A FRACTAL RATE MODEL FOR ADSORPTION KINETICS AT SOLID/SOLUTION INTERFACE

by

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Langmuir's linear rate equation has limited applications in the adsorption kinetics at solid/solution interface. Considering the fractal properties of adsorption surfaces, a fractal derivative model is proposed, its initial slope agrees well with Azizian-Fallah's modified rate equation.

Key words: *adsorption kinetics, fractal derivative model, fractal calculus*

Introduction

Due to fast development of nanotechnology, porous fibers with nanoscale porosity [1-9] can be easily fabricated through fast or sudden solvent evaporation [8, 9], and they have been widely applied to adsorption of heavy mental ions [2]. A fast and accurate prediction of adsorption effect at initial stage is of great importance in practical applications.

The rate eq. (1) is an important tool to dealing with adsorption kinetics at the solid/solution interface, Langmuir's linear rate equation can be written in the form [10]:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k(q_\mathrm{e} - q) \tag{1}$$

where k is the rate constant of sorption, q_e – the amount of metal ions absorbed at equilibrium, and q – the amount of metal ions on the surface of the sorbent.

Equation (1) is linear, and its solution can be easily obtained, which reads:

$$q = q_\mathrm{e}(1 - \mathrm{e}^{-kt}) \tag{2}$$

In most practical applications, its adsorption property at initial stage is of great interest:

$$\frac{q}{q_\mathrm{e}} = kt, \quad t \ll 1 \tag{3}$$

Though eq. (1) is simple, but its prediction accuracy is low, and many modifications were appeared in literature. Here is the Azizian-Fallah's modification [11]:

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$$\frac{\mathrm{d}q}{\mathrm{d}t} = k\frac{q_\mathrm{e}^{n-1}}{q^n}(q_\mathrm{e}^n - q^n) \tag{4}$$

Its solution reads:

$$q = q_\mathrm{e}(1-\mathrm{e}^{-nk't})^{1/n} \tag{5}$$

where $k' = kq_\mathrm{e}^{n-1}$, n is an empirical parameter. The adsorption property at initial period becomes:

$$\frac{q}{q_\mathrm{e}} = k''(0)t^{1/n}, \quad t \ll 1 \tag{6}$$

It is obvious that the slope at initial stage can be adjusted by the empirical parameter.

Fractal derivative model

Haerifar and Azizian [12] found fractal properties of adsorption processes at the solid/solution interface, and proposed a fractal-like adsorption kinetics. According to Haerifar and Azizian's finding [12], the adsorption kinetics can be described using a fractal derivative [13]:

$$\frac{\mathrm{D}q}{\mathrm{D}t^\alpha} = \Gamma(1+\alpha)\lim_{\Delta t = t_A - t_B \to L_0}\frac{u(t_A)-u(t_B)}{(t_A - t_B)^\alpha} \tag{7}$$

The fractal derivative defined in eq. (7) was first proposed in 2011 [14], its physical explanation was given in [15], it can be cataloged into local fractional calculus. It was proved that the fractal dimensions are relative to the fractional order of fractional dimensional equations [15, 16]. Now the fractal derivative models have been widely applied in engineering [17-23].

According to fractal properties of adsorption process [12], eq. (1) can be modified:

$$\frac{\mathrm{D}q}{\mathrm{D}t^\alpha} = k(q_\mathrm{e} - q) \tag{8}$$

Equation (8) can be solved by a fractional Taylor series method [23]. Using the fractional complex transformation (also called as He-Li transformation or the two scale transformation [13, 24, 25]:

$$s = t^\alpha \tag{9}$$

Equation (8) becomes:

$$\frac{\mathrm{d}q}{\mathrm{d}s} = k(q_e - q) \tag{10}$$

Fractional complex transformation [13, 23] is an approximate transformation to convert a space/time to its continuous partner. It is useful mathematic tool to treatment of fractional calculus and fractal differential equations [24-32].

We obtain the solution of eq. (10) in the form:

$$q = q_e[1 - \exp(-ks)] = q_e[1 - \exp(-kt^{\alpha})] \tag{11}$$

The adsorption property at initial period becomes:

$$\frac{q}{q_e} = k\alpha t^{\alpha-1} \tag{12}$$

It is obvious that eq. (12) is equivalent to eq. (6), revealing our fractal model is reliable.

Discussion and conclusions

Very recently, a fractal surface coverage model was proposed to have a fast and accurate insight into the arsenic concentration in an electrochemical sensor with great success, the paradox arising in its classic surface coverage model can be completely solved [33]. The adsorption kinetics can be also explained by the geometrical potential theory [34-36]. In [37] authors successfully applied the theory to explain nanofiber membrane's highly selective adsorption property. All these works are helpful to further improve the rate equation with a suitable geometrical potential as a modification of Langmuir adsorption isotherm.

This paper gives a fractal modification of the simplest rate equation, while the prediction accuracy is same as that by Azizian-Fallah's modification [11]. The fractal order can be determined experimentally. This paper gives a new approach to the rate equation, and it can be easily to be applied to dealing with various adsorption processes.

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