

A COMPARISON OF CHEMISORPTION KINETIC MODELS APPLIED TO POLLUTANT REMOVAL ON VARIOUS SORBENTS

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A comparison of kinetic models describing the sorption of pollutants has been reviewed. The rate models evaluated include the Elovich equation, the pseudo-first order equation and the pseudo-second order equation. Results show that chemisorption processes could be rate limiting in the sorption step. The pseudo-second order equation may be applied for chemisorption processes with a high degree of correlation in several literature cases where a pseudo-first order rate mechanism has been arbitrarily assumed.

Keywords: sorption; kinetics; Elovich equation; pseudo-first order and pseudo-second order.

INTRODUCTION

Many attempts have been made to formulate a general expression describing the kinetics of sorption on solid surfaces for liquid-solid phase sorption systems. The pseudo-first order equation was first represented by Lagergren¹ for the sorption of oxalic acid and malonic acid onto charcoal. Several applications of the Lagergren equation have been widely applied throughout the years. An early application of the pseudo-first order rate equation of Lagergren was the sorption of cellulose triacetate from chloroform onto calcium silicate by Trivedi *et al.*². Numerous studies report first order Lagergren kinetics for the sorption of metals such as the sorption of As(III) from aqueous solutions by haematite³, the sorption of nickel(II) from aqueous solutions by Woolastonite and china clay^{4,5}, the sorption of chromium(VI) by bismuth trioxide⁶, the sorption of cadmium(II) onto hydrous ceric oxide⁷, the sorption of chromium(III) by natural moss and chromium(VI) by copper-coated moss⁸, the sorption of mercury(II) onto hydrous zirconium oxide⁹, the sorption of lead(II) onto kaolinitic clay¹⁰, the sorption of arsenite(III) and arsenate(V) using basic yttrium carbonate¹¹ and the sorption of arsenic(V) on haematite and feldspar¹²; of dyes such as the sorption of Omega Chrome Red ME (OCRME) using a 1:1 ratio of fly ash and coal¹³, the sorption of Methylene Blue on water hyacinth roots¹⁴, the sorption of Orlamar Red BG (ORBG) by *Fomitopsis carnea*¹⁵, the sorption of Congo Red, Procin Orange and Rhodamine-B by waste orange peel¹⁶, the sorption of Congo Red on red mud¹⁷ and the sorption of Acid Blue 29 and Reactive Blue 3 on chrome sludge¹⁸. Others studies utilizing the pseudo-first order model include the sorption of Acid Violet dye onto waste banana pith¹⁹ and the sorption of fluoride, phosphate and arsenate(V) using lanthanum-impregnated silica gel²⁰.

This present paper presents a literature review of over 250 systems analysed by the Lagergren pseudo-first order

kinetic model. Three of these results have been analysed and compared by the pseudo-second order rate mechanism and the Elovich equation, for the sorption of phosphate onto tamarind nut shell activated carbon²¹ and the sorption of Pb(II) and Cu(II) onto bottom ash²².

DISCUSSION

In order to investigate the mechanism of sorption and potential rate controlling steps such as mass transport and chemical reaction processes, kinetic models have been used to test experimental data. These kinetic models included the pseudo-first order equation, the pseudo-second order equation and the Elovich equation.

The Pseudo-First Order Equation

The pseudo-first order equation of Lagergren¹ is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

where q_e and q_t are the sorption capacity at equilibrium and at time t , respectively (mg g^{-1}) and k_1 is the rate constant of pseudo-first order sorption (1 min^{-1}). After integration and applying boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of equation (1) becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad (2)$$

The equation applicable to experimental results generally differs from a true first order equation in two ways²³:

- The parameter $k_1(q_e - q_t)$ does not represent the number of available sites.
- The parameter $\log(q_e)$ is an adjustable parameter and often it is found not equal to the intercept of a plot of $\log(q_e - q_t)$ against t , whereas in a true first order $\log(q_e)$

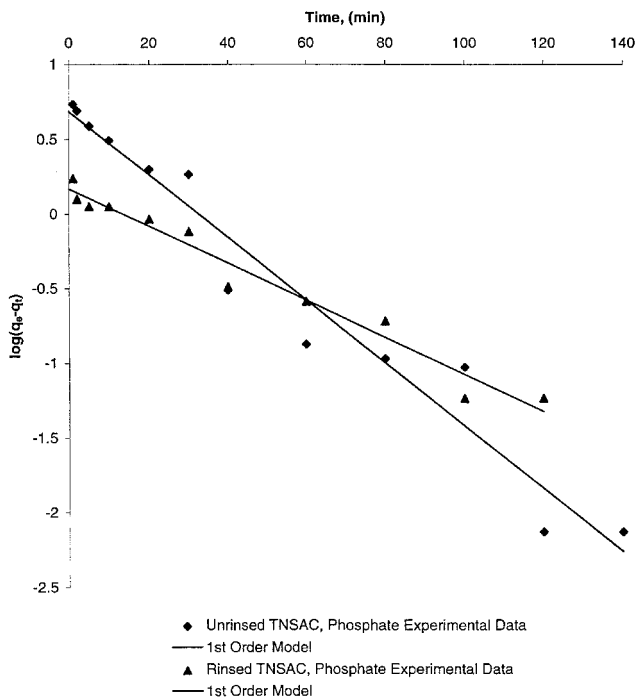


Figure 1. Pseudo-first order sorption kinetics of phosphate onto tamarind nut shell activated carbon (TNSAC).

should be equal to the intercept of a plot of $\log(q_e - q_t)$ against t .

In order to fit equation (2) to experimental data, the equilibrium sorption capacity, q_e , must be known. In many cases q_e is unknown and as chemisorption tends to become unmeasurably slow, the amount sorbed is still significantly smaller than the equilibrium amount²⁴. In most cases in the literature, the pseudo-first order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial 20 to 30 minutes of the sorption process. Furthermore, one has to find some means of extrapolating the experimental data to $t = \infty$, or treat q_e as an adjustable parameter to be determined by trial and error. For this reason, it is necessary to use trial and error to obtain the equilibrium sorption capacity, q_e , to analyse the pseudo-first order model kinetics. In over 50% of literature references, based on analysing sorption kinetics, the authors did not measure an equilibrium isotherm.

The Pseudo-Second Order Equation

If the rate of sorption is a second order mechanism, the pseudo-second order chemisorption kinetic rate equation is expressed as:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (3)$$

where q_e and q_t are the sorption capacity at equilibrium and at time t , respectively (mg g^{-1}) and k is the rate constant of pseudo-second order sorption ($\text{g mg}^{-1} \text{min}^{-1}$). For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of equation (3) becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \quad (4)$$

which is the integrated rate law for a pseudo-second order reaction. Equation (4) can be rearranged to obtain:

$$q_t = \frac{t}{\frac{1}{kq_e^2} + \frac{t}{q_e}} \quad (5)$$

which has a linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (6)$$

where h can be regarded as the initial sorption rate as $q_t/t \rightarrow 0$, hence:

$$h = kq_e^2 \quad (7)$$

Equation (6) can be written as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \quad (8)$$

Equation (6) does not have the disadvantage of the problem with assigning an effective q_e . If pseudo-second order kinetics are applicable, the plot of t/q_t against t of equation (6) should give a linear relationship, from which q_e , k and h can be determined from the slope and intercept of the plot and there is no need to know any parameter beforehand.

The Elovich Equation

The Elovich equation is generally expressed as follows²⁵:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (9)$$

where q_t is the sorption capacity at time t (mg g^{-1}), α is the initial sorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and β is the desorption constant (g mg^{-1}) during any one experiment.

To simplify the Elovich equation, Chien and Clayton²⁶ assumed $\alpha\beta t \gg 1$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ equation (9) becomes²⁷:

$$q_t = \beta \ln(\alpha\beta) + \ln(t) \quad (10)$$

Thus, the constants can be obtained from the slope and the intercept of a straight line plot of q_t against $\ln(t)$. Equation (10) will be used to test the applicability of the Elovich equation to the kinetics of sorption.

Analysis of Data from the Literature

The pseudo-first order equation has been adequately employed to describe reactions. However, it is typically expressed in a range of reaction only^{5,28}. The data of Bhargava and Sheldarkar²¹ for the sorption of phosphate onto unrinsed tamarind nut shell activated carbon (TNSAC) and rinsed tamarind nut shell activated carbon were plotted according to equation (2) and the results are shown in Figure 1. The equilibrium capacity q_e was obtained by trial and error and the correlation coefficients are 0.957 for unrinsed TNSAC and 0.967 for TNSAC. The plot of t/q_t against t of equation (6) is shown in Figure 2 for the same data. The correlation coefficients are extremely high (>0.998). The pseudo-second order equation is based on the sorption capacity on the solid phase. It deserves particular attention in the present discussion because, contrary to the other models, it predicts the behaviour

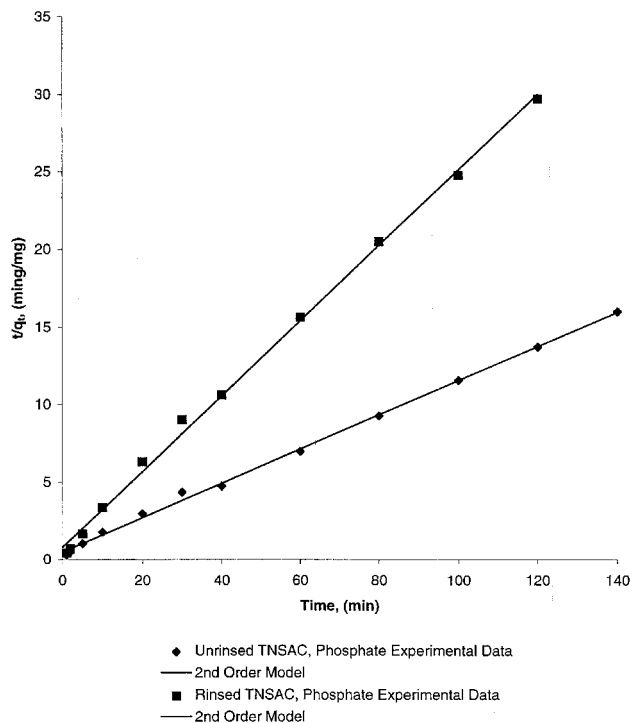


Figure 2. Pseudo-second order sorption kinetics of phosphate onto tamarind nut shell activated carbon (TNSAC).

over the whole range of studies supporting a pseudo-second order equation and is in agreement with chemisorption being the rate controlling step. In addition, the same data are also plotted with the Elovich equation (10) and the results are shown in Figure 3. The correlation coefficients are 0.967 for unrinsed TNSAC and 0.933 for TNSAC.

Other data from the literature were also tested by plotting t/q_t against t for the sorption of lead(II) and copper(II) onto bottom ash according to equation (6)²². The agreement of experimental data and the pseudo-second order equation is much better than those for the other two equations. The sorption of lead(II) and copper(II) onto bottom ash were plotted with excellent correlation coefficients—0.990 for lead and 1.00 for copper—and the results are shown in Figure 4.

Numerous applications of the Lagergren equation have been reported. A comparison of the rate constant models of pseudo-first order systems is given in Table 1. Boyd *et al.*⁵⁰ proposed that if the film diffusion is rate controlling, the slope of the plots of equation (2) will vary inversely with the particle size, the film thickness and with the distribution coefficient, k ; if the sorption rate controlling step is chemical exchange, the slope will be independent of particle diameter and flow rate and will depend only on the concentration of the sorbate in solution and the temperature. In the case of the sorption of mercury(II) onto hydrous zirconium oxide⁹, the rate constant is independent of concentration. The mechanism of sorption may not be ion exchange or chemically rate controlling. For the sorption of arsenic(V) onto haematite¹², the rate constant is independent of agitation but dependent on temperature. The mechanism of arsenic(V) sorption onto haematite may be chemically rate controlling. The rate constant for the sorption of cadmium(II) onto Fe(III)/Cr(III) hydroxide is

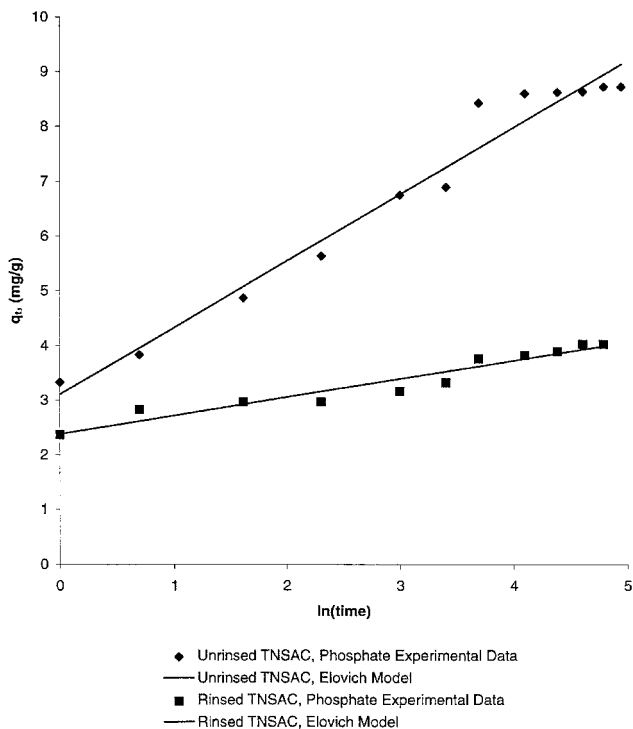


Figure 3. Elovich equation of phosphate onto tamarind nut shell activated carbon (TNSAC).

dependent on concentration and temperature⁴³. The mechanism of sorption of cadmium(II) onto Fe(III)/Cr(III) hydroxide may be chemically rate controlling. However, in the case of the sorption of Acid Brilliant Blue, Direct Red 12 B, chromium(VI) and lead(II) onto biogas residual slurry^{35,44–46}, the rate constant is dependent on concentration and particle size. For the sorption of phenolic compounds on fly ash and impregnated fly ash³⁹,

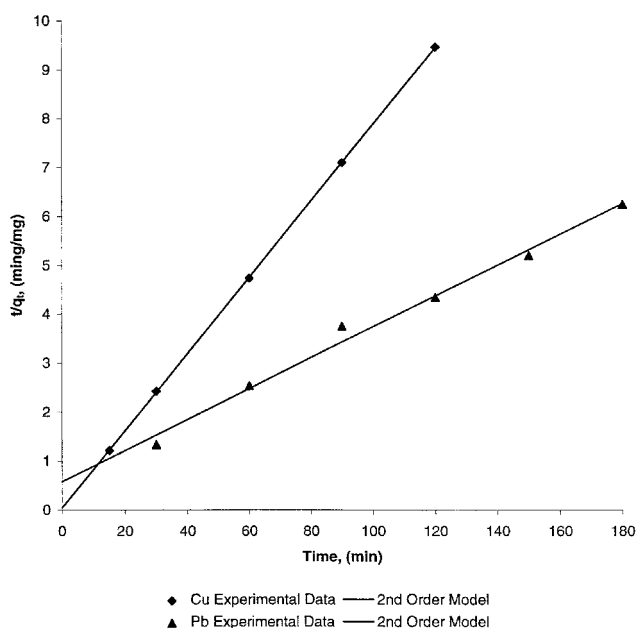


Figure 4. Pseudo-second order sorption kinetics of lead(II) and copper(II) onto bottom ash.

Table 1. A comparison of the rate constant of the pseudo-first order kinetic model.

Sorbent	Solute	k , min ⁻¹	Condition	Reference
Fly ash/Wollastonite	Cr(VI)	3.1×10^{-2}	30°C	Panday <i>et al.</i> ²⁹
Fly ash	Cu(II)	6.93×10^{-2}	30°C	Panday <i>et al.</i> ³⁰
Fly ash	Victoria Blue	1.7×10^{-2}	25°C	Khare <i>et al.</i> ³¹
Haematite	As(III)	0.734	20°C	Singh <i>et al.</i> ³
		0.683	30°C	
		0.673	40°C	
1:1 Fly ash and coal	OCRME	2.92×10^{-2}	30°C	Gupta <i>et al.</i> ¹³
		2.90×10^{-2}	40°C	
		2.84×10^{-2}	50°C	
Fly ash	Fluoride	1.81×10^{-2}	30°C	Chaturvedi <i>et al.</i> ³²
		4.01×10^{-2}	40°C	
		5.31×10^{-2}	50°C	
Wollastonite	Ni(II)	1.02×10^{-2}	30°C	Sharma <i>et al.</i> ⁴
China clay	Ni(II)	9.2×10^{-2}	30°C	Sharma <i>et al.</i> ⁵
		8.0×10^{-2}	40°C	
		8.2×10^{-2}	50°C	
Banana pith	Acid violet	1.3×10^{-1}	20 mg dm ⁻³	Namasivayam and Kanchana ¹⁹
		3.7×10^{-2}	50 mg dm ⁻³	
		2.5×10^{-2}	75 mg dm ⁻³	
		1.8×10^{-2}	100 mg dm ⁻³	
Biogas residual slurry	Congo Red	2.8×10^{-2}	20 mg dm ⁻³	Namasivayam and Yamuna ³³
		2.6×10^{-2}	20 mg dm ⁻³	
		5.0×10^{-3}	100 mg dm ⁻³	
		5.0×10^{-3}	200 mg dm ⁻³	
Biogas residual slurry	Rhodamine-B	2.9×10^{-2}	20 mg dm ⁻³	Namasivayam and Yamuna ³⁴
		2.4×10^{-2}	50 mg dm ⁻³	
		1.6×10^{-2}	100 mg dm ⁻³	
		1.1×10^{-2}	200 mg dm ⁻³	
Biogas residual slurry	Acid Brilliant Blue	1.50×10^{-1}	20 mg dm ⁻³	Yamuna and Namasivayam ³⁵
		6.63×10^{-3}	50 mg dm ⁻³	
		5.57×10^{-3}	75 mg dm ⁻³	
		4.76×10^{-3}	100 mg dm ⁻³	
Biogas residual slurry	Acid Brilliant Blue	8.55×10^{-3}	53–75 μ m	Yamuna and Namasivayam ³⁵
		6.63×10^{-3}	75–150 μ m	
		6.00×10^{-3}	150–250 μ m	
		3.00×10^{-3}	250–500 μ m	
Bicarbonate-treated peanut hulls	Hg(II)	5.43×10^{-2}	10 mg dm ⁻³	Namasivayam and Periasamy ³⁶
		4.39×10^{-2}	15 mg dm ⁻³	
		6.09×10^{-2}	20 mg dm ⁻³	
Commercial granular activated carbon	Hg(II)	3.76×10^{-2}	10 mg dm ⁻³	Namasivayam and Periasamy ³⁶
		1.92×10^{-2}	15 mg dm ⁻³	
		1.94×10^{-2}	20 mg dm ⁻³	
Fe(III)/Cr(III) hydroxide	Cr(VI)	7.59×10^{-2}	24°C	Namasivayam and Ranganathan ³⁷
		8.06×10^{-2}	29°C	
		8.75×10^{-2}	38°C	
Fe(III)/Cr(III) hydroxide	Paraquat	1.83	10 mg dm ⁻³	Namasivayam <i>et al.</i> ³⁸
		1.24	20 mg dm ⁻³	
		0.500	40 mg dm ⁻³	
Fly ash and impregnated fly ash	Phenol	1.68×10^{-2}	150 μ m	Singh and Rawat ³⁹
		1.84×10^{-2}	100 μ m	
		1.89×10^{-2}	45 μ m	
Fly ash and impregnated fly ash	<i>o</i> -Cresol	1.40×10^{-2}	150 μ m	Singh and Rawat ³⁹
		1.55×10^{-2}	100 μ m	
		1.69×10^{-2}	45 μ m	
Fly ash and impregnated fly ash	<i>m</i> -Cresol	1.60×10^{-2}	150 μ m	Singh and Rawat ³⁹
		1.68×10^{-2}	100 μ m	
		1.79×10^{-2}	45 μ m	
Fly ash and impregnated fly ash	<i>p</i> -Cresol	1.80×10^{-2}	150 μ m	Singh and Rawat ³⁹
		1.92×10^{-2}	100 μ m	
		2.09×10^{-2}	45 μ m	
Fly ash and impregnated fly ash	<i>o</i> -Nitrophenol	1.96×10^{-2}	150 μ m	Singh and Rawat ³⁹
		2.09×10^{-2}	100 μ m	
		2.25×10^{-2}	45 μ m	
Fly ash and impregnated fly ash	<i>m</i> -Nitrophenol	2.04×10^{-2}	150 μ m	Singh and Rawat ³⁹
		2.16×10^{-2}	100 μ m	
		2.35×10^{-2}	45 μ m	
Fly ash and impregnated fly ash	<i>p</i> -Nitrophenol	2.20×10^{-2}	150 μ m	Singh and Rawat ³⁹
		2.36×10^{-2}	100 μ m	
		2.53×10^{-2}	45 μ m	
Fly ash and impregnated fly ash	Phenol	1.71×10^{-2}	pH 2.0	Singh and Rawat ³⁹
		1.69×10^{-2}	pH 4.0	
		1.68×10^{-2}	pH 6.5	
		1.60×10^{-2}	pH 8.0	
		1.71×10^{-2}	pH 10.0	

Table 1. continued

Sorbent	Solute	k, min^{-1}	Condition	Reference
Fly ash and impregnated fly ash	<i>o</i> -Cresol	1.47×10^{-2}	pH 2.0	Singh and Rawat ³⁹
		1.42×10^{-2}	pH 4.0	
		1.40×10^{-2}	pH 6.5	
		1.30×10^{-2}	pH 8.0	
		1.17×10^{-2}	pH 10.0	
Fly ash and impregnated fly ash	<i>m</i> -Cresol	1.70×10^{-2}	pH 2.0	Singh and Rawat ³⁹
		1.65×10^{-2}	pH 4.0	
		1.60×10^{-2}	pH 6.5	
		1.50×10^{-2}	pH 8.0	
		1.34×10^{-2}	pH 10.0	
Fly ash and impregnated fly ash	<i>p</i> -Cresol	2.03×10^{-2}	pH 2.0	Singh and Rawat ³⁹
		1.93×10^{-2}	pH 4.0	
		1.80×10^{-2}	pH 6.5	
		1.69×10^{-2}	pH 8.0	
		1.58×10^{-2}	pH 10.0	
Fly ash and impregnated fly ash	<i>o</i> -Nitrophenol	2.24×10^{-2}	pH 2.0	Singh and Rawat ³⁹
		2.08×10^{-2}	pH 4.0	
		1.96×10^{-2}	pH 6.5	
		1.75×10^{-2}	pH 8.0	
		1.64×10^{-2}	pH 10.0	
Fly ash and impregnated fly ash	<i>m</i> -Nitrophenol	2.33×10^{-2}	pH 2.0	Singh and Rawat ³⁹
		2.21×10^{-2}	pH 4.0	
		2.04×10^{-2}	pH 6.5	
		1.83×10^{-3}	pH 8.0	
		1.76×10^{-2}	pH 10.0	
Fly ash and impregnated fly ash	<i>p</i> -Nitrophenol	2.50×10^{-2}	pH 2.0	Singh and Rawat ³⁹
		2.37×10^{-2}	pH 4.0	
		2.20×10^{-2}	pH 6.5	
		2.00×10^{-2}	pH 8.0	
		1.89×10^{-2}	pH 10.0	
Fly ash and impregnated fly ash	Phenol	1.68×10^{-2}	30°C	Singh and Rawat ³⁹
		1.72×10^{-2}	40°C	
		1.84×10^{-2}	50°C	
Fly ash and impregnated fly ash	<i>o</i> -Cresol	1.40×10^{-2}	30°C	Singh and Rawat ³⁹
		1.49×10^{-2}	40°C	
		1.63×10^{-2}	50°C	
Fly ash and impregnated fly ash	<i>m</i> -Cresol	1.60×10^{-2}	30°C	Singh and Rawat ³⁹
		1.70×10^{-2}	40°C	
		1.79×10^{-2}	50°C	
Fly ash and impregnated fly ash	<i>p</i> -Cresol	1.80×10^{-2}	30°C	Singh and Rawat ³⁹
		1.96×10^{-2}	40°C	
		2.03×10^{-2}	50°C	
Fly ash and impregnated fly ash	<i>o</i> -Nitrophenol	1.96×10^{-2}	30°C	Singh and Rawat ³⁹
		2.05×10^{-2}	40°C	
		2.14×10^{-2}	50°C	
Fly ash and impregnated fly ash	<i>m</i> -Nitrophenol	2.04×10^{-2}	30°C	Singh and Rawat ³⁹
		2.14×10^{-2}	40°C	
		2.29×10^{-2}	50°C	
Fly ash and impregnated fly ash	<i>p</i> -Nitrophenol	2.20×10^{-2}	30°C	Singh and Rawat ³⁹
		2.38×10^{-2}	40°C	
		2.54×10^{-2}	50°C	
Bi ₂ O ₃	Cr(VI)	3.88×10^{-2}	30°C	Bhutani and Kumari ⁶
		3.94×10^{-2}	35°C	
		4.33×10^{-2}	40°C	
		5.70×10^{-2}	45°C	
		6.22×10^{-2}	50°C	
Peanut hull carbon	Cd(II)	5.36×10^{-2}	10 mg dm ⁻³	Periasamy and Namasivayam ⁴⁰
		6.03×10^{-2}	15 mg dm ⁻³	
		4.48×10^{-2}	20 mg dm ⁻³	
Commercial granular activated carbon	Cd(II)	1.09×10^{-2}	10 mg dm ⁻³	Periasamy and Namasivayam ⁴⁰
		9.2×10^{-3}	15 mg dm ⁻³	
		8.0×10^{-3}	20 mg dm ⁻³	
Peanut hull carbon	Pb(II)	5.03×10^{-2}	10 mg dm ⁻³	Periasamy and Namasivayam ⁴¹
		5.63×10^{-2}	15 mg dm ⁻³	
		6.02×10^{-2}	20 mg dm ⁻³	
Commercial granular activated carbon	Pb(II)	1.40×10^{-2}	10 mg dm ⁻³	Periasamy and Namasivayam ⁴¹
		1.43×10^{-2}	15 mg dm ⁻³	
		1.50×10^{-2}	20 mg dm ⁻³	
Peanut hull carbon	Ni(II)	4.61×10^{-2}	10 mg dm ⁻³	Periasamy and Namasivayam ⁴²
		4.25×10^{-2}	15 mg dm ⁻³	
		2.88×10^{-2}	20 mg dm ⁻³	
Commercial granular activated carbon	Ni(II)	1.04×10^{-2}	10 mg dm ⁻³	Periasamy and Namasivayam ⁴²
		1.09×10^{-2}	15 mg dm ⁻³	
		1.18×10^{-2}	20 mg dm ⁻³	

Table 1. continued

Sorbent	Solute	k, min^{-1}	Condition	Reference
Fe(III)/Cr(III) hydroxide	Cd(II)	1.33×10^{-2}	20°C	Namasivayam and Ranganathan ⁴³
		1.38×10^{-2}	30°C	
Fe(III)/Cr(III) hydroxide	Cd(II)	1.40×10^{-2}	40°C	Namasivayam and Ranganathan ⁴³
		1.24×10^{-2}	50 mg dm ⁻³	
		1.38×10^{-2}	80 mg dm ⁻³	
		9.0×10^{-3}	110 mg dm ⁻³	
Water hyacinth roots	Methylene Blue	7.8×10^{-3}	140 mg dm ⁻³	Low <i>et al.</i> ¹⁴
		6.9×10^{-2}	100 mg dm ⁻³	
		6.4×10^{-2}	250 mg dm ⁻³	
Moss	Cr(III)	4.2×10^{-2}	500 mg dm ⁻³	Lee <i>et al.</i> ⁸
		4.06×10^{-4}	5 mg dm ⁻³	
		2.46×10^{-4}	10 mg dm ⁻³	
Moss	Cr(VI)	1.89×10^{-4}	20 mg dm ⁻³	Lee <i>et al.</i> ⁸
		5.87×10^{-3}	5 mg dm ⁻³	
		4.65×10^{-3}	10 mg dm ⁻³	
Biogas residual slurry	Direct red 12 B	4.58×10^{-3}	20 mg dm ⁻³	Namasivayam and Yamuna ⁴⁴
		1.03×10^{-2}	10 mg dm ⁻³	
		8.3×10^{-3}	20 mg dm ⁻³	
Biogas residual slurry	Direct red 12 B	5.8×10^{-3}	50 mg dm ⁻³	Namasivayam and Yamuna ⁴⁴
		4.1×10^{-3}	75 mg dm ⁻³	
		9.0×10^{-3}	53– μm	
Biogas residual slurry	Cr(VI)	8.3×10^{-3}	75–150 μm	Namasivayam and Yamuna ⁴⁵
		8.1×10^{-3}	150–250 μm	
		6.0×10^{-3}	250–500 μm	
Biogas residual slurry	Cr(VI)	1.15×10^{-2}	10 mg dm ⁻³	Namasivayam and Yamuna ⁴⁵
		1.28×10^{-2}	20 mg dm ⁻³	
		7.80×10^{-3}	30 mg dm ⁻³	
Biogas residual slurry	Cr(VI)	8.30×10^{-3}	40 mg dm ⁻³	Namasivayam and Yamuna ⁴⁵
		1.94×10^{-2}	53–75 μm	
		1.28×10^{-2}	75–150 μm	
Biogas residual slurry	Pb(II)	1.18×10^{-2}	250–500 μm	Namasivayam and Yamuna ⁴⁶
		1.75×10^{-1}	20 mg dm ⁻³	
		1.39×10^{-1}	50 mg dm ⁻³	
Biogas residual slurry	Pb(II)	1.03×10^{-1}	75 mg dm ⁻³	Namasivayam and Yamuna ⁴⁶
		1.56×10^{-2}	100 mg dm ⁻³	
		7.56×10^{-2}	75–150 μm	
Hydrous ceric oxide	Cd(II)	5.58×10^{-2}	250–500 μm	Mishra and Singh ⁷
		4.52×10^{-2}	>500 μm	
		5.75×10^{-2}	30°C	
Hydrous zirconium oxide	Hg(II)	6.72×10^{-2}	40°C	Mishra <i>et al.</i> ⁹
		7.83×10^{-2}	50°C	
		8.52×10^{-2}	60°C	
		8.44×10^{-2}	1.0×10^{-3} mol dm ⁻³	
Kaolinitic clay	Pb(II)	8.44×10^{-2}	1.0×10^{-4} mol dm ⁻³	Orumwense ¹⁰
		8.20×10^{-2}	1.0×10^{-5} mol dm ⁻³	
		8.44×10^{-2}	1.0×10^{-6} mol dm ⁻³	
		8.44×10^{-2}	1.0×10^{-7} mol dm ⁻³	
		8.32×10^{-2}	1.0×10^{-8} mol dm ⁻³	
		5.8×10^{-3}	30°C	
Feldspar	As(V)	6.5×10^{-3}	40°C	Singh <i>et al.</i> ¹²
		8.3×10^{-3}	50°C	
		6.35×10^{-2}	20°C	
Feldspar	As(V)	6.67×10^{-2}	30°C	Singh <i>et al.</i> ¹²
		3.22×10^{-2}	40°C	
		5.27×10^{-2}	50 rev/min	
		5.58×10^{-2}	75 rev/min	
Haematite	As(V)	5.87×10^{-2}	100 rev/min	Singh <i>et al.</i> ¹²
		6.35×10^{-2}	125 rev/min	
		0.116	20°C	
Haematite	As(V)	0.106	30°C	Singh <i>et al.</i> ¹²
		0.104	40°C	
		0.114	50 rev/min	
Peanut hull carbon	Cu(II)	0.116	75 rev/min	Periasamy and Namasivayam ⁴⁷
		3.26×10^{-2}	100 rev/min	
		3.52×10^{-2}	125 rev/min	
		3.37×10^{-2}	10 mg dm ⁻³	
Granular activated carbon	Cu(II)	9.2×10^{-3}	15 mg dm ⁻³	Periasamy and Namasivayam ⁴⁷
		9.2×10^{-3}	20 mg dm ⁻³	
		1.10×10^{-2}	10 mg dm ⁻³	
Lanthanum-impregnated silica gel	F	1.70×10^{-2}	15 mg dm ⁻³	Wasay <i>et al.</i> ²⁰
			20 mg dm ⁻³	

Table 1. continued

Sorbent	Solute	k , min ⁻¹	Condition	Reference
Lanthanum-impregnated silica gel	P	1.70×10^{-2}	20°C	Wasay <i>et al.</i> ²⁰
Lanthanum-impregnated silica gel	As(V)	2.99×10^{-2}	20°C	Wasay <i>et al.</i> ²⁰
Basic yttrium carbonate	As(III)	4.9×10^{-3}	20°C	Wasay <i>et al.</i> ¹¹
Basic yttrium carbonate	As(V)	7.05×10^{-2}	20°C	Wasay <i>et al.</i> ¹¹
<i>Fomitopsis Carneae</i>	Orlamer red BG	1.32×10^{-3}	0.05 g dm ⁻³	Mittal and Gupta ¹⁵
		1.87×10^{-3}	0.10 g dm ⁻³	
		3.17×10^{-3}	0.25 g dm ⁻³	
		3.18×10^{-3}	0.35 g dm ⁻³	
Orange peel	Congo red	4.06×10^{-2}	20 mg dm ⁻³	Namasivayam <i>et al.</i> ¹⁶
		4.94×10^{-2}	40 mg dm ⁻³	
		3.57×10^{-2}	50 mg dm ⁻³	
Orange peel	Procion orange	1.37×10^{-1}	10 mg dm ⁻³	Namasivayam <i>et al.</i> ¹⁶
		1.03×10^{-1}	20 mg dm ⁻³	
		1.55×10^{-1}	30 mg dm ⁻³	
		8.34×10^{-2}	40 mg dm ⁻³	
Orange peel	Rhodamine-B	9.95×10^{-2}	10 mg dm ⁻³	Namasivayam <i>et al.</i> ¹⁶
		2.34×10^{-1}	20 mg dm ⁻³	
		2.71×10^{-1}	30 mg dm ⁻³	
		2.99×10^{-1}	40 mg dm ⁻³	
Chrome sludge	Acid blue 29	3.2×10^{-3}	10°C	Lee <i>et al.</i> ¹⁸
		3.0×10^{-3}	25°C	
		2.9×10^{-3}	50°C	
Chrome sludge	Reactive blue 2	6.3×10^{-3}	10°C	Lee <i>et al.</i> ¹⁸
		5.0×10^{-3}	25°C	
		2.6×10^{-3}	50°C	
Fe(III)/Cr(III) hydroxide	Hg(II)	2.42×10^{-1}	10 mg dm ⁻³	Namasivayam and Senthikumar ⁴⁸
		9.8×10^{-2}	20 mg dm ⁻³	
		1.01×10^{-1}	30 mg dm ⁻³	
		8.3×10^{-2}	40 mg dm ⁻³	
Coirpith carbon	Cu(II)	1.97×10^{-2}	20 mg dm ⁻³	Namasivayam and Kadirvelu ⁴⁹
		2.65×10^{-2}	30 mg dm ⁻³	
		3.22×10^{-2}	40 mg dm ⁻³	
		3.41×10^{-2}	50 mg dm ⁻³	
Red mud	Congo red	3.34×10^{-2}	10 mg dm ⁻³	Namasivayam and Arasi ¹⁷
		6.66×10^{-2}	20 mg dm ⁻³	
		7.55×10^{-2}	30 mg dm ⁻³	
		3.57×10^{-2}	40 mg dm ⁻³	

the rate constant is dependent on concentration and temperature.

Diffusional mass transport models applied to sorption systems have not been reviewed in this paper, but their role is extremely important particularly in processes where ion exchange and ionic bonding are not as prevalent as in chemisorption processes. The diffusion models are usually based on one or more of the following mechanistic steps:

- (1) external mass transport across the boundary layer surrounding the particle;
- (2) diffusional mass transfer within the internal structure of the adsorbent particle by a pore, surface, branched pore or a combination of these mechanisms;
- (3) adsorption at a surface site.

The diffusional mass transport models have been developed extensively for the removal of organics and dyestuffs from wastewaters. Pore diffusion models with external mass transport have been developed for the adsorption of phenolic compounds onto activated carbon⁵¹ and acid dyes onto bagasse pith⁵².

Homogeneous solid surface diffusion models have been developed for the adsorption of phenol onto activated carbon using the Crank-Nicolson finite difference method to solve the diffusion equation⁵³, the adsorption of phenolic

compounds onto carbon using orthogonal collocation to solve the diffusion equation⁵⁴ and the adsorption of basic dyes onto silica⁵⁵ and basic dyes onto activated carbon⁵⁶, using a semi-analytical solution to solve the diffusion equation. Branched pore diffusion models based on macro-, meso- and micropore diffusion have been developed for phenol adsorption⁵⁷ and dye adsorption on activated carbon⁵⁸.

The application of variable surface diffusivity to the HSDM has been studied in several cases⁵⁹⁻⁶¹.

A pore-solid diffusion model has been developed and used to describe the adsorption of organics onto activated carbon^{62,63}.

In the case of these diffusional mass transport models, the solutions involve a reasonable degree of mathematical complexity.

CONCLUSIONS

It appears that the majority of adsorption studies reported in the literature are represented as pseudo-first order rate mechanisms. In many instances this model is restricted to a limited fraction of the reaction range and other available kinetic models have not been used to test and correlate the data. The limited data from the literature which has been tested in the present paper indicate that system variables

should be more extensively tested and that several kinetic models and correlation coefficients should be used to test experimental sorption data if a mechanism cannot be confirmed. The variables should include: agitation speed, sorbent diameter, solute concentration, sorbent mass and solute temperature.

NOMENCLATURE

α	constant in Elovich equation
β	exponent in Elovich equation
h	initial dye sorption rate, mg pollutant/g sorbent min
k_1	pseudo-first order rate constant, min ⁻¹
k	pseudo-second order rate constant, g sorbent/mg pollutant min
q_e	equilibrium mass of pollutant sorbed on sorbent, mg pollutant/g sorbent
q_t	mass of pollutant sorbed at time t , mg pollutant/g sorbent
t	contact time, min

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