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Analytical models for describing cation adsorption/desorption kinetics as considering the electrostatic field from surface charges of particles

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A B S T R A C T

Surface charges of particles together with the adsorbed counter ions in diffuse layer can set up a strong electrostatic field around the particles in aqueous solution. The existent kinetic models for describing cation exchange on solid/liquid interface were either empirical or semi-empirical, and in which the electrostatic field is not considered. In this paper, as considering the important effect of electrostatic field around particles on cations adsorption/desorption, for the first time the dynamic distribution equations of cations in diffuse layer for adsorption and desorption processes in both flow method and batch technique have been established. Those equations clearly show how the cation concentration changes with time in different position of diffuse layer during the cation exchange process, and the corresponding new kinetic models have been obtained upon them. The new models indicate that, in both flow method and batch technique, for the adsorption process, experimental results should appear zero order kinetic process caused by the strong force adsorption in the initial stage of adsorption, and then transform to the first order kinetic process of the weak force adsorption; and for the desorption process, however, only first order kinetic process may exist. The new models are essentially different from the classic apparent or empirical kinetic models since all the parameters have their defined physical meanings in the new models, thus the rate parameters in the new models have the potential to theoretically predict. Theoretical analyses also indicated that, the adsorption/desorption rate in flow method experiment will be much higher than that in batch technique experiment.

1. Introduction

Surface charges of solid particles together with the adsorbed counter ions in diffuse layer can set up a strong electrostatic field around the particles. The existent kinetic models for describing the cation exchange were either empirical or semi-empirical, e.g. the Freundlich equation [1,2], the Elovich equation [3,4], the parabolic diffusion equation, and the zero order, first order kinetic equation and so on [5–9]; and most importantly, in all of those classic equations the electrostatic field was not considered. Therefore it will be very important to establish analytical models for cation adsorption/desorption process in which the important effect of electrostatic field around particles to be taken into account.

Ion diffusion and adsorption were taken as two different and separate processes in former studies. But actually there are two different adsorption processes for ions on charged particle surface: adsorption occurring in diffuse layer (DL) via electrostatic force (exchange adsorption) and adsorption occurring at solid surface caused by surface complexation (specific adsorption) [10]. Recent studies have shown that ion diffusion and ion adsorption in DL via electrostatic force are essentially the same one process [11–13]. For the electrostatic adsorption, an adsorbed ion via the electrostatic force in DL is not fixed at an “adsorption site” at particle surface, but it is randomly distributed in DL and obeys the Boltzmann distribution law, hence the adsorbed ions in DL do not lose their chemical natures, the only difference between cations in DL (adsorption phase) and in bulk solution (solution phase) is their mobility or activity, and the former is much lower than the latter because of the electrostatic attractive force.

Usually, if a cation species can be chemically adsorbed on the particle surface, it still can be physically adsorbed simultaneously by the electrostatic force in DL. Therefore it is very important to distinguish these two different and coincident processes in an experiment. Unfortunately, only the overall kinetic rate of cation adsorption, which includes the electrostatic force adsorption and the chemical bond

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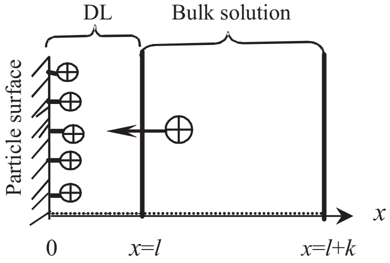

Fig. 1. A conceptual diagram of cation adsorption exchange in batch technique experiment.

adsorption, could be determined in an experiment [10]. Thus the establishment of the exact analytical models for describing the electrostatic force adsorption/diffusion in DL is critical in evaluating the chemical adsorption rate from the experimental data.

As considering the adsorption/diffusion in an external electric field, the complex Fokker-Planck equation with time-dependent potential will be employed. Unfortunately, because of the inherit complexity, the analytical solution of the Fokker-Planck equation with a time-dependent potential still remained a challenge. Recently, the new theories established by Li and Wu make it possible, and based on the new theory, the adsorption and desorption kinetic models of ions for electrostatic force adsorption could be obtained from the following equations theoretically [11,14,15]:

$$\frac{\partial A_i(x,t)}{\partial t} = D_p \frac{\partial^2 A_i(x,t)}{\partial x^2} \tag{1}$$

and

$$J_i(x,t) = D_{p_i} \frac{dA_i(x,t)}{dx} \tag{2}$$

where A_i is apparent concentration of ith ion species, and it can be expressed as:

$$A_i(x,t) = f_i(x,t) \exp\left[\frac{Z_i F \varphi(x,t)}{RT}\right] \tag{3}$$

and J_i is apparent flux, and it is defined:

$$J_i(x,t) = j_i(x,t) \exp\left[\frac{Z_i F \varphi(x,t)}{RT}\right] \tag{4}$$

where $f_i(x, t)$ is the concentration of the ith ion species at a distance x away from particle surface; $j_i(x, t)$ is the flux of the ion species; $\varphi(x, t)$ is the electric potential in the electric field of DL; Z_i is the charges of the ion species; F is the Faraday constant; R is the gas constant; T is the absolute temperature; D_{pi} is the diffusion coefficient of the ion species.

In this study, we will establish analytical new models for describing cation adsorption and desorption kinetics in both miscible displacement method (flow method) [5,16–18], and batch technique [19], which are widely applied to ion exchange research. For those new models, the electrostatic effect around particles on cation adsorption/desorption will be systematically taken into account.

However, recent studied have shown that, for solution with high electrolyte concentration, non-electrostatic forces (e.g. ionic dispersion forces) in ion adsorption behaviour will become importance [20]. In this study, we ignored the non-electrostatic forces, thus the obtained results may be applicable for a relative low electrolyte concentration condition ($\leq$0.1 mol/l).

2. The dynamic distribution of cation in DL for the adsorption and desorption processes in exchange

2.1. The dynamic distribution of cation in DL in batch technique experiment

2.1.1. Exchange adsorption process of cations in batch technique experiment

The cation exchange adsorption process can be illustrated as Fig. 1 in batch technique experiment. The exchange adsorption means the adsorption process is actually an exchange process, thus before adding the new exchange cation species in the bulk solution, another cation species has existed in the DL.

Supposing that the concentration of ith adsorbed cation species in the bulk solution is initially f_{i0}, and that in the bulk solution the $\varphi(x) = 0$; also considering the concentration of the ith cation species in the DL is initially zero. The dynamic distribution of the exchange adsorption cation in DL is a solution of Eq. (1) with the initial condition:

$$A_i(x,0) = 0 \cdot e^{ZF\varphi(x,0)/RT} = 0 \tag{5}$$

and the boundary condition based on Eq. (2) and the "apparent mass conservation" law [14]:

$$\frac{d[k \cdot A_i(x,t)]}{dt} = -D_{pi} \left.\frac{dA_i(x,t)}{dx}\right|_{x=l} \tag{6}$$

where k is the average thickness of bulk solution, it can be estimated from the following equation: $k = (V - mSl)/mS$, in which V is the total volume of liquid, m is the mass of sample, S is the specific surface area of the sample, l is the average thickness of DL, and $(V - mSl)$ is the volume of the bulk solution.