studied. On the basis of the results it was defined that the process of sorption of zinc and iron ions on the cation exchanger proceeds by an ion-exchange mechanism. The kinetics of this process is a combination of external and internal diffusion kinetics (with some predominance of external diffusion kinetics) and is better described by the pseudo-second order reaction model. In addition, a certain contribution to the overall speed of the process is made by the interaction of the sorbed ions with the functional groups of the cation exchanger.

1. Introduction

The sources of heavy metals entering the water are emissions from industrial enterprises, as well as corrosive water supply equipment. There are various ways to purify water from heavy metal compounds. The most promising method of purifying water from heavy metals is ion exchange.

It is necessary to use complex-forming ion exchangers, which possess high affinity for polyvalent and heavy metals in order to solve technological problems associated with obtaining high-purity substances in the processes of separation, recovery, concentration of rare and non-ferrous metals. Such compounds include phosphorus-containing cation exchangers with phosphoric acid groups (Saladze & Kopilova-Valova, 1980; Kopilova *et al.,* 1992).

The aim of this work is to study the effectiveness of phosphorus-containing sorbent based on butadiene-styrene rubber of the DSKK grade, used to remove Zn(II) and Fe(III) ions from aqueous solutions. The method of synthesis of phosphorus-containing sorbent by chemical modification (oxidative chlorophosphorylation reaction) of industrial polymer - butadiene-styrene rubber was developed by our scientists and described earlier (Karimova *et al.,* 2017; Maharramov *et al.,* 2003; Azizov *et al.,* 2003; Dasa *et al.,* 2019;

Howell *et al.,* 2019; Hui *et al.,* 2019). It was found that this reaction proceeds using readily available commercial reagents under mild conditions and using simple equipment. This paper presents the influence of various parameters, such as the concentration of the initial Zn(II) and Fe(III) solution, the pH of the solution, the sorbent mass, contact time and temperature.

The study of sorption kinetics makes it possible to determine the rate of attainment of equilibrium, the maximum working capacity of an ion exchanger for a certain solution composition, and the mechanism of interaction of metal ions with ion exchanger during sorption (Sag *et al.,* 2019; Sun *et al.,* 2020; Abdel-Hakim *et al.,* 2021).

2.   Experiments and results

Phosphorus-containing sorbent was synthesized on the basis of butadiene-styrene rubber using PCl_3, CCl_4, H_2SO_4 and O_2 (Karimova *et al.,* 2017; Maharramov *et al.,* 2003; Azizov *et al.,* 2003). Butadiene-styrene rubber was purchased from the Voronezh Synthetic Rubber Manufactory (Russia). PCl_3, CCl_4, H_2SO_4 were purchased from Vecton (Russia) and used without further purification. It should be emphasized that during the polymer modification reaction, a crosslinking process occurs between macromolecular chains. As a result, cross-linked products with various functional groups, such as: -$P(O)Cl_2$ (phosphonium dichloride) and -$OP(O)Cl_2$ (phosphorus dichloride), which were converted by the hydrolysis reaction to phosphonate (-$P(O)(OH)_2$) and phosphate (-$OP(O)(OH)_2$) groups, respectively.

The modified butadiene-styrene rubber was used as the sorbent for studying the sorption behavior of Zn(II) and Fe(III) ions in aqueous solution. The working solutions of zinc sulfate were prepared by dissolving a sample of $ZnSO_4 \times 7H_2O$ in an appropriate amount of distilled water. The ferric chloride working solution was prepared by dissolving the $FeCl_3 \times 6H_2O$ sample in an appropriate amount of distilled water. The pH value in the solution was established using an acetate-ammonia buffer solution.

The concentrations of $ZnSO_4 \times 7H_2O$, $FeCl_3 \times 6H_2O$ before and after sorption are determined using a photometric colorimeter with an optical density determination at a wavelength of 490 nm.

Preliminary experiments began with the aim of studying the effect of the pH of the solution, sorbent mass, contact time, temperature and the initial concentration of metal ions on the sorption of Zn(II) and Fe(III) ions by a phosphorus-containing sorbent. Precisely weighed amounts of sorbent (0.05 g) were placed in flasks and filled with $ZnSO_4 \times 7H_2O$ and $FeCl_3 \times 6H_2O$ solutions of different initial concentrations. In this case, the initial concentrations of the samples were changed in the range from 10^{-4} to 5×10^{-2} M. When studying the effect of the sorbent mass on sorption, the mass of the sorbent was varied in the range from 0.01 to 0.1 g. The solutions of Zn(II) and Fe(III) with a pH of 1 to 11 were used in order to determine the effect of the pH of the solution. A study of the dependence of the sorption on contact time was carried out using 0.3 g of sorbent and 90 ml of $ZnSO_4 \times 7H_2O$ and $FeCl_3 \times 6H_2O$ solutions with 10^{-3} M concentration and changing the contact time in a range from 3 to 65 minutes, and temperatures of 25, 35 and 50°C. In recent experiments, the sample was taken every 3-5 minutes and analyzed on a spectrophotometer. The sorption capacity ($mg \cdot g^{-1}$) and the degree of adsorption (%) were calculated using equations (1) and (2):

$$SC = (c_0 - c_e)\frac{V}{m} \tag{1}$$

$$R = \frac{100(c_0 - c_e)}{c_0} \qquad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations of Zn(II) and Fe(III) ions in the solution, respectively (mg·ml^{-1}), V is the volume of the solution (ml), and m is the sorbent mass (g).

The results show that 10^{-3} M solutions, 0.05g adsorbent, was used as the optimal concentration for studying the effect of pH on the sorption of ions. Based on the results obtained, adsorption isotherms are determined.

The results are statistically processed using standard methods (Alosmanov, 2011; Polyanskiy *et al.,* 1976; Kokotov & Pasechnik, 1960). The average error of the experiment was estimated to be less than 4%.

Most of the electronic transitions in the molecules appear in the range 200-750 nm, where 200-400 nm refers to the near-ultraviolet region.

UV-spectroscopy

Fig. 1 shows the ultraviolet spectra of the phosphorus-containing polymeric sorbent based on butadiene-styrene rubber before and after adsorption.

As can be seen, unsaturated hydrocarbons with isolated double bonds have an intense absorption band due to the transition $\pi \rightarrow \pi^*$ in the region of 170-200 nm, which is observed in all cases. Electronic spectra of benzene derivatives in which the aromatic chromophore is conjugated with other chromophores have a peculiar character. In this case the spectrum contains three peaks (two from the aromatic nucleus and one from another chromophore), all of them shifted to the long-wave region and their intensity is higher than for benzene (Bukov *et al.,* 2006). Thus peaks at 250-270 nm, 265-280 nm, and 270-285 nm for various samples, respectively, are observed. Samples containing metal ions give peaks in the region of 300-350 nm.

Thermogravimetric analysis

TG analysis is widely used to evaluate the thermostability of polymers. This type of measurement is performed quickly and requires a very small amount of sample. TG and DTG curves typical for the polymer, synthesized sorbent and sorbent after sorption of Zn(II) and Fe(III) ions are shown in Fig. 2-5.

It is seen that degradation in all cases proceeds in three stages. However, the characteristic temperatures for the specific samples are different. The characteristic temperatures of degradation stages are shifted to lower values with decreasing rate of heating, and each stage appeared more distinct, separated from other stages.

The plots obtained for all the studied samples show a very similar shape of TG and DTG for the first decomposition step. Based on the experimental conditions (synthesis, pretreatment) and the structure of the polymers (porous and cross-linked), it seems that the mass loss at this step is due to the removal of physically adsorbed water located in the pores and water connected by hydrogen bonds with functional groups.

According to the literature data (Iditoiu *et al.*, 1999), the values of mass loss at the first stage attributed to evaporation of physically adsorbed water existing in the pores and water connected by hydrogen bonds with functional groups varied (from 4 to 22%) for cross-linked polymers.
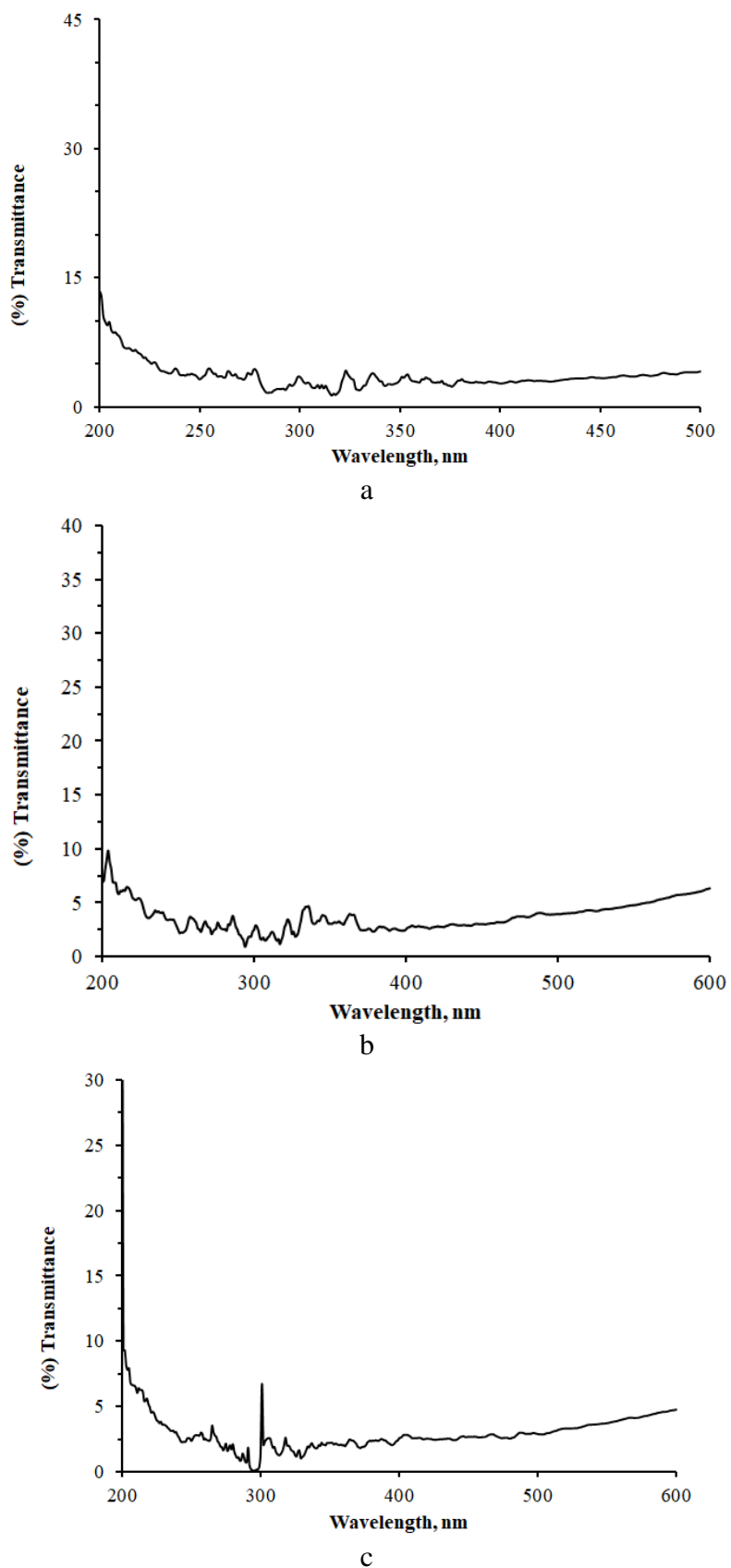
a

b

c

Fig. 1. UV-spectra or the phosphorus-containing polymeric sorbent based on butadiene-styrene rubber: a-before adsorption ions, b-after adsorption zinc ions, c- after adsorption iron ions

This depends on several factors. In (Iditoiu *et al.*, 1999), the authors showed that in the same polymer matrix, the forms of functional groups (acidic or sodium salt), the size of pellet samples, their microstructure, and the heating rate play an important role. The results obtained in this study show that the temperature characteristics of this first stage lie in the range of 20 to 150 °C and the relatively small mass loss ranges from 1 to 4 %.

Considering that in our case the polymers studied have the same polymer matrix, degree of cross-linking and granule size, the mass loss in all cases is approximately the same and ranges between 4 and 9 %. The same can't be said for the original polymer that didn't undergo modification. In that case, the loss of mass occurs at higher temperatures and has a higher value. These differences can be explained by the nature of the functional group and their hygro-peakness.

The second stages of degradation (Fig. 2-5) are also approximately the same for the modified samples. When heated from 245 to 300 °C the weight loss varies from 14 to 18%, and for the unmodified sample at 465 °C the weight loss differs between the studied samples more significantly.

The second stage of decomposition is characterized by relatively higher values of mass loss than in the first stage. In this stage, the mass loss is the result of the conversion/decomposition of functional groups. The process starts with a dehydration reaction of phosphonate and phosphate groups in the polymers and the DTG curves are slightly more complex.

The magnitude of the mass loss depends on the molecular weight of the decomposition products.

The third stage of the decomposition is also characterized by a considerable mass loss (from 8 to 39 %). This stage can be attributed to the detachment of a side group from the polymer chain, depolymerization and separation of large organic molecules formed at the second stage. What cannot be said for the initial butadiene styrene rubber. Here the mass loss is practically 100%.

Finally, the residual amounts of polymers are compared.

For the other polymers, the values were moderate to close. In general, the residue values are in the range of 25 % to 50 %, which is typical for cross-linked functional groups of polymers.

It is well known that thermal degradation of cross-linked polymers under nonisothermal conditions is a very complex heterogeneous process. The main stages of heterogeneous decomposition reactions of solid materials are as follows: (I) reagents and heat transfer to the phase separation surface, (II) interface rearrangement with solid reagent flow, (III) transfer of volatile products from the reaction space (Vlad *et al.,* 2003).

The kinetics of the sorption

The kinetics of the sorption of ions from aqueous solutions with phosphorus-containing cation exchanger synthesized on the basis of butadiene-styrene rubber was comparatively studied in this paper under static conditions. The phosphorus-containing cation exchanger was synthesized on the basis of industrial polymer – butadiene-styrene rubber of the DSSK brand by the reaction of oxidative chlorophosphorylation using PCl_3 in the presence of oxygen, followed by hydrolysis of the resulting modificant. The method of obtaining the sorbent is described in the early works (Karimova *et al.,* 2017). The pH value in the solution is established using an acetate-ammonia buffer solution.
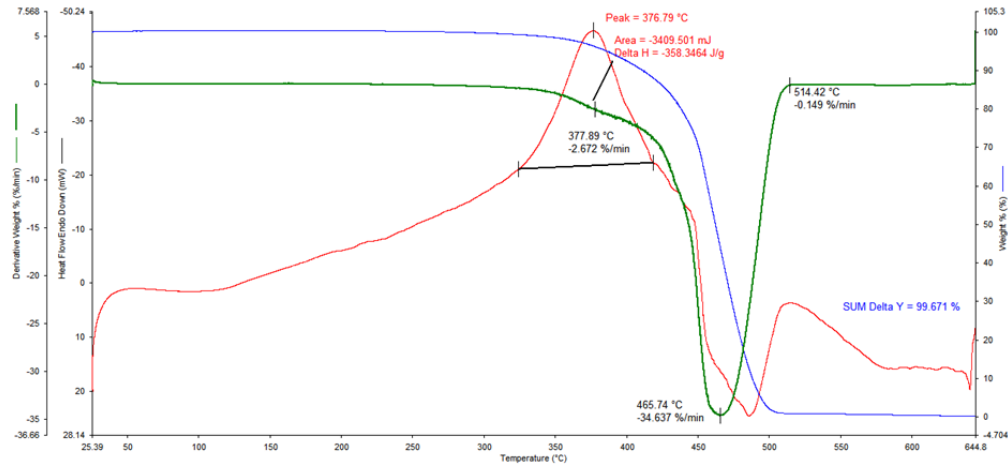
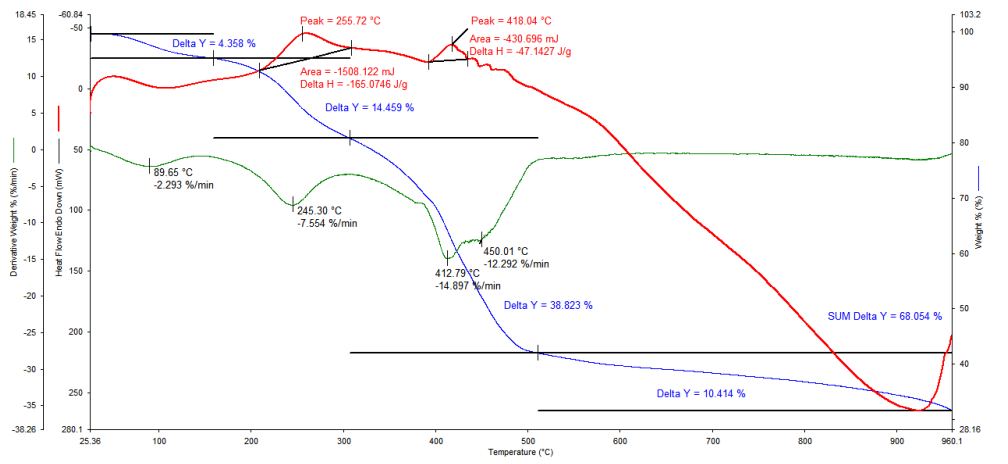**Fig. 2.** TG and DTG curves of DSSK butadiene styrene rubber

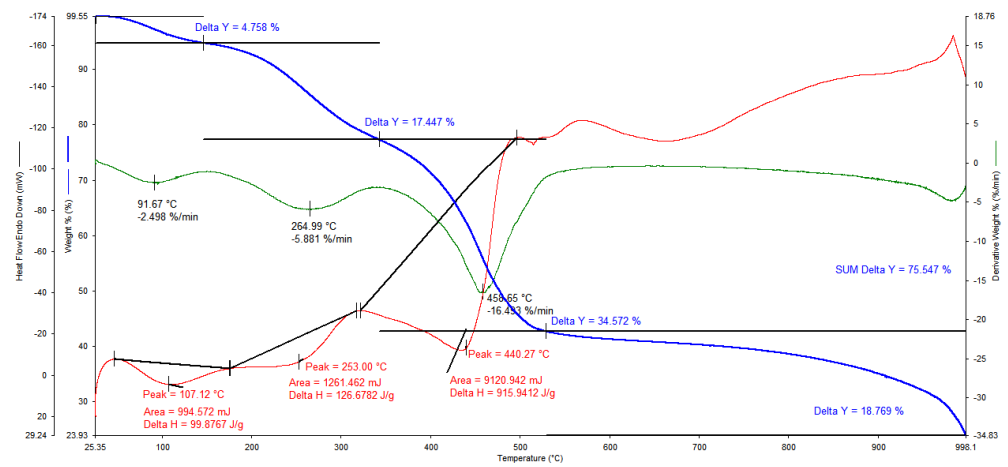**Fig. 3.** TG and DTG curves of the modified polymer

Fig. 4. TG and DTG curves of the sorbent after sorption of Zn(II) ions
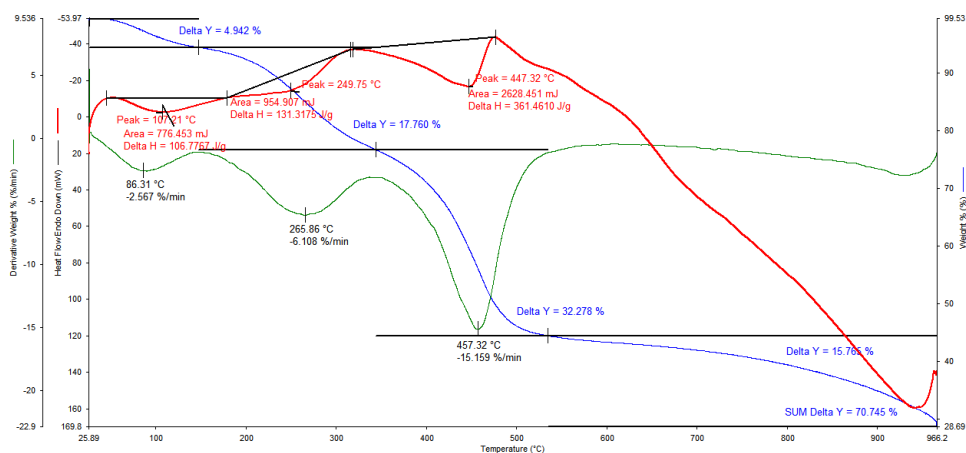
Fig. 5. TG and DTG curves of the modified sorbent after sorption of Fe(III) ions

A 200 ml flask equipped with a magnetic stirrer is used in order to study the sorption kinetics by limited volume method[6]. 90 ml of a previously prepared solution with a component concentration of 10^{-3} mol·L^{-1} is placed in a flask. The experiments were carried out at a constant temperature of $23 \pm 2°C$ and pH 6 (the indicated acidity of the medium is optimal). 0.3 g (in terms of absolutely dry) cation exchanger was placed in the solution. Analysis of the content of elements in all solutions was performed by spectrophotometric method. The volume of taken samples did not exceed 2% of the total volume.

Fig. 6 shows the dependence of the sorption of ions on time using the synthesized phosphorus-containing sorbent. It is seen that for the phosphorus-containing sorbent achieving equilibrium cationite-salt solution occurs after 65 minutes.

It is known that the sorption process is complex and multi-stage, and the cumulative consideration of all stages of this process is difficult to implement, therefore, it is usually resorted to simplifications using the principle of the limiting stage (Maharramov *et al.*, 2003).

The contribution of external diffusion to the sorption of ions on the phosphorus-containing rubber sorbent can be described by the equation
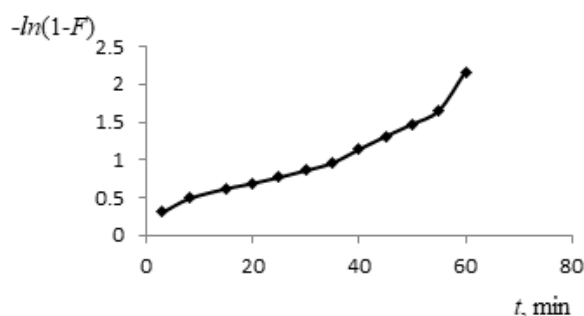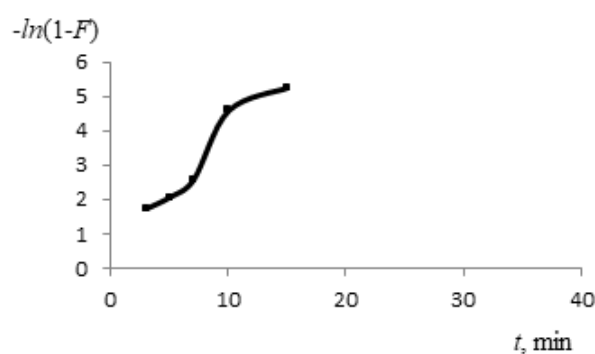
$$ln(1 - F) = -\gamma \cdot t, \tag{3}$$

where F is the rate at which equilibrium is reached, calculated by formula $F = {a_t}/{a_e}$ (a_t – the amount of sorption (mmol/g) at time t, a_e is the amount of sorption in the equilibrium state (mmol/g)); γ is some constant value for these conditions; t - sorption time (min).

a

97

b
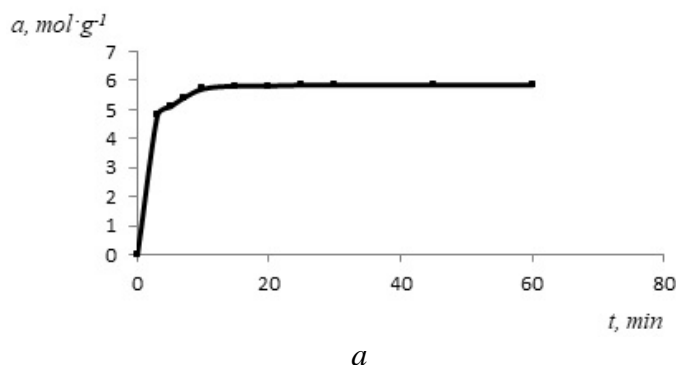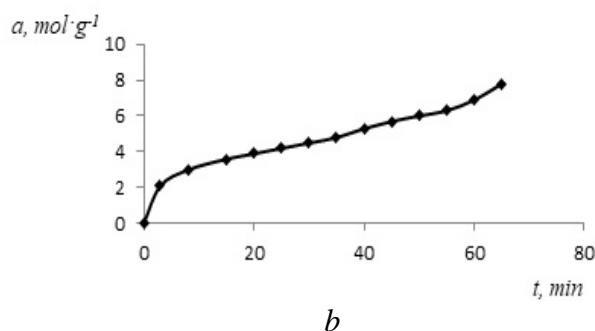
Fig. 6. Kinetic curves of sorption: a - of zinc ions, b - of iron ions

The dependence $-ln(1-F) = f(t)$ is shown in Fig.7.

a

b

**Fig. 7.** Dependence of $-ln(1-F)$ on time t for sorption of: a - of zinc ions, b - of iron ions

As can be seen from Fig. 7, only in the initial sections there is a rectilinear dependence of the function $-\ln(1-F) = f(t)$, and the kinetic curves do not describe only the external diffusion mechanism throughout the entire process. In the course of the process, the influence of the external diffusion factor decreases, while the intradiffusion factor increases, and for the phosphorus-containing cation exchanger synthesized by us this effect occurs much earlier than for the industrial cation exchanger. This means that the process proceeds in a mixed diffusion mode, i.e. It is controlled by diffusion in the solution film and diffusion in the cationite grain (Azizov *et al.*, 2003). In order to evaluate the contribution of internal diffusion to the sorption process, the following empirical equation is used

$$a_t = k_d \cdot t^{1/2}, \tag{4}$$

where a_t is the amount of sorbed ion per unit cation exchange mass at time t, mol/g; k_d is the rate constant of internal diffusion, mmol·g $^{-1}$·min$^{-0.5}$; t-sorption time, min.

Evidence that the stage limiting the sorption process is internal diffusion is the observance of a rectilinear relationship in the coordinates a_t - $t^{1/2}$ (Fig. 8).

a

b
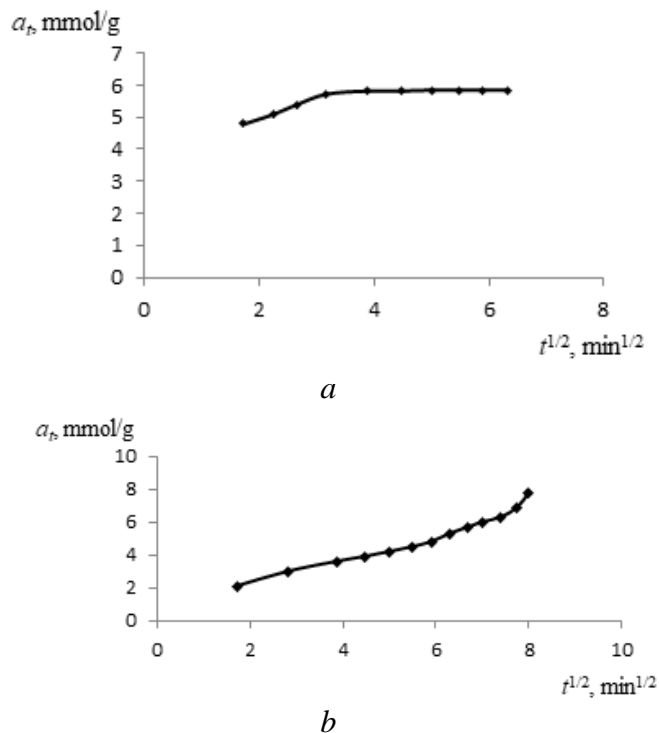
Fig. 8. Dependence a_t - $t^{1/2}$ for sorption of: a - of zinc ions, b - of iron ions

In most cases this dependence is multilinear and is characterized by 2-3 sections, and is described by the equation

$$a_t = k_d \cdot t^{1/2} + A, \qquad (5)$$

where *A* is the segment cut off on the ordinate axis of the $a_t = f(t^{1/2})$ dependence.

The quantity *A* in equation (3) characterizes the thickness of the boundary layer. The initial section describes the diffusion of sorbate through the solution layer to the surface of the sorbent (external diffusion kinetics). The second section, from whose slope the rate of internal diffusion is determined, describes the intrinsic diffusion process itself (Polyanskiy *et al.*, 1976). It should be noted that in all cases, the process of diffusion of iron ions on the phosphorus-containing sorbent synthesized on the basis of butadiene-styrene rubber is described by equation (3), i.e. there is a mixed kinetics. In this case, the kinetic parameters corresponding to internal diffusion characterize the slope angle of the second section; the segment cut off by the continuation of this straight line on the ordinate axis is proportional to the thickness of the film surrounding the ion exchanger grain (Kokotov & Pasechnik, 1960; Guibal *et al.*, 1998). The rate constants of the external and internal diffusions are presented in Table 1.

Table 1. The rate constants of the external and internal diffusions

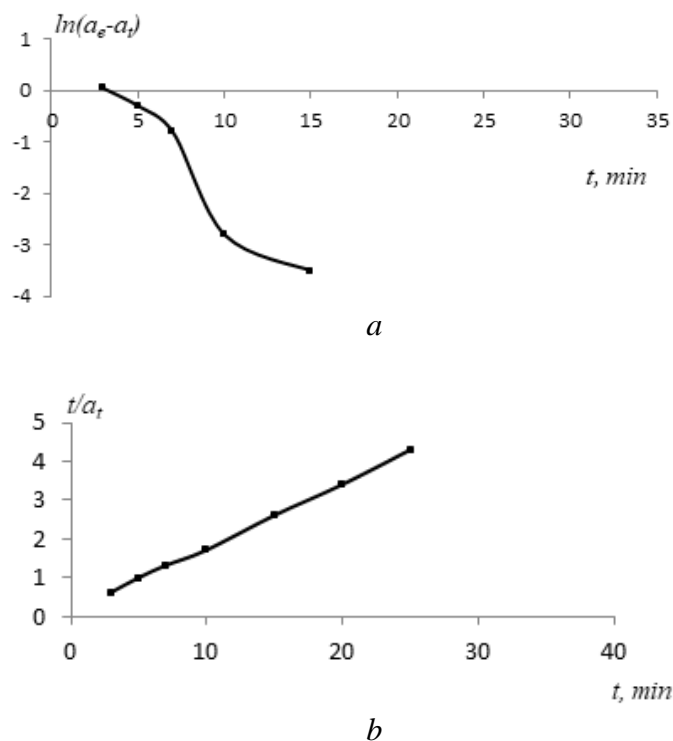| İon	The rate constants of the external diffusion		The rate constants of the internal diffusion		
	γ	R^2	k_d, mmol·g^{-1} min$^{-0,5}$	A	R^2
Zn(II)	0,3881	0,8866	0,1993	4,7925	0,7118
Fe(III)	0,0312	0,9136	0,8152	0,3879	0,952

R - is the correlation coefficient

It is assumed that a substantial contribution to the kinetics of the entire process can be made by the sorption proper phase. Therefore, to describe the pattern of this kinetic stage, the pseudo-first and pseudo-second order patterns of the reaction were used, which in linear form are expressed by the equations

$$ln(a_e - a_t) = ln a_e - k_1 \cdot t, \tag{6}$$

$$t/a_t = 1/(k_2 \cdot a_e^2) + (1/a_e) \cdot t, \tag{7}$$

where a_e and a_t - the value of equilibrium sorption and the value of sorption at time t, respectively, mmol/g; k_1, k_2 are the rate constants of the sorption of the pseudo-first (min^{-1}) and pseudo-second orders (g/mmol·min), respectively. According to the equation (6) the $ln(a_e-a_t)$-t dependence must represent a straight line from which the values of k_1 and a_e can be determined. Fig. 6.1 and 6.2 shows the dependences $ln(a_e - a_t)$ - t and t/a_t - t. The values of k_1 and a_e calculated from these dependencies are given in Table 2.

a

b

Fig. 9. Dependencies: a - $ln(a_e - a_t)$ - t; b - t/a_t - t of zinc ions
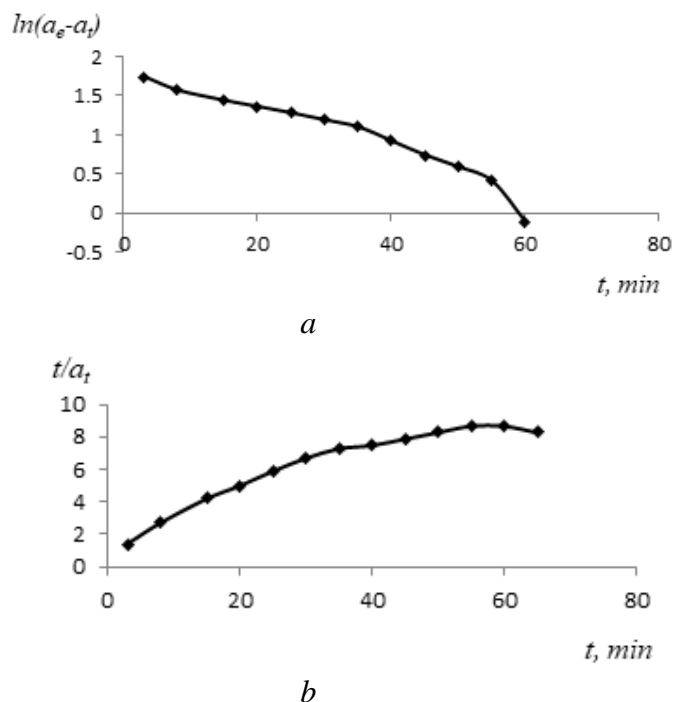
a

b

Fig. 10. Dependencies: a - $ln(a_e - a_t) - t$; b - $t/a_t - t$ of iron ions

Table 2. The rate constants of the external and internal diffusions

İon	The pseudo-first-order model			The pseudo-second-order model		
	a_e	k_1	R^2	a_e	k_2	R^2
Zn(II)	13,7816	0,3259	0,9308	6,0168	0,2562	0,9991
Fe(III)	6,7727	0,0278	0,9302	8,8809	0,0052	0,8918

It should be noted that, in spite of sufficiently high correlation coefficients, the values of a_e, obtained from the line $ln(a_e - a_t) - t$, in most cases do not coincide with the experimental values of a_e. From the dependences $t/a_t - t$, according to equation (7), k_2 and a_e were calculated.

3.   Conclusion

In this study, the sorption capacity of the phosopher-containing sorbent is studied synthesized by oxidative chlorophosphorylation of butadiene-styrene rubber followed by hydrolysis with respect to Zn(II) and Fe(III) ions, determining the influence of various parameters such as the pH of the solution, the initial concentration of the salt, the sorbent mass, phase contact time and temperature. Experimental results have shown that a phosphorus-containing sorbent based on butadiene-styrene rubber can be successfully used to extract ions from aqueous solutions.

As a result of processing the kinetic curves of sorption of ions on the phosphorus-containing sorbent synthesized on the basis of butadiene-styrene rubber, it is defined that the mechanism of the process is rather complicated. The low concentration of the iron salt solution leads to the fact that diffusion of the solution film contributes to the overall process speed. The mixed diffusion mechanism indicates the effect of diffusion on the cationite grain. The application of the equations of chemical kinetics has shown that a certain contribution to the overall process speed is made by the interaction stage of the

sorbed ions with the functional groups of the cation exchanger. The results obtained can be useful in developing the sorption technology for purification of natural and waste water from iron ions using phosphorus-containing sorbent based on butadiene-styrene rubber.

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