



KINETICS OF ACID DYE ADSORPTION ON GAC

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Abstract—This work involves the treatment of simulated industrial waste water containing acid dye-stuffs with granular activated carbon adsorption selected as the treatment method. Predicting the rate at which adsorption takes place for a given system is probably the single most important factor for adsorber design, with adsorbate residence time and ultimately the reactor dimensions controlled by the system's kinetics. A fixed volume stirred tank reactor was used to study the kinetics of adsorption in a single component system. Process parameters including the rate of agitation, dye concentration and phase ratio were studied with results being modelled using a dual resistance external mass transfer and solid diffusivity model. A single value of solid diffusivity described the adsorption decay curves in most instances and also indicated that chemisorption is the likely process of acid dye adsorption onto activated carbon. © 1999 Elsevier Science Ltd. All rights reserved

Key words—adsorption, activated carbon, dyes, solid diffusion, external mass transfer, stirred tank reactor

NOMENCLATURE

- C = concentration (mg dm^{-3})
 C_0 = initial solute concentration (mg dm^{-3})
 C_s = solute concentration at the particle surface (mg dm^{-3})
 D = diffusion coefficient in Fick's law
 d_p = average particle diameter (μm , cm)
 D_s = solid diffusivity ($\text{cm}^2 \text{s}^{-1}$)
 k_f = fluid-particle mass transfer coefficient (cm s^{-1})
 q_i = intraparticle solute concentration in HSDM model (mg g^{-1})
 q_s = solid phase concentration at particle surface (mg g^{-1})
 \bar{q} = average concentration of solute in particle (mg g^{-1})
 r = radial distance from centre of particle, $0 \leq r \leq R$ (cm)
 R = radius of adsorbent particle (cm , μm)
 S_p = particle surface area (cm^2)
 t = time (s , min , hr)
 V = volume (dm^3)
 V_p = particle volume (dm^3)
 W = weight of adsorbent (g)

Greek symbols:

- ε_p = particle voidage
 ρ = density (g cm^{-3})

INTRODUCTION

In this study into the kinetics of adsorption, the granular activated carbon Filtrasorb 400 (Chemviron Carbon) was used as the adsorbent and acid dyestuff Tectilon Red 2B (Ciba-Geigy) as the adsorbate. Granular activated carbon ensured rapid adsorption and the dye concentrations can be calculated using spectrophotometry.

Resistance to mass transfer in adsorption processes can be described by two processes; resistance due to external mass transfer though the particle boundary layer and resistance due to intraparticle diffusion. Furusawa and Smith (1973) proposed a model to describe external mass transfer by two methods, using linear and non-linear isotherms, these models were successfully applied to the adsorption of dyestuffs by McKay (1983). A simple model proposed by Spahn and Schlunder (1975a,b) was also used to model the acid dye-carbon system by Walker (1995).

The description of batch adsorption processes by two resistance models including external mass transfer and intraparticle diffusional resistance has been developed by several authors. The major differences in the models are due to the mechanism of intraparticle diffusion proposed, namely pore diffusion, solid diffusion or a combination of both. The film pore diffusion models are based on the unreacted shrinking core model proposed by Levenspiel (1962) and use analytical expressions to describe diffusion in terms of the effective diffusion coefficient, D_{eff} . A graphical differentiation solution to the model was proposed by Spahn and Schlunder (1975a,b) with

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McKay (1984) further developing the model by using the constraint of a saturated isotherm.

Solid phase diffusion is the dominant effect in intraparticle mass transfer therefore solid diffusion models have been developed by many authors. The film homogeneous solid diffusion model developed by Matthews and Weber (1977) from measurements of phenol removal by activated carbon, assumes external mass transfer dominance in the initial stages of adsorption. Al-Duri (1988) successfully employed the model to describe dye adsorption and multicomponent systems. Gilliland *et al.* (1974) reported the strong concentration dependence of D_s and attributed this phenomenon to changes in energies of adsorption with surface coverage. Peel *et al.* (1981) developed the "branched pore kinetic model" for activated carbon adsorption in which the carbon particles were considered to be bi-porous with pore diffusion dominating in the macropores and solid diffusion occurring in the micropores. The branched pore model has been successfully used by Al-Duri *et al.* (1990) for dye adsorption.

MATHEMATICAL MODEL

This model is based on studies carried out by Matthews and Weber (1977) who proposed a dual resistance model combining external mass transfer and solid phase diffusion for batch studies which was later modified by McKay *et al.* (1983). They assumed the adsorbent particles to be identical spheres of radius, R , with the concentration of the solute in the particle at distance, r , from the centre and time, t , given by $q_i(r, t)$, assuming spherical geometry. The rate of change of q_i with distance

and time is given by the diffusional equation

$$\frac{\partial q_i}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q_i}{\partial r} \right) \quad (1)$$

with the boundary conditions:

$$r = 0, \quad \frac{\partial q_i}{\partial r} = 0 \quad (2)$$

$$q_i(R, t) = q_s(t) \quad (3)$$

It is assumed that the diffusional coefficient, D , in equation 1 is constant and that the first boundary condition represents the state of the particle at $t = 0$ and the second shows that the concentration at the surface of the particle varies with time.

The model uses the isotherm described by Redlich and Peterson (1956) and describes the mass transfer of the solute from the liquid phase to the particle by:

$$\frac{d\bar{q}}{dt} = \frac{k_f S_p}{V_p \rho (1 - \varepsilon)} (C - C_s) \quad (4)$$

where S_p is the particle surface area, ρ the particle density, V_p the particle volume, ε the particle porosity, k_f the external mass transfer coefficient and $\bar{q}(t)$ the average particle solute concentration which is defined below

$$\bar{q}(t) = \frac{3}{R^3} \int_0^R q_i(r, t) r^2 dr \quad (5)$$

As the particles are assumed to be spherical, equation 4 can be reduced to:

$$\frac{d\bar{q}}{dt} = \frac{3k_f}{R\rho(1 - \varepsilon)} (C - C_s) \quad (6)$$

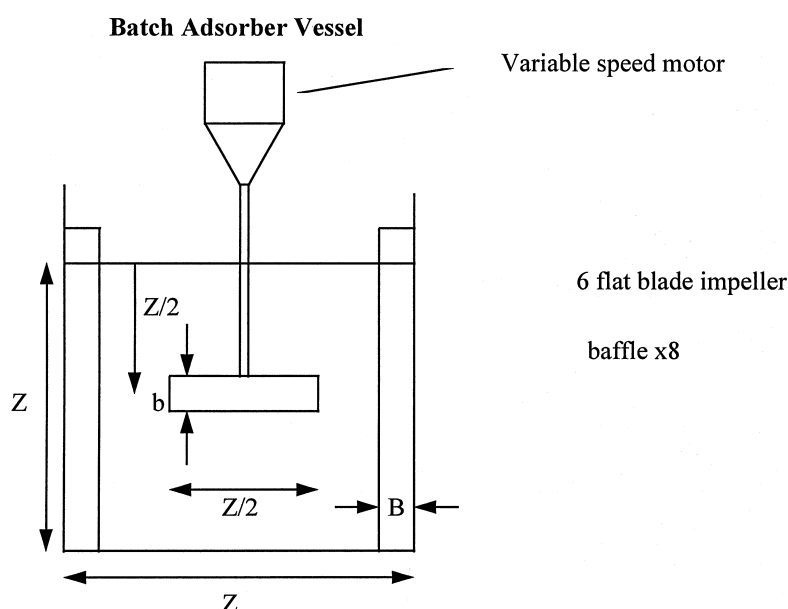


Fig. 1. Batch adsorber vessel.

Table 1. Adsorber specifications

Item	Description	Dimensions
B	width of baffles	$(3/40) \cdot Z$
L	height of impeller	$Z/2$
b	width of impeller blade	$Z/10$
D_m	impeller diameter	$Z/2$

The bulk solute concentration is defined as

$$C = C_0 - \frac{W}{V} \bar{q} \quad (7)$$

equations 1–7 can be solved by the introduction of dimensionless variables which are described by McKay *et al.* (1983) and with the solution of this model calculated by numerical analysis. Thus the concentration time profile for a batch adsorption may be calculated and compared with experimental results.

EXPERIMENTAL METHODS

Contact time experiments provided the kinetic data in the form of concentration decay vs time curves. The gradients of such curves were interpolated to give useful design parameters such as external and internal mass transfer coefficients. In the contact time experimental runs a fixed mass of carbon, of known particle size, was brought into contact with a fixed volume of solution ($1.71 \approx 1700$ g) at a prefixed initial dye concentration and agitation rate. The dye solution comprised of liquid dyestuffs as supplied by the manufacturer and de-ionised water. A schematic diagram of the apparatus is shown in Fig. 1 with dimensions in Table 1. At the instant of sorbate–sorbent contact, mixing at a fixed rate of agitation was started. Samples (2 ml) were taken from the solution at regular time intervals over a 4 h period. This small sample volume ensures that the reactor volume remains essentially constant throughout the course of the experiment. The samples were then ana-

lysed in a Perkin-Elmer spectrophotometer at a wavelength of 503 nm and the dye concentration then calculated from a calibration curve. Process variables under investigation included mass of adsorbent to volume of solution ratio, agitation rate and concentration of the adsorbate in the liquid phase.

RESULTS AND DISCUSSION

This modified model was used to describe the kinetic decay curves for Tectilon Red (TR2B) adsorbing onto granular activated carbon F400 under a range of conditions. The results from the model were expressed in terms of a plot of experimental and modelled dimensionless solute concentration vs time and in terms of external mass transfer coefficient, k_f , and a solid diffusivity, D_s , for each particular system.

The shape of this decay curve is governed by the external mass transfer coefficient, k_f , and the solid diffusivity, D_s with the equilibrium of the system described by the Redlich–Peterson isotherm. This model has proved successful in a range of adsorption systems including, acid dyes adsorbing onto peat by Allen *et al.* (1988), basic dyes adsorbing onto activated carbon by Al-Duri (1988) and basic dyes adsorbing onto peat and lignite by Murray (1995).

The performance of this model is illustrated in Figs 2–4 which show experimental and theoretical decay curves at various conditions. Using a constant value of D_s , the model displays a very good fit over the course of most of the experiments although there is a slight deviation in some of the initial stages due to under-estimation of the external mass transfer coefficient.

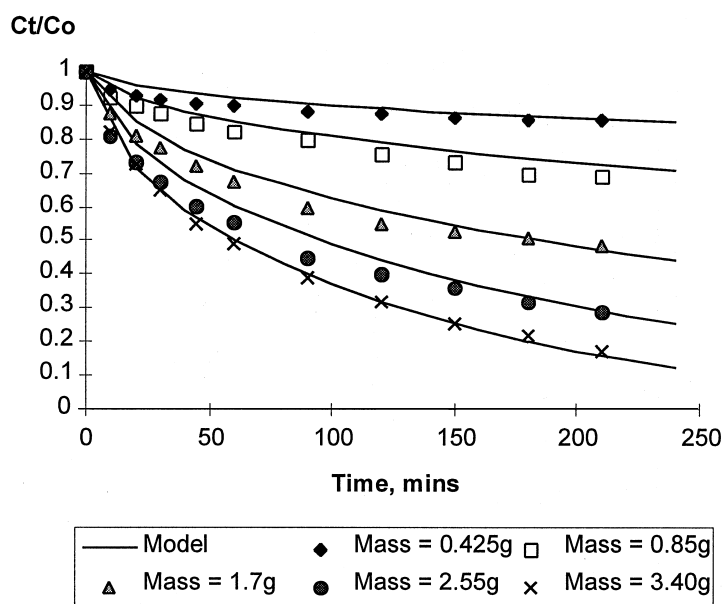


Fig. 2. Effect of mass of adsorbent on adsorption of TR2B $C_0 = 200$ mg/l, $d_p = 355$ – 500 μ m, agitation = 500 rpm.

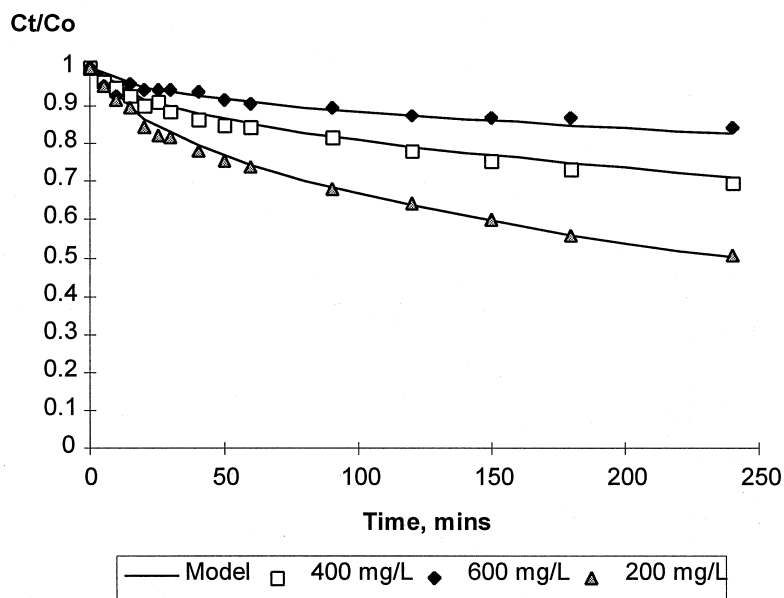


Fig. 3. Effect of initial concentration on adsorption of TR2B carbon mass = 1.7 g, $d_p = 355\text{--}500\ \mu\text{m}$, agitation = 500 rpm.

The rate of intraparticle diffusion is determined by the solid diffusivity, D_s , which when increased, increases the rate of adsorption. The rate of adsorption and the magnitude of D_s are dependent upon the nature of the adsorption process, for physisorption processes the magnitude of D_s ranges from 10^{-2} – 10^{-5} (cm^2/s) and for chemisorption systems 10^{-5} – 10^{-13} (cm^2/s). This may be explained by the stronger bonds holding the molecules tighter to the adsorbent pore walls thus lowering the rate of molecular migration. D_s remains constant for variation in adsorbent mass and agitation speed as predicted by theory, see Table 2.

However, D_s did vary slightly with change in initial dye concentration. Diffusivity should be independent of bulk solute concentration for the solid diffusion model, however Miyahara and Okazaki (1992) reported an increase in solid diffusivity with concentration during the adsorption of nitrobenzene onto activated carbon. Our results indicate that there is a slight decrease in diffusivity with increased dye concentration for Tectilon Red. This phenomenon may be due to collisions between dye molecules at high concentrations increasing the diffusional resistance within the particle. The trend may be due to dye agglomeration at high bulk

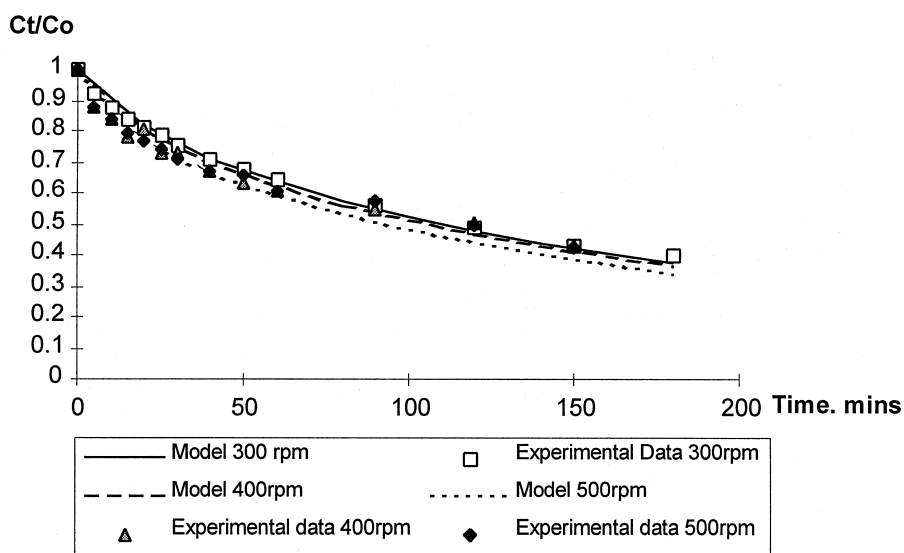


Fig. 4. Effect of agitation rate on adsorption of TR2B carbon mass = 1.7 g, $C_0 = 200\ \text{mg/l}$, $d_p = 355\text{--}500\ \mu\text{m}$.

Table 2. Kinetic parameters for the adsorption of TR2B to achieve accurate correlation of experimental and theoretical data

System	$k_f \times 10^{-3}$ (cm/s)	$D_s \times 10^{-9}$ (cm ² /s)
<i>Mass (g)</i>		
0.425	2.8	1.5
0.85	2.8	1.5
1.7	2.8	1.5
2.55	2.8	1.5
3.4	2.8	1.5
<i>Agitation (rpm)</i>		
300	1.1	1.5
400	1.8	1.5
500	2.8	1.5
<i>Concentration (mg/dm³)</i>		
100	2.8	1.5
200	2.8	1.5
400	2.8	1.6
600	2.8	1.6
1000	2.8	1.7

liquid concentrations which would further increase the diffusional resistance. Dye agglomeration may also cause blockage of the smaller pores within the carbon structure.

Initial values of k_f used in this model were related to values obtained from the single resistance models by Walker *et al.* (1995). However the magnitude of the external mass transfer coefficient needed to be increased by around 40%. A more accurate approximation for k_f using single resistance models would take the form of a linearisation of the first 10 min rather than the first 20 min of the C_t/C_0 vs time curve. External mass transfer coefficients determined using single resistance models in this work gave reasonable approximations for k_f compared to Murray (1995).

CONCLUSIONS

The rate at which acid dye adsorption occurs was found to be dependent upon several process parameters. Concentration decay curves were modelled effectively by the dual resistance modified Matthews–Weber model. Constant values for the external mass transfer coefficient and solid diffusivity successfully described adsorption with variation in adsorbent mass. Results of external mass transfer for variation in agitation rate correlated well with other authors with a single solid diffusivity describing adsorption. In order to obtain best fit of experimental and theoretical data, a decrease in solid diffusivity was needed for decrease in solute concentration. The value of solid diffusivity also indicated that chemisorption is the likely process of acid dye adsorption onto activated carbon.

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