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ARTICLES

Mathematical Modeling in the Development of Indicator Tubes for Determining Chromium(VI) in Natural Waters

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Abstract—The adsorption dynamics of the chromium(VI) complex of 1,5-diphenylcarbazide on the KU-2-8 strongly acidic cation exchanger was studied. A mathematical model was developed that adequately describes the processes in the system and provides recommendations on the procedure for determining chromium(VI) in natural water using an indicator tube. The experimental data were evaluated by processing model solutions of the composition of natural surface waters.

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Recently, indicator tubes packed with a solid substrate have become widespread in controlling the pollution of inland and littoral waters by toxic components of various natures. Their advantage is in simplicity and ease of operation in determining hazardous substances at a level of their maximum permissible concentrations (MPCs) or lower. Indicator tubes combine adsorption preconcentration with the visual colorimetric determination of toxic substances; although, there are other procedures for rapid determination [1, 2]. In developing indicator tubes, it is necessary to consider the adsorption–desorption of the studied substances in a dynamic mode as a multistage heterogeneous process involving certain regularities of mass transfer, when adsorbent particles are flown around with the continuous liquid phase of the test solution, and certain hydrodynamic conditions [3, 4].

The method of mathematical modeling can be successfully implemented to reduce the time spent for the development of test methods for determining various substances. The approaches of mathematical modeling were used to optimize the adsorption process and to reduce the experimental data in the studies of, for example, the preparation conditions of butadiene [5], the liquid-phase separation of dicarboxylic acids [6], and the adsorption of the decomposition products of reducing sugars [7]. The data obtained enabled the study of the effect of many parameters over a wide range of their variation and the optimization of the adsorption processes both over a whole cycle and at the regeneration stage and showed the high efficiency of the developed calculation methods.

It should be noted that various models of the general theory of mass transfer are used in the works on the analysis of mass transfer in ion exchange [8, 9]. Three main models commonly known in the theory and practice are used to describe mass transfer in the stationary adsorbent layer: (1) film, (2) penetration, and (3) boundary-layer models. Here, the first two models disregarding the hydrodynamic characteristics of the process are in a worse agreement with the experimental data than the boundary-layer models [3, 4, 8, 9].

Therefore, the model of mass transfer used in this work is based on the boundary-layer theory described in [4, 8, 9].

Chromium(VI) is one of the most toxic elements whose concentration in both natural and industrial water should be strictly controlled. The need for the rapid determination of chromium(VI) at the time of sample collection is caused by its ability to be adsorbed on the walls of a vessel during the transportation of the test sample and to partially transform into chromium(III) in the presence of reductants. To determine chromium(VI) in water, a rather selective and sensitive reaction with 1,5-diphenylcarbazide (DPC) is used [10]. In this reaction, diphenylcarbazide reduces Cr(VI) to Cr(III) yielding the oxidized form of the reagent, diphenylcarbazone. In solutions with pH ≈ 1, the latter forms a positively charged stable complex with chromium(III) ions, chromium(III) diphenylcarbazonate (DPCAT–Cr(III)), which has an exact stoichiometry and a red–violet color (λ_{max} = 540 nm). The chemical analytical characteristics of this complex observed in its adsorption recovery from an test solution allow one to use chromatography or solid-phase colorimetry [11]. Various adsorbents either with ion-exchange properties (cation and anion exchangers) or without them (foams, membranes, films, and others) are used as substrates for the components of such an analytical system. In these cases, the substrate can participate in the adsorption process in different ways [12–17]. In the cited articles, the detection limit for chromium(VI) in natural waters was at a level of 0.002–0.032 mg/L, which indicated a high sensitivity of the proposed procedures; however, the procedures were labor-intensive and time-consuming, which reduced their effectiveness. It is obvious that

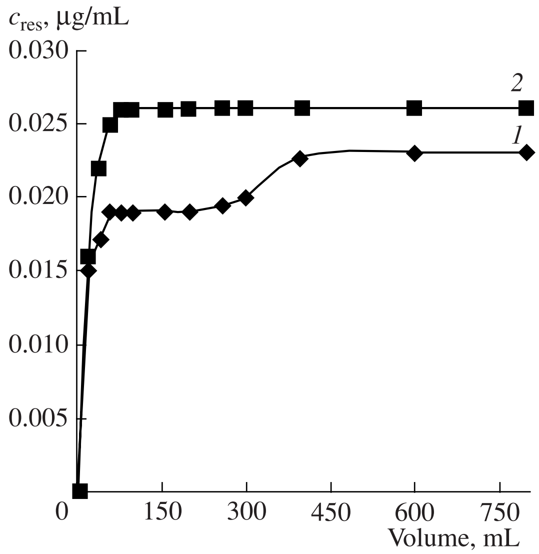

Fig. 1. Adsorption dynamics of the DPCAT–Cr(III) complex on the KU-2-8 cation exchanger; d_c = 1.00 cm, m_a = 0.50 g, c_{in} = 0.10 μg/mL, V_v: (*1*) 6.00 and (*2*) 10.00 mL/min.

the effectiveness of any procedure is related to its rapidity, while the latter is known to be characterized by the kinetics of the process the procedure is based on. In studying the kinetics of processes occurring in a heterogeneous systems of solid adsorbent–adsorbate solution, the following factors limiting the processes are mainly considered: (1) internal diffusion, (2) external diffusion, and (3) chemical reaction [15–18]. The effect of one or another parameter in the sited works was studied by both experimental and theoretical methods with the use of mathematical modeling.

Earlier, we have shown the potentials of using a KU-2-8 sulfonic cation exchanger as an adsorbent for recovering the DPCAT–Cr(III) complex for determining Cr(VI) in natural waters [19]. The recovering of the complex from the analyzed solution and its immobilization on the surface of KU-2-8 contributed to an increase in its time stability. The maximum stability (more than a week) was observed at the temperature of +5°C; in this case, the fraction of the decomposed complex was less than 30% [20]. The literature data on the study of the regularities of adsorption dynamics showed that the method of mathematical modeling was not used earlier for the processes in the system of DPCAT–Cr(III)–KU-2-8.

With respect to the aforesaid, the goals of this work were to study the adsorption dynamics of the DPCAT–Cr(III) complex on a KU-2-8 strongly acidic cation exchanger, to construct a mathematical model that adequately describes the processes occurring in the system, and to provide recommendations on implementing a rapid procedure for determining chromium(VI) in natural water using an indicator tube.

EXPERIMENTAL

We used a KU-2-8 cation exchanger with a particle diameter (d_p) of 0.43–0.50 mm. One-half gram portions of the adsorbent (m_a) were placed in glass tubes (columns) with a diameter (d_c) of 1.00 cm. An aqueous solution of the DPCAT–Cr(III) complex, prepared by the procedure described in [10], with an initial Cr(VI) concentration (c_{in}) of 0.10 μg/mL was passed through an adsorbent layer at 18–20°C. A laminar flow mode was maintained through the experiment in the range of flow rates (V_v) from 0.30 to 16.00 mL/min. The residual concentration of DPCAT–Cr(III) (c_{res}) in the eluate was controlled spectrophotometrically at the outlet from the adsorbent layer [10].

RESULTS AND DISCUSSION

It should be noted that the adsorption isotherm of DPCAT–Cr(III) on KU-2-8 obtained at the beginning of the study was categorized as *L*(3) type in the Giles classification system [21], which indicated the formation of both monolayers and polylayers on the surface of the cation exchanger.

The experiments with the flow rate of the complex solution passing through the adsorbent varied form 0.30 to 16.00 mL/min resulted in dynamic curves of two types: (1) with two plateaus and (2) with one plateau; this was in agreement with the above type of the adsorption isotherm. The former type of adsorption curve was observed in the range of V_v = 0.30–6.00 mL/min, while the latter at V_v = 8.00–16.00 mL/min. The typical curves obtained at a fixed V_v are presented in Fig. 1, curves *1* and *2*. The first plateau (curve *1*) indicates the beginning of the formation of a stable monolayer of the adsorbed complex on the cation exchanger because of the Coulomb interactions forces between the positively charged complex and the negatively charged surface of KU-2-8. The additional immobilization of the complex is due to hydrophobic interactions between the phenyl rings of the DPCAT–Cr(III) molecules and the phenyl and, probably, vinyl groups of the styrene–divinylbenzene matrix of KU-2-8. In this case, the adsorption monolayer of the complex makes the surface of the cation-exchanger particles more hydrophobic. The second plateau signifies that the formation of successive adsorption polylayers of the complex on the hydrophobized surface can occur primarily because of hydrophobic interactions resulting from weak electrostatic forces. The second type consists of curves with one lengthy plateau (Fig. 1, curve *2*) obtained at rather high flow rates V_v = 8.00–16.00 mL/min, when a stable primary monolayer formed nearly over the whole height (depth) of the adsorbent layer. The polylayers do not form because weak hydrophobic forces cannot retain additional adsorption layers of the complex at the noted values of V_v, which is also evidenced by the initial increase in c_{res}

at the outlet of the column with the increase in the volume of the complex solution [22].

In the analysis of the dynamic curves obtained and their mathematical treatment, a linear flow rate, so-called critical flow rate, (V_{cr}) of the DPCAT–Cr(III) solution passing through the stationary layer of KU-2-8 was determined to be equal to 17.94 mL/min. Above this flow rate, the formation of adsorption polylayers is completely excluded [23]. The dependence plotted in Fig. 2 shows the same value of V_{cr} found for different concentrations of the adsorbed complex. It should be noted that the mathematical model proposed in this work can be used with lower V_v with respect to the relative deviation (error) of the theoretical data from the experimental data. For example, relative error was 3–20% at V_v = 8.00–14.00 mL/min and only 1–2% at $V_v \geq 16.00$ mL/min. Therefore, at linear flow rates close or equal to V_{cr}, the results obtained using the conventional procedures of mathematical modeling for the adsorption processes obeying the ion-exchange mechanism in the stationary adsorbent layers are the best fit to the experimental data.

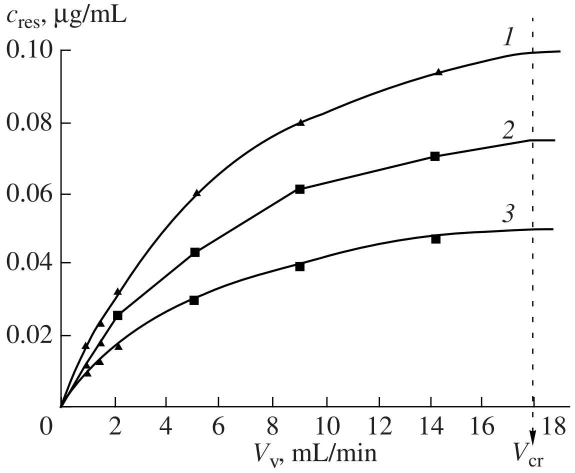

Fig. 2. Residual concentration of the DPCAT–Cr(III) complex as a function of the flow rate of its solution passing through a layer of the KU-2-8 cation exchanger; d_c = 1.00 cm, m_a = 0.50 g, c_{in}: (*1*) 0.10, (*2*) 0.75, and (*3*) 0.05 μg/mL.

Some hydrodynamic, mass-transfer, and kinetic regularities of the adsorption of the DPCAT–Cr(VI) complex were then studied, namely, the effect of different initial concentrations of the complex solution (c_{in} = 0.10–0.25 μg/mL) and the phase contact time (τ_{cont} = 0.2–1.0 min) at the variation of the weight of KU-2-8 (m_a = 0.50–3.00 g). It is known that the mass transfer coefficient β is one of the important parameters of heterogeneous systems in mathematical modeling. This coefficient was calculated from the equation $\beta = 4.2505 \times 10^{-3} + 1.7218\mathrm{Re}^{0.3632}$ developed earlier (Re was the Reynolds number) [22]. To describe mathematically the adsorption dynamics in the studied heterogeneous system of KU-2-8–DPCAT–Cr(III), we used the sign model presented in [8, 9], which consisted of the following:

$$\frac{\partial c_{res}}{\partial \tau} + V_v \frac{\partial c_{res}}{\partial x} + \frac{\partial \bar{c}}{\partial \tau} = D_L \frac{\partial^2 c_{res}}{\partial x^2}, \tag{1}$$

material-balance equations using a coefficient of longitudinal diffusion;

$$\frac{\partial \bar{c}}{\partial \tau} = \beta(c_{res} - c^*), \tag{2}$$

equations of adsorption kinetics;

$$\bar{c} = \frac{c^*}{a + bc^*}, \tag{3}$$

equations of adsorption isotherms; and the initial and boundary conditions necessary to solve the system of Eqs. (1)–(3).

$$\left.\begin{array}{r} \tau = 0: c_{res} = c_{in}; \quad \bar{c} = 0 \\ x = 0: c_{res} = c_{in} \\ x = \infty: c_{res} = 0 \end{array}\right| . \tag{4}$$

Here, c_{res} was the residual concentration of the DPCAT–Cr(III) complex in the solution, $\bar{c}$ was the concentration of the DPCAT–Cr(III) complex in the phase of the KU-2-8 cation exchanger, c^* was the equilibrium concentration of the DPCAT–Cr(III) complex at the adsorbent particle–solution boundary, c_{in} was the initial concentration of the DPCAT–Cr(III) complex in the solution, D_L is the coefficient of longitudinal diffusion, τ was the time of adsorption, V_v was the flow rate of the liquid phase, x was a coordinate, β was the mass transfer coefficient, and a and b were experimental constants.

With regard to the initial and boundary conditions (4), the system of Eqs. (1)–(3) was solved using the implicit differential procedure described in [8, 9], which allowed us to study the effect of different parameters (V_v, c_{in}, β, D_L, d_c, and m_a) on the adsorption recovery of the DPCAT–Cr(III) complex by a layer of KU-2-8. The time the equilibrium is reached in the system is known as one of the factors responsible for the efficiency of dynamic adsorption. By varying the above parameters, we obtained a number of dependences were for the time of equalizing of c_{res} on the flow rate for adsorbent portions of different weights packed in columns of different diameters, which are graphically presented in Figs. 3 and 4. The equalizing time (τ_{eq}) is the time when the residual and initial concentrations of DPCAT–

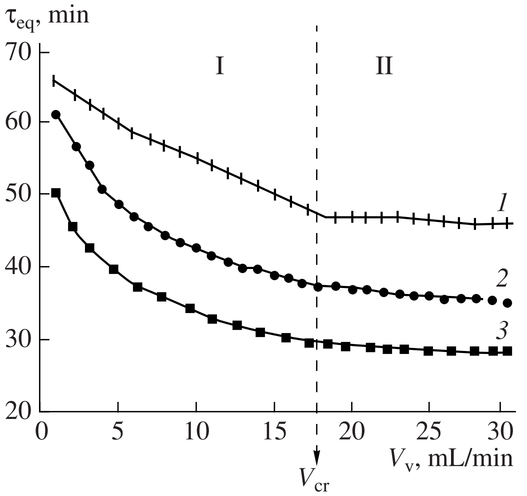

Fig. 3. Equalizing time of the residual concentration of the DPCAT–Cr(III) complex as a function of the flow rate of its solution passing through a layer of the KU-2-8 cation exchanger; d_c (*1*) 1.00, (*2*) 0.50, and (*3*) 0.25 cm, m_a = 0.50 g, c_{in} = 0.10 μg/mL.

Cr(III) become equal with regard to the possible experimental error, which should not exceed 5%; that is, $c_{res} = 0.95c_{in}$. As follows from Fig. 3, the equalizing time decreases in the range of V_v = 2.00–17.94 mL/min regardless of the value of d_c (region I). When the flow rate reaches the value of V_{cr} = 17.94 mL/min, the equalizing time becomes constant, and it remains unchanged with further increase in the flow rate (region II). This proves once again that only surface monolayers are formed throughout all of the adsorbent material.

Figure 4 presents an example of the dependences of τ_{eq} on the initial concentration of DPCAT–Cr(III) at constant m_a and variable d_c (Fig. 4a) and at constant d_c and variable m_a (Fig. 4b). As follows from Fig. 4a, an increase in c_{in} decreased the values of τ_{eq} for all the studied d_c. A similar dependence was observed for a fixed column diameter with different m_a; however, the contribution of the latter was small. The noted peculiarity allowed the conclusion that the column diameter d_c had a greater effect on the mass transfer process than the weight of adsorbent. This fact was confirmed by the experimental data obtained in the study of the effect of d_c and m_a on the adsorption recovery of the complex on the KU-2-8 cation exchanger. For example, in varying the weight of adsorbent from 0.50 to 3.00 g, τ_{eq} was 15–20 min, while in changing column diameter in the range of 0.40–1.00 cm, τ_{eq} was 30–130 min [19].

The mathematical treatment of the dependences characterizing the effects of m_a, d_c, and c_{in} at the moment when a dynamic equilibrium was reached in the system (Fig. 4) according to the equality of $c_{res} = 0.95c_{in}$ resulted in the following equations:

$$\tau_{eq} = e + f\ln d_c + gm_a, \quad (5)$$

$$\tau_{eq} = e + fc_{in} + gm_a, \quad (6)$$

$$\tau_{eq} = e + fc_{in} + g/d_c. \quad (7)$$

Here, *e*, *f*, and *g* are the coefficients whose numerical values are presented in Tables 1–3. The difference between the experimental values and the values calculated using the proposed Eqs. (5)–(7) is 10–15%. High values of correlation coefficients (r^2) for the given equations unambiguously indicate that the equations correspond, to a high degree, to the dependences obtained by the proposed mathematical model.

Thus, the adsorption dynamics of the DPCAT–Cr(III) complex on the KU-2-8 cation exchanger was studied in this work with the aim to develop indicator tubes of the type of solid adsorbent–adsorbate solutions. On the basis of the experimental data obtained, a

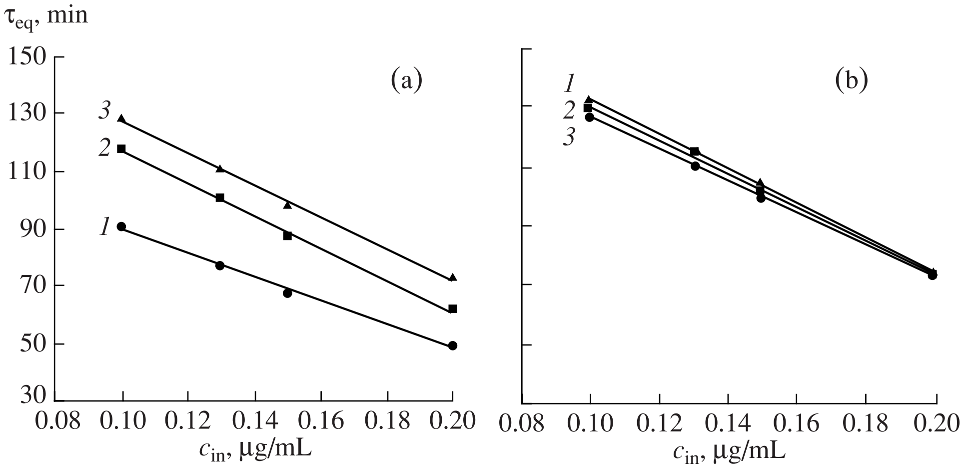

Fig. 4. Equalizing time of the residual concentration of the DPCAT–Cr(III) complex as a function of initial concentration (a) at a constant adsorbent weight of 1.00 g and column diameter of (*1*) 0.25, (*2*) 0.50, and (*3*) 1.00 cm and (b) at a constant column diameter of 1.00 cm and adsorbent weight of (*1*) 0.25, (*2*) 0.50, and (*3*) 1.00 g.

Table 1. Numerical values of coefficients of Eq. (5) at the specified values of c_{in} (μg/mL)

Coefficient	0.10	0.13	0.15	0.20
e	136.1943	124.0803	100.1502	73.4112
f	38.7804	28.3367	23.6763	16.8153
g	–2.4079	–2.7300	–2.8922	–0.8190
r^2	0.8891	0.9982	0.9816	0.9993

Table 2. Numerical values of coefficients of Eq. (6) at the specified values of d_c (cm)

Coefficient	0.25	0.50	1.00
e	109.7343	175.8788	189.6944
f	–297.3279	–563.2157	–569.5588
g	–0.0906	–2.8166	–4.4239
r^2	0.9932	0.9984	0.9976

Table 3. Numerical values of coefficients of Eq. (7) at the specified values of m_a (g)

Coefficient	0.25	0.50	1.00
e	191.9764	192.2051	185.7095
f	–545.1245	–535.1928	–509.5629
g	–9.8417	–10.3896	–10.1259
r^2	0.9865	0.9897	0.9863

mathematical model of indicator tubes was constructed, which considered the peculiarities of heterogeneous processes occurring in the chemical systems of this type. The developed type of indicator tubes provides the determination of chromium(VI) at a level of MPC or lower using different methods of detecting the analytical signal, namely, solid-phase spectrophotometry, visual colorimetry, and a linear-coloristic method. In the last case, the optimal flow rate of passing the complex solution should not be less than the critical flow rate; according to the experimental data, the role of tube diameter is considerable. The volume of the analyzed adsorbate solution is 300–500 mL for all alternative procedures using the indicator tubes. The experimental data were tested using model solutions whose composition corresponded to natural surface waters [24]. Here, sample preparation included the formation of the DPCAT-Cr(III) complex in the sample in the presence of a total amount of more than ten cations and five anions at their maximum possible concentrations. It was observed that only Ca^{2+} and Fe^{3+} ions slightly affected the photometric reaction. If the complex is recovered from the test water sample under the optimum conditions of indicator tube operation, the shape and quantitative properties of the dynamic elution curves are only slightly distorted. Some minor changes are possible in the kinetics of the formation of a complex monolayer on the surface of KU-2-8. It should be noted that the constructed mathematical model both takes into account chemical analytical and adsorption properties of such heterogeneous systems and explains the dependence of the performance characteristics of the results of analysis on the rate of processes involved in the recovery of the adsorbate from the test solution into the indicator tube. In general, the use of mathematical modeling allows the optimization of the recovery of one or another component from the solution and the reduction of the experimental data.

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