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ИЗУЧЕНИЕ СОРБЦИИ ИОНОВ Cr(III) ФОСФОРСОДЕРЖАЩИМ ПОЛИМЕРНЫМ СОРБЕНТОМ

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В статье представлены результаты исследования по сорбции ионов Cr(III) из водных растворов с использованием фосфорсодержащего сорбента на основе бутадиен-стирольного каучука марки ДССК. Данный сорбент был синтезирован реакцией окислительного хлорфосфорилирования бутадиен-стирольного каучука марки ДССК с использованием PCl_3, CCl_4, H_2SO_4 и O_2 в лабораторных условиях. Изучено влияние различных параметров, таких как pH раствора, начальная концентрация ионов металла, масса сорбента, время контакта фаз и температура на эффективность сорбции ионов Cr(III). Сорбционная емкость и степень сорбции были вычислены на основании данных по концентрациям, полученным при анализе проб на масс спектрометре ISP MS 7700e. Установлено снижение степени сорбции ионов Cr(III) в кислых и щелочных средах, а оптимальным условием для сорбции является слабокислая среда. Повышение температуры и массы сорбента положительно влияют на сорбцию. Степень сорбции уменьшается с увеличением начальной концентрации ионов Cr(III). Это указывает на то, что фосфорсодержащий сорбент на основе бутадиен-стирольного каучука марки ДССК имеет ограниченное число активных центров для сорбции, а при более низких концентрациях почти все ионы Cr(III) сорбировались. Однако увеличение начальной концентрации ионов Cr(III) приводит к быстрому насыщению поверхности сорбента. Также установлено, что при комнатной температуре равновесие устанавливается уже через 40 мин. Результаты эксперимента показали, что фософрсодержащий сорбент на основе бутадиен-стирольного каучука марки ДССК может быть успешно использован для извлечения ионов Cr(III) из водных растворов.

Ключевые слова: удаление, полимерный сорбент, сорбция, хром

STUDY OF SORPTION OF Cr(III) IONS BY PHOSPHORUS-CONTAINING POLYMER SORBENT

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The paper presents the results of a study on the sorption of Cr(III) ions from aqueous solutions using phosphorus-containing sorbent based on butadiene-styrene rubber of the DSKK

brand. This sorbent was synthesized by the reaction of oxidative chlorophosphorylation of butadiene-styrene rubber of the DSKK brand using PCl_3, CCl_4, H_2SO_4 and O_2 under laboratory conditions. The effect of various parameters, such as the pH of the solution, the initial concentration of metal ions, the sorbent mass, the contact time of the phases, and the temperature on the sorption efficiency of Cr(III) ions have been studied. The sorption capacity and the degree of sorption were calculated on the basis of the concentration data obtained from the analysis of samples on the ISP MS 7700e mass spectrometer. A decrease in the degree of sorption of Cr(III) ions in acidic and alkaline media is established, and an acid-poor medium is the optimal condition for sorption. The increase in the temperature and mass of the sorbent positively affects sorption. The degree of sorption decreases with increasing initial concentration of Cr(III) ions. This indicates that the phosphorus-containing sorbent based on butadiene-styrene rubber of the DSSC brand has a limited number of active sites for sorption, and at lower concentrations almost all Cr(III) ions were sorbed. However, an increase in the initial concentration of Cr(III) ions leads to a rapid saturation of the surface of the sorbent. It has also been established that equilibrium is established at room temperature after 40 min. Experimental results have shown that a phosphorus-based sorbent based on butadiene-styrene rubber can be successfully used to extract Cr(III) ions from aqueous solutions.

Key words: removal, polymer sorbent, sorption, chromium

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INTRODUCTION

One of the main sources of water pollution is industrial production. A serious problem is the removal from the wastewater of chromium (III) and chromium (VI) ions. The most promising way to remove these pollutants is the sorption method [1].

Compared with other methods, sorption is superior in design simplicity, initial cost, ease of operation and insensitivity to toxic substances. This method uses a large number of suitable sorbents, such as activated carbon [2], inexpensive adsorbents (natural, industrial, as well as synthetic materials, wastes) [3] and polymeric materials (sorbent and resins) [4]. Adsorption on activated charcoal is one of the effective methods of wastewater treatment. However, such coals are expensive adsorbents and are produced in small amounts [1].

The aim of this work was to study the efficiency of phosphorus-containing sorbent based on butadiene-styrene rubber of the DSKK grade, used to remove Cr(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 [5, 6]. 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 solution of Cr(III), the pH of the solution, the sorbent mass, contact time and temperature.

EXPERIMENTAL

As the sorbent for studying the sorption behavior of Cr(III) ions in aqueous solution, modified butadiene-styrene rubber was used. Phosphorus-containing sorbent was synthesized on the basis of butadiene-styrene rubber using PCl_3, CCl_4, H_2SO_4 and O_2 [6]. 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.

A working solution of chromium nitrate was prepared by dissolving the sample of $Cr(NO_3)_3$ in an appropriate amount of distilled water. The pH value in the solution was established using an acetate-ammonia buffer solution.

The concentrations of $Cr(NO_3)_3$ after sorption were established using an ISP MS 7700e mass spectrometer.

Preliminary experiments began with the aim of studying the effect of the pH of the solution, sorbent mass, contact time, temperature and initial concentration of metal ions on the sorption of Cr(III) ions by a phosphorus-containing sorbent. Precisely weighed amounts of sorbent (0.05g) were placed in flasks and filled with solutions of $Cr(NO_3)_3$ with different initial concentrations. At that, the initial concentrations of the samples were changed in the range from 402.6 to 11197.5 $mg \cdot L^{-1}$. When studying the effect of sorbent mass on sorption, the sorbent mass was varied in the range from 0.01 to 0.1 g. To determine the effect of the pH of the solution, solutions of chromium (III) nitrate with a pH of 1 to 11 were used. A study of the dependence of the contact time on sorption was carried out using 0.3 g of sorbent and 0,09 l of 5094.3 $mg \cdot L^{-1}$ $Cr(NO_3)_3$ solution and changing the contact time in range from 3 to 35 min, and temperatures of 25, 35 and 50 °C. In recent experiments, the sample was taken every 3-5 min and analyzed on a mass spectrometer. The sorption capacity (SC) (mg/g) and the degree of adsorption (R) (%) were calculated using equations (1) and (2)

$$\mathrm{SC} = (\mathrm{c}_0 - \mathrm{c}_\mathrm{e})\frac{V}{\mathrm{m}} \quad (1)$$

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

where c_0 and c_e are the initial and equilibrium concentrations of Cr(III) ions in the solution, respectively ($mg \cdot L^{-1}$), V is the volume of the solution (L), and m is the sorbent mass (g).

The results showed that 5094.3 $mg \cdot L^{-1}$ $Cr(NO_3)_3$ was used as the optimum concentration for the study of the effect of pH on the sorption of Cr(III) ions, and the mass of the adsorbent was 0.05 g. Based on the results obtained, adsorption isotherms are determined.

The results were statistically processed using standard methods [7, 8]. The average error of the experiment was estimated to be less than 4%.

RESULTS AND DISCUSSION

Description of the reaction and characteristics of the phosphorus-containing polymeric sorbent

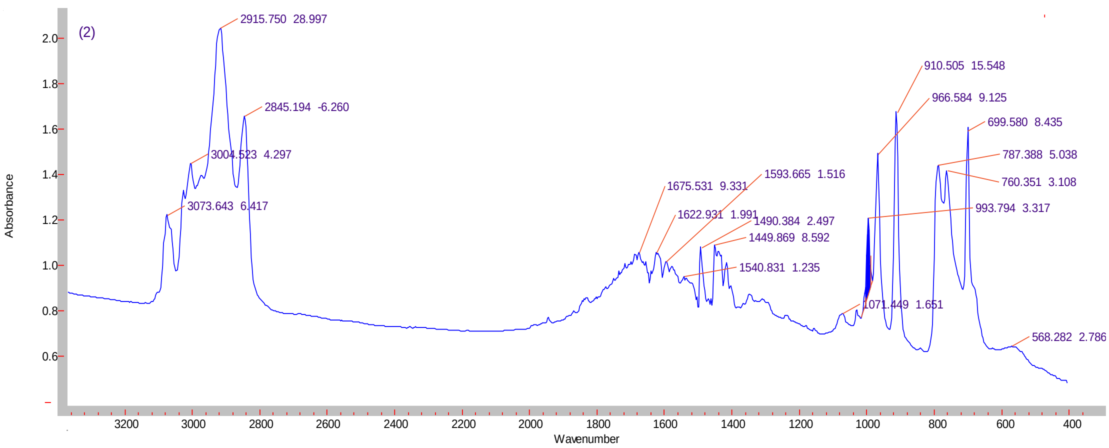
Synthesis of phosphorus-containing sorbent was described in earlier works [6]. It should be emphasized that during the polymer modification reaction, a crosslinking process occurs between macromolecular chains. As a result, we obtained cross-linked products with various functional groups, such as: $-P(O)Cl_2$ (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. Synthesized phosphorus-based sorbent based on butadiene-styrene rubber is a dark brown powder with a cross-linked structure, insoluble in organic solvents, mineral acids and alkalis [9, 10].

Fig. 1 shows the infrared spectrum of the polimer before and after modificate. In the IR spectrum of the modified the absorption bands of 1050-1030 sm^{-1} correspond to the phosphorus atom bound to the alkyl part of the polymer via oxygen. The absorption bands of 1240-1190 sm^{-1} show the attachment of phosphorus through oxygen to the aromatic part of the polymer. In polymers, the bound OH- group gives a signal in the region of 3400-3200 sm^{-1}. For solids, only one broad band is observed. The absorption band at 1720 sm^{-1} corresponds to the group -CO-O- attached to the aromatic part of the polymer, as well as to the double-bonded sites of the polymer. The first overtone *v*C=O (about 1720 sm^{-1}) also lies at 3500-3400 sm^{-1}, but is characterized by low intensity [11].

Effect of solution pH

The pH of the solution is one of the most important experimental factors, which determines the sorption selectivity during sorption on sorbents. The pH value determines the specific surface charge of the sorbent and the ionic dissociation of Cr(III) ions in the solution [12]. This physico-chemical parameter, because of its effect on the degree of protonation and the dissociation of functional groups, is very important for a phosphorus-containing polymer-based sorbent [10].

Table 1 shows the results of an investigation of the effect of the pH of the solution on the sorption of Cr(III) ions. As can be seen from Fig. 2, an increase in the pH of the solution from 1 to 6 led to an increase in the R value from 18.4 to 61.2%, and a further increase in the pH of the solution from 6 to 11 resulted in a decrease in R from 61.2 to 30%. The highest values of removal efficiency were obtained in weakly acidic solutions (pH 6). This is due to the fact that at low pH values (pH<3) the functional groups of the sorbent are protonated [10].



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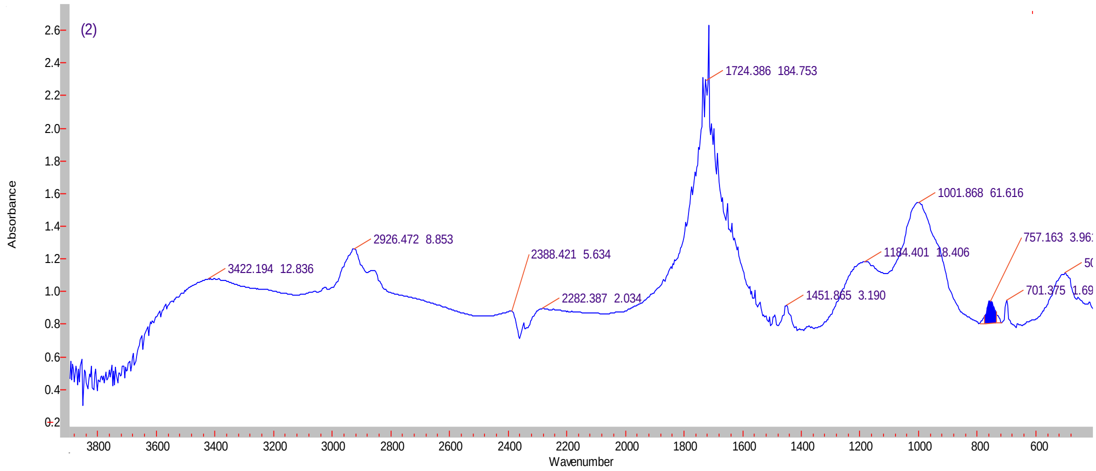

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Fig. 1. The effect of the pH of the medium on the degree of sorption of Cr(III)
Рис. 1. Влияние pH среды на степень сорбции ионов Cr(III)

Table 1

The influence of the pH of the medium on the sorption of Cr(III)
***Таблица 1*. Влияние pH среды на степень сорбции ионов Cr(III)**

pH	1	2	3	4	5	6	7	8	9	10	11
SC, $mg \cdot g^{-1}$	281	594	647	782	930	935	916	783	674	619	459
R, %	18.4	38.7	42.3	51	60.4	61.2	59.7	51.2	44	40.1	30

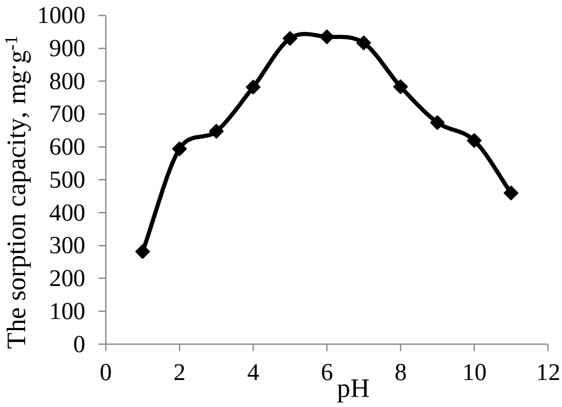

Fig. 2. Influence of the weight of phosphorus-containing sorbent on the degree of sorption of Cr(III)
Рис. 2. Влияние массы фосфорсодержащего сорбента на сорбцию ионов Cr(III)

The removal efficiency decreases at high pH values due to the abundance of OH- and/or due to ion repulsion between the negatively charged sorbent functional groups and the anionic molecules of the chromium salt.

As a result, a further initial pH of 6.0 was chosen for further sorption experiments.

Effect of sorbent mass

Table 2 and Fig. 3 show the effect of sorbent mass on the degree of sorption. As can be seen, the value of the sorption degree increased with increasing sorbent mass to 0.1 g (corresponding to 71.1% of the initial amount of Cr(III) ions sorbed on the phosphorus-containing sorbent). The increase in the degree of sorption can be associated with an increase in the number of active functional groups associated with the presence of a large sorption surface.

Table 2

The influence of the weight of the phosphorus-containing sorbent on the sorption of Cr(III)
***Таблица 2.* Влияние массы фосфорсодержащего сорбента на сорбцию ионов Cr(III)**

The weight of sorbent, g	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1
SC, $mg \cdot g^{-1}$	3234	1895	1373	1097	935	827	755	669	601	544
R, %	42.3	49.6	53.9	57.4	61.2	64.9	69.2	70	70.8	71.1

Table 3

Effect of the initial concentration of Cr(III) ions on sorption
***Таблица 3.* Влияние начальной концентрации ионов Cr(III) на сорбцию**

C_0, $mg \cdot L^{-1}$	402.6	2459.4	5094.3	7159.6	9856.3	11197.5
SC, $mg \cdot g^{-1}$	12	171	935	948	980	990
R, %	9.6	23.2	61.2	44.1	33.1	29.5

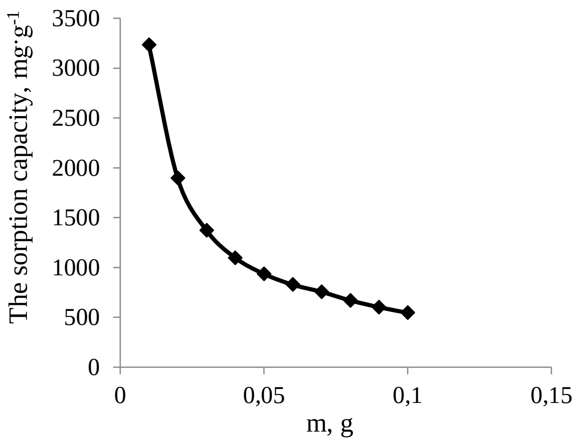

Fig. 3. Influence of the initial concentration of Cr(III) ions on the sorption capacity
Рис. 3. Влияние начальной концентрации ионов Cr(III) на степень сорбции

The effect of the initial concentration of Cr(III)

The initial concentration of sorbates is the main factor in sorption processes, since it affects the ion distribution between the solid and liquid phases [13, 14]. The result of this study is shown in Table 3 and is shown in Fig. 4.

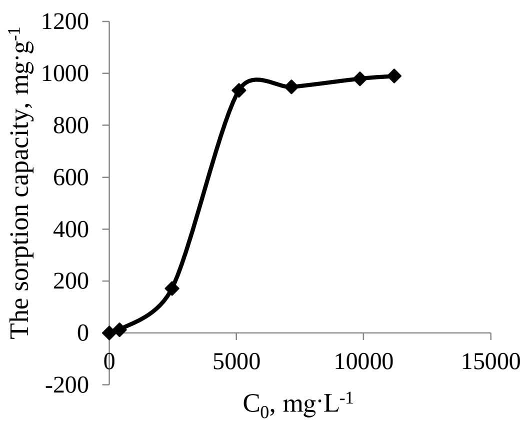

Fig. 4. Effect of contact time and temperature on the sorption capacity
Рис. 4. Влияние времени контакта и температуры на сорбционную емкость

The degree of sorption increases with an increase in the initial concentration to 5094.3 $mg \cdot L^{-1}$ and reaches a maximum value (R = 61.2%). In this concentration range, the adsorbate molecules can interact with the active sites of the sorbent, and therefore the degree of sorption was relatively high. A further increase in the initial concentration of Cr(III) ions leads to a decrease in the degree of sorption. This indicates that the phosphorus-containing sorbent has a limited number of active sites for sorption, and at lower concentrations, almost all Cr(III) ions are sorbed. However, an increase in the initial concentration of Cr(III) ions leads to a rapid saturation of the surface of the sorbent [15].

The effect of contact time and temperature

Experiments have shown that the sorption of Cr(III) ions occurs rapidly in the first 5 minutes and becomes slower near equilibrium. The results of the experiment are presented in Table 4. Fig. 4 shows the effect of contact time and the effect of temperature on the sorption of Cr(III) ions.

With an increase in temperature from 25 to 50 °C, the degree of sorption increases, if equilibrium is reached at 25 °C in 40 min, then at 35 °C it is established after 25 min, and at 50 °C – after 20 min.

Table 4

The effect of contact time and temperature on the sorption of Cr(III)
***Таблица 4.* Влияние времени контакта и температуры на сорбцию ионов Cr(III)**

The contact time, t, min	25 °C		35 °C		50 °C	
	SC, $mg \cdot g^{-1}$	R, %	SC, $mg \cdot g^{-1}$	R, %	SC, $mg \cdot g^{-1}$	R, %
3	936	61.2	1064	69.6	1269	83
5	1024	67	1189	77.8	1315	86
7	1119	73.2	1200	78.5	1382	90.4
10	1181	77.3	1239	81	1392	91.1
15	1281	83.8	1308	85.6	1422	93
20	1313	86	1327	86.8	1519	99.4
25	1428	93.4	1527.8	99.9	1528	100
30	1494	97.7	1528	100		
35	1519	99.4				
40	1528	100				

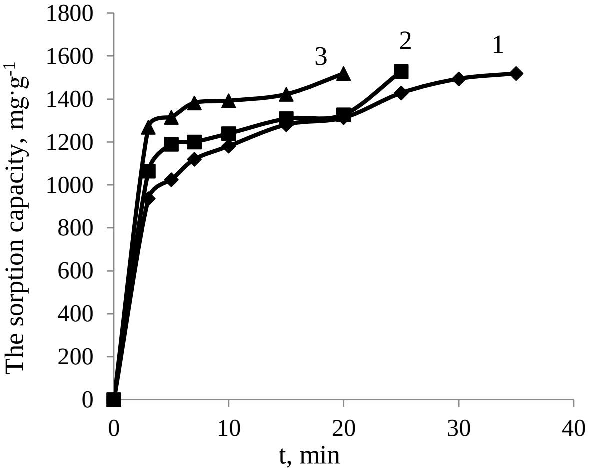

Fig. 5. Effect of contact time and temperature on the sorption capacity: 1 – 25 °C, 2 – 35 °C, 3 – 50 °C
Рис. 5. Влияние времени контакта и температуры на сорбционную емкость: 1 – 25 °C, 2 – 35 °C, 3 – 50 °C

This result can be associated with an increase in the mobility of Cr(III) ions and an increase in the number of active sites on the surface of the sorbent [16]. On the other hand, in nature, the sorption of Cr(III) ions on a phosphorus-containing sorbent is an endothermic process and can include chemical sorption. The endothermic nature of the sorption of pollutants has also been reported in other studies of our scientists, namely: the sorption of Pb^{+2} on a cellulose-based sorbent, the adsorption of Pb^{+2} on phosphate-modified kaolinite clay, the sorption of Cu^{+2} on a wood fern and the adsorption of a water-soluble dye on a functionalized resin [17-20].

CONCLUSION

In this study, the sorption capacity of a phosphorus-containing sorbent synthesized by oxidative chlorophosphorylation of butadiene-styrene rubber followed by hydrolysis with respect to Cr(III) ions was studied by determining the effect of various parameters such as the pH of the solution, the initial concentration of the $Cr(NO_3)_3$ salt, mass of sorbent, contact time of phases and temperature. Experimental results have shown that a phosphorus-based sorbent based on butadiene-styrene rubber can be successfully used to extract Cr(III) ions from aqueous solutions.

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