Surface mass transfer processes using activated date pits as adsorbent

A Gaid*, F Kaoua, N Mederres and M Khodjsa
Industrial Chemistry Institute, University of Sciences and Technology Houari Boumedienne, PO Box 32, El Alia, Algiers

Abstract

The factors affecting the initial rate of adsorption of some organic compounds onto activated date pits, have been investigated in detail. Phenol, aniline, methylene blue, procion red and humic substances were employed to test this adsorbent.

The applicability of the Langmuir isotherm for the present system has been tested and the surface mass transfer coefficient and the surface diffusion coefficient at 20°C determined. The kinetics of adsorption indicates that the process is diffusion controlled.

Nomenclature

D_p : effective pore-volume diffusion coefficient (L^2/T)
D_{eff} : effective surface diffusion coefficient (L^2/T)
ε : intraparticle-void fraction (dimensionless)
r : radial coordinate (L)
C_o : initial liquid concentration (M/V)
C_t : external liquid concentration at time t (M/V)
C_{eq} : liquid equilibrium concentration (M/V)
C_s : surface-phase concentration (M/V)
t : time (T)
ρ_a : apparent density of adsorbent (M/V)
q : solid-phase concentration (M/M)
q_e : solid equilibrium concentration (M/M)
K : Langmuir constant (V/M)
Q_o : Langmuir constant related to the adsorption capacity (M/M)
b : Langmuir constant related to the energy of adsorption (V/M)
k,n : Freundlich isotherm parameters
q_t : average solid-phase concentration (M/M)
β_s : mass transfer coefficient between bulk liquid and outer surface of particle (L/T)
m : mass of adsorbent particles per unit volume of liquid (M/V)
S_s : outer surface area of adsorbent particles per unit volume of particle-free liquid (M^{-1})
V : volume of liquid in the adsorber (V)
M : mass of particles in the adsorber (M)
τ : rate constant for adsorption (T^{-1})
ϕ : rate constant for pore diffusion ($T^{-1/2}$)

Introduction

Many organics in water and waste water may be toxic to man and aquatic inhabitants.

Adsorption on activated carbon is an acceptable treatment method for the removal of these organic substances. The adsorption process in water and waste-water purification usually involves fixed-bed columns for which the equilibrium and kinetic design parameters are usually determined in laboratory studies.

The kinetic parameters govern the physical size of the adsorber. The external and internal mass transfer coefficients, usually represented as β_s and D_{eff} for film transfer resistance and intra-particle diffusion respectively, can be estimated for design purposes.

The objective of the present study was to determine these coefficients for an adsorption system using activated date pits as adsorbent.

Agitated baffled vessels were employed to contact aqueous solutions of organic substances (phenol, aniline, methylene blue, procion red and humic substances) with activated carbon particles.

Theory

Kinetic studies

The study of the kinetics of adsorption at the solid-solution interface is of great significance in water and waste-water treatment as it defines the solute uptake rate, which in turn governs the residence time of the adsorption process.

It is necessary to study the kinetics of adsorption in batch systems in order to determine the rate-limiting step in the adsorption process.

The mechanism of solute adsorption onto an adsorbent comprises several steps. For the purposes of this work the overall adsorption process is assumed to occur in the following three steps:

- mass transfer of solute from bulk solution to the particle surface;
- adsorption of solute onto sites; and
- internal diffusion of solute via either a pore diffusion model, or a homogeneous solid phase diffusion model.

The rate constants of adsorption and pore diffusion were determined using equations of Lagergren and Bill(1868) and Weber and Morris (1963) respectively, which are as follows :

Rate constant for adsorption

$$\log (q_e - q) = \log q_e - (\tau / 2.3)\, t \qquad (1)$$

Rate constant for pore diffusion

$$C_t / C_o = \phi\, t^{0.5} \qquad (2)$$

* To whom all correspondence should be addressed.
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Mass transfer coefficient

For calculation of the mass transfer coefficient, it is assumed that in a well agitated adsorber, the mixing in the liquid phase is rapid and hence the concentration of adsorbate in the liquid phase and the concentration m of carbon particles in the liquid are virtually uniform throughout the vessel (Panday et al., 1985).

Consequently m is determined from the measured mass of adsorbent and volume of particle-free liquid as shown in Eq.(3):

$$m = M/V \qquad (3)$$

The change in organic substance solution concentration with respect to time is related to the fluid-particle mass transfer coefficient by Eqs. (4) and (5)

$$dC_t / dt = -\beta_s S_s (C_t - C_s) \qquad (4)$$

$$C_t = C_o \text{ at } t = 0 \qquad (5)$$

Assuming smooth spherical particles, the surface area for mass transfer to the particles can be obtained from m using Eq. (6) :

$$S_s = \frac{6\,m}{d_p \rho_a (1 - \varepsilon)} \qquad (6)$$

The mass transfer coefficient is given by Eq.(7) :

$$\frac{C_t}{C_o} = \frac{1}{1 + mK} + \frac{mK}{1 + mK} \exp\left(-\frac{1+mK}{mK}\beta_s S_s t\right) \qquad (7)$$

As $t \rightarrow 0$, surface mass transfer will predominate. A plot of $\mathrm{Ln}\left(\frac{C_t}{C_o} - \frac{1}{1+mK}\right)$ versus t will yield a straight line with intercept $(mK/(1 + mK))$ and slope $\left(-\frac{1+mK}{mK}\beta_s S_s\right)$, from which the surface mass transfer coefficient β_s can be obtained. The Langmuir constant K is obtained by multiplying Q_o and b.

Intraparticle diffusion

Internal transfer of organic substances of the solid particle is governed by pore diffusion , in which case the adsorbate diffuses through the fluid-filled pores in its original form, and by solid-phase diffusion, in which case the adsorbate is transfered in its adsorbed form, usually via surface diffusion, along the pore walls.

To derive the fundamental equations for the process, it is assumed that :

- the system is isothermal,
- there is no resistance from adsorption. desorption at the active sites, and
- the velocity is high enough to render external mass transfer resistance negligible.

Assuming that the spherical adsorbent particles are well dispersed and that equilibrium is represented by a Freundlich isotherm, the following system of equations is obtained from mass balances (Koballa and Dudukovic, 1977) :

$$\frac{\varepsilon}{r^2}\frac{d}{dr}\left(D_p r^2 \frac{dC}{dr}\right) + \rho_a \frac{1}{r^2}\frac{d}{dr}\left(D_{eff} r^2 \frac{dq}{dr}\right) = \varepsilon\frac{dC}{dt} + \rho_a \frac{dq}{dt} \qquad (8)$$

$$q = kC^{1/n} \qquad (9)$$

$$dq/dr = 0 \qquad r = 0 \qquad (10)$$

$$q = 0 \qquad t = 0 \qquad (11)$$

$$C = 0 \qquad t = 0 \qquad (12)$$

If surface diffusion is assumed to be the main internal transfer mechanism, simplification of Eq.(8) yields :

$$\frac{dq}{dt} = \frac{1}{r^2}\frac{d}{dr}\left(D_{eff} r^2 \frac{dq}{dr}\right) \qquad (13)$$

If D_{eff} is constant, using Eqs. (9) to (12), Eq. (13) can be integrated (Crank , 1965), to give:

$$\frac{q_t}{q_e} = \frac{C_o - C_t}{C_o - C_{eq}} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{\pi^2 D_{eff} n^2 t}{r^2}\right) \qquad (14)$$

The simplified form is given by :

$$\frac{C_o - C_t}{C_o - C_{eq}} = \left[1 - \exp\left(-\frac{D_{eff}\pi^2 t}{r^2}\right)\right]^{1/2} \qquad (15)$$

The plot of $\mathrm{Ln}\left[1 - (C_o - C_t / C_o - C_{eq})^2\right]$ versus t produces straight lines with a slope of $(-D_{eff}\pi^2/r^2)$, from which intraparticle diffusion coefficient Ds can be obtained. In order to interpret correctly the adsorption curves measured over large changes in concentration, it is necessary to solve the diffusion equation for the appropriate functional dependance of the diffusivity on sorbate concentrations.

Experimental procedure

Materials

The solutes used were obtained from MERCK chemical suppliers. The isotherms were all determined using distilled water and all the chemicals studied were readily soluble in water. The granular activated carbon was manufactured in the laboratory (Gaid and Kaoua, 1991) .

Table 1 shows the physical properties of this carbon.The carbon was washed with distilled water and dried using a tray drier at 105°C for 24 h. The batch adsorber vessel was a baffled 1.2 dm^3 beaker and the volume of solution used on each run was 1.0 dm^3. Precisely weighed activated carbon doses between 0.5 and 10 $g \cdot \ell^{-1}$ were added. A rotating contactor was used to facilitate the mixing of the carbon in the test solution.

The Langmuir constants of the relevant adsorbates,obtained earlier (Gaid and Kaoua, 1991), are listed in Table 2 .

The study was conducted at ambient temperature (20°C). The organic solution was placed in a batch adsorber vessel containing different amounts of pre-weighed activated carbon.

Samples were removed from the batch after a certain time, and filtered through Whatman Glass Fiber Paper (GF/F, pore diameter 0.7 µm) to remove any remaining activated carbon. The filtrate was subsequently analysed to determine the residual solution concentration of the adsorbate.

TABLE 1 PHYSICAL PROPERTIES OF ACTIVATED DATE PITS	
Total surface area (m^2/g)	806
Particle density (wetted in water)	0.524
Porosity	0.2
Iodine number (mg/g)	655
CCl_4 number (%)	36
Ash (%)	4.5
Moisture (%)	3.0
Particle size (mm)	1.2

TABLE 2 LANGMUIR CONSTANTS FOR ACTIVATED CARBON			
Organic substances	**Qo** ($mg \cdot g^{-1}$)	**b** ($\ell \cdot mg^{-1}$)	**K** ($\ell \cdot g^{-1}$)
Phenol	90	0.083	7.47
Aniline	51	0.090	4.59
Humic substances	21	0.019	0.40
Methylene blue	52	0.086	4.47
Procion red	38	0.066	2.50

Analytical measurements

A Pye Unicam UV spectrophotometer was used to determine concentrations of organic substances. Table 3 lists the methods and wavelengths of all organic substances used.

TABLE 3 UVWAVELENGTHS FOR ORGANIC SUBSTANCES OF INTEREST		
Organic substance	**Analytical method**	**Wavelength (in nm)**
Phenol	Aminoantipyrine	510
Aniline	K Ferricyanure	720
Humic substances	-	280
Methylene blue	-	280
Procion red	-	500

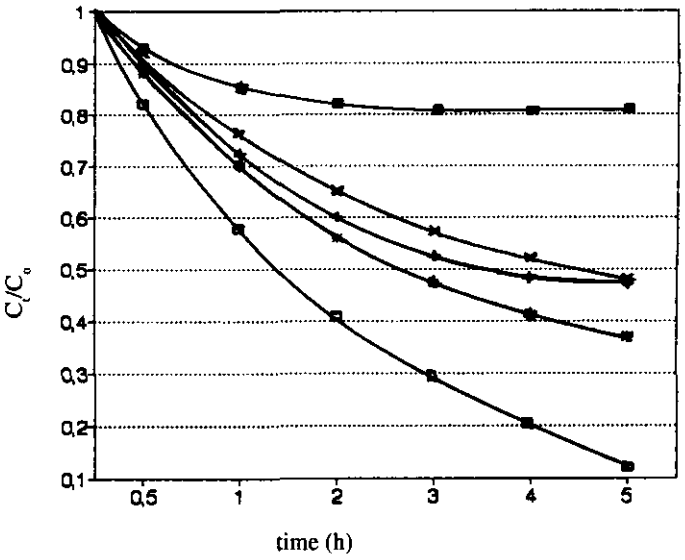

Figure 1
Kinetics of organic substances adsorption
(Conditions : C_o : 100 mg·ℓ$^{-1}$; T : 20°C
speed : 1 010 r·min^{-1}; M : 6 g·ℓ$^{-1}$)
□ *Phenol*
✱ *Aniline*
× *Methylene blue*
\+ *Procion red*
■ *Humic substances*

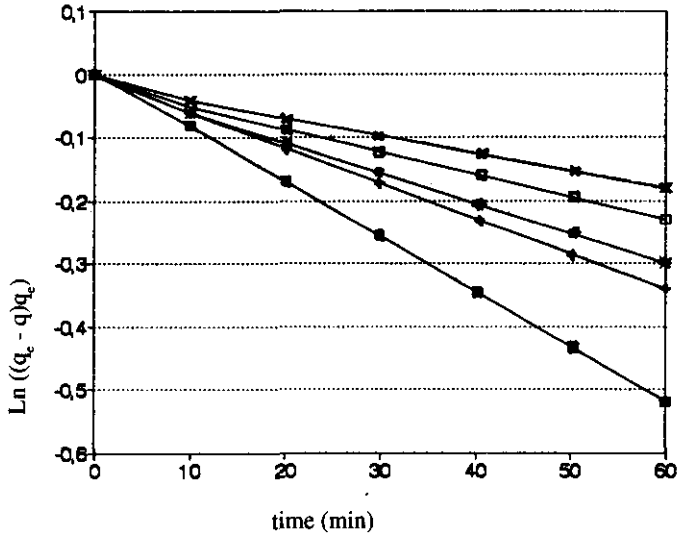

Figure 2
Plots of rate constants for adsorption of organic substances onto activated date pits (20°C)

Results and discussion

Rate constants for adsorption (τ) and pore diffusion (ϕ)

Figure 1 shows the adsorption isotherms of the adsorbents which were studied.Straight line plots of log $[(q_e - q)/q_e]$ versus time (Fig. 2) suggest the applicability of the Lagergren equation. However, the plots of C_t/C_o versus t 0.5 (Fig. 3), although linear for a wide range of contact period, do not pass through the origin. This suggests that the mechanism involved in the process of the organic substances uptake by activated date pits is complex and that both the boundary layer diffusion effect and intraparticle diffusion contribute to the rate-determining step (Poots et al.,1978).

The initial curved portion of the graphs is being attributed to the boundary layer diffusion effect, whereas the linear portion is due to the intraparticle diffusion of adsorbate.

The rate constants for adsorption and pore diffusion calculated from the slopes of the respective plots are listed in Table 4. In a rapidly stirred batch reactor, the adsorbate molecules diffuse into the interior of the porous adsorbent. In diffusion studies rate processes are usually expressed in terms of the square-root of time. A plot of the amount of organic substance adsorbed per g of

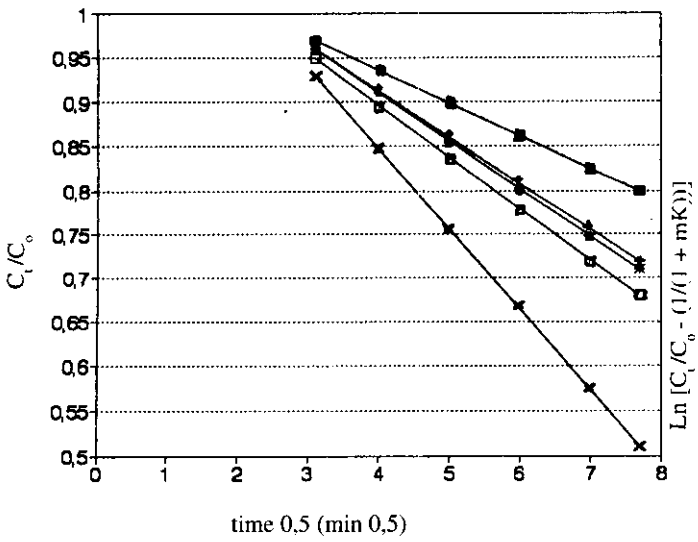

Figure 3
Plots of rate constants for pore diffusion (20°C)

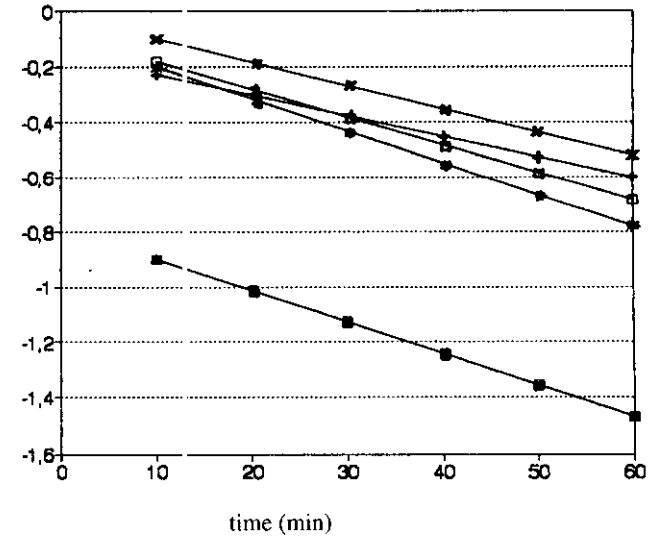

Figure 4
Plots of mass transfer coefficients for adsorption of organic substances onto activated date pits (20°C)

TABLE 4
τ, ϕ, β_s and D_{eff} PARAMETERS FOR THE ADSORPTION OF ORGANIC SUBSTANCES ON ACTIVATED DATE PITS
(Co = 80 mg·l^{-1} sp = 1 010 r·min^{-1}
m =6 g·l^{-1}, T = 20°C)

Organic substances	τ min^{-1}	ϕ $min^{-0.5}$	β_s $cm·s^{-1}$	D_{eff} $cm^2·s^{-1}$
Phenol	9.54×10^{-3}	7.90×10^{-2}	8.33×10^{-4}	1.90×10^{-6}
Aniline	7.00×10^{-3}	4.33×10^{-2}	6.11×10^{-4}	2.93×10^{-7}
Methylene B	6.90×10^{-3}	5.20×10^{-2}	6.00×10^{-4}	1.10×10^{-6}
Procion red	1.40×10^{-2}	4.50×10^{-2}	1.24×10^{-3}	2.55×10^{-7}
Humic Substances	1.99×10^{-2}	3.2×10^{-2}	1.73×10^{-3}	7.60×10^{-7}

adsorbent against square-root of time (Fig. 3) although linear for a wide range of contact period, passes through the origin.

This suggests that the mechanism involved in the uptake of an organic substance (contaminant, compound) by activated date pits is governed by the boundary layer diffusion effect and the intraparticle diffusion (Poots et al., 1976; Panday et al., 1985; Huang and Blankenship, 1984).

These rate parameters have different units; therefore, the rate values cannot be compared.

However, the values of ϕ indicated that the best adsorption was for phenol which has a rate constant for pore diffusion in the order to 7.90×10^{-2} $min^{-0.5}$.

The rate constant for adsorption values confirmed this result. τ for phenol was lower (9.54×10^{-3} min^{-1}) than that obtained for the other organic substances studied.

Mass transfer coefficient results

The plots of Ln [(Ct/Co) - [1/ (1 + mK)]] against t give straight lines (Fig. 4).

The mass transfer coefficients were calculated from the slopes and intercepts of the plots, and are listed in Table 4.

These values indicate that the velocity of the adsorbent transport from bulk to the solid phase is rapid enough to suggest the use of activated date pits for the removal of these organic substances from water and waste waters.

The product of β_s and S_s has the unit of rate ($time^{-1}$) and is approximately equal to the rate of adsorption ($\beta_s S_s \sim \tau$), (Table 5) indicating that the rate of adsorption is diffusion controlled.

TABLE 5
CALCULATED τ, β_s and $\beta_s S_s$ FOR ORGANIC SUBSTANCES

Organic substances	τ s^{-1}	β_s $cm·s^{-1}$	$\beta_s S_s$ s^{-1}
Phenol	0.572	8.33×10^{-4}	0.595
Aniline	0.420	6.11×10^{-4}	0.436
MethyleneB	0.414	6.00×10^{-4}	0.429
Procionred	0.840	1.24×10^{-3}	0.886
Humic substances	1.190	1.73×10^{-3}	1.236

TABLE 6
β_s AND D_{eff} COEFFICIENTS FOR THE ADSORPTION OF DYES ON ADSORBENTS (T = 20°C)

D_{eff} $cm^2 \cdot s^{-1}$	Author	Adsorbent	Dye	β_s $cm \cdot s^{-1}$
0.87×10^{-7}	McKay and Allen[1980]	Peat	Acid Blue 25	0.45×10^{-4}
0.30×10^{-8}	McKay et al.[1988]	Peat	Disperse blue 7	0.76×10^{-4}
0.50×10^{-6}	Spahn and Schundler[1975]	Activated carbon	Crystal violet	0.23×10^{-2}
1.10×10^{-6}	This study	Activated carbon	Methylene blue	6.00×10^{-4}
2.550×10^{-7}	This study	Activated carbon	Procion red	1.24×10^{-3}
1.92×10^{-10} (at 30° C)	Khare et al.[1988]	Wallastonite	Crystal violet	3.39×10^{-5} (at 30°C)
2.8×10^{-6}	Kaoua et al.[1988]	Bentonite	Methylene blue	1.42×10^{-9}

The values obtained for dyes (methylene blue and procion red) compare favourably with those obtained in several studies using activated carbon and other adsorbents (McKay and Allen, 1980; McKay et al., 1988; Spahn, 1975).

The only other information relating to mass transfer coefficients and diffusivities is based on small organic molecules, not large ionic species.

In the case of phenol, values for β_s and D_{eff} of 4.30×10^{-4} $cm \cdot s^{-1}$ and 0.20×10^{-6} $cm^2 \cdot s^{-1}$ respectively, have been reported (Spahn, 1975; McKay and Allen, 1980) . These are in the same order as our values.

For any one organic substance, a single external mass transfer coefficient and external diffusivity are sufficient to describe that particular system for all variations in activated carbon mass and initial organic substance concentration. The values of the external mass transfer coefficients in Table 6 show considerable divergence. There are 2 main reasons likely for this effect: firstly, the chemical affinity between the different compounds and the activated carbon, and secondly, the size of the molecule which will affect its mobility within the carbon.

The dye ions and humic substances are large organic molecules, but there is some difference between molecular volumes.

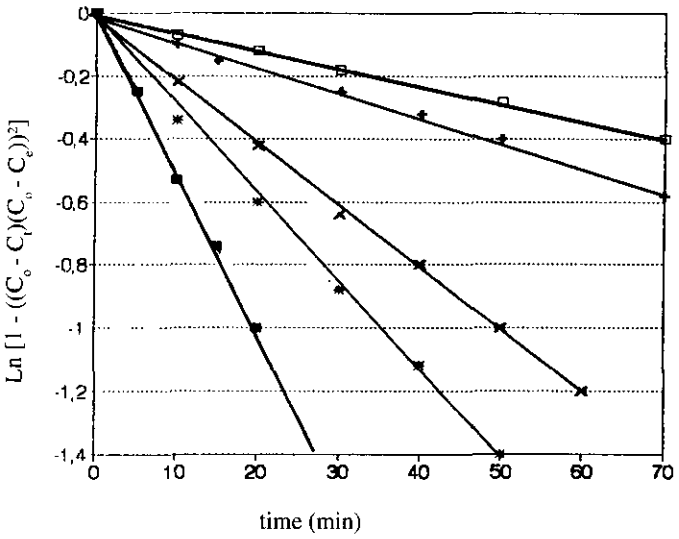

Figure 5
Plots of intraparticle diffusion coefficients of organic substances

Intraparticle diffusion results

Figure 5 shows typical experimental Ln [1- $((C_o - C_t)(C_o - C_e))^2$] versus t for various organic compounds but at the same initial liquid concentration (C_o), solid concentration (M) and temperature. Values of D_{eff} are listed in Table 4, and are calculated for a particle radius of 1.2 mm.

Results show that the intraparticle effect is much less important for procion red and aniline than for phenol and methylene blue. The slope of the experimental curve at any time is proportional to the rate of adsorption. The variation in effective diffusion coefficients in Table 4 describing the internal mass transfer process shows a similar relative variation to the external mass transfer coefficients and it would appear that the major controlling factors are the size of the molecule and the chemical affinity between compound and activated carbon. This effect supports the postulated mechanism of pore diffusion since the adsorption affinity is between the compound in solution entrained in the activated carbon pores and the internal sites on the adsorbent.

Conclusions

The adsorption capacity of 5 organic substances (phenol, aniline, methylene blue, procion red, humic substances) in aqueous solutions onto activated date pits has been studied. The results show the suitability of activated date pits carbon for the removal of these organic compounds.

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