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KINETICS OF POLLUTANT SORPTION BY BIOSORBENTS: REVIEW

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ABSTRACT

A review of the mechanisms of solute sorption onto various biosorbents has been performed. The mechanisms have been subdivided into reaction based systems and diffusion based systems and the literature has been reviewed in accordance with these two groups. The range of solute-sorbent systems reviewed include metal ions, dyestuffs and several organic substances in aqueous systems onto a wide range of biosorbents and mineral earths. Extensive tables are presented summarising isotherm types, sorption capacities, kinetic models which have been applied particularly to biosorbent systems but also to many other adsorbent materials.

Key Words: Biosorbents, Kinetics, Sorption.

1. INTRODUCTION

Sorption systems have been investigated to assess their suitability for application in the field of water pollution control. The cost and performance of a product or the mode of application are always of concern to control process efficiency. Therefore the sorption capacity and required contact time are two of the most important parameters to understand. Two important physicochemical aspects for evaluation of a sorption process as a unit operation are the equilibrium of the sorption and the sorption kinetics. Sorption equilibrium is established when the concentration of sorbate in the bulk solution is in dynamic balance with that of the interface. An equilibrium analysis is the most important fundamental information required to evaluate the affinity or capacity of a sorbent. However, thermodynamic data can predict only the final state of a system from an initial non-equilibrium mode. It is therefore important to determine how sorption rates depend on the

Table 1. Kinetic Equations Used by Taylor *et al*[25].

Reaction Order	Equation	Equation Number
zero order	$q_t^* = q_0^* + k_0 t$	(13)
first-order reaction	$\ln(q_t) = \ln(q_0) + k_1 t$	(14)
second-order reaction	$\frac{1}{q_t} = \frac{1}{q_0} + k_2 t$	(15)
third-order reaction	$\frac{1}{q_t^2} = \frac{1}{q_0^2} + k_3 t$	(16)
Parabolic diffusion	$q = \alpha + k_d \sqrt{t}$	(17)
Elovich-type equation	$q_t = q_0 + \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$	(18)

Key : $q = q_0$ at $t = 0$

concentrations of sorbate in solution and how rates are affected by sorption capacity or by the character of the sorbent. From the kinetic analysis, the solute uptake rate, which determines the residence time required for completion of the sorption reaction, may be established.

Sorption processes may include ion exchange, chelation, physical and chemical sorption. When the chemical reaction at the solid phase is rapid and is not associated with solid-phase transport processes, the liquid-phase transport process determines the overall rate of reaction, e.g., transport in the bulk liquid phase, diffusion across the liquid film surrounding the solid particles, diffusion in liquid-filled macropores[1]. Sorption mechanisms depend on the sorbate-sorbent interaction and the system conditions. Therefore it is impossible to classify sorption mechanisms by the solute type. This is demonstrated in Tables 2 to 4. Table 2 presents a list of metal ion systems and summarises the isotherm type, the sorption capacity and the sorption mechanism. These can be seen to vary widely from system to system. Other pollutant sorption systems have been classified by the solute type in Tables 3 and 4 for dye-sorbent and organic-sorbent systems respectively. However, further analysis of these data and systems are required in order to understand and predict the diffusion and kinetic transport mechanisms which control their uptake rates.

This work gives an overview of the main approaches to determining rate equations for sorption systems using biosorbents. The solutes in the sorption systems in this paper are aqueous phase pollutants such as metal ions, dyestuffs and contaminating organic compounds. The majority of the sorbents reviewed are materials of biological organic compounds and a few inorganic sorbents such as sili-

Table 2. Sorption of Metal Ions on Biosorbents.

Isotherm: L = Langmuir & F = Freundlich

Material	Metal	Reference	Isotherm Type X_m (mg/g)	Kinetics/Diffusion
Activated carbon from bicarbonate–treated peanut hulls	Hg(II)	Namasivayam & Periasamy[56] (1993)	L, 109.89	Film & pore diffusion
Activated carbon from commercial	Hg(II)	Namasivayam & Periasamy[56] (1993)	L, 12.38	Film & pore diffusion
Activated coconut shell	Cr(VI)	Rao et al.[14] (1992)	Nil	1st order
Activated carbon-carbonized ground hust	Cr(III)	Periasamy et al.[15] (1991)	F, 5.61 at pH 2	1st order
		Periasamy et al.[15] (1991)	F, 3.54 in tap water	1st order
Antimony (V) phosphate cation exchanger	Pesticide Phosphamidon	Varshney et al.[24] (1996)	Nil	1st & 2nd Orders
Banana pith	Cu(II)	Lee et al.[8] (1995)	L, 8.55 at pH 4.5	1st order
		Lee et al.[8] (1995)	L, 13.46 in synthetic solution	1st order
Beech leaves	Al(III)	Salim et al.[40] (1992)	F	Intraparticle diffusion
	Ca(II)	Salim et al.[40] (1992)	F	Intraparticle diffusion
	Cd(II)	Salim et al.[40] (1992)	F	Intraparticle diffusion
	Cu(II)	Salim et al.[40] (1992)	F	Intraparticle diffusion
	Mg(II)	Salim et al.[40] (1992)	F	Intraparticle diffusion
	Ni(II)	Salim et al.[40] (1992)	F	Intraparticle diffusion
	Pb(II)	Salim et al.[40] (1992)	F	Intraparticle diffusion
China clay	Ni(II)	Sharma et al.[50] (1991)	30°C, L, 5.06	Intraparticle diffusion
		Sharma et al.[50] (1991)	40°C, L, 1.34	Intraparticle diffusion
		Sharma et al.[50] (1991)	50°C, L, 0.80	Intraparticle diffusion

Chitosan	Cu(II)	Findon et al.[43] (1993)	L, 40 & F	Boundary layer (intraparticle) diffusion
Chrome sludge	Cr(III)	Lee et al.[8] (1995)	L, 24.04	Nil
Coconut husk with dye coated form (CHRY)	Cu(II)	Low et al.[9] (1995)	L, 12.27	Nil
Coconut husk with dye coated form (CHAB9)	Cu(II)	Low et al.[9] (1995)	L, 8.13	Nil
Coconut husk with dye coated form (CHAB5)	Cu(II)	Low et al.[9] (1995)	L, 7.75	Nil
Coconut husk with NH	Cu(II)	Low et al.[9] (1995)	L, 3.07	Nil
Coconut shell	Cd(II)	Bhattacharya & Venkobachar[4] (1984)	F	Film diffusion
Dried water hyacinth roots	Cu(II)	Low et al.[68] (1994)	L, 20.90	Nil
Dye-treated oil palm fiber	Cu(II)	Low et al.[69] (1993)	L, 15.87	Nil
Feldspar	As(V)	Singh et al.[53,54] (1988, 1996)	20°C, L, 0.21	Film & pore diffusions
		Singh et al.[53,54] (1988, 1996)	30°C, L, 0.18	Film & pore diffusions
		Singh et al.[53,54] (1988, 1996)	40°C, L, 0.16	Film & pore diffusions
Haematite	As(V)	Singh et al.[53,54] (1988, 1996)	20°C, L, 0.22	Film & pore diffusions
		Singh et al.[53,54] (1988, 1996)	30°C, L, 0.20	Film & pore diffusions
		Singh et al.[53,54] (1988, 1996)	40°C, L, 0.19	Film & pore diffusions

(*continued*)

Table 2. Continued.

Isotherm: L = Langmuir & F = Freundlich

Material	Metal	Reference	Isotherm Type X_m (mg/g)	Kinetics/Diffusion
Hematite	Cr(II)	Singh et al.[59] (1993)	20°C, L, 2.70	Boundary layer (intraparticle) diffusion
		Singh et al.[59] (1993)	30°C, L, 2.86	
		Singh et al.[59] (1993)	40°C, L, 3.13 (all in (umol/g))	
Hydrous ferric oxide	Cd(II)	Dzombak & Morel[22] (1986)	L & F	2nd order
Kaolinitic	Pb(II)	Orumwense[65] (1996)	30°C, L, 4.76	Boundary layer (intraparticle) diffusion
		Orumwense[65] (1996)	40°C, L, 5.41	
		Orumwense[65] (1996)	50°C, L, 6.46	
Leaf mould	Cr(V)		pH L F	
		Sharmar & Forster[20,21] (1994, 1996)	1.5, 27.6, 0.81	2nd order
		Sharmar & Forster[20,21] (1994, 1996)	2.0, 43.1, 1.56	2nd order
		Sharmar & Forster[20,21] (1994, 1996)	2.5, 23.4, 3.80	2nd order
		Sharmar & Forster[20,21] (1994, 1996)	3.0, 8.9, 1.81	2nd order
		Sharmar & Forster[20,21] (1994, 1996)	4.0, 7.1, 0.98	2nd order
		Sharmar & Forster[20,21] (1994, 1996)	6.0, 3.9, 1.26	2nd order
		Sharmar & Forster[20,21] (1994, 1996)	10.0, 2.5, 0.98	2nd order

Mixed soil	Zn	Taylor et al.[25] (1995)	Nil	Elovich
Modified ground nut husts	Cd(II)	Okieimen et al.[35] (1991)	L, 0.38 (mmolg^{-1})	Particle diffusion
	Pb(II)	Okieimen et al.[35] (1991)	L, 0.19 (mmolg^{-1})	Particle diffusion
Moss	Cu(II)	Lee & Low[70] (1989)	L, 27.10	Nil
Oil-palm fibre	Cu(II)	Low et al.[69] (1993)	L, 1.98	Nil
Peat	Al(III)	Allen et al.[33] (1992)	Nil	External film diffusion
	Cu(II)	Allen et al.[33] (1992)	Nil	External film diffusion
	Cd(II)	Allen et al.[33] (1992)	Nil	External film diffusion
	Pb(II)	Allen et al.[33] (1992)	Nil	External film diffusion
	Zn(II)	Allen et al.[33] (1992)	Nil	External film diffusion
Peat (horticultural)	Cu	Viragraghavan & Dronamraju[45] (1993)	5°C, L,7.68, F,8.25	Intraparticle diffusion
		Viragraghavan & Dronamraju[45] (1993)	10°C, L,7.83, F,7.56	Intraparticle diffusion
		Viragraghavan & Dronamraju[45] (1993)	15°C, L,6.93, F,5.75	Intraparticle diffusion
		Viragraghavan & Dronamraju[45] (1993)	21°C, L,6.91, F,6.46	Intraparticle diffusion
	Ni	Viragraghavan & Dronamraju[45] (1993)	5°C, L,4.69, F,4.45	Intraparticle diffusion
		Viragraghavan & Dronamraju[45] (1993)	10°C, L,6.64, F,8.94	Intraparticle diffusion
		Viragraghavan & Dronamraju[45] (1993)	15°C, L,9.74, F,7.83	Intraparticle diffusion
		Viragraghavan & Dronamraju[45] (1993)	21°C, L,7.03, F,6.82	Intraparticle diffusion

(*continued*)

Table 2. Continued.

Isotherm: L = Langmuir & F = Freundlich

Material	Metal	Reference	Isotherm Type X_m (mg/g)	Kinetics/Diffusion
	Zn	Viragraghavan & Dronamraju[45] (1993)	5°C, L,13.3, F,13.4	Intraparticle diffusion
		Viragraghavan & Dronamraju[45] (1993)	10°C, L,10.6, F,10.3	Intraparticle diffusion
		Viragraghavan & Dronamraju[45] (1993)	15°C, L,8.40, F,6.49	Intraparticle diffusion
		Viragraghavan & Dronamraju[45] (1993)	21°C, L,7.27, F,6.03	Intraparticle diffusion
Sphagnum moss	Pb(II)	Ho & McKay[89] (1999)	Nil	Pseudo 2nd order
Sphagnum moss peat	Cr(VI)		pH L F	
		Sharma & Forster[17] (1993)	1.5, 119.0, 0.41	2nd order
		Sharma & Forster[17] (1993)	2.0, 65.8, 1.49	2nd order
		Sharma & Forster[17] (1993)	2.5, 36.4, 4.18	2nd order
		Sharma & Forster[17] (1993)	3.0, 26.5, 3.89	2nd order
		Sharma & Forster[17] (1993)	4.0, 21.7, 1.35	2nd order
		Sharma & Forster[17] (1993)	6.0, 15.3, 1.05	2nd order
		Sharma & Forster[17] (1993)	10.0, 6.5, 1.03	2nd order

Sphagnum moss peat	Cu(II)		pH L F	
		Ho et al.[18](1994)	2.0, 3.85, 0.42	2nd order
		Ho et al.[18](1994)	3.0, 12.4 2.74	2nd order
		Ho et al.[18](1994)	4.0, 15.4, 4.34	2nd order
		Ho et al.[18](1994)	4.5, 15.8, 4.41	2nd order
		Ho et al.[18](1994)	5.0, 16.4, 4.50	2nd order
Unicellular yeast–Scaaharomyces cerevisiae	Cu(II)	Huang et al.[55](1990)	L, 2.93 & F	Film & pore diffusions
Waste Fe(III)/Cr(II)	Cd(II)		T(C), (L & F)	Intraparticle diffusion
		Namasivayam & Ranganathan[60] (1995)	20, L, 39.00	Intraparticle diffusion
		Namasivayam & Ranganathan[60] (1995)	30, L, 40.49	Intraparticle diffusion
		Namasivayam & Ranganathan[60] (1995)	40, L, 47.17	Intraparticle diffusion
Water hyacinth roots	Cr(III)	Low & Lee[64] (1996)	L, 9.48 at 25°C	Intraparticle diffusion
Waste tea, Turkish coffee, exhausted coffee, nut shell and walnut shell	Al(III)	Orhan & Büyükgüngör[16] (1993)	Nil	1st order
	Cd(II)	Orhan & Büyükgüngör[16] (1993)	Nil	1st order
	Cr(V)	Orhan & Büyükgüngör[16] (1993)	Nil	1st order

Table 3. Sorption of Dyes on Biosorbents.

Isotherm: L = Langmuir & F = Freundlich

Material	Dye	Reference	Isotherm Type X_m (mg/g)	Kinetics/Diffusion
Activated carbon	Basic Red 22	McKay et al.[71] (1987)	L, 708	Nil
	Basic Yellow 21	McKay et al.[71] (1987)	L, 628	Nil
	Basic Blue 69	McKay et al.[71] (1987)	L, 871	Nil
Activated carbon	Napthol Green B	Juang & Swei[63] (1996)	Nil	Boundary layer (intraparticle) diffusion
	Rhodamine B	Juang & Swei[63] (1996)	Nil	
Activated carbon	Basic dye	McKay[72] (1983)	Nil	Pore diffusion
Activated carbon (Filrtasorb 400)	Basic Blue 69	McKay & Al-Duri[73,74] (1988,1988)	F, L=656	Pore diffusion & pore models
	Basic Yellow 21	McKay & Al-Duri[73,74] (1988,1988)	F, L=241	Pore diffusion & pore models
	Basic Red 22	McKay & Al-Duri[73,74] (1988,1988)	F, L=245	Pore diffusion & pore models
Bagasse pith	Acid Blue 25	McKay et al.[75] (1997)	L, 21.7	Nil
	Acid Red 114	McKay et al.[75] (1997)	L, 22.9	Nil
	Basic Blue 69	McKay et al.[75] (1997)	L, 15.5	Nil
	Basic Red 22	McKay et al.[75] (1997)	L, 77.6	Nil
Banana pith	Acid Violet	Namasivayam & Kanchana[13] (1992)	L, 13.1	Nil
Bagasse pith	Dye	El-Geundi[104](1986)	Nil	Intraparticle diffusion

Bentonite	Safranine (BR)	McKay et al.[111](1984)	L, 120	Nil
	Congo Red (DirR)	McKay et al.[111](1984)	L, 50	Nil
	Foron Brill (DispR)	McKay et al.[111](1984)	L, 26	Nil
	Methylene Blue (BB)	McKay et al.[111](1984)	L, 150	Nil
	Sandolan Blue (AB)	McKay et al.[111](1984)	L, 20	Nil
	Foron Blue (DispB)	McKay et al.[111](1984)	L, 40	Nil
Biogas residual slurry	Direct Red 12B	Namasivayam & Yamuna[47] (1995)	L, 12.3	Boundary layer diffusion
Biogas residual slurry	Acid Brilliant Blue	Yamuna et al.[46] (1993)	L, 13.7	Nil
Biogas waste slurry	Congo Red	Namasivayam & Yamuna[41] (1992)	Nil	Boundary layer diffusion
Biogas waste slurry	Congo Red	Namasivayam & Kanchana[76] (1993)	L, 4.05	Nil
Biogas waste slurry	Acid Brilliant Blue	Yamuna & Namasivayam[46] (1993)	L, 0.04 at pH 2.56	Intraparticle diffusion
Biogas waste slurry	Rhodamine–B	Namasivayam & Yamuna[42] (1992)	F	Intraparticle diffusion
Carbon	Deorlene Yellow	McKay[77] (1982)	L, 200	Nil
	Disperse Blue 7	McKay[77] (1982)	L, 25	Nil
	Victoria Blue	McKay[77] (1982)	L, 5.5	Nil
Carbonized spent bleaching earth	Basic Blue 3	Low et al.[64] (1996)	L, 120.6	Nil
	Methylene Blue	Low et al.[64] (1996)	L, 94.5	Nil
Chitin	Acid Blue 25	McKay et al.[78] (1983)	L, 190	External mass transfer
	Acid Blue 158	McKay et al.[78] (1983)	L, 200	External mass transfer
	Mordant Yellow 5	McKay et al.[78] (1983)	L, 50	External mass transfer
	Direct Red 84	McKay et al.[78] (1983)	L, 40	External mass transfer

(*continued*)

Table 3. Continued.

Isotherm: L = Langmuir & F = Freundlich

Material	Dye	Reference	Isotherm Type X_m (mg/g)	Kinetics/Diffusion
Fly ash & coal	Omega Chrome Red ME	Gupta et al.[49] (1990)	30°C, 0.765	Nil
		Gupta et al.[49] (1990)	40°C, 0.783	Nil
		Gupta et al.[49] (1990)	50°C, 0.428 (L type for all)	Nil
Fomito psis carnea	Orlamar Red BG (ORBG)	Mittal & Gupta[10] (1996)	F, 503.1	1st order
	Orlamar Blue G (OBG)	Mittal & Gupta[10] (1996)	F, 545.2	1st order
	Orlamar Red GTL (ORGTL)	Mittal & Gupta[10] (1996)	F, 643.9	1st order
Fuller's earth	Acid Blue 25	McKay et al.[79] (1985)	L, 220	Nil
	Basic Blue 69	McKay et al.[79] (1985)	L, 1200	Nil
Handwood sawdust	Telon blue (Acid Blue 25)	Asfour et al.[58] (1985)	Nil	Boundary layer diffusion
Lignite	Basic Red 22	Allen et al.[80] (1988)	L, 235	Nil
	Basic Yellow 21	Allen et al.[80] (1988)	L, 390	Nil
Low cost agricultural by-product	Dye	Nawar & Doma[93] (1989)	Nil	Intraparticle diffusion
Peat	Acid Blue 25	Poots et al.[37] (1976)	L, 13.0	Nil
Peat	Basic Blue 3	Allen et al.[81] (1988)	L, 390	Nil
	Basic Red 22	Allen et al.[81] (1988)	L, 240	Nil
	Basic Yellow 21	Allen et al.[81] (1988)	L, 300	Nil
Red mud	Congo Red	Namasivayam et al.[12] (1997)	L, 4.05	Nil

Silica	Acid Blue 25	McKay & Alexander[82] (1978)	<5.0	Nil
	Basic Blue 69	McKay et al.[83] (1981)	L, 25.0	Nil
Sulfonated coal	Basic Blue 9	Atul et al.[84] (1996)	L, 113.3	Nil
	Basic Violet 10	Atul et al.[84] (1996)	L, 66.7	Nil
Sphagnum peat moss (Portadown)	Basic 69	McKay & Allen[30] (1980)	L	Diffusion
	Telon blue	McKay et al.[31] (1981)	L	Diffusion
Sphagnum peat moss	Telon blue (Acid Blue 25)	Poots et al.[37] (1976a)	L & F	Boundary layer diffusion
Waste banana pith	Acid Violet Color	Namasivayam & Kanchana[13] (1992)	L, 13.10	1st order
			Nil	Intraparticle diffusion
Waste banana pith	Congo Red	Namasivayam et al.[11] (1996)	L, 20.29	Nil
Water hyacinth	Methylene Blue	Low et al.[9] (1995)	L, 128.9	1st order & intraparticle diffusion
	Victoria Blue	Low et al.[9] (1995)	L, 145.4	
Waste orange peel	Congo Red	Deo & Ali[85] (1993)	L, 22.44	Nil
Waste orange peel	Congo Red	Namasivayam et al.[11] (1996)	L, 22.44 & F	1st order
	Procin Orange	Namasivayam et al.[11] (1996)	L, 1.33 & F	1st order
	Rhodamine B	Namasivayam et al.[11] (1996)	L, 3.23 & F	1st order
Waste red mud	Congo Red	Namasivayam & Arasi[12] (1997)	L, 4.05	1st order
Wood	Astrazone	McKay & Poots[86] (1980)	L, 98.5	Intraparticle diffusion
	Telon	McKay & Poots[86] (1980)	L, 83	Intraparticle diffusion
Wood	Acid Blue 25	Poots et al.[37] (1976b)	L, 8.3	Intraparticle diffusion
Wood fiber	Napththalene Orange G	Medley & Andrews[66] (1959)	Nil	Boundary layer (intra-particle) diffusion

Table 4. Sorption of Organic Substances on Biosorbents

Isotherm: L = Langmuir & F = Freundlich

Material	Organic	Reference	Isotherm Type X_m (mg/g)	Kinetics/Diffusion
Activated carbon fibers	Lysozyme	Juang et al.[62] (1996)	Nil	Boundary layer (intraparticle) diffusion
	β-lactoglobulin	Juang et al.[62] (1996)	Nil	Boundary layer (intraparticle) diffusion
	Hamoglobin	Juang et al.[62] (1996)	Nil	Boundary layer (intraparticle) diffusion
	Phenol	Juang et al.[62] (1996)	Nil	Boundary layer (intraparticle) diffusion
Algae	Lauryl benzyl sulphonate	Fernadez et al.[91] (1995)	F	Intraparticle diffusion control
Glycol	Oxalic acid	Tien & Thodos[101] (1960)	F	Film pore diffusion
Activated carbon	Organic	Fritz & Schlunder[107] (1981)	Nil	Solid diffusion mass transfer
Activated carbon	Phenol	Moon & Lee[108] (1983)	Nil	Solid diffusion mass transfer
Activated carbon	Gases hydrocarbon	Costa et al.[120] (1985)	Nil	Solid diffusion mass transfer

Activated carbon	Phenol	McKay[87] (1988)	L, 320–380	External & internal mass transfer
	p-chlorophenol	McKay[87] (1988)	L, 400–460	External & internal mass transfer
	Sodium dodecyl sulphate	McKay[87] (1988)	L, 430–470	External & internal mass transfer
Granular activated carbons	Benzenesulfonate	Weber & Morris[36] (1964)	L, 29 at 30°C	Nil
		Weber & Morris[36] (1964)	L, 35 at 9.5°C	Nil
		Weber & Morris[36] (1964)	L, 26 at 48.5°C	Nil
Granular activated carbons	Para-toluenesulfonate	Weber & Morris[36] (1964)	L, 43	Nil
	2-hexyl-toluenesulfonate	Weber & Morris[36] (1964)	L, 83	Nil
	2-octyl-toluenesulfonate	Weber & Morris[36] (1964)	L, 101	Nil
	2-decyl-toluenesulfonate	Weber & Morris[36] (1964)	L, 119	Nil
	2-dodecyl-toluenesulfonate	Weber & Morris[36] (1964)	L, 139	Nil
Granular activated carbons	3-dodecyl-toluenesulfonate	Weber & Morris[36] (1964)	L, 139	Nil
	6-dodecyl-toluenesulfonate	Weber & Morris[36] (1964)	L, 139	Nil
	2-tetradecyl-toluenesulfonate	Weber & Morris[36] (1964)	L, 164	Nil

(*continued*)

Table 4. Continued

Isotherm: L = Langmuir & F = Freundlich

Material	Organic	Reference	Isotherm Type X_m (mg/g)	Kinetics/Diffusion
	Ortho-nitrochlorobenzene	Weber & Morris[36] (1964)	L, 220	Nil
	Para-nitrochlorobenzene	Weber & Morris[36] (1964)	L, 240	Nil
	Phenol	Weber & Morris[36] (1964)	L, 103 (all at 30°C)	Nil
Fly ash	Phenol	Singh & Rawat[51] (1994)	Nil	Intrapartice/Film diffusion
	o-Cresol	Singh & Rawat[51] (1994)	Nil	Intrapartice/Film diffusion
	m-Cresol	Singh & Rawat[51] (1994)	Nil	Intrapartice/Film diffusion
	p-Cresol	Singh & Rawat[51] (1994)	Nil	Intrapartice/Film diffusion
	o-Nitrophenol	Singh & Rawat[51] (1994)	Nil	Intrapartice/Film diffusion
	m-Nitrophenol	Singh & Rawat[51] (1994)	Nil	Intrapartice/Film diffusion
	P-Nitrophenol	Singh & Rawat[51] (1994)	Nil	Intrapartice/Film diffusion

Impregnated fly ash	Phenol	Singh & Rawat[51] (1994)	Nil	Intrapartice/Film diffusion
	o-Cresol	Singh & Rawat[51] (1994)	Nil	Intrapartice/Film diffusion
	m-Cresol	Singh & Rawat[51] (1994)	Nil	Intrapartice/Film diffusion
	p-Cresol	Singh & Rawat[51] (1994)	Nil	Intrapartice/Film diffusion
	o-Nitrophenol	Singh & Rawat[51] (1994)	Nil	Intrapartice/Film diffusion
	m-Nitrophenol	Singh & Rawat[51] (1994)	Nil	Intrapartice/Film diffusion
	P-Nitrophenol	Singh & Rawat[51] (1994)	Nil	Intrapartice/Film diffusion
Silica	Lysozyme	Sarkar & Chattoraj[67] (1993)	Nil	Film diffusion
	β-lactoglobulin	Sarkar & Chattoraj[67] (1993)	Nil	Film diffusion
	Hamoglobin	Sarkar & Chattoraj[67] (1993)	Nil	Film diffusion

cates and Fullers earth have been included for comparison purposes. To predict the time to achieve the equilibrium state of sorption and to establish the reaction mechanism, a knowledge of the rate equations explaining the reaction system is required. A number of equations have been used to describe kinetic reactions in biosorbents[2–6]. These include first-order, second-order and two-constant rate equations.

2. SORPTION REACTION MODELS

2.1. First-Order Forward Reaction

The Lagergren rate equation[2] may have been the first rate equation for the sorption in liquid/solid systems based on solid capacity. The Lagergren rate equation (equation 1) is the most widely used rate equation for sorption of a solute from a liquid solution.

$$\frac{dq_t}{dt} = k_1(q_m - q_t) \tag{1}$$

Integrating this for the initial and end conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_{t,}$ equation (1) may be rearranged for linearised data plotting as shown by equation (2):

$$\log(q_m - q_t) = \log(q_m) - \frac{k_1}{2.303}\, t \tag{2}$$

When equation (2) is applied and the parameter q_m is evaluated, using experimental data, it generally differs from a true first-order equation in two ways[1]:

- The parameter q_m does not represent the number of available sites.
- The parameter $\log(q_m)$ is an adjustable parameter and it is not often equal to the intercept of a plot of $\log(q_m - q_t)$ against t, whereas in a true first order system, $\log(q_m)$ should be equal to the intercept of a plot of $\log(q_m - q_t)$ against t. In fact, equation (2) is only an approximate solution to the first order rate mechanism.

In order to fit equation (2) to experimental data, the equilibrium sorption capacity, q_m, should be known. In many cases q_m is unknown, as chemisorption tends to become unmeasurably slow while the amount sorbed is still significantly smaller than the equilibrium amount[7]. In most cases from the literature, the pseudo-first order equation of Lagergren does not fit well over the range of contact times under investigation. Furthermore, one has to find some means of extrapolating the experimental data to $t = \infty$, or treat q_m as an adjustable parameter to be determined by trial and error. For this reason, it is necessary to use a trial and error solution method to obtain the equilibrium sorption capacity, q_m.

In 1947, Boyd *et al*[3] developed a rate equation to explain rates of ion-exchange sorption of ions from aqueous solutions by organic zeolites. In cases of diffusion though a boundary liquid film and sorption kinetics as a chemical phenomenon, the authors concluded that a mass action rate equation for sorption kinetics as the chemical phenomenon and a diffusion equation for diffusion though a boundary liquid film are the same as the first order rate equation of Lagergren. They also concluded that if film diffusion is rate controlling, the constant of the rate equation will vary inversely with the particle size and the film thickness; if the exchange is chemically rate controlled, the rate constant will be independent of particle diameter and flow rate and it will depend only on the concentrations of the ions in solution and the temperature.

Numerous studies report first-order Lagergren kinetics for the sorption of metals using biosorbents, such as the sorption of chromium(III) by natural moss and chromium(VI) by copper-coated moss[8], the sorption of Methylene Blue on water hyacinth roots[9], the sorption of Orlamar Red BG (ORBG) by *Fomitopsis carnea*[10], the sorption of Congo Red, Procin Orange and Rhodamine-B by waste orange peel[11], the sorption of Congo Red on Red mud[12] and the sorption of Acid Violet onto waste banana pith[13].

Rao *et al*[14] reported a first order reaction kinetic model, based on solution concentration for the sorption of chromium(VI) onto prepared activated coconut shell carbons.

2.2. First-Order Reversible Reaction

A reversible first order rate expression based on solution concentration (Bhattacharya and Venkobachar, 1984) is given by equation (3):

$$-\ln\left(1 - \frac{X_t}{X_e}\right) = k't \tag{3}$$

Equation (3) can be rearranged to equation (4) which provides a linearised form for plotting as In[1-*u(t)*] versus time, t,

$$\ln[1 - u(t)] = -k't$$
$$\text{where } u(t) = \frac{X_t}{X_e} \tag{4}$$

This model has been applied for the sorption of chromium(VI) onto the activated carbon prepared using carbonised groundnut husk[15], for the sorption of chromium(VI), aluminium(III) and cadmium(II) onto the waste tea, Turkish coffee, exhausted coffee, nut shell and walnut shell by Orhan and Büyükgüngör[16].

2.3. Second-Order Reaction

One possible mechanism to describe metal removal by peat is:

$$P + M \overset{K^1}{\Leftrightarrow} PM,$$
$$\text{with } K' = (PM)/(P)(M) = k_f/k_r \tag{5}$$

Based on this equation, Gosset *et al*[5] developed a technique for obtaining the binding kinetic constant k_f. This required the following assumptions:

- the reverse reaction, k_r, is negligible;
- the peat metal anion stoichiometry is constant for all experimental conditions and equal to one metal ion per binding site;
- the overall kinetics are limited by the binding reaction itself and not the diffusion of species.

Gosset *et al*[5] developed an expression to describe these reactions:

$$k_f = \frac{1}{(PM)_{\lim} - (M)_{in}} \cdot \ln\left[\frac{(M)_{in}}{(PM)_{\lim}} \cdot \left(\frac{(PM)_{\lim} - (PM)}{(M)_{in} - (PM)}\right)\right] \tag{6}$$

This model has been applied for the sorption of chromium(VI), copper(II) and nickel(II) onto sphagnum moss peat[17–19] and for the sorption of chromium(VI) onto leaf mould [20,21].

Dzombak and Morel[22] developed a reversible second-order rate expression for the surface complexation reaction shown in equation (7):

$$\frac{d(XC)}{dt} = k_f(X)(C) - k_b(XC) \tag{7}$$

After including the appropriate mole balance equations for X_t and C_t and algebraic manipulation, equation (7) can be rewritten as:

$$\frac{d(XC)}{dt} = k_f(XC)^2 - (XC)[k_f(X_t) + k_f(C_t) + k_b] + k_f(X_tC_t) \tag{8}$$

The authors used a fourth-order Runge-Kutta formula to solve equation (8) and determined values of k_f and k_r by trial and error that enabled data fitting of the kinetics of Cd^{2+} sorption on hydrous ferric oxide.

2.4. Langmuir-Hinshelwood Kinetics

The Langmuir-Hinshelwood kinetic expression has been applied to describe the sorption kinetics of metal ions onto humic acids[23]. The Langmuir-Hinshelwood equation is as follows:

$$-\frac{dC_t}{dt} = \frac{k_1 C_t}{1 + k_0 C_t} \tag{9}$$

Rearranging equation (9) gives:

$$\frac{\ln\left(\frac{C_0}{C_t}\right)}{C_0 - C_t} + k_0 = \frac{k_1 t}{C_0 - C_A t} \tag{10}$$

The standard equations for first-order and second-order reactions have been applied to describe the sorption of phosphamidon on an antimony(V) phosphate cation exchanger as a multistep process[24]. The rate equations for the two reactions are shown:

$$\log C = \log C_0 - \left(\frac{k_a}{2.303}\right) t \tag{11}$$

$$\frac{1}{C} - \frac{1}{C_0} = k_a t \tag{12}$$

2.5. Various Order Reaction Models

Taylor *et al*[25] have analysed five equations for the sorption of zinc. The equations used are shown in Table 1.

The authors concluded that zinc sorption kinetics by soils were best described by the Elovich[25] equation.

3. SORPTION DIFFUSION MODELS

The sorption process can be described by four consecutive steps:

1. transport in the bulk of the solution;
2. diffusion across the liquid film surrounding the sorbent particles;
3. particle diffusion in the liquid contained in the pores and in the sorbate along the pore walls;
4. sorption and desorption within the particle and on the external surface.

Any of the four previous steps may be the rate controlling factor or any combination of the steps. Transport in the solution is sometimes rate determining in large scale field processes[1]. Many experimental sorption systems are designed to eliminate the effect of transport in the solution by rapid mixing so that it does not become rate limiting[26].

3.1 Film Diffusion Control

Boyd *et al*[3] represented a film diffusion model as follows:

$$\log(q_m - q_t) = \log(q_m) - \left(\frac{R}{2.303}\right) t \tag{19}$$

Equation (19) is the same form as equation (2) indicating that differentiating between film diffusion control and pseudo-first order reaction control will be difficult. However, carrying out a series of sorption studies at different agitation speeds usually demonstrates that film diffusion has a much stronger dependence on agitation. In agitated sorption studies, film diffusion is usually only rate controlling for the first few minutes.

3.2 Particle Diffusion Control

Boyd *et al*[3] represented a particle diffusion model as follows:

$$\frac{q_t}{q_m} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D_i \pi^2 n^2 t}{r^2}\right) \tag{20}$$

The lines representing the above expression converge asymptotically over time since the higher terms of the summation become small and are negligible. Therefore, equation (20) can be rewritten in the following simplified form:

$$1 - \frac{q_t}{q_m} = \frac{6}{\pi^2} \exp\left(-\frac{D_i \pi^2}{r^2}\right) t \tag{21}$$

and

$$1 - \frac{q_t}{q_m} = \frac{6}{\pi^2} \exp(-k')t \tag{22}$$

where

$$k' \text{ is the overall rate constant as } k' = \frac{D_i \pi^2}{r^2} \tag{23}$$

Skopp and Warrick[27] developed a similar equation based on a theory describing heat flow as presented by Carslaw and Jaeger[28]. Enfield *et al*[29] reported an approach similar to the diffusion-limited model of Skopp and Warrick[27] except they assumed the soil particles were spherical:

$$S_{avg} = F(C) - \frac{6F(C)}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{k_d \pi^2 n^2 t}{r^2}\right) \tag{24}$$

McKay and Allen[30] presented an equation based on external film diffusion which can be used to determine external mass transfer coefficients. This equation is one of the most widely used equations for the sorption of a solute from a liquid solution. It may be represented:

$$\ln\left(\frac{C_t}{C_0} - \frac{1}{1 + m_s K}\right) = \ln\left(\frac{m_s K}{1 + m_s K}\right) - \frac{1 + m_s K}{m_s K}\beta_l S_s t, \tag{25}$$

K is the Langmuir isotherm equilibrium constant for the system. The surface area for external mass transfer to the particles can be obtained from m_s which is defined as the concentration of the adsorbent in the liquid phase:

$$m_s = \frac{M}{V} \tag{26}$$

The specific surface, S_s, of a particle for external mass transfer is:

$$S_s = \frac{\delta m_s}{d_p \rho_p (1 - \varepsilon_p)} \tag{27}$$

The external mass transfer coefficient can now be obtained from equation (25).

Several studies report mass transfer coefficients for the sorption of dyes using biosorbents, such as the sorption of Telon Blue and Basic Blue 69 from aqueous solutions by peat[30,31], the sorption of Acid Blue 25, Acid Blue 158, Mordant Yellow 5 and Direct Red 84 by chitin[32], the sorption of Basic Blue 69 and Acid Blue 25 onto wood[31]. The same equation was used for the sorption of metals, such as the sorption of lead(II), cadmium(II), copper(II), zinc(II) and aluminium(III) onto peat[33].

Chanda *et al*[34] developed a simple equation for particle diffusion controlled sorption processes as follows:

$$\ln\left(1 - \frac{X_t}{X_e}\right) = -k_p t \tag{28}$$

This equation has been applied for the sorption of cadmium(II) and lead(II) by modified groundnut husks from aqueous solutions[35].

4. PORE DIFFUSION CONTROL

According to Weber and Morris[36] if the rate limiting step is intraparticle diffusion, a plot of solute sorbed against square root of contact time should yield a straight line passing through the origin[37]. The most widely applied intraparticle diffusion equation for biosorption system is given by Weber and Morris[38]:

$$q_t = k_d t^{1/2} \tag{29}$$

Numerous researchers have found that this equation described the kinetics of sorption of dyes in biosorbents. In a batch reactor with rapid stirring, the intraparticle diffusion is often the rate controlling step in many sorption processes such as the sorption of dye namely AB 25, AB 158, MY 5 and DR 84 onto chitin[39]; the sorption of cadmium(II) by beech leaves[40]; the sorption of Congo Red and Rhodamine-B by biogas waste slurry [41,42]; the sorption of copper ions by chitosan[43]; the sorption of Methylene Blue by water hyacinth roots[9]; the sorption of Orlamar Red BG, Orlamar Blue G and Orlamer Red GTL by dead macro fungus *Fomitopsis carnea*[10]. However numerous studies report intraparticle diffusion is not the only rate controlling step for the sorption of dyes using biosorbents such as the sorption of Acid Blue onto wood and peat[37,44]; the sorption of color from synthetic wastewaters by waste banana pith[13]; the removal of copper, nickel and zinc by peat[45] and the sorption of Acid Brilliant Blue and Direct red 12 B by biogas waste slurry[46,47].

The pore diffusion coefficients for intraparticle transport can be described using the following equation[4]:

$$\overline{D} = \frac{0.03}{t_{1/2}} r_0^2 \tag{30}$$

This equation has been applied to describe the kinetics of several sorption systems[4,48–54]. Equation (30) has been used successfully to describe the experimental sorption results showing that intraparticle diffusion is the rate limiting step in sorption of nickel (II) from aqueous solution by China clay by Sharma *et al*[50]. However, it does not always fully describe the kinetics of sorption systems in which intraparticle diffusion is a rate controlling step. Bhattacharya and Venkobachar[4] reported that the rate limiting stage of the sorption of cadmium(II) by crushed coconut shell from solution is partly film diffusion. Singh *et al*[53,54] concluded that both film and pore diffusion are involved in the removal of arsenic(V) from aqueous by haematite and feldspar.

The same result on the mechanism of intraparticle diffusion was also reported for the sorption of metal ions using biosorbents. Intraparticle diffusion is often the rate-limiting step in many sorption processes such as the sorption of copper(II) onto treated unicellular yeast, *Saccharomyces cerevisiae*[55], the sorption of mercury(II) onto activated carbon prepared from bicarbonate-treated peanut hulls[56]. However numerous studies report intraparticle diffusion is not the only rate controlling step for the sorption of metal ions using biosorbents. Several authors[10,42,43,46,49,57–65,54] report that plots of sorption capacity against the square root of time are linear while the initial curved portions of the graphs may be attributed to boundary layer diffusion effects[66]. This linear portion is due to intraparticle diffusion effects (Weber and Morris, 1963). Furthermore, a number of workers have found the kinetics of sorption are characterized by two steps such as the sorption of proteins, lysozyme, β-lactoglobulin and haemoglobin onto silica from water[67]; the sorption of phenol and its derivatives on activated carbon fibers[62]; the sorption of Naphthol Green B and Rhodamine B by activated carbon[63].

5. PSEUDO-SECOND ORDER RATE CONTROL

If the rate of sorption is dependent on a second order equation based on the sorbate uptake, the pseudo-second order chemisorption kinetics may be expressed as:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2, \tag{31}$$

For initial and end conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$; the integrated form of equation (31) becomes:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t, \tag{32}$$

If pseudo-second order kinetics are applicable to the pollutant-biosorbent system then the plot of t/q_t against t of equation (32) should give a linear relationship. The value q_e and k can be determined from the slope and intercept and there is no need to know any parameter beforehand. The pseudo-second order kinetics model has been applied successfully to several biosorption systems [88,89].

6. SORPTION MODEL SELECTION

Due to the large array of models, as shown in this paper, the selection of a sorption model for testing is not an easy or obvious choice. Furthermore, the mathematical model should be consistent with a proposed mechanism for sorption although the identification of a potential mechanism alone is usually not sufficient to define the rate controlling kinetic or diffusion process. The model choices are represented in Figure 1.

Figure 1 shows three main sorption model options, any one or group of models may be responsible for the rate controlling step. An additional complicating factor is that the initial rate controlling process may change throughout the duration of the sorption process, for example, initially external film diffusion, may give way to reaction which after a further time period may become diffusion controlled. Therefore, in order to identify the correct sorption model usually involves selecting and testing several models and system variables over the entire sorption range, from t = zero until sorbent saturation is achieved.

6.1. Step 1–Mechanism

A preliminary appraisal of the sorbent-sorbate system may provide information indicating the sorption mechanism. For instance, are there any chemical

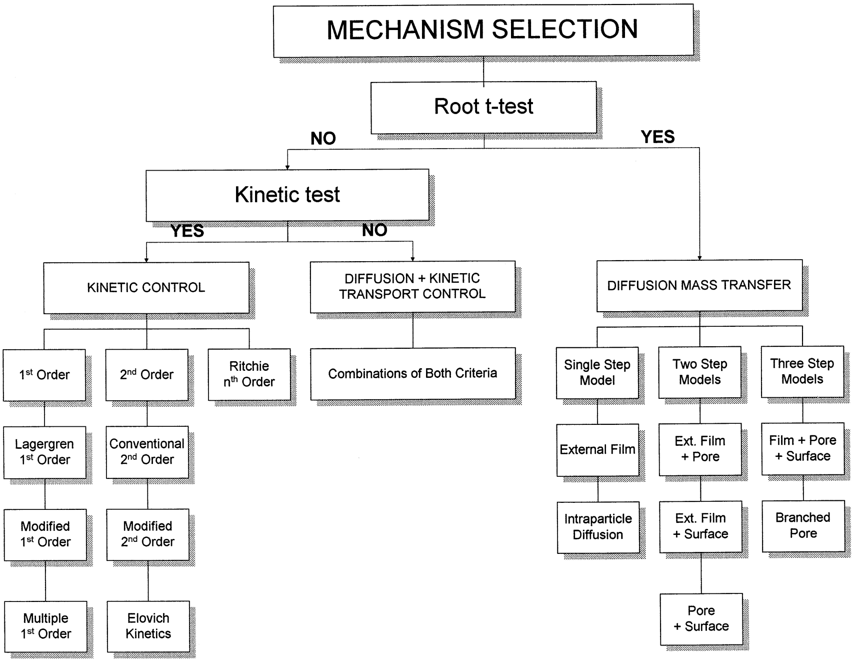

Figure 1. Sorption Model Selection for System Design.

groups on the sorbent which can undergo chemical reaction to form a chemical bond. Acid groups on the sorbent could provide ion exchange sites for metal ions and ionic dyes, amine groups can provide a lone pair of electrons for chelation with metal ions etc. Relatively inert sorbent surfaces may only provide physical sites for diffusional controlled bond formation.

In order to identify the exact mechanism it is necessary to carry out experiments to study several system variables, namely, initial concentration, sorbent particle size, solution temperature, solution pH and agitation and analyse the data for different order kinetic reactions or for pore/solid phase diffusion mechanisms. The correlation coefficients between experimental and theoretical data will provide the 'best fit' model. The suitability of this model still needs to be confirmed by proposing a mechanism appropriate to the sorption model. The difference between kinetic sorption and diffusion sorption can be confirmed by analysing experimental data in a number of ways. Usually more than one system variable is required as several different mathematical model equations can fit a limited number of experimental data points with a high degree of accuracy.

6.2. Step 2–Kinetic versus Diffusion Control

The distinction between these two processes is often difficult to characterise. For example, the removal of a metal ion from an effluent by an ion exchanger is obviously an ion-exchange mechanism, which is often rapid and not rate controlling. Rate control could be the intraparticle diffusion of the metal ions throughout the pores of the ion exchange sorbent. As a very general guideline, from the literature presented in this paper, if equilibrium is achieved within three hours, the process is usually kinetic controlled and above twenty four hours, it is diffusion controlled. Either or both kinetic and sorption processes may be rate controlling in the three to twenty four hour period. Another very general guideline is that changes in pH have a greater effect on the sorption of solutes in reaction controlled sorption processes.

A more appropriate quantitative approach to distinguishing between kinetic and diffusion rate control is to perform the square root of contact time analysis according to equation (29). A plot of the amount of pollutant adsorbed, q_t, against the square root of time, $t^{0.5}$, yields a straight line plot of slope k_d, a diffusional rate parameter. This straight line, passing through the origin, indicates intraparticle diffusion control. This approach has been successful in many cases[36,40,90,10,91]. In cases of adsorbents whose pore size range is extensive including micro-, meso- and macropores up to three linear sections have been obtained [92,93]. Additional confirmation of a diffusion mechanism should be obtained by analysing the effect of the system variables on k_d. For intraparticle diffusion controlling systems: - k_d should vary linearly with reciprocal particle diameter; the product of k_d times sorbent mass should vary linearly with sorbent mass. Furthermore, it is possible to determine the sorption energy by carrying out sorption studies at different temperatures. The rates of reaction sorption increase more rapidly than those of diffusion processes with temperature. When k_d is plotted against reciprocal temperature (Arrhenius plot) for diffusion controlled processes the energy of adsorption is usually less than 25–30 kJ/mol.

$$k_d = A_{\exp}\left(-\frac{E}{RT}\right) \tag{33}$$

Kinetic sorption processes usually have energies greater than 25–30 kJ/mol and diffusion sorption processes, in which no electrons are transferred or shared between the sorbed molecules/ions and the sorbent surface. The theoretical equations for intraparticle diffusion indicate that the concentration dependence of a diffusion-adsorption process will give k_d values that vary with the square root of concentration. If the rate controlling step is surface mass transfer then k_d will vary with the reciprocal of particle diameter. It is advisable to study at least two or three variables prior to concluding which sorption process is rate controlling.

6.3. Step 3–Kinetic versus Combined Mass Transport

In order to distinguish between a reaction kinetic model and a model controlled by coupled reaction and diffusion, it is necessary to carry out a kinetic analysis. Linearisation of data and statistical analysis of data using correlation coefficients enables the "best fit" model to be determined. The conventional kinetic equations are given by (11) to (15) and the more appropriate (for sorption systems) linearised pseudo-order equations are given by (2), (4), (5) and equations (32) and (34) for the Ritchie[94] nth order reactions respectively. The rate equation is:

$$\frac{d\theta}{dt} = k_2'(1 - \theta)^n \tag{34}$$

Integrating gives:

$$\frac{1}{(1 - \theta)^n} = (n - 1)k_2't + 1 \qquad \text{for n} \neq 1 \tag{35}$$

Therefore, the reaction order n can be obtained.

6.4. Step 4–External Film Transport

When the plots in step 2 or step 3 do not pass through the origin, this is indicative of some degree of external film mass transfer or boundary layer control. For most systems reported in the literature, there is some evidence of film resistance in the initial stages of the sorption process. However, the concentration driving force, bulk concentration minus surface liquid concentration, decreases rapidly and so its influence is usually limited to the early stages of adsorption. Equation (19) describes film transport and is analogous to the pseudo-first order equation (2), however, a series of agitation and particle size variation experiments will usually distinguish which mechanism is controlling.

External film diffusion can be identified on a theoretical basis by plotting the mathematical function for kinetic sorption (first order, second order etc.) against time or for diffusion sorption (q_t) versus square root of time. If the plots do not go through the origin it is indicative of external film control and the film mass transfer parameter can be determined from equations (19) or (25). External film diffusion is best identified by carrying out a series of agitated batch contact time experiments at different agitation speeds. Agitation shears the film boundary layer reducing this mass transfer resistance and can be easily seen from plots of solute concentration versus time. As the agitation speed is changed, the rate controlling process may also change from film to reaction or diffusion. Another 'external' phenomenon is a surface enhancement often associated with highly energetic heterogeneous surfaces. This results in a high rapid uptake of solute on the sorbent before the system stabilizes. This effect is seen on similar plots to those used in the identification of external film mass transport, but in this case, varying agitation speed has little influence on the rate of uptake.

6.5. Step 5–Diffusion Model Selection

The main diffusion models are based on pore diffusion, D_p, homogenous solid phase diffusion, D_s, or a combined resistance model [95,96], sometimes incorporating pore size distribution [97,98].

Equations (36) and (37) represent the pore diffusion equation for a diffusion rate N_t:

$$N_t = \frac{D_{eff}\partial}{r^2\partial r}\left(r^2\,\frac{\partial Cr}{\partial r}\right) \tag{36}$$

$$N_t = D_{eff}\left[\frac{\partial^2 C_t}{\partial r^2} + \frac{1\partial C}{r\partial r}\right] \tag{37}$$

It has been found that most compounds, typical of wastewater dissolved components, exhibit adsorption isotherms of the favourable type, i.e., isotherms that tend to approach irreversibility and reflect the Langmuir shape [99,100,36]. Hence extended research work has been done on applying the film-pore diffusion model for predicting the rate of adsorption of pollutants existent in wastewaters. Following many studies on porous particles and their properties[101], most work on pore diffusion has been based on activated carbon systems [102,39,103]. However, studies have extended to biosorbents using bagasse pith[104] and peat[105] and good results were obtained. It was found that a single value of the effective diffusivity D_{eff} succeeded in describing the rate of intraparticle diffusion on a narrow range of experimental conditions. However, in the case of solid diffusion mass transfer control equations (38) and (39) must be solved:

$$\frac{dq}{dt} = \frac{D_s\partial}{r^2\partial r}\left(r^2\,\frac{\partial q_i}{\partial r}\right) \tag{38}$$

$$= D_s\left[\frac{\partial^2 q_i}{\partial r^2} + \frac{2\partial q_i}{r\partial r}\right] \tag{39}$$

where q ($mg\cdot g^{-1}$) is the average solid phase concentration; q_i ($mg\cdot g^{-1}$) is the point solid phase concentration and is a function of the radial position r and time t. D_s ($cm^2\cdot s^{-1}$) is the solid diffusivity and is assumed–for mathematical convenience–to be constant over the process. The average solid concentration q is related to the point solid concentration q_i by:

$$q_t = \frac{3}{R^3}\int_0^R q_i\,(r,t)r^2 dr \tag{40}$$

These equations have been solved in several places in literature using Crank-Nicolson's numerical finite difference method [106,107,108]. Details of this method can be found in literature[109]. Liapis and Rippin[110] adopted orthogonal collocation, another numerical approach. McKay *et al*[111] presented a solution which solves numerically for t and analytically for x, yielding accurate results over a wide range of system conditions.

A linear driving force (LDF) model for approximating the uptake rates by spherical pellets, was first proposed by Glueckauf and Coates[112]. Since the work of Glueckauf and Coates, several investigators have attempted to improve the LDF model with various degrees of success [113–116]. More recent, Yao[117] and Yao and Tien[118] analysed the relationship between the LDF model and the approximate solutions of the intrapellet diffusion equation. These solutions have been presented by Tien[119].

Pore diffusivities are constant and closely linked to the molecular diffusivity of the sorbate, D_L, as shown by equation (41).

$$D_p = \frac{\varepsilon_p D_L}{\tau} \tag{41}$$

It is frequently recognised that the D_p used in the pore diffusion model is essentially an effective diffusivity, D_{eff}, which is better represented as:

$$D_{eff} = D_p + e_s D_s \frac{\partial q}{\partial c} \tag{42}$$

The use of this equation in combined pore-surface diffusion models has been investigated by a number of workers[103,120–124].

Solid diffusivities are known to vary as a function of surface coverage and temperature although they are often assumed constant over limited concentration ranges. Usually statistical correlation fitting of data is used to select between the best model. However, Ruckenstein[125] defined a parameter, α, based on pore size and structure to define the relative importance of macropore and/or micropore diffusion.

In reality, many diffusion controlled processes are a combination of pore and surface diffusion. Masamune and Smith[95,96] represented a two resistance model in equation (43).

$$\varepsilon_p D_p \frac{\partial c_p}{\partial r} + (1 - \varepsilon_p) D_s \frac{\partial q}{\partial r} = k_f (c_b - c_p) \qquad \text{for } r = R \tag{43}$$

with the condition when $\frac{\partial c_p}{\partial r} = 0$ and $r = 0$.

Zogorski *et al*[126] had described adsorption by an initial rapid uptake followed by a slow diffusion period that would take several hours to reach equilibrium. This slow approach to equilibrium had been attributed to the presence of another resistance that has not been accounted for in the previous models. The film-pore and solid diffusion models both assumed structurally homogeneous adsorbent without attempts to relate the adsorption rate to the sorbent's internal structure. However, Beck and Schultz[127] found that diffusion within solid particles is related to the ratio of molecular diameters of the diffusing particles to the diameters of pores. As the ($d_{molecule}/d_{pore}$) ratio becomes larger, multidirectional interactions between pore walls and sorbate molecules become significant and control the diffusion rate. They are therefore responsible for the slow approach to equilibrium.

The branched-pore diffusion model is based on a detailed description of the carbon particle[97]. Activated carbon has particles with a polydisperse structure, i.e., a network of pores of a wide size range interspersed throughout the particle. The branched-pore model approximates this size distribution in two ranges occupying two regions: namely, the macropore region where $d_p \geq$ nm, and the micropore region where $d_p <$ nm. Diffusion through macropores is mainly described by solid diffusion, while in the micropores multidirectional interactions are significant. Hence, they are responsible for micropore diffusion.

The branched pore model equations[97,98] are:

$$f\,\frac{\partial q_M}{\partial t} = \frac{fD_s\partial}{r^2\partial r}\left(r^2\,\frac{\partial q_m}{\partial r}\right) - R_b \tag{44}$$

$$(1-f)\,\frac{\partial q_m}{\partial t} = (1-f)\,\frac{D_e\partial}{r^2\partial r}\left[(D_e)_m r^2\,\frac{\partial q_m}{\partial r}\right] + R_b \tag{45}$$

$$q = fq_M + (1-f)q_m \tag{46}$$

where

f = Volume fraction occupied by the macropore region

q_M and q_m = Adsorbed-phase region in the macropopre and micropore regions, respectively

$(D_e)_M$ and $(D_e)_m$ = Effective intrapellet diffusivities of the two regions

R_b = Rate of transfer of the diffusing species from the macropore to the micropore region (per unit pellet volume)

The selection of the most appropriate diffusion model requires a statistical analysis to assess the degree of correlation between the models.

6.6. Step 6–Sorbent Selection Criteria

Based on available literature it is very difficult to categorise sorbent-sorbate systems as following any specific sorption model. Too little analysis of data has been performed and only a limited number of system variables have been analysed

Table 5. Model Application by Classification of Surface Type.

Sorbate Type	Example	Sorbent Type	Example	Sorption Model
Polar Organic	Phenol Non-Ionic Chlorinated Organics, Dyes	Low Surface Activity	Pith, Straw, Biomass, Wood, Lignite, Cellulosics, Chitosan, Carbon	Diffusion
Ions	Cu, Cd, Ni, Ionic Dyes	Ionic Sites	Ion Exchangers, Peat	Reaction Kinetics
Ions	Cu, Cd, Ni, Ionic Dyes	Lower Surface Activity	Lignite, Pith, Biomass, Carbons, Chitosan	Diffusion + Kinetics
Non-Polar Organics	Hydrocarbons	Low Surface Activity	Pith, Straw, Biomass etc.	Surface Diffusion

by most researchers. From the limited data available some general guidelines are available for agitated batch sorption systems (see Table 5).

Additional attention must be given to agitation, affecting film diffusion, sorbent microporosity, affecting pore and surface diffusion, and solution pH affecting sorption capacity and sorption rates of ionic species.

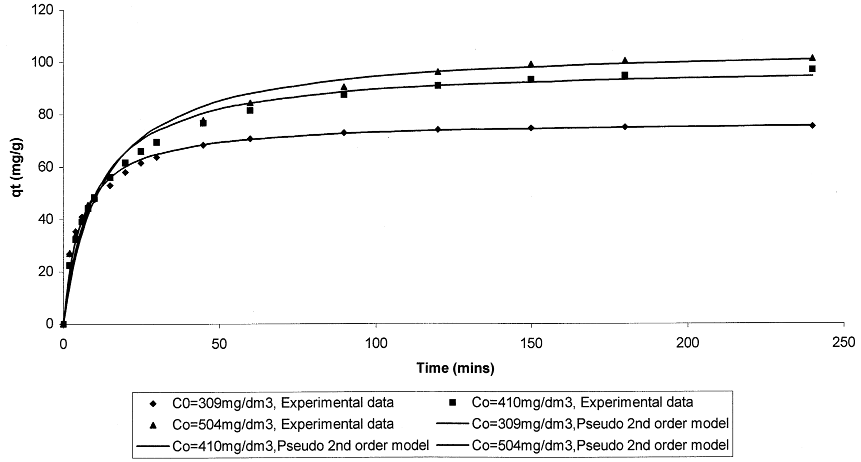

Figure 2. Plot of sorbed amount versus time for lead (II) at various initial concentrations

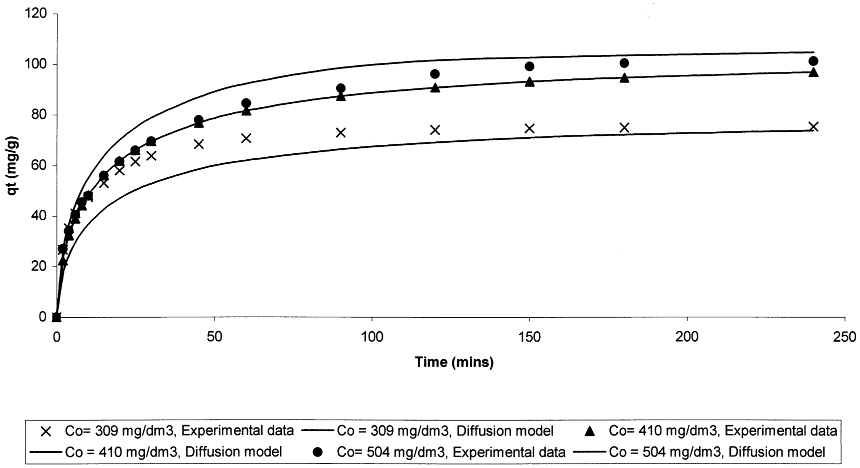

Figure 3. Plot of sorbed amount versus time for lead (II) at various initial concentrations.

7. COMPARISONS OF SORPTION MODELS FOR KINETIC AND DIFFUSION

Some comparisons of model applications to different adsorption systems can be made. Figures 2 and 3 show plots of data for the adsorption of lead ions onto peat. Figure 2 shows the theoretical plots for a pseudo-second order kinetic model[128,129] compared with experimental data. Figure 3 shows the theoretical plots of an intraparticle diffusion model based on $t^{0.5}$ applied to the same experimental data. The sum of the errors squared (SSE) analysed has been applied to the results and are shown in Table 6. The pseudo-second order kinetic model correlates the experimental data the best. The system is the sorption of lead ions mostly

Table 6. Comparison of Sum of Square Errors Squared (SSE) for Sorption Kinetic and Diffusion Models of Lead onto Peat[128,129].

	$SSE = \sum\left[\frac{(q_{t,\exp t} - q_{t,theo})^2}{q_{t,\exp t}^{\;2}}\right]$	
Concentrations (mg/dm^3)	Pseudo 2nd Order	Diffusion
309	0.018125	10.0323
410	0.097431	0.108563
504	0.110381	0.304261

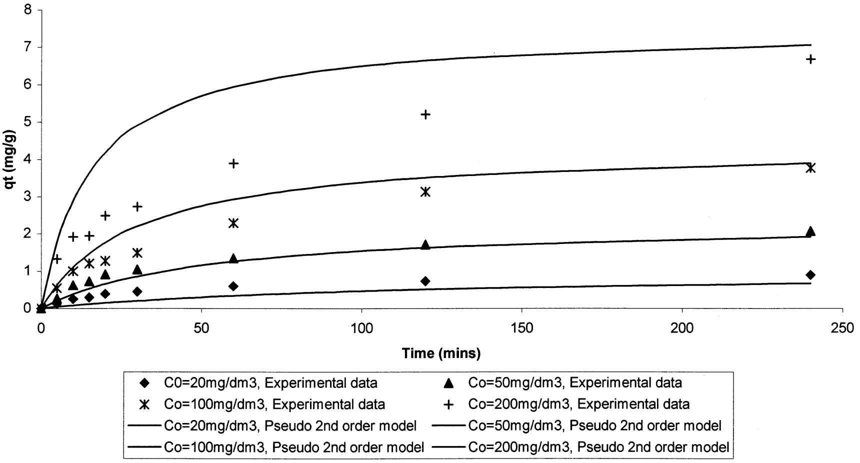

Figure 4. Plot of sorbed amount versus time for Acid Blue 25 at various initial concentrations.

exchanging with hydrogen ions of the humic and fulvic acids in peat typical of an exchange reaction.

Figures 4 and 5 compare the same models, namely the pseudo-second order kinetic reaction [130,131] with the intraparticle diffusion model[130,131] respectively,

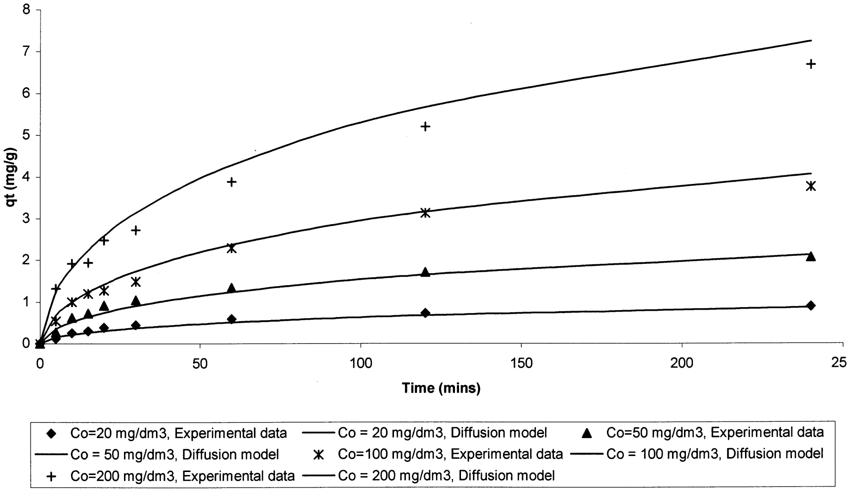

Figure 5. Plot of sorbed amount versus time for acid blue 25 at various initial concentrations.

Table 7. Comparison of Sum of Square Errors Squared (SSE) for Sorption Kinetic and Diffusion Models of Acid Blue 25 onto Wood[130,131].

	$\mathrm{SSE} = \sum \left[\frac{(q_{t,\exp t} - q_{t,theo})^2}{q_{t,\exp t}^2} \right]$	
Concentrations (mg/dm^3)	Pseudo 2nd Order	Diffusion
20	2.339314	0.187388
50	0.413764	0.187034
100	0.549910	0.103603
200	2.613616	0.074538

for the adsorption of Acid Blue 25 dye onto wood. The models are compared on the basis of an SSE analysis shown in Table 7. The diffusion model fits the experimental data significantly better than the kinetic model. The conclusion fits the experimental system in which an organic compound is adsorbing by diffusion onto a relatively chemically inert wood adsorbent.

A third system is compared in Figures 6 and 7 using the second order model and the diffusion model[132], respectively. The SSE analysis is presented in Table 8 and demonstrate that the pseudo-second order kinetic model is a better fit for the adsorption of Basic Blue dye 69 on peat. However, with exception of the lowest concentration ($C_o = 20\text{mg/dm}^3$), for which it is known that a single diffusion mech-

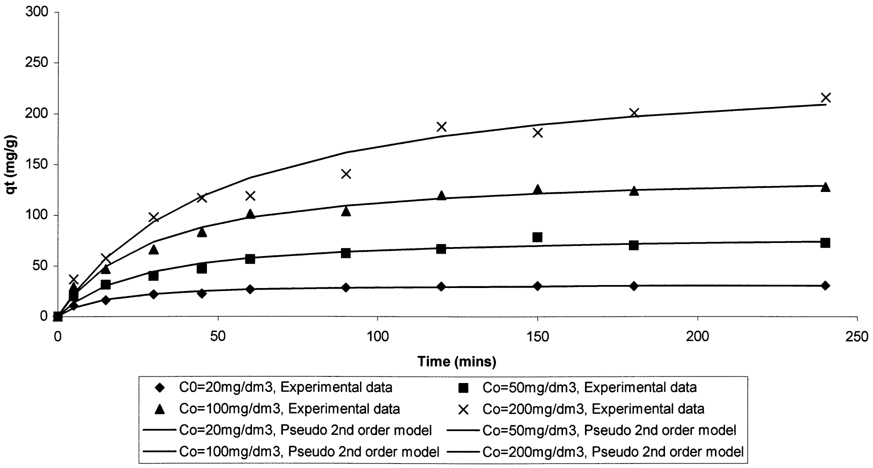

Figure 6. Plot of sorbed amount versus time for Astrazon Blue (BB69) at various initial concentrations.

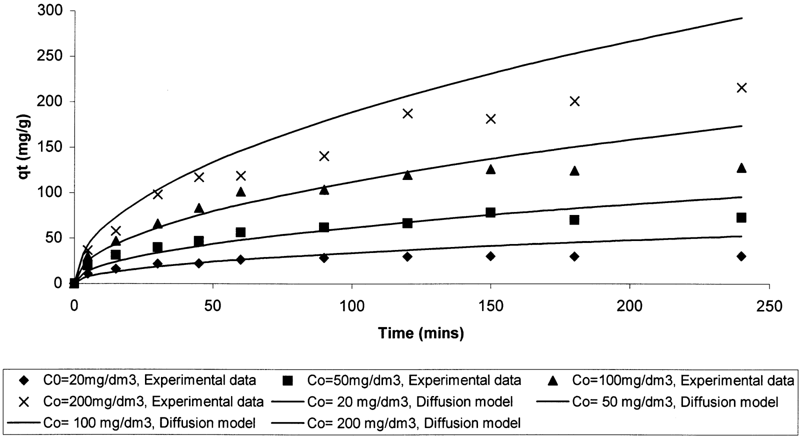

Figure 7. Plot of sorbed amount versus time for Astrazone Blue (BB69) at various initial concentrations.

anism does not work well, the SSE values are much closer than in the other two systems. The kinetic model would be slightly favoured, because basic dyes are known to ionise to a degree in aqueous solutions to from coloured cations; these could then exchange with the hydrogen ions of peat. However, it is possible in this system that there could also be a contribution from a diffusion controlled process.

It should be emphasised that these systems and models were selected only as examples since a full analysis should be performed, based on testing several kinetic and several diffusion models for each system.

Table 8. Comparison of Sum of Errors Squared (SSE) for Sorption Kinetic and Diffusion Models of Astrazon Blue (BB69) onto Sphagnum Moss Peat[132].

	$\mathrm{SSE} = \sum \left[\frac{(q_{t,\exp t} - q_{t,theo})^2}{q_{t,\exp t}^{\ 2}} \right]$	
Concentrations (mg/dm^3)	Pseudo 2nd Order	Diffusion
20	0.059344	1.137346
50	0.142145	0.343148
100	0.105048	0.243305
200	0.202826	0.509083

8. CONCLUSIONS

The use of cheap biosorbents for the treatment of aqueous effluents to remove dyes, metal ions and various organics has been recognised as a major potential development in the area of biosorption during the past ten years. The increase in the number of papers in the literature during this period demonstrates this and these papers have been reviewed in the present work.

This paper reports that several kinetic and diffusion sorption mechanisms have been used to analyse the experimental data. The various models have been presented and their methods of solution which can be used to determine rate parameters and diffusion coefficients. The kinetic sorption models include zero order, first order, pseudo-first order, second order, pseudo-second order, reversible reaction models, third order, Langmuir-Hinshelwood, and Elovich Kinetics. Two models for determining the mass transfer coefficients for external film sorption control and two solutions for intraparticle diffusion sorption have been presented.

It is usually necessary to carry out experimental studies using several variables and test the data in order to confirm whether the mechanism is film diffusion, kinetic sorption, diffusion sorption or a combination of these processes.

In the literature references reviewed in the present paper, dealing with the sorption of pollutants onto biosorbents and other sorbents, only ten percent consider the possibility of more than one sorption process. In general, authors select one model for testing, usually the pseudo-first order process, and report the experimental data have a ‘satisfactory fit’ with the acceptance of the theoretical model based on a correlation coefficient analysis. Furthermore, many papers only report the effect of one process variable in the paper, perform a model analysis, and this is not sufficient to provide absolute confirmation of the sorption process mechanism.

9. ACKNOWLEDGEMENT

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10. NOTATION

$\overline{D}$	the coefficient of intraparticle diffusion (cm^2/s)
α	the fractional attainment of equilibrium (−)
(C)	concentration of Cd^{2+} (mg/dm^3)
$(D_e)_M$	the effective intrapellet diffusivities of the adsorbed-phase region in the macropore region (cm^2S)

$(D_e)_m$	the effective intrapellet diffusivities of the adsorbed-phase region in the micropore region (cm^2S)
(M)	the concentration of free metal in solution, (mg/dm^3)
$(M)_{in}$	the initial free metal concentration, (mg/dm^3)
(P)	the concentration of peat binding sites, (mg/dm^3)
(PM)	the concentration of metal bound to peat, (mg/dm^3)
(PM)	the variable bound metal concentration, (mg/dm^3)
$(PM)_{lim}$	the equilibrium bound metal concentration, (mg/dm^3)
(X)	concentration of $FeOH_2^+$ (mg/dm^3)
(XC)	concentration of $FeOCdOH_2^+$ (mg/dm^3)
A	metal ion
C	the concentration of phosphamidon in solution (mg/dm^3)
C_0	the concentration at the start of the reaction (mg/dm^3)
C_A	metal concentration in solution (mg/dm^3)
D_{eff}	the effective diffusivity (cm^2)
D_i	the internal diffusion coefficient (cm^2/s)
D_p	the pore diffusion (cm^2S)
D_s	the homogenouos solid phase diffusion cm^2/s)
$d_{molecule}/d_{pore}$	the molecular diameter to pore diameter ratio
d_p	the particle diameter (cm)
F(C)	function describing the amount of P that can be sorbed at equilibrium as a function of solution concentration ($\mu g/g$)
f	volume fraction occupied by the macropore region
H	humic acid
k	the rate constant of pseudo-second order sorption, (g/mg-min)
K	Langmuir isotherm equilibrium constant (dm^3/g)
K'	the apparent conditional stability constant, (l/mg)
k’	overall rate constant
k_0	zero-order reaction rate constant of LH model, (mg/g min)
k_1	first-order reaction rate constant of LH model (min^{-1})
k_a	the sorption rate constant
k_b	the forward binding kinetic constant (l/mgmin)
k_d	diffusion coefficient ($mg/g\ min^{0.5}$)
k_L	the Lagergren rate constant of first order sorption, (l/min)
k_2	second order rate constant (g/mg min)
k_3	third order rate constant (g^2mg^2 min)
k_p	the rate coefficient for particle diffusion control corresponding to particle size of the sorbent
k_r	the kinetic constant for desorption (1/min)
n	number of expansion terms used to solve equation (20)

q	the average solid phase concentration (mg/g)
q_e	the sorption capacity at equilibrium (mg/g)
q_M	the adsorbed-phase region in the macropore (mg/g)
q_m	the amount of solute sorbed at infinity (mg/g)
q_i	the point solid phase concentration (mg/g)
q_o	the amount of solute sorbed at time $t = 0$ (mg/g)
q_t	amount of solute sorbed on the surface of the sorbent at any time, t, (mg/g)
r	particle radius (cm)
R	Universal gas constant (kJ/molK)
r_0	the radius of sorbent (cm)
S_{avg}	average concentration of P in the soil particle(μg/g)
S_s	specific particle surface (cm^{-1})
SSE	Sum of square errors squared
t	the reaction time (min)
$t_{1/2}$	time for the uptake of half amount of sorbate sorbed (min)
$u(t)$	the fractional attainment (−)
V	volume of solution (cm^3)
X	the fractional conversion of sorbate (−)
X_e	the fractional conversion of sorbate at equilibrium (−)

GREEK LETTERS

α	initial solute sorption rate (mg solute/g min)
β	desorption constant (g/mg solute)
β_L	external mass transfer coefficient (cm/s)
θ	fractional surface coverage (−)
ε_P	particle voidage (−)
ρ_P	sorbent particle density (g/cm^3)

SUBSCRIPTS

b	binding reaction
e	equilibrium condition
f	forward reaction
i	internal/intraparticle
o	time, $t = o$
p	particle
r	reverse reaction
t	time

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