UOT 541.183

REMOVAL OF Fe(III) IONS USING PHOSPHORUS-CONTAINING SORBENT ON THE BASIS OF BUTADIENE-STYRENE RUBBER**E.S.Karimova, A.A.Azizov, R.M.Alosmanov***Baku State University**afinabdu@rambler.ru*

Received 28.02.2019

Phosphorus-containing polymeric sorbent on the basis butadiene–styrene rubber was used to remove Fe(III) ions 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, contact time, and temperature.

Keywords: removal, polymer sorbent, sorption, iron.

Introduction

Heavy metal compounds are one of the most toxic substances. Contained in drinking water ions of heavy metals, getting into animal organisms, block enzyme systems, what leads to a sharp disruption of their life. 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. So in one of the promising methods of water purification from copper(II) ions is ion exchange [1]. For the purification of chromium-containing effluents, technologies using high-efficiency redox sorbent of iron(II) hydroxide are used [2]. Among heavy metals in drinking water, iron is usually at its maximum concentrations, which has both natural and man-made sources. The most common methods of deironing today are cleaning methods using sand and anthracite backfill. However, these fillings do not provide the required level of water purification, and dangerous to human health toxic aromatic organic compounds can be released from the anthracite backfill. In addition, filters with sand and anthracite backfill are quite cumbersome because of the low absorptive capacity of the fillers [3].

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) [4] and polymeric materials (sorbent and resins) [3].

The aim of this work was to study the effectiveness of phosphorus-containing sorbent based on butadiene-styrene rubber, used to remove 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 [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 Fe(III) solution, the pH of the solution, the sorbent mass, contact time and temperature.

Experimental part

The modified butadiene–styrene rubber was used as the sorbent for studying the sorption behavior of Fe(III) ions in aqueous solution. 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.

The ferric chloride working solution was prepared by dissolving the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 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 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ after sorption were 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 Fe(III) ions by a phosphorus-containing sorbent. Precisely weighed amount of sorbent (0.05 g) was placed in flasks and filled with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solutions of different initial concentrations. In this case, the initial concentrations of the samples were changed in the range from $0.9 \cdot 10^{-3}$ to $2.6 \cdot 10^{-3} \text{M}$. 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 iron(III) chloride 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 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution with $1.5 \cdot 10^{-3} \text{M}$ concentration and changing the contact time in a range from 3 to 65 min, and temperatures of 25, 35 and 50°C . In recent experiments, the sample was taken every 3–5 min and analyzed on a spectrophotometer. The sorption capacity (SC, mg/g) and the degree of adsorption (%) were calculated using equations (1) and (2)

$$\text{SC} = (C_0 - C_e) \frac{V}{m}, \quad (1)$$

$$R = \frac{100(C_0 - C_e)}{C_0}, \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations of Fe(III) ions in the solution, respectively (mg/ml), V is the volume of the solution (ml), and m is the sorbent mass (g).

The results showed that $1.5 \cdot 10^{-3} \text{M}$ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 0.05 g adsorbent was used as the optimal concentration for studying the effect of pH on the sorption of Fe(III) ions. 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, cross-linked products with various functional groups, such as: $-\text{P}(\text{O})\text{Cl}_2$ (phosphonium dichloride) and $-\text{OP}(\text{O})\text{Cl}_2$ (phosphorus dichloride), which were converted by the hydrolysis reaction to phosphonate ($-\text{P}(\text{O})(\text{OH})_2$) and phosphate ($-\text{OP}(\text{O})(\text{OH})_2$) groups, respectively. The synthesized phosphorus-containing sorbent on the basis of butadiene-styrene rubber is a dark brown powder with a cross-linked structure, insoluble in organic solvents, mineral acids and alkalis [9, 10].

UV-spectroscopy

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

Fig. 1. UV-spectra of the phosphorus-containing polymeric sorbent on the basis of butadiene-styrene rubber: *a* – before and *b* – after adsorption of iron.

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 Fe(III) ions in the solution [11]. 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 sorbent on the basis of polymer [10].

Table 1 shows the results of investigating the effect of the solution pH on the sorption of Fe(III) ions.

Table 1. The influence of the medium pH on the sorption of Fe(III) ions

pH	1	2	3	4	5	6	7	8	9	10	11
SC, mg/g	1.8	2.4	3.3	5.4	7	7.2	5.4	4.5	2.7	2.1	1.5
R, %	23	31	43	69	89	90.7	71	63.7	34.7	26.6	19

As can be seen from Figure 2, an increase in the pH of the solution from 1 to 6 led to an increase in the R value from 23 to 90.7%, and a further increase in the pH of the solution from 6 to 11 resulted in a decrease in R from 90.7 to 19%.

Fig. 2. The effect of the pH of the medium on the sorption of Fe(III) ions.

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].

Table 2. Influence of the weight of the phosphorus-containing sorbent on the sorption of Fe(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/g	1.8	3	5.2	6	7.2	7.8	8	8	8	8
R, %	23.3	53.3	64.7	80.7	90.7	96	100	100	100	100

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

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

Effect of sorbent mass

Table 2 and Figure 3 show the effect of sorbent weight on the sorption capacity.

Fig. 3. Influence of the weight of phosphorus-containing sorbent on the sorption of Fe(III) ions.

As can be seen, the value of the degree increases with increasing of sorbent mass to 0.06 g (corresponding to 96% of the initial amount of Fe(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.

The effect of the initial concentration of Fe(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 [12, 13]. The result of this study is shown in Table 3 and is shown in Figure 4.

The maximum value of the sorption degree is observed at a concentration $1.5 \cdot 10^{-3}$ M (90.7%). The degree of sorption decreases with increasing initial concentration of Fe(III) ions.

This indicates that the phosphorus-containing sorbent has a limited number of active sites for sorption, and at lower concentrations, almost all Fe(III) ions are sorbed. However, an increase in the initial concentration of Fe(III) ions leads to a rapid saturation of the sorbent surface.

The effect of contact time

Experiments have shown that the sorption of Fe(III) ions occurs rapidly in the first 8 minutes and becomes slower near equilibrium.

The results of the experiment are presented in Table 4. Figure 5 shows the effect of the contact time on the sorption of Fe(III) ions.

The effect of temperature

With an increase in temperature from 25 to 50°C, the degree of sorption increases if, at 25°C, equilibrium is reached after 70 minutes, then at 35°C it is established after 65 min, and at 50°C – after 55 minutes. This can be seen from the Table 5 and Figure 6.

Table 3. Effect of initial concentration of Fe(III) ions on the sorption

C_0 , M	$0.9 \cdot 10^{-3}$	$1.1 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	$2.2 \cdot 10^{-3}$	$2.6 \cdot 10^{-3}$
SC, mg/g	1.2	2.1	7.2	6.8	4.7	3.8
R, %	22.2	36.4	90.7	76.5	41	26.9

Table 4. Effect of contact time on the sorption of Fe(III) ions

The contact time, t , min	3	8	15	20	25	30	35	40	45	50	55	60	65
SC, mg/g	2.1	3	3.6	3.9	4.2	4.5	4.8	5.3	5.7	6	6.3	6.9	7.8
R, %	27.3	42.7	46.7	48.7	53.3	56	60	66.7	71.3	75.3	78.7	86.7	96

Fig. 4. Influence of the initial concentration of Fe(III) ions on the sorption.

Fig. 5. The effect of contact time on the sorption of Fe(III) ions.

Table 5. The effect of temperature on the sorption of Fe(III) ions

The contact time, t , min	25°C		35°C		50°C	
	SC, mg/g	R, %	SC, mg/g	R, %	SC, mg/g	R, %
5	2.1	27.3	2.4	31.3	5.4	65.3
10	3	42.7	3	48.7	5.7	73.3
15	3.6	46.7	3.9	50	6	77.3
20	3.9	48.7	4.2	52	6.3	78.7
25	4.2	53.3	4.5	56	6.5	80.7
30	4.5	56	4.8	62	6.6	82
35	4.8	60	5.1	62	6.7	82.7
40	5.3	66.7	5.7	71.3	6.9	84.7
45	5.7	71.3	6	77.3	7.5	92.7
50	6	75.3	6.9	84.7	7.8	98
55	6.3	78.7	7.5	92.7	8	100
60	6.9	86.7	7.8	98		
65	7.8	96	8	100		
70	8	100				

Fig. 6. Effect of temperature on the sorption of Fe(III) ions.

This result can be associated with an increase in the mobility of Fe(III) ions and an increase in the number of active sites on the surface of the sorbent. On the other hand, in nature, sorption of Fe(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 [14–16].

Adsorption isotherms

Adsorption isotherms define the equilibrium relationship between adsorbent and adsorbate. In other words, the adsorption isotherms serve to describe how the adsorbed molecules interact with adsorbents when the process approaches equilibrium. The results obtained in this study were analyzed using the Langmuir, Freundlich and Dubinin-Radushkevich isotherm equations.

Langmuir isotherm

The Langmuir model is used to determine the homogeneity of the adsorption process. According to this model, the adsorbent's surface is homogeneous, each active site on the adsorbent's surface has the ability to sorb only one adsorbate molecule, and there is no interaction between the adsorbed molecules. In addition, in terms of energy, the active sites are equivalent to each other. The linear Langmuir isotherm equation is [17]:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}}, \quad (3)$$

where C_e is the concentration of the iron remaining in the solution at equilibrium (mg/L) and q_e is the amount of iron adsorbed at equilibrium (mg/g). The $q_{\max}$ constant is the adsorbent's maximum monolayer adsorption capacity (mg/g) and K_L is the adsorption constant (L/mg) and is related to the free energy of adsorption.

Linear plots of C_e/q_e versus C_e showed that the iron adsorption on the phosphorus-containing sorbent followed the Langmuir isotherm. The values of the $q_{\max}$ and K_L were calculated from the slope and intercept of the plot, respectively.

The Langmuir isotherm's essential characteristics may be described through R_L , a dimensionless constant separation factor or equilibrium parameter. R_L may be represented as [18]:

$$R_L = \frac{1}{1 + K_L C_0}, \quad (4)$$

where K_L (L/mg⁻¹) refers to the Langmuir constant and C_0 is the adsorbate's initial concentration (mg/L⁻¹). The R_L value indicates the adsorption nature to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

Freundlich isotherm

The Freundlich isotherm model involves heterogeneous surface adsorption sites that have different adsorption energies and provides no information about the monolayer adsorption

capacity. The linear form of the Freundlich isotherm model equation is [19]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e, \quad (5)$$

where K_F (mg/g) and n are the Freundlich isotherm constants related to adsorption capacity and adsorption intensity, respectively. The value of $1/n$ is the degree of heterogeneity of phosphorus-containing sorbent. The linear plots of $\ln q_e$ versus $\ln C_e$ show that the adsorption of iron on phosphorus-containing sorbent follows the Freundlich isotherm. The values of Freundlich constants, that is, K_F and $1/n$, were calculated from the intercept and slope of the linear plot, respectively.

Dublin-Radushkevich isotherm

The Dublin-Radushkevich (D-R) isotherm was selected to assess the adsorbent's porosity. The linear form of the D-R isotherm equation is [20]:

$$\ln q_e = \ln q_s - K_{D-R} \varepsilon^2, \quad (6)$$

where q_s is the theoretical saturation capacity (mg/g), K_{D-R} is the D-R isotherm constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2/kJ^2), and ε is the Polanyi potential that is related to the equilibrium concentration as follows:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right), \quad (7)$$

where R ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$) is the gas constant and T (K) is the absolute temperature. The linear plots of $\ln q_e$ versus ε^2 show that the adsorption of iron on the sorbent follows the D-R isotherm (plot not shown). The values of q_s and K_{D-R} were calculated from the intercept and slope using linear regression.

The obtained different isotherm parameters are shown in Table 6.

Table 6. Langmuir, Freundlich and Dubinin-Radushkevich isotherm parameters for the adsorption of iron on the phosphorus-containing polymeric sorbent on the basis of butadiene-styrene rubber

Langmuir			
Maximum adsorption capacity ($q_{\max}$, mg/g)	Langmuir adsorption constant (K_L , L/mg ⁻¹)	Separation factor (R_L)	Correlation coefficient (r^2)
2.34	0.26	0–1	0.826
Freundlich			
Freundlich isotherm constant (K_F , mg/g)	Degree of heterogeneity (1/n)	Correlation coefficient (r^2)	
10.7	–0.3856	0.6534	
Dubinin-Radushkevich			
Theoretical saturation capacity (q_s , mg/g)	Dubinin-Radushkevich isotherm constant (K_{D-R} , mol ² /kJ ⁻²)	Correlation coefficient (r^2)	
4.4	3·10 ⁻⁷	0.902	

Conclusions

In the present study the sorption capacity of the phosphorus-containing sorbent synthesized by oxidative chlorophosphorylation of butadiene-styrene rubber followed by hydrolysis with respect to Fe(III) ions was studied, determining the influence of various parameters such as the pH of the solution, the initial concentration of the salt $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 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 Fe(III) ions from aqueous solutions.

References

1. Tataeva S.D., Akhmedov S.A., Gamzaeva U.G. Sorbtciia medi(II) na anionitakh s immobilizovannoi formazanovoi gruppirovkoi // Sorbtionnye i khromatograficheskie protsessy. 2005. T. 5. Vyp. 5. S. 696–703.
2. Demirbas A. Agricultural based activated carbons for the removal of dyes from aqueous solutions // J. Hazard. Mater. 2009. V. 167. P. 1–9.
3. Gupta V., Suhas K. Application of low-cost adsorbents for dye removal // Journal of Environ. Managem. 2009. V. 90. P. 2313–2342.
4. Panić V., Šešlija S.I., Nešić A.R. Adsorption of azo dyes on polymer materials // Hem. Ind. 2013. V. 67. P. 881–899.

5. Magerramov A.M., Alosmanov R.M., Melikova A.Ia. Fosfokhlorigovanie polibutadiena fosfor(III)khloridom v prisutstvii kisloroda // *Izv. vuzov. Himiia i him. tekhnologiya*. 2003. T. 46. № 6. С. 25–27.
6. Pat. № 0108. Az. R. Fəza quruluşlu polibutadien fosfon turşusunun [2,3-dimetil-1-fenil-5-pirazalon] monoimidi uran (VI)-nın sorbenti kimi / Əzizov A., Rəhimov R., Alosmanov R. 2003
7. Harris D.C. Quantitative Chemical Analysis. New York: W.H. Free man. 2007. P. 51–64.
8. Pollard J.H., Handbook of Numerical and Statistical Techniques. Cambridge University Press, Cambridge. 1977. P. 374.
9. Alosmanov R.M., Azizov A.A., Magerramov A.M. IAMR-spektroskopicheskoe issledovanie fosforsoderzhashchego polimernogo sorbenta // *Rossiiskii Zhurn. obshch. himii*. 2011. T. 81. № 7. С. 23–24.
10. Alosmanov R.M., Azizov A.A., Maharramov A.M. acid base sorption properties of phosphorus containing polymeric sorbent // *Mater. Res. Innovations*. 2010. V. 14. No 5. P. 414–418.
11. Saladadze K.M., Kopilova-Valova V.D. Kompleksnye ionnye teploobmenniki. M: Nauka, 1980. С. 336.
12. Ramazanov A.Sh., Esmail G.K. Sorbtionnoe koncentrirovaniye ionov medi, tsinka, kadmiia i svintsa iz vodny`kh rastvorov prirodnoi glinoi // *Vest. Dagestanskogo gos. Un.* 2014. Vyp. 1. С. 179–183.
13. Eremin O.V., E`pova E.S., Rusal` O.S. Sorbtciia ionov tsinka iz vodnykh rastvorov prirodnym clinoptilovlitovym tufom // *Uspehi sovremennogo estestvoznaniia*. 2015. № 10. С. 86–91.
14. Ho Y.S., Wase D.A., Forster C.F. Removal of lead ions from aqueous solution using sphagnum moss peat as adsorbent // *Water SA*. 1996. V. 22. P. 219–224.
15. Unuabonah E.I., Adebawale K.O. Kinetic and thermodynamic studies of the adsorption of lead(II) ions onto phosphate-modified kaolinite clay // *J. Hazard. Mater.* 2007. V. 144. P. 386–395.
16. Ho Y.S., Huang C.T., Huang H.W. Equilibrium sorption isotherm for metal ions on tree fern // *Process Biochem*. 2002. V. 37. P. 1421–1430.
17. Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum // *Journal of the American Chemical Society*. 1918. P. 1361.
18. Hall K.R., L.C.Eagleton, A.Acrivos and T.Vermeulen. Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions // *Instrumental&Engineering Chemistry Fundamentals*. 1996. P. 212.
19. Freundlich H.M.F. Über die adsorption in lösungen Z. // *Phys. Chemi*. 1906. P. 385–470.
20. Dublin M.M., Radushkevich L.V. Equation of the characteristic curve of activated charcoal // *Proceeding of the Union of Soviet Socialist Republics Academy of Sciences of the USSR. Phys. Chem. Section*. 1947. V. 55. P. 331–337.

Fe(III) İONLARIN ÇIXARILMASI MƏQSƏDİ İLƏ BUTADİEN–STİROL KAUCUK ƏSASINDA FOSFORTƏRKİBLİ SORBENTİN İSTİFADƏSİ

E.S.Kərimova, A.Ə.Əzizov, R.M.Alosmanov

Fe(III) ionlarını sudan çıxarmaq üçün butadien-stirol kauçukun əsasında fosfortərkibli sorbent istifadə edilmişdir. Sorbsiyanın məhlulun pH göstəricisindən, metal ionlarının ilkin konsentrasiyasından, sorbent kütləsindən, faza təmas vaxtından və temperaturdan asılılığının öyrənilməsi məqsədi ilə tədqiqatlar aparılıb.

Açar sözlər: çıxarmaq, polimer sorbenti, sorbsiya, dəmir.

УДАЛЕНИЕ ИОНОВ Fe(III) С ИСПОЛЬЗОВАНИЕМ ФОСФОРСОДЕРЖАЩЕГО СОРБЕНТА НА ОСНОВЕ БУТАДИЕН–СТИРОЛЬНОГО КАУЧУКА

Э.С.Керимова, А.А.Азизов, Р.М.Алосманов

Фосфорсодержащий полимерный сорбент на основе бутадиен-стирольного каучука использовали для удаления ионов Fe(III) из воды. Проводили исследования по изучению сорбционных характеристик, определяя влияния различных параметров, таких как pH раствора, начальная концентрация ионов металла, масса сорбента, время контакта фаз и температура.

Ключевые слова: удаление, полимерный сорбент, сорбция, железо.