INORGANIC MATERIALS AND NANOMATERIALS

Extraction Of Indium from Sulfuric Acid Solutions To Carbon Composites Modified With Nanotubes

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The regularities of the sorption extraction of indium from sulfuric acid solutions using composites based on activated carbons modified with carbon nanotubes are considered. Their surface was studied by scanning electron microscopy. The equilibrium and kinetic characteristics of the sorbents are obtained. Indium sorption isotherms have a convex shape and are described by the Langmuir equation. The approximation of kinetic data using pseudo-first and pseudo-second order models, internal diffusion, and Elovich showed that the highest correlation coefficient is observed when using a pseudo-second order model. The process of indium sorption is limited by external diffusion. The efficiency of the carbon composite during the extraction of indium in four sorption-desorption cycles has been verified.

Keywords: indium, sorption, carbon composite, carbon nanotubes, sulfuric acid solution, ion exchange

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INTRODUCTION

Rare metals, including indium, are widely used in science-intensive areas of industrial production. Since there are no world industrial reserves of its ores, the main sources are various wastes and intermediate products of tin, lead and zinc production. The average indium content in them varies from 0.001 to 0.1% [1].

A possible source of it could be the fumarole emissions of the Kudryavy volcano, located on Iturup Island (Sakhalin Region), which contain, along with indium, significant quantities of other valuable elements such as rhenium, germanium, and molybdenum [2].

From solutions formed during hydrometallurgical processing of wastes and intermediate products, indium is extracted using extraction [3]. The emerging difficulties in preparing large volumes of reagents, as well as contamination of zinc production solutions with organic reagents, affect its further production [4].

For extracting indium from solutions, the sorption method is also used. Various materials are used for this purpose, such as resins (cationites and ampholytes) [4]. Besides resins and various impregnates, the possibility of indium sorption is studied using composites [5], natural zeolites [6], activated carbons [7], including those modified with hyperbranched polyethylenimine [8], and carbon nanotubes [9]. The co-sorption of indium and gallium was studied using iron(II) hexacyanoferrate [10]. The possibility of indium sorption by ampholytes in the presence of iron ions has also been investigated [11].

The aim of this work is to study the sorption characteristics of a composite for extracting indium from sulfuric acid solutions based on activated carbon with carbon nanotubes attached to its surface.

EXPERIMENTAL PART

In this work, samples of carbon composite based on activated carbon Tatsorb (LLC "NPO Povolzhsky Sorbents Plant "Tatsorb", Kazan), obtained from coconut shell, were used for indium extraction. These samples were produced at the D.I. Mendeleev Russian University of Chemical Technology: Tatsorb-CNT-1, modified with multi-walled carbon nanotubes of the "Global CO" brand (LLC "Global CO", Khimki) with a diameter of 15-45 nm, and Tatsorb-CNT-2, modified with multi-walled carbon nanotubes of the "Taunit" brand (LLC "Nanotechcenter", Tambov) with a diameter of 20-50 nm. In both cases, the content of nanotubes was 0.001%.

The activated carbon was treated with dispersed nanotubes and dried at a temperature of 60°C. For comparison, unmodified carbon of the "Tatsorb" brand was selected.

The surface morphology of the carbon composite was investigated using scanning electron microscopy (**SEM**) on an electron microscope JSM 6510LV (Jeol, Japan).

Indium sorption was studied under static conditions from a sulfuric acid solution (pH 3.50 ± 0.05). A solution with an indium concentration of 20 mg/l was added to the sorbent sample at a ratio of sorbent (g) to solution volume (ml) of 1 : 500. The phase contact was carried out with intensive stirring (150 rpm) for 24 hours on a Loip LS-210 orbital shaker (Russia). The phases were separated by decantation, and the indium concentration was determined by photometric analysis method [12]. The sorption capacity (***SC***) was calculated using the formula:

$$SC = (C_{\mathrm{init}} - C_{\mathrm{eq}})\ V / g\ , (1)$$

where C_{init} is the concentration in the initial solution, mg/l; C_{eq} is the concentration in the solution after sorption, mg/l; V is the volume of the solution, l; g is the mass of the sorbent sample, g.

The sorption degree (α, %) was calculated by the ratio:

$$\alpha = \frac{(C\text{исх}-\text{Сравн})}{C\text{исх}} \times 100, (2)$$

where C_{init} is the indium concentration in the initial solution, mg/l; C_{eq} is the indium concentration in the solution after sorption, mg/l.

Sorption isotherms were obtained by the method of variable volumes. A solution with a volume of 50-250 ml was added to a 0.1 g sorbent sample. The pH of the solution was 3.5 ± 0.05, the indium concentration in the initial solution was 20 mg/l.

Desorption was carried out under static conditions by contacting the indium-saturated composite with an eluent – an acidic aqueous solution of hydrochloric acid with a pH of 4.5 ± 0.05, acidity was regulated using 6 M HCl at a phase ratio of 1 : 100 (g : ml). The number of desorption contacts was three.

The desorption degree (β, %) was calculated using the formula:

$$\beta = \frac{\mathrm{C\,In\,эл}\ \ V\mathrm{эл}}{\mathrm{CEисх}\ \ m} \times 100, (3)$$

where $C_{\mathrm{In\ el}}$ is the indium concentration in the eluate, mg/l; V_{el} is the volume of eluent, l; SC_{init} is the initial capacity of the composite, mg/g; m is the sample of the indium-saturated composite, g.

The kinetics of indium sorption was studied using the limited solution volume method with intensive stirring (160 rpm), the contact time varied from 10 to 240 min, the ratio of the sorbent sample (g) to the solution volume (ml) was 1 : 500.

To study the sorbent stability under cyclic operation, tests were conducted, including four stages of sorption-desorption under the conditions described above.

RESULTS AND DISCUSSION

According to SEM images (Fig. 1), the carbon nanomodified composite is covered with long tangled bundles of carbon nanotubes.

The isotherms of indium sorption by carbon materials have a convex shape (Fig. 2) and can be described by the Langmuir equation [13] in linearized form (4):

$$C/CE = C/CE_{\infty} + 1/(CE_{\infty} \cdot K), (4)$$

where CE is the sorption capacity, mg/g; CE_{∞} is the maximum sorption capacity, mg/g; K is the Langmuir constant, ml/g; C is the equilibrium concentration of metal in solution after sorption, mg/l.

Taking into account the data from the linearized isotherms of indium sorption, the maximum sorption capacity for indium was calculated, as well as the Langmuir constants (Table 1).

To determine the time of sorption equilibrium, integral kinetic curves were obtained (Fig. 3), the course of which shows that 170-180 min is required to establish equilibrium sorption of indium on composites, while for the unmodified sorbent - more than 200 min.

Data on the rate of indium sorption by carbon sorbents were processed using the following kinetic models [14]:

1. Pseudo-first order model: $\lg(Qe - Qt) = \lg Q_e - \frac{k_1}{2.303}\tau$.
2. Pseudo-second order model: $\frac{\tau}{Qt} = \frac{1}{k_2 Q_e^2} + \frac{1}{Qe}\tau$.
3. Internal diffusion model: $Q_t = k_{\mathrm{id}} \cdot \sqrt{\tau} + C$.
4. Elovich model: $Q_t = \frac{1}{\beta} \cdot \ln(\alpha\,\beta) + \frac{1}{\beta} \cdot \ln\tau$,

where Q_e – equilibrium sorption capacity, mg/g; Q_t – sorption capacity at time t , mg/g; k_1 (k_2) – rate constant of pseudo-first (pseudo-second) order, min $^{-1}$ (g mg $^{-1}$ min $^{-1}$); k_{id} – intraparticle diffusion rate constant, mg g $^{-1}$ min $^{-0.5}$; α – initial rate of sorption process, g mg $^{-1}$ min $^{-1}$; β – Elovich rate constant, g mg $^{-1}$.

Approximation of kinetic data using these models (Fig. 4) showed that the highest correlation coefficient (Table 2) is observed when applying the pseudo-second order model.

Processing according to the pseudo-second order model (Tatsorb-CNT-1, $R^2 = 0.9986$, Tatsorb-CNT-2, $R^2 = 0.9981$) shows that the process modeled by the Langmuir equation for a limited volume can be approximately described by the pseudo-second order equation, but the applicability of the aforementioned equation is not related to the kinetic mechanism [15, 16]. From the processing of kinetic data using the intraparticle diffusion model (Tatsorb-CNT-1, $R^2 = 0.9496$; Tatsorb-CNT-2, $R^2 = 0.9295$) (Fig. 4c), it can be seen that the line does not pass through the origin, therefore it can be concluded that the sorption of rhenium by the carbon composite occurs in the external diffusion region [17].

Considering the mechanism of indium sorption by the carbon composite, in addition to physical sorption in the pores of activated carbon, one should take into account its partial sorption by carbon nanotubes located on the sorbent surface, which acquires a negative charge (R^-) at pH >3.46 (isoelectric point). The interaction of the indium cation in this case can proceed according to the equation [9]:

$$In^{3+} + 3R^{-}_{CNT} \leftrightarrow In^{+}R^{-}_{3CNT}. \quad (5)$$

This is confirmed by the fact that when comparing sorption capacities obtained under the same conditions, the capacity of Tatsorb-CNT-1 and Tatsorb-CNT-2 composites, coated with nanotubes, is 12.6 and 9.7% higher than that of unmodified Tatsorb activated carbon.

The stability of properties of nanomodified Tatsorb-CNT-1 and Tatsorb-CNT-2 composites was evaluated during four sorption-desorption cycles. The degree of indium sorption by Tatsorb-CNT-1 composite after four cycles decreased by 4%, the degree of desorption - by 7%, in the case of Tatsorb-CNT-2 - by 3.5 and 6%, respectively. The degree of indium sorption by "Tatsorb" activated carbon, chosen for comparison, and the degree of desorption decreased to a much greater extent - by 5.0 and 6.2 times, respectively. The decrease in sorbent characteristics is associated with its mechanical degradation. Activated carbons in the absence of carbon nanotubes undergo greater destruction than composites based on them.

CONCLUSION

Based on the equilibrium, kinetic, and operational characteristics of indium sorption obtained in this work, Tatsorb-CNT-1 and Tatsorb-CNT-2 carbon composites can be used for the extraction of indium from dilute sulfuric acid solutions purified from foreign components that affect the sorption process.

The kinetic data of indium sorption by carbon nanocomposite are described with a high degree of correlation according to the pseudo-second-order and internal diffusion models. Indium sorption occurs in the external diffusion region.

Testing the stability of the carbon composite in cyclic tests showed that the degree of sorption of Tatsorb-CNT-1 and Tatsorb-CNT-2 composites for indium, compared to unmodified Tatsorb activated carbon, decreased significantly less over four cycles.

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CONFLICT OF INTEREST

The authors declare that they have no known financial conflicts of interest or personal relationships that could have influenced the work presented in this article.

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Table 1. Maximum capacity values and Langmuir constant

Composite	Maximum sorption capacity, mg/g	Langmuir constant, ml/g
Tatsorb-CNT-1	34.5	12.2 ± 0.5
Tatsorb-CNT-2	27.6	9.1 ± 0.5
Tatsorb	21.0	8.4 ± 0.5

Table 2. Values of indium sorption rate constants by carbon sorbents

Model							
pseudo-first order		pseudo-second order		intraparticle diffusion		Elovich	
k_1, min $^{-1}$	R^2	k_2, g mg $^{-1}$ min $^{-1}$	R^2	k_{id}, mg g $^{-1}$ min $^{-0.5}$	R^2	β, g mg $^{-1}$	R^2
Tatsorb-CNT-1							
0.017	0.9704	0.100	0.9986	0.0172	0.9496	2.07	0.8345
Tatsorb-CNT-2							
0.02	0.9642	0.103	0.9981	0.0168	0.9295	2.15	0.7959
Tatsorb							
0.015	0.9371	0.199	0.9918	0.0161	0.9681	2.14	0.917

FIGURE CAPTIONS

Fig. 1. Surface of modified activated carbon covered with carbon nanotubes, magnification ×15000 (a) and ×50000 (b).

Fig. 2. Indium sorption isotherms by nanomodified composite and activated carbon (a) and their anamorphoses (b): *1* - Tatsorb-CNT-1, *2* - Tatsorb-CNT-2, *3* - Tatsorb.

Fig. 3. Integral kinetic curves of indium sorption from sulfuric acid solutions by carbon composites and unmodified activated carbon: *1* - Tatsorb-CNT-1, *2* - Tatsorb-CNT-2, *3* - Tatsorb.

Fig. 4. Dependencies $\lg(Q_e - Q_t) = f(\tau)$ (a); $t/Q_t = f(\tau)$ (b); $Q_t = f(\sqrt{\tau})$ (c); $Q_t = f(\ln \tau)$ (d); for indium sorption by carbon composites and activated carbon: *1* - Tatsorb-CNT-1, *2* - Tatsorb-CNT-2, *3* - Tatsorb.

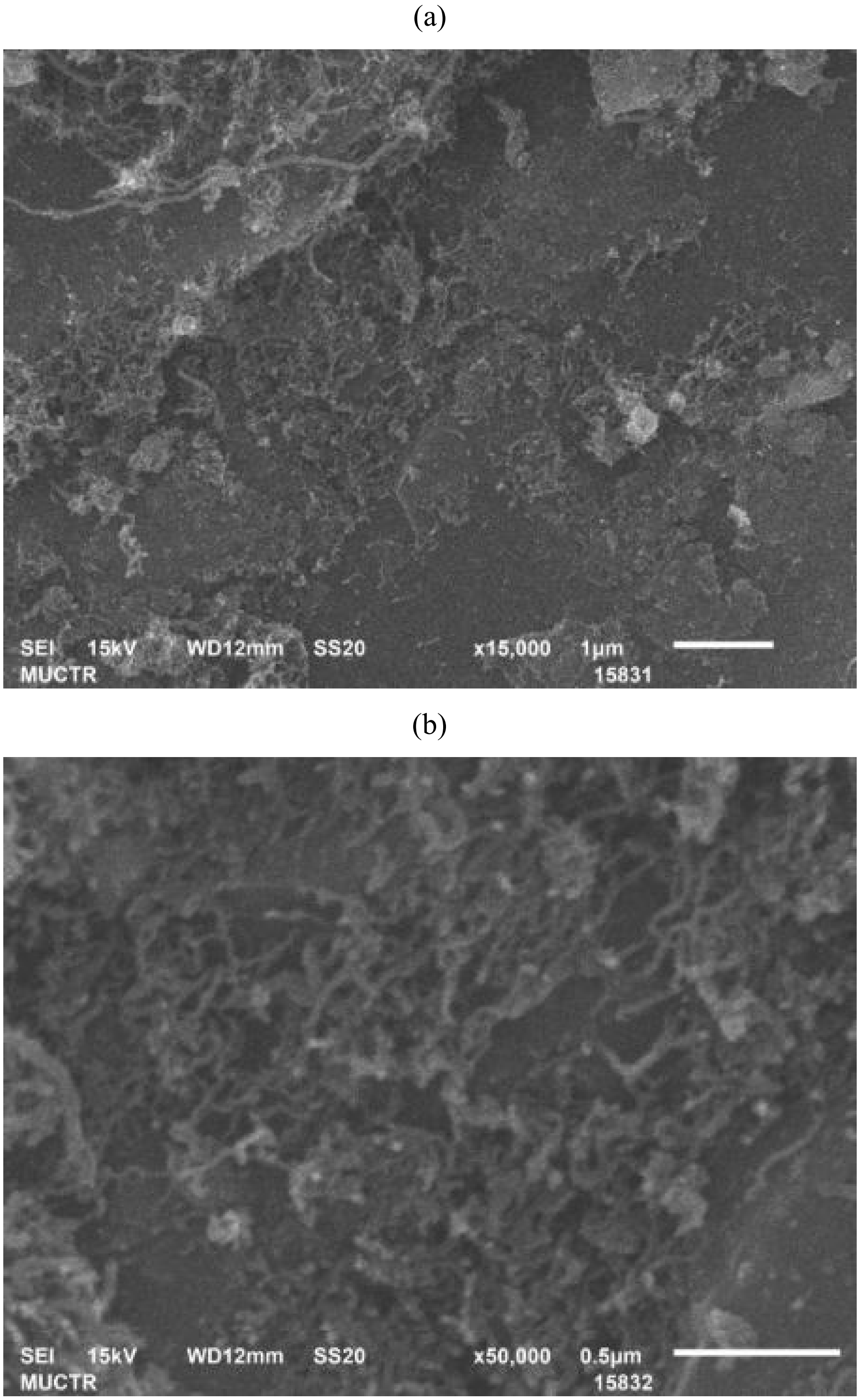
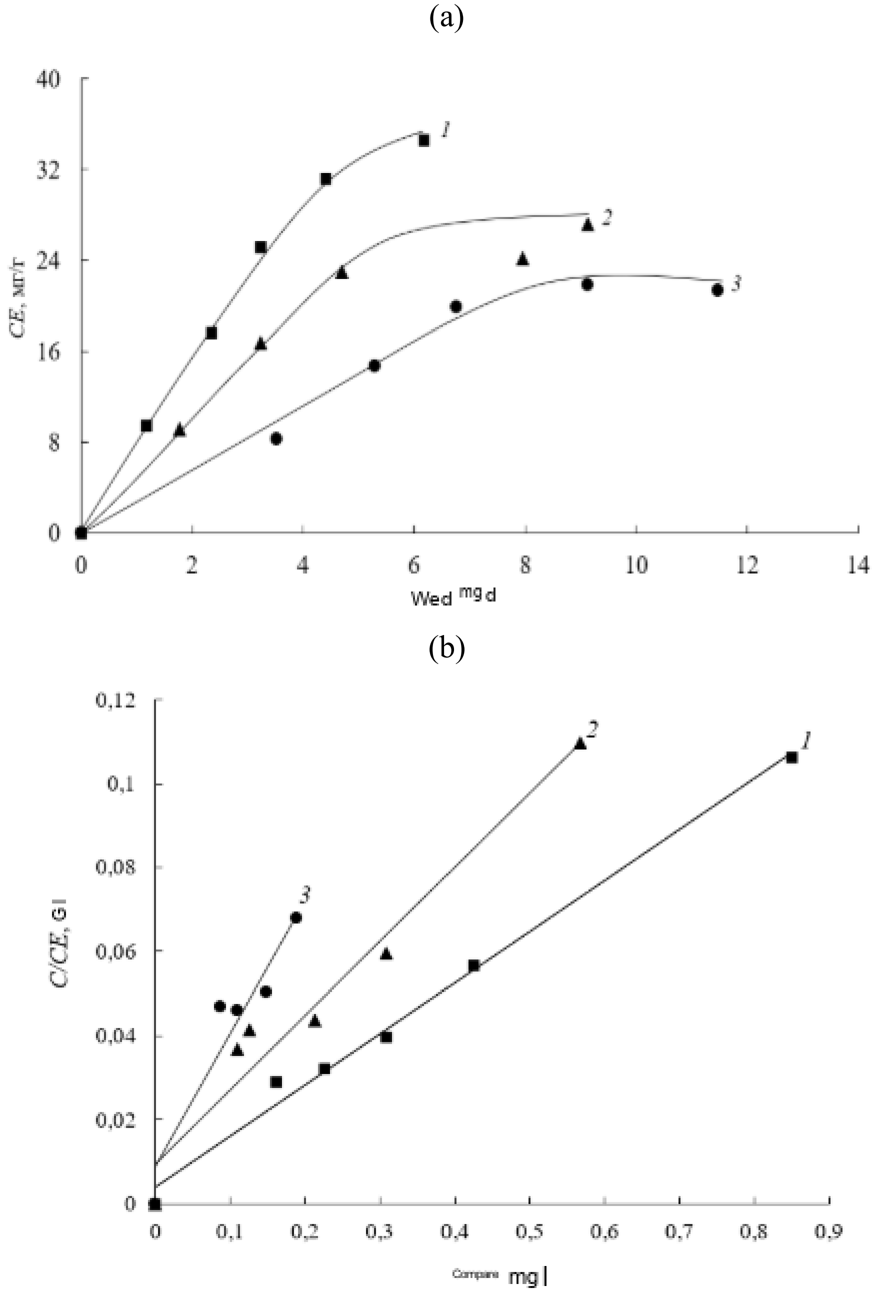

(a)
SEI 15kV WD12mm SS20 x15,000 1μm
MUCTR 15831
(b)
SEI 15kV WD12mm SS20 x50,000 0.5μm
MUCTR 15832

Fig. 1.


(a)
40
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24
16
8
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2
3
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6
8
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12
14
Wed mg d
(b)
0,12
0,1
0,08
0,06
0,04
0,02
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C/CE, Gl
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0,1
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Fig. 2.

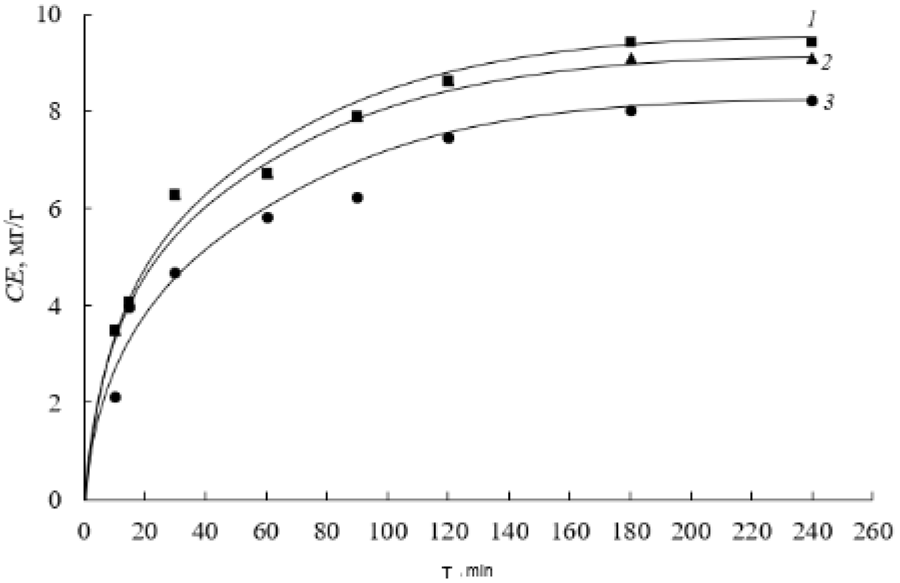
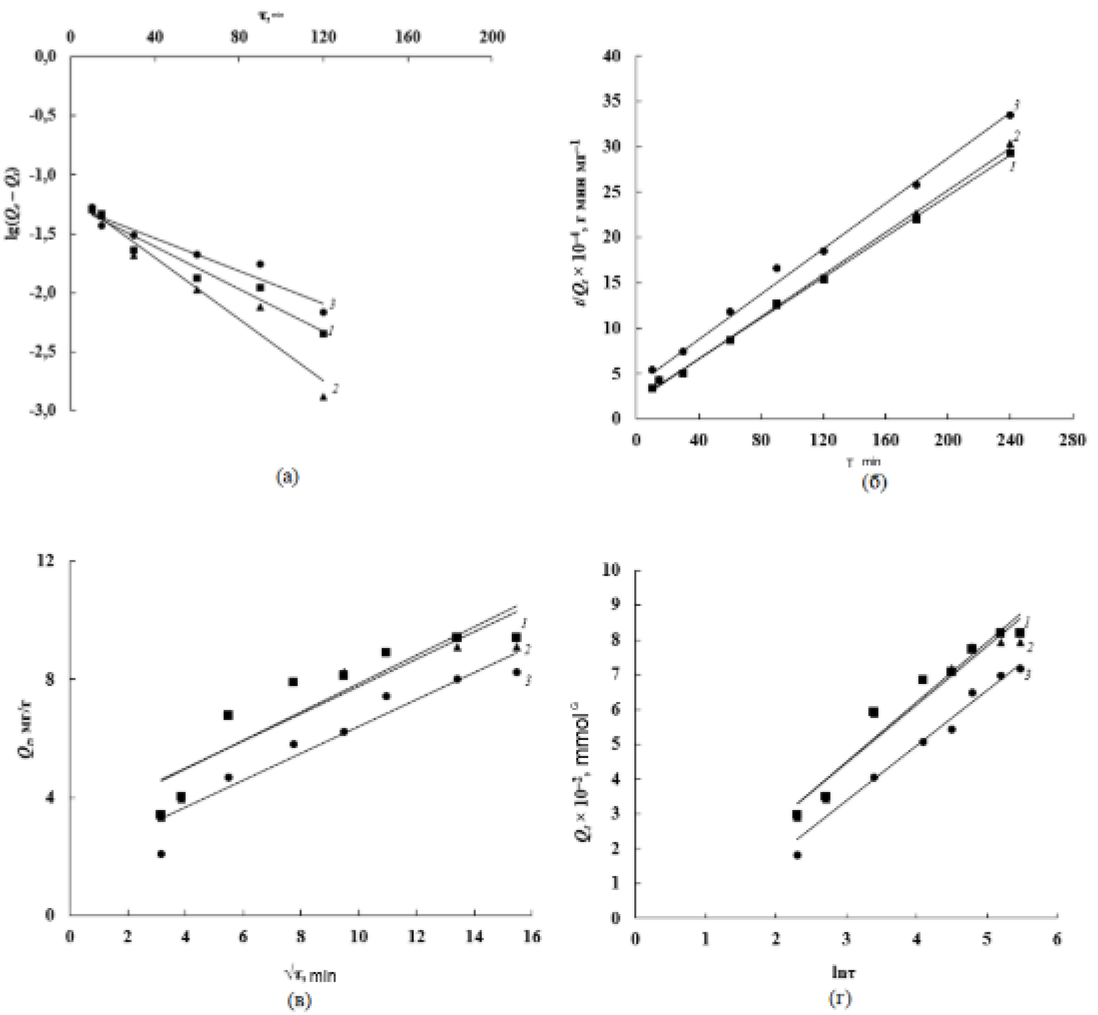


Fig. 3.



(a)

(б)

(в)

(г)

Fig. 4