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Research article
Научная статья

Theoretical and experimental justification of kinetic and isotherm equations for gold adsorption from solutions onto activated carbon considering intraparticle mass transfer

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Abstract: This study continues the research presented in our previous article [1], which examined the process of gold adsorption from gold cyanide solutions onto activated carbon (AC) over a relatively short time interval – up to 40 h – during which adsorption occurred predominantly within the near-surface layer of the sorbent. The aim of the present work was to improve the previously developed mathematical model of gold adsorption onto activated carbon from gold cyanide solutions [1] by incorporating the intraparticle mass transfer stage into the model. This goal was achieved by adding an additional term to the adsorption kinetics equation that accounts for gold sorption driven by intraparticle mass transfer. This modification preserved the entire theoretical framework of adsorption described by the earlier kinetics equation, incorporating it as a special case within a more general sorption model based on the improved kinetics equation. An analytical solution to the modified equation was derived, from which a new-type adsorption isotherm was obtained in analytical form. The paper presents the derivation and analysis of this new-type isotherm equation and its identification based on experimental data.

Keywords: gold, kinetics, adsorption, activated carbon (AC), adsorption isotherm, cyanide solution, intraparticle mass transfer rate constant, mathematical modeling.

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Теоретическое и экспериментальное обоснование уравнений кинетики и изотермы сорбции золота из растворов на активированный уголь с учетом внутридиффузионного массопереноса

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Аннотация: Настоящая работа является продолжением предыдущей статьи [1], в которой рассматривался процесс адсорбции золота из золотоцианистых растворов на активированный уголь (АУ) в течение относительно короткого отрезка времени –

до 40 ч. При этом процесс адсорбции протекал в тонком приповерхностном слое сорбента. Целью данного исследования являлось усовершенствование разработанной нами ранее математической модели адсорбции золота на активированный уголь из золотоцианистых растворов [1] в направлении учета в ней внутридиффузионной стадии массопереноса золота. Поставленная задача была достигнута путем включения в уравнение кинетики адсорбции еще одного члена, описывающего сорбцию золота за счет внутридиффузионного массопереноса. Такая модернизация уравнения кинетики позволила полностью сохранить всю теорию адсорбции, описываемую предыдущим уравнением кинетики, и включить ее как частный случай в более общую теорию сорбции с учетом усовершенствованного уравнения кинетики. Получено аналитическое решение предложенного уравнения, из которого аналитически выводится изотерма нового типа. Приведены вывод и анализ уравнения изотермы нового типа, а также выполнена идентификация по экспериментальным данным.

Ключевые слова: золото, кинетика, сорбция, активированный уголь (АУ), изотерма сорбции, цианистый раствор, константа скорости внутридиффузионного массопереноса, математическое моделирование.

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Introduction

A significant increase in the duration of gold adsorption from two days or more — as well as the loading of activated carbon (AC) beyond 40—60 % of its total maximum gold capacity, causes the process kinetics to shift toward a stage limited by intraparticle mass transfer[1] [1]. Accordingly, it becomes necessary to derive a new kinetic equation for the adsorption of gold from gold cyanide solutions onto activated carbon, taking into account this limiting factor. The resulting solution must adequately describe the process kinetics both at the near-surface adsorption stage and as it transitions into the stage governed by intraparticle mass transfer. Additionally, the analytical solution should allow for the derivation of the adsorption isotherm equation. oth the kinetic and isotherm equations must be identified using experimental adsorption kinetic curves and isotherm data, based on four physical constants introduced during the development of the kinetic model. These constants, whose numerical values are determined during the identification procedure, must be linked to the specific ionic composition of the solution and to a particular grade of activated carbon. Once identified, they will serve as physical constants under the given conditions and may be used for predictive calculations of both equilibrium adsorption values and kinetic parameters under conditions matching those of the experimental data. The identification of the kinetic equation solution using experimental curves should reveal how the fourth model parameter depends not only on the initial gold concentration in the solution and the AC loading in the adsorption column volume, but also on the time-varying conditions of intraparticle mass transfer during the adsorption process.

The main objective of this study was to develop a mathematical model of gold adsorption from gold cyanide solutions onto activated carbon that would reliably describe the process under various initial gold concentrations and AC loadings in the closed volume of an adsorption column. A key indicator of the model's validity is that the adsorption isotherm equation was derived analytically from the solution of the adsorption kinetics equation. As the results presented here show good agreement with experimental data, they can be applied in practical calculations for countercurrent industrial adsorption process flowsheets using activated carbon, provided the specific operating conditions are taken into account.

The developed mathematical model was identified based on experimental data obtained at the Irgiredmet Research Institute (Russia), using standard methodologies for investigating the kinetics of gold adsorption from synthetically prepared gold cyanide solutions onto regenerated activated carbon of the NORIT-3515 grade.

Research methodology

The adsorption isotherm of gold onto activated carbon of the NORIT-3515 grade was determined using the static method with constant AC mass of 1.5 g and varying gold concentrations ranging from 3.2 to 39.8 mg/dm^3 in gold cyanide solutions containing 176.0 mg/dm^3 NaCN (pH = 10.8). The temperature of

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[1] Termed *intradiffusion* in the authors' earlier work [1]; here, *intraparticle mass transfer* is used to reflect a broader mechanism.

the solutions during the experiments was maintained within the range of 20—22 °C. The adsorber was a cylindrical vessel made of organic glass with a flat bottom, equipped with a stirrer and rotation speed controller, which ensured uniform suspension of the adsorbent throughout the entire volume of the solution [1]. The height-to-diameter ratio of the adsorber was 2.5:1.0. The solution volume for each experiment was 3 dm^3, and the total time required to achieve one equilibrium isotherm value was 216 h. At predetermined time intervals from the start of the experiment, samples were collected to construct the kinetic curves.

The gold concentration in the solutions was measured using an ICE 3300 atomic absorption spectrophotometer (Thermo Fisher Scientific, USA) at the certified analytical center of Irgiredmet OJSC [1]

Theoretical basis for selecting the form of the adsorption kinetics equation considering intraparticle mass transfer (intradiffusion), its solution, and derivation of the isotherm equation

The theoretical concepts of gold adsorption kinetics onto activated carbon presented earlier [1] remain valid at low degrees of AC particle saturation, when $Au(CN)_2^-$ is primarily concentrated within a thin near-surface shell of the adsorbent granule, with a thickness not exceeding 20 % of the particle's effective radius. Under these conditions, the adsorption kinetics are adequately described by Equation (1), while the adsorption isotherm is described by a modified Langmuir equation (2):

$$\frac{dC_\text{y}}{dt} = K_1(C_0 - C_\text{y})\left(\frac{m}{V}C_\text{p}\right) - K_2C_\text{y}, \qquad (1)$$

$$C_{\text{y}2} = \frac{C_0\, m/VC_\text{p}}{K_2/K_1 + C_\text{p}\, m/V}, \qquad (2)$$

where C_y is the gold content in 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 adsorbent, mg/g; K_1 is the adsorption rate constant, dm^3/(mg·h); K_2 is the desorption rate constant, h^{-1}; m is the carbon mass, g; V is the solution volume, dm^3; t is time, h; $C_{\text{y}2}$ is the equilibrium gold content in the carbon for a given equilibrium gold concentration (C_p), mg/dm^3.

However, under practical conditions, as demonstrated by experiments conducted by researchers at the Irgiredmet Research Institute using standard methodologies for synthetically prepared gold cyanide solutions with regenerated NORIT-3515 activated carbon as the adsorbent (Figs. 1—3), an increase in the duration of the adsorption process from 40—50 h to 200 h or more results in two notable effects. First, the gold content in the carbon continues to increase while gold remains in the cyanide solution at a concentration exceeding the equilibrium value C_p, as defined by isotherm (2). Second, the shape of the experimental kinetic curve changes in such a way that it can no longer be adequately described by Equation (1). A theoretical explanation for this phenomenon becomes possible if we adopt the hypothesis that the rate-limiting stage of gold adsorption shifts to intraparticle mass transfer from the near-surface layer into the interior of the adsorbent particle. This stage is characterized by the inward movement of a spherical adsorption front within the particle — that is, from the outer surface toward the center of the granule [2; 3]. In this interpretation, the value C_0 acquires the meaning of the total ultimate gold content per unit mass of activated carbon. Practically, this means that in a fully saturated adsorbent granule, where the adsorption front has reached the center, the local gold content throughout the particle volume equals C_0. Assuming that within the region already traversed by the adsorption front in the adsorbent granule, the gold content is equal to C_0, the current gold content in the carbon (C_y) can, with sufficient accuracy, be determined by the following expression:

$$C_\text{y} = \frac{C_0V_{\text{дз}}}{V_\text{з}} = \frac{C_0\left(\frac{4}{3}\pi R^3 - \frac{4}{3}\pi r^3\right)}{\frac{4}{3}\pi R^3} = C_0\left(1 - \frac{r^3}{R^3}\right), \qquad (3)$$

where $V_{\text{дз}}$ is the volume of the adsorbent particle saturated with gold; $V_\text{з}$ is the total volume of the adsorbent particle; R is the adsorbent average particle radius; r is the radius of the central core not yet saturated with gold.

To account for intraparticle mass transfer, it is necessary to introduce an additional term into the kinetics equation (1), which should adequately reflect the kinetics of internal gold transport within the adsorbent. According to the law of mass action, this term must be proportional to the product of the current gold content in the carbon (C_y) and the concentration of active sites in the adsorbent that are still free of gold, expressed as ($C_0 - C_\text{y}$). This assumption holds true if we accept the premise that the adsorption front is diffuse under real conditions — that is, its boundary extends over a finite thickness, within which a concentration gradient of adsorbed $Au(CN)_2^-$ ions is formed along the radius of the adsorbent particle. If the adsorption front had a sharply defined spherical boundary, the factor C_y would appear with an exponent of 2/3, reflecting its proportionality to the surface area of a sphere. In such a case, only those adsorbed $Au(CN)_2^-$ ions located at the boundary of the spherical adsorption front would interact with the remaining active sites. The number of these ions would be proportional to the surface area of the spherical front. Numerical simulations confirmed the validity of the assumption regarding the diffuseness of the adsorption front.

Taking this into account, the kinetics equation takes the following form:

$$\frac{dC_y}{dt} = K_1(C_0 - C_y)\frac{m}{V}C_p - K_2C_y + K_3(C_0 - C_y)C_y, \quad (4)$$

where K_3 is the rate constant of intraparticle mass transfer, s^{-1}.

Using the material balance equation for a closed system:

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

after simple transformations, the kinetics equation (4) can be reduced to a mass-action-type equation with a known solution [4]:

$$C_y = \frac{C_{y2}\left(\frac{C_{y0} - C_{y1}}{C_{y0} - C_{y2}}\right)\exp\left\{K_3\left[K_{13}\left(\frac{m}{V}\right)^2 - 1\right](C_{y1} - C_{y2})t\right\} - C_{y1}}{\left(\frac{C_{y0} - C_{y1}}{C_{y0} - C_{y2}}\right)\exp\left\{K_3\left[K_{13}\left(\frac{m}{V}\right)^2 - 1\right](C_{y1} - C_{y2})t\right\} - 1}, \quad (6)$$

$$C_{y1} = \frac{-b + \sqrt{b^2 - 4ac}}{2a}, \quad (7)$$

$$C_{y2} = \frac{-b - \sqrt{b^2 - 4ac}}{2a}, \quad (8)$$

$$a = K_{13}\left(\frac{m}{V}\right)^2 - 1, \quad (9)$$

$$b = -\left[K_{13}\frac{m}{V}\left(\frac{m}{V}C_0 + C_{p0} + \frac{m}{V}C_{y0}\right) + K_{23} - C_0\right], \quad (10)$$

$$c = K_{13}\frac{m}{V}C_0\left(C_{p0} + \frac{m}{V}C_{y0}\right). \quad (11)$$

Here, $K_{13} = K_1/K_3$ and $K_{23} = K_2/K_3$ — are the equilibrium constants of adsorption and desorption, respectively, with reference to the rate-limiting stage of the process — intraparticle mass transfer.

The coefficients K_{13}, K_{23}, and C_0 are true identification constants whose values are determined by fitting the isotherm equation (8) to experimental data obtained over a wide range of C_{p0} and m/V. This isotherm is of a new type, as it does not correspond to any of the known isotherm models. It establishes a relationship between the equilibrium values of C_{y2} and the initial process parameters — C_{p0}, C_{y0}, m, and V — in a closed system. The identification coefficients K_{13}, K_{23}, and C_0 can be regarded as physical constants that are specific to the adsorption conditions and the type of adsorbent used. The constant C_0 represents the total ultimate adsorption capacity of the activated carbon. The identification parameter K_3 defines the rate constant of intraparticle mass transfer. This parameter varies over time, and its change reflects the dependence of the mass transfer rate on the degree of gold saturation within the adsorbent particles. Furthermore, K_3 is also influenced by the initial gold concentration in the solution (C_{p0}) and the activated carbon loading (m/V) n the solution volume of the adsorption column. Therefore, K_3 is an identification parameter whose functional dependence on C_{p0}, m/V, and time t must be determined through numerical simulations and theoretical analysis, supported by experimental data.

The solution presented in Equation (6) has a notable property: as the adsorption time tends toward infinity, it approaches a limiting equilibrium value C_{y2}. This means that C_{y2} represents the equilibrium gold loading on the activated carbon (C_y) that is inherently contained in the solution to the kinetic Equation (6). Alternatively, C_{y2} может быть найдено исходя из заданных начальных условий по выражению (8), which defines an adsorption isotherm of a new type. This equation enables the calculation of equilibrium values of C_y based on the known identification constants K_{13}, K_{23}, and C_0, as well as the specified initial values C_{y0}, C_{p0}, m, and V, under batch adsorption conditions in a closed system. y combining Equation (8) with the material balance equation (5), an isotherm equation is readily derived that describes the relationship between the equilibrium gold loading on the carbon ($C_y = C_{y2}$) and the corresponding equilibrium gold concentration in the solution (C_p):

$$C_{y2} = \frac{-(K_{13}\, m/VC_p + K_{23} - C_0) - \sqrt{(K_{13}\, m/VC_p + K_{23} - C_0)^2 + 4K_{13}C_0C_p\, m/V}}{2}. \quad (12)$$

From this, the inverse isotherm can be obtained:

$$C_p = \frac{C_{y2}^2 + C_{y2}(K_{23} - C_0)}{K_{13}\, m/V\,(C_0 - C_{y2})}. \quad (13)$$

Here, C_{y2} is calculated using Equation (8), in combination with Equations (9)—(11). Thus, both equilibrium gold loading C_y and equilibrium solution concentration C_p an be predicted in advance for any given combination of initial process parameters C_{p0}, C_{y0}, m, and V, provided that the identification constants K_{13}, K_{23}, and C_0 are known.

Identification of the mathematical model for gold adsorption dynamics onto activated carbon based on experimental kinetic curves and the adsorption isotherm

The isotherm derived in Equation (8) was identified using the initial parameters C_{p0}, C_{y0}, m, and V, and along with Equation (12), based on experimental data for the equilibrium concentration C_p . This yielded the following constants [5]: $K_{13} = 8.004$, $K_{23} = 83.519$, and $C_0 = 82.632$. These values may be considered reference characteristics for the investigated activated carbon grade (NORIT-3515) and the specified experimental conditions.

Subsequent identification of the solution to the kinetic Equation (6), with respect to the identification parameter K_3 and experimental kinetic curves, was performed using theoretical concepts of the gold adsorption process on activated carbon [6—12] and analysis of the experimental data. As a first approximation, a functional expression was obtained for K_3, allowing its dependence to be considered as a function of the degree of gold saturation in the activated carbon particles and, consequently, on the process time (t), the initial gold concentration in the solution (C_{p0}), and the carbon loading per unit solution volume (m/V). For adequately determine the time dependence of K_3, an important requirement is that the adsorption process must proceed continuously during the kinetic experiments on gold adsorption onto activated carbon:

$$K_3 = \frac{K_{03}}{\sqrt[3]{C_{p0}\dfrac{m}{V}}\,t^{\frac{1}{3}}}, \qquad (14)$$

where $K_{03} = 0.00073$ is true identification constant for the intraparticle mass transfer rate. This constant is independent of both process parameters and time.

Expression (8) and the resulting isotherm (12) represent a new type of adsorption isotherm that relates the equilibrium values of C_y to the initial values of the process parameters C_{p0} and m/V in closed systems. This differs from classical isotherms, which relate the equilibrium values of C_p and C_y, equiring one of the parameters to be determined experimentally. Together, isotherms (8) and (12), in combination with the kinetic Equation (6), provide an adequate description of both the equilibrium gold loading on activated carbon under any initial concentration in solution and the kinetics of the gold adsorption process at extended contact times and a broad range of carbon loadings (m/V).

For brevity, the newly introduced isotherm model — represented by Equation (8) together with the intermediate Equations (9)—(11), and its derivative form Equation (12) — will hereafter be referred to as the "MEGA isotherm" [13]. Notably, the MEGA isotherm expression excludes all kinetic parameters that were previously required to describe the process dynamics, including the coefficient K_3, which depends on the degree of gold saturation in activated carbon particles and, therefore, on the adsorption time t. Moreover, K_3 is also a function of the initial gold concentration in the solution and the carbon loading (m/V) per unit volume of the adsorption apparatus or process stage.

The identified constants K_{13}, K_{23}, and C_0, as well as the functional dependence of K_{13} on C_{p0}, m/V , and t, allow for an accurate description of both the adsorption kinetics (Figs. 1 and 2) and the adsorption isotherm (Fig. 3) of gold from gold cyanide solutions onto activated carbon (see table). The kinetic and isotherm plots include confidence intervals for the experimen-

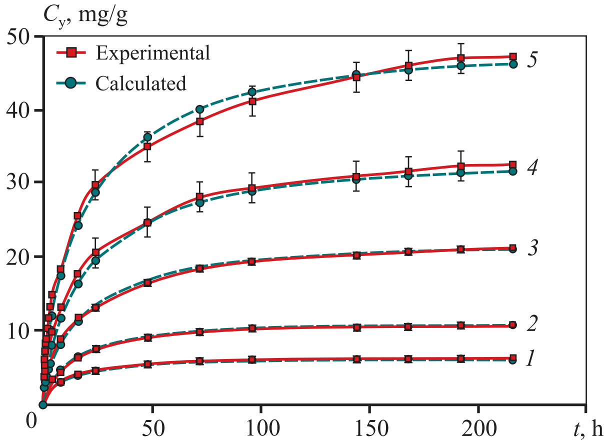

Fig. 1. Kinetic curves of $Au(CN)_2^-$ adsorption onto activated carbon at different initial gold concentrations in the solution and different AC loadings $m/V = 0.5$ g/dm^3 ($m = 1.5$ g, $V = 3$ dm^3)

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 $Au(CN)_2^-$ 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

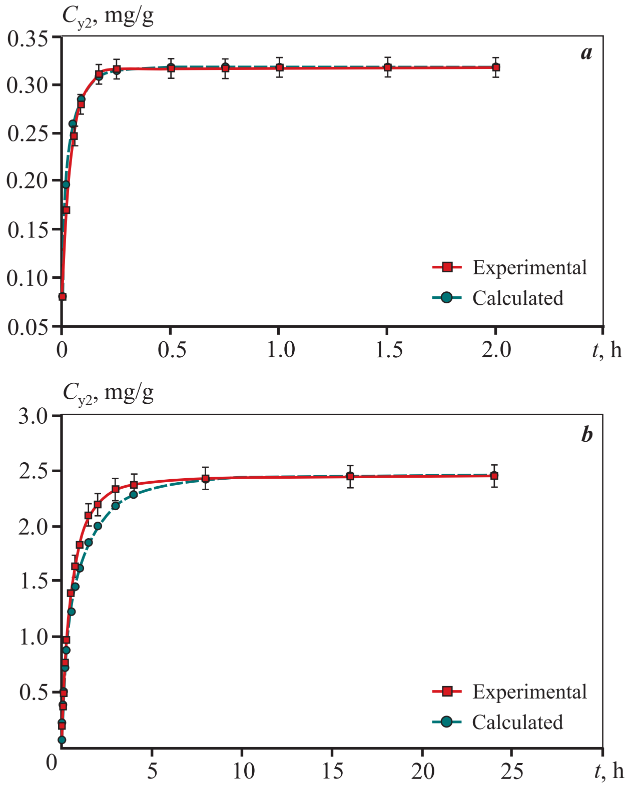

Fig. 2. Kinetic curves of Au(CN)$_2^-$ adsorption onto activated carbon at an initial gold concentration in the solution C_{p0} = 11.9 mg/dm^3 and carbon loading m/V = 50 g/dm^3 (m = 75 g, V = 1.5 dm^3) (***a***) and 5 g/dm^3 (m = 7,5 g, V = 1,5 dm^3) (***b***)

Рис. 2. Кинетические кривые адсорбции Au(CN)$_2^-$ на АУ при начальной концентрации золота в растворе C_{p0} = 11,9 мг/дм^3 и загрузке АУ m/V = 50 г/дм^3 (m = 75 г, V = 1,5 дм^3) (***a***) и 5 г/дм^3 (m = 7,5 г, V = 1,5 дм^3) (***b***)

tal data points, calculated at a confidence level of $P = 0.95$ [1].

The degree of agreement between the calculated results and the experimental data confirms that the applied physicochemical concepts of gold adsorption onto activated carbon from gold cyanide solutions, as well as the derived adsorption kinetics equation with its analytical solution, provide an adequate mathematical framework for describing the process. This model can be used both for predictive purposes and for the development of optimal discrete and continuous, co-current and counter-current technological process flowsheets.

Comparative evaluation of the developed mathematical model and existing Fleming models

The most commonly used and practically applied models for describing the kinetics of gold adsorption onto activated carbon are Fleming's "*Kn*" and "*Kk*" models [14—16].

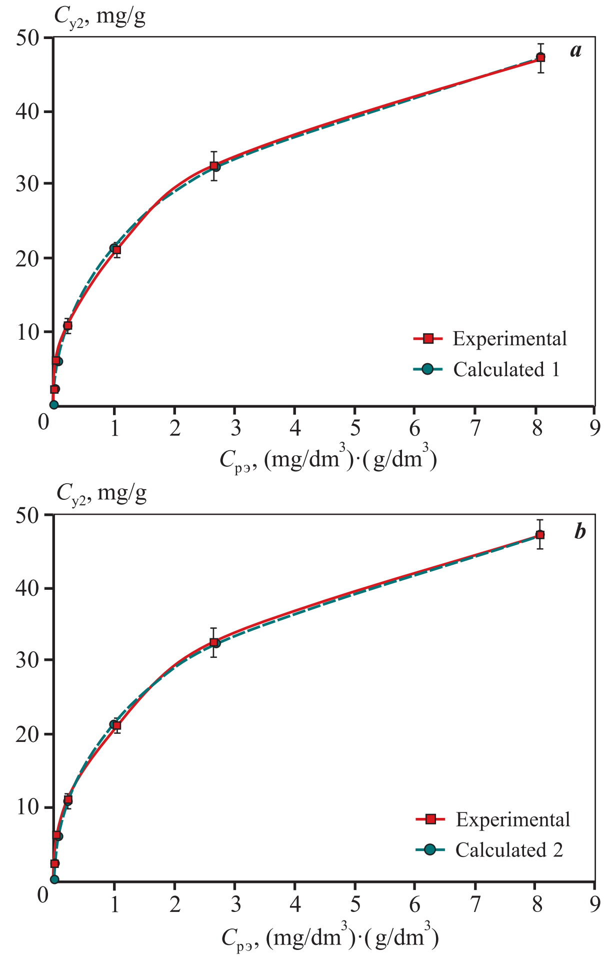

Fig. 3. MEGA isotherms: experimental and calculated curves

a – calculation using Equation (8),
b – calculated using Equation (12)

Рис. 3. Экспериментальные и расчетная изотермы МЕГА

a – расчет по формуле (8), ***b*** – по (12)

The *Kn* model is expressed as:

$$C_y - C_{y0} = KC_p t^n. \tag{15}$$

For batch adsorption processes in a closed system, the material balance equation must be added:

$$C_p = C_{p0} - \frac{m}{V}(C_y - C_{y0}). \tag{16}$$

The resulting solution takes the following form:

$$C_y = C_{y0} + \frac{KC_{p0}t^n}{1 + K\frac{m}{V}t^n}. \tag{17}$$

From this, it follows that as $t \to \infty$

$$C_y = C_{y0} + \frac{m}{V}C_{p0}, \tag{18}$$

Experimental and calculated data of the MEGA isotherm

Экспериментальные и расчетные данные изотермы МЕГА

Parameter	Experiment No.						
	1	*2*	*3*	*4*	*5*	*6*	*7*
Experimental isothermal values значения ($C_{y2\,exp}$)	0.318	2.45	6.34	10.98	21.3	32.68	47.28
Isothermal values C_{y2}, calculated using initial values C_{p0}, C_{y0}, m, V and Equation (8)	0.318	2.46	6.19	10.97	21.53	32.48	47.34
Isothermal values C_{y2}, calculated using Equation (12) and equilibrium concentrations of gold using Equation (13)	0.326	2.462	6.186	10.975	21.531	32.481	47.343
Experimental equilibrium gold concentrations in solution (C_p)	0	0	0.07	0.45	2.09	5.3	16.2
Experimental equilibrium gold concentrations in solution. $C_{pэ} = C_p m/V$ – generalized parameter	0	0	0.035	0.225	1.045	2.65	8.1
Equilibrium gold concentration in solution (C_p), calculated using Equation (13)	0.000012	0.00257	0.143	0.454	1.974	5.4	16.168
Equilibrium gold concentrations in solution calculated using Equation (13). $C_{pэ} = C_p m/V$ – generalized parameter	0.0006	0.01285	0.0715	0.227	0.987	2.7	8.084

In other words, the model implies that adsorption will proceed until all gold is removed from the solution and fully absorbed by the activated carbon — an outcome that contradicts the physicochemical understanding of the process and the behavior described by the adsorption isotherm.

Under practical conditions, where free cyanide is present in solution (as is typically the case), the adsorption process is accompanied by desorption. As a result, equilibrium is established at certain concentrations, and the collection of these equilibrium states forms the adsorption isotherm. Under such conditions, the adsorption process can never proceed to completion, meaning that some residual concentration of the adsorbate must always remain in the solution. These residual concentrations — particularly at high sorbent loadings — can become so low that they fall below the detection limits of standard analytical methods. This may lead to the mistaken conclusion that the adsorption process has gone to completion.

This phenomenon can be readily explained by the hypothesis that gold desorption proceeds through the formation of intermediate species derived from $Au(CN)_2^-$ within the carbon sorbent, in which one CN^--ion is replaced by a hydroxyl ion OH^-. The resulting intermediate partially decomposes to form , which — due to its weak interaction with the carbon lattice and relatively small molecular size — tends to desorb. However, for this desorption to proceed, free cyanide must be present in the solution to convert Au(CN) back into the soluble $Au(CN)_2^-$ complex. In the absence of free cyanide, water-insoluble AuCN remains within the structure of the carbon sorbent, and desorption does not occur [17—20].

For practical purposes, when modeling gold adsorption kinetics over limited time intervals and within a restricted range of C_{p0} and m/V values, the use of the *Kn* model may be acceptable as a first approximation for fitting kinetic curves — especially given that many such curves can be adequately approximated by a power-law function. If an experimental kinetic curve is available, it is often permissible — within specific time intervals — to fit it using the *Kn* model by identifying suitable values of *K* and *n* that minimize the root-mean-square relative deviation between the experimental and model-predicted curves. To that end, the original *Kn* kinetic equation for a closed system (Equation 17) can be rewritten as:

$$\frac{C_{yi} - C_{y0}}{C_{p0} - \frac{m}{V}(C_{yi} - C_{y0})} = Kt_i^n, \qquad (19)$$

where C_{yi} and ti are the values of the experimental data points along the kinetic curve, and *K* and *n* are the identification constants to be determined. Taking the logarithm of this expression yields a linearized form of the kinetic equation, from allows the identification constants *K* and *n* to be estimated in a first approximation using the least squares method:

$$\ln\left(\frac{C_{yi}-C_{y0}}{C_{p0}-\frac{m}{V}(C_{yi}-C_{y0})}\right)=\ln K+n\ln t_i\,. \qquad (20)$$

The resulting values of *K* and *n* are then refined directly using Equation (17) by minimizing the sum of squared relative deviations between the experimental C_{yi} values and those calculated from the model. It is important to note that the values of *K* and *n* obtained using this procedure are valid only under the specific experimental conditions used to obtain the kinetic curve employed in the identification process. If the conditions are altered and a new kinetic curve is obtained, new values of *K* and *n* must be determined accordingly.

Since the identification constants *K* and *n* in Fleming's *Kn* model lack clear physical meaning, their functional dependence on external conditions also lacks a well-defined interpretation. As an empirical model, it provides limited scientific or predictive value beyond that of conventional regression approaches. When applying this model in practice, it is essential to take into account the specific assumptions and conditions under which it was developed and, most importantly, the purposes it was originally intended to serve. All semi-empirical models share a fundamental limitation: they are based on physically undefined parameters and tend to yield physically inconsistent results when extrapolated to limiting cases, which diminishes their theoretical rigor and predictive reliability.

Fleming's *Kk* model (1984) offers only marginal improvements over the *Kn* model. While the parameters it employs have a somewhat clearer physical interpretation — particularly *K*, which functions as an equilibrium constant — the model inherently incorporates a Henry-type isotherm. This imposes significant constraints on its applicability for designing real-world technological flowsheets.

In contrast, the theoretical model of gold adsorption onto activated carbon developed in this study offers a more consistent and scientifically grounded description when fitted to specific empirical kinetic data. Unlike Fleming's models, it is derived from fundamental principles and allows for the analytical derivation of a new type of isotherm — referred to as the MEGA isotherm — directly from the kinetic equation. This isotherm provides an accurate description of the experimentally obtained adsorption curve and enables the calculation of equilibrium values of C_y (Equation 12) and C_p (Equation 13) across a wide range of initial conditions, including carbon loading and the initial concentrations of gold in solution (C_{p0}) and in regenerated activated carbon (C_{y0}).

Conclusion

Unlike Fleming's *Kk*- and *Km* models, the kinetic model of gold adsorption from gold cyanide solutions onto activated carbon presented in this work is developed on the basis of well-established fundamental theoretical principles. All parameters introduced into the model have clear physical meaning, and both the adsorption kinetics equation and the resulting new-type adsorption isotherm adequately describe the complete set of experimental data obtained for both adsorption kinetics and isotherm. The experimental data were collected over a wide range of process parameters, including initial gold concentrations in solution from C_{p0} = 3.2 to 39.8 mg/dm^3 and activated carbon loadings ranging from m/V = 0.5 to 50 g/dm^3. These values cover nearly the entire practical range of initial gold concentrations and sorbent loadings typically encountered in real-world gold adsorption systems.

The mathematical model of adsorption dynamics and the MEGA isotherm proposed in this study enable an accurate description of gold adsorption onto activated carbon from gold cyanide solutions. This applies both to predictive modeling and to the design and optimization of technological process flowsheets [21—23]. The generality of the developed model is largely determined by the structure of the proposed kinetics equation and its analytical solution, from which the MEGA isotherm is derived.

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