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Estimate of Effective Diffusivity Starting from the Phenol Adsorption Profiles on an Activated Carbon in Discontinuous Suspension

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Abstract

This study consists on developing a model of internal diffusion with adsorption in a porous particle in order to estimate its effective diffusivity. For this purpose, the particle is put in suspension in an isothermal perfectly agitated reactor in transient state (closed system). The adopted model is based on the adsorption equilibrium on the internal porous surface and assumes that the external concentration varies with time in the external transfer resistance absence. The proposed model equations are numerically solved using the finite differences technique. Experimental concentration profiles of adsorption of dyes either on a commercial activated carbon are smoothed to suit the proposed model. A good agreement between experimental theory profiles is obtained.

Keywords: Kinetic adsorption; Media porous; Numerical solution; Diffusion coefficient

Notation

c: Pore fluid solute concentration, mg/l

C : Fluid phase solute concentration, mg/l

C_0 : Initial concentration, mg/l

K_L : Langmuir adsorption parameter, l/mg

D_e : Diffusion coefficient, cm^2/s

K_L : Mass transfer coefficient, cm/s

q_m : Adsorption capacity per unit adsorbent volume, mg/cm^3

r : Radial coordinate for particle, cm

R_p : Particle radius, cm

T : Time, mn

V : Solution volume, cm^3

V_p : volume of particles,cm^3

m : solid mass, mg

γ : intercept of tangent to adsorption isotherm

ε_p : particle porosity

ρ : apparent density particles, g/cm^3

Introduction

In literature kinetic adsorption in porous middle has occupied a topic place in researches. Such a phenomen can be caused in solution contains active carbon (porous middle). Many important processes in chemical engineering include modeling of diffusion within particles or fluid spheroids. Accurate, but still computationally simple, solutions to these diffusion equations are, therefore, of great importance. Diffusion in adsorption processes has been subject to many studies since the classical approximate solution by Glueckauf [1]. In that solution, the mass transfer within the spherical particles is described by assuming that the mass- transfer rate depends linearly on the difference between the average concentration within the sphere and the surface concentration, along with the assumption of a constant (time -independent) mass-transfer coefficient. Since then that assumption has been used widely in the adsorber modeling. Furthermore, It has been shown that the linear driving force assumption (LDF) is equivalent to assuming a concentration profile within the particles. Both these approaches are used to ease the complicated solution of the time-dependent material balances in the absorbers [2-6]. In this paper, we research the solution of diffusion equation with the numerical methods and analytic methods.

Diffusion Model

Modeling of diffusion within spherical particles is often an important part of modeling of many processes relevant to chemical engineering such as adsorption. The accurate solution to the differential equations describing diffusion is quite a complicated task involving calculation of infinite series. In view of the highly porous structure of the adsorbent studies and of the relatively low adsorption capacity for different colorant, the pore diffusion model was used to fit the data. We assume the particles are spherical and of radius R_p, that they have an intraparticle porosity ε_p, and that local equilibrium exists at each point within a bead between the pore liquid and the adsorbent surface. The external mass transfer resistance was neglected.

With these assumptions the model is represented by the following conservation equations and boundary conditions. For the particles

$$[\varepsilon_P + (1 - \varepsilon_P)\frac{\partial q}{\partial c}]\frac{\partial c}{\partial t} = \frac{\varepsilon_P}{r^2} D_e \frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r}\right) \quad (1)$$

In this equation, D_e and q represents the effective pore diffusivity and the concentration in the adsorbed phase respectively.

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With the boundary conditions

$$r = 0, \frac{\partial c}{\partial r} = 0 \quad (1a)$$

$$r = R_p, \; c = C \quad (1b)$$

$$t = 0, \; c = 0 \quad (1c)$$

'c' represents the concentration in the pore fluid.

At first time we considered that the equilibrium is instantaneous and the concentration in the pore fluid c equal at the initial concentration C_0.

We showed that the adsorption of coloring was well represented by the Freundlich isotherm. Thus, the bracketed term on the left-hand side of eq. (1) can be approximated as

$$\frac{\partial c}{\partial t}\left[1+\frac{1-\varepsilon_p}{\varepsilon_p}K_F\right] = \frac{D_e}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right) \quad (2)$$

When K_F represent the Freundlich constant.

The implicit method of Crank-Nicolson was used to solve the model equations numerically for different values of D_e and we used Matlab logitiel. If we represent the rapport of concentration with the time, we find the subsequent ensuing for various diffusion constant (Figures 1-4).

When the equilibrium does not happen instantantaneously and the concentration in the external fluid C variable varies with the time, the model is represented by the conservation equations (1) and boundary conditions (1a), (1b), (1c), and by the equation for the liquid in the vessel

$$\frac{dC}{dt} = -a_p \varepsilon_p D_e \left(\frac{\partial c}{\partial r}\right)_{r=Rp} \quad (3)$$

$$t=0, \; C=C_0 \quad (3a)$$

In these equations, $a_p = 3V_p/VR_p$ is the surface area of the particles per unit volume of liquid and C is the concentration in the external fluid. At equilibrium c=C and, thus, the term in brackets on the left-hand side of eq. (1) can be obtained from the adsorption isotherms. When the adsorption isotherm is linear, (1) and (3) can be solved analytically. The adsorption isotherm is represented by $[\varepsilon_p C + (1-\varepsilon_p) q] = mC + \gamma$, where m and γ are constants, we obtain

$$\frac{q}{q_\infty} = 1 - 6B(1+b)\sum_{k=1}^{\infty}\frac{\exp(-p_k{}^2 D_e t / mR_p{}^2)}{B^2 p_k{}^2 + 9(1+B)} \quad (4)$$

Where

$$\tan p_k = \frac{3p_k}{3+Bp_k{}^2} \quad (4a)$$

In these equations, $q_\infty = B(mC_0 + \gamma)/(1+B)$ and $B = V/mV_p$.

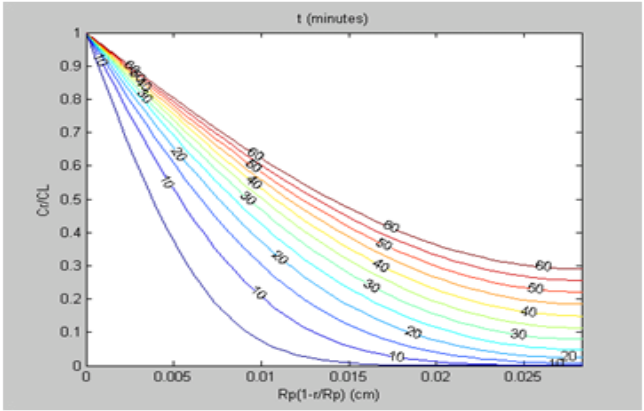

Figure 1: Intrapartical kinetic adsorption with Diffusion coefficient $D_e = 1*10^{-7}cm^2/s$.

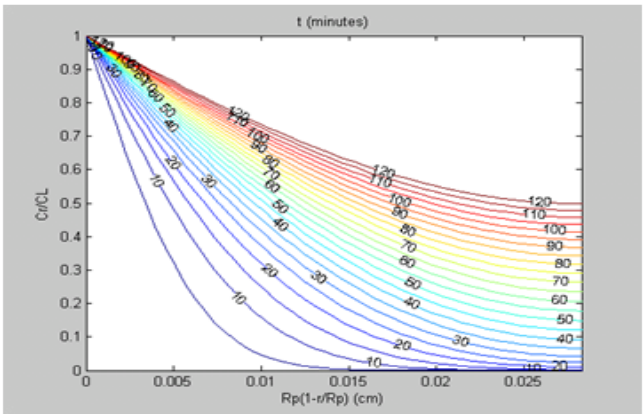

Figure 2: Intrapartical kinetic adsorption with Diffusion coefficient $D_e = 8*10^{-8}cm^2/s$.

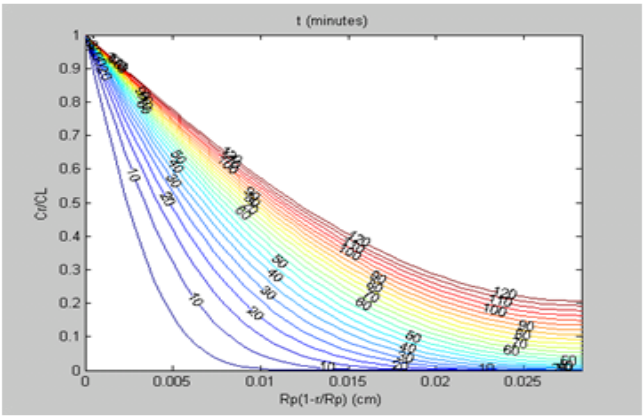

Figure 3: Intrapartical kinetic adsorption with Diffusion coefficient $D_e = 4*10^{-8}cm^2/s$.

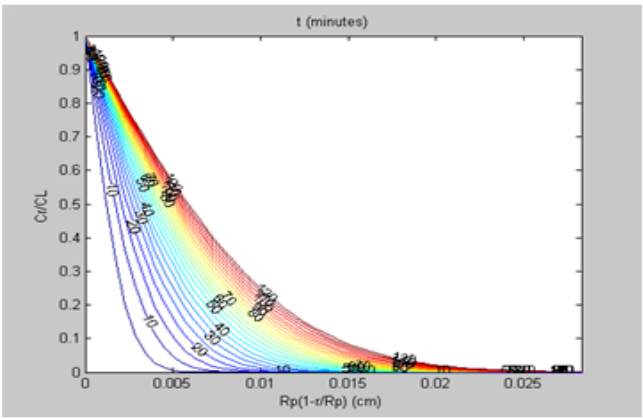

Figure 4: Intrapartical kinetic adsorption with Diffusion coefficient $D_e = 1*10^{-8}cm^2/s$.

Where the isotherm is non-linear and a finite concentration step is applied, however, a numerical solution is required in general. In this part we showed that the adsorption of coloring was well represented by the langmuir isotherm. Thus, the bracketed term on the left-hand side of eq.(1) can be approximated as

$$\frac{\partial c}{\partial t}\left[1+\frac{1-\varepsilon_p}{\varepsilon_p}\frac{K_L.q_m}{\left(1+K_L c\right)^2}\right]=\frac{D_e}{r^2}\frac{\partial}{\partial_r}\left(r^2\frac{\partial c}{\partial r}\right) \quad (5)$$

Where K_L represent Langmuir adsorption parameter.

q_m represent adsorption capacity per unit adsorbant volume.

Validation of the Model

Several work was interested in the study of the kinetics of adsorption of organic molecules or mineral ions in solution by a porous solid. As example work of Grzegorczyk et al. [7], on the adsorption of an amino acid by a porous solid with the use of the operating conditions specified by Table 1 gave very important results. We propose to use these results to test and validate the model developed in our work. Grzegorczyk et al. [7], also used the method of orthogonal collocation based on the use of the finite element to numerically solve the model of the equations of diffusion for various values of the coefficient of diffusion D_e.

In the first simulation, the experimental results published by Grzegorczyk et al. [7], are smoothed by our model for various values of effective diffusivity. It is noticed that this model is in good agreement with the experiments of Grzegorczyk and et al. [7].

Figures 5- 7 represent smoothing by our kinetic model of the experiments of Grzegorczyk by three types of activated carbon.

The values of effective diffusivity thus estimated by our model and the model of Grzegorczyk et al. [7], for the three types of the activated carbon, are represented in Table 2.

Adsorbent	activated carbon (1)	activated carbon (2)	activated carbon (3)
r_P (mm)	0.283	0.302	0.241
ε_p	0.62	0.51	0.66
C_0 (mol/l)	25×10^{-3}	25×10^{-3}	25×10^{-3}
K_L (l/mol)	34	27	69
W (mg)	10	10	10
V (l)	0.1	0.1	0.1
q (mol/g)	0.77×10^{-3}	1.42×10^{-3}	1.22×10^{-3}

Table 1: Operating conditions of the adsorption of phenylalanine on various adsorbents [7].

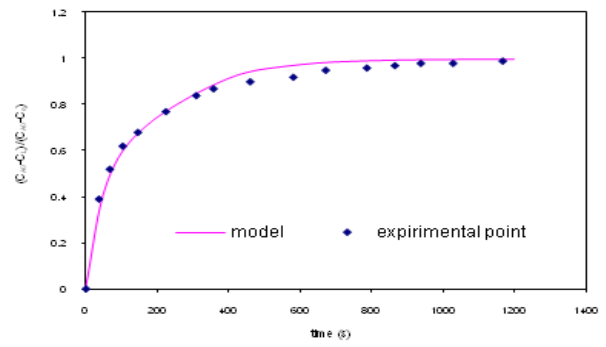

Figure 5: Smoothing of the kinetic experiments of Grzegorczyk et al. by the model suggested (adsorption of phenylanine by the standard adsorbent (1)).

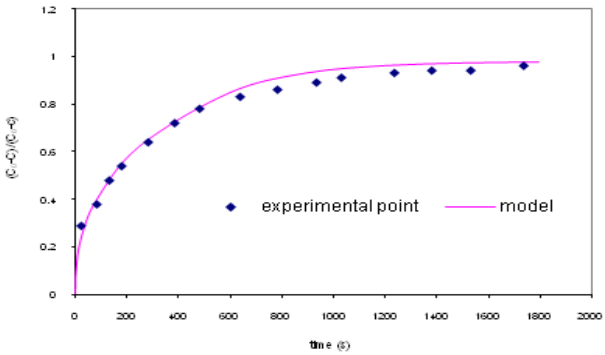

Figure 6: Smoothing of the kinetic experiments of Grzegorczyk et al. by the model suggested (adsorption of phenylanine by the standard adsorbent (2)).

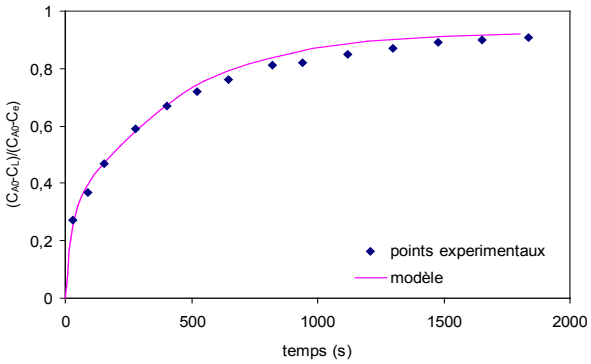

Figure 7: Smoothing of the kinetic experiments of Grzegorczyk et al. by the model suggested (adsorption of phenylanine by the standard adsorbent (3)).

For the three types of the activated carbon, the values of effective diffusivity estimated by the model of Grzegorczyk et al. are of the same order of magnitude as those estimated by our model, which proves in additional the great agreement between our model and also the model of Grzegorczyk et al. [7].

Adsorption of Phenol on Activated Carbon of Norit Type

For elimination by adsorption of phenol in aqueous mediums, one uses in this part an activated carbon of Norit type of average diameter equalizes with 940 µm, the volume of the aqueous phenol solution used is 800 ml to which one adds a mass W=1600 Mg of activated carbon to a temperature fixed θ=40°C. With the same method the implicit method of Crank-Nicolson was used to solve the model equations numerically for different values of D_e and we used Matlab logitiel, the values of R_P, ε_P, q_m, K_L, ρ, V, and V_P are given for the experimental resulting find about Najjar [8], with Norit activated carbon. One represents the evolution of the relative fraction of solution adsorbable of phenol by Norit consistent with time for various concentrations initial C_0, one obtains Figures 8-10.

It is noted that our model is in concord with the experimental points. One notes the values of effective diffusivity estimated by our model for various initial concentrations C_0 of phenol in Table 3.

For the adsorption of phenol on activated carbon of Norit type, when initial concentration C_0 increases the value of the effective

	Standard activated carbon (1)	Standard activated carbon (2)	Standard activated carbon (3)
Effective diffusivity estimated by Grzegorczyk et al. (cm^2/s).	1.5×10^{-6}	0.86×10^{-6}	0.52×10^{-6}
Effective diffusivity estimated by our model (cm^2/s).	3.5×10^{-6}	1.5×10^{-6}	1×10^{-6}

Table 2: Estimate of the effective diffusivity for the three types of activated carbon.

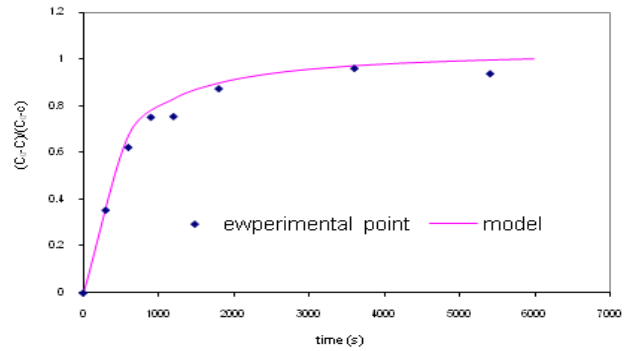

Figure 8: Fraction relating of aqueous solution adsorbed to the balance of phenol by Norit for an initial concentration C_0=25 mg/l.

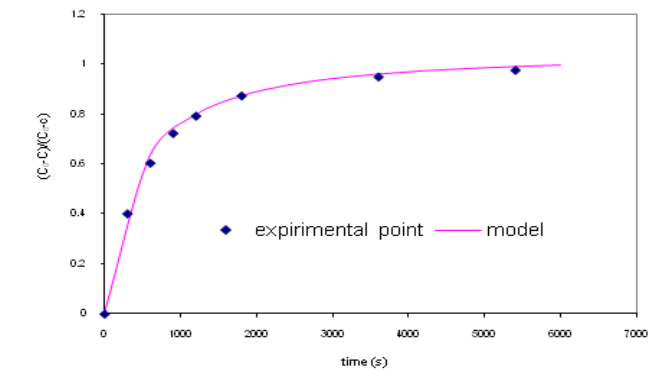

Figure 9: Fraction relating of aqueous solution adsorbed to the balance of phenol by Norit for an initial concentration C_0=50 mg/l.

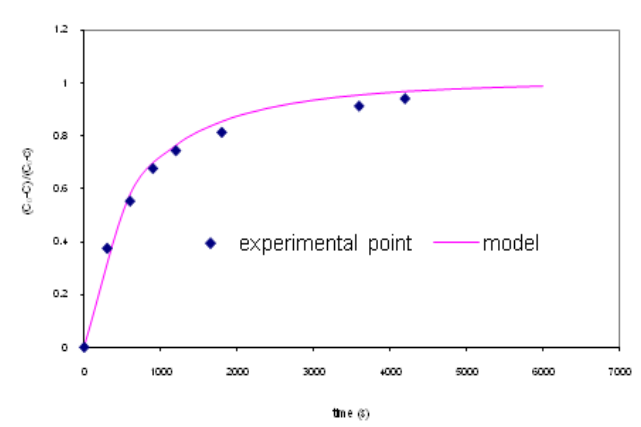

Figure 10: Fraction relating of aqueous solution adsorbed to the balance of phenol by Norit for an initial concentration C_0=100 mg/l.

Initial phenol concentration in solution C_0 (mg/l)	100	50	25
Effective diffusivity D_e (cm^2/s)	9×10^{-8}	3×10^{-7}	2×10^{-6}

Table 3: Estimate of the effective phenol diffusivity in activated carbon produced starting from Norit.

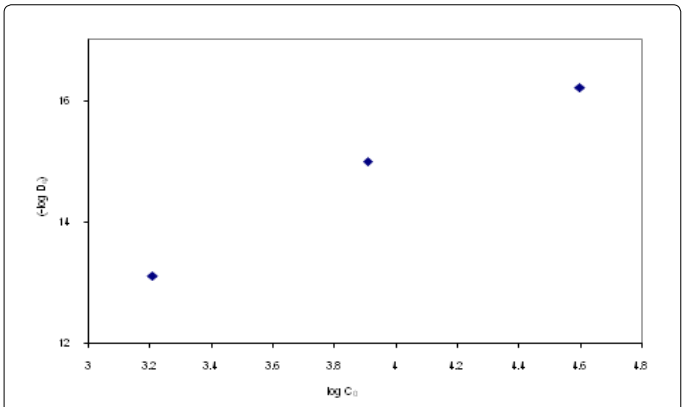

Figure 11: Variation of (-log D_e) according to log C_0 for the adsorption of phenol by the Norit.

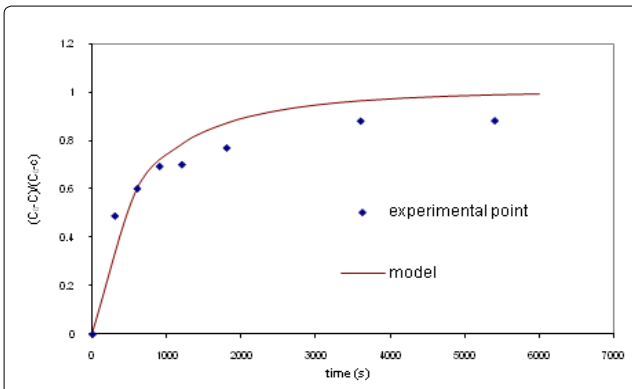

Figure 12: Fraction relating of aqueous solution adsorbed to the balance of phenol by Norit for an initial concentration C_0=200 mg/l.

diffusivity D_e decreases, then one can deduce that effective diffusivity depends on the initial concentration. Figure 11 represents the evolution of (- log D_e) according to log C_0.

For the adsorption of phenol on produced activated carbon of Norit type, the effective diffusivity De varies in opposite direction with initial concentration C_0. One can deduce that effective diffusivity depends on the initial concentration. So now one represents the relative fraction of adsorbed phenol aqueous solution by Norit according to time for great initial concentrations phenol C_0 in the solution, then one obtains Figures 12 and 13. It is noted that for the high initial phenol concentrations in solution C_0= 200 mg/l and C_0= 300 mg/l, the model does not follow the experimental points perfectly.

Conclusion

This work represents a numerical study of kinetic adsorption in porous solid of particles, when the adsorption isotherm is linear the diffusion equations can be solved analytically but when the isotherm is non-linear, a numerical solution is required in general. Several methods are used to obtain the solution, for example the method implicit of Crank-Nicolson. The numerically resulting of diffusion model

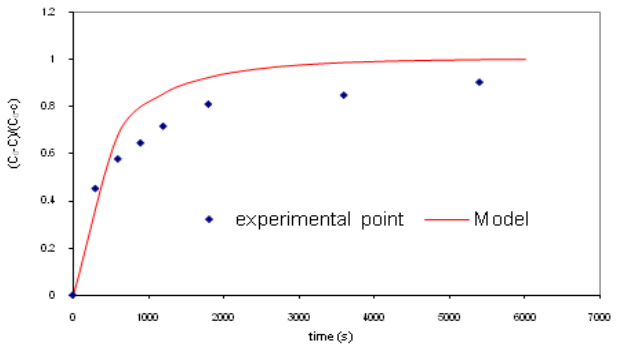

Figure 13: Fraction relating of aqueous solution adsorbed to the balance of phenol by Norit for an initial concentration C_0=300 mg/l.

calculated were then compared with the experimental and the diffusion coefficient D_e that smoothed experimental curve.

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