Chapter 2 Adsorption of Dyes

Abstract Adsorption is one of the most commonly used, traditional separation technologies utilized for separation. Since it is an equilibrium-governed process, the process efficiency is excellent, but the throughput is relatively low. Nevertheless, because of its simplicity, this is one of the normally used technologies for dye removal from aqueous stream. Therefore, it is imperative to understand the modeling aspects of such adsorbent-based systems which is necessary for design and implementation of the technology. Additionally, the chapter describes the characteristics of the different commonly used adsorbents and its applicability.

Keywords Adsorbent • Chrysoidine • Eosin • Congo red • Activated charcoal

The word "adsorption" was formulated in 1881 by German physicist Heinrich Kayser to differentiate between the surface phenomena and intermolecular penetration. Adsorption can be divided into physical and chemical adsorption. Physical adsorption is controlled by the physical forces such as van der Waals forces, hydrophobicity, hydrogen bond, polarity, static interaction, dipole-dipole interaction, $\pi - \pi$ interaction, etc. When the species are adsorbed to the surface of the adsorbent by means of strong chemical interactions or bonding, it is referred to as chemisorption. The extent of adsorption depends on the nature of adsorbate such as molecular weight, molecular structure, molecular size, polarity, and solution concentration. It is also dependent on the surface properties of adsorbent such as particle size, porosity, surface area, surface charge, etc. The primary advantages of adsorption processes are:

- 1. Simple in design
- 2. Relatively safe and easy to operate
- 3. Inexpensive (compared to other separation processes)
- 4. Provides sludge-free cleaning operations (Gupta et al. [2000\)](#page-45-0).

Selection of a suitable adsorbent is the primary concern for adopting adsorption in any process industries. The performance of the process is often limited by the equilibrium capacity of the adsorbent.

2.1 Application of Adsorption in the Treatment of Process **Wastewater**

Various low-cost adsorbents for treatment of effluent containing heavy metals have been studied by various researchers in the past. Most of these adsorbents are prepared from the waste or by-products of other process plants or naturally occurring materials. A list of most commonly used low-cost adsorbents for heavy metal removal that is prepared from naturally occurring materials and processes are presented in Table [2.1.](#page-1-0)

2.2 Experimental Studies of Dye Adsorption

In the following sections, adsorption of chrysoidine, eosin, and Congo red by commercial activated carbon (CAC) has been presented.

2.2.1 Batch Adsorption

The batch adsorption is typically carried out in the solution phase containing dyes. The effects of agitation time and initial dye concentration on the percentage adsorption of dye by activated carbon at room temperature are shown in Figs. [2.1a](#page-2-0), [2.1b](#page-2-1), and [2.1c](#page-3-0) for chrysoidine, eosin, and Congo red. For all the cases, the percentage adsorption increases with agitation time for different initial dye concentration and attains equilibrium after some time.

Metals	Adsorbent	Adsorption capacity (mg/g)	Reference
Zn^{2+}	Blast-furnace slag	103.3	83
	Powdered waste slag	168.0	147
$\frac{\overline{Ni^{2+}}}{\overline{Cu^{2+}}}$	Red mud	160.0	112
	Blast-furnace slag	133.3	83
	Red mud	106.4	153
Cr^{6+}	Waste slurry	640.0	459
	Tea industry waste	455.0	165
$\frac{\overline{Hg}^{2+}}{\mathrm{Cd}^{2+}}$	Waste slurry	560.0	159
	Fly ash	207.3	152
	Waste slurry	1030.0	159
$\overline{V^{5+}}$	Waste metal sludge	24.8	97
As^{3+}, As^{5+}	Acid-activated laterite	24.5, 8.0	

Table 2.1 Low-cost high-capacity metal ion adsorbents

From Fig. [2.1a](#page-2-0), it may be observed that for all initial chrysoidine concentration, the percentage adsorption is found to be constant beyond 80 min. This indicates that equilibrium is attained at about 80 min for initial dye concentration in the range of 100–400 mg/L. It is also clear that the extent of adsorption depends on the initial dye concentration. For dye solution of lower initial concentration (up to 100 mg/L), the adsorption is very fast and almost 100% adsorption is achieved quickly. The dye adsorption at equilibrium decreases from 100% to about 94% as the dye concentration increases from 100 to 400 mg/L.

It is clear from Fig. [2.1b](#page-2-1) that up to an initial eosin concentration of 100 mg/L, more than 99% adsorption is achieved within 5 min. For an initial concentration of 200 mg/L, the percentage adsorption increases until 90 min and becomes constant thereafter. For a feed concentration of 400 mg/L, the percentage adsorption increases rapidly for about 90 min, and the increase becomes gradual thereafter.

For 210 min of operation, the dye adsorption is 99.6% for an initial dye concentration of 100 mg/L but only 72.3% for 400 mg/L.

Figure [2.1c](#page-3-0) describes the variation of Congo red adsorption with time for different initial dye concentration. The percentage adsorption of Congo red is found to be constant beyond 50 min. This indicates that the equilibrium is attained within 50 min for the range of initial dye concentrations. It is also clear that the extent of adsorption depends on the initial dye concentration. For dye solution of lower initial concentration, the adsorption is very fast and 90% of adsorption is achieved quickly. The percentage dye adsorption at equilibrium decreases from 90% to 28% as the dye concentration increases from 50 to 545 mg/L.

The effects of adsorbent dose on the extent of chrysoidine adsorption are shown in Fig. [2.2](#page-4-0) for initial dye concentrations of 700 mg/L. It is clear from the figure that percentage adsorption increases with time up to 80 min and also with adsorbent dose. Percentage adsorption increases from about 77 to 99% when the adsorbent dose increases from 0.75 to 1.40 g/L. This increase in percentage adsorption may be due to the fact that the number of available sites for adsorption increases with adsorbent dose.

The pH of the solution has significant influence in the rate of adsorption. The percentage dye adsorption at different pH is shown in Figs. [2.3a,](#page-4-1) [2.3b](#page-5-0), and [2.3c](#page-5-1) for chrysoidine, eosin, and Congo red, respectively. Figure [2.3a](#page-4-1) describes the variation of chrysoidine adsorption at different pH for an initial dye concentration of 400 mg/L. The color of chrysoidine dye in aqueous medium is red (λ_{max} : 457 nm) in acidic pH but changes its color from red to yellow (λ_{max} : 442 nm) in basic pH. This is due to the presence of chromophore in the structure of chrysoidine. A chromophore is any structural feature (in this case, $-N = N-$) which produces light absorption in the ultraviolet region or color in the visible region. An auxochrome is any group (in this case $-NH_2$) which, although not a chromophore, leads to a red shift when attached to a chromophore. Thus, the combination of chromophore and auxochrome behaves as a new chromophore. Bathochromic effect (red shift) and

hypsochromic effect (blue shift) are the shifting of the absorption band to the longer and shorter wavelengths (Finar [1973](#page-44-0)). Therefore, due to blue shift, chrysoidine changes its color in basic pH.

Adsorption followed by desorption technique is generally used to get the more concentrated form of the dye solution. One of the most common desorption technique is the pH treatment. But problem arises for the dyes which are highly pH sensitive, like chrysoidine as discussed in the previous paragraph.

Most of the activated carbon contains some oxygen complexes on the surface, e.g., (a) strongly carboxylic groups, (b) carbonyl groups, and (c) phenolic groups (Motoyuki [1990](#page-46-0)). These groups are nucleophilic in nature and potential adsorbing sites. In acidic pH, these active sites get blocked by hydrogen ion leading to reduction in adsorption. Hence, adsorption of chrysoidine on activated carbon is less in acidic pH. It is found from Fig. [2.3a](#page-4-1) that at pH 2.6, adsorption is nearly 62%

for the feed dye concentrations of 400 mg/L at the end of experiment. The percentage adsorption decreases from about 98 to 40%, when pH decreases from 11.1 to 2.6. From Fig. [2.3a,](#page-4-1) it may be observed that the adsorption of this dye is more at the basic pH.

The percentage of eosin adsorption at different pH levels are shown in Fig. [2.3b](#page-5-0) for an initial dye concentration of 100 mg/L. pH plays an important role on adsorption capacity by influencing the chemistry of both the dye molecule and the activated carbon in aqueous solution. Eosin is a dipolar molecule at low pH. Activated carbon contains oxygen complexes on its surface, e.g., strongly carboxylic groups, carbonyl groups, and phenolic groups (Motoyuki [1990\)](#page-46-0). These groups are nucleophilic in nature. With decrease in pH of the dye solution, more dye molecules are protonated and get adsorbed on the surface of the activated carbon. It can be observed from Fig. [2.3b](#page-5-0) that at pH 2, adsorption is about 100% for an initial

dye concentration of 100 mg/L. Percentage adsorption decreases with increase in pH. For the initial dye concentration of 100 mg/L, the removal is 91% for a pH of 12.

The percentage of Congo red adsorption at different pH has been shown in Fig. [2.3c](#page-5-1) for the initial dye concentrations of 200 mg/L. The initial pH of dye solution plays an important role particularly on the adsorption capacity by influencing the chemistry of both dye molecule and activated carbon in aqueous solution. Congo red is a dipolar molecular at lower pH and exists as anionic form at higher pH as shown in Fig. [2.3c](#page-5-1). The sodium and potassium salt of anionic Congo red in aqueous medium is red in color in basic pH up to 10. Above the pH value of 10, the degree of red color changes from the original one. It has also been found that as the pH decreases, the color of Congo red solution changes from red to dark blue. Therefore, the pH of the medium needs to be maintained between 5 and 10 to treat Congo red. These variations of color with pH suggest that the extent and nature of ionic character of Congo red molecule depend on the pH of the medium. The variations in the extent of adsorption of Congo red on activated carbon with pH are due to the difference in ionic character of the dye molecule. With decrease in pH of dye solution, more dye molecules are protonated and chemisorbed on the nucleophilic sites of the surface of CAC. It is found from the figure that at pH 2, adsorption is about 100%. On the other hand, the percentage adsorption decreases with increase in pH of the dye solution. This is because at higher pH, dye molecules exist in anionic form, and due to interionic repulsion, less adsorption takes place. For the feed dye concentration of 200 mg/L, the percentage adsorption decreases to 25% at the end of the experiment when the pH is 12. From Fig. [2.3c](#page-5-1), it may be observed that the adsorption of Congo red is maximum at the acidic pH. Therefore, when Congo red is present in the solution as red color, the operating pH for maximum adsorption should be kept at 5.

Effects of temperature on the extent of adsorption are shown in Figs. [2.4a,](#page-7-0) [2.4b](#page-7-1), and [2.4c](#page-8-0) for chrysoidine, eosin, and Congo red, respectively. Adsorption experiments are carried out for aqueous solution of chrysoidine for two different concentrations (400 and 700 mg/L) at three different temperatures (30, 50, and 70 °C) and at a pH of 4.4. It has been observed that the adsorption capacity increases significantly with temperature as shown in Fig. [2.4a](#page-7-0) for the initial chrysoidine concentration of 400 mg/L. The percentage adsorption increases from about 94 to 99% for the feed dye concentration of 400 mg/L and about 80 to 87% for the feed dye concentration of 700 mg/L, at the end of experiment, when temperature is raised from 30 to 70 °C. This endothermic nature of adsorption is due to the positive ΔH^0 value as shown in Table [2.4a](#page-13-0).

In order to observe the effect of temperature on the adsorption capacity, experiments are carried out for 100 mg/L eosin at three different temperatures (30, 40, and 50 °C) using 1.0 g of activated carbon per liter of the solution. It has been observed that with increase in temperature, adsorption capacity decreases as shown in Fig. [2.4b.](#page-7-1) This is due to the negative value of ΔH^0 value (refer to Table [2.4b](#page-14-0)).

Experiments are carried out to observe the effect of temperature on the extent of adsorption for Congo red of different initial concentration (50, 100, and 200 mg/L)

in aqueous solution at three different temperatures (e.g., 30, 40, and 50 $^{\circ}$ C) and at neutral pH. It has been observed that the adsorption capacity increases significantly with temperature as shown in Fig. [2.4c](#page-8-0) for the initial Congo red concentration of 100 mg/L. This is because of positive ΔH^0 value as shown in Table [2.4c](#page-14-1).

The thermodynamic parameters ΔG^0 , ΔS , and ΔH^0 for the adsorption of chrysoidine, eosin, and Congo red have been determined by using the following equations (Khan et al. [1995](#page-46-1)):

$$
\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{2.1}
$$

$$
\log(q_e/C_e) = \frac{\Delta S^0}{2.303R} + \frac{-\Delta H^0}{2.303RT}
$$
 (2.2)

where q_e is the amount of dye adsorbed per unit mass of activated carbon (mg/g), C_e is equilibrium concentration (mg/L), and T is temperature in Kelvin. q_e/C_e is called the adsorption affinity. It may be noted here that the experimental data considered here for the calculation of the thermodynamic parameters, namely, ΔG^0 , ΔH^0 , and ΔS^0 , are in the linear range of the equilibrium adsorption isotherm (e.g., for chrysoidine, q_e varies from 2.5 to 3.0 mmol/g and C_e varies from 0.012 to 0.2 mmol/L as shown in Fig. [2.5a](#page-10-0)). The values of Gibbs free energy (ΔG^0) have been calculated by knowing the enthalpy of adsorption (ΔH^0) and the entropy of adsorption (ΔS^0). ΔS^0 and ΔH^0 are obtained from a plot of log(q_e/C_e) versus $\frac{1}{T}$, from Eq. ([2.2](#page-7-2)). Once these two parameters are obtained, ΔG^0 is determined from Eq. [\(2.1\)](#page-7-3). The values of ΔG^0 , ΔH^0 , and ΔS^0 are listed in Tables [2.2a,](#page-9-0) [2.2b](#page-9-1) and [2.2c](#page-9-2) for chrysoidine, eosin, and Congo red, respectively.

Gibbs free energy (ΔG^0) for all the three dyes is negative (as shown in Tables [2.2a,](#page-9-0) [2.2b,](#page-9-1) [2.2c](#page-9-2)). This indicates that the adsorption process is spontaneous for all the three dyes. Adsorption of chrysoidine and Congo red is endothermic in nature (since ΔH^0 value is positive; refer to Tables [2.2a](#page-9-0) and [2.2c](#page-9-2)). On the other hand, eosin adsorption is exothermic in nature (as ΔH^0 value is negative; refer to Table [2.2b](#page-9-1)). The positive value of ΔS^0 for chrysoidine and Congo red (refer to Tables [2.2a](#page-9-0) and [2.2c](#page-9-2)) dictates that the adsorbed dye molecules on the activated carbon surface are organized in a more random fashion compared to those in the aqueous phase. Similar observations have been reported in the literature (Bhattacharyya and Sharma [2003](#page-43-0)). For eosin, the negative value of ΔS^0 (refer to Table [2.2b\)](#page-9-1) suggests decreased randomness at the solid solution interface during adsorption (Manju et al. [1998\)](#page-46-2).

Adsorbent	Chrysoidine	ΔH^0	ΔS^0		$-\Delta G^{0}(kJ/mol)$ at temperature	
(g/L)	(mg/L)	(kJ/mol)	(J/mol.K)	303 K	323 K	343 K
0.5	400	43.6	171.4	8.3	11.8	15.2
1.0	700	48.9	180.9	5.9	9.6	13.2
Mean		46.3	176.2		10.7	14.2

Table 2.2a Thermodynamic parameters for adsorption of chrysoidine in activated charcoal at different temperature and dye concentrations

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Table 2.2b Thermodynamic parameters for adsorption of eosin in activated charcoal at different temperature and 100 mg/L of eosin

			$A = \Delta G^0$ (kJ/mol) at temperature			
Eosin (mg/L)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol.K)	303 K	313 K	323 K	
100	27.0	52.6	11.0	10.5	10.0	

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Table 2.2c Thermodynamic parameters for adsorption of Congo red in activated charcoal at different temperature and dye concentrations

			$-\Delta G^0(kJ/mol)$ at temperature		
Congo red (mg/L)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol.K)	303 K	313 K	323 K
50	21.5	86.8	4.8	5.7	6.6
100	51.1	178.1	2.9	4.6	6.4
200	10.1	34.5	0.3	0.67	1.0
Mean	27.6	99.8	2.7	3.7	4.7

2.2.1.1 Langmuir Adsorption Isotherm

Langmuir adsorption isotherm is applicable to explain the equilibrium data for many adsorption processes. The basic assumption of this process is the formation of monolayer of adsorbate on the outer surface of adsorbent, and after that no further adsorption takes place. The expression of the Langmuir model is given as follows (Ozacar and Sengil [2003\)](#page-47-0):

$$
q_{\rm e} = \frac{QbC_{\rm e}}{1 + bC_{\rm e}}\tag{2.3}
$$

A linear form of this expression is

$$
\frac{1}{q_{e}} = \frac{1}{Q} + \frac{1}{Qb} \cdot \frac{1}{C_{e}}
$$
\n(2.4)

where q_e is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g) and C_e is the equilibrium concentration of adsorbate (mg/L). The constant Q and

b are the Langmuir constants and are the significance of adsorption capacity (mg/g) and energy of adsorption (l/mg), respectively. Values of Q and b are calculated from the intercept and slope of the plot $1/q_e$ versus $1/C_e$.

2.2.1.2 Freundlich Adsorption Isotherm

This model is an indicative of the extent of heterogeneity of the surface of adsorbent and is given as follows:

$$
q_{\rm e} = K_{\rm F} C_{\rm e}^{1/n} \tag{2.5}
$$

where K_F and n are Freundlich constants. A linear form of the Freundlich expression is as follows:

$$
\log q_{\rm e} = \log K_{\rm F} + \frac{1}{n} \log C_{\rm e} \tag{2.6}
$$

The constants K_F and *n* are the Freundlich constants and are the significance of adsorption capacity and intensity of adsorption, respectively. Values of K_F and n are calculated from the intercept and slope of the plot $log q_e$ versus $log C_e$.

Adsorption isotherms of chrysoidine, eosin, and Congo red on activated carbon at 30 °C are shown in Figs. [2.5a](#page-10-0), [2.5b](#page-11-0), and [2.5c,](#page-11-1) respectively. The coefficients of these two isotherm models for the three dyes are given in Table [2.3](#page-11-2). These data provide information on the amount of activated carbon required to adsorb a particular mass of dye under specified system conditions. Correlation coefficients are evaluated by fitting the experimental adsorption equilibrium data for three dyes separately using both Langmuir and Freundlich adsorption isotherms and are also shown in Table [2.3](#page-11-2). It is found from the correlation coefficients (r^2) that adsorption

Table 2.3 Langmuir and Freundlich isotherm constants for adsorption of dyes on activated charcoal

isotherm for the present three dye-activated charcoal systems is best explained by Freundlich equation.

2.2.1.3 Adsorption Kinetics

The kinetics of adsorption of chrysoidine, eosin, and Congo red on activated carbon have been described using both first- and pseudo-second-order model. The Lagergren's equation for first-order kinetics is as follows:

$$
\log(q_{\rm e} - q_{\rm t}) = \log q_{\rm e} - \frac{k_1 t}{2.303} \tag{2.7}
$$

The expression for pseudo-second-order rate equation is given as (Ho et al. [1996\)](#page-45-1)

$$
\frac{t}{q_{\rm t}} = \frac{1}{k_2 q_{\rm e}^2} + \frac{t}{q_{\rm e}}\tag{2.8}
$$

where q_e and q_t are the amounts of dye adsorbed (mg/g) at equilibrium and at any time t and k_1 is the rate constant (min^{-1}) . Figures [2.6a](#page-12-0), [2.6b](#page-13-1), and [2.6c](#page-13-2) show (t/q_t) versus t plot for pseudo-second-order kinetics for chrysoidine, eosin, and Congo red, respectively. In Eq. (2.8) (2.8) , k_2 (g/mg min) is the rate constant for the pseudosecond-order adsorption kinetics. The slope of the plot (t/q_t) versus t gives the value of q_e , and from the intercept, k_2 can be calculated. The values of k_1 , k_2 , and correlation coefficients (r^2) , both in the first and pseudo-second-order kinetics, are presented in Tables [2.4a,](#page-13-0) [2.4b,](#page-14-0) and [2.4c](#page-14-1) for chrysoidine, eosin, and Congo red, respectively. It may be observed from Tables [2.4a](#page-13-0), [2.4b](#page-14-0), and [2.4c](#page-14-1) that the adsorption of chrysoidine, eosin, and Congo red on activated carbon follows pseudo-second-order kinetics more closely.

Table 2.4a Comparison of the first- and second-order adsorption rate constants, calculated and experimental q_e value for chrysoidine on activated charcoal

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		First-order			Pseudo-second-order		
Eosin (c_0) (mg/L)	q_e , exp t (mg/g)	q_e , fit (mg/g)	k_1 (1/min)	r^2	q_e, fit (mg/g)	k_2 (g/mg) min)	
Feed CAC: 1.0 g/L							
200	175.0	152.3	6.7×10^{-2}	0.91	173.4	5.4×10^{-4}	0.998
400	286.0	232.2	4.4×10^{-2}	0.86	302.1	4.3×10^{-4}	0.998

Table 2.4b Comparison of the first- and second-order adsorption rate constants, calculated and experimental q_e value for eosin on activated charcoal

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Table 2.4c Comparison of the first- and second-order adsorption rate constants, calculated and experimental q_e value for Congo red on activated charcoal

		First-order				Pseudo-second-order	
Congo red (c_0) (mg/L)	q_e , exp t (mg/g)	q_e , fit (mg/g)	k_1 (1/min)		q_e, fit (mg/g)	k_2 (g/mg min)	
Feed CAC: 1.0 g/L							
50	45.7	2.2	1.8×10^{-2} 0.925		45.9	12×10^{-2}	0.999
$\overline{100}$	76.2	75.0	4.1×10^{-2} 0.879		88.5	5.3×10^{-2}	0.987
380	171.1	119.0	12.9×10^{-2}	0.964	181.8	4.5×10^{-2}	0.997
545	183.1	144.8	3.0×10^{-2}	0.978	207.5	2.5×10^{-2}	0.995

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2.2.2 Column Adsorption

Column adsorptions studies are essential for design of industrial scale fixed-bed adsorber system. Figure [2.7](#page-15-0) shows the breakthrough curves for different bed depths. It may be observed from Fig. 2.8 that the breakthrough time (duration for zero column outlet concentration) increases from 18 to 39 h, when the bed depth is increased from 4.5×10^{-2} m to 7.0×10^{-2} m, for the same flow rate of 0.18 L/hr. The shape and the gradient of the breakthrough curves for the two bed depths are almost identical.

2.3 Generalized Shrinking Core Model for Batch Adsorption Data

To develop a mathematical model that describes the adsorption dynamics, the following information are generally required:

1. A complete description of equilibrium behavior, i.e., the maximum level of adsorption attained in a sorbent/sorbate system as a function of the sorbate liquid-phase concentration

2. Mathematical representation of associated rate of adsorption, which is controlled by the resistances within the sorbent particles

In adsorption, mainly two resistances prevail – the external liquid film resistance and the resistance in the adsorbent particle. The intraparticle diffusion resistance may be neglected for solutes that exhibit strong solid to liquid-phase equilibrium solute distribution, in the initial period of operation. However, even for such systems, the above assumption leads to errors that are substantial beyond the first few minutes if the agitation is high (Mathews and Weber [1976](#page-46-3)). So, both the resistances are important for kinetic study (Chatzopoulos et al. [1993;](#page-43-1) McKay [1984;](#page-46-4) Costa et al. [1987;](#page-44-1) Komiyama and Smith [1974](#page-46-5); Liapis and Rippin [1977](#page-46-6)).

The external liquid film resistance is characterized by the external liquid film mass transfer coefficient (k_f) . The mass transport within the adsorbent particles is assumed to be a pore diffusion (Dedrick and Beckman 1967; Weber and Rumer [1965;](#page-49-0) Furusawa and Smith [1973](#page-44-2); McKay 1982) or homogeneous solid diffusion process (McKay 1982; Hand et al. [1983](#page-45-2); Kapoor et al. [1989](#page-45-3)).

The pore diffusion model outlined in this paper is based on the unreacted shrinking core model (Yen 1968; Levenspiel [1972](#page-46-7)) with pseudo-steady-state approximation. This model has mostly been applied to gas-solid non-catalytic reactions, but a number of liquid-solid reactions also have been analyzed using this model (Neretnieks [1976;](#page-47-1) Spahn and Schlunder 1975). In the pore diffusion model, there is adsorption of the adsorbate into the pores with a cocurrent solute distributed all along the pore wall.

The assumptions made in this model are as follows:

- (a) Pore diffusivity is independent of concentration.
- (b) Adsorption isotherm is irreversible.
- (c) Pseudo-steady-state approximation is valid.
- (d) The driving force in both film and particle mass transfer is directly proportional.
- (e) Adsorbent particles are spherical.

The major limitation of this model is that it is specific to the nature of isotherm. This means that the model available in literature is most suitable for Langmuir-type isotherm, i.e., formation of a monolayer of adsorbate on the adsorbent. Besides, this model is only applicable for higher initial adsorbate concentration in solution so that the batch process operating line intercepts the invariant zone of isotherm. For example, for Astrazone blue-silica system, the literature model is applicable for $C_0 >> 200$ mg/lit (McKay [1984\)](#page-46-4). The present model, which is more generalized, overcomes the above limitations. The model proposed, here in, can be applied to wide ranges of initial adsorbate concentrations for all possible nature of isotherms. The system reported here is adsorption of Astrazone blue dye on Sorbsil Silica.

The equations considered for the kinetics of the adsorption process for spherical adsorbent particles for the present model are as follows:

The mass transfer from external liquid phase can be written as

$$
N(t) = 4\pi R^2 K_f (C_t - C_{\text{et}})
$$
\n(2.9)

The diffusion of solute through the pores as per Fick's law can be written as

$$
N(t) = \frac{4\pi D_{\rm p} C_{\rm et}}{\left[\frac{1}{R_{\rm f}} - \frac{1}{R}\right]}
$$
\n(2.10)

where D_p is the effective diffusivity in the porous adsorbent (Fogler [1997](#page-44-3)).

The mass balance on a spherical element of adsorbate particle can be written as

$$
N(t) = -4\pi R_f^2 Y_{\text{et}} \rho \left[\frac{dR_f}{dt} \right]
$$
 (2.11)

The average concentration on adsorbent particle can be written as

$$
\overline{Y_{t}} = Y_{et} \left[1 - \left(\frac{R_{f}}{R} \right)^{3} \right]
$$
 (2.12)

The differential mass balance over the system by equating the decrease in adsorbate concentration in the solution with the accumulation of the adsorbate in the adsorbent can be written as

$$
N(t) = -V\left(\frac{dC_t}{dt}\right) = W\left(\frac{d\overline{Y_t}}{dt}\right) \tag{2.13}
$$

The dimensionless terms used for simplification are as follows:

$$
C_{t}^{*} = \frac{C_{t}}{C_{0}}, r = \frac{R_{f}}{R}, Bi = \frac{k_{f}R}{D_{p}}, Ch = \frac{W}{VC_{0}}, C_{et}^{*} = \frac{C_{et}}{C_{0}} \text{ and } \tau = \frac{D_{p}t}{R^{2}}
$$

Simplifying Eqs. (2.9) and (2.10)

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$$
C_{\text{et}}^* = \frac{Bi(1-r)C_{\text{t}}^*}{[r+Bi(1-r)]} = g_1(C_{\text{t}}^*, r)
$$
\n(2.14)

Now differentiating the above equation with respect to τ

$$
\frac{dC_{\text{et}}^*}{d\tau} = \frac{Bi(1-r)}{r + Bi(1-r)} \frac{dC_t^*}{d\tau} - \frac{BiC_t^*}{\left[r + Bi(1-r)\right]^2} \frac{dr}{d\tau} \tag{2.15}
$$

From the equilibrium relationship

$$
Y_{\rm e}(t) = g_2(C_{\rm et}^*)
$$
\n(2.16)

where g_2 is any equilibrium isotherm relationship. Simplifying Eqs. ([2.9](#page-16-0)) and ([2.11](#page-16-2))

$$
\left(\frac{dr}{d\tau}\right) = \frac{-Bi\left(\frac{C_0}{\rho Y_e}\right)\left(C_t^* - C_{\text{et}}^*\right)}{r^2} \tag{2.17}
$$

Simplifying Eqs. (2.12) (2.12) and (2.13)

$$
\left(\frac{dC_t^*}{d\tau}\right) + Ch\left(1 - r^3\right) \left(\frac{dY_{\text{et}}}{d\tau}\right) = 3Ch \cdot Y_{\text{et}} r^2 \left(\frac{dr}{d\tau}\right) \tag{2.18}
$$

For Langmuir isotherm

$$
Y_{\rm et} = \frac{Y_s C_{\rm et}}{1 + k_0 C_{\rm et}} = \frac{Y_s C_0 C_{\rm et}^*}{1 + k_0 C_0 C_{\rm et}^*} = \frac{Y_{\rm es} C_{\rm et}^*}{1 + k_0^* C_{\rm et}^*}
$$
(2.19)

where $Y_{\text{es}} = Y_{\text{s}} C_0$ and $k_0^* = k_0 C_0$.

The time derivative of Eq. (2.19) (2.19) (2.19) becomes

$$
\frac{dY_{\text{et}}}{d\tau} = \frac{Y_{\text{es}}}{\left(1 + k_0^* C_{\text{et}}^*\right)^2} \frac{dC_{\text{et}}^*}{d\tau} \tag{2.20}
$$

Combining Eqs. [\(2.14\)](#page-16-5), ([2.18](#page-17-1)), and [\(2.20\)](#page-17-2) and after algebraic manipulation, the following expression is obtained (for Langmuir-type isotherm):

$$
\left(\frac{dC_t^*}{d\tau}\right) = \left(N\middle/M\right)\left(\frac{dr}{d\tau}\right) \tag{2.21}
$$

where $M = 1 + Ch(1 - r^3) \frac{Y_{\text{es}}Bi(1 - r)}{(1 + L^* C^*)^2 [r + r(1 - r^3)]}$ $(1 + k_0^* C_{\text{et}}^*)^2 [r + (1 - r)Bi]$ and, $N = 3ChY_{\text{et}}r^2 + \frac{ChY_{\text{es}}Bi(1 - r^3)\tilde{C}_t^*}{(1 + k^*C^*)^2[r + (1 - r^3)]}$ $\frac{(1 + k_0^* C_{\text{et}}^*)^2 [r + (1 - r)Bi]^2}{(1 + k_0^* C_{\text{et}}^*)^2 [r + (1 - r)Bi]^2}$. Using Eq. ([2.14](#page-16-5)), Eq. ([2.17](#page-17-3)) may be written as

2.3 Generalized Shrinking Core Model for Batch Adsorption Data 67

$$
\frac{dr}{d\tau} = \frac{-Bi\left(\frac{C_0}{\rho r_e}\right)\left(C_t^* - C_{\text{et}}^*\right)}{r^2} = f_1\left(C_t^*, r\right) \tag{2.22}
$$

Using Eqs. (2.14) (2.14) (2.14) and (2.22) , Eq. (2.21) (2.21) (2.21) may be expressed as

$$
\left(\frac{dC_t^*}{d\tau}\right) = \frac{N(C_t^*, r)f_1(C_t^*, r)}{M(C_t^*, r)} = f_2(C_t^*, r)
$$
\n(2.23)

The initial conditions for Eqs. [\(2.22](#page-17-4)) and ([2.23](#page-18-0)), $C_0 = 1.0$ and $r = 1.0$ at time, $\tau = 0.0$. Equations [\(2.22\)](#page-17-4) and ([2.23](#page-18-0)) can be solved to find the bulk concentration at any time " t " if we know all the process parameters. The two process parameters – the external mass transfer coefficient (k_f) and internal effective diffusivity (D_p) – are unknown to us. These two parameters are estimated by optimizing the experimental concentration profile as outlined in the next section.

2.3.1 Numerical Analysis

The above set of equations are numerically solved using fourth-order Runge-Kutta of step size (d τ) of the order 10⁻⁵ along with a nonlinear optimization technique (Levenberg-Marquardt) to estimate the two process parameters described above, so that the experiment kinetic profile (i.e., bulk concentration versus time) is matched. For this purpose, optimization subroutine UNLSF/DUNLSF from IMSL math library has been used.

The adsorption systems studied here encompass Radke-Prausnitz isotherm (Tables [2.5](#page-19-0) and [2.6](#page-19-1)). The systems considered here are (1) Astrazone blue dye on silica, (2) para-nitrophenol on granular activated carbon from Lurgi, and (3) toluene on F300 activated carbon. The experimental data on kinetics and the isotherm constants have been reported in literature (McKay [1984](#page-46-4); Costa et al. [1987;](#page-44-1) Chatzopoulos et al. [1993](#page-43-1)).

The adsorption of Astrazone blue on silica follows Langmuir isotherm (McKay [1984\)](#page-46-4). The isotherm constants are $Y_s = 0.5$ lit/g and $K_0 = 0.016$ lit/mg, where Y_e in mg/g and C_e in mg/l. For $W = 17$ g, $V = 1.7$ l, $R = 0.3025$ mm, and $\rho = 2.2$ g/cc, the concentration decay data for $C_0 = 520$ mg/l has been used to determine the unknown process parameters using the above numerical procedure as shown in Fig. [2.8a.](#page-20-0) The estimated values of the parameters are as follows: $k_f = 130.0 \times 10^{-6}$ cm/s and $D_p = 16.16 \times 10^{-9}$ cm²/s. These values of k_f and D_p are used to simulate the adsorption kinetics for different operating conditions. It is interesting to note that the estimated values of k_f and D_p are close to the values reported by Mckay [\(1984](#page-46-4)), i.e., $k_f = 80 \times 10^{-6}$ cm/s and $D_p = 18 \times 10^{-9}$ cm²/s. The experimental observations and the model-simulated concentration profiles for different initial dye

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concentrations, masses of silica, and particle sizes of silica have been shown in Figs. [2.8b,](#page-20-1) [2.8c](#page-20-2) and [2.8d,](#page-21-0) respectively. From the above figures, it may be observed that beyond 120 min (2 h) of the process, the model underpredicts the bulk concentration profile. This may be due to the increase of the resistance inside the micropores which inhibits the process of adsorption. The present model can be used for multicomponent adsorption processes and also with concentration-dependent diffusivity. The model is useful to estimate k_f and D_p values, which are required for the design of fixed-bed adsorber.

2.4 Discussion of Mathematical Model Analysis

The adsorption experiments in the fixed-bed column are carried out to study the adsorption dynamics and quantify the breakthrough curve. One of the crucial aspects of design of adsorption columns for any separation process is the prediction of the breakthrough time. This is necessary to estimate the lifetime of the adsorption bed and its process efficiency. There have been several mathematical models developed in the past based on different assumption justifying the simplicity in the calculations.

2.4.1 Thomas Model (Thomas [1944\)](#page-48-3)

Thomas solution is the most general and widely used equation for modeling performance of fixed-bed adsorption. The Thomas model assumes second-order reversible Langmuir kinetics of the adsorption-desorption process. Ideally the model is suitable for situations where the external and internal diffusion resistances are small. This is particularly true for adsorption scenarios in most liquid systems and therefore is most relevant for adsorption in aqueous environment. The expression describing the output concentration C_t/C_0 is given by

where k_{Th} is the model parameter obtained from nonlinear regression of the output concentration with time. The parameter q_e is the maximum adsorption capacity of the adsorbent.

2.4.2 Adams-Bohart Model (Bohart and Adams [1920](#page-43-2))

The Adams-Bohart model considers that the adsorption rate is proportional to both the adsorbent leftover capacity and the concentration of the adsorbate species in the solution. The Adams-Bohart model is originally applied for prediction of adsorption behavior in gas-solid systems, but later on extended to liquid streams. It assumes that the adsorption rate is proportional to the residual capacity of the adsorbent and adsorbate concentration. Since the external mass transfer is not taken into account, it is particularly not suitable for describing the system at high flow rate and concentration. Theoretically, the model is applicable for predictions at early times, when $C/C_0 \ll 1$. The mathematical equation describing the output concentration is represented by Eq. [\(2.25\)](#page-21-1):

$$
\frac{c_{\rm t}}{c_0} = \exp\left(k_{\rm AB}c_0t - k_{\rm AB}q_{\rm e}\frac{Z}{Q}\right) \tag{2.25}
$$

where k_{AB} is the model parameter obtained from nonlinear regression of the experimental data.

2.4.3 Yoon-Nelson Model (Yoon and Nelson [1984](#page-49-1))

The Yoon-Nelson model is based on the assumption that the probability of adsorption for each molecule decreases proportionately on the probabilities of the adsorbate adsorption and breakthrough. One of the features of the model is that the product of the parameters $K_{vn}\tau_{vn}$ is constant for a particular adsorbent-adsorbate combination and independent on the operating conditions. This is a fairly simple model which does not require any knowledge of the adsorption capacity or type of the adsorbent:

$$
\frac{c_t}{c_0 - c_t} = \exp(k_{\rm{YN}}t - \tau k_{\rm{YN}}) \tag{2.26}
$$

where τ and k_{YN} are the model parameters obtained from nonlinear regression of the experimental data.

2.4.4 Clark Model (Clark [1987\)](#page-44-4)

This model is based on the application of the mass transfer concept in combination with Freundlich equilibrium isotherm. The adsorption equilibrium isotherm satisfying Freundlich relationship can only be used for predicting the breakthrough profile of the adsorption column. The semiempirical relationship is presented in Eq. ([2.27](#page-22-0)):

$$
\frac{c_t}{c_0} = \left(\frac{1}{1 + A \exp(-rt)}\right)^{1/(n-1)}
$$
\n(2.27)

where A and r are the model constants obtained from nonlinear regression analysis. The constant 1/n is obtained from the Freundlich isotherm equation.

2.4.5 Bed Depth/Service Time (BDST) Model (Goel et al. [2005](#page-44-5))

The BDST model is the linearized form of the Adams-Bohart model. The main consideration here is the assumption that the intraparticle diffusion and external mass transfer resistance is negligible and the adsorption kinetics is controlled by the surface chemical reaction between the adsorbate and adsorbent, which is generally uncommon in real systems. The popularity of the BDST is due to its simplicity in predicting breakthrough behavior owing to its rapid analysis. The expression predicting the breakthrough profile (C_t/C_0) is given by

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$$
\frac{c_0}{c_t} = 1 + K_{\text{BDST}} \exp\left(\frac{q_e Z}{Q} - c_0 t\right) \tag{2.28}
$$

where K_{BDST} is the model parameter determined by the nonlinear regression analysis of the experimental data. Although the BDST model provides a simple and comprehensive approach for evaluating sorption column test, its validity is limited and does not involve any sound understanding of the implicit transport mechanism (Bohart and Adams [1920;](#page-43-2) Poots et al. [1976a;](#page-47-2) Faust and Aly [1987\)](#page-44-6). One of the major limitations of this model is the symmetry of the logistic function (S-shaped curve) around its midpoint $t = N_0 Z / C_0 U_0$ and $C = C_0 / 2$, which is not true for most breakthrough profiles. Therefore, a more detailed adsorption bed modeling based on the physical transport laws of pore diffusion is necessary for accuracy of the model prediction and scaling up of the process.

2.4.6 Pore Diffusion-Adsorption Model

The 1D single species convective-diffusive equation (Kunii and Levenspiel [1991](#page-46-8)) is described by Eq. ([2.29](#page-23-0)):

$$
\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \left(\frac{3k_f}{a_p}\right) \left(\frac{1-\epsilon}{\epsilon}\right) \rho_s (C - C_e)
$$
(2.29)

where the generation term accounted is dependent on the solid-fluid mass transfer rate and is linearly proportional to the concentration difference and C_e is the adsorbate concentration at the adsorbent-bulk interface. The solution of Eq. ([2.29](#page-23-0)) provides information of the transient solute concentration at various bed depths. In deriving Eq. [\(2.29\)](#page-23-0), by the material balance analysis, it is inherently assumed that all the interparticle void space in the bed is saturated and the fluid velocity is uniform and unhindered throughout. The initial and boundary conditions of Eq. ([2.29](#page-23-0)) are

at
$$
t = 0, C = C_0
$$
 for $z = 0$ and $C = 0$ for $0 < z \le L$ (2.30a)

$$
at z = 0, \quad D_L \frac{\partial C}{\partial z} + V(C_0 - C) = 0 \tag{2.30b}
$$

and at
$$
z = L
$$
, $\frac{\partial C}{\partial z} = 0$ (2.30c)

The intra-pellet adsorption is described by the pore diffusion transport model. Intraparticle mass transport is characterized by the pore diffusion coefficient D_n . The mass balance equation for the liquid phase (pore) in a spherical particle can be written as

$$
\varepsilon_{\rm p} \frac{\partial C_{\rm p}}{\partial t} + (1 - \varepsilon_{\rm p}) \rho_{\rm s} \frac{\partial q}{\partial t} = D_{\rm p} \left(\frac{\partial^2 C_{\rm p}}{\partial r^2} + \frac{2}{r} \frac{\partial C_{\rm p}}{\partial r} \right) \tag{2.31}
$$

where C_p is the contaminant concentration inside the particle and ε_p is particle porosity. Assuming instantaneous equilibrium $\frac{\partial q}{\partial t} = \frac{\partial C_{\rm p}}{\partial t}$ ∂q $rac{vq}{\partial C_p}$. Modifying Eq. [\(2.31\)](#page-23-1), we get (Singha et al. [2012\)](#page-48-4),

$$
\frac{\partial C_{\mathbf{p}}}{\partial t} = \frac{1}{\left[1 + \left(1 - \epsilon_{\mathbf{p}}\right)\rho_s \frac{\partial q}{\partial C_{\mathbf{p}}}\right]} \left(\frac{D_{\mathbf{p}}}{\epsilon_{\mathbf{p}}}\right) \left(\frac{\partial^2 C_{\mathbf{p}}}{\partial r^2} + \frac{2}{r} \frac{\partial C_{\mathbf{p}}}{\partial r}\right) \tag{2.32}
$$

The initial condition ($t = 0$) is given by $C_p = 0$ for $0 < r < a_p$.

The symmetry condition at the particle center $(r = 0)$ and continuity of the concentration on the external surface of the adsorbent bed are simultaneously expressed as

$$
at r = 0, \frac{\partial C_p}{\partial r} = 0
$$
 (2.33a)

and at
$$
r = a_p, k_f (C_p - C_e) = D_p \varepsilon_p \frac{\partial C_p}{\partial r}
$$
 (2.33b)

2.5 Various Types of Adsorbents Used for Dye Adsorption

A summary of the various low-cost adsorbents for dye removal as studied by several researchers in the past is presented in Tables [2.7,](#page-25-0) [2.8](#page-29-0) and [2.9.](#page-37-0) Natural materials or the wastes/by-products of industries or synthetically prepared materials, which cost less and can be used as such or after some minor treatment as adsorbents, are generally called low-cost adsorbents. Generally, the low-cost adsorbents are usually branded as substitutes for activated carbons because of their similar wide usage; however, in a clear sense, they are essentially substitutes for all available expensive adsorbents. These alternative low-cost adsorbents (Gupta et al. [2009](#page-45-4)) may be categorized in two ways (1) based on their availability, for, e.g., natural materials such as coal, wood, lignite, peat, etc., or agricultural/industrial/ domestic wastes; or by-products such as sludge, slag, red mud, fly ash, etc., or synthesized products; and (2) depending on their nature, for, e.g., organic or inorganic. The adsorbents listed in Table [2.7](#page-25-0), [2.8,](#page-29-0) and [2.9](#page-37-0) provide useful information about the type and capacity of alternative adsorbents without going into too much detail of the preparation process.

		Surface	Adsorption capacity	Concentration	
Adsorbent	Adsorbate	area (m^2/g)	(mg/g)	range (mg/L)	Source
GAC Filtrasorb 400	Acid blue 40	1100	57.5 mg/g	$25 - 200$	Ozacar and Sengil (2002)
Filtrasorb F 400	Acid blue 80	1200	112.3 mg/g	\equiv	Choy et al. (2000)
Filtrasorb F 400	Acid red 114	1200	103.5 mg/g	\equiv	Choy et al. (2000)
Filtrasorb F 400	Acid red 88	\equiv	109 mg/g		Venkata Mohan et al. (1999)
Filtrasorb F 400	Acid yel- low 117	1200	155.8 mg/g	\equiv	Choy et al. (2000)
GAC Filtrasorb 400	Acid yel- low 17	1100	133.3	$25 - 200$	Ozacar and Sengil (2002)
PAC	Acid brown 283	1026	22	$30 - 250$	Martin et al. (2003)
AC-charcoal	Acid blue	$\overline{}$	100.9	$10 - 25$	Choy et al.
	Acid yellow		128.8		(1999)
	Acid red 114		101		
AC rice husk	Acid blue	352	50	$1 - 50$	Mohamed (2004)
Blast furnace sludge	Acid blue 113	28	2.1	\equiv	Jain et al. (2003c)
Bentonite	Acid blue 193	767	740.5		Ozcan et al. (2004)
Wood sawdust raw	Acid blue 25	$\overline{}$	5.92	$\overline{}$	Ho and McKay (1998a)
Treated cotton	Acid blue 25	$\overline{}$	589	\equiv	Bouzaida and Rammah (2002)
Chitosan	Acid blue 25	\equiv	77.4	\equiv	Martel et al. (2001)
Hazelnut shell	Acid blue 25	$\overline{}$	60.2	50-500	Ferrero (2007)
Sawdust-walnut	Acid blue 25	$\overline{}$	37	50-500	Ferrero (2007)
Sawdust-cherry	Acid blue 25	$\overline{}$	32	50-500	Ferrero (2007)

Table 2.7 Adsorption capacities of commercial activated carbon and other alternative adsorbents for removal of acid dyes

Table 2.7 (continued)

Table 2.7 (continued)

Table 2.7 (continued)

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Table 2.8 (continued) Table 2.8 (continued)

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Table 2.8 (continued) Table 2.8 (continued)

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Table 2.9 (continued) Table 2.9 (continued)

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