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Design of an adsorption column for methylene blue abatement over silica: From batch to continuous modeling

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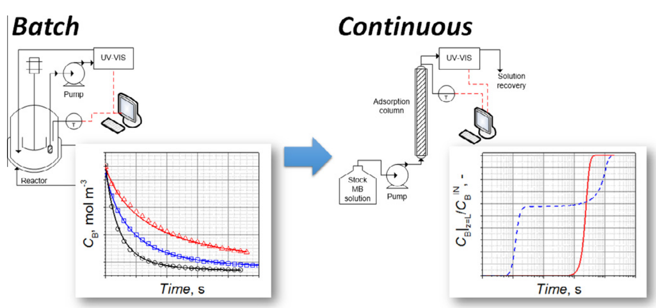
HIGHLIGHTS

- Transient intraparticle model for fluid–solid adsorption kinetics.
- The PDEs system solved with method of lines.
- Methylene blue adsorption over silica used as a model system.
- Physical parameters fitted on the batch experimental data.
- Adsorption columns can be strictly simulated.

GRAPHICAL ABSTRACT



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ABSTRACT

Scale-up processes are a central feature of chemical engineering science and technology. In this field, researchers' efforts focus on the development of mathematical models that could be able to interpret physical and chemical phenomena on several dimension scales. Adsorption systems are typical operation units that fall in the mentioned category. In fact, moving from the particle to the fixed bed scale, a further dimension represented by the column axial coordinate is added to the system (and, for larger columns, also the column radial coordinate). In a previous work, an Adsorption Dynamic Intraparticle Model (ADIM) has been proposed and validated by the authors for adsorption batch systems. In the present paper, an attempt to implement the model equations for continuous systems has been made. For validation purposes, an adequate experimental investigation has been obtained by carrying out adsorption experiments both on batch and in continuous devices by using a model system that is represented by *aqueous methylene blue over silica*. Starting from batch experiments, where some fundamental mass transfer parameters, such as the surface diffusivity (D_S), the tortuosity factor (τ) and the mass transfer coefficient (k_m), have been determined, the ADIM model has been extended to the prediction of the breakthrough curves obtained in continuous system, obtaining good agreements with the collected experimental data. In this way, it has been demonstrated that the ADIM model is a powerful, flexible tool for adsorption modeling over increasing dimension scales.

1. Introduction

Fluid–solid adsorption is a common industrial technique that is normally used for both product separation and wastewater treatment. In the field of water purification, the removal of dyes from wastewaters is an argument of great interest in chemical engineer-

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Nomenclature

List of symbols

a_{sp}	geometrical specific surface area, $m^2 \cdot m^{-3}$
b	Langmuir affinity parameter, $m^3_{liq,P} \cdot mol^{-1}$
C_0	adsorbate initial concentration, $mol \cdot m^{-3}$
C_B	solute bulk concentration, $mol \cdot m^{-3}_{BULK}$
C_B^{IN}	column feed concentration, $mol \cdot m^{-3}_{BULK}$
C_L	solute concentration in the liquid of the pores, $mol \cdot m^{-3}_{liq,P}$
C_S	solute concentration in the solid, $mol \cdot m^{-3}_{sol,P}$
$C_{S,*}$	saturation solute solid concentration, $mol \cdot m^{-3}_{sol,P}$
D_0	molecular diffusivity, $m^2 \cdot s^{-1}$
D_P	pore diffusivity based on the cross sectional area, $m^2 \cdot s^{-1}$
D_S	surface diffusivity, $m^2 \cdot s^{-1}$
D_Z	axial dispersion coefficient, $m^2 \cdot s^{-1}$
K_F	Freundlich adsorption constant, $(mol \cdot m^{-3}) \cdot (mol \cdot m^{-3})^{-n}$
k_m	mass transfer coefficient, $m \cdot s^{-1}$
L	column length, m
n	adsorption intensity, –
Q	volumetric flow-rate, $cm^3 \cdot min^{-1}$
r_P	particle radial coordinate, m
R_P	particle radius, m
Re	Reynolds number, –
s	shape factor, –
Sc	Schmidt number, –
S_P	particle external surface area, m^2
t	time, s
T	temperature, K
u	flow velocity, $m \cdot s^{-1}$
V_P	particle volume, m^3
w_{ADS}	adsorbent mass, g
z	column axial coordinate, m

Greek symbols

ε	solid particle porosity
ε'	volumetric ratio between the bulk volume and the overall particle volume, $m^3_{BULK} \cdot m_P^{-3}$
ε_v	column void fraction, –
η_{ADS}	adsorption efficiency, –
μ	water viscosity, $Kg \cdot m^{-1} \cdot s^{-1}$
ρ	water density, $Kg \cdot m^{-3}$
τ	tortuosity factor, –

ing science. Over 100,000 kinds of dyes are produced every year with a production of more than $7 \cdot 10^5$ tonnes y^{-1}; they are widely used in a variety of industries like textile, leather, paper and others [1,2]. By considering such employment, the dye removal is a key factor both for environmental and quality aspects. In fact, even concentrations less than 1 ppm of dyes can give an undesirable highly visible color to water [2] and some dyes, or their degradation products, may be toxic and carcinogens [3]. For this reason, numerous techniques for water de-colorization have been developed like coagulation, flocculation, several kinds of physical, chemical and biological degradations and the use of cation exchange membranes [1,2]. Beside these, the adsorption on solid adsorbents is a technique that shows many attractive features. The advantages of this technology are represented by low costs, simplicity of design, ease of operation and insensitivity to toxic substances [4]. The cheapness of the method is mostly dependent on the adsorbent choice, for example by using non-conventional low-cost adsorbents (active carbon from natural waste sources, i.e. pinewood, rice husk, tree fern, vine, sugar cane dust, banana pith, corncob, coal sewage sludge, fly ashes [1]) or natural materials, such as clays and silica.

In order to properly design an adsorption column for dyes removal, it is necessary to perform an intensive batch investigation on both the equilibrium and the kinetics of the couple adsorbate/adsorbent. Some important physical and chemical properties can be determined with a correct experimentation, such as the equilibrium dye concentration on the adsorbent, the diffusivity of the adsorbate in both the external film of the liquid–solid interface, the internal diffusivity and the surface diffusivity [5]. All the mentioned properties are of crucial importance in design of an adsorption column and are only measurable univocally by performing batch experiments. In the present work, a model system has been taken into account, that is the adsorption of methylene blue over silica. Methylene blue (MB) has been chosen as adsorbate molecule, because it is widely used in industry for dying cotton, wood and silk [2] and its release in the environment can generate health disease to human and animals such as eye burns or permanent injuries to eyes [2,6]. Even if in the literature there are already some papers dealing with the removal of MB by adsorption using siliceous adsorbents, the collected data are not enough detailed to design an adsorption column, because lacking of either the equilibrium [7] or kinetic data [8–13]. For this reason, the sorption of methylene blue on raw silica has been explored in this paper, designing two experimental devices useful to collect adsorption kinetics data and carrying out a systematic study to explore the effect of stirring rate, mass of adsorbent, dye initial concentration, solid particle size in batch conditions, and of length of packing and particle dimensions in continuous conditions.

All the collected experimental data have been interpreted with a dynamic intraparticle model (ADIM) previously developed and validated for batch systems [14,15].

2. Materials and methods

2.1. Adsorbent and adsorbate properties

In performing equilibrium and kinetic experiments, raw silica cylindrical pellets Aerolyst™ 355 were used as adsorbent material without any type of pre-treatment. A morphological characterization of the solid was made by physisorption of N_2 at 78 K. Physical properties of the solid are listed in Table 1.

The average equivalent particle radius has been calculated as reported in the literature [16], that is the radius of a sphere of equal volume ($R_P = 6 \cdot V_P/S_P$). This value has been considered as the integration extreme of the mass balance intraparticle equations.

Trihydrate methylene blue powder has been provided by ICN Biomedicals, Inc. (M.W. = 373.9 $g \cdot mol^{-1}$, CAS: 7220-79-3) and was used to realize a stock solution at concentration of $1 \cdot 10^{-2}$ $mol \cdot m^{-3}$ then diluted when necessary. Dye concentration was detected by UV analysis by using a Jasco UV-975 detector. Among the various peaks characterizing the methylene blue spectrum, the

Table 1
Adsorbent physical properties.

Property, unit	Value
Surface area (BET), $m^2 \cdot g^{-1}$	144.8
Pore specific volume, $m^3 \cdot g^{-1}$	$0.90 \cdot 10^{-6}$
Pore size range, nm	10–100
Average particle length, m	$(4.50 \pm 0.35) \cdot 10^{-3}$
Average particle diameter, m	$(2.35 \pm 0.27) \cdot 10^{-3}$
Average equivalent radius R_P, m	$(1.40 \pm 0.15) \cdot 10^{-3}$
Bulk density, $g \cdot m^{-3}$	$2.65 \cdot 10^6$
Porosity ε, –	0.71