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# A dynamic intraparticle model for fluid–solid adsorption kinetics

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ABSTRACT

The fluid–solid adsorption batch kinetics is surely one of the most popular topic in the chemical engineering science. The water purification from pollutant components, such as metals and organic compounds, can be considered one of the main application of this field. Even if the topic is of a great scientific and industrial interest, the modeling of the mentioned systems is by now far to be reliable. As a matter of fact, most of the models reported in the literature are based on semi empirical approaches that describe the adsorption experimental data on the basis of equilibria and the kinetic terms. In this paper, a new modeling approach is proposed for adsorption kinetics investigation performed in batch reactors with a fluid–solid system. In particular, the mass balances have been developed by taking into account for both the external and internal mass transfer diffusion limitations, solving the dynamic partial differential equations (PDEs) system along the radius of the sorbent particles, considering both the fluid and solid phases that constitute the sorbent particle. From a numerical point of view, the solution of this type of problem is very challenging because it involves the simultaneous solution of many PDEs, ODEs and AEs. Here, physical parameters have to be evaluated either from existing correlations or by direct measurements. This fact makes the model predictable. In order to test the model, some Cu(II) and Pb(II) adsorption tests, taken from literature, using different kind of silica have been interpreted. The presented model can be considered of great interest, as it is the starting point for designing continuous adsorption columns for water purification.

## 1. Introduction

The fluid–solid adsorption can be considered an evergreen problem in the chemical engineering topics. A great amount of paper is published every year with the aim of investigating the sorption of chemicals, both organic and inorganic, on sorbents of different nature that can be either commercial or natural. These studies are usually divided into two parts: equilibrium and kinetic investigations. In the first case, different kind of adsorption isotherms have been already developed, and are accurately reviewed by Febrianto et al. (2009).

The investigation of the adsorption kinetics are usually performed in batch reactors, where a known amount of both sorbent and adsorbate are charged, by fixing temperature, stirring rate and all the physical–chemical variables that constitute the system. In this way, it is possible to measure the evolution with time of the adsorbate concentration in the bulk phase along the experiment time. The data collected in such a way are nowadays described with simplified approaches (Ho, 2006; Liu and Shen, 2008; Febrianto et al., 2009; Qiu et al., 2009) based on kinetic expressions with related mass balances. In particular, different models have been proposed. In general these models can be divide into three categories (Febrianto et al., 2009; Qiu et al., 2009): (i) adsorption reaction models (ARM), where the adsorption phenomenon is expressed such as a reaction rate expression; (ii) adsorption diffusion models (ADM), where the diffusion paths of the sorbate are taken into account; and (iii) double exponential model (DEM) where both external and internal diffusion terms are taken into account. The mentioned models are briefly reported in Table 1.

All the reported equations are usually applied to the adsorption kinetic data by fitting the related adjustable parameters. Even if the fitting can be considered more than satisfactory, it is hard to find a physical meaning of the fitted parameters in all the mentioned cases. Duong D. Do in 1998 has published an extensive book devoted to the field, solving adsorption problems for gas–solid adsorption systems, where the bulk concentration has been considered constant, so neglecting the bulk mass balance. This point is of particular relevance, because, by including the bulk mass balance, it would be possible to describe systems where the sorbate is very diluted or systems with high sorbent/solute ratio.

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### List of symbols

| | |
|---|---|
| $a_i$ | Elovich's equation parameters |
| $a_{sp}$ | geometrical specific surface area ($m^2/m^3$) |
| $a_{sp,I}$ | sorbent specific surface area ($m^2/m^3$) |
| $b$ | Langmuir adsorption constant ($m^3_{liq,P}/mol$) |
| $C_B$ | solute bulk concentration ($mol/m^3_{BULK}$) |
| $C_A$ | concentration of metal in solution at time $t$ ($mol/m^3$) |
| $C_{A,e}$ | adsorbate equilibrium concentration ($mol/m^3$) |
| $C_{A,i}$ | liquid–particle interface adsorbate concentration ($mol/m^3$) |
| $C_L$ | solute concentration in the liquid of the pores ($mol/m^3_{liq,P}$) |
| $C_S$ | solute concentration in the solid ($mol/m^3_{sol,P}$) |
| $C_{S,I}$ | solute concentration on the solid surface ($mol/m^2$) |
| $C_{S,*}$ | saturation solute solid concentration ($mol/m^3_{sol,P}$) |
| $D^0_{AB}$ | ion diffusivity ($m^2/s$) |
| $D_{Cu(II)}$ | Cu(II) ion diffusivity ($m^2/s$) |
| $D_i$ | Wilczak and Keinath parameters ($mol/m^3$) |
| $D_e$ | effective diffusivity liquid film diffusion coefficient ($m^2/s$) |
| $d_P$ | pore diameter (nm) |
| $D_P$ | pore diffusivity based on the cross sectional area ($m^2/s$) |
| $D_{Pb(II)}$ | Pb(II) ion diffusivity ($m^2/s$) |
| $D_S$ | superficial diffusivity ($m^2/s$) |
| $F$ | Faraday (96.5 C/g-equiv) |
| $J, J_P, J_S$ | overall, void and adsorbate phase transport fluxes ($mol/m^2/s$) |
| $k_i$ | kinetic constant |
| $k_m$ | mass transfer coefficient (m/s) |
| $L$ | mobility constant ($m^2$ mol/J/s) |
| $m_a$ | adsorbent amount in the solution ($g/m^3$) |
| $q$ | amount adsorbed at time $t$ |
| $q_\infty$ | average amount adsorbed at infinite time |
| $\bar{q}$ | average amount adsorbed at time $t$ |
| $q_e$ | amount adsorbed |
| $R_g$ | ideal gas constant (J/(mol K)) |
| $r_P$ | particle radial direction (m) |
| $R_P$ | particle radius (m) |
| *Shape* | shape factor |
| $S_0$ | particle surface area per volume ($m^2/m^3$) |
| $t$ | time (s) |
| $T$ | temperature (K) |
| *th* | film thickness (m) |
| $z_+, z_-$ | valences of, respectively, cation and anion |

*Greek symbols*

| | |
|---|---|
| $\varepsilon$ | particle porosity ($m^3_{liq,P}/m^3_P$) |
| $\varepsilon'$ | volumetric ratio between the bulk volume and the overall particle volume ($m^3_{BULK}/m^3_P$) |
| $\lambda^0_+, \lambda^0_-$ | limiting zero concentration ionic conductances (($A/m^2$) (V/m) (g-equiv/$m^3$)) |
| $\mu, \mu_0$ | chemical potential |
| $\tau$ | tortuosity factor |

For example, pollutant removal from liquid streams is one of the mentioned cases (Chiron et al., 2003; Lu et al., 2006; Mohan and Pittman, 2007; Febrianto et al., 2009). This model solves one of the main problems of the adsorption kinetics, relating it to the diffusion paths that characterize the system. In the present paper, starting from the mentioned model, we developed a more general fluid–solid adsorption model, including both the mass balances for bulk and particle phases. In particular, both the external and internal mass transfer limitations have been taken into account, introducing only physical parameters to describe the adsorption kinetics. The model has been applied to a case study, that is Cu(II) and Pb(II) removal from water with silica based sorbents with good results. As it can be guessed, the presented work is a good starting point for the realization of a much more sophisticated model that could be useful to design continuous adsorption columns.

## 2. Theory

A correct investigation of the fluid–solid adsorption kinetics needs to define all the possible diffusion and equilibria phenomena. In particular, four different steps have been taken into account in our model, in agreement with literature findings (Pignatello and Zing, 1996): (i) diffusion from the bulk to the particle surface; (ii) diffusion from the pore mouth into pore (pore liquid diffusion); (iii) equilibrium between the liquid and the solid phase; and (iv) diffusion of the adsorbate molecule on the sorbent surface. A scheme of the adopted adsorption mechanism is reported in Fig. 1.

None of the defined steps has been considered rate determining, in this way all the physical phenomena are taken into account. Thus, the proposed model takes into account the existence of three different domains. First of all, the liquid bulk that contains the solute dissolved in the solvent. By considering a batch reactor, the solute bulk concentration ($C_B$) can be assumed constant till the liquid film surrounding the particle. Of course, the mass flux between the bulk and the liquid, that is inside the particle pore, must be considered, so the solute concentration at the catalyst surface can be different from the bulk one. Two different domains can be distinguished inside the particle: (i) a liquid side, where the solute diffuses from the outer particle surface to the center of the particle and (ii) a solid side, where the solute concentration reaches the equilibrium inside the particle through one of the possible mechanism that can be found in the literature (Febrianto et al., 2009). In our case, the Langmuir mechanism has been considered. Moreover, the solute can diffuse also on the sorbent surface, with a diffusivity parameter that strongly depends on the interactions between the solute and the sorbent.

For clearness purposes, a summary of the assumed hypothesis is reported below:

1. Monomodal particles size.
2. Average porosity and tortuosity of the particle.
3. Adsorption equilibrium in the pore.
4. Particle mass balance adaptable on the basis of the shape factor.
5. Isothermal system.

The bulk liquid phase mass balance can be written as in Eq. (1). In the mentioned equation, the accumulation term was considered equal to the solute flux from the bulk to the liquid phase inside the pores of the particles. Here $\varepsilon'$ represents the volumetric ratio between the bulk liquid volume and the overall particle volume. This term is needed for dimensional purposes and is necessary to express the influence of the bulk volume/solid volume ratio on the adsorption kinetics.

$$\varepsilon' \cdot \frac{\partial C_B(t)}{\partial t} = -k_m \cdot a_{sp} \cdot (C_B(t) - C_L(t, r_P)|_{R_P}) \qquad (1)$$

The flux was considered proportional to the mass transfer coefficient ($k_m$) and the geometric specific surface area, this last calculated assuming that all the solid particles can be considered as spheres of the same radius, Eq. (2).

$$a_{sp} = \frac{3}{R_P} \qquad (2)$$