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Numerical simulation of the adsorption process of copper for phosphoric acid purification

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ABSTRACT

In this paper, a numerical study of the adsorption phenomenon of copper present in phosphoric acid is presented. The process is carried out batch wise using dates stones and activated carbon as solid supports. The governing equations for the adsorption phenomenon were discretisized by finite differences method using the explicit scheme where the conditions of stability are ensured. A computing code was developed to determine all the structures of diffusion of heavy metals solutions into the pores of adsorption particles. In order to assess the code reliability, the obtained results were compared to the values reported in the literature and a maximum deviation of 1.49% was shown. The application of the computing code for the case of the adsorption of copper onto the two considered solid supports and using the obtained experimental data enabled the calculation of the superficial intraparticle diffusion coefficient D_s, as well as the mass transfer coefficient K_f.

Keywords: Superficial diffusion; Mass transfer coefficient; Adsorption; Cations; Dates stones; Activated carbon

1. Introduction

The use of adsorption onto natural materials like dates stones for the elimination of heavy metals present in phosphoric acid is getting frequent. This can provide interesting substitutes to the commonly used but expensive adsorbent, namely activated carbon. In the present study, a numerical simulation was carried out in order to assess the performance of dates stones to retain copper ions present in phosphoric acid solutions by also considering activated carbon. Therefore, the knowledge of key parameters such as the mass transfer and the diffusion coefficients is of great importance.

In many research works, technical solutions were put forward for the estimation of these parameters. One can cite Roy et al. [1] who applied the orthogonal collocation method to solve the partial differential equations which describe the diffusion phenomenon in an unsteady state, followed by the use of Laplace transform. Their results were compared with those obtained by Traegner and Suidan [2]. The performance of this treatment depends on several factors such as the kinetics of adsorption and equilibria, the reactor hydrodynamic, the competition induced between the metallic cations present in the phosphoric acid, etc.

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The aim of the present study is to develop a simulation code for the adsorption taking place in a batch reactor, based on the equilibrium and kinetic parameters.

The theoretical approach relies on the homogeneous surface diffusion model (HSDM) which takes into account the outside mass transfer coefficient (K_f) and the superficial diffusion coefficient (D_s) to model the adsorption kinetic as reported by Weber and Chakravorty [3], Mathews and Weber [4], and Crittenden and Weber [5] to describe adsorption processes and where the necessary equations require the introduction of kinetic parameters.

A priori an experimental work is carried out in a batch reactor to determine the Freundlich isotherm parameters which, once injected in the calculation code, enable to obtain the superficial diffusion coefficients.

The simulation programs were first assessed by means of results reported in the literature and then applied to the case of purification of phosphoric acid by adsorption onto dates stones and activated carbon for the elimination of copper metallic cations, namely copper.

2. The mathematical model

In a spherical coordinates system, the diffusion equation in a transient regime involves terms of first and second order in the Laplacian. In a dimensional form, the radial difference for an axi-symmetric problem can be written as follows:

$$\frac{\mathrm{d}C_b}{\mathrm{d}t}V = -M\frac{\mathrm{d}q_{avg}}{\mathrm{d}t} \tag{1}$$

$$q_{avg} = \frac{3}{(d_p/2)^2}\int_0^{d_p/2} q(r,t)r^2\mathrm{d}r \tag{2}$$

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q}{\partial r}\right) \tag{3}$$

$$q(r,0) = 0 \tag{4}$$

$$\frac{\partial q}{\partial r} = 0 \quad \text{for} \quad r = 0 \tag{5}$$

$$\rho_p D_s\frac{\partial q}{\partial r} = K_f(C_b - C_s) \tag{6}$$

$$q_s = KC_s^n \tag{7}$$

Putting $n=1$ in Eq. (7) gives the case of linear adsorption, whereas for $n=0$, the HSDM becomes a simple case of diffusion in a sphere where the solution is constant, as presented by Carslaw and Jaeger [6]. For $n \neq 0$ and $n \neq 1$, a nonlinearization problem does occur.

The dimensional form of the previous equations is obtained by using the following dimensional variables:

$$C_b^* = C/C_0; \quad T = 4D_{st}/d_p^2; \quad R = 2r/d_p; \quad q^* = q/q_0$$

These represent the dimensional concentration of the adsorbent phase, time, and radial distance, respectively.

The dimensional the Biot number (Bi) and the distribution variable (D_g) are defined as follows:

$$\mathrm{Bi} = \frac{K_f d_p C_0}{2D_s\rho_p q_0}; \quad D_g = \frac{M}{V}\frac{q_0}{C_0}$$

The dimensional equations are then obtained as follows [1]:

$$C_b^* + D_g \cdot q_{avg}^* = 1 \tag{8}$$

$$q_{avg} = 3\int_0^1 q^* \cdot R\,\mathrm{d}R \tag{9}$$

$$\frac{\partial q^*}{\partial T} = \frac{1}{R^2}\frac{\mathrm{d}}{\mathrm{d}R}\left(R^2\frac{\mathrm{d}q^*}{\mathrm{d}R}\right) \tag{10}$$

$$q^*(R,0) = 0 \tag{11}$$

$$\frac{\partial q^*(0,T)}{\partial R} = 0 \tag{12}$$

$$\frac{\partial q^*(1,T)}{\partial R} = \mathrm{Bi}(C_b^* - C_s^*) \tag{13}$$

$$q_s^* = C_s^{*n} \tag{14}$$

3. Numerical resolution method

Eq. (10) is discretisized by means of the explicit scheme which is stable if the ratio $\lambda = \frac{\Delta t}{\Delta r^2} \leq \frac{1}{2}$, Saatdjian [7]. The grid points are uniformly located and the Gauss Seidel method is used for the resolution, taking into account the initial and boundary conditions are satisfied. Eq. (9) is then integrated by means of the trapezoidal rule to obtain directly the C_b^* values from Eq. (8).

An initial value of C_s at $t = 0$ is taken as zero, Mohellebi, and Lakel [8] and is introduced in Eq. (13), where the C_b^* values are compared to those obtained from Eq. (8). If the difference is reasonable, the actual value of C_s is considered, otherwise C_s is recalculated as follows [1]:

$$C_s = C_s \pm \frac{C_{b1}^* - C_{b2}^*}{z}; \tag{15}$$

where z is a factor which can be constant or increases with the number of iterations. If the new Cvalue is different enough from the actual one then the difference between C_{b1} and C_{b2} is high, indicating a use of a high value for z, for a slow convergence and a long compilation time. If the initial value of C_s is close to that of the actual one, then a small value of z can be used according within the interval $5 \leq z \leq 20$ [1]. The exact values of C_s are then used to calculate q_s^* by means of Eq. (14).

4. Results and discussion

4.1. Validation of the computing code

In order to assess the computing code developed in the present work, the data reported in Ref. [1] were used and introduced as input and the results are shown in Fig. 1 and compared to the values obtained therein. It can be seen that both sets of values are close with a maximum deviation of about 1.49%, indicating a reliable code.

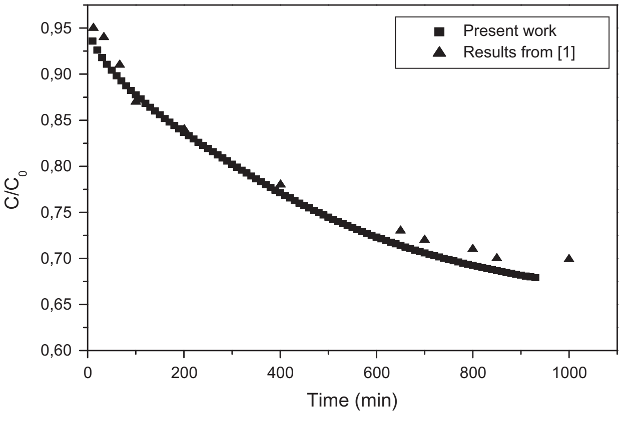

Fig. 1. Validation of the developed calculation code.

4.2. Modeling of the adsorption of Cu^{+2} present in H_3PO_4 in a batch reactor

A priori, for this case, the value of the parameters K_f and D_s are unknown and hence the procedure of their calculation is according the following steps:

(1) Calculation of the mass transfer coefficient K_f by means of the method used in [8–11].

K_f is defined by the following relation as follows:

$$\frac{\partial q}{\partial t} = K_f A (C - C_s) \tag{16}$$

where C and C_s are the concentrations of the solute in the liquid and in the solid particles, respectively, in (g/cm^3), A is the specific surface area per unit mass of dates stones (cm^2 g^{-1}) and q is the retention capacity, both are defined as follows:

$$q = \frac{(C_s - C)V}{M} \tag{17}$$

$$A = \frac{6}{d_p \rho_p} \tag{18}$$

Deriving Eq. (17) and using Eq. (16) as well as the following boundary conditions:

$$t \to 0; \quad C_s \to 0; \quad C_0 = 0$$

Gives the following expression:

$$\left[\frac{dC}{dt}\right] = -K_f S C_0 \tag{19}$$

Table 1
Experimental data

Parameters	Adsorption of Cu onto	
	Dates stones	Activated carbon
d_p (cm)	2e−4	5.1e−4
ρ_p (g/cm^3)	0.75e−3	0.125e−2
K_f	0.19493	1.1253
n	0.417	1.541
C_0 (g/cm^3)	6e−6	6e−6

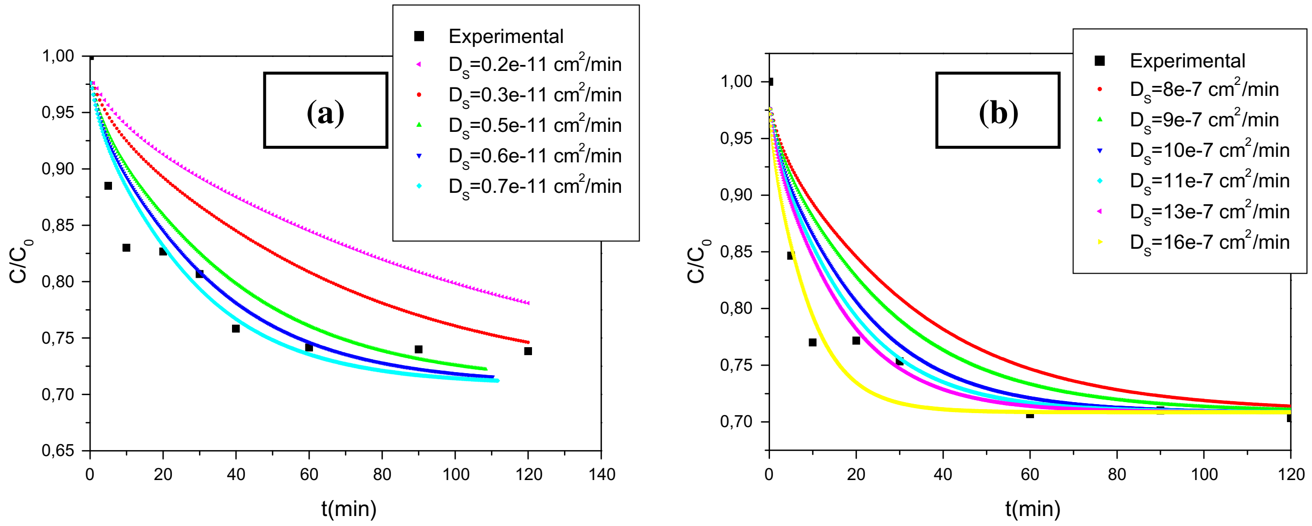

Fig. 2. Diffusion (D_s) coefficients using (a) dates stones and (b) activated carbon, as solid supports.

With:

$$S = \frac{6\, r_{SL}}{d_p \rho_p} \tag{20}$$

ρ_p is the apparent density of the support in (g/cm^3) and r_{SL} is the concentration of the support (g/cm^3).

From the slope at the origin of the experimentally obtained curve giving C/C_0 vs. time, the mass transfer coefficient value K_f can be determined.

(2) By means of the calculation code, an initial value of the diffusion coefficient D_s is assumed, and hence the values of C/C_0 vs. time are obtained, and in the mean time the accuracy of the values of C_s and the stability of the explicit scheme are also obtained.

(3) A trial and error approach as applied in [12] is adopted for the determination of D_s and consists on adjusting the numerically determined curve to the experimental, by comparing the calculated and the experimental values of C/C_0, when varying with time. If the deviation is satisfactory then the D_s value obtained is corrected, otherwise D_s is changed before repeating step 2.

4.3. Experimental data

The experimental data used in the calculation code for the adsorption of the copper cation onto dates stones and activated carbon are given in Table 1.

4.4. Application of computing code for the case of the adsorption of copper

Fig. 2 shows, for copper cations and the two solid supports, the variations of the dimensional concentration C/C_0 with time, where several values of D_s were tried till a calculated curve was close enough to the experimental one.

Table 2
Calculated mass transfer (K_f) and diffusion (D_s) coefficients

Coefficient	Adsorption of Cu^{+2}	
	Dates stones	Activated carbon
K_f (cm m^{-1})	3.536	2.6451
D_s (cm^2 m^{-1})	0.7e–11	1.3e–8

The obtained results according to the procedure described above, concerning the diffusion and the mass transfer coefficients are presented in Table 2.

The results of diffusivity coefficients reproduced the analogous viewpoint that film diffusion is quite a dominant step in the biosorption of Cu(II) [13].

5. Conclusion

In the present work, a numerical approach was developed to determine the mass transfer (K_f) and the superficial diffusion (D_s) coefficients. These are the two key parameters which are required for any modeling of the elimination of heavy metal cations, such as Cu^{+2} from phosphoric acid, by means of adsorption onto solid supports like dates stones. The used numerical resolution method was that of finite differences, based on the Gauss Seidel method for the equations resolution.

The developed code was validated by comparison with results reported in the literature [1], and the maximum deviation was 1.49%, hence providing a reliable code. The mass transfer coefficient (K_f) was determined from the experimental results by means of the slope at the origin used in [8].

The superficial diffusion coefficient D_s was determined by means of the trial and error method used in [12] and accurate results were obtained.

Symbols

A — specific surface of support (cm^2 g^{-1})
Bi — Biot number based on surface diffusion
$C_b(t)$ — bulk liquid phase adsorbate concentration (g/cm^3)
$C_b^*(t)$ — non dimensional bulk liquid concentration
$C_s(t)$ — liquid phase adsorbate concentration at solid–liquid interface (g/cm^3)
C_0 — initial liquid phase concentration (g/cm^3)
d_p — adsorbate particle diameter (cm)
D_g — surface distribution parameter
D_s — surface diffusion coefficient (cm/s^2)
K — Freunlich isotherm capacity constant
K_f — liquid film mass transfer coefficient (cm/s)
M — total mass of support in closed batch test (g)
n — Freunlich isotherm constant
$q(r,t)$ — adsorbed phase adsorbate concentration (mg g^{-1})
q_{avg} — average adsorbed phase adsorbate concentration (mg g^{-1})
q_{avg}^* — non dimensional average surface concentration
$q_s(t)$ — adsorbed phase adsorbate concentration at solid–liquid interface (mg g^{-1})
ρ_p — apparent particle density (g/cm^3)
q_0 — initial adsorbed phase adsorbate concentration (mg g^{-1})
r — radial coordinate (cm)
r_{SL} — concentration of support (g/cm^3)
t — time (min)
T — dimensionless time
V — liquid volume in closed batch test (cm^3)

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