

ADSORPTION OF Fe (III) IONS BY SYNTHETIC POLYMER BASED ADSORBENT

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Abstract. In this work adsorption of ferric (III) ions by a synthetic adsorbent on the base of maleic anhydride styrene copolymer and 1,3,5-triazine was studied. Adsorption characteristics of this adsorbent with respect to Fe (III) ions were studied. Various parameters affecting adsorption process, particularly, the value of the optimal pH, contact time, the effect of ionic strength, the effect of the initial ferric (III) ions concentration were studied. Results have shown that the maximum adsorption capacity of the product over ferric ions is $367.21 \text{ mg} \cdot \text{g}^{-1}$ at $\text{pH} = 4$.

Keywords: Adsorption, Fe (III), synthetic adsorbent, 1,3,5-triazine, preconcentration.

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1. Introduction

During the last years the quality of water worsened. Heavy metal ions are among the most dangerous pollutants of wastewaters. 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 and 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 (Jun *et al.*, 2012, Mostafa *et al.*, 2014).

Many techniques were used in order to extract different types of pollutants from wastewater. Among them adsorption technique takes a special place due to the ease of operation, scale up, economic cost and the variety of available adsorbents (Khalid *et al.*, 2015).

The aim of this work is to study the adsorption of Fe (III) ions from its aqueous solutions by a polymeric chelating-forming adsorbent based on copolymer of styrene with maleic anhydride and 1,3,5-triazine (Alieva *et al.*, 2017, Oztaş *et al.*, 2008, Purnaratrie, 2015, Rongdong *et al.*, 2017). Various adsorption characteristics, in particular the effect of pH, contact time, ionic strength, initial concentration of the metal ion, were studied during the studies. The process of desorption was also studied and the

optimum eluent was established. Several adsorption isotherm and kinetic models have been studied (Sukpreabprom *et al.*, 2014).

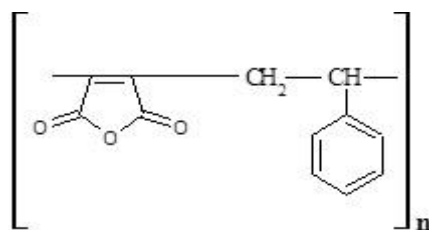
2. Research method and research

Preparation of solutions. The initial solution of Fe (III) ions with concentration of $10^{-2} \text{ mol}\cdot\text{L}^{-1}$ was prepared by using 10^{-1} M FeCl_3 solution, prepared by dissolving reduced iron in HCl and HNO_3 . 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(diazen-2,1-diyl)bis(benzene-1,3,5-triol) $\text{C}_{18}\text{H}_{18}\text{O}_6\text{N}_4$ (R) (Bulatov & Kalikin, 1972). Absorbances of solutions were measured on KFK-2 and optimal pH = 5 and $\lambda = 490 \text{ nm}$ were established.

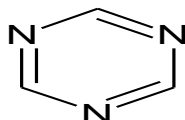
Buffer solutions from 1 to 5 were prepared on the basis of 0.1 N solutions of CH_3COOH and $\text{NH}_3\cdot\text{H}_2\text{O}$.

To study the effect of ionic strength on the adsorption capacity of the sorbent, $2 \text{ mol}\cdot\text{L}^{-1}$ of KCl solution was used, as well as $2 \text{ mol}\cdot\text{L}^{-1}$ of KOH solution to study the desorption process.

For the synthesis of the adsorbent, maleic anhydride styrene copolymer and 1,3,5-1,3,5-triazine were used.

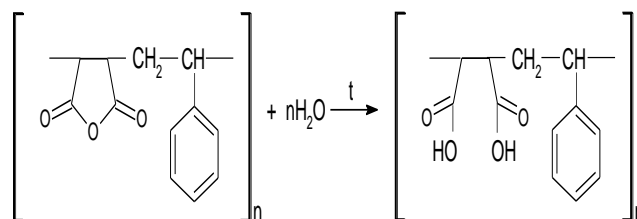


Scheme 1. Molecular structure of the copolymer of styrene with maleic anhydride

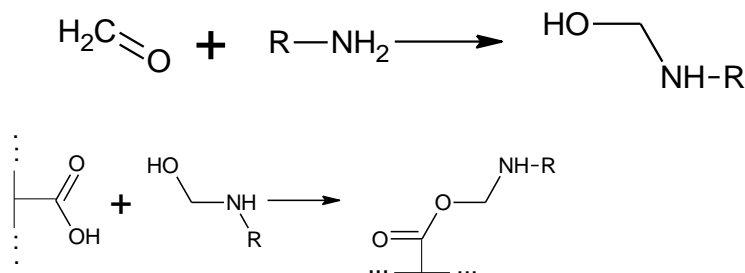


Scheme 2. Molecular structure of 1,3,5-triazine

Synthesis of adsorbent. Synthesis of the adsorbent was carried out according to a known technique (Akbarov & Akbarov, 2002). As the polymer matrix for the synthesis of the sorbent, maleic anhydride styrene copolymer and 1,3,5-triazine were used. For that purpose, 3 g of polymer were added to the round bottom flask. Subsequently, the appropriate amount of 1,3,5-triazine was weighed, dissolved in alcohol 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 $60\text{-}70^\circ\text{C}$, 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 adsorption 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. Adsorption 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 ($10^{-2} \text{ mol}\cdot\text{L}^{-1}$) 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 5.0, and final concentrations of Fe (III) ions were measured with the reagent 2,2'-([1,1'-biphenyl]-4,4'-diylbis(diazene-2,1-diyl)bis(benzene-1,3,5-triol)) $\text{C}_{18}\text{H}_{18}\text{O}_6\text{N}_4$ (R) on the photoelectrocolorimeter KFK-2 at $\lambda=490 \text{ nm}$.

The degree of metal ion extraction was calculated by the following formulas:

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

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

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 adsorbent mass (mg).

The desorption process. Adsorption regeneration is one of the critical steps. This work also includes desorption studies. 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 $10^{-2} \text{ mol}\cdot\text{L}^{-1}$ Fe (III) solution and 18 ml of pH 4.0 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 $0.5 \text{ mol}\cdot\text{L}^{-1}$ 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 $2 \text{ mol}\cdot\text{L}^{-1}$ 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 (Mostafa *et al.*,2014).

Equipment. The absorbances of the solutions were measured on photoelectrocalorimeter KFK-2 in a cuvette with a layer thickness $l = 1$. pH values measured on the pH meter Ionomer I-130.

3. Results and Discussions

Effect of pH on the degree of extraction of Fe (III). 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 adsorbent was weighed and added to the flask. Further, 2 ml of a $10^{-2} \text{ mol}\cdot\text{L}^{-1}$ 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 absorbances 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 4.0. Further adsorption experiments were carried out at a given pH value 4.0. A graphic representation of the data is shown in Fig. 1:

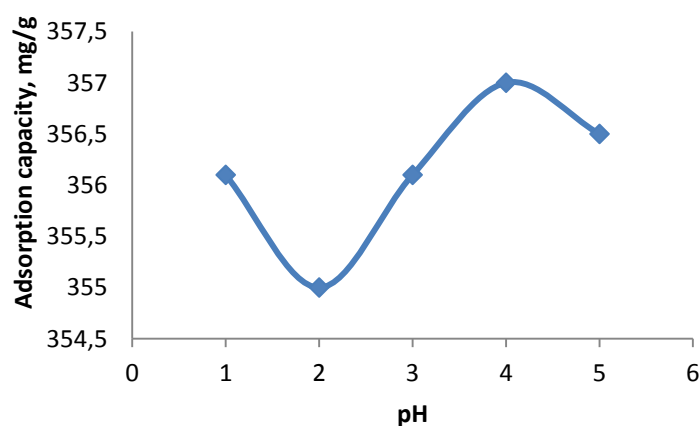


Figure 1. Effect of pH on adsorption capacity $m_{\text{adsorb.}}=30 \text{ mg}$, $V_{\text{gen.}}=20 \text{ ml}$, $C_{\text{Me}}=10^{-2} \text{ mol}\cdot\text{L}^{-1}$

Effect of contact time. The effect of time on the sorption capacity of the Fe (III) metal ion is shown in Fig. 2. In order to study this parameter, measurements were made in the range from 0 to 240 minutes. The equilibrium concentrations of metal ions in the sample were determined at the appropriate time intervals at KFK-2 and $\lambda = 490 \text{ nm}$.

As can be seen from Fig. 2, in the period from 0 to 90 minutes, the degree of sorption gradually increases, and from 120 minutes remains constant. This indicates the attainment of complete adsorption equilibrium.

Effect of ionic strength on the adsorption capacity. In the course of this work, the influence of ionic strength on the degree of extraction of the Fe (III) ion was investigated. For these purposes, $2 \text{ mol}\cdot\text{L}^{-1}$ potassium chloride KCl solution was used. Studies have shown that within the range of $\mu = 0.2\text{-}1.4 \text{ mol}\cdot\text{L}^{-1}$, 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.

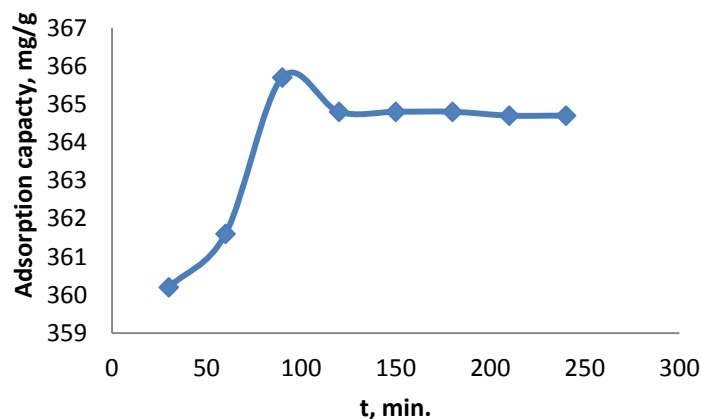


Figure 2. Effect of contact time on adsorption capacity
 $m_{\text{adsorb.}}=30$ mg, $V_{\text{gen.}}=20$ ml, $C_{\text{Me}}=10^{-2}$ mol·L⁻¹, pH=4

Effect of the initial concentration of Fe (III) ions. In the course of the experiment, the effect of the initial metal ion concentration on the degree of adsorption by the synthesized adsorbent was studied. For this purpose, the concentration range of Fe (III) ions was used from $0.2 \cdot 10^{-3}$ mol·L⁻¹ to $10.0 \cdot 10^{-3}$ mol·L⁻¹. For this, 30 mg of sorbent were weighed, the corresponding volumes of the metal ion solution and pH 4.0 were added. After 120 minutes, absorbances of the homogeneous solutions on KFK-2 were measured with a buffer solution pH 5.0 at $\lambda = 490$ 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 Fig. 3 and Table 1.

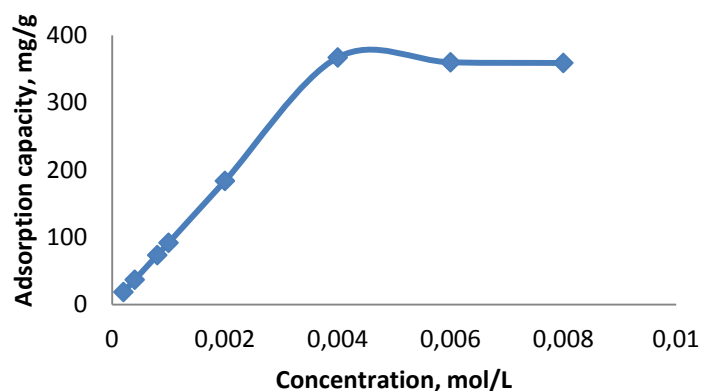


Figure 3. Effect of initial metal ion concentration on the adsorption capacity
 $m_{\text{adsorb.}}=30$ mg, $V_{\text{gen.}}=20$ ml, $C_{\text{Me}}=10^{-2}$ mol·L⁻¹, pH=4, t=120 min.

The results of the studies showed that the greatest sorption capacity is observed at a Fe (III) concentration of $4.0 \cdot 10^{-3}$ mol·L⁻¹.

Table 1. Extraction degree of Fe (III) ions by a synthesized sorbent ($m_{\text{adsorb.}}=30$ mg, $V_{\text{gen.}}=20$ ml, $C_{\text{Me}}=10^{-2}$ mol·L⁻¹, pH=4, t=120 min.)

$C_{\text{Me}}, \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$	0,2	0,4	0,8	1,0	2,0	4,0	6,0	8,0
R, %	44	55	69	75	82	85	84	83,9

Results of the present work were compared with the literature data and given in Table 2 below.

Table 2. Comparison of adsorption capacities of different adsorbents for the adsorption of Fe(III) ions ($m_{\text{adsorb.}}=30$ mg, $V_{\text{gen.}}=20$ ml, $C_{\text{Me}}=10^{-2}$ mol·L⁻¹, pH=4, t=120 min.)

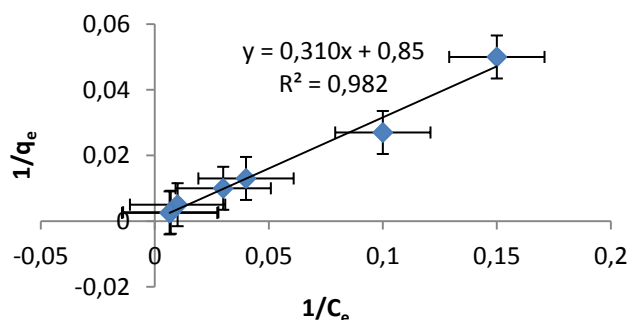
Adsorbent	Maximum adsorption capacity ($q_{\text{max}}, \text{mg} \cdot \text{g}^{-1}$)	Reference
Hen eggshell	18.8	Rotliwala, Chevli and Maheshvari (2017)
Olive cake	58.47	Zaid Ahmed Al-Anber and Mohammad Al-Anber (2008)
Acanthace aeactivated carbon	503	Hussain, Mohammed, Nallu and Arivoli(2012)
Husk of Cicerarientinum	72.16	Ahalya, Kanamadi and Ramachandra (2006)
Malein-anhydride styrene copolymer+1,3,5-triazine	367,21	Present Work

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⁻¹) is concentration of adsorbate in the aqueous phase at equilibrium, q_e (mmol·g⁻¹) is the equilibrium adsorption capacity, q_m is equal to q_e for the complete monolayer and K_L (L·mmol⁻¹) is the Langmuir isotherm constant.

Linear plot of dependence of $1/q_e$ versus $1/C_e$ is shown in Fig. 4. The values of the q_{max} and K_L were calculated from the slope and the intercept of the plot, respectively.

**Figure 4.** Langmuir isotherm model ($m_{\text{adsorb.}}=30$ mg, $V_{\text{gen.}}=20$ ml, $C_{\text{Me}}=10^{-2}$ mol·L⁻¹, pH=4, t=120 min.)

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

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

where b is the Langmuir constant ($L \cdot \text{mmol}^{-1}$), C_0 is the initial concentration of adsorbate ($\text{mmol} \cdot L^{-1}$). 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 0.97, which shows that adsorption is favorable under the specified experimental conditions by Langmuir model. Also the value of the coefficient of regression $R^2=0.98$ 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 ($\text{mmol} \cdot L^{-1}$) is adsorbate concentration at equilibrium, q_e ($\text{mmol} \cdot \text{g}^{-1}$) 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 Fig. 5. The values of K_F and $1/n$ were calculated from the slope and intercept of the plot, respectively.

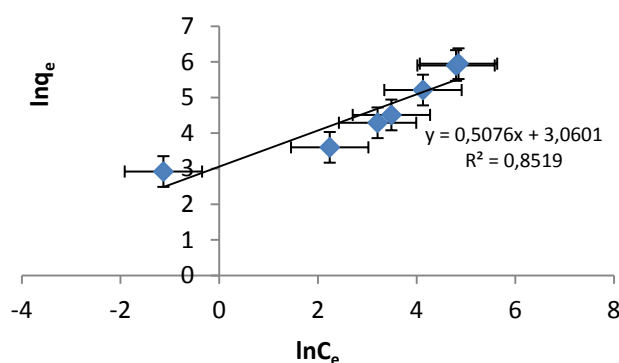


Figure 5. Freundlich isotherm model
($m_{\text{adsorb.}}=30 \text{ mg}$, $V_{\text{gen.}}=20 \text{ ml}$, $C_{\text{Me}}=10^{-2} \text{ mol} \cdot L^{-1}$, $\text{pH}=4$, $t=120 \text{ min.}$)

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 almost equal to 1 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 $1/n = 0.507$, which indicates to normal adsorption process.

Results are shown in Table 3.

Table 3. Langmuir and Freundlich isotherm parameters
($m_{\text{adsorb.}}=30 \text{ mg}$, $V_{\text{gen.}}=20 \text{ ml}$, $C_{\text{Me}}=10^{-2} \text{ mol} \cdot L^{-1}$, $\text{pH}=4$, $t=120 \text{ min.}$)

Adsorbent	Langmuir				Freundlich		
	(q_{max} , $\text{mg} \cdot \text{g}^{-1}$)	(K_L , $L \cdot \text{mg}^{-1}$)	(R_L)	(R^2)	(K_F , $\text{mg} \cdot \text{g}^{-1}$)	($1/n$)	(R^2)
S	1.176	2.83	0.97	0.98	21	0.507	0.851

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:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

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 Fig. 6.

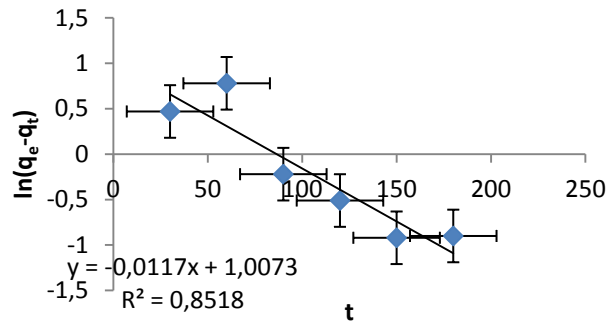


Figure 6. Pseudo-first-order kinetic model
($m_{\text{adsorb.}}=30 \text{ mg}$, $V_{\text{gen.}}=20 \text{ ml}$, $C_{\text{Me}}=10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\text{pH}=4$, $t=120 \text{ min.}$)

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:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

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

The plot of dependence of $\frac{t}{q_t}$ versus t is shown in Fig. 7.

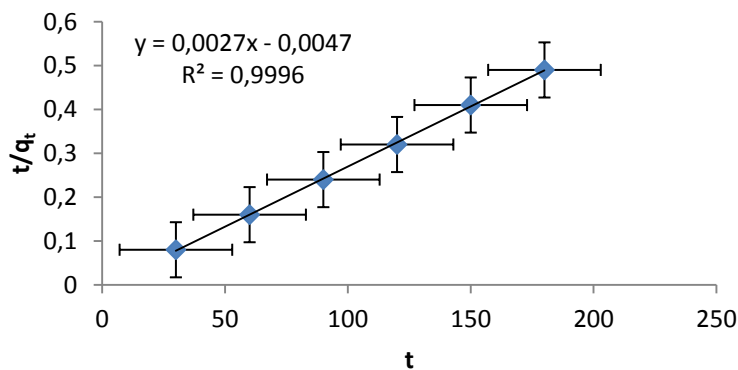


Figure 7. Pseudo-second-order kinetic model
($m_{\text{adsorb.}}=30 \text{ mg}$, $V_{\text{gen.}}=20 \text{ ml}$, $C_{\text{Me}}=10^{-2} \text{ mol} \cdot \text{L}^{-1}$, $\text{pH}=4$, $t=120 \text{ min.}$)

Values of k_2 and q_e were evaluated from the intercept and slope of the plot of $\frac{t}{q_t}$ 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 4.

Table 4. Adsorption kinetic parameters

	Pseudo-first-order				Pseudo-second-order		
	$q_e(\text{exp}), \text{mg}\cdot\text{g}^{-1}$	$k_1, (\text{min}^{-1})$	$q_e(\text{cal}), \text{mg}\cdot\text{g}^{-1}$	(R^2)	$k_2, (\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1})$	$q_e(\text{cal}), \text{mg}\cdot\text{g}^{-1}$	(R^2)
S	361.27	-0.011	2.7	0.851	-0.004	500	0.999

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⁻¹solutions of HNO₃, HCl, H₂SO₄ and CH₃COOH acids. The results of the studies have shown that maximum desorption ability over Fe(III) ions shows 0.5 mol·L⁻¹solution of HNO₃. Investigation have shown 5 times possible using of adsorbent after regeneration.

4. 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 361.27 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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