Theoretical analysis of the pseudo-second order kinetic model of adsorption. Application to the adsorption of Ag(I) to mesoporous silica microspheres functionalized with thiol groups

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HIGHLIGHTS

▶ Equation for the rate constant in the pseudo-second order kinetic model is proposed.
▶ This rate constant is correlated to the diffusion coefficient in spherical particles.
▶ The adsorption of Ag(I) within mesoporous spherical particles is studied.
▶ The adsorption data are fitted by the spherical diffusion model.
▶ The diffusion coefficient value depends on the saturation ratio for adsorption.

ARTICLE INFO

ABSTRACT

There is no universally accepted theoretical interpretation of the rate constant of the pseudo-second order kinetic model of adsorption. This study proposes a relationship for the rate constant of the pseudo-second order adsorption model based on the diffusion mass transfer of the adsorbate within spherical homogeneous adsorbent microspheres. This relationship provides a new interpretation of the physical meaning of the rate constant mentioned above.

A detailed study of the adsorption of Ag(I) onto and within isolated mesoporous silica microspheres functionalized with thiol groups has been conducted. The experimental data were fitted successfully by the pseudo-second order model resulting in the determination of the values of the corresponding apparent diffusion coefficient (D_{Ag}) and the adsorbate adsorbed on the surface of the particles (q_s). The latter value was found to be almost equal to the corresponding equilibrium value (q_e). The logarithm of the value of D_{Ag} increased linearly from 2.5×10^{-17} m²/s to 6×10^{-16} m²/s with the decrease in the saturation ratio (q_s/q_{max} where q_{max} is the maximum amount of Ag adsorbed).

1. Introduction

The overall kinetics of adsorbate adsorption is dependent on both the actual adsorption of the adsorbate onto the adsorption sites, defined by the corresponding kinetic and equilibrium constants, and its mass transfer towards these sites, characterized by the corresponding diffusion coefficient. Adsorption kinetic studies in liquid/solid systems are often conducted under batch conditions where the transient adsorbate concentration in the solution is fitted by a suitable kinetic model. Among these models the pseudo-first order and pseudo-second order models have been used most frequently [1,2]. The physical meaning of the rate constant in the pseudo-first order kinetic model, also known as the Lagergren equation (Eq. (1) and its solution Eq. (2) for $q = 0$ at $t = 0$) [3], is well understood in terms of the direct proportionality between the rate of adsorption and the distance of the system from equilibrium.

$$\frac{dq}{dt} = k_1(q_e - q) \tag{1}$$

$$\ln \frac{(q_e - q)}{q_e} = -k_1 t \tag{2}$$

where q and q_e are the transient and equilibrium amount of adsorbate adsorbed.

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