

# Sorption And Physicochemical Properties of A Phosphorylated Mercerised Cotton Cellulose

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## Research Article

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# Abstract

A process of a mercerised cotton cellulose sample phosphorylation has been investigated. After oxidation a phosphorus content was determined by spectrophotometric analysis and it was in a range of 0.179 to 0.950 mmol g<sup>-1</sup>. A significant decrease in the tensile strength of the sample was found upon an increase of phosphoric acid concentration in a phosphorylating solution. Phosphorylated mercerized fabric contents more phosphorous as unmercerized fabric in 3 times. The sorption properties of phosphorylated cotton cellulose in aqueous solution containing Cu<sup>2+</sup> were characterized. The maximum of static exchange capacity was found to be 1.48 ± 0.11 mmol g<sup>-1</sup> for phosphorylated cotton with content 0.898 ± 0.090 mmol g<sup>-1</sup> of phosphorus. The sorption of Cu<sup>2+</sup> by single phosphorus-containing group occurs for samples with not exceeding 0.80 mmol g<sup>-1</sup> of phosphorus. The preliminary studies of uranium(VI) micro quantities of radionuclides <sup>241</sup>Am, <sup>233</sup>U and <sup>239</sup>Pu sorption from aqueous solution with phosphorylated textile demonstrated the high efficiency.

## Introduction

Cellulose is one of the most abundant biomaterials in the nature. It is a linear syndiotactic homopolymer formed by glucopyranose units linked to each other through b-(1,4)-glycosidic bonds. Due to the free hydroxyl groups bonded with the pyranose ring, cellulose undergoes chemical reactions as primary and secondary alcohols. Formation of ethers and esters, carboxylation, sulfation, phosphorylation, amination and other modifications of cellulose are used and aimed at the initial structure of polymer save (Bykov and Ershov 1996, 2009; Suflet et al. 2006; Klemm et al. 2012; Luneva and Ezovitova 2014; Lehtonen et al. 2020). Chemical modifications of cellulose by introducing the functional groups provide new properties and applicability. Cellulose materials are widely used in the field of water filtration, heavy metals sorption, and development of new non-biodegradable products for medicine and fire-retardant materials (Kettunen et al. 2011; Klemm et al. 2011; Mat Zain 2014; Nair et al. 2014; Ghanadpour et al. 2015; Mautner et al. 2015; Werber et al. 2016; Ferrer et al. 2017; Voisin et al. 2017). The phosphorylated cellulose is of the great interest for investigation and could be one of the most promising material. It is well-known that phosphorus-containing groups are introduced and linked covalently to cellulose molecule after various chemical treatments with P<sub>2</sub>O<sub>5</sub>, PCl<sub>5</sub>, PCl<sub>3</sub>, POCl<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, et al (Sander and Steininger 1968; Granja et al. 2001; Gospodinova et al. 2002; Luneva and Ezovitova 2014; Ghanadpour et al. 2015; Lehtonen et al. 2020). However, the mercerized cotton phosphorylation process studies are rather sparse. Mercerization of cellulose significantly increases its chemical activity in the esterification processes. The phosphorylated mercerised cotton materials can be used as an active and easily impregnated sorbents in filters, a base for defined compositions applying to the different material surface, and as for disinfecting purposes as well (Sud et al. 2008; Ojedokun and Bello 2016). Development of special flushable compositions allow to reused textile after disappearance of disinfecting action.

Current study brings new insights in the properties of the phosphorylated mercerised cotton cellulose.

# Experimental Materials And Methods

## Cotton cellulose treatment

The commercially available mercerized cotton cellulose sample with specific density  $390 \pm 9 \text{ g/m}^2$ , plain-weave texture, fiber diameter  $250 \pm 30 \mu\text{m}$ , thickness  $700 \pm 50 \mu\text{m}$  was used.

The dried sample containing no more than 10% moisture was impregnated with the solution of  $2.80 \text{ mol g}^{-1}$  urea and phosphoric acid (of  $0.200$  to  $2.403 \text{ mol g}^{-1}$ ) at  $80^\circ\text{C}$  for 1 hour (the ratio of sample to liquid was 1:10). The impregnated sample was squeezed to a mass 2 times more than the dry sample mass and dried at  $70^\circ\text{C}$  for at least 5 hours and then at  $145 \div 150^\circ\text{C}$  for 1,5 hours. After phosphorylation, the sample was washed three times with hot and cold distilled water and impregnated with the solution of  $0.10 \text{ mol L}^{-1}$  HCl at room temperature for 1 hour. The sample was washed three times with cold distilled water again and was dried at  $70^\circ\text{C}$  for at least 5 hours.

## Phosphorus content determination

The phosphorus content was determined before and after phosphorylation by the spectrophotometric method based on the color intensity of the Sn(II) reduced phosphorus molybdenum complex. To convert the phosphorus contained in the sample to phosphate ions, 500 mg sample was treated with a 25 ml hot mixture consisting of 3 volumes of concentrated sulfuric acid and 1 volume of 60% hydrogen peroxide. This reaction allowed to dissolve the sample completely and was accompanied by the release of gases. After that the solution was heated at  $175^\circ\text{C}$  for 1 hour in order to decompose the unreacted excess of hydrogen peroxide then the solution was transferred to a flask and diluted with distilled water. It should be noticed that all used solutions and distilled water were previously thermostabilized in a water thermostat to a temperature of  $25^\circ\text{C}$ . Then 0.500 ml of the sample was transferred to a 50 ml flask and diluted with distilled water. After thorough mixing, 2 ml of 2% sulfurous ammonium molybdate  $(\text{NH}_4)_2\text{MoO}_4$  was added and 0.200 ml of 3.5%  $\text{SnCl}_2$  was added in 5 min. The solution was mixed at  $25^\circ\text{C}$  for 15 min. The optical density of the blue phosphor-molybdenum reduced complex was detected at a wavelength of 700 nm (a 5.00 cm thick Cuvette was used). The experimental molar absorption coefficient of this complex was found to be equal to  $\varepsilon_{700 \text{ HM}} = (2.485 \pm 0.023) \times 10^4 \text{ cm}^{-1} \text{ L mol}^{-1}$ . According to the previously obtained calibration graph, the phosphorus content was determined as  $\text{mmol g}^{-1}$  or mass percentages.

## Infrared spectroscopy

IR analysis of the samples was accomplished by the FT-02 INFRALUM IR spectrometer in the range of  $400 \div 4000 \text{ cm}^{-1}$ . 200 ÷ 300 mg of the sample were thoroughly ground with twice recrystallized KBr to obtain a homogeneous mixture with a 0.5% cellulose material mass fraction.

## Acid-Base Titration

The potentiometric titration of the phosphorylated mercerized cotton cellulose was performed with 0.100 mol L<sup>-1</sup> NaOH using the pH meter «ECOTEST 120» (glass electrode combined with silver chloride reference electrode).

## Tensile strength

Tensile testing was performed using the Zwick Roell Z010. The width of the sample was shown to be 20 mm, the thickness – 0.70 mm, the preload value – 0.10 N, the stretching speed – 20 mm/min. The standard maximum breaking force was measured until at least 5 reproducible results were obtained. The results were processed using t-test statistics.

## Sorption characteristics

The sorption characteristics of the samples were determined by the example of sorption of macroquantities of Cu<sup>2+</sup> and UO<sub>2</sub><sup>2+</sup> ions and microquantities of radionuclides <sup>241</sup>Am, <sup>233</sup>U and <sup>239</sup>Pu.

## Sorption of Cu<sup>2+</sup> and UO<sub>2</sub><sup>2+</sup>

The sorption properties of the sample were studied as a model system of Cu<sup>2+</sup> and UO<sub>2</sub><sup>2+</sup> sorption from 1 ÷ 200 mmol L<sup>-1</sup> CuSO<sub>4</sub> solutions and 20 mmol L<sup>-1</sup> UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> solutions. About 0.5 g of textile sample (precision of weighing – ±0.0001 g) were soaked in pH 3.0 solution at 20°C for 5 days while stirring (the ratio of «sample» to «liquid» was 1:50). The pH changes after sorption was detected to be no more than 0.5. The Cu<sup>2+</sup> concentration before and after sample soaking in the solution was determined spectrophotometrically with the Cary Varian 100 device based on the ammonia complex color intensity at λ = 630 nm in the presence of a 1000-fold excess of the ligand (ε<sub>630</sub> = 69.5 ± 0.5 cm<sup>-1</sup> L mol<sup>-1</sup>). The UO<sub>2</sub><sup>2+</sup> concentration in the solution was determined spectrophotometrically with the Shimadzu UV 3100 device based on the color intensity at λ = 420 nm. The values of the static capacity were determined by the formula:

$$SEC = \frac{(C_0 - C_{eq}) \cdot V_s}{m_t},$$

where SEC – the static exchange capacity for copper or uranyl ions, mmol g<sup>-1</sup>; C<sub>0</sub> – initial copper or uranyl ions concentration in the solution, mmol L<sup>-1</sup>; C<sub>eq</sub> – equilibrium copper or uranyl ions concentration in the solution, mmol L<sup>-1</sup>; V<sub>s</sub> – the volume of solution, L; m<sub>t</sub> – the mass of textile, g.

## Sorption of radionuclides <sup>241</sup>Am, <sup>233</sup>U and <sup>239</sup>Pu

Caution! <sup>241</sup>Am, <sup>233</sup>U и <sup>239</sup>Pu are highly radioactive isotopes and must be handled in dedicated facilities with equipment suitable for radioactive materials.

About 0.1 g of textile sample (precision of weighing –  $\pm 0.0001$  g) were soaked in solution at 20°C for 48 h while stirring (the ratio of «sample» to «liquid» was 1:200). In the filtrate above solid phase was determined specific activity of radionuclides  $^{241}\text{Am}$ ,  $^{233}\text{U}$  или  $^{239}\text{Pu}$ .

The sorption of  $^{241}\text{Am}$  and  $^{233}\text{U}$  were carry out from Moscow tap water with the following composition,  $\text{mg L}^{-1}$ :  $\text{Na}^+ - 6 \div 8$ ;  $\text{K}^+ - 4 \div 5$ ;  $\text{Mg}^{2+} - 15 \div 17$ ;  $\text{Ca}^{2+} - 52 \div 56$ ;  $\text{Cl}^- - 6 \div 8$ ;  $\text{SO}_4^{2-} - 36 \div 38$ ;  $\text{HCO}_3^- - 200 \div 205$ ; total mineral content –  $310 \div 330$ ; hardness –  $3.6 \div 3.8 \text{ mmol L}^{-1}$ ;  $\text{pH} = 7.3 \div 7.8$ . The amount of corresponding radionuclide (about  $10^5 \text{ Bq L}^{-1} \approx 4.3 \text{ mg L}^{-1} \text{ }^{233}\text{U}$ ) were added to liquid phase the and kept for 120 h to establish hydrolytic equilibrium between the radioactive and inactive components of the solution. The solution for investigation of plutonium sorption contained  $1.0 \text{ mol L}^{-1} \text{ HNO}_3$  and about  $10^6 \text{ Bq L}^{-1} \text{ }^{239}\text{Pu}$  and its was prepared by dissolving 1.0 mg  $[\text{N}(\text{CH}_3)_4]_2\text{Pu}(\text{NO}_3)_6$  in an aliquot of  $3.0 \text{ mol L}^{-1} \text{ HNO}_3$  and by diluting with water. The textile samples added in the resulting solution and soaked with him. After establish sorption equilibrium partition coefficient was determinated by formula:

$$K_d = \frac{A_0 - A_{eq}}{A_{eq}} \cdot \frac{V_S}{m_t},$$

where  $K_d$  – the partition coefficient,  $\text{ml g}^{-1}$ ;  $A_0$  and  $A_{eq}$  – initial and equilibrium specific activity of radionuclides,  $\text{Bq L}^{-1}$ ;  $V_S$  – the volume of solution, ml;  $m_t$  – the mass of textile, g.

The specific activity of  $^{241}\text{Am}$  in solutions was determined by a radiometric method from intensity of 59 keV  $\gamma$ -line using an SKS-50M spectrometric complex («Green Star Technologies»). The specific activities of  $^{233}\text{U}$  and  $^{239}\text{Pu}$  in solutions were determined by an alpha-spectrometric method from intensities 4.9 MeV and 5.2 MeV lines, respectively, using an low-background semiconductor alpha spectrometer ALPHA-ARIA («ORTEC»).

## Results And Discussion

Mercerization was carried out to improve sample wettability which is associated with effect of sliding and smoothness of cellulose fibers, and to reduce the edge angle of wetting. Moreover, mercerization improved absorptive properties and imparted a greater affinity for dyes and various chemical finishes. After sample impregnation with NaOH followed by washing, its protonation-deprotonation occurred and resulted in surface hydrophilization with an increase in the hydrophilic-lipophilic balance of the sample.

Phosphorylation of mercerized cotton cellulose was accompanied by both external material and structural changes. The sample had a yellowish color after heating up to 145°C, the intensity of which was subsequently washed out by hot and cold distilled water. The strength characteristics were noticeably changed. According to the results on tensile strength investigation the heat treatment did not reduce the sample strength characteristics during phosphorylation in the absence of  $\text{H}_3\text{PO}_4$ . The standard maximum tear force for untreated and phosphorylated sample was observed to be equal  $17.2 \pm$

0.5 and  $17.9 \pm 0.6$  MPa. The difference within the statistical margin of error indicates that there were no changes in the molecular and supramolecular structure after both mercerization and heat treatment of the cotton cellulose sample. However, the strength characteristics of the sample were reduced by almost 2 times (Fig. 1) despite on low  $\text{H}_3\text{PO}_4$  concentration ( $0.20 \text{ mol L}^{-1}$ ). Apparently, it was caused by changes in the structure of the molecules and partial destruction which seemed to increase with raising concentration of phosphoric acid in the phosphorylating solution. It should be noticed that the complete destruction of the sample was not observed with  $\text{H}_3\text{PO}_4$  concentration up to  $2.403 \text{ mol L}^{-1}$ .

The phosphorus content was determined as phosphate ions concentration after wet oxidation of phosphorylated mercerized cotton. The sample wet oxidation was carried out by using a hot concentrated sulfuric acid (98%, 3 volumes) and hydrogen peroxide (60%, 1 volume). After sample complete dissolution and discoloration of the solution, heating was performed to decompose the excess hydrogen peroxide completely. It is known that all phosphorus of the phosphorylated sample transforms into phosphoric acid.

Table 1  
Results on phosphorus content determination in the cotton cellulose sample before and after phosphorylation obtained by the spectrophotometric method based on the color intensity of the reduced phosphorus molybdenum complex.

Nº	$\text{C}(\text{H}_3\text{PO}_4)$ , $\text{mol L}^{-1}$	Content P, wt. %	n(P) in 1 g textile, $\text{mmol g}^{-1}$
1	0	$0.062 \pm 0.006$	$0.0201 \pm 0.0020$
2	0.201	$0.55 \pm 0.06$	$0.179 \pm 0.018$
3	0.399	$1.28 \pm 0.13$	$0.414 \pm 0.041$
4	0.601	$1.49 \pm 0.15$	$0.481 \pm 0.048$
5	0.802	$1.89 \pm 0.19$	$0.611 \pm 0.061$
6	1.01	$2.31 \pm 0.23$	$0.745 \pm 0.075$
7	1.20	$2.48 \pm 0.25$	$0.802 \pm 0.080$
8	1.40	$2.78 \pm 0.28$	$0.898 \pm 0.090$
9	1.60	$2.90 \pm 0.29$	$0.938 \pm 0.094$
10	1.80	$2.73 \pm 0.27$	$0.881 \pm 0.088$
11	2.00	$2.94 \pm 0.29$	$0.950 \pm 0.095$
12	2.20	$2.53 \pm 0.25$	$0.816 \pm 0.082$
13	2.40	$2.73 \pm 0.27$	$0.881 \pm 0.088$

The data shown an obvious increase in phosphorus content in the sample which corresponds to the rising phosphoric acid concentration in the phosphorylating solution. The number of phosphorus-

containing groups per 1 g of the sample increased from 0.179 to 0.950 mmol along with phosphoric acid concentration increased from 0.201 to 2.00 mol L<sup>-1</sup>. However, a further increase in the acid concentration did not lead to a phosphorus content increase and was constant within the statistical error.

For comparison the unmercerized cotton fabric was phosphorylated and phosphorus content in its was determined. Unmercerized cotton fabric is more hydrophobic material and is poorly impregnated with aqueous solutions. Therefore, phosphorylation process of the fabric is difficult. In Fig. 3 shows the phosphorus content in phosphorylated mercerized and unmercerized fabric versus phosphoric acid concentration in phosphorylating solution. It is seen that the phosphorus content increases as growing of phosphoric acid concentration both for mercerized fabric and unmercerized. But phosphorus content increases unlinear to about 3 wt. % in mercerized and to about 1 wt. % in unmercerized fabric. Mercerized fabric contents phosphorous more 3 times as unmercerized fabric.

The study results of the mercerized cotton cellulose samples using IR spectroscopy are shown in the Fig. 2.

According to Suflet and Lehtonen (Suflet et al. 2006; Lehtonen et al. 2020), the mercerized cotton cellulose had specific IR wavenumbers: O-H groups stretching vibrations at 3400 ÷ 3500 cm<sup>-1</sup>, CH<sub>2</sub>-groups – at 2800 ÷ 2900 cm<sup>-1</sup> and C–O–C-elements of glycosidic bonds – at 1166 and 1115 cm<sup>-1</sup>. Several additional bands in the IR spectrum of phosphorylated cotton cellulose was obtained. The absorption band at 1720 cm<sup>-1</sup> appeared due to carbonyl groups which probably were arisen from the pyranose ring opening. Presumably, it can indicate a partial oxidation of the sample. Moreover, the absorption band at 1210 cm<sup>-1</sup> and 830 cm<sup>-1</sup> occurs for bonds valence vibrations P = O and P–O–C respectively. The absence of additional bands in the region of 2800 ÷ 2900 cm<sup>-1</sup> and the shoulder at 920 ÷ 1000 cm<sup>-1</sup>, coming from P–O–H valence vibrations, indicates the absence of the pointed functional groups. Furthermore, the appropriate potentiometric titration curve could not be provided due to the inflection point absence. This fact could be the evidence that there were no functional phosphorus-containing groups with hydrogen which could be substituted.

It is known that modified phosphorylated cotton cellulose can be used as a heavy toxic metals sorbent (Hokkanen et al. 2014; Sirviö et al. 2016; Guo et al. 2018). The cotton cellulose sorption properties were studied using Cu<sup>2+</sup> sorption from solutions with different phosphoric acid concentrations (pH = 3, t = 20°C) as a model system. The significant increase of a sorption capacity was shown in the presence of phosphorus-containing groups. The adsorption isotherms shape and their non-linearity indicated an intricate mechanism of the adsorption process. Presumably chemisorption occurs on the surface due to complexation along with Cu<sup>2+</sup> physical adsorption. The data obtained were described by the Langmuir monomolecular adsorption model, as a Fig. 3. The plateau corresponds to saturation of sorption centers and formation of a monomolecular layer according to the equation:

$$SEC = SEC_{\infty} \cdot \frac{K \cdot C(Cu^{2+})}{1 + K \cdot C(Cu^{2+})}$$

where SEC – the static exchange capacity,  $\text{mmol g}^{-1}$ ;  $SEC_{\infty}$  – the limit static exchange capacity,  $\text{mmol g}^{-1}$ ; K – the exchange equilibrium constant – the ratio of sorption rates constants to desorption rates constants,  $\text{L mmol}^{-1}$ ;  $C(Cu^{2+})$  – copper ions concentration in the solution,  $\text{mmol L}^{-1}$ .

However, a further increase in SEC along with an increase in the  $Cu^{2+}$  sorbed concentration indicated the polymolecular nature of sorption. In this case, the branch rise of the sorption isotherm at more than  $125 \text{ mmol L}^{-1}$  of  $Cu^{2+}$  is explained by the additional copper amounts sorption and the appearance of the second and subsequent adsorption layers, as well as occurrence of chemisorption.

Thereby it is appropriate to compare the maximum static exchange capacity of the monomolecular layers  $SEC_{\infty}$  of different phosphorylated cotton cellulose samples (Fig. 4).

It is clear that sample phosphorylation with even low concentrations of phosphoric acid turned out to lead to an increase in the maximum sorption capacity. The results confirmed that chemical reaction of phosphate groups addition to the monomer units of cotton cellulose was dealt with. In addition, the initial part of the curve shows an increase in the  $Cu^{2+}$  sorption capacity along with an increase in the concentration of  $H_3PO_4$  in the phosphorylating solution. The  $SEC_{\infty}$  maximum ( $1.48 \pm 0.11 \text{ mmol g}^{-1}$ ) can be observed with  $1.40 \text{ mol L}^{-1}$  of  $H_3PO_4$ . The maximum sorption capacity was not changed with up to  $1.80 \text{ mol L}^{-1}$  of  $H_3PO_4$  within statistical error. A further increase in  $H_3PO_4$  concentration caused a significant decrease in  $SEC_{\infty}$ . Furthermore, considering a dependence between a  $Cu^{2+}$  sorbed amount and a phosphorus content it can be concluded that a linear correlation exists (Fig. 6). A  $Cu^{2+}$  were coordinated in the ratio  $n(Cu^{2+}):n(P) = 1:1$  with no more than  $0.80 \text{ mmol g}^{-1}$  of phosphorus content. The exchange equilibrium constant for samples with phosphorus content no more  $0.80 \text{ mmol g}^{-1}$  was  $0.0803 \pm 0.0087 \text{ L mmol}^{-1}$ . For samples with phosphorus content  $0.80 \text{ mmol g}^{-1}$  and more the exchange constant was equal  $0.0331 \pm 0.0077 \text{ L mmol}^{-1}$ . The efficiency of  $Cu^{2+}$  sorption became higher with more than  $0.80 \text{ mmol g}^{-1}$  of phosphorus content and the ratio  $n(Cu^{2+}):n(P) = 1:1$  did not match. It can be explained by the bidenticity of phosphorus-containing groups and their ability to coordinate more metal ions than in the 1:1 ratio. Such kind of proportionality is typical for complexation reaction and sorption with chemical nature.

The isotherm of uranyl ions sorption was obtained from a sample phosphorylated with  $0.802 \text{ mol L}^{-1}$   $H_3PO_4$  solutions (phosphorus content –  $1.89 \pm 0.19 \text{ wt. \%}$ ;  $n(P) = 0.611 \pm 0.061 \text{ mmol g}^{-1}$ ) (Fig. 7).

It is shown that the obtained experimental data are well described by the Langmuir equation. The maximum static exchange capacity ( $SEC_{\infty}$ ) and the exchange equilibrium constant (K) for the uranyl ions sorption by a the phosphorylated textile sample were  $0.822 \pm 0.014 \text{ mmol g}^{-1}$  and  $1.844 \pm 0.11 \text{ L mmol}^{-1}$

<sup>1</sup>. The high values of the exchange constants and the convex shape of the sorption isotherms indicates that the uranyl ions sorption by phosphorylated cellulose samples is highly selectivity.

The dependence of the static exchange capacity  $UO_2^{2+}$  on the phosphorus content in textile samples is shown in Fig. 8.

The presented results (Fig. 8) shown that increasing of phosphorus content in samples leads to growth of the uranyl-ions capacity. It indicated an increasing of ionogenic groups number in the composition of sorbents when more concentrated solutions of phosphoric acid are used in the phosphorylating. Higher absolute values of static exchange capacity for uranyl ions in comparison with static exchange capacity for copper are apparently associated with the formation of stronger uranium compounds with phosphate groups on cellulose.

The dependence of the distribution coefficients ( $K_d$ ) for the radionuclides  $^{241}\text{Am}$ ,  $^{233}\text{U}$  and  $^{239}\text{Pu}$  on the phosphorus content in the samples of phosphorylated cellulose is shown in Fig. 9.

The presented in Fig. 9 results demonstrated no statistically significant change of radionuclides  $^{241}\text{Am}$ ,  $^{233}\text{U}$  and  $^{239}\text{Pu}$  sorption while increasing of the phosphorus content in the textile sorbents. The average values of the partition coefficient ( $K_d$ ) was for the radionuclides  $965 \pm 13$ ,  $1600 \pm 32$ , and  $734 \pm 25 \text{ ml g}^{-1}$ , respectively. In the case of  $^{241}\text{Am}$  and  $^{233}\text{U}$  the observed effect is apparently associated with the fact that these radionuclides in tap water can be in a hydrolyzed forms, i.e. corresponding hydroxides or radiocolloids. Sorption of these forms of radionuclides occurs due to physical adsorption on the sorbent surface and does not depend on the degree of phosphorylation of the cellulose. The absence of the effect of the phosphorus content on the sorption of  $^{239}\text{Pu}$  may be due to the high complexing ability of phosphate groups with respect to  $\text{Pu}^{4+}$  ions. In this case, almost complete sorption (more than 99%) of microquantities of plutonium from the acidic solution occurs despite change of ionogenic groups concentration at sorbent. It should be noted that physical adsorption of hydrolyzed and polymeric forms of plutonium (which can be formed in  $1.0 \text{ mol L}^{-1} \text{ HNO}_3$ ) be able to occur.

According to the results it was concluded that there is a great opportunity to apply mercerized phosphorylated cotton cellulose as a radioactive actinides sorbent due to such a significant static exchange capacity of uranyl ions. This sorbent allows to compact ash into cement matrices and dispose of a radioactive waste.

## Conclusion

Mercerization of cellulose improves its wettability and leads to hydrophilization of the surface. Moreover, the mercerized cotton fabrics is commercially available and is widely used in other branch of industrial. Therefore it is very perspective materials for modification with other functional groups and investigation its physicochemical properties. Cotton cellulose phosphorylation reduces its strength and leads to significant tissue destruction with high phosphoric acid concentrations (more than  $2.40 \text{ mol L}^{-1}$ ).

According to IR spectroscopy and potentiometric titration of mercerized phosphorylated cotton cellulose results it was found that functional groups  $P=O$  and  $C-O-P$  is present in the structure modified cellulose. The absence of a significant increase in the  $Pu^{4+}$  sorption with an increase in phosphorus content may indicate the absence of a hydroxyl group on the phosphorus atom. The behaviour is observed in the case of mono- and dialkyl phosphoric acids, which give extremely strong complexes with tetravalent f-elements ions. Sorption of microquantity of actinides in different oxidation states from tap water shows that the presence of noticeable amounts of bicarbonate ion levels out the difference in the sorption behavior of the studied elements. It allow to assume that significant contribution of physical sorption and the formation of radiocolloids takes place under the studied conditions. In the case of  $Pu^{4+}$  sorption, the pattern is observed that is typical of the interaction of tetravalent f-elements ions with trialkyl phosphates. It is confirms the assumption of the presence of a phosphoryl group in modified cellulose in a form close to trialkyl phosphate.

Data analysis of mercerized phosphorylated cellulose static exchange capacity indicates a complete polymolecular character of adsorption mechanism, which is described by the Langmuir equation. It was found that coordination of a copper ion occurs by a single phosphorus-containing group ( $n(Cu^{2+}):n(P) = 1:1$ ) with  $0.80 \text{ mmol g}^{-1}$  of phosphorus in the sample.

In addition, cotton cellulose is a cheap and commercially available raw material for the production of woven materials with various purposes. The mercerization process is a simple method which could be implemented and used for manufacturing. Thus, the results obtained are of a great interest for development new woven materials with a high phosphorus content, which will sorb heavy and carcinogenic metal. Moreover, the observed high sorption capacity of uranyl opens up new possibilities for disposal of radioactive actinides by ash cementation after complete oxidation (combustion) of the spent sorbent.

The obtained results make it possible to offer the obtained phosphorylated cellulose for use, e.g. as a material suitable for collecting and removing small volumes of technological solutions containing valuable or hazardous metals for recuperation or waste disposal.

## Declarations

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**Availability of data and material** (data transparency). Not applicable

**Code availability** (software application or custom code). Not applicable

**Authors' contributions.** It was equal.

**Ethics approval** (include appropriate approvals or waivers). Not applicable

**Consent to participate** (include appropriate statements). Not applicable

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## Figures

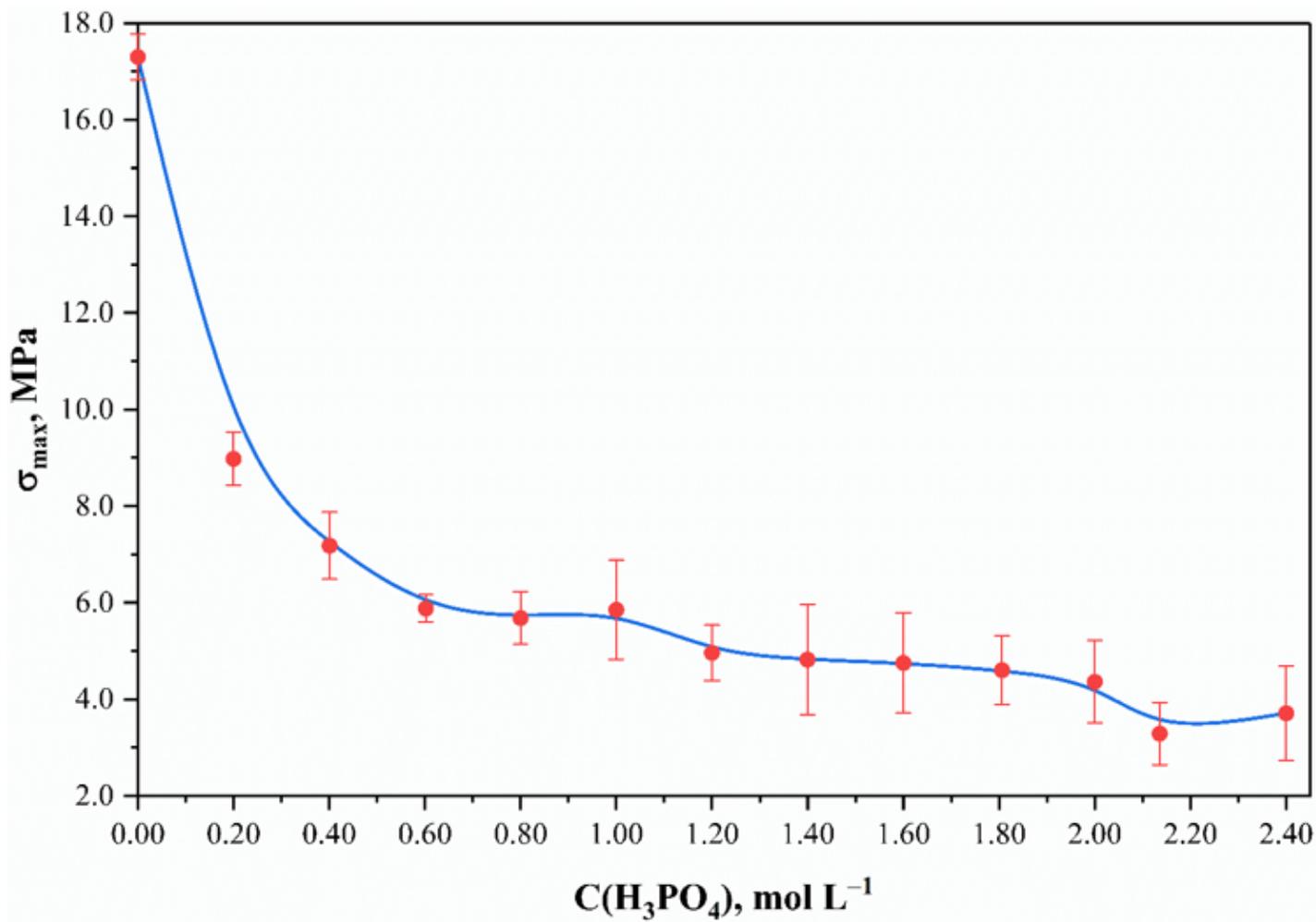
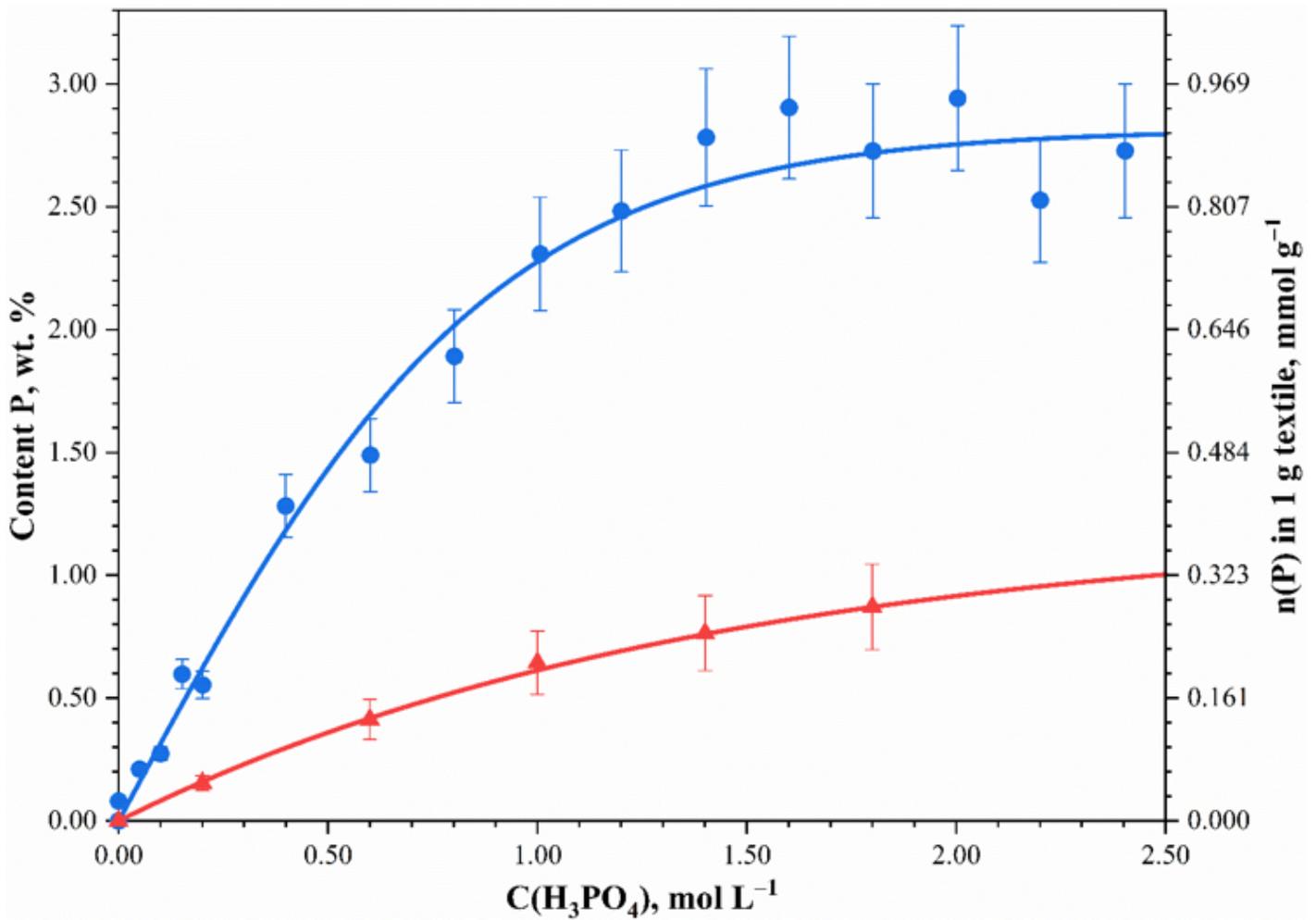


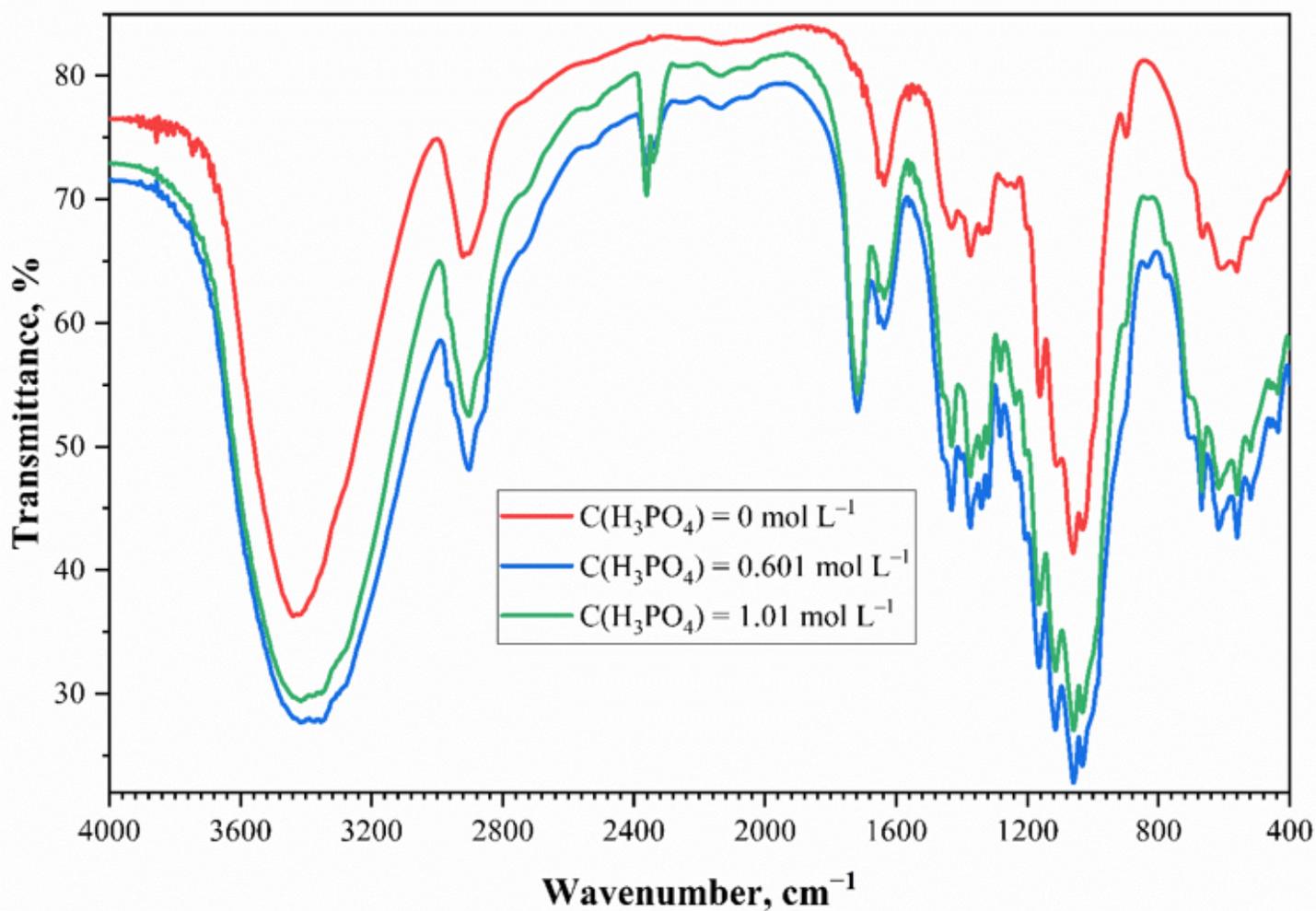
Figure 1

Effect of phosphoric acid content on the standard maximum tensile strength for cotton.



**Figure 2**

The phosphorus content (wt. % and mol in 1 g textile) in phosphorylated mercerized (circles) and unmercerized (triangles) fabric versus phosphoric acid concentration in phosphorylating solution.



**Figure 3**

The IR spectrum of the mercerized cotton cellulose and the phosphorylated cotton cellulose treated solutions with different phosphoric acid concentrations.

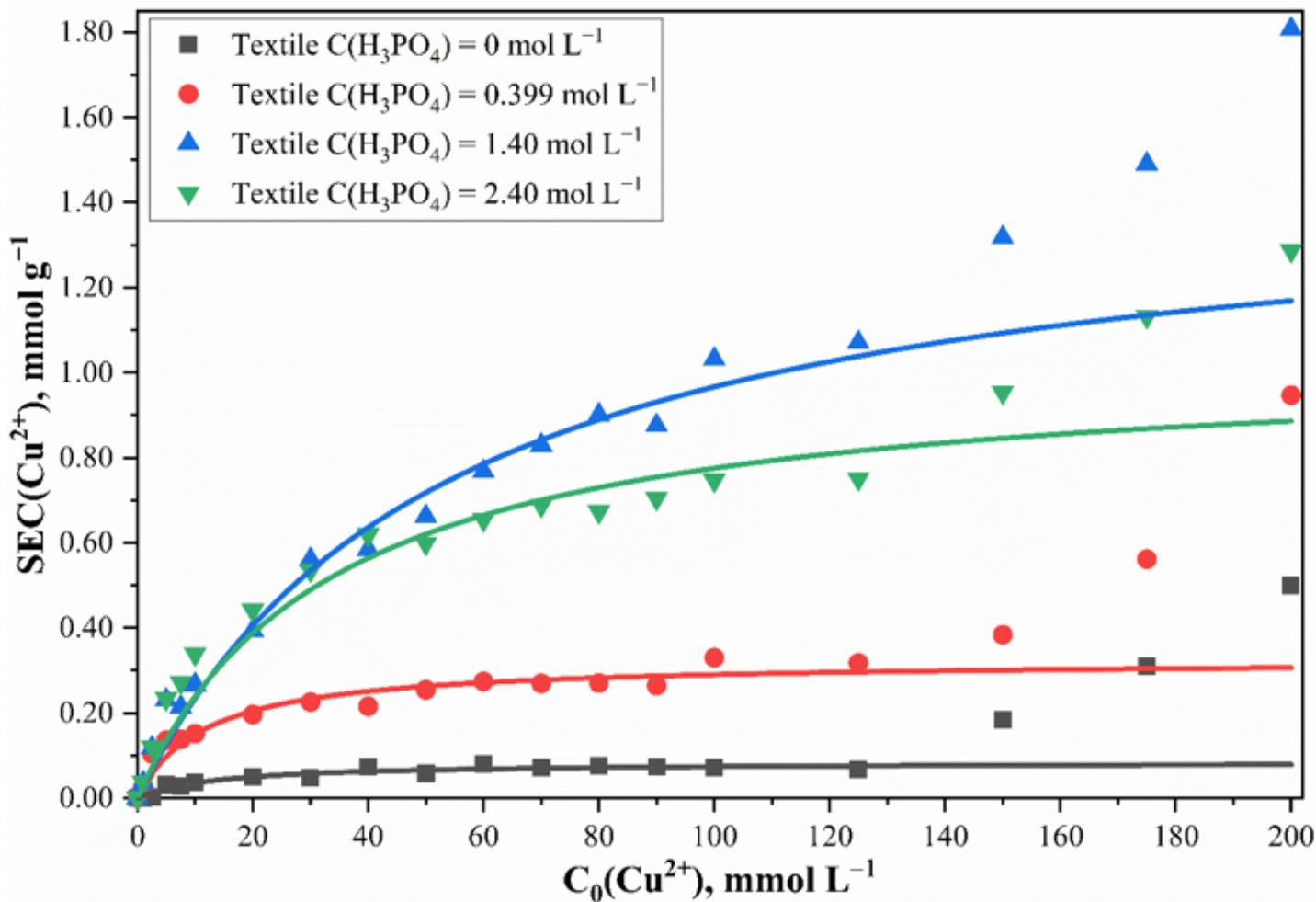


Figure 4

A Cu<sup>2+</sup> sorption isotherms of cotton cellulose samples phosphorylated with different concentration of phosphoric acid solutions: points – experimental data, lines – calculated values according to the Langmuir equation. The temperature of the solutions during sorption experiments was  $t = 20^\circ\text{C}$ .

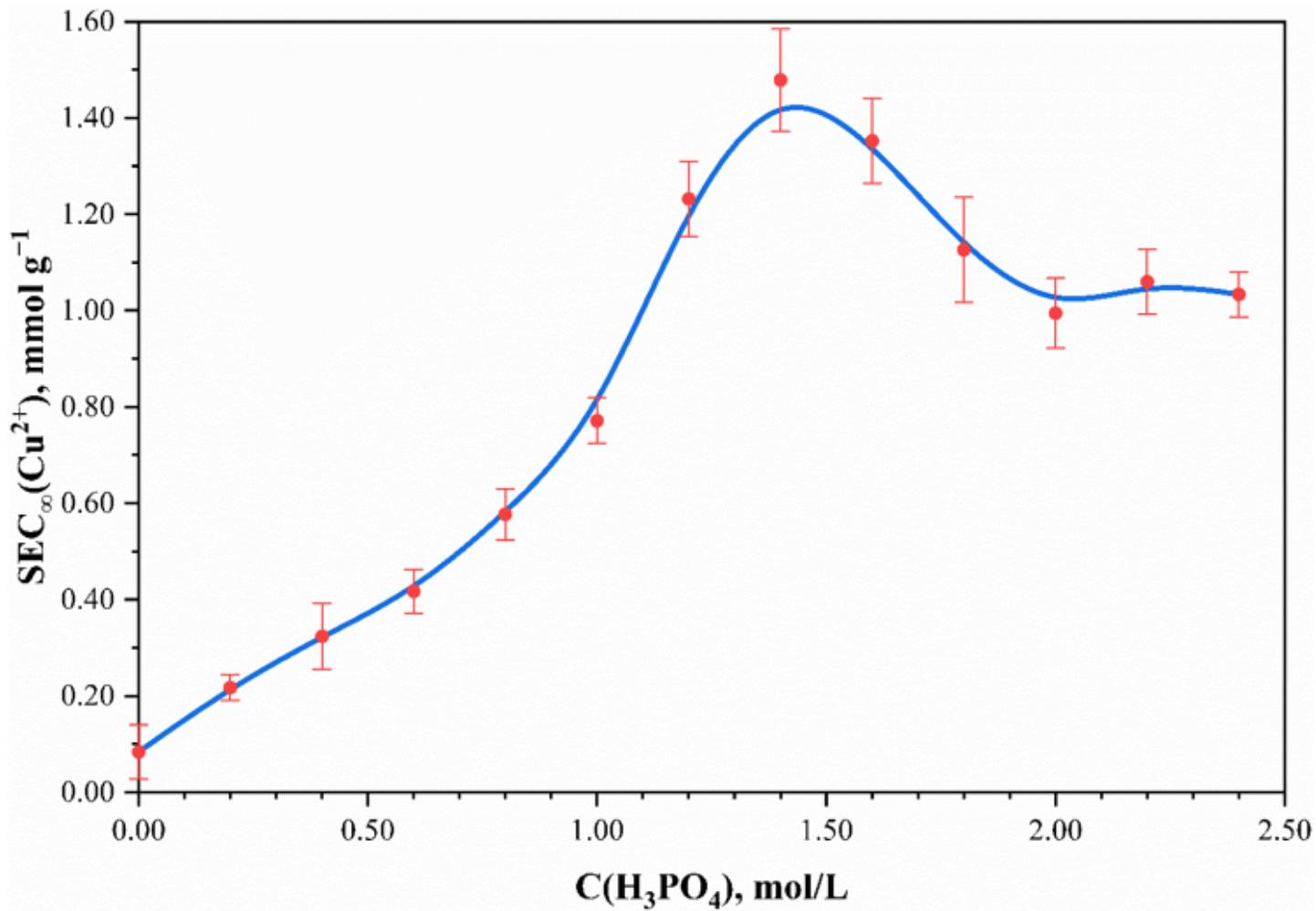
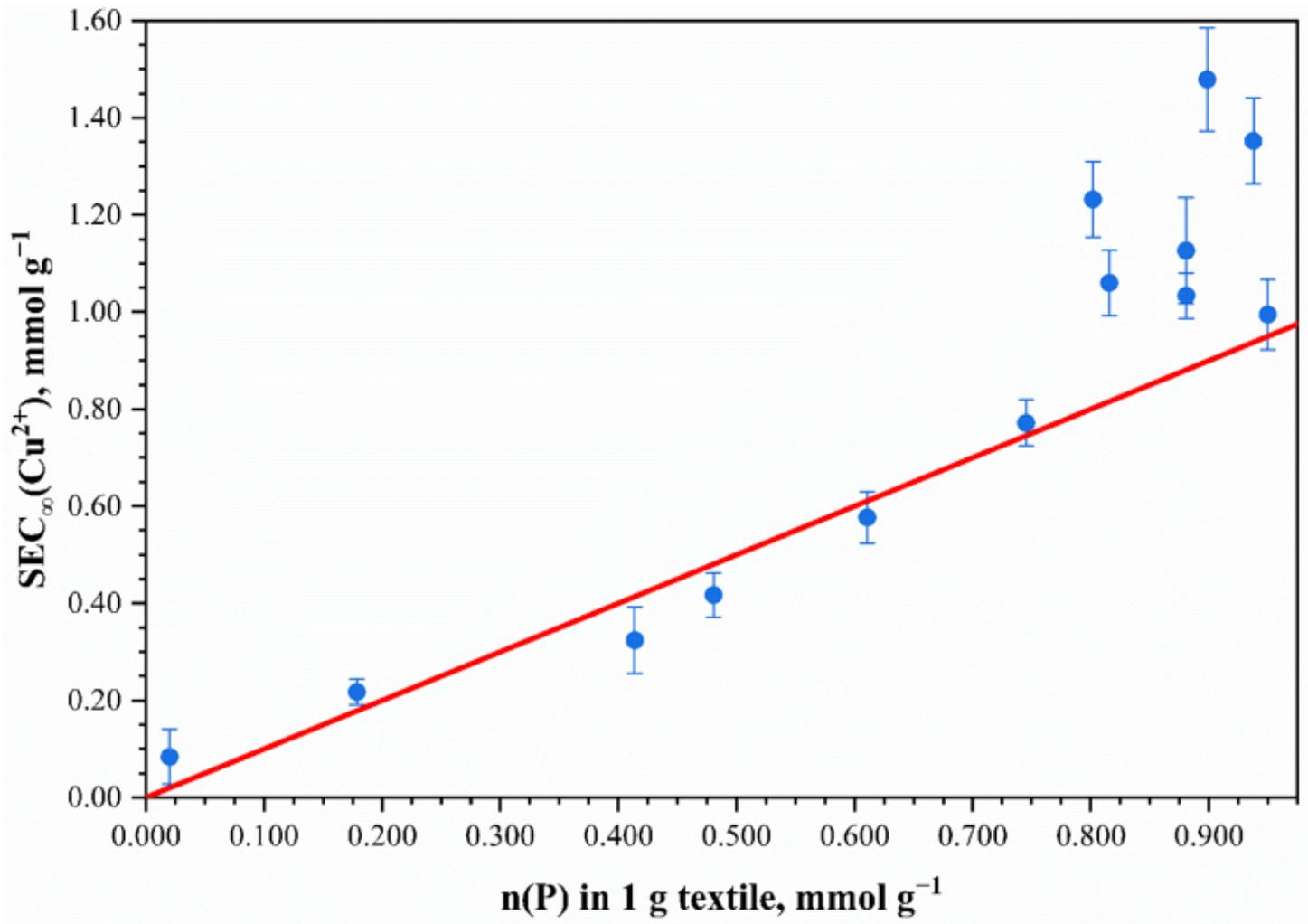


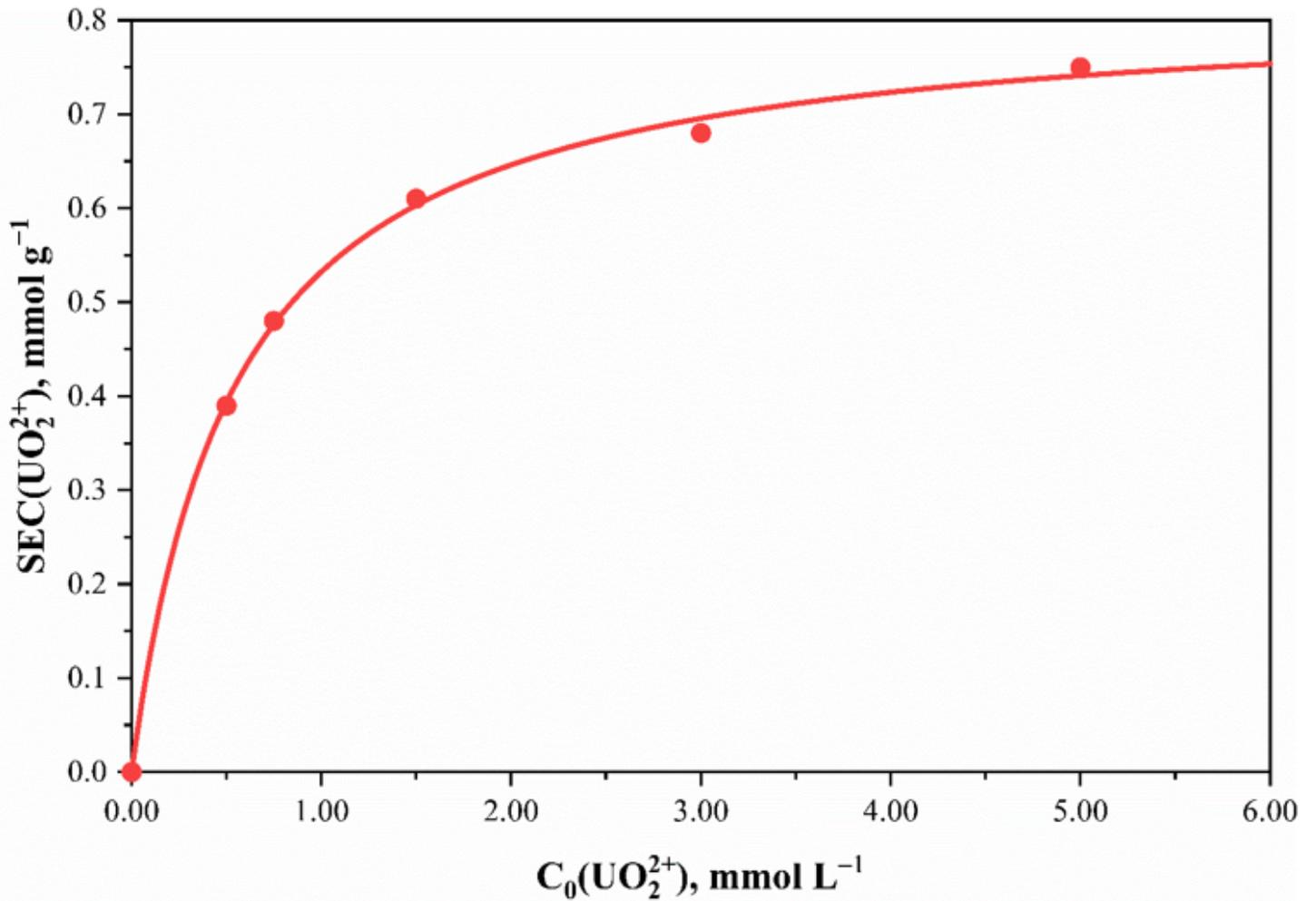
Figure 5

Effect of phosphoric acid concentration on the maximum static exchange capacity  $\text{SEC}_\infty$  ( $t = 20^\circ\text{C}$ ) of phosphorylated cotton cellulose samples related to  $\text{Cu}^{2+}$ .



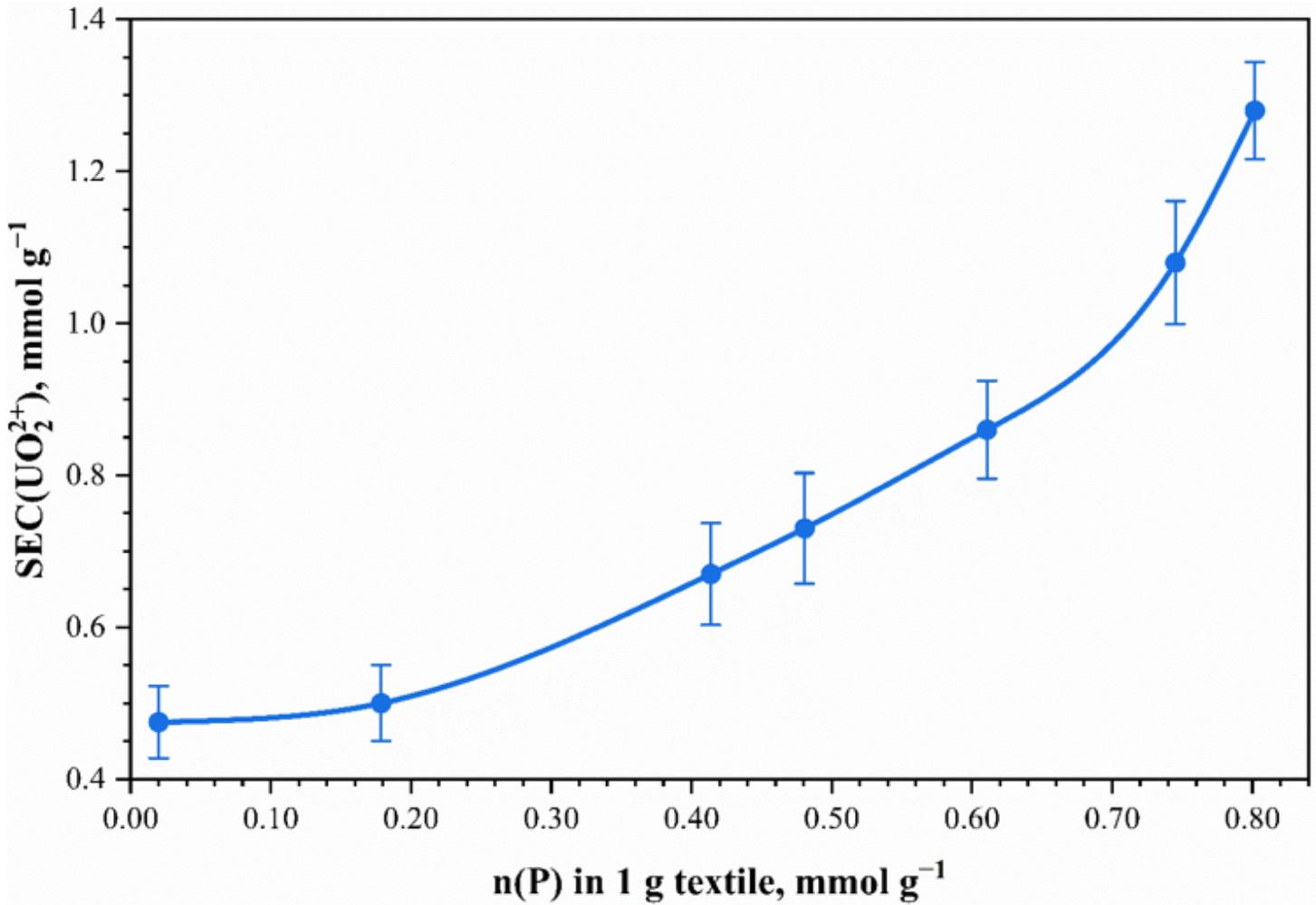
**Figure 6**

Effect of phosphorus content in mercerized phosphorylated cotton cellulose on the maximum static exchange capacity  $SEC_{\infty}$  ( $t = 20^{\circ}\text{C}$ ) related to  $\text{Cu}^{2+}$  points – experimental data, the line corresponds to the ratio  $n(\text{Cu}^{2+}):n(\text{P}) = 1:1$ .



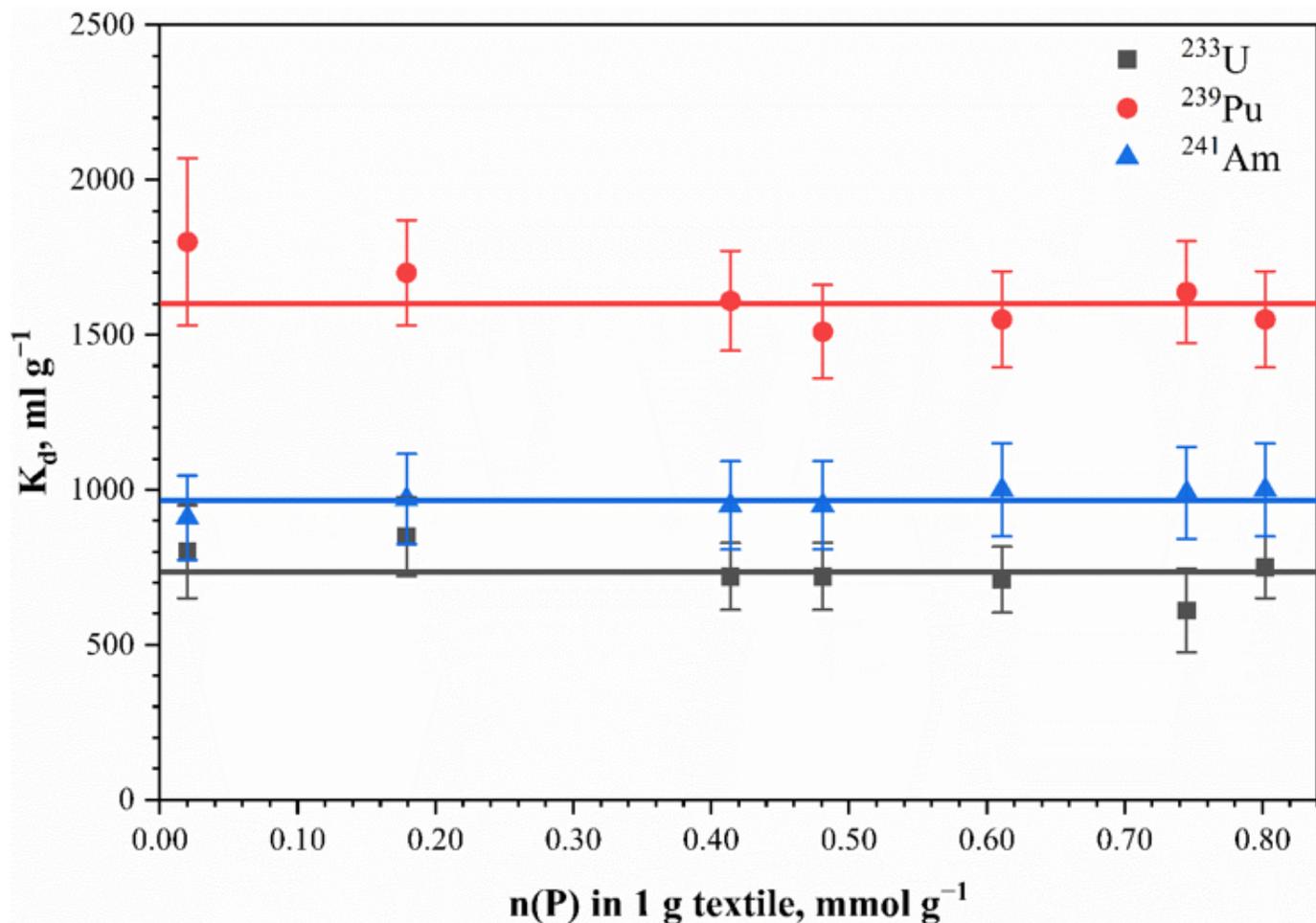
**Figure 7**

A  $\text{UO}_2^{2+}$  sorption isotherm of cotton cellulose samples phosphorylated with  $0.802 \text{ mol L}^{-1}$   $\text{H}_3\text{PO}_4$  solutions (phosphorus content –  $1.89 \pm 0.19 \text{ wt. \%}$ ;  $n(\text{P}) = 0.611 \pm 0.061 \text{ mmol g}^{-1}$ ): points – experimental data, lines – calculated values according to the Langmuir equation. The temperature of the solutions during sorption experiments was  $t = 20^\circ\text{C}$ .



**Figure 8**

Effect of phosphorus content in mercerized phosphorylated cotton cellulose on the static exchange capacity SEC from 20  $\text{mmol L}^{-1}$   $\text{UO}_2^{2+}$  solutions: points – experimental data, the line corresponds to the ratio  $n(\text{Cu}^{2+}):n(\text{P}) = 1:1$ . The temperature of the solutions during sorption experiments was  $t = 20^\circ\text{C}$ .



**Figure 9**

Effect of phosphorus content in mercerized phosphorylated cotton cellulose on the partition coefficient related to different radionuclides: points – experimental data, lines correspond to the partition coefficients. The sorption of <sup>241</sup>Am and <sup>233</sup>U were carry out from Moscow tap water; sorption of <sup>239</sup>Pu were carry out from 1.0 mol L<sup>-1</sup> HNO<sub>3</sub> solution.