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# Development and solution of the kinetics equation and adsorption isotherm for gold adsorption from cyanide solutions onto activated carbon

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**Abstract:** This paper presents the results of theoretical and experimental studies on the process of gold adsorption from cyanide solutions onto activated carbon (AC). One of the objectives of the study was to identify the functional relationship between the mass loading of AC in the volume of the adsorption column solution and the kinetics of the process. To achieve this, a modified adsorption kinetics equation (considering the heterogeneity of the process) was proposed, which incorporates the solid phase of the carbon sorbent in the unit volume of solution as a third intermediate agent of adsorption interaction between the adsorbate ions and the free active sites of the AC. As a result, a modified third-order adsorption kinetics equation for gold adsorption on AC was derived, taking into account the solid phase loading of AC in the solution volume, along with its analytical solutions under conditions of constant gold content in the initial solution and the process conducted in a closed volume with varying gold concentrations in the solution according to the material balance equation. The relationship between the solutions of the kinetic equation and the adsorption isotherm equation was established. From the solutions of the kinetic equation, a modified Langmuir isotherm equation was derived, which allows determining the equilibrium concentrations of gold on the AC and in the solution a priori under the condition that the process is conducted in a closed volume, with known initial gold contents in the solution and on the AC, as well as with a known AC loading in the adsorber volume. The theoretical dependencies of the adsorption and desorption rate constants on temperature, convective, and diffusion parameters are discussed. The presented mathematical model of adsorption kinetics is valid under the conditions of gold adsorption on AC from gold cyanide solutions with an adsorption time of up to 2 days and a sorbent capacity utilization degree of 40–60%.

**Keywords:** gold, kinetics, adsorption, carbon adsorbent, adsorption isotherm, cyanide solution, reaction rate constant, mathematical modeling.

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# Разработка и решение уравнения кинетики и изотермы адсорбции золота из цианистых растворов на активированный уголь

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**Аннотация:** Представлены результаты теоретических и экспериментальных исследований процесса адсорбции золота из цианистых растворов на активированный уголь (АУ). Одной из задач работы было выявление функциональной зависимости между загрузкой массы АУ в объеме раствора адсорбционной колонны и кинетикой процесса. Для ее решения предложено модифицированное уравнение кинетики адсорбции (с учетом гетерогенности процесса) в виде включения твердой фазы угольного сорбента в единице объема раствора в качестве третьего промежуточного агента адсорбционного взаимодействия между ионами адсорбата и свободными активными центрами АУ. В результате получены модифицированное уравнение кинетики адсорбции золота на АУ 3-го порядка с учетом твердой фазы загрузки АУ в объеме раствора и его аналитические решения при условиях постоянства содержания золота в исходном растворе и проведения процесса в замкнутом объеме с изменяющейся концентрацией золота в растворе согласно уравнению материального баланса. Установлена взаимосвязь между решениями кинетического уравнения и уравнением изотермы адсорбции. Из решений кинетического уравнения получено модифицированное уравнение изотермы Ленгмюра, позволяющее находить равновесные концентрации золота на АУ и в растворе доопытно при условии проведения процесса в замкнутом объеме и известных начальных значениях содержаний золота в растворе и на АУ, а также при известной загрузке АУ в объеме адсорбера. Обсуждены теоретические зависимости констант скоростей адсорбции и десорбции от температуры, конвективных и диффузионных параметров. Представленная математическая модель кинетики адсорбции справедлива для условий проведения процесса адсорбции золота на АУ из золотоцианистых растворов при времени адсорбции до 2 суток и степени заполнения полной предельной емкости сорбента 40–60 %.

**Ключевые слова:** золото, кинетика, адсорбция, угольный адсорбент, изотерма адсорбции, цианистый раствор, константа скорости реакции, математическое моделирование.

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## Introduction

A fundamental problem in the field of carbon-sorption technology for the extraction of gold from gold-cyanide solutions is the lack of a universally accepted, theoretically grounded kinetics equation that can adequately describe both the dynamics and statics of the sorption process, taking into account variable operating factors — such as the concentrations of metal and the mass of activated carbon (AC) in the solution volume. Of the currently existing equations, the most widely used in practice are two semi-empirical Fleming kinetics equations [1—3]. The first of these cannot, in principle, adequately represent the sorption process because it does not assume the existence of an isotherm, while the second is only valid for a sorption process with a linear isotherm, which in our case is unacceptable as it contradicts experimental data.

Therefore, it is necessary to select a theoretically grounded adsorption kinetics equation from the existing developments in this field and, if needed, refine it to qualitatively align with the currently established patterns of the adsorption process. One of the main conditions should be the possibility of analytically deriving an isotherm equation from the selected kinetics equation. For further refinement of the mathematical model to quantitatively correspond to the kinetic characteristics of the adsorption process, a series of standard experimental studies must be conducted to obtain kinetic curves under various initial conditions for the determining operating factors — such as the initial concentration of gold in the solution and the carbon loading in the adsorber volume. The experimental kinetic curves and the isotherm curve can be used to identify the predictive mathematical model, with the final result being the numerical values of the identification constants that correspond to the characteristic properties of the carbon sorbent.

Thus, the objective of this work was to attempt to solve a fundamental problem in the theory and practice of gold adsorption from gold-cyanide solutions onto activated carbon — the theoretical justification of the physical meaning of the proposed kinetics equation and the adsorption process isotherm equation to create a predictive mathematical model capable of adequately describing the dynamics of the adsorption process at a quantitative level, within the framework of developing industrial process schemes and optimizing their operation. This study precedes a subsequent series of articles dedicated to the problem of modeling noble metal sorption processes onto AC, addressing issues of intradiffusion kinetics, countercurrent sorption processes from solutions and pulps (CIL and CIP processes).

## 1. Research methodology

To construct the isotherm for gold adsorption onto activated carbon (NORIT-3515), a static method with constant AC mass of 1.5 g and varying gold concentrations from 3.2 to 39.8 mg/dm$^3$ in cyanide solutions with NaCN concentration = 176.0 mg/dm$^3$, pH = 10.8, was used. The solution temperature was maintained between 20—22 °C throughout the experiments.

The adsorber was a circular vessel made of organic glass with a flat bottom and an agitation device equipped with a stirrer speed regulator. The height-to-diameter ratio of the adsorber was 2.5 : 1.0, with a solution volume of 3 dm$^3$ for each experiment. The total time required to achieve one equilibrium isotherm value was 216 hours. Samples were taken at regular intervals from the start of the experiment to construct kinetic curves.

The gold concentration in the solutions was determined using an atomic absorption spectrophotometer ICE 3300 (Thermo Fisher Scientific, USA) at the certified analytical center of "Irgiredmet" OJSC (Certificate No. 222.0132/RA.RU.311866/2021 for measurement methodology accreditation). The standard deviation of reproducibility for gold concentrations in solutions ranging from 0.01—0.10 mg/dm$^3$ was between 0.003 to 0.007 with an error margin of ±0.006 to ±0.014 mg/dm$^3$ at a confidence level of $P = 0.95$. The error margins at $P = 0.95$ for the concentration ranges 0.2—1.0 mg/dm$^3$ were ±0.04 to ±0.08 mg/dm$^3$, for 3.0—10.0 mg/dm$^3$ were ±0.2 to ±0.5 mg/dm$^3$, and for 20.0—50.0 mg/dm$^3$ were ±1.0 to ±2.5 mg/dm$^3$. The experimental results were statistically processed, calculating the mean, standard deviation, and confidence intervals for reproducibility for each isotherm point and kinetic curve.

## 1.1. Theoretical foundations of gold adsorption kinetics from cyanide solutions onto activated carbon

### 1.1.1. Theoretical justification for choosing a third-order kinetics equation

Experimental modeling of the adsorption kinetics process can be conducted in two ways. In the first case, adsorption occurs under conditions of constant gold content in the solution, while in the second, it occurs in a closed volume with continuously changing gold concentration in the solution according to the material balance. Although the adsorption mechanism and the kinetics equation describing the process remain unchanged, the solutions to the kinetics equations differ in each case and have different practical applications. [4; 5] The solution obtained from the kinetics equation for adsorption in a closed volume, taking into account additional conditions related to the ionic composition of the solution and its continuous flow through the adsorbers, can be directly used in the calculations of a continuous countercurrent gold adsorption process onto activated carbon [6—10], carried out in a series of sequentially arranged adsorption apparatus.

The widely accepted gold adsorption kinetics equation from cyanide solutions onto AC, considering the reversibility of the adsorption process and the existence of a sorbent's maximum capacity, is as follows:

$$\frac{dC_y}{dt} = K_1(C_0 - C_y)C_p - K_2C_y, \qquad (1)$$

where $C_y$ is the gold content in the loaded carbon, mg/g; $C_p$ is the gold concentration in the solution, mg/dm$^3$; $C_0$ is the maximum adsorption capacity of the sorbent, mg/g; $K_1$ is the adsorption rate constant, dm$^3$/(mg·h); $K_2$ is the desorption rate constant, h$^{-1}$; $t$ is time, h.

This is the classical form of the equation for a reversible second-order homogeneous chemical reaction, and since it describes a heterogeneous adsorption process, it is assumed a priori that the mass of the solid-phase adsorbent in the adsorption process is constant and is automatically considered in the adsorption rate constant. For the practical application of the kinetics equation (1), whose behavior largely depends on the adsorbent loading, it is necessary to establish a functional relationship between the adsorption rate and the mass of AC in the solution. This issue can be addressed by considering that the heterogeneous physicochemical process of $AuCN_2^-$ adsorption onto AC has a third-order interaction, unlike the second-order homogeneous chemical reaction (1).

The difference between these two processes is that in a chemical reaction, two substances, evenly dissolved in a liquid, interact with equal probability at any point in the solution, whereas in the adsorption process, the ions dissolved in the liquid phase have different probabilities of reaching the adsorbent surface depending on their location to interact with the free active sites contained in the finely dispersed solid phase of the adsorbent distributed in the liquid phase of the solution.

Thus, the act of paired interaction between an adsorbate ion and the active sites of the adsorbent is divided into two sequential processes: the first is the transport of the adsorbate ion in the solution phase to the surface of the adsorbent's solid phase, and the second is the interaction of some ions that have reached the surface with the free active sites of the adsorbent, while another portion desorbs back into the solution phase.

The kinetics of the adsorption process is critically influenced by internal operational parameters such as the loading of a certain mass of AC per unit volume of solution and the gold concentration in the solution. Since adsorption is a mass-statistical process, it must obey the law of mass action. This means that the intensity of any paired interactions is always directly proportional to the product of the concentrations of the interacting agents. If the interaction of agents occurs indirectly through an intermediate stage that screens out some portion of one of the agents, the intensity of the final paired interaction of these agents will equal the product of the remaining concentration of the agent that passed through the intermediate stage and the concentration of the second agent.

According to the law of mass action, the product $C_p \cdot m/V$ characterizes the intensity of the first interaction of dissolved $AuCN_2^-$ with the surface of the solid phase of the adsorbent granules, where $m/V$ (g/dm$^3$) represents the content, or loading, of the adsorbent mass ($m$, g) per unit volume of solution ($V$, dm$^3$). This parameter includes all the physicochemical characteristics of the adsorbent, including granule size, effective surface area, porosity, and its nature, which should be reflected in the rate constant $K_1$.

The intensity of the second paired interaction between the $AuCN_2^-$ ions that have reached the solid phase surface and the free active sites of the adsorbent will be proportional, according to the law of mass action, to the product $C_p \cdot m/V$ and the content of free active sites in the mass of the adsorbent's solid phase $C_0 - C_y$, i.e. $C_p \cdot m/V \cdot (C_0 - C_y)$.

Based on the above concepts of the $AuCN_2^-$ adsorption process onto AC, we record the third-order adsorption kinetics differential equation considering the heterogeneity and reversibility of the process:

$$\frac{dC_y}{dt} = K_1(C_0 - C_y)\left(C_p \frac{m}{V}\right) - K_2 C_y, \qquad (2)$$

where $K_1$ is the adsorption rate constant, (dm$^3$)$^2$/(g·mg·h).

This equation is valid only for the first two stages of adsorption: convective mass transfer and film-near-surface diffusion, i.e., approximately up to 40—60 % of the full capacity of the carbon [1—3]. This work is limited to considering only these two fastest stages of the adsorption process. It is assumed that in the initial period, up to about 2 days, the contribution of the third, slower and significantly longer intradiffusion stage is negligible.

### 1.1.2. Analytical solutions of the kinetics equation and derivation of the isotherm equation

The first analytical solution of the kinetics equation (2) is obtained under the condition that the gold concentration in the solution is constant and equal to $C_{p0}$. In practice, such conditions can be realized with a low AC loading in a large volume of solution (in the unlimited case).

The particular solution of equation (2), assuming $C_p$ = const and for the initial conditions $C_p = C_{p0}$, $C_y = C_{y0}$, at $t = 0$, will have the form:

$$C_y = \frac{K_1 C_0 C_{p0}\, m/V}{K_1 C_{p0}\, m/V + K_2}\left(1 - e^{-(K_1 C_{p0} m/V + K_2)t}\right) + \\ + C_{y0} e^{-(K_1 C_{p0} m/V + K_2)t}, \qquad (3)$$

where $C_{y0}$ is the initial gold content in the carbon, mg/g; $C_{p0}$ is the initial constant gold concentration in the cyanide solution, mg/dm$^3$.

The solution (3) shows that at $t \to \infty$, $e^{-(K_1 C_{p0} m/V + K_2)t} \to 0$, and therefore, the value will tend towards its isothermal value determined by the expression:

$$C_y = \frac{C_0 C_{p0}\, m/V}{C_{p0}\, m/V + K_2/K_1}, \qquad (4)$$

which represents a modified form of the Langmuir isotherm considering the loading $m/V$ of the adsorbent in the adsorber volume. Given that $C_{p0}$ = const, the time required to reach the equilibrium value $C_y$, can be quite long, sometimes taking months.

To solve the kinetics equation (2) under adsorption conditions in a closed volume, it must be supplemented by the material balance equation:

$$(C_y - C_{y0})m = (C_{p0} - C_p)V, \qquad (5)$$

where $m$ is the mass of the carbon, g; $V$ is the solution volume, dm$^3$; $C_{p0}$ is the initial gold concentration in the cyanide solution, mg/dm$^3$.

From equation (5), the expression for the current value $C_p$ can be found as:

$$C_p = C_{p0} - \frac{m}{V}(C_y - C_{y0}), \qquad (6)$$

substituting this into (2), we obtain a nonlinear first-order differential equation with the right-hand side in the form of a quadratic trinomial relative to $C_y$ with constant coefficients:

$$\frac{dC_{\text{y}}}{dt} = K_1\left(\frac{m}{V}\right)^2 {C_{\text{y}}}^2 - \left[K_1C_0\left(\frac{m}{V}\right)^2 + K_1C_{\text{p0}}\frac{m}{V} + K_1\left(\frac{m}{V}\right)^2 C_{\text{y0}} + K_2\right]C_{\text{y}} + K_1C_0C_{\text{p0}}\frac{m}{V} + K_1\left(\frac{m}{V}\right)^2 C_0C_{\text{y0}}. \quad (7)$$

It is known that a quadratic trinomial can always be represented as the product of two linear binomials if its roots are known, which can be found by equating the right side of equation (7) to zero:

$$C_{\text{y1}} = 0{,}5\left[C_0 + \frac{V}{m}C_{\text{p0}} + C_{\text{y0}} + \frac{K_2}{K_1}\left(\frac{V}{m}\right)^2\right] + \sqrt{0{,}25\left[C_0 + \frac{V}{m}C_{\text{p0}} + C_{\text{y0}} + \frac{K_2}{K_1}\left(\frac{V}{m}\right)^2\right]^2 - \left[\frac{V}{m}C_0\left(C_{\text{p0}} + C_{\text{y0}}\frac{m}{V}\right)\right]}, \quad (8)$$

$$C_{\text{y2}} = 0{,}5\left[C_0 + \frac{V}{m}C_{\text{p0}} + C_{\text{y0}} + \frac{K_2}{K_1}\left(\frac{V}{m}\right)^2\right] - \sqrt{0{,}25\left[C_0 + \frac{V}{m}C_{\text{p0}} + C_{\text{y0}} + \frac{K_2}{K_1}\left(\frac{V}{m}\right)^2\right]^2 - \left[\frac{V}{m}C_0\left(C_{\text{p0}} + C_{\text{y0}}\frac{m}{V}\right)\right]}. \quad (9)$$

Knowing the roots $C_{\text{y1}}$ and $C_{\text{y2}}$, equation (7) can be rewritten as:

$$\frac{dC_{\text{y}}}{dt} = K_1\left(\frac{m}{V}\right)^2 (C_{\text{y}} - C_{\text{y1}})(C_{\text{y}} - C_{\text{y2}}). \quad (10)$$

This expression represents the mass-action equation with a known solution [11]. In our case, it looks as follows:

$$C_{\text{y}} = \frac{c_1 C_{y2} e^{K_1(m/V)^2(C_{\text{y1}} - C_{\text{y2}})t} - c_2 K_1 (m/V)^2 C_{\text{y1}}}{c_1 e^{K_1(m/V)^2(C_{\text{y1}} - C_{\text{y2}})t} - c_2 K_1 (m/V)^2}, \quad (11)$$

where $c_1$ and $c_2$ are arbitrary constants.

Thus, (11) is effectively the solution of two equations: the differential kinetics equation and the material balance equation, so the particular solution for the initial conditions $t = 0$, $C_{\text{y}} = C_{\text{y0}}$ and $C_{\text{p}} = C_{\text{p0}}$ has the form

$$C_{\text{y}} = \frac{C_{\text{y2}}\left(\dfrac{C_{\text{y0}} - C_{\text{y1}}}{C_{\text{y0}} - C_{\text{y2}}}\right) \cdot e^{K_1(m/V)^2(C_{\text{y1}} - C_{\text{y2}})t} - C_{\text{y1}}}{\left(\dfrac{C_{\text{y0}} - C_{\text{y1}}}{C_{\text{y0}} - C_{\text{y2}}}\right) \cdot e^{K_1(m/V)^2(C_{\text{y1}} - C_{\text{y2}})t} - 1}. \quad (12)$$

Analysis of solution (12) shows that at $t \to \infty$ the value $C_{\text{y}} = C_{\text{y2}}$. Since $C_{\text{y}}$ in each specific case, at different values of $C_{\text{p0}}$, $C_{\text{y0}}$ and $t \to \infty$ will tend toward the isothermal value, equal to $C_{\text{y2}}$, meaning that $C_{\text{y2}}$ should represent the isothermal point for the kinetics curve, and the collection of these points for different values of $C_{\text{p0}}$ will form the isothermal curve. Therefore, the dependence of $C_{\text{y2}}$ on the final equilibrium concentration of gold in the solution $C_{\text{p}}$, which can be obtained from the material balance equation, is the isotherm equation.

Returning to expression (9), it is evident that $C_{\text{y2}}$ depends on many parameters, including the initial gold concentration in the solution $C_{\text{p0}}$ its content in the regenerated carbon $C_{\text{y0}}$, as well as the mass loading of carbon $m/V$ in the adsorber volume. Since the isotherm equation must link $C_{\text{y2}}$ with the final equilibrium gold concentration in the solution $C_{\text{p}}$, from the material balance equation (5) for a given value of $C_{\text{y2}}$ we find the value of $C_{\text{p}}$.

Expressing $C_{\text{p0}}$ and $C_{\text{y0}}$ through the equilibrium values $C_{\text{y2}}$ and $C_{\text{p}}$ and substituting them into expression (9), after a series of elementary transformations, we obtain an equation linking $C_{\text{y2}}$ with $C_{\text{p}}$ and $m/V$:

$$C_{\text{y2}} = \frac{C_0 C_{\text{p}}\, m/V}{K_2/K_1 + C_{\text{p}}\, m/V}, \quad (13)$$

where $C_{\text{y2}}$ is the equilibrium gold content, mg/g; $C_0$ is the maximum adsorption capacity of the sorbent, mg/g; $C_{\text{p}}$ is the equilibrium gold concentration in the solution, mg/dm$^3$; $m$ is the mass of carbon, g; $V$ is the volume of solution, dm$^3$; $K_1$ is the adsorption rate constant, (dm$^3$)$^2$/(g·mg·h); $K_2$ is the desorption rate constant, h$^{-1}$.

Thus, the root $C_{\text{y2}}$ is the equilibrium isothermal gold content on the carbon for a given equilibrium gold concentration in the solution $C_{\text{p}}$, and these quantities are linked by equation (13), which is a modified Langmuir isotherm equation adjusted for carbon loading. That is, the Langmuir isotherm, as expected, is valid for adsorption in a closed volume. Considering expression (9), which directly links $C_{\text{y2}}$ with the initial parameters $C_{\text{p0}}$, $m$, $V$, and $C_{\text{y0}}$, note that there is a possibility of predictive determination of $C_{\text{y2}}$ under given initial conditions, which, in turn, allows finding the equilibrium gold concentration in the solution:

$$C_{\text{p}} = \frac{\dfrac{C_{\text{y2}}K_2}{K_1}\,\dfrac{V}{m}}{C_0 - C_{\text{y2}}}. \quad (13.1)$$

## 2. Results and discussion

### 2.1. Identification of the adsorption mathematical model based on experimental data: calculated and experimental kinetics and isotherm curves

The identification of the model coefficients was conducted using the isotherm equation (9) obtained from experimental isothermal values. The first approximation of the coefficients $K_{21}$ and $C_0$ was determined using the least squares method based on the linearized isotherm equation. The refinement or adjustment of the coefficients was performed iteratively based on the criterion of the sum of squares of deviations between the calculated and experimental isotherm values.

The identification of the isotherm (9), considering that $K_{21} = K_2/K_1$ is a constant value, allowed for the determination of the numerical values of the constants $K_{21} = 1.753$ g·mg/(dm$^3$)$^2$ и $C_0 = 56.996$ mg/g, which are valid over a wide range of varying internal operational parameters for adsorption kinetics: the initial gold concentration in the solution $C_{p0}$ and the mass of AC ($m$) loaded in the adsorber volume $V$: $3.2 < C_{p0} < 39.8$ mg/dm$^3$ и $0.5 < m/V < 50$ г/dm$^3$.

These parameter ranges cover the full spectrum of practically encountered scenarios for gold concentrations in solutions and AC loadings in adsorbers. The values of $K_{21}$ and $C_0$ for this specific type of AC are physical constants that do not need to be determined each time the technological parameters are changed. In contrast, the identification parameter $K_1$ depends on the internal operational conditions,

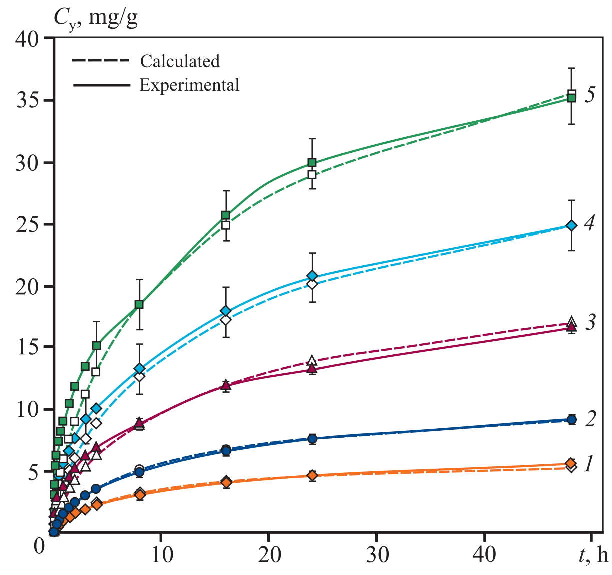

**Fig. 1.** Kinetic curves of $AuCN_2^-$ adsorption onto activated carbon at different initial gold concentrations in the solution and AC loading $m/V = 0.5$ g/dm$^3$ ($m = 1.5$ g, $V = 3$ dm$^3$)

***1*** – $C_{p0} = 3.2$, ***2*** – 5.9, ***3*** – 12.7, ***4*** – 21.6, ***5*** – 39.8 mg/ dm$^3$

**Рис. 1.** Кинетические кривые адсорбции $AuCN_2^-$ на активированном угле при различной начальной концентрации золота в растворе и загрузке АУ $m/V = 0{,}5$ г/дм$^3$ ($m = 1{,}5$ г, $V = 3$ дм$^3$)

***1*** – $C_{p0} = 3{,}2$, ***2*** – 5,9, ***3*** – 12,7, ***4*** – 21,6, ***5*** – 39,8 мг/дм$^3$

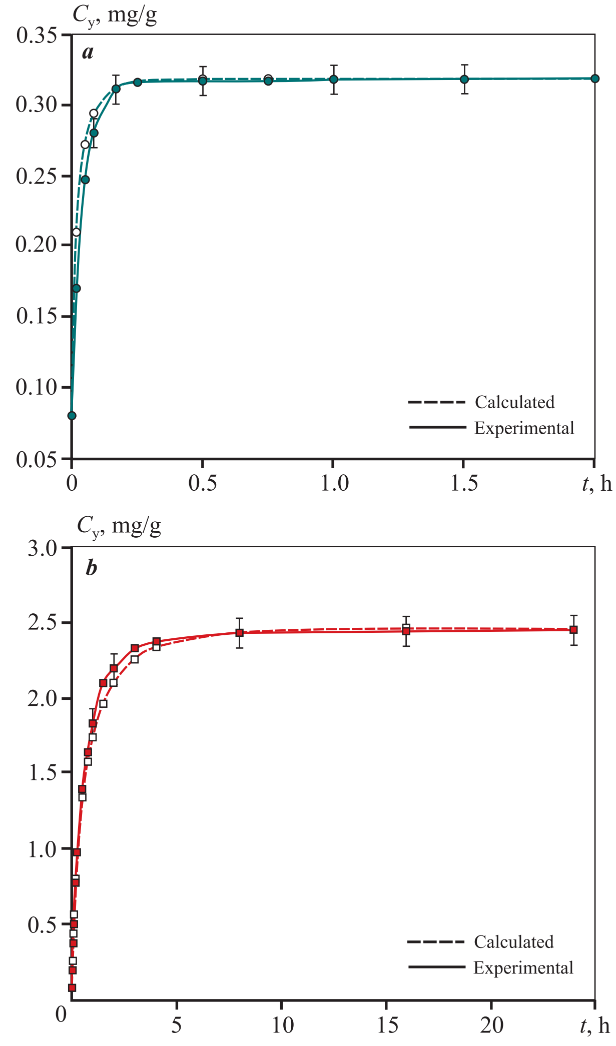

**Fig. 2.** Kinetic curves of $AuCN_2^-$ adsorption onto activated carbon at the initial gold concentration in solution $C_{p0} = 11.9$ mg/dm$^3$ and AC loading $m/V = 50$ g/dm$^3$ (***a***) and $m/V = 5$ g/dm$^3$ (***b***)

***a*** – $m = 75$ g, $V = 1.5$ dm$^3$; ***b*** – $m = 7.5$ g, $V = 1.5$ dm$^3$

**Рис. 2.** Кинетические кривые адсорбции $AuCN_2^-$ на АУ при начальной концентрации золота в растворе $C_{p0} = 11{,}9$ мг/дм$^3$ и загрузке АУ $m/V = 50$ г/дм$^3$ (***a***) и 5 г/дм$^3$ (***b***)

***a*** – $m = 75$ г, $V = 1{,}5$ дм$^3$; ***b*** – $m = 7{,}5$ г, $V = 1{,}5$ дм$^3$

and for solution (12) to be applicable in practical calculations, it is necessary to find the functional dependence of $K_1$ on $C_{\text{p}0}$ and $m/V$. Only in this case does expression (12) become a mathematical model with predictive properties that can be practically applied for calculating and optimizing the technological process of gold sorption from gold-cyanide solutions onto AC (Fig. 1 and 2).

During the identification of (12) based on the set of experimental kinetic curves obtained under various $C_{\text{p}0}$ and $m/V$, a functional dependence of $K_1$ on these parameters was found. Further computational studies showed that the constant $K_1$ depends not only on internal operational parameters but also on time: this dependence is inversely proportional to $\sqrt[3]{t}$. Considering this pattern, the final form of the functional dependence of $K_1$ on $C_{\text{p}0}$, $m/V$ and $t$ is as follows:

$$K_1 = \frac{K_{01}}{\sqrt[3]{C_{\text{p}0}\, m/V}\,\sqrt[3]{t}}, \tag{14}$$

where $K_{01} = 0.0098$ is the adsorption rate identification constant, independent of internal operational parameters and time.

The identification parameter $K_1$ in equation (14) is a functional dependence on operational factors and time. The coefficient $K_1$ is a part of $K_{01}$ as an identification constant, obtained from the collective values of $K_1$, during the identification of kinetic curves at different values of $C_{\text{p}0}$ and $m/V$. The time dependence is related not to time itself but to changes in the sorption conditions during the filling of the sorbent grains with the adsorbed metal.

## 2.2. Analysis of the modified isotherm equation under conditions of limiting transitions to Henry, Freundlich, and maximum adsorption isotherms

Analysis of equation (13) shows that at low values of $C_{\text{p}}$ and small carbon loadings $m/V$, we obtain a linear isotherm because in this case $K_2 >> K_1 C_{\text{p}}\, m/V$, and the terms $K_1 C_{\text{p}}\, m/V$ in the denominator can be neglected, resulting in:

$$C_{\text{y}} = \frac{K_1}{K_2} C_0 C_{\text{p}} \frac{m}{V}. \tag{15}$$

Considering that the adsorption and desorption rate constants ($K_1$ and $K_2$) depend not only on internal but also on external operational parameters, such as temperature and stirring speed, their temperature dependence, according to the Arrhenius equation, can be represented as:

$$K_1 = K'_{10}\, e^{\frac{-E_1}{RT}}, \tag{16}$$

$$K_2 = K'_{20}\, e^{\frac{-E_2}{RT}}, \tag{17}$$

where $K'_{10}$ and $K'_{20}$ are the pre-exponential factors for the adsorption and desorption rate constants, depending on internal operational parameters and stirring speed; $E_1$ and $E_2$ are the activation energies for adsorption and desorption, kcal/mol; $T$ is temperature, K; $R = 9872$ cal/(K·mol) is the universal molar gas constant.

Therefore,

$$\Gamma = \frac{K_{10}}{K_{20}}\, e^{\frac{-(E_1-E_2)}{RT}}\, C_0. \tag{18}$$

Taking this expression into account, equation (15) becomes a modified form of the Henry linear isotherm, considering the carbon loading ($m/V$), per unit solution volume, and in its final form, it will appear as follows:

$$C_{\text{y}} = \Gamma C_{\text{p}} \frac{m}{V}. \tag{19}$$

At large values of $C_{\text{p}}$ and $m/V$, when $K_1 C_{\text{p}}\, m/V >> K_2$, the term $K_2$ can be neglected. In this case, $C_{\text{y}}$ will approach the maximum equilibrium capacity of the adsorbent, i.e., $C_{\text{y}} \to C_0$. For moderate values of the product $C_{\text{p}} \cdot m/V$ within a relatively narrow range of varying gold concentrations in the solution and moderate carbon loading, the Langmuir isotherm can be approximated by the modified Freundlich isotherm [12]:

$$C_{\text{y}} = K\left(C_{\text{p}} \frac{m}{V}\right)^{\alpha}, \tag{20}$$

where α is the identification constant.

Thus, if at least one kinetic curve and an experimental adsorption isotherm are available, obtained over a sufficiently wide range of varying gold concentrations in the solution and AC loadings, then by identifying the isotherm (13) based on this data and solving the kinetics equation (3) or (12) using the constants $K_1$, $K_2$, and $C_0$ as identification coefficients, it is always possible to achieve the required accuracy in describing these curves by selecting appropriate values for $K_1$, $K_2$, $C_0$.

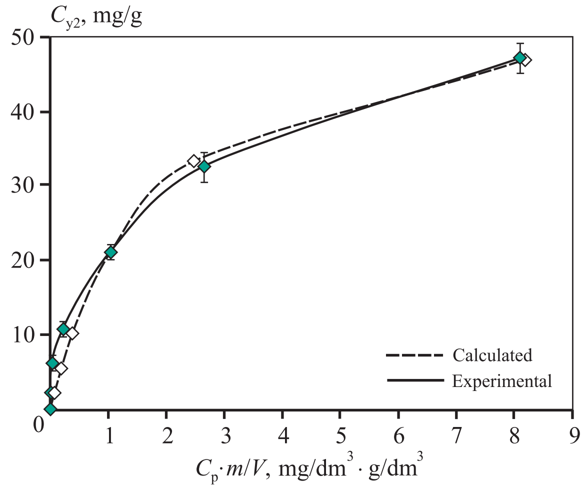

**Fig. 3.** Experimental and calculated adsorption isotherm according to formula (9)

**Рис. 3.** Экспериментальная и расчетная по формуле (9) изотермы адсорбции

When graphically representing the obtained modified isotherms (Fig. 3), the generalized parameter $C_{p0} \cdot m/V$ or $C_p \cdot m/V$ should be plotted along the x-axis. The found constants $K_1$, $K_2$, and $C_0$ can be used to calculate the equilibrium values of $C_{y2}$ and $C_p$, as well as the concentrations $C_y$ and $C_p$ for various time points within the same range of initial conditions where the experimental curves used for identification were obtained.

The same result can be achieved by identifying the solution (12) based on the points of the experimental kinetics curves of the adsorption process using these parameters. The solution (12), obtained within the framework of the proposed adsorption process kinetics equation operating in a closed volume, and its analysis, including the derivation of the modified Langmuir isotherm equation, demonstrate the adequacy of the theoretical justification for selecting the kinetics equation to the real process of gold adsorption from cyanide solutions onto AC.

## 2.3. Theoretical justification of the functional dependencies of adsorption and desorption rate constants on external operational factors and diffusion coefficient

In practice, adsorption proceeds through a multistage mechanism with successive periods where different stages limit the process [13—17]. Initially, the process is limited by convective mass transfer in the solution, and the process speed is entirely determined by the stirring rate of the solution. As the surface layer of the adsorbent becomes saturated with the target component, the process gradually transitions to the next stage, which is subsequently limited by the film-surface diffusion rate. According to the authors of works [1—3; 18], when the adsorbent reaches 40—60 % saturation, the process shifts to the intradiffusion stage, which is not reflected in equation (2), meaning this equation and its solution are valid only for the adsorption process during the first two stages, which corresponds well with experimental data.

Identifying solution (12), which represents a theoretical kinetic curve derived from the points of experimental kinetic curves using three identification coefficients $K_1$, $K_2$, and $C_0$, provides calculated kinetic curves that nearly coincide with experimental ones within the accuracy limits of the experiments (see Fig. 1 and 2). The graphs of the kinetics indicate the confidence interval for the points of experimental values, calculated with a reliability of $P = 0.95$; the accuracy ranges for different gold concentrations in the solution are provided above in the “Research Methodology” section.

The identification coefficients have clear physical meaning and can be further experimentally studied to reveal their functional dependence not only on the internal operational parameters established by us but also on various external conditions and internal characteristics of the adsorbent, as they represent integral characteristics. The influence of stirring speed and temperature on the values of $K_1$, $K_2$ can be determined based on general theoretical concepts.

The adsorption and desorption rate constants ($K_1$, $K_2$) depend on external operational parameters — stirring speed $\vartheta$ and temperature $T$ — as well as on the internal characteristic of the adsorbent—diffusion coefficient ($D$). The general functional structure of these constants, depending on external conditions considering the temperature dependence based on the Arrhenius equation [19] and the internal characteristic—diffusion coefficient, can be represented as follows:

$$K_1 = K_{10} f(\beta, D) e^{\frac{-E_1}{RT}}, \tag{21}$$

$$K_2 = K_{20} f(\beta, D) e^{\frac{-E_2}{RT}}, \tag{22}$$

where $K_{10}$ and $K_{20}$ are identification parameters that do not depend on external operational parameters and the diffusion coefficient but depend on the internal operational parameters $C_{p0}$ and $m/V$; $f(\beta, D)$ is the generalized mass transfer coefficient in the adsorption process —

a function depending on $\beta$ and $D$; $\beta$ is the convective mass transfer coefficient, directly proportional to the stirring speed $\vartheta$ as $\beta = \alpha\vartheta$; $D$ is the generalized coefficient of film-surface diffusion of gold in AC.

The unit act of mass transfer of the gold cyanide complex from the solution to AC consists of two sequentially occurring processes. The first is mass transfer within the solution volume from areas of current concentration $\vartheta$ to areas of depleted concentration, i.e., directly to the adsorption surface of the carbon granules. The rate of this process entirely depends on the solution stirring rate $C_{\text{p}}$ and represents convective mass transfer. The second process is film and diffusion mass transfer in the near-surface thin layer of the carbon granules, i.e., in the macro- and micropores of the adsorbent. The overall result of the sequential micro-processes occurring within the solution volume and on the surface of the carbon adsorbent granules during mass transfer can be approximately represented as a mass exchange process depending on a certain generalized mass transfer coefficient ($K$), inverse to the total mass transfer resistance ($r$). This coefficient depends both on the stirring conditions of the solution and the physicochemical characteristics of the carbon adsorbent.

It is known that mass transfer resistance in sequential processes follows the law of additive resistances for mass exchange processes [20]. Considering this, we can write the expression for the total mass transfer resistance ($r$) in the adsorption process. We assume that the convective $r_{\text{к}}$ and diffusion $r_{\text{д}}$ resistances are expressed by formulas inversely dependent on the convective ($\beta$) and diffusion ($D$) mass transfer coefficients:

$$r_{\text{к}} = \frac{1}{\beta}, \tag{23}$$

$$r_{\text{д}} = \frac{1}{D}. \tag{24}$$

The total resistance for sequential mass transfer processes, according to the law of additive resistances, will be equal to:

$$r = r_{\text{к}} + r_{\text{д}} = \frac{1}{\beta} + \frac{1}{D}. \tag{25}$$

Therefore, the expression for the generalized mass transfer coefficient will have the form:

$$K = \frac{1}{r} = \frac{\beta D}{\beta + D}. \tag{26}$$

Since $\beta = \alpha\vartheta$, we can finally write:

$$K = \frac{\alpha\,\vartheta\,D}{\alpha\,\vartheta + D}. \tag{27}$$

The sought function $f(\beta, D)$ is the generalized mass transfer coefficient, i.e., $K = f(\beta, D)$. Considering the obtained relationships, the rate constants $K_1$ and $K_2$ are described by the following equations:

$$K_1 = K_{10}\frac{\alpha\vartheta D}{\alpha\vartheta + D}\, e^{\frac{-E_1}{RT}}, \tag{28}$$

$$K_2 = K_{20}\frac{\alpha\vartheta D}{\alpha\vartheta + D}\, e^{\frac{-E_2}{RT}}. \tag{29}$$

The presented expressions (28), (29) reflect one of the fundamental patterns of adsorption processes, namely the proportional, or linear, dependence of the adsorption process rate on the stirring speed. As it increases (at low values), the adsorption rate increases proportionally, with the kinetic curve rising linearly. At a moderate stirring speed, its increase leads to a nonlinear change in the adsorption process rate, expressed by a bending of the kinetic curve and its gradual flattening. At higher stirring speeds, the adsorption process rate stops increasing, characterized by the curve reaching a plateau.

This is partly related to the concept of limiting stages of the adsorption process — either the convective mass transfer stage, if the adsorption rate depends on the stirring speed, or the surface (film) mass transfer stage, or purely intradiffusion stage [20—22].

Another important factor that confirms the validity of the obtained expressions for the constants $K_1$ and $K_2$ is that the kinetic parameters $\beta$ and $D$ are incorporated into the constants $K_1$ and $K_2$ in such a way that in the isotherm equation (9), they mutually cancel out and do not affect the behavior of the isotherm curve, which is fully consistent with the theoretical concepts of isothermal equilibrium states.

## Conclusion

Based on the theoretical concepts of the adsorption mechanism of $\text{AuCN}_2^-$ from cyanide solutions onto activated carbon, a third-order adsorption kinetics equation was proposed, taking into account the loading of activated carbon per unit volume of solution. This allowed for the derivation of adequate analytical solutions not only for the kinetics but also for the adsorption isotherm. The resulting isotherm equation is derived from the solution of the kinetics equation, enabling the calculation of equilibrium isothermal values $C_{\text{y}}$ and $C_{\text{p}}$ for various initial parameters $C_{\text{y}0}$, $C_{\text{p}0}$, $m$, and $V$. The developed mathematical model allows for the determination of standardized physical constants $C_0$ and $K_{21}$ based on experimental adsorption isotherm data for different types of carbon under standard conditions.

The theoretical justification for the functional dependencies of the physical constants of adsorption and desorption rates on external operational parameters (such as temperature and stirring speed) and the internal physicochemical characteristics of the adsorbent (such as the diffusion coefficient) has been presented. The obtained results can be used for practical calculations in optimizing the technological process of gold adsorption from cyanide solutions, provided the contact time between the carbon adsorbent and the cyanide solution does not exceed 2 days.

## References

1. Nicol M. J., Fleming C. A., Cromberge G. The absorption of gold cyanide onto activated carbon. I. The kinetics of absorption from pulps. *Journal of the Southern African Institute of Mining and Metallurgy*. 1984; 84 (2):50—54.
2. Nicol M. J., Fleming C. A., Cromberge G. The absorption of gold cyanide onto activated carbon. II. Application of the kinetic model to multistage absorption circuits. *Journal of the Southern African Institute of Mining and Metallurgy*. 1984; 84 (3):70—78.
3. Nicol M. J., Fleming C. A. The absorption of gold cyanide onto activated carbon. III. Factors influencing the rate of loading and the equilibrium. *Journal of the Southern African Institute of Mining and Metallurgy*. 1984;84(4):85—93.
4. Vegter N.M. The distribution of gold in activated carbon during adsorption from cyanide solutions. *Hydrometallurgy*. 1992; 30(1-3):229—242. https://doi.org/10.1016/0304-386X(92)90086-F
5. Jinsong X., Rajashekhar M., Twinney J., Ghahreman A. A review on adsorption mechanism of gold cyanide complex onto activation carbon. *Journal of Industrial and Engineering Chemistry*. 2022;111:35—42. https://doi.org/10.1016/j.jiec.2022.04.014
6. Buah W. K., Darmey J. and Osei F. Effects of maturity of coconut shells on gold adsorption efficiencies of derived activated carbons. *Ghana Mining Journal*. 2019;19(2): 50—54. https://doi.org/10.4314/gm.v19i2.7
7. Khosravi R., Azizi A., Ghaedrahmati R., Gupta V.K, Agarwal S. Adsorption of gold from cyanide leaching solution onto activated carbon originating from coconut shell — Optimization, kinetics and equilibrium studies. *Journal of Industrial and Engineering Chemistry*. 2017;54:464—471. http://dx.doi.org/10.1016/j.jiec.2017.06.036
8. Efremova S.V., Kablanbekov A.A., Anarbekov K.K., Bunchuk L.V., Sukharnikov Y.I., Bogdanovich N.I., Terlikbaeva A.Z., Zharmenov A.A. Carbon sorbent based on special fine coke for the extraction of gold. *Solid Fuel Chemistry*. 2019; 53(4):18—25. (In Russ.). https://doi.org/10.1134/S0023117719040066
   Ефремова С.В., Кабланбеков А.А., Анарбеков К.К., Бунчук Л.В., Сухарников Ю.И., Богданович Н.И., Терликбаева А.Ж., Жарменов А.А. Углеродный сорбент на основе мелочи спецкокса для извлечения золота для извлечения золота. *Химия твердого топлива*. 2019;53(4):18—25. https://doi.org/10.1134/S0023117719040066
9. Larin A.V. Material balance equations and their solutions in linear adsorption dynamics. *Protection of Metals and Physical Chemistry of Surfaces*. 2022;58(1):3—7 (In Russ.). https://doi.org/10.31857/S0044185622010132
   Ларин А.В. Уравнения материального баланса и их решения в линейной динамике адсорбции. *Физикохимия поверхности и защита материалов*. 2022;58(1): 3—7. https://doi.org/10.31857/S0044185622010132
10. Elshin V.V., Kolodin A.A., Ovsyukov A.E. Measurement of gold concentration in cyanide solutions. *Vestnik Irkutskogo gosudarstvennogo tekhnicheskogo universiteta*. 2010;5(45):187—194. (In Russ.). https://www.elibrary.ru/item.asp?id=15255131
    Ёлшин В.В., Колодин А.А., Овсюков А.Е. Измерение концентрации золота в цианистых растворах. *Вестник Иркутского государственного технического университета*. 2010;5(45):187—194. https://www.elibrary.ru/item.asp?id=15255131
11. Kamke E. Differentialgleichungen. Leipzig: Akademische Veragsgesellschaft Geest & Portig K.-G., 1962. 336 p.
12. Adamson A. Physical chemistry of surfaces. New York: Wiley, 1976. 698 p.
13. Jianping J., Yuexin H., Hui L., Yangyang H., Yongjun P., Xiaotian G., Wei Y. Mineral phase and structure changes during roasting of fine-grained carbonaceous gold ores and their effects on gold leaching efficiency. *Chinese Journal of Chemical Engineering*. 2019;27(5):1184—1190. https://doi.org/10.1016/j.cjche.2018.08.006
14. Lobanov V.G., Timofeev E.I.. Development and implementation of modern technology of cyanide leaching of gold from gravity concentrates. *Metallurg*. 2017;(6):75—79. (In Russ.). https://doi.org/10.1007/s11015-017-0522-9
    Лобанов В.Г., Тимофеев Е.И. Разработка и внедрение современной технологии цианистого выщелачивания золота из гравитационных концентратов. *Металлург*. 2017;(6):75—79. https://doi.org/10.1007/s11015-017-0522-9
15. Schwaab M., Steffani E., Barbosa-Coutinho E., Severo Júnior J.B.. Critical analysis of adsorption/diffusion

modelling as a function of time square root. *Chemical Engineering Science*. 2017;173:179—186.
https://doi.org/10.1016/j.ces.2017.07.037

16. McLaughlin J., Agar G.E. Development and application of a first order rate equation for modelling the dissolution of gold in cyanide solution. *Minerals Engineering*. 1991;4(12):1305—1314.
https://doi.org/10.1016/0892-6875(91)90174-T
17. Voiloshnikov G.I., Murashova O.N., Byvaltsev A.V. Mathematical modeling and optimization of the countercurrent sorption process of gold extraction. *Vestnik Irkutskogo gosudarstvennogo tekhnicheskogo universiteta*. 2010;6(46):183—188. (In Russ.).
https://www.elibrary.ru/item.asp?id=15486093
Войлошников Г.И., Мурашова О.Н., Бывальцев А.В. Математическое моделирование и оптимизация противоточного сорбционного процесса извлечения золота. *Вестник Иркутского государственного технического университета*. 2010; 6(46):183—188.
https://www.elibrary.ru/item.asp?id=15486093
18. Chu K.H. Extracting surface diffusion coefficients from batch adsorption measurement data: application of the classic Langmuir kinetics model. *Environmental Technology*. 2017;40(5):543—552.
https://doi.org/10.1080/09593330.2017.1397767
19. Stiller W. Arrhenius equation and non-equilibrium kinetics: 100 years Arrhenius equation. Leipzig: BSB B.G. Teubner, 1989. 160 p.
20. Ibragimova R.I., Grebennikov S.F., Guryanov V.V., Fedyukevich V.A., Vorobyev-Desyatovsky N.V. Effect of the porous structure of activated carbon on the adsorption kinetics of gold (I) cyanide complex. *Russian Journal of Physical Chemistry A*. 2014;88(2):1052—1057.
https://doi.org/10.7868/S0044453714060168
Ибрагимова Р.И., Гребенников С.Ф., Гурьянов В.В., Федюкевич В.А., Воробъев-Десятовский Н.В. Влияние пористой структуры активированного угля на кинетику адсорбции цианидного комплекса золота (I). *Журнал Физической химии*. 2014;88(2):1052—1057.
https://doi.org/10.7868/S0044453714060168
21. Inglezakis V.J., Fyrillas M.M., Park J. Variable diffusivity homogeneous surface diffusion model and analysis of merits and fallacies of simplified adsorption kinetics equations. *Journal of Hazardous Materials*. 2019;367:224—245.
http://dx.doi.org/10.1016/j.jhazmat.2018.12.023
22. Tukmakov D.A. Mathematical model of non-stationary sorption in a two-phase medium taking into account the spatial unequality of the distribution of the micro-component concentration distribution in the sorbent phase. *Vestnik Tverskogo gosudarstvennogo universiteta. Seriya Khimiya*. 2019;38(4):26—35. (In Russ.).
https://doi.org/10.26456/vtchem2019.4.3
Тукмаков Д.А. Математическая модель нестационарной сорбции в двухфазной среде, учитывающая пространственную неравномерность распределения концентрации микрокомпонента в фазе сорбента. *Вестник ТвГУ. Серия Химия*. 2019;38(4):26—35.
https://doi.org/10.26456/vtchem2019.4.3

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**A.P. Mironov** – processed the experimental data, contributed to manuscript writing, and participated in the discussion of the results.

**A.A. Lisitsyna** – performed mathematical processing of the experimental data, contributed to manuscript writing, and participated in the discussion of the results.

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