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Multi-resistance kinetic models for biosorption of Cd by raw and immobilized citrus peels in batch and packed-bed columns

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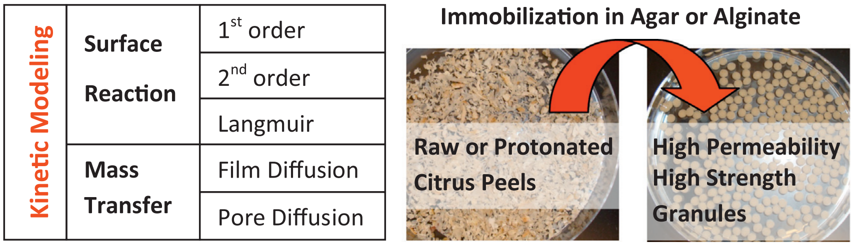
HIGHLIGHTS

- Citrus peels were immobilized in agar and alginate to produce stable granules.
- Batch kinetics were described by 3 surface reaction and 4 mass transfer models.
- A number of models were identified as analogous, which was largely unnoticed so far.
- Sensitivity analysis shows different rate limiting factors for granules and raw peels.
- A dual resistance mass transfer model predicted breakthrough curves *a priori*.

GRAPHICAL ABSTRACT



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ABSTRACT

Biosorbents should be of suitable size and stability for successful use in packed-bed columns, a reactor type commonly used in industrial sorption or ion exchange processes. Two polymeric materials (calcium alginate and agar) were investigated for immobilization of citrus peels to improve biosorbent properties. By varying relevant parameters such as initial concentration, flow rate, and bed height, immobilized peels and raw peels pre-saturated with calcium and hydrogen ions were compared for cadmium biosorption in equilibrium and kinetic batch experiments as well as in fixed-bed reactors. The batch equilibrium was described by Langmuir and Freundlich isotherms, with the following affinity sequence: protonated raw peels (PRP) ≈ protonated alginate-immobilized peels (PALP) > agar-immobilized peels (AGP) > calcinated raw peels (CRP). The Langmuir uptake capacity followed the order PALP > CRP > PRP > AGP. Batch kinetics was described by three mass transfer models (based on external resistance, intraparticle resistance, and both) and by three surface reaction models (pseudo first order, pseudo second order, and Langmuir kinetics). Frequently used mass transfer models such as Weber-Morris, Boyd, and Urano were reviewed, revealing that these models are different approximations of the same parent model. The suitability of using Weber-Morris and Boyd plots to determine the dominating mass transfer resistance was critically evaluated, and mathematically analogous models were identified. Breakthrough curves were simulated by a surface reaction model (Bohart–Adams) and were predicted *a priori* by a mass transfer model (Klinkenberg) using external and intraparticle mass transfer coefficients from engineering correlation and batch kinetic data, respectively.

Abbreviations: AGP, agar-immobilized peels; ALP, alginate-immobilized peels; CRP, calcium-saturated raw peels; LDF, linear driving force; MTM, mass transfer modeling; PALP, protonated alginate-immobilized peels; PFO, pseudo first order; PRP, protonated peels; PSO, pseudo second order; SRM, surface reaction modeling.

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Nomenclature

Symbol	Definition
A	area of cross section of fixed-bed column (cm^2)
b	Langmuir affinity constant, Eq. (13) (L/mg)
B	parameter in Eqs. (20)–(24) (= $\pi^2 D_s/R^2$) (min^{-1})
Bi	Biot number, i.e., ratio of external film diffusivity to intraparticle diffusivity (= $R\ k_f/D_s$) (–)
C	concentration of sorbate in aqueous phase at time t (min) (mg/L)
C_0	initial or influent sorbate concentration in batch or fixed-bed reactor (mg/L)
C_∞	value of C at t_∞ for batch experiment (mg/L)
C_e	equilibrium sorbate concentration in aqueous phase (mg/L)
C_i	aqueous sorbate concentration at sorbate–sorbent interface (mg/L)
D	diffusion coefficient of sorbate in aqueous phase (cm^2/min)
D_s	diffusion coefficient of sorbate within the sorbent (cm^2/min)
F	saturation fraction (= q/q_∞) (–)
h	bed height (cm)
K	equilibrium constant for linear isotherm, Eq. (15) (L/g)
k_1	pseudo-first-order rate constant, Eq. (11) (1/min)
k_2	pseudo-second-order rate constant, Eq. (12) (g/(mg min))
k_{ad}	second-order forward rate constant, Eq. (10) (L/(mg min))
k_{BA}	rate constant, Eq. (18) (mL/(mg min))
k_{de}	first-order reverse rate constant, Eq. (10) (1/min)
k_f	external or film mass transfer coefficient, Eq. (4) (cm/min)
K_f	overall fluid phase mass transfer coefficient, Eq. (37) (cm/min)
K_F	Freundlich isotherm parameter ($L^{1/\mu}/(g\ mg^{1/\mu-1})$)
k_S	intraparticle mass transfer coefficient, Eq. (7) (cm/min)
K_S	overall solid phase mass transfer coefficient (cm/min)
M	mass of sorbent in the reactor (batch/fixed bed) (g)
n	integer used in Eqs. (20), (25), (29), (30) to define infinite series (–)
N_0	Bohart–Adams parameter, Eq. (18) (mg/mL)
q	average concentration of sorbate within the sorbent at time t (mg/g)
Q	flow rate (mL/min)
q'	sorbate concentration within sorbent at a radius r from sorbent center (mg/g)
q_∞	value of q at t_∞ (mg/g)
q_{BA}	parameter in BA model, Eq. (19) (mg/g)
q_{bt}	value of q at breakthrough time (mg/g)
q_e	equilibrium sorbate concentration in sorbent (mg/g)
q_i	concentration of sorbate within sorbent at interface (mg/g)
q_m	Langmuir maximum uptake (mg/g)
R	radius of sorbent particle (cm)
Re	Reynolds number (= $2\ R\ u/\nu$) (–)
S’	sorbent particle surface area per volume of liquid in reactor (= $(1-\varepsilon)\ S_0/\varepsilon = S_0 M/(V_s\ \rho)$) ($cm^{-1}$)
S_0	sorbent particle surface area per unit particle volume (= $3/R$) (cm^{-1})
Sc	Schmidt number (= ν/D) (–)
Sh	Sherwood number (= $2\ k_f\ R/D$) (–)
t_b	breakthrough time (min)
t_∞	duration of batch experiment or saturation time in fixed-bed experiment (min)
u	superficial velocity within column (= Q/A) (cm/h)
v	interstitial velocity within column (= u/ε) (cm/h)
V	volume of reactor (batch or fixed bed) (mL)
V_s	volume of aqueous phase (= $V\ \varepsilon$) (mL)
Z	axial distance coordinate, positive in flow direction (vertical upflow) (cm)
α	ratio of sorbate remaining in liquid phase to sorbate bound, Eq. (25) (–)
β	parameter used in Eqs. (29), (30) (–)
γ	parameter used in Eq. (25) (–)
ε	void fraction in column (–)
ε_p	sorbent porosity (–)
ρ_b	density of packed bed (= M/V) (g/mL)
ρ	density of sorbent (= $M/(V\ (1-\varepsilon))$) (g/mL)
μ	Freundlich isotherm exponent (–)
ν	kinematic viscosity of water at 25 °C (cm^2/min)
ξ	dimensionless distance (= $h\ K_f\ S_0/(\varepsilon\ v\ (1-\varepsilon))$) used in Eq. (35) (–)
τ	dimensionless time $(= S_0 K_f (vt - h)/(K\ \rho\ v))$ used in Eq. (35) (–)

1. Introduction

For industrial application of biosorption as a low-cost metal removal alternative to processes such as ion exchange, packed-bed columns are generally regarded as the best reactor type, since their large solid/liquid concentration difference creates a strong driving force that results in high effluent quality. Application in packed-bed columns requires the sorbent to be sufficiently rigid. Past research has shown that citrus peels can be successfully used in packed-bed reactors [1], but some citrus peel types have caused clogging and disintegration problems in packed-bed reactors, though they performed well in batch mode. The use of citrus peels necessitates appropriate processing, as done in the present work, to make the biosorbent suitable for use in a column reactor regardless of its initial shape and size. Immobilization of microbial biomass within natural or synthetic polymeric matrices has been effective in this regard; however, such processing has not been widely explored for agro-based biomass. Listed in order of increasing cost according to Sigma Chemical Company, 2011 (http://www.sigmaaldrich.com), the most commonly used immobilization matrices are alginate, agar, silica gel, polysulfone, agarose, and polyacrylamide [2]. Alginate and agar were chosen as matrix materials in this study because of their low cost and ease of preparation. The first of two main objectives of the present work was to determine a suitable immobilization method for citrus peels, producing a stable biosorbent with high uptake (affinity and capacity), as well as favorable kinetics.

The second main objective was to evaluate kinetic models for batch and column application. The goal of the present research was to employ a simple analytically solvable two-parameter model for *a priori* prediction of breakthrough curves without adjusting any model parameters, but rather using parameters from other sources, such as batch experiments. A number of articles have been published on various narrow aspects of this topic, such as modeling biosorption kinetics either in batch or in columns using either native or processed biosorbents, considering either mass transfer or surface reaction as the rate-limiting step. However, in none of these studies is an analytical solution for mass transfer in both