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Fractal Nature of Sorption Kinetics

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The generalization of sorption kinetics equations is given within the context of fractal conception. Using the fractional integrodifferentiation technique, we derived a new class of solutions that takes memory effects into account. Satisfactory agreement with experimental data has been found.

In recent years, the tendency of revision of the fundamental tenets of the heat and mass exchange theory was outlined. It should be pointed out that two fundamental factors hinder the development of the adequate quantitative theory of heterogeneous systems. This is the space inhomogeneity and multiphase behavior of a system. The description of space structure features of heterogeneous systems using Euclidean geometry is limited, and it is necessary to invoke notions of the fractional dimension geometry. The multiphase behavior of the system leads to the necessity of the development of a radically new approach for the study of sorption kinetics. The interface of two phases represents the special condition of the substance that is intermediate between interacting phases. Such an intermediate substance condition is characterized by the availability of fluctuations, its complicated correlation nature, and the absence of the traditional structure of a relaxation-time hierarchy. The complicated space- and time-correlation character leads to the existence of memory effects and self-organization. It is beyond the scope of traditional statistical physics methods to describe such properties.

One intensively developing area is connected with the use of the fractal conception.[1−12] The wide area of application of this conception in various branches of natural sciences is related to two features. The first is connected with the use of the Haussdorff−Besikovich fractional-dimension geometry approach. As a result, it is possible to develop an adequate description of the systems with a complicated space structure. These systems cannot be described using Euclidean geometry. The second feature is connected with the use of the mathematical technique of the fractional integrodifferentiation.[13−16] Using this formalism, it is possible to take into account the complicated nature of the nonlinear phenomena such as memory effects and space correlations.

In this work, the attempt to develop the quantitative sorption model (as a special case of electrosorption) on the basis of the fractional integrodifferentiation formalism to explain the experimental data[17−19] has been made. The basic idea of the experiment is the measurement of the concentration difference of Sr^{2+} and Ca^{2+} cations in their salt solutions before and after filtration through the cell with polarized or unpolarized activated carbon and the establishment of the time dependence of the concentration difference. Thus, the time dependence of the quantity of cation adsorption is determined.

The mathematical description of electrosorption is realized by a set of equations consisting of the equation of balance (conservation law of substance), kinetic equations for components participating in the sorption process, equations of electrodynamics, and equations of adsorption isotherms giving the relationship between the concentration of substance in a solution and on a sorbent surface. In general, the equations have a complicated integrodifferential form. Therefore, various approximate models with precise determination of the their applicability boundary are applied. The fundamental feature of the considered process is that during the substance sorption from a liquid phase onto the surface of a solid phase with further diffusion in the solid phase, kinetic factors depend on the sought solutions, and the problem becomes nonlinear. Moreover, at different stages of an adsorption, it is necessary to use different equations.

The initial equations that take into account the marked features of fractional derivatives of time and space have the following form:

$$\frac{\partial^\alpha}{t_0\,\partial\tau^\alpha}(C_\mathrm{f}(x,t)+C_\mathrm{s}(x,t))+\frac{\partial^\beta}{l_0\,\partial\xi^\beta}q(x,t)=0 \qquad (1)$$

$$q(x,t)=D_\mathrm{f}\frac{\partial^\beta}{l_0\,\partial\xi^\beta}C_\mathrm{f}(x,t)+D_\mathrm{s}\frac{\partial^\beta}{l_0\,\partial\xi^\beta}C_\mathrm{s}(x,t)-uC_\mathrm{f}-vC_\mathrm{f}+C_\mathrm{f}u_\mathrm{f}\frac{\partial\varphi}{\partial\xi}+C_\mathrm{s}u_\mathrm{s}\frac{\partial\varphi}{\partial\xi} \qquad (2)$$

where $0 < \alpha$ and $\beta \le 1$. When $\alpha = \beta = 1$, eqs 1 and 2 transform to the traditional form.[21] C_f is the density of substance transmitted by a liquid, C_s is the density of the adsorbed substance, $q(x, t)$ is the fluid flow with the substance, D_f and D_s are the diffusivities defining their diffusion contributions to the fluid flow with the substance, u and v are the velocities of the liquid and the substance defining their convective streams, and u_sf represents the absolute velocities of ions at the single strength of a field $E = -\mathrm{grad}\ \varphi$.

In eqs 1 and 2, the fractional derivative is defined[14] by

$$\frac{\mathrm{d}^\alpha C(x,t)}{\mathrm{d}t^\alpha}=\frac{1}{\Gamma(1-\alpha)}\frac{\mathrm{d}}{\mathrm{d}t}\int_0^t\frac{C(x,\tau)}{(x-\tau)^\alpha}\,\mathrm{d}\tau$$

The fractional derivative with respect to the dimensionless space variable ξ is defined similarly.

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Equations 1 and 2 are supplemented by the isotherm sorption equation on the boundary between liquid and solid phases:

$$C_s = \varphi(C_f, E) \tag{3}$$

The expression for the flow $q(x, t)$ in each case has these features and presents a separate problem. The strict solution of this expression is made on the basis of the kinetic equation with a consequent averaging procedure. Equation 3 also has a form that depends on the adsorption isotherm, taking into account the features of the interphase.

The solution of eqs 1 and 2 depends on the mechanisms of the adsorption process and the filtration mode. We will consider the simple case of an inner diffusion mode, when eqs 1, 2, and 3 lead to the equation ($C_s \rightarrow C$):

$$\frac{d^\alpha \tilde{C}(\tau)}{d\tau^\alpha} - \frac{\tilde{C}(\tau = 0)}{\Gamma(1-\alpha)\tau^\alpha} = 1 - \tilde{C}(\tau) \tag{4}$$

The second summand on the left side of eq 4 is defined as the fractional derivative $d^\alpha\tilde{C}(\tau = 0)/d\tau^\alpha = \tilde{C}(\tau = 0)/\Gamma(1 - \alpha)\tau^\alpha$, where $\tilde{C}(\tau) = C(\tau)/C_0$, $\tau = t/t_0$, t_0 is the characteristic time of the inner diffusion process, and C_0 is the saturated concentration of the solid phase. For the solution of eq 4, we use the Laplace transform $\tilde{C}(p) = \int_0^\infty \exp(-p\tau)\, \tilde{C}(\tau)\, d\tau$. For $\tilde{C}(p)$ from eq 4, we obtain $\tilde{C}(p) = [(1 + p^\alpha)\cdot\tilde{C}(\tau = 0)]/[p(1 + p^\alpha)]$. Using the inverse Laplace transformation, we have $\tilde{C}(\tau) = 1 - [1 - \tilde{C}(\tau = 0)]E_{\alpha,1}(-\tau^\alpha)$, where $E_{\alpha,\beta}(\xi)$ is the Mittag–Leffler function,[12] $E_{\alpha,\beta}(\xi^\alpha) = \sum_{k=0}^\infty(\xi^{\alpha k}/(\Gamma(\alpha k + \beta))$ for $\alpha > 0, \beta > 0$.

The solution of eq 4 depends on the initial conditions and the value of α. For $0 < \alpha \leq 1$ and for the initial condition $\tilde{C}(\tau = 0) = 0$, we obtain

$$C(\tau) = C_0[1 - E_{\alpha,1}(-\tau^\alpha)] \tag{5}$$

At $\alpha = 1$, from eq 5 we have $E_{1,1}(-\tau) = \exp(-\tau)$:

$$C(\tau) = C_0(1 - \exp(-\tau)) \tag{6}$$

This solution is the same as the earlier known one. In the case when $\alpha = 0.5$, we have $E_{1/2,1}(-\tau^{1/2}) = \exp(\tau)[1 - \mathrm{erf}(\sqrt{\tau})]$ and eq 5 takes the following form:

$$C(\tau) = C_0[1 - \exp(\tau)(\mathrm{erfc}(\sqrt{\tau}))] \tag{7}$$

The transformation of the functional form of the solution from eq 6 to 7 corresponds to the variation of the state and properties of substance. The reasons responsible for the use of eqs 6 and 7 are not included in a variation of the t_0 parameter. Thus, a variation of α supplements the description of substance properties and, as we will show below, more exactly describes the experimental data. Moreover, the range of α variation in eq 4 can be $n < \alpha \leq n + 1$, where $n = 0, 1, 2, ...$ For $1 < \alpha \leq 2$, we have

$$C(\tau) = C_0[1 - E_{\alpha,1}(-\tau^\alpha)] - A\tau^{\alpha-1}E_{\alpha,\alpha}(-\tau^\alpha) \tag{8}$$

Except for the initial condition $\tilde{C}(\tau = 0) = 0$, eq 8 must satisfy another condition:

$$\frac{(d^{\alpha-1})}{(d\tau^{\alpha-1})}C(\tau)|_{\tau=0} = -A$$

Figure 1 shows the results of the numerical solution of eq 5 for various values of α and t_0 together with experimental data for the adsorption of Ca^{2+} and Sr^{2+} ions on unpolarized activated carbon $\mathscr{K}$-2 reported in ref 17. The best agreement with experimental data for Ca^{2+} was observed for $\alpha = 0.75$. For the adsorption of Sr^{2+} ions, in contrast to the adsorption of Ca^{2+} ions, to explain the experimental results, it is necessary to take into account the variation of α with time. Thus, the process of the adsorption of Sr^{2+} ions has multifractal character. As analysis showed, the agreement between calculated and experimental data is good only at certain values of t_0: for Ca^{2+}, $t_0 = 10$ h; for Sr^{2+}, $t_0 = 13$ h. The derived values of t_0 correspond to the value of $C/C_0 = 0.6$ for the studied ions. The time dependence of α is shown in Figure 2. As one can see from this Figure, the essential difference in the sorption kinetics of Ca^{2+} and Sr^{2+} ions is observed in the initial stage.

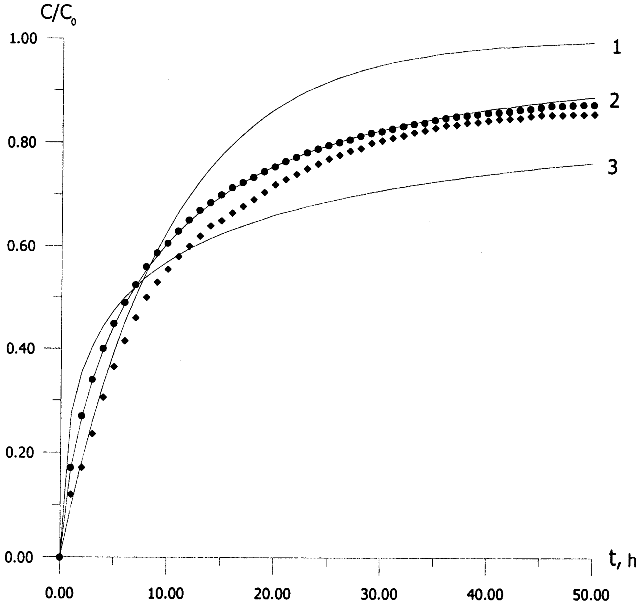

Figure 1. Time dependence of C/C_0 for unpolarized activated carbon. Curves 1−3: calculated results. 1: $\alpha = 1$. 2: $\alpha = 0.75$. 3: $\alpha = 0.5$. (●) Experimental data for Ca^{2+}. (◆) Experimental data for Sr^{2+}.

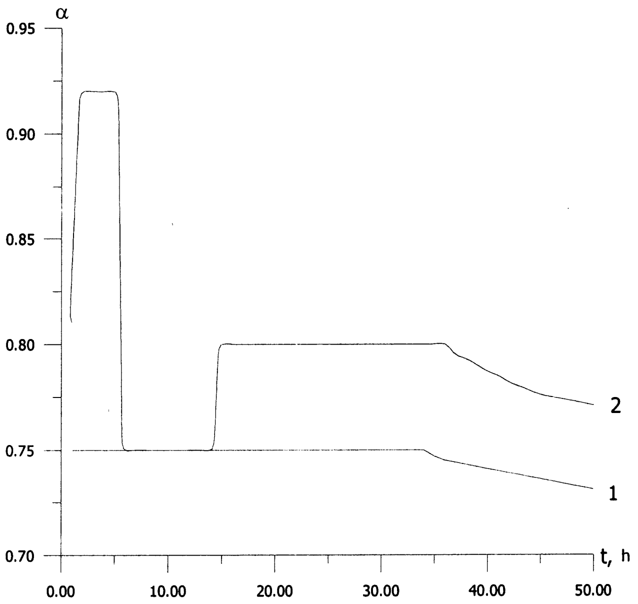

Figure 2. Time dependence of α for unpolarized activated carbon. 1: For Ca^{2+}; 2: for Sr^{2+}.

It is interesting that on the polarized sorbents electrosorption curves are explained by eq 8 with a variation of α within the range from 1 to 2. For the explanation of experimental results

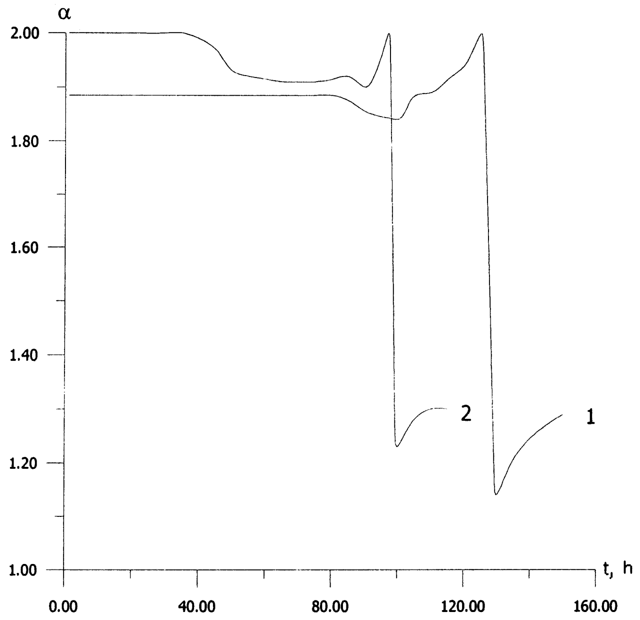

Figure 3. Time dependence of α for anode-polarized activated carbon. 1: For Ca^{2+}; 2: for Sr^{2+}.

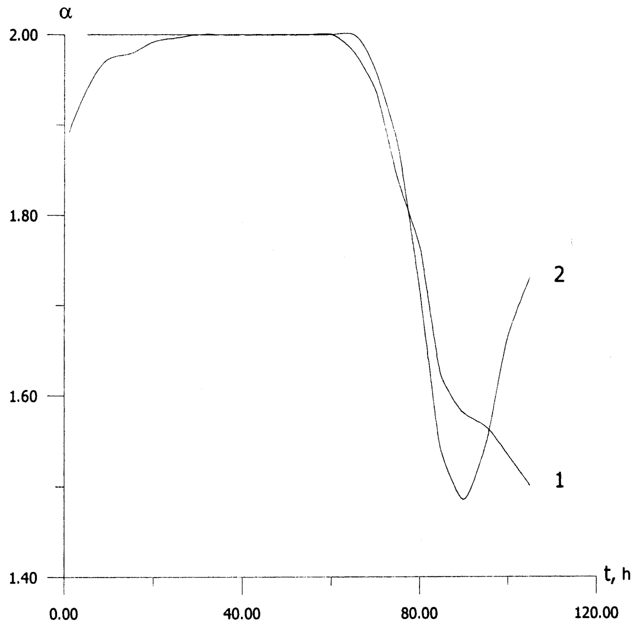

Figure 4. Time dependence of α for cathode-polarized carbon. 1: For Ca^{2+}, 2: for Sr^{2+}.

reported in refs 17 and19, it is necessary to take into account the variation of α with time. As the analysis showed, the agreement between the calculated and experimental data is good at certain values of t_0 that correspond to the time of saturation of the solid phase. For Ca^{2+} ions, t_0 is equal to 150 and 95 h for adsorption on anode- and cathode-polarized carbon, respectively. In the case of Sr^{2+} ions, t_0 is equal to 115 and 106 h for anode- and cathode-polarized carbon, respectively. The time dependence of α for electrosorption on anode- and cathode-polarized carbon is shown in Figures 3 and 4. Figure 3 shows abrupt changes in the α parameter with time. It is remarkable that at the time where the abrupt change of the values of parameter α takes place the destruction of the anode (at 95 h for Sr^{2+} ions and 120 h for Ca^{2+} ions) was observed visually. This testifies that the parameter α is not a simple adjustable parameter but that it has direct relationship with the sorbent structure.

In the case of cathode-polarized sorbents, we did not visually observe their destruction; however, a drastic decrease of the parameter α after 65 h of sorption can testify to certain structural modifications of activated carbon, which can be connected, for example, with the intercalation of ions into interplanar spaces of carbon.

The physical means of parameter t_0 is the characteristic time of the inner diffusion process $t_0 = d_{equ}^2/\pi^2 D_{eff}$, where D_{eff} is the effective diffusivity of the cation in the activated carbon pores and $d_{equ} = (l - k/\pi^2)d$ is the characteristic size of the adsorbent particles (d is the diameter of the particle, $k = 0.6$ at $2l/d > 4$, and l is the length of the cylindrical part of the particle); in our case $d_{eq} = 7.5 \times 10^{-2}$ cm. Using calculated values of t_0 and d_{eq}, we obtained the values of diffusivity D for cations: $D_{Ca^{2+}} = 1.58 \times 10^{-8}$ cm^2/s and $D_{Sr^{2+}} = 1.22 \times 10^{-8}$ cm^2/s for the adsorption without polarization. For an adsorption on polarized sorbents, the results are the following: for the anode-polarized sorbent, $D_{Ca^{2+}} = 1.06 \times 10^{-9}$ cm^2/s and $D_{Sr^{2+}} = 1.38 \times 10^{-9}$ cm^2/s. For the cathode-polarized sorbent, $D_{Ca^{2+}} = 1.67 \times 10^{-9}$ cm^2/s and $D_{Sr^{2+}} = 1.15 \times 10^{-9}$ cm^2/s. The calculated values of diffusivities agree satisfactorily with the data reported by other authors.

There are two adjustable parameters (α and t_0) in eq 5 to explain the experimental data. There is a fundamental difference between these parameters. If under the change of t_0 the form of solution is not varied, then the varying of α leads to the change of the functional form of the solution. Moreover, as the calculations indicate, there is a correlation between α and t_0. The calculated and the experimental data show good agreement only at certain values of these parameters. It is fundamentally important that the values of α are varied with time. By this, we mean that the variation of the differential equation form is the result of substance property changes. The establishment of regularities in the fractal dimension variation becomes the important problem of the developed fractal conception and needs special investigation.

Thus, using the fractional integrodifferentiation approach, it is possible to get well-known solutions and to realize their nontrivial generalization. The fractional derivative approach is a fundamentally new method of the quantitative description of the time and space nonlocal processes. In this case, the fractal dimension becomes the most important magnitude in the fractal conception. The fundamental nature of this magnitude is that it determines the order of fractional derivatives and fractional integrals and is an “operating” parameter of the theory that is analogous to that in the physics of open systems.[21]

Another important feature is connected with the property of self-similarity of the fractal structures. Contrary to traditional methods of the system description on the basis of various averaging procedures, when an “erasing” of the microscopic level of description takes place, the self-affine structure of the medium is taken into account in the fractal conception, and thereby within the framework of this conception, the microscopic and macroscopic levels of the system description are integrated. As a result, it is possible to restore more detailed information using experimental data on the macroscopic level.

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