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ADSORPTION STUDY OF Fe(III) IONS BY MASC-2-AMINO-4-NITROPHENOL

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Adsorption of ferric(III) ions by a chelating synthetic sorbent based on the copolymer of styrene with maleic anhydride (MASC) and 2-amino-4-nitrophenol was studied. Adsorption characteristics of the sorbent with respect to Fe(III) ions have been investigated. Various parameters influencing adsorption – optimal pH, the ionic strength, the time necessary for establishing complete sorption equilibrium, the initial concentration of metal ions were studied. It was shown that the maximum adsorption capacity of the sorbent with respect to ferric ions is 373.33 mg/g at pH=5. Several adsorption isotherm and kinetic models have been explored and the most relevant to our experimental data has been revealed.

Keywords: sorption, Fe(III), chelate-forming sorbent, preconcentration.

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Introduction

Iron is found in chemical wastewater, metallurgical, machine-building, metalworking, petrochemical, textile, chemical-pharmaceutical and other industries. When the iron content is more than 1 mg/l, the water becomes brown. In connection with the growth of industrial production, there is an increase in the consumption of natural water and, as a result, an increase in generated wastewater. Insufficiently treated wastewater is the main source of pollution and clogging of natural reservoirs, lead to significant physicochemical changes in the properties and composition of water, making it unsuitable for household use. The most common toxic impurities of wastewater are heavy metals. Sources of these impurities are waters of textile, leather, electroplating, chemical and machine-building enterprises, as well as ore and mine enterprises production [1, 2].

The aim of this work is to study the sorption of Fe(III) ions from its aqueous solutions by a polymeric chelating-forming sorbent based on a copolymer of styrene with maleic anhydride and 2-amino-4-nitrophenol [3–6]. Various sorption characteristics, in particular the effect of pH, time, ionic strength, initial concentration of the metal ion, were studied. The process of desorption was also investigated and the optimum eluent was established. Several adsorption isotherm and kinetic models have been studied [7].

Experimental part

Preparation of solutions. The initial metal solution of Fe(III) ions with concentration of $5 \cdot 10^{-3}$ mol/L was prepared by using 10^{-1} M FeCl₃ solution, prepared by dissolving reduced iron in HCl and HNO₃. The equilibrium concentrations of Fe(III) ions in the solution were determined with the help of the corresponding reagent 2,2'-([1,1'-biphenyl]-4,4'-diylbis(diazene-2,1-diyl))bis(benzene-1,3,5-triol) C₁₈H₁₈O₆N₄ (R) [8]. Optical densities of the solutions were measured on KFK-2 and optimal pH=5 and $\lambda=490$ nm were established.

Buffer solutions from 1 to 5 were prepared on the basis of 0.1 N solutions of CH₃COOH and NH₃·H₂O. To study the effect of ionic strength on the sorption capacity of the sorbent, 2 mol/L KCl solution was used, as well as 2 mol/L KOH solution to study the desorption process. For the synthesis of the sorbent, a styrene maleic anhydride copolymer (Scheme 1) and 2-amino-4-nitrophenol (Scheme 2) were used.

Scheme 1. Molecular structure of a copolymer of styrene with maleic anhydride.

Scheme 2. Molecular structure of 2-amino-4-nitrophenol.

Synthesis of sorbent. Synthesis of the sorbent was carried out according to a known technique [1]. As the polymer matrix for the synthesis of the sorbent, styrene maleic anhydride copolymer and 2-amino-4-nitrophenol were used. For that purpose, 3 g of polymer were added to the round bottom flask. Subsequently, the appropriate amount of 2-amino-4-nitrophenol was weighed, dissolved in water and added to the original contents of the flask. The synthesis was carried out in the presence of formalin, as a cross-linking agent. The reaction was carried out at a temperature of 60–70°C, for 30–40 minutes. During the reaction, the following transformations were observed:

Since the process is carried out in an aqueous medium, the anhydride groups of the polymer undergo hydrolysis.

Scheme 3. The mechanism of the sorption process.

As a result of the mutual influence of formaldehyde and amine, an unstable carbonylamine is formed. The resulting carbonylamine interacts with the carboxyl groups of the macromolecule and thus the amine is introduced into the macromolecule.

At the end, the resulting synthesis product is passed through a filter paper, washed, dried, ground and used for further research.

Preconcentration. Sorption studies of Fe (III) ions were carried out at room temperature. For each experiment, 2 ml of a solution of a metal ion with a known concentration ($5 \cdot 10^{-3}$ mol/L) was added to 50 ml conical flasks. In each flask, 30 mg of sorbent and corresponding pH were added. The pH of the solutions was monitored using a pH meter Ionomer-130. The resulting mixture was kept for 24 hours. The contents of the flask were then passed through a filter paper and the liquid phase was separated from the solid phase.

Subsequently, 1 ml samples were taken from each flask, diluted with a buffer solution of pH 5, and final concentrations of Fe (III) ions were measured with the reagent 2,2'-([1,1'-bi-phenyl]-4,4'-diylbis(diazen-2,1-diyl))bis(benzene-1,3,5-triol) $C_{18}H_{18}O_6N_4$ (R) on the photoelectrocolorimeter KFK-2 at $\lambda = 490$ nm. The degree of metal ion extraction was calculated by the following formulas:

$$R_{\%} = \frac{C_0 - C_e}{C_e} 100, \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m}, \quad (2)$$

where C_0 is the initial concentration of the metal ion ($\text{mol}\cdot\text{L}^{-1}$), C_e is the equilibrium concentration of the metal ion ($\text{mol}\cdot\text{L}^{-1}$), V is the volume of the solution (L), and m is the sorbent mass (mg).

The desorption process. Desorption studies were carried out using different inorganic acids of the same concentration, namely: $0.5 \text{ mol}\cdot\text{L}^{-1}$ solutions of HNO_3 , HCl , H_2SO_4 and CH_3COOH acids. To carry out the experiment, 30 mg of sorbent were weighed into 4 flasks, 2 ml of a $5\cdot 10^{-3} \text{ mol/L Fe (III)}$ solution and 18 ml of pH 5.0 were added and left for 24 hours. Subsequently, the solid portion of the solution was separated from the liquid by filtration. To the filtered portion was added 20 ml of 0.5 mol/L solutions of HNO_3 , HCl , H_2SO_4 and CH_3COOH acids.

Tightly closed and left for 24 hours. At the end of the day, the liquid portion of the solution was again separated from the solid. 1 ml was then taken from the homogeneous solution, 1-2 ml of a 2 mol/L solution of KOH was added, diluted with a buffer solution of pH 5.0, and final concentrations of Fe (III) ions were determined with (R) on KFK-2 [2].

Equipment. Absorbances of solutions were measured on photoelectrocalorimeter KFK-2 in a cuvette with a layer thickness $l = 1$. pH values measured on the pH meter IonomerI-130. The IR spectrum of the sorbent was taken on a Varian 3600 Fourier spectrometer in the region from 400 to 4000 cm^{-1} .

Results and discussions

Sorbent structure. The result of stud-

ying the structure of the sorbent is shown in Figure 1.

As can be seen from Figure 1, the following functional groups are present in the structure of the sorbent. The vibrational frequencies are observed in IR spectra of sorbent: at $3600\text{--}3100 \text{ cm}^{-1}$ [valence oscillations of the --OH group in the carboxyl group, the covalent vibrations of the group --NH ($3400\text{--}3200 \text{ cm}^{-1}$)], $1780\text{--}1750 \text{ cm}^{-1}$ (valence oscillations of the C=O group of the carboxyl group), $1570\text{--}1540 \text{ cm}^{-1}$ (the valence oscillations of the C--N group and the deformation vibrations of the N--H group), $725\text{--}675 \text{ cm}^{-1}$ (deformation vibrations of the C--C group in the benzene ring)

Effect of pH on the degree of Fe(III) extraction. One of the most important parameters that affect the degree of sorption is pH, so studying the effect of this parameter is an important task. For this purpose, 30 mg of sorbent was weighed and added to the flask. Further, 2 ml of a $5\cdot 10^{-3} \text{ mol/L}$ metal ion solution and 18 ml of an appropriate pH of 1 to 5 were added. The contents of the flask were stored for 24 hours.

After a day, the solid portion of the solution was separated from the liquid and the optical densities of the homogeneous solutions were measured on a KFK-2 photoelectrocalorimeter with a buffer solution pH 5.0 at a wavelength 490 nm . The results of the studies showed that the greatest metal recovery is observed at a pH value 5.0. Further sorption experiments were carried out at a given pH value 5.0. A graphic representation of the data is shown in Figure 2.

Fig.1. IR spectra of adsorbent.

Fig. 2. Effect of pH on adsorption capacity
 $m_{\text{sorb.}}=30 \text{ mg}$, $V_{\text{gen.}}=20 \text{ ml}$, $C_{\text{Me}}=5 \cdot 10^{-3} \text{ mol/L}^{-1}$.

The influence of time on the degree of the metal ion extraction. The effect of time on the sorption capacity of the Fe(III) metal ion is shown in Figure 3. In order to study this parameter, measurements were made in the range from 0 to 270 min. The equilibrium concentrations of metal ions in the sample were determined at the appropriate time intervals on KFK-2 and $\lambda = 490 \text{ nm}$.

Fig.3. Effect of time on adsorption capacity
 $m_{\text{sorb.}}=30 \text{ mg}$, $V_{\text{gen.}}=20 \text{ ml}$, $C_{\text{Me}}=5 \cdot 10^{-3} \text{ mol/L}^{-1}$.

As can be seen from Figure 3, in the period from 0 to 120 min, the degree of sorption gradually increases, and from 150 min remains constant. This indicates to the attainment of complete sorption equilibrium.

Effect of ionic strength on the sorption capacity of the sorbent. In the course of this work, the influence of ionic strength on the degree of the Fe(III) ion extraction was investigated. For these purposes, 2 mol/L potassium chloride KCl solution was used.

Studies have shown that within the range of $\mu = (0.2-1.4) \text{ mol/L}$, the presence of K^+ and

Cl^- ions has a negligible effect on the extraction of metal ion and practically does not affect the adsorption capacity of the adsorbent.

Effect of the initial concentration of Fe(III) ions on the adsorption capacity. In the course of the experiment, the effect of the initial metal ion concentration on the degree of adsorption by the synthesized sorbent was studied. For this purpose, the concentration range of Fe (III) ions was used from $0.1 \cdot 10^{-3} \text{ mol/L}$ to $6 \cdot 10^{-3} \text{ mol/L}$. For this, 30 mg of sorbent were weighed, the corresponding volumes of the metal ion solution and pH 5.0 were added. After 150 minutes, the optical densities of the homogeneous solutions on KFK-2 were measured with a buffer solution pH 5.0 at $\lambda = 490 \text{ nm}$. The degree of extraction of the metal ion by the adsorbent was calculated using the well-known formula (1). The results are graphically depicted in Figure 4 and Table 1.

Fig.4. Effect of initial metal ion concentration on the adsorption capacity. $m_{\text{sorb.}}=30 \text{ mg}$, $V_{\text{gen.}}=20 \text{ ml}$, $C_{\text{Me}}=5 \cdot 10^{-3} \text{ mol/L}^{-1}$.

Table 1. Extraction degree of Fe(III) ions by a synthesized sorbent

$C_{\text{Me}}, \times 10^{-3} \text{ mol/L}$	0.1	0.2	0.4	0.8	1	2	4	6
R, %	42	58	69	75	82	85	95	93

The results of the studies showed that the greatest sorption capacity is observed at a Fe(III) concentration of $4 \cdot 10^{-3} \text{ mol/L}$.

The desorption process. This work also involves studying the reverse process-desorption. The presence of the necessary eluents for

desorbing the metal ion is an important task. In our article, this process is carried out by using different inorganic acids with the same concentration, in particular 0.5 mol/L solutions of HNO_3 , HCl , H_2SO_4 and CH_3COOH acids. The results of the studies have shown that maximum desorption ability over Fe(III) ions shows 0.5 mol/L solution of HNO_3 .

Langmuir isotherm

Langmuir model can be described using the following equation [Langmuir 1918]

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

where C_e (mmol/L) is concentration of adsorbate in the aqueous phase at equilibrium, q_e (mmol/g) is the equilibrium adsorption capacity, q_m is equal to q_e for the complete monolayer and K_L ($\text{L}/\text{mmol}^{-1}$) is the Langmuir isotherm constant.

Linear plot of dependence of $1/q_e$ versus $1/C_e$ is shown in Figure 5. The values of the q_{max} and K_L were calculated from the slope and the intercept of the plot, respectively.

Fig.5. Langmuir isotherm model.

The essential characteristic of the Langmuir isotherm can be represented by a separation factor called equilibrium parameter (R_L) and has the following form:

$$R = \frac{1}{1 + bC_0}, \quad (4)$$

where b is the Langmuir constant (L/mmol), C_0 is the initial concentration of adsorbate (mmol/L). The value R_L indicates the isotherm type. A value between 0 and 1 shows favorable adsorption process.

Results show that R_L lies between 0 and 1 and is equal to 0.99, which shows that adsorption is favorable under the specified experimental conditions by Langmuir model. Also the value of the coefficient of regression $R^2=0.9382$ indicates that isotherm model fits good with experimental adsorption data.

Freundlich isotherm

The Freundlich model is described by the following equation [Freundlich 1906]

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

where C_e (mmol/L) is adsorbate concentration at equilibrium, q_e (mmol/g) is the equilibrium adsorption capacity, K_F is the Freundlich constant and $1/n$ the heterogeneity factor.

The plot of dependence of $\ln q_e$ versus $\ln C_e$ is shown in Figure 6. The values of K_F and $1/n$ were calculated from the slope and intercept of the plot, respectively.

Fig.6. Freundlich isotherm model.

K_F indicates capacity of adsorption process (mg/g), n provides an approximation of adsorption intensity. A favourable adsorption is estimated when the value of n is 1–10. Results show that the value of n is equal to 1.66 for, which indicates favorable adsorption process. On the other hand $1/n$ is considered as a function of adsorption strength. If value of $1/n$ is lower than 1 it means a normal adsorption, if $1/n > 1$ it shows cooperative adsorption. In our case $1/n = 0.602$, which indicates to normal adsorption process.

Dubinin-Radushkevich isotherm

The Dubinin–Radushkevich (D-R) model is used to explain adsorbent's porosity. The iso-

therm is obtained on the basis of the following equation [Dubinin 1947]

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

where q_s is the theoretical saturation capacity (mmol/g), k_{D-R} is the D-R isotherm constant related to the free energy of adsorption, and ε is 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 ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) is the gas constant and T (300 K) is the absolute temperature.

Adsorption energy was calculated by the following equation:

$$E = \frac{1}{\sqrt{2k_{D-R}}}, \quad (8)$$

Linear plots of $\ln q_e$ versus ε^2 are given in Figure 7. The values of q_s and k_{D-R} are calculated from the intercept and slope.

The value of R^2 is equal to 0.8829. E is equal to 3.5 kJ/mol. If E lies between 8 and 16 kJ/mol then it shows chemisorptions process, while the value of E lower than 8 kJ mol⁻¹ means physical adsorption process. So in our case 3.5 kJ/mol value of E means that physical adsorption process is observed between S and Fe(III).

Pseudo-first-order model

The adsorption kinetic data in this model is rated using pseudo-first-order equation (Lagergren's equation). It helps to evaluate the adsorption degree by adsorption capacity. The equation is as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \quad (9)$$

where q_e and q_t are adsorption capacities at equilibrium and time t (min), respectively ($\text{mg} \cdot \text{g}^{-1}$) and k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}).

The plot of dependence of $\ln(q_e - q_t)$ versus t is shown in Figure 8.

Fig.7. Dubinin-Raduskhevich isotherm model.

Fig.8. Pseudo-first-order kinetic model.

Table 2. Langmuir, Freundlich and Dubinin-Raduskhevich isotherm parameters

Adsorbent	Langmuir				Freundlich			Dubinin- Raduskhevich			
	($q_{\max}$, $\text{mg} \cdot \text{g}^{-1}$)	(K_L , $\text{L} \cdot \text{mg}^{-1}$)	(R_L)	(R^2)	(K_F , $\text{mg} \cdot \text{g}^{-1}$)	($1/n$)	(R^2)	(q_s , $\text{mg} \cdot \text{g}^{-1}$)	(E , $\text{kJ} \cdot \text{mol}^{-1}$)	(k_{D-R} , $\text{mol}^2 \cdot \text{kJ}^{-2}$)	(R^2)
S	13.44	24.08	0.99	0.93	0.35	0.60	0.75	384.25	3.5	$4 \cdot 10^{-8}$	0.88

Values of k_1 and q_e were calculated from slope and intercept of the plot of $\ln(q_e - q_t)$ versus t . The large difference between the experiment q_e value $q_{e(\text{exp})}$ and the calculated q_e value $q_{e(\text{cal})}$ shows that pseudo-first order kinetic model was poor fit for the adsorption process of sorbent S for Fe(III).

Pseudo-second-order model

Adsorption kinetics can also be explained by using pseudo-second-order model. For that purpose the following equation is used:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

where k_2 is the rate constant of pseudo-second-order adsorption ($\text{g/mg} \cdot \text{min}^{-1}$) and $k q_e^2$ is the initial adsorption rate ($\text{mg/g} \cdot \text{min}^{-1}$).

The plot of dependence of t/q_t versus t is shown in Figure 9.

Fig.9. Pseudo-second-order kinetic model.

Values of k_2 and q_e were evaluated from the intercept and slope of the plot of t/q_t versus t . For pseudo-second order kinetic model we can see that the experiment q_e value $q_{e(\text{exp})}$ and the calculated q_e value $q_{e(\text{cal})}$ are close to each other, so that adsorption process of synthesized sorbent S for Fe(III) can be well described by the pseudo-second order kinetic model.

Results of kinetic studies are shown in Table 3.

Table 3. Adsorption kinetic parameters

Adsorbent	Pseudo-first-order				Pseudo-second-order		
	$q_e(\text{exp})$, mg/g	k_1 , (min^{-1})	$q_e(\text{cal})$, mg/g	(R^2)	k_2 , ($\text{g/mg} \cdot \text{min}^{-1}$)	$q_e(\text{cal})$, mg/g	(R^2)
S	373.33	0.0106	20.16	0.8514	1.36	435	1

Conclusion

The results of the investigations are quite high, in particular, when studying the effect of the initial concentration of metal ions on the sorption capacity of the sorbent, the maximum sorption capacity of the sorbent is 373.33 mg/g. The foregoing allows us to assume the possibility of using the synthesized sorbent, based on a copolymer of styrene with maleic anhydride and m-aminophenol, for extracting Fe (III) ions from various natural and industrial objects.

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References

1. Akperov O.G., Akperov E.O. Praktikum po vysokomolekuliarnoi himii. Baku, 2002. 231 s.
2. Alieva A.F., Eyyubova E.J., Huseynov F.E., Shamilov N.T., Chiragov F.M.. Adsorption study of some sorbents based on maleic anhydride styrene copolymer and sulfodimezine and triazine as linkable amines. New materials, compounds and applications. 2017. V. 1. No 1. P. 27–35
3. Bulatov M.I., Kalikin I.P. Praktikum po fotometricheskomu i spektrofotometricheskim metodam analiza. L.: Himiia, 1972. 407 s.
4. Jun D., Ren F.L., Tao Ch.Y. Adsorption Behavior of Fe(II) and Fe(III) Ions on Thiourea Cross-Linked Chitosan with Fe(III) as Template. Molecules. 2012. V. 17. P. 4388–4399.
5. Mostafa M.H.Kh., Al-Wakeel K.Z., Abd El Rehim S.S., Abd El Monem H. Adsorption of Fe(III) from Aqueous Medium onto Glycine-Modified Chitosan Resin: Equilibrium and Kinetic Studies. J. Dispersion Sci. Technology. 2014. V. 35. No 12. P. 1691–1698.

6. Oztaş N.A., Karabakan A., Topal Ö. Removal of Fe(III) ion from aqueous solution by adsorption on raw and treated clinoptilolite samples. Microporous and Mesoporous Materials, 2008. V. 111. No 1. P. 200–205
7. Purnaratne A.R.F.I. Comparative Adsorption of Fe(II) and Cd(II) Ions on Glutaraldehyde Cross-linked Chitosan-coated Cristobalite. Oriental J. Chem. 2015. V. 31. P. 2071–2076.
8. Rongdong D., Yuan H., Jiangang K., Zuo W. Adsorption of Fe(III) on smithsonite surfaces and implications for flotation. Colloids and Surfaces. A Physicochem. Eng. Aspects. 2017. V. 8. No 12. P. 542–555.
9. Sukpreabprom H., Arquero O., Naksata W., Sooksamiti P., Janhom S. Isotherm, Kinetic and Thermodynamic Studies of the Adsorption of Cd(II) and Zn(II) Ions from Aqueous Solutions onto Bottom Ash. Int. J. Environmental Sci. and Development. 2014. V. 5. No 2. P. 165–170.

Fe(III) MASS-2-AMINO-4-NİTROFENOL İLƏ SORBSİYASININ ÖYRƏNİLMƏSİ

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Məqalə dəmir(III) ionlarının malein anhidridinin stirol ilə birgə sopolimeri və 2-amino-4-nitrofenol əsasında sintez edilmiş xelatəmələgətirici sintetik sorbent tərəfindən adsorbsiyasının öyrənilməsinə həsr edilmişdir. Sorbentin Fe(III) ionlarına qarşı sorbsion xüsusiyyətləri öyrənilmişdir. Tədqiqat zamanı sorbsiyaya təsir edən müxtəlif parametrlər, xüsusilə, optimal pH, ion qüvvəsinin təsiri, zamandan asılılıq, metal ionlarının ilkin qatılığının təsiri öyrənilmişdir. Araşdırmalar göstərir ki, maksimum sorbsiya tutmu mühitin pH=5 qiymətində 373.33 mq/q təşkil edir. Tədqiqat zamanı bəzi sorbsiya izotermiləri və kinetikaı öyrənilmişdir.

Açar sözlər: sorbsiya, Fe(III), xelatəmələgətirici sorbent, qatılşdırılma.

ИЗУЧЕНИЕ СОРБЦИИ ИОНОВ Fe(III) С МА-2-АМИНО-4-НИТРОФЕНОЛОМ

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Исследована адсорбция ионов железа(III) хелатообразующим синтетическим сорбентом на основе сополимера стирола с малеиновым ангидридом (МАСС) и 2-амино-4-нитрофенолом. Изучены адсорбционные характеристики сорбента по отношению к ионам Fe(III). Исследовано влияние различных параметров на адсорбцию – оптимального pH, ионной силы, времени необходимого для установления полного сорбционного равновесия, начальной концентрации ионов металлов. Показано, что максимальная адсорбционная емкость сорбента по отношению к ионам трехвалентного железа составляет 373.33 мг/г при pH=5. Изучено несколько изотермических и кинетических моделей адсорбции и выявлена наиболее соответствующая нашим экспериментальным данным.

Ключевые слова: сорбция, Fe(III), хелатообразующий сорбент, концентрирование.