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Study of Potassium Sorption by Porous Substrates of Birch Bark

E. V. VEPRIKOVA, S. A. KUZNETSOVA, N. V. CHESNOKOV, and B. N. KUZNETSOV

*Institute of Chemistry and Chemical Technology, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, Russia**E-mail: inm@icct.ru*

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Abstract

Potassium sorption processes from aqueous solutions of KH_2PO_4 , K_2HPO_4 , K_3PO_4 , KCl , and KNO_3 by porous substrates of bast and birch bark were studied. The effect of the nature of the salts on potassium sorption was found. It was demonstrated that the investigated salts by their capacity to potassium sorption could be placed in the following row: $\text{K}_3\text{PO}_4 > \text{K}_2\text{HPO}_4 > \text{KCl} > \text{KNO}_3 > \text{KH}_2\text{PO}_4$. Comparison of sorption of potassium and phosphates from solutions of phosphorus-containing salts was made. The effect of pH of solutions and the background electrolyte on potassium sorption from various salt solutions was studied. It was found that the application of the background electrolyte exerted a positive effect on potassium sorption from solutions of KH_2PO_4 , KCl and KNO_3 . It was demonstrated on an example of potassium chloride and potassium nitrate that an increase in the pH of solutions of the salts to 10.7 led to a larger increase in potassium sorption in comparison with the effect reached in the presence of the background electrolyte. It was found that the highest sorption of potassium (A_∞) was reached from solutions of K_3PO_4 and KCl (pH 10.8) and amounts to 32.55 и 30.20 mg/g, respectively. Potassium sorption isotherms obtained under various conditions, for which values of the constant KL and the limiting sorption A_∞ were determined according to the Langmuir equation, are given. Potassium sorption values were calculated using these significations and compared with the experimental data. It was demonstrated that porous substrates of bast and birch bark showed close sorption activities in relation to potassium. The substrates investigated exceed activated carbon of birch wood

Key words: birch bark, porous substrate, potassium, sorption, desorption, prolonged action

INTRODUCTION

Birch refers to the major forest forming deciduous species in the territory of Russia and is widely used in various sectors of timber manufacturing industry. When obtaining wood large-tonnage birch bark wastes are accumulated. From the viewpoint of environmental management, such wastes are regarded as valuable secondary raw materials that should be fully processed. Industrial utilization of birch bark is mainly limited by the production of tar and decorative items of birch bark. The major part of wastes is burned or disposed in dumps, which increases negative technogenic impacts on the environment.

An important area of rational disposal of wood wastes is obtaining organomineral fertilizers on their basis, the application of which is a necessary condition for efficient and sustainable operation of agrosystems [1, 2]. Prolonged action fertilizers that have a capacity to a long, slow release of nutrients into the soil take a special place among fertilizers. Their application leads to a decrease in washing out of active elements by groundwater, which allows reducing amounts of traditional water-soluble fertilizers [2].

One way to ensure prolonged effects of fertilizers is the application of porous carriers and materials with sorption or ion-exchange properties to attach various nutrients to them. The

literature proposes to use natural zeolites and peat as carriers of active components [3, 4]. However, the application of peat and wood wastes is preferable, since soil is enriched by a set of organic nutrients.

Works [5–7] demonstrate an opportunity to obtain biocomposite minerals with prolonged effects based on porous substrates of bast and birch bark. To remove polyphenol substances negatively affecting the development of plants and of the porous structure of the substrate treatment of raw materials with a 1.5 % alkaline solution was proposed in these works. Although potassium biocomposite fertilizers showed ability to slow isolation of the active component for a long time, fast washing out of potassium chloride for the first 30 min is typical for them [7]. Therefore, search for preparation methods that allow increasing resistance of biocomposites to washing out potassium with water is an important task. The preparation of the biocomposite fertilizers proposed was performed by impregnation of substrates of bast and birch bark with a solution of KCl that is widely used for the preparation of applied catalysts. The ability of substrates to the interaction with the applied compound will determine the contribution of adsorption to its fastening on their surface, therefore, the determination of sorption activity of substrates in relation to potassium is of great importance. Adsorption is a promising application technique of the required compound, since one can have an effect on the strength of binding of the sorbed component with the substrate surface. Additionally, adsorption allows ensuring a higher dispersion of the active component in the carrier due to various interactions [8]. This is especially crucial for the development of biocomposite fertilizers with slow release of the active component applied.

It should be noted that the process of potassium sorption from aqueous solutions has been well studied for ion exchangers of various types [9, 10]. As demonstrated by analysis of the literature over the last 5–8 years, information on this matter for sorbents of wood wastes is almost absent.

The work purpose is the study of potassium sorption from aqueous solutions of various salts by porous substrates of bast and birch bark.

EXPERIMENTAL

Air-dry (moisture content of $(7.5 \pm 0.5) \%$) silver birch bark (*Betula pendula* Roth.) and bast separated therefrom were used as raw materials for the preparation of porous substrates (PS) with the following fraction composition (mass %): 0.25–0.50 mm – 23.7; 0.50–1.00 mm – 76.3. The content of silver bark in a sample of birch bark was $(45 \pm 1) \text{ mass } \%$.

Porous substrates were obtained by treatment of bast and birch bark with a 1.5 % aqueous NaOH solution at a temperature of $(80 \pm 5) ^\circ\text{C}$ in a hydromodulus 5 for 1 h followed by washing out with water and neutralization according to the technique described in [11]. The resulting substrates were dried at $(50 \pm 5) ^\circ\text{C}$ until the air-dry condition.

Potassium sorption isotherms were constructed using model KH_2PO_4 , K_2HPO_4 , K_3PO_4 , KCl and KNO_3 solutions. The potassium concentration in the solutions was varied in a range of 12.5 to 700.5 mg/L. Sorption in the remaining experiments was performed from solutions with the initial potassium concentration of $(657.0 \pm 7.5) \text{ mg/L}$. To prepare the salts solutions distilled water with pH of 6.3 ± 0.1 was used.

Sodium chloride, the concentration of which is solutions of potassium salts was varied from 0.5 to 2.0 mass %, was used as the background electrolyte. The pH values of 10.8 in model solutions of KCl and KNO_3 were set using a KOH 5.0 % solution.

Sorption was carried out under static conditions with shaking (intensity of (120 ± 10) vibrations/min) of a sample weight of the PS (0.2 g) with models of solutions (50 mL) at a temperature of $(20 \pm 1) ^\circ\text{C}$. The kinetics of sorption was studied by varying the length of the process from 5 to 90 min. Sorption duration in all the remaining experiments was 24 h.

A change of the potassium concentration in solutions in the sorption-desorption process was determined by the atomic emission method using an Analyst-400 device. A change in the concentration of potassium phosphates (recalculated for phosphorus) was determined by the differential photometry method according to State Standard GOST 200851.2–75. The sorptive capacity (A , mg/g) of porous substrates of bast and birch bark was calculated according to a

change in potassium and phosphorus concentrations.

According to Langmuir adsorption isotherm reduced to linear form, A_∞ and K_L for potassium sorption processes were calculated:

$$1/A = 1/(A_\infty K_L) C_{eq} + 1/A_\infty \quad (1)$$

where A is potassium sorption, mg/g; A_∞ is limiting sorption, mg/g; C_{eq} – equilibrium potassium concentration, mg/L; K_L is Langmuir equation constant, L/mg.

With provision for the obtained values of A_∞ and K_L , potassium sorption values were calculated and their comparison with the experimental data was made.

The method of the least squares was similarly applied to determine A_∞ and K_L in accordance with the generally accepted rules [12], by minimizing the function:

$$F(A_\infty, K_L) = \sum_i (A_i - f(C_{eqi}, A_\infty, K_L))^2 \quad (2)$$

where f is the Langmuir isotherm.

The calculations were carried out using the Statgraphics Centurion XVI software package; DOE block (Design of Experiment). The significance level was 0.05.

Filling degree of a porous substrate (F) was determined according to a ratio of the maximum experimental value of potassium sorption (A_{max}) to the value of the limiting sorption (A_∞) [13]:

$$F = A_{max}/A_\infty \quad (3)$$

The specific surface (S_{sp}) was determined by low-temperature nitrogen adsorption using a Sorbtometr-M device.

RESULTS AND DISCUSSION

It was determined that PS of bast and birch bark differed from each other by their sorption activity in relation to potassium and significantly exceeded birch activated carbon (BAC) selected as a comparison sample (Table 1). It is obvious that the development degree of porous structure (524.6 m²/g for BAC, 2.4 and 3.2 m²/g for PS of bast and birch bark) does not affect potassium sorption from various salt solutions.

In case of potassium sorption from KH_2PO_4 , K_2HPO_4 and K_3PO_4 solutions, one can trace the A_∞ dependence on a change in pH values of model solutions that is driven by an increase in a salt concentration. The greatest sorption is reached from K_3PO_4 solutions, where an increase in salt concentration leads to an increase in alkalinity. Potassium sorption is minimal from KH_2PO_4 acid salt solutions (see Table 1). The dependence of potassium sorption on pH of solutions is probably driven by the effect of electrostatic interactions between substrate surface and K^+ ions. Obviously, a negative charge of the substrate surface increases with increasing of alkalinity of model solutions of K_2HPO_4 and K_3PO_4 , and potassium attraction to it is enhanced. This will contribute to increase in its sorption [14].

On an example of a substrate of birch bark bast, it was demonstrated that potassium adsorption processes from model solutions of K_2HPO_4 and K_3PO_4 were described by Langmuir isotherms (type I) according to the BET

TABLE 1

Potassium sorption from various salt solutions by porous substrates (PS) of bast and birch bark

Potassium salts	pH of model solutions*	A_∞ , mg/g		
		PS of birch bark bast	PS of birch bark	BAC
KCl	6.3–6.1	8.42	9.13	3.35
KNO ₃	6.3–6.0	3.73	3.55	1.45
KH ₂ PO ₄	6.1–4.4	0.75**	0.65**	–
K ₂ HPO ₄	6.2–7.9	10.40	10.45	7.25
K ₃ PO ₄	6.8–12.6	32.55	31.44	11.72

Note. A_∞ is the limiting sorption of potassium; dash – does not absorb.

* Values are given for a range of potassium concentration of 12.5–700 mg/L.

** The maximum sorption value is given.

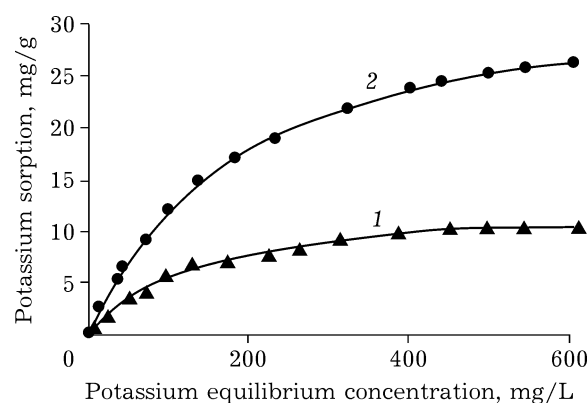


Fig. 1. Potassium sorption isotherms from solutions of K_2HPO_4 (1) and K_3PO_4 (2) by a porous substrate of birch bark bast: lines are calculated according to the Langmuir equation and Table 4 data; points represent experimental data.

classification corresponding to monolayer sorption (Fig. 1) [13]. In solutions of K_2HPO_4 with the potassium equilibrium concentration of ≥ 550 mg/L, its limiting sorption (10.42 mg/g) is reached. It was found that an increase in potassium concentration in a solution of K_3PO_4 of over (715 ± 5) mg/L led to a decrease in its sorption due to instability of the substrate in concentrated solutions of phosphates. It should be noted that differences in potassium sorption from solutions of these salts by substrates based on bast and birch bark in the investigated concentration range does not exceed ± 2.5 mg/g.

Analysis of Fig. 2 data demonstrates that potassium sorption from solutions of KH_2PO_4 decreases with increasing their concentration. Concentration values of solutions, with which potassium sorption is terminated, differ for substrates of bast and birch bark and are amount to ≥ 400 and 250 mg/g, respectively. It is obvi-

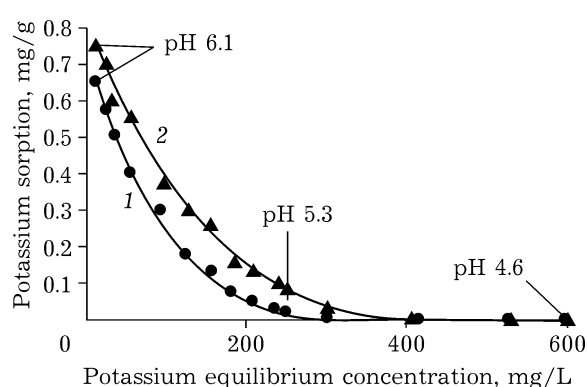


Fig. 2. Potassium sorption from a solution of KH_2PO_4 by porous substrates of birch bark (1) and bast (2).

ous an increase in acidity of solutions with the increase in their concentrations leads to enhancement of electrostatic repulsions of positively charged substrates surfaces and K^+ cations.

The introduction of NaCl into a solution of KH_2PO_4 as a background electrolyte substantially increases potassium sorption due to shielding by the salt of electric repulsions typical for this system. Herewith, screening effect increases with the increase of the amount of NaCl that is added to a solution of dihydrophosphate. Reverse effect of its action is observed in case of potassium sorption from a solution of K_2HPO_4 in the presence of the background electrolyte that is potassium sorption decreases on average in four times due to shielding attraction to the substrate surface. It was found that introduction of NaCl to a solution of K_3PO_4 led to a smaller decrease of potassium sorption in comparison with $c K_2HPO_4$ (Table 2).

TABLE 2

Effect of a background electrolyte NaCl on potassium sorption from phosphate salt solutions by porous substrates (PS) of bast and birch bark. The initial concentration of potassium in model solutions is (657.0 ± 7.5) mg/g

NaCl concentration, mass %	Potassium sorption (in mg/g) from a solution of					
	KH_2PO_4		K_2HPO_4		K_3PO_4	
	PS of bast	PS of birch bark	PS of bast	PS of birch bark	PS of bast	PS of birch bark
0	0	0	10.42	10.25	25.78	25.19
0.5	2.45	2.31	8.48	8.32	25.15	24.95
1.0	5.78	5.64	5.36	5.14	24.66	24.25
2.0	7.54	7.47	2.62	2.25	23.54	23.43
3.5	7.71	7.68	2.43	2.11	22.14	22.12

TABLE 3

Sorption of potassium and phosphates from various salt solutions by substrates of bast and birch bark, mg/g

Potassium phosphates	Substrate of birch bark bast			Substrate of birch bark		
	A_K	A_P	$A_{c/P}$	A_K	A_P	$A_{c/P}$
KH_2PO_4	7.54	2.18	5.96	7.47	5.05	5.91
K_2HPO_4	10.42	5.28	4.12	10.25	5.71	4.05
K_3PO_4	25.78	1.69	6.79	25.19	1.66	6.64

Note. A_K , A_P are experimental values of sorption of potassium and phosphorus, respectively; $A_{c/P}$ is the calculated value of sorption of phosphorus.

Apparently, a background electrolyte weakly shields strong attraction of potassium to substrates surface driven by the pH value of 12.4 of model phosphate solution. An increase in electrolyte concentration by more than 2.0 mass % weakly affects potassium sorption.

It should be noted that observed changes in sorption for substrates of bast and bark are similar and differ little for their values (see Table 2).

It is interesting to compare sorption of potassium and phosphates from solutions of their salts that are represent typical water-soluble phosphorus-potassium fertilizers [2].

Table 3 presents sorption values of potassium (A_K) and phosphates (A_P), in recalculation for phosphorus) by PS of bast and birch bark from solutions of salts, the initial potassium concentration in which was (657.0 ± 7.5) mg/L. Background electrolyte that is 2.0 mass % NaCl was used in case of KH_2PO_4 . Table 3 also gives phosphorus sorption values $A_{c/P}$ calculated on the basis of the assumption that potassium and phosphorus are sorbed in the stoichiometric ratio.

A_P values of obtained for a substrate of bast in a solution of KH_2PO_4 is 2.7 times lower than the calculated value unlike the data for a substrate of birch bark. Low ability of the substrate of bast to sorb phosphates may be due to the lower content of active phenoxy radicals and Fe^{3+} ions on its surface compare to the substrate of birch bark [5]. A_P values are substantially lower than calculated $A_{c/P}$ (see Table 3) in case of sorption of phosphates from a solution of K_3PO_4 . The observed difference is probably driven by strong electrostatic repulsions of phosphate ions and the surface of substrates in an alkaline solution of the salt complicating their sorption.

It was found that the introduction of sodium chloride into a solution of K_3PO_4 in an amount of 2.0 and 3.5 mass % led to an insignificant increase in sorption of phosphates by substrates of bast and bark that is on average by 5–10 %.

The impact of effects of electrostatic interaction on potassium sorption from solutions of

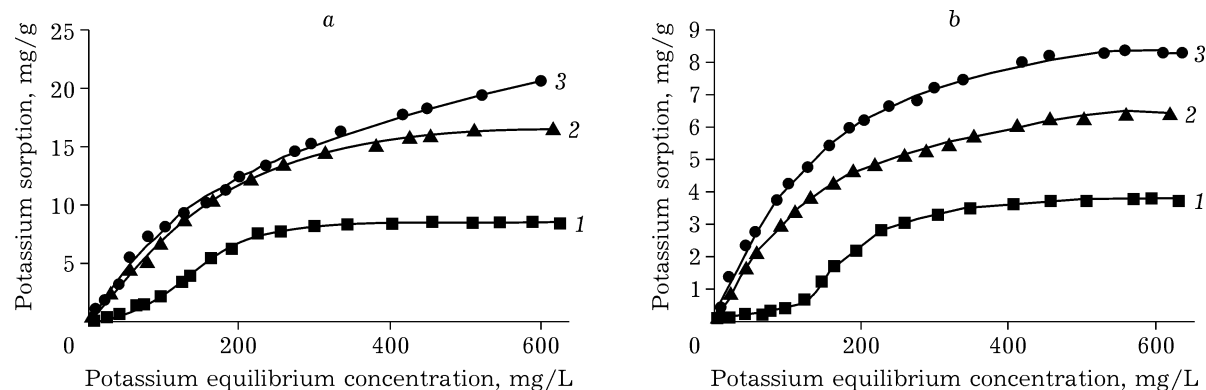


Fig. 3. Potassium sorption isotherms from solutions of KCl (a) and KNO_3 (b) by a porous substrate of birch bark bast: 1 – pH 6.2; 2 – pH 6.2, the background electrolyte (2 % NaCl); 3 – pH 10.8; curves 2 and 3 are calculated according to the Langmuir equation and Table 4 data; points are experimental values.

KCl и KNO₃ was studied on an example of the substrate of birch bark bast. It should be noted that pH values of solutions of these salts are changed very little with increasing concentrations (see Table 1).

It was found that potassium adsorption processes from solutions of potassium chloride and potassium nitrate were described by similar isotherms and differed only by sorption values (Fig. 3). The introduction of a background electrolyte into the solutions or an increase in their pH values to 10.8 leads to a change in the form of isotherms. Thus, with pH of solutions of the salts of 6.2 in the absence of NaCl, one can highlight a concave plot on isotherms in the region of equilibrium concentrations of potassium from 0 to 100–160 mg/L (see Fig. 3, curve 1).

Apparently, electrostatic interaction effects exert a strong effect on sorption from low-concentrated solutions [14]. By shielding electrostatic repulsions, the background electrolyte leads to a substantial increase in potassium sorption in the studied range of its concentrations (see Fig. 3, curve 2).

It should be noted that an increase in alkalinity of KNO₃ solutions to 10.8 leads to a greater increase in potassium sorption in comparison with the effect of the background electrolyte. A positive effect of pH in case of KCl is observed in solutions with the equilibrium concentration of over 350 mg/L (see Fig. 3, curve 3).

Comparison of potassium sorption results from solutions of KCl and KNO₃ demonstrates that the maximum values were obtained for KCl. This difference may be driven by the effect of the anion nature that is its sizes, electronegativity, mobility *etc.* It is known that pref-

erably individual ions are sorbed from solutions of such salts. The formation probability of ion associates in such solutions is very low and does not affect the sorption process [9, 14].

Table 4 gives determination results of A_{∞} и K_L according to eqn. (1) and the least squares method. Equation (1) was used to process experimental results obtained for solutions of K₃PO₄ and KCl (in the presence of the background electrolyte and with pH of 10.8). The Least squares method was used in the remaining cases.

To compare maximum experimental potassium sorption values $A_{\max}$ with limiting sorption values A_{∞} the occupation density of substrate F (eqn. 3) was calculated. The maximum values are reached for solutions of K₃PO₄ and KNO₃, which testifies a high occupation density of the sorption layer in the studied range of their concentrations.

Figures 1 and 3, *a* give experimental data on potassium sorption from solutions of K₃PO₄ and KCl (in the presence of NaCl and with pH of 10.8) and isotherms, for calculations of which A_{∞} and K_L values determined by eqn. (1) and presented in Table 4, were used. Comparison of the data cited indicates compliance of experimental and calculated data.

The usefulness of the Least squares method to determine A_{∞} and K_L in case of potassium hydrophosphate and potassium nitrate (in the presence of 2 % NaCl and pH of 10.8) is demonstrated by Table 5 data that presents calculation results of these parameters by eqn. (1). Additionally, Table 5 gives maximum values of potassium sorption $A_{\max}$ reached in solutions of various salts with appropriate values of maximum equilibrium concentration of potassium

TABLE 4

Langmuir isotherms parameters for potassium sorption from various salt solutions by a porous substrate of birch bark bast

Potassium salts	A_{∞} , mg/g	K_L , L/mg	R^2	F
K ₃ PO ₄	32.55	$0.566 \cdot 10^{-2}$	0.998	0.81
KCl (in the presence of 2 % NaCl)	26.88	$0.339 \cdot 10^{-2}$	0.979	0.61
KCl (pH 10.8)	30.20	$0.333 \cdot 10^{-2}$	0.988	0.68
K ₂ HPO ₄	15.69	$0.483 \cdot 10^{-2}$	0.998	0.66
KNO ₃ (in the presence of 2 % NaCl)	8.67	$0.571 \cdot 10^{-2}$	0.997	0.74
KNO ₃ (pH 10.8)	10.56	$0.672 \cdot 10^{-2}$	0.999	0.79

Note. F is the degree of filling of the substrate; R^2 is the approximation coefficient.

TABLE 5

Langmuir isotherms parameters for potassium sorption from solutions of K_2HPO_4 and KNO_3 by a porous substrate of birch bark bast calculated by eqn. (1)

Potassium salts	Isotherm parameters			C_{eq}^{max} , mg/L	A_{max} , mg/g	A_{max}^{eq} , mg/g
	A_{∞} , mg/g	K_L , L/mg	R^2			
K_2HPO_4	15.78	$0.835 \cdot 10^{-2}$	0.985	615.42	10.42	13.21
KNO_3 (in the presence of 2 % NaCl)	20.77	$0.145 \cdot 10^{-2}$	0.977	615.51	6.42	9.80
KNO_3 (pH 10.8)	17.70	$0.110 \cdot 10^{-2}$	0.979	630.47	8.31	7.25

Note. R^2 is the approximation coefficient.

C_{eq}^{max} and A_{max}^{eq} values calculated by the Langmuir equation.

Comparison of experimental A_{max} and calculated A_{max}^{eq} values of potassium sorption detected their substantial differences for solutions of K_2HPO_4 and KNO_3 (in the presence of 2 % NaCl) – in 1.27 and 1.53 times, respectively. A_{max} and A_{max}^{eq} values in case of KNO_3 (pH 10.8) differ less – in 1.15 times. However, it was found that the experimental data in the region of equilibrium concentrations of potassium up to 100 mg/L exceeded the calculated values of sorption by 2.4–3.0 times.

The application of the least squares method allowed specifying A_{∞} and K_L values (see Tables 4 and 5). Thus, potassium sorption isotherms from the studied solutions of potassium hydrophosphate and potassium nitrate calculated using these values agree with experimental results (see Figs. 1 and 3, b).

Kinetics of potassium sorption by a substrate of bast from solutions of K_3PO_4 and KCl (pH of

10.8), where its maximum adsorption is reached, was studied (see Table 4).

Analysis of Fig. 4 data demonstrates that a change in pH values in a solution of potassium chloride from 6.2 to 10.8 leads not only to an increase in sorption but also to time reduction of reaching the equilibrium in 1.5 times.

Sorption equilibrium in alkaline solutions of the studied salts is reached for approximately equal periods of time – for 40 and 45 min for KCl and K_3PO_4 , respectively.

CONCLUSION

The effect of the nature of salts on potassium sorption from aqueous solutions by PS based on birch bark was detected resulting from the research carried out. It was found that the salts studied by the capacity to potassium sorption could be placed in the following row: $K_3PO_4 > K_2HPO_4 > KCl > KNO_3 > KH_2PO_4$. It was demonstrated that PS of bast and birch bark showed close sorption activities in relation to potassium.

It was found that an increase in alkalinity of solutions led to an increase in potassium sorption from solutions of its salts. The application of a background electrolyte exerts a positive effect on potassium sorption only from solutions of KH_2PO_4 , KCl and KNO_3 . On an example of KCl and KNO_3 , it was demonstrated that an increase in pH of solutions up to 10.8 led to a larger increase in potassium sorption in comparison with a background electrolyte.

Studies demonstrated that maximum potassium sorption by substrates based on birch bark bast was reached from solutions of K_3PO_4 and KCl (pH of 10.8) – A_{∞} is 32.55 and 30.20 mg/g, respectively.

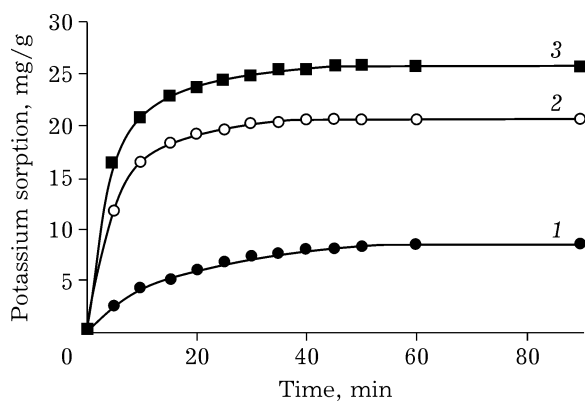


Fig. 4. Kinetics of potassium sorption by a substrate of birch bark bast: 1 – KCl, pH 6.2; 2 – KCl, pH 10.8; 3 – K_3PO_4 , pH 12.4.

It was found that PS by their sorption properties, PS of bast and birch bark exceeded active carbon (birch activated carbon).

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