A FRACTAL LANGMUIR KINETIC EQUATION AND ITS SOLUTION STRUCTURE

by

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The Langmuir kinetic equation is analyzed by the variational iteration method, its solution property is revealed analytically. The effects of desorption time and adsorption coefficient on the solution properties are also discussed, and a fractal modification of Langmuir kinetic equation is suggested.

Key words: *homotopy equation, Lagrange multiplier, variational principle, fractal calculus*

Introduction

The Langmuir kinetic equation is well-known in electrochemistry and surface science, it can be generally written [1]:

$$\frac{d\sigma}{dt} + \frac{1}{\tau}\sigma - kn = 0, \ \ \sigma(0) = \sigma_0 \tag{1}$$

where σ is the adsorbed particle's surface concentration, n – the bulk concentration, and τ and k are desorption time and adsorption coefficient, respectively.

Langmuir kinetics has been widely applied to study of adsorption/desorption properties of porous media [2-6]. The kinetic equation given in eq. (1) can be equivalently written in an integral equation [1]:

$$\sigma(t) = k\tau \int_0^{\infty} \frac{1}{\tau} \exp\left(-\frac{s}{\tau}\right) n(t-s) ds \tag{2}$$

Equation (2) shows a relaxation process of the surface concentration. This paper will study the solution property of eq. (1) by the variational iteration method [7-9].

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Solution property of Langmuir kinetic equation

The variational iteration method has been widely used to solve various linear and non-linear problems. For linear case, an exact solution can be obtained. The variational iteration algorithm for eq. (1) can be expressed [7-9]:

$$\sigma_{n+1}(t) = \sigma_n(t) + \int_0^t \lambda \left\{ \frac{\mathrm{d}\sigma_n(s)}{ds} + \frac{1}{\tau}\sigma_n(s) - kn \right\} \mathrm{d}s \tag{3}$$

where λ is the Lagrange multiplier, which is determined by the variational theory [10-13]. By the standard process of the variational iteration method, the multiplier can be identified:

$$\lambda = -\exp\left(\frac{s-t}{\tau}\right) \tag{4}$$

As eq. (1) is a linear equation, and the Lagrange multiplier is identified exactly, so we begin with an initial guess $\sigma_0(t) = \sigma_0$, we can obtain the following exact solution:

$$\sigma = \sigma_0 + \int_0^t kn \exp\left(\frac{s-t}{\tau}\right) \mathrm{d}s \tag{5}$$

The terminal value of σ when time tends to infinity is:

$$\sigma(\infty) = \tau kn \tag{6}$$

We use a homotopy equation [14-17] to describe the solution property:

$$\sigma(t) = p(t)\sigma_0 + [1 - p(t)]\sigma(\infty) = \sigma(\infty) + p(t)[\sigma_0 - \sigma(\infty)] \tag{7}$$

where p is a homotopy function satisfying $p(0) = 1$ and $p(\infty) = 0$. Considering the relaxation process of eq. (5):

$$p(t) = \exp\left(-\frac{kn}{\tau}t\right) \tag{8}$$

So an approximate solution can be expressed:

$$\sigma(t) = \tau kn + (\sigma_0 - \tau kn)\exp\left(-\frac{kn}{\tau}t\right) \tag{9}$$

In the aforementioned analysis, the desorption time is considered as a constant. In most case it is a function of time, so eq. (1) can be modified:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}t} + \frac{1}{\tau(t)}\sigma - kn = 0, \ \ \sigma(0) = \sigma_0 \tag{10}$$

This is also a linear equation, so its exact solution can be obtained by the variational iteration method:

$$\sigma = \sigma_0 + \int_0^t kn \exp\left\{ \int_0^s \frac{1}{\tau(\xi)}\mathrm{d}\xi - \int_0^t \frac{1}{\tau(\xi)}\mathrm{d}\xi \right\} \mathrm{d}s \tag{11}$$

The adsorption coefficient depends upon σ, so eq. (1) becomes:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}t} + \frac{1}{\tau}\sigma - k(\sigma)n = 0, \ \ \sigma(0) = \sigma_0 \tag{12}$$

If $k(\sigma)$ is a non-linear function, eq. (12) can be solved approximately the following variational iteration algorithm:

$$\sigma_{n+1} = \sigma_0 + \int_0^t k(\sigma_n) n \exp\left\{\int_0^s \frac{1}{\tau(\xi)}\mathrm{d}\xi - \int_0^t \frac{1}{\tau(\xi)}\mathrm{d}\xi\right\}\mathrm{d}s \tag{13}$$

A fractal modification of Langmuir kinetic equation

Many experimental studies show that σ is a function of t^α instead of t [18-28]:

$$\sigma \propto t^\alpha \tag{14}$$

This property can be best described by a fractal derivative model:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}t^\alpha} + \frac{1}{\tau}\sigma - kn = 0 \tag{15}$$

where $\mathrm{d}\sigma/\mathrm{d}t^\alpha$ is the fractal derivative defined [22-28]:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}t^\alpha}(t_0) = \Gamma(1+\alpha) \lim_{\substack{t-t_0 \to \Delta t \\ \Delta t \neq 0}} \frac{\sigma(t) - \sigma(t_0)}{(t-t_0)^\alpha} \tag{16}$$

where α is the two-scale fractal dimension and Δt – the minimal time interval beyond which the solution property becomes uncertain.

Conclusion

This paper study the solution structure of the Langmuir kinetic equation by the variational iteration method, where the Lagrange multiplier is identified by the variational principle. For the non-linear kinetic equation, an exact solution structure is obtained. The effects of desorption time and adsorption coefficient on the solution structure are also elucidated, and a fractal partner of Langmuir kinetic equation is suggested.

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