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Pseudo-second order model for sorption processes

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Abstract

A literature review of the use of sorbents and biosorbents to treat polluted aqueous effluents containing dyes/organics or metal ions has been conducted. Over 70 systems have been reported since 1984 and over 43 of these reported the mechanism as being a pseudo-first order kinetic mechanism. Three sorption kinetic models are presented in this paper and have been used to test 11 of the literature systems previously reported as first order kinetics and one system previously reported as a second order process. In all 12 systems, the highest correlation coefficients were obtained for the pseudo-second order kinetic model. © 1999 Elsevier Science Ireland Ltd. All rights reserved.

Keywords: Kinetics; Sorption; Pseudo-second order

1. Introduction

The sorption of pollutants from aqueous solution plays an important role in wastewater treatment since it eliminates the need for huge sludge-handling processes. Well-designed sorption processes have high efficiency resulting in a high-quality effluent after treatment which can be recycled. Furthermore, if low-cost sorbents or sorbent regeneration is feasible then the sorbent material cost can be kept low. It is therefore understandable that the study of sorption kinetics in wastewater treatment is significant as it provides valuable insights into the reaction pathways and into the mechanism of sorption reactions. In addition, the kinetics describe the solute uptake rate which in turn controls the residence time of sorbate uptake at the solid–solution interface. Therefore, it is important to be able to predict the rate at which pollutant is removed from aqueous solutions in order to design appropriate sorption treatment plants. To develop sorption kinetics, a knowledge of the rate law describing the sorption system is required. The rate law is determined by experimentation and it cannot be inferred by more examination of the overall chemical reaction equation. The rate law has three primary requirements [1]:

- A knowledge of all the molecular details of the reaction including the energetics and stereochemistry.
- Interatomic distances and angles throughout the course of the reaction.
- The individual molecular steps involved in the mechanism.

1.1. Simple sorption kinetic systems

Numerous sorption systems have been investigated particularly during the past 15 years. Most of these have been reported as first order kinetic processes. Bhattacharya and Venkobachar [2] presented a simple first order reversible kinetic model, based on solution concentration for the sorption of cadmium(II) from liquid phase onto both Giridih coal and crushed coconut shell, as a reversible reaction with an equilibrium being established between two liquid and solid phases. This model has been applied to several other sorption systems (Table 1).

The pseudo-first order rate equation of Lagergren [3] has long been widely applied. In 1947, Boyd et al. [4] developed a rate equation which considered rates of ion-exchange adsorption in the exchange adsorption of

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ions from aqueous solutions by organic zeolites. In the cases of diffusion through a boundary liquid film and adsorption kinetics as a chemical phenomenon, the authors concluded that a mass action rate equation for adsorption kinetics as a chemical phenomenon and a diffusion equation for diffusion through a boundary liquid film are the same as the pseudo-first order rate equation of Lagergren. They also concluded that if film diffusion is rate controlling, the constant of the equation will vary inversely with the particle size and the film thickness; if the exchange is chemically rate controlled, the constant of the equation will be independent of particle diameter and flow rate and will depend only on the concentrations of the ions in solution and the temperature. The earlier application of the pseudo-first order rate equation of Lagergren to the sorption of cellulose triacetate from chloroform on calcium silicate was undertaken by Trivedi et al. [5]. Numerous studies report pseudo-first order Lagergren kinetics for the sorption of metals, such as the sorption of arsenite(III) from aqueous solutions by haematite [6] and the sorption of nickel(II) from aqueous solutions by wollastonite and china clay [7,8]. Several other metal sorption examples are listed in Table 1. The same first pseudo-order model was used for the sorption of dyes, such as the sorption of Omega Chrome Red ME (OCRME) using a 1:1 ratio of fly ash and coal [9], and the sorption of Methylene Blue on water hyacinth roots [10]. Table 1 shows a number of other pseudo-first order dye sorption systems.

In addition, Seki and Suzuki [11] reported that the kinetics of lead(II) sorption on a composite biopolymer sorbent of alginic acid and humic acid can be approximated to a pseudo-first order reaction with the Lagergren expression based on metal complexation.

Research work has been conducted using pseudo-second order kinetics for sorption reactions; for instance, Gosset et al. [12] reported batch metal removal by peat. Sharma and Forster [13–15] reported that the kinetics of the sorption of chromium(VI) using peat, leaf mould and granular activated carbon follow a pseudo-second order reaction rate. Ho et al. [16–18] reported that sorption of copper(II) and nickel(II) using peat in single- and bi-solute systems follows a similar second order reaction mechanism. Other examples for metal ions and dyes are given in Table 1.

Moreale and Van Bladel [19] developed an empirical model for the sorption of *p*-chloroaniline using Soignies and Heverlee I soils. The order of the reaction was calculated to be 1.92 and 1.93 for Soignies and Heverlee I soils respectively. Dzombak and Morel [20] found that the kinetics of cadmium(II) sorption on hydrous ferric oxide can be described by a second order rate equation and the kinetics of sorption should correspond to a reversible second order reaction at low sorbate/sorbent ratios (first order at very low ratios), and two competitive reversible second order reactions at higher sorbate/sorbent ratios.

1.2. Complex sorption kinetic systems

Singh et al. [21] reported that the sorption of mercury(II) by kaolinite obeyed multiple first order kinetics. Varshney et al. [22] proposed that the kinetics of sorption of the pesticide phosphamidon on beads of antimony(V) phosphate cation exchanger followed second order kinetics during the first 15 min, but afterwards, up to 180 min, it is a first order reaction. Sarkar and Chattoraj [23] have shown that the sorption of proteins such as lysozyme, β-lactoglobulin and hemoglobin from aqueous solution to the surface of silica powder follow first order Lagergren kinetics with two kinetic constants. Atun and Sismanoglu [24] found that the sorption of 4,4′-isopropylidene diphenol (Bis-phenol A) and diphenylolpropane-4,4′-diosyacetic acid (Bis acid A2) on kaolinite-type clay follows a first order process. However, at low concentrations of Bis-phenol A the mechanism follows a first order rate expression with two kinetic steps. Comber et al. [25] reported a complex multi-step processes, with equilibration times varying from minutes to weeks, for the sorption of cadmium(II), copper(II) and zinc(II) onto natural suspended particulate matter in the Humber estuary. It is often incorrect to apply simple kinetic models such as first- or second-order rate equations to a sorption with solid surfaces which are rarely homogeneous and because the effects of transport phenomena and chemical reactions are often experimentally inseparable [26].

Salim et al. [27] reported that the sorption of cadmium(II) on beech leaves is a first order reaction based on the solution concentration with respect to cadmium(II). Salim et al. [28] reported that the interaction between lead(II) and cypress leaves followed a fractional order of 0.7 based on the solution concentration with respect to lead(II). In the case of column studies the kinetics of copper(II) and lead(II) sorption onto polysulfone and algae complex follow the first order rate law based on the sorption capacity of the solid [29], and the kinetics of isoproturon sorption onto soil follow a reversible first order process henceforward described as the distance-from-equilibrium rate law [30]. Locke et al. [31] reported that the kinetics of acifluorfen sorption onto soil follow a first order process. Chien and Clayton [32] reported that the Elovich equation may be used to describe the kinetics of phosphate sorption in soils. Taylor et al. [33] reported that zinc sorption kinetics by 12 Alabama soils was best described by the Elovich equa-

Table 1
Comparison of mechanisms of sorption from the literature

Sorbent	Solute	Model	Reference
Giridih coal and Coconut shell	Cd(II)	^{s}1st order	Bhattacharya and Venkobachar [2]
Fly ash/Wollastonite	Cr(VI)	1st order	Panday et al. [42]
Fly ash	Cu(II)	1st order	Panday et al. [43]
Peat	Cu(II), Cd(II), Ni(II) and Zn(II)	2nd order	Gosset et al. [12]
Hydrous ferric oxide	Cd(II)	2nd order	Dzombak and Morel [20]
Fly ash	Victoria Blue	1st order	Khare et al. [34]
Peat	Pb(II)	2nd order	Ho and McKay [44]
Wollastonite	Fe(II)	1st order	Singh et al. [35]
Fly ash	OCRME	^{s}1st order	Gupta et al. [45]
1:1 Fly ash and coal	OCRME	1st order	Gupta et al. [45]
Fly ash	Floride	1st order	Chaturvedi et al. [46]
Peat	CN^-	2nd order	Cancela et al. [47]
Wollastonite	Ni(II)	1st order	Sharma et al. [7]
China clay	Ni(II)	1st order	Sharma et al. [8]
Groundnut husk carbon	Cr(VI)	^{s}1st order	Periasamy et al. [48]
Banana pith	Acid violet	1st order	Namasivayam and Kanchana [49]
Beech leaves	Cd(II)	*1st order	Salim et al. [27]
Coconut shell carbons	Cr(VI)	^{s}1st order	Rao et al. [50]
Biogas residual slurry	Congo Red	1st order	Namasivayam and Yamuna [51]
Biogas residual slurry	Rhodamine-B	1st order	Namasivayam and Yamuna [52]
Biogas residual slurry	Acid Brilliant Blue	1st order	Yamuna and Namasivayam [53]
Peanut hull carbon	Hg(II)	1st order	Namasivayam and Periasamy [54]
Waste tea, Turkish coffee, Exhausted coffee, Nut shell and Walnut shell	Cr(VI), Cd(II), Al(III)	^{s}1st order	Orhan and Büyükgüngör [55]
Peat	Cr(VI)	2nd order	Sharma and Forster [13]
Silica	Lysozyme. β-Lactoglobulin and Hemoglobin	^{m}1st order	Sarkar and Chattoraj [23]
Fe(III)/Cr(III) hydroxide	Cr(VI)	1st order	Namasivayam and Ranganathan [56]
Fe(III)/Cr(III) hydroxide	Paraquat	1st order	Namasivayam et al. [57]
Fly ash and Impregnated fly ash	Phenol, *o*-Cresol, *m*-Cresol, *p*-Cresol, *o*-Nitrophenol, *m*-Nitrophenol and *p*-Nitrophenol	1st order	Singh and Rawat [38]
Bi_2O_3	Cr(VI)	1st order	Bhutani and Kumari [39]
Peanut hull carbon	Cd(II)	1st order	Periasamy and Namasivayam [58]
Leaf mould	Cr(VI)	2nd order	Sharma and Forster [14]
Cypress leaves	Pb(II)	0.7 order	Salim et al. [28]
Peat	Cu(II)	2nd order	Ho et al. [16]
Peanut hull carbon	Pb(II)	1st order	Periasamy and Namasivayam [59]
Peanut hull carbon	Ni(II)	1st order	Periasamy and Namasivayam [60]
Peat	Ni(II)	2nd order	Ho et al. [17]
Fe(III)/Cr(III) hydroxide	Cd(II)	1st order	Namasivayam and Ranganathan [61]
Water hyacinth roots	Merthylene Blue	1st order	Low et al. [10]
Moss and Copper-coated moss	Cr(III) and Cr(VI)	1st order	Lee et al. [62]
Algae	Lauryl benzyl sulphonate	2nd order	Fernadez et al. [63]
Biogas residual slurry	Direct red 12 B	1st order	Namasivayam and Yamuna [64]
Biogas residual slurry	Cr(VI)	1st order	Namasivayam and Yamuna [65]

Table 1 (Continued)

Sorbent	Solute	Model	Reference
Biogas residual slurry	Pb(II)	1st order	Namasivayam and Yamuna [66]
Activated carbon	CN^-	[s]1st order	van Deventer and van der Merwe [67]
Hydrous ceric oxide	Cd(II)	1st order	Mishra and Singh [68]
Hydrous zirconium oxide	Hg(II)	1st order	Mishra et al. [69]
Kaolinitic clay	Pb(II)	1st order	Orumwense [70]
Immobilized bimomass	Cu(II) and Pb(II)	1st order	Ramelow et al. [29]
Feldspar	As(V)	1st order	Singh et al. [71]
Haematite	As(V)	1st order	Singh et al. [71]
Fly ash	Cr(VI)	[s]1st order	Dasmahapatra et al. [72]
Kaolinite	Hg(II)	[m]1st order	Singh et al. [21]
Peanut hull carbon	Cu(II)	1st order	Periasamy and Namasivayam [73]
Lanthanum-impregnated silica gel	F, P and As(V)	1st order	Wasay et al. [74]
Basic yttrium carbonate	As(III) and As(V)	1st order	Wasay et al. [75]
Peat	Cu(II) and Ni(II)	2nd order	Ho et al. [18]
Acitvated carbon	Cr(VI)	2nd order	Sharma and Forster [15]
Biopolymers	Pb(II)	1st order	Seki and Suzuki [11]
Fomitopsis Crania	Orlamar Red BG	1st order	Mittal and Gupta [76]
Kaolinite	Bis Acid A2	1st order	Atun and Sismanogly [24]
	Bisphenol A	[m]1st order	
Antimony(V) phosphate cation exchanger	Pesticide phosphamidon	[m,s]1st and 2nd order	Varshney et al. [22]
Orange peel	Congo Red, Procion Orange and Rhodamine-B	1st order	Namasivayam et al. [77]
Chrome sludge	Acid Blue 29 and Reactive Blue 2	1st order	Lee et al. [78]
Fe(III)/Cr(III) hydroxide	Hg(II)	1st order	Namasivayam and Senthilkumar [79]
Coirpith carbon	Cu(II)	1st order	Namasivayam and Kadirvelu [80]
Red mud	Congo red	1st order	Namasivayam and Arasi [81]
Soil	Isoproturon	[+]1st order	Worrall et al.[30]
Soil	Acifluorfen	*1st order	Locke et al. [31]
Soil	Hg(II)	2nd order	Yin et al. [82]
Chitin	Acid blue 193, Acid blue 40, Direct yellow 44, Direct blue 78	2nd order	Kim et al. [83]
Fly ash	*o*-xylene	[s]1st order	Banerjee et al. [84]

[s] 1st Order: a first order rate expression based on solution concentration.
[m] 1st Order: multiple first order kinetics.
* 1st Order: a first order rate expression based on solid.
[+] 1st Order: distance-from-equilibrium rate law.

tion when six models were tested, namely, zero-, first-, second-, third-order, parabolic diffusion and Elovich. These data are summarized in Table 1.

In the present work, a correlative kinetic analysis approach to the sorption process has been adopted and various sorption parameters such as the equilibrium sorption capacity, percent metal ion removal, rate constants and initial sorption rate, can be calculated from the experimental data by the pseudo-second order rate low. A pseudo-second order kinetic model is presented and discussed. Furthermore, data from the literature have been analysed and a comparison of the best fit sorption mechanisms has been made with the mechanisms proposed in the literature.

2. Materials and methods

The experimental data discussed and analysed by the pseudo-second order kinetic mechanism, proposed in this paper, have been reported previously in the literature. The experimental data analysed are the sorption of Victoria Blue dye onto fly ash by Khare et al. [34], the sorption of Fe(II) onto wollastonite by Sinjgh et al.

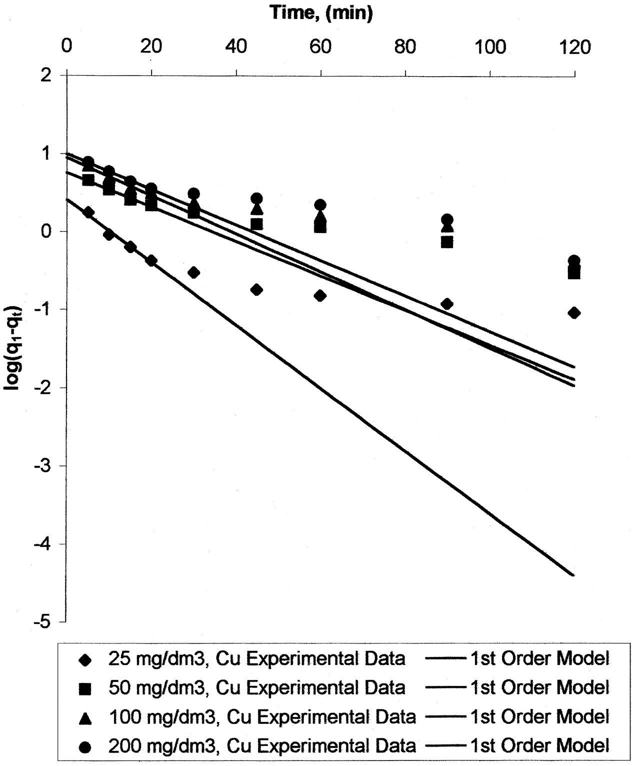

Fig. 1. Pseudo-first order sorption kinetics of copper(II) onto peat at various initial concentrations.

[35], the sorption of nickel(II) onto wollastonite by Sharma et al. [7], the sorption of copper(II) and lead(II) onto bottom ash by Kaur et al. [36], the sorption of cadmium(II) onto beech leaves by Salim et al. [27], the sorption of phosphate onto the tamarind nut shell activated carbon (TNSAC) by Bhargava and Sheldarkar [37], the sorption of *o*-cresol (OCL) and *p*-nitrophenol (PNP) onto fly ash by Singh and Rawat [38], the sorption of chromium(VI) onto bismuth trioxide by Bhutani and Kumari [39], the sorption of lead(II) onto cypress leaves by Salim et al. [28], the sorption of copper(II) onto peat by Ho et al. [16] and the sorption of cadmium(II) onto decaying leaves by Sayrafi et al. [40].

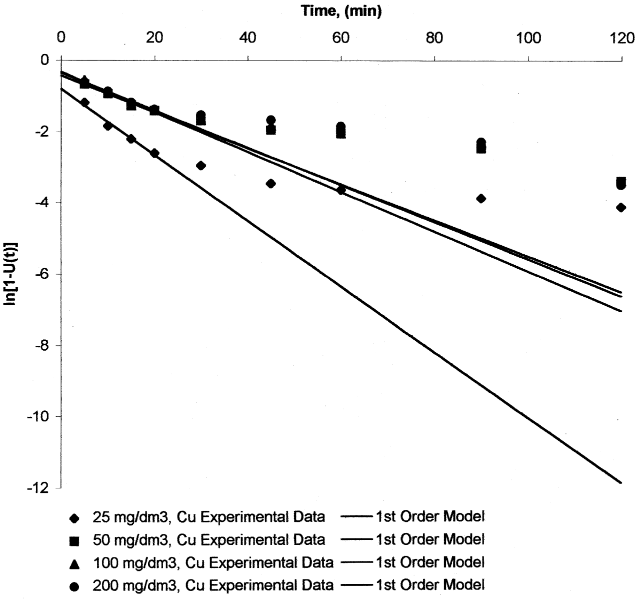

Fig. 2. First order sorption kinetics of copper(II) onto peat at various initial concentrations.

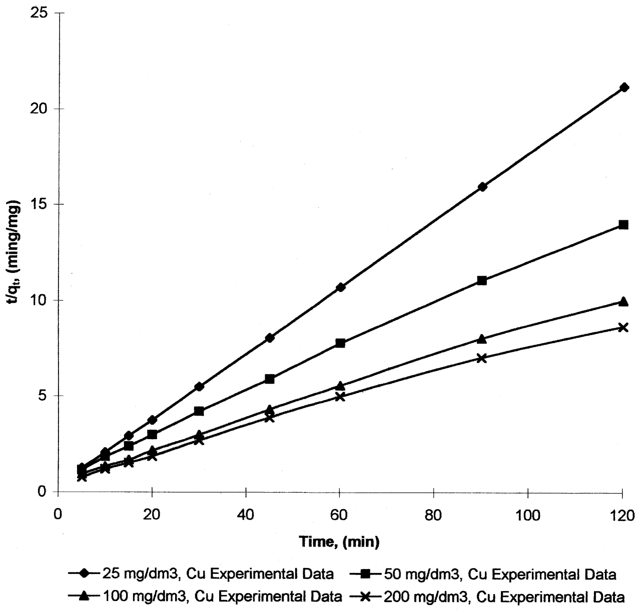

Fig. 3. Pseudo-second order sorption kinetics of copper(II) onto peat at various initial concentrations.

3. Theoretical models

Several models can be used to express the mechanism of solute sorption onto a sorbent. In order to investigate the mechanism of sorption, characteristic constants of sorption were determined using a pseudo-first order equation of Lagergren [3] based on solid capacity, a first order equation of Bhattacharya and Venkobachar [2] based on solution concentration, and a pseudo-second order equation based on solid phase sorption respectively.

A kinetic model for sorption analysis is the pseudo-first order rate expression of Lagergren [3] in the form:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_{\mathrm{S1}}(q_1 - q_t) \tag{1}$$

Integrating this for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, Eq. (1) may be rearranged for linearized data plotting as shown by Eq. (2):

$$\log(q_1 - q_t) = \log(q_1) - \frac{k_{\mathrm{S1}}}{2.303}t \tag{2}$$

where

Table 2
Comparison of the mechanisms of sorption for literature and pseudo-second order model

Sorbent	Solute	Best fit model	Literature mechanism
Fly ash	Victoria Blue	Pseudo 2nd order	Pseudo 1st order
Wollastonite	Ni(II)	Pseudo 2nd order	Pseudo 1st order
Bi_2O_3	Cr(VI)	Pseudo 2nd order	Pseudo 1st order
Peat	Cu(II)	Pseudo 2nd order	2nd order
Fly ash	OCL and PNP	Pseudo 2nd order	Pseudo 1st order
PHC and GAC	Cu(II)	Pseudo 2nd order	Pseudo 1st order
Beech leaves	Cd(II)	Pseudo 2nd order	*1st Order
Cypress leaves	Pb(II)	Pseudo 2nd order	*0.7 Order
Fly ash	OCRME	Pseudo 2nd order	^{s}1st order
Bottom ash	Cu(II) and Pb(II)	Pseudo 2nd order	None
TNSAC	Phosphate	Pseudo 2nd order	Diffusion
Reed leaves	Cd(II)	Pseudo 2nd order	None

* 1st Order: a first order rate expression based on solid with $t^{0.5}$.

^{s} 1st Order: a first order rate expression based on solution concentration.

k_{S1} is the rate constant of first order sorption (1/min),
q_1 is the amount of solute sorbed at equilibrium (mg/g),
q_t is amount of solute sorbed on the surface of the sorbent at any time t (mg/g).

A reversible first order rate expression based on solution concentration may be represented [2] by Eq. (3):

$$\frac{dC_B}{dt} = -\frac{dC_A}{dt} = C_{A*}\frac{dX_A}{dt} = k_1C_A - k_2C_B$$

$$= k_1(C_{A*} - C_{A*}X_A) - k_2(C_{B*} - C_{A*}X_A) \qquad (3)$$

Since $C_B = C_{B*}X_B = -C_{A*}X_A$ where

C_B	is the concentration of sorbate on the sorbent at any time,
C_A	is the concentration of sorbate in solution at any time.
C_{A*} and C_{B*}	are the initial concentrations of sorbate on the sorbent and in solution, respectively,
X_A	is the fractional conversion of soluted sorbate,
k_1 and k_2	are the first order rate constants.

At equilibrium conditions

$$\frac{dC_B}{dt} = \frac{dC_A}{dt} = 0 \qquad (4)$$

and

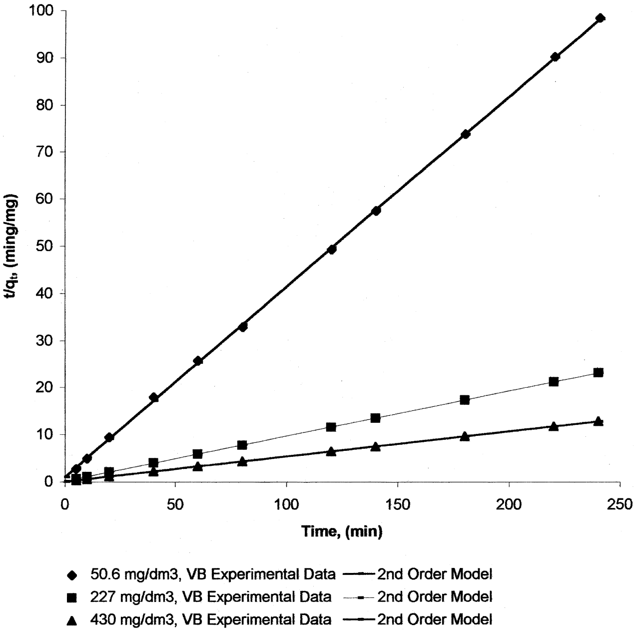

Fig. 4. Pseudo-second order sorption kinetics of Victoria Blue onto fly ash at various initial concentrations.

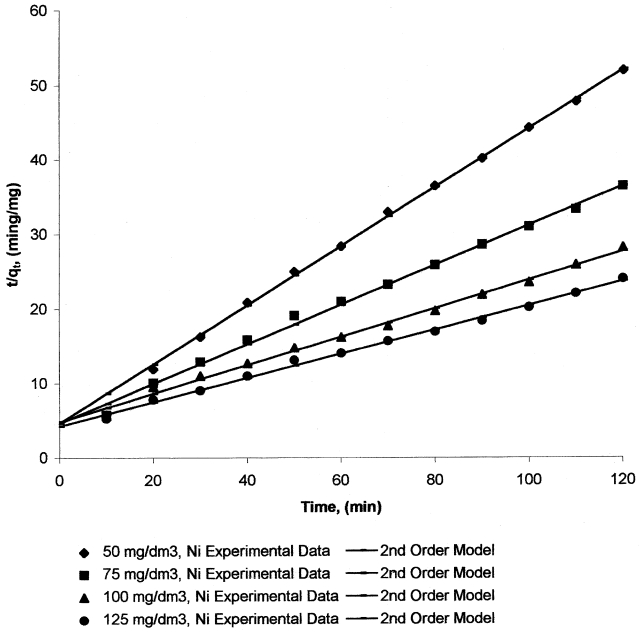

Fig. 5. Pseudo-second order sorption kinetics of nickel(II) onto wollastonite at various initial concentrations.

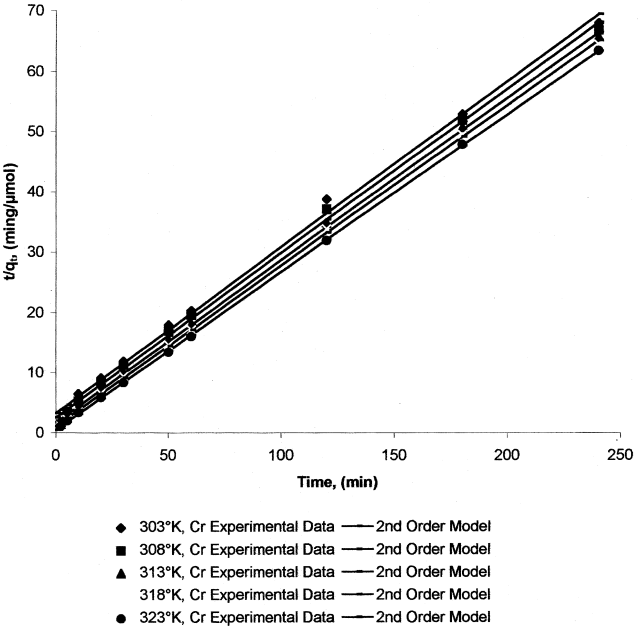

Fig. 6. Pseudo-second order sorption kinetics of chromium(VI) onto bismuth trioxide at various temperatures.

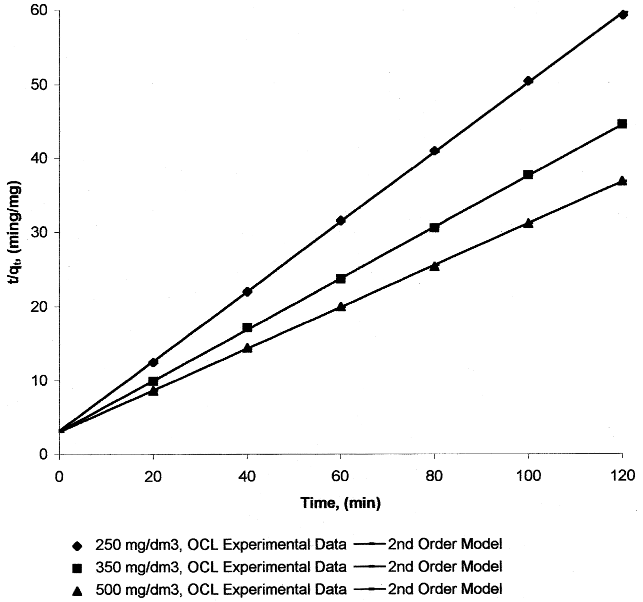

Fig. 8. Pseudo-second order sorption kinetics of *o*-cresol onto fly ash at various initial concentrations.

$$X_{\mathrm{Ac}} = \frac{K_{\mathrm{c}} - \dfrac{C_{\mathrm{B*}}}{C_{\mathrm{A*}}}}{K_{\mathrm{c}} + 1} \tag{5}$$

where

X_{ac} is the fractional conversion of soluted sorbate at equilibrium,

K_{c} is the equilibrium constant defined by Eq. (7)

Rearranging Eq. (5) gives an expression for K_{c} in terms of X_{Ac}:

$$K_{\mathrm{c}} = \frac{\dfrac{C_{\mathrm{B*}}}{C_{\mathrm{A*}}} + X_{\mathrm{Ac}}}{1 - X_{\mathrm{Ac}}} \tag{6}$$

$$K_{\mathrm{c}} = \frac{C_{\mathrm{Bc}}}{C_{\mathrm{Ac}}} = \frac{C_{\mathrm{B*}} + C_{\mathrm{A*}}X_{\mathrm{Ac}}}{C_{\mathrm{A*}} - C_{\mathrm{A*}}X_{\mathrm{Ac}}} = \frac{k_1}{k_2} \tag{7}$$

where

C_{Bc} and C_{Ac} are the equilibrium concentrations for soluted sorbate on the sorbent and solution, respectively.

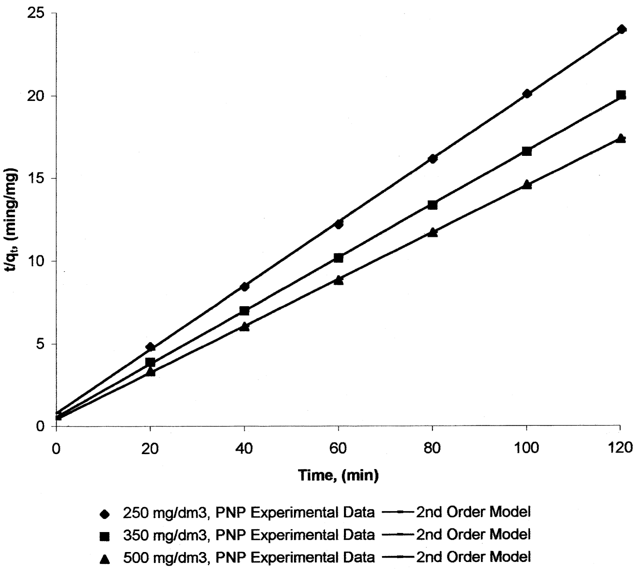

Fig. 7. Pseudo-second order sorption kinetics of *p*-nitrophenol onto fly ash at various initial concentrations.

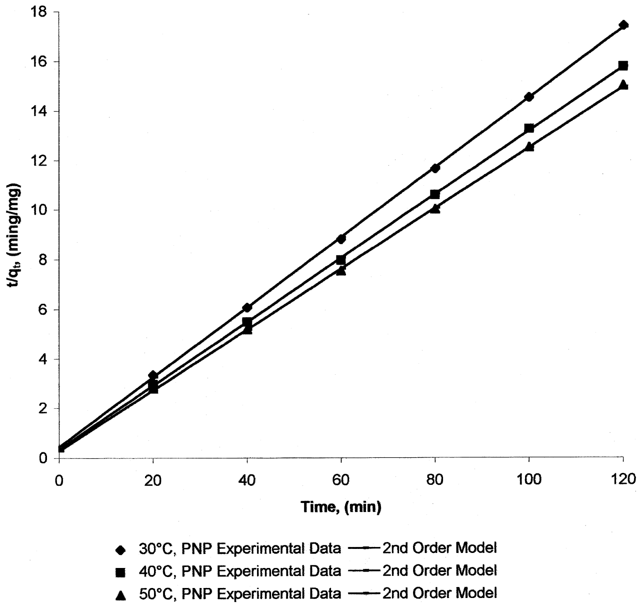

Fig. 9. Pseudo-second order sorption kinetics of *p*-nitrophenol onto fly ash at various temperatures.

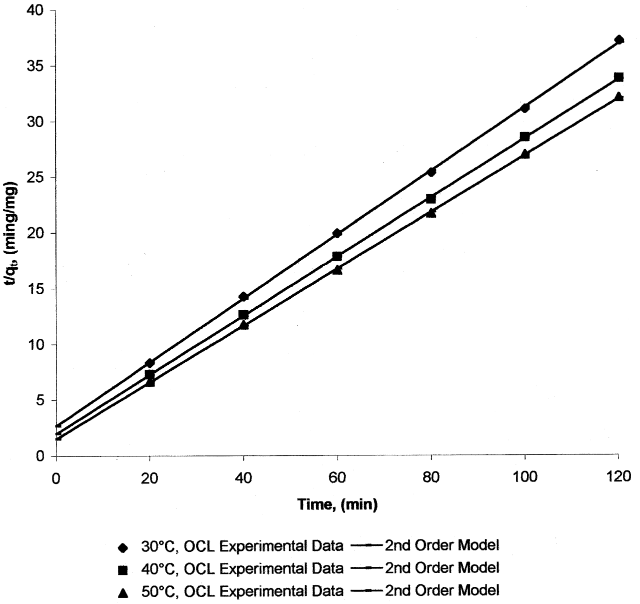

Fig. 10. Pseudo-second order sorption kinetics of *o*-cresol onto fly ash at various temperatures.

The rate equation in terms of equilibrium conversion can be obtained from Eqs. (3), (5) and (6) as follows:

1. substituting for $k_2 = k_1/k_c$ in Eq. (3);
2. substituting K_c by Eq. (6).

Now, Eq. (3) becomes:

$$k_1\left(\frac{C_{B*}}{C_{A*}} + X_{Ac} - \frac{C_{B*}X_A}{C_{A*}} - X_AX_{Ac}\right)$$

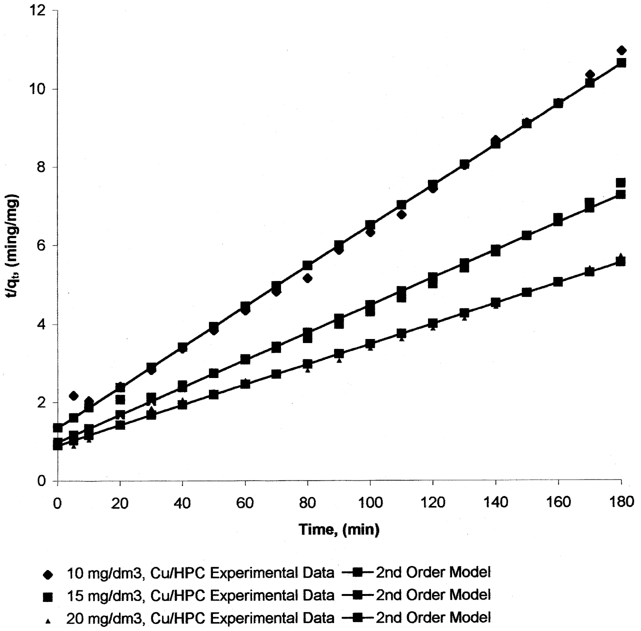

Fig. 11. Pseudo-second order sorption kinetics of copper(II) onto peanut hull carbon (PHC) at various initial concentrations.

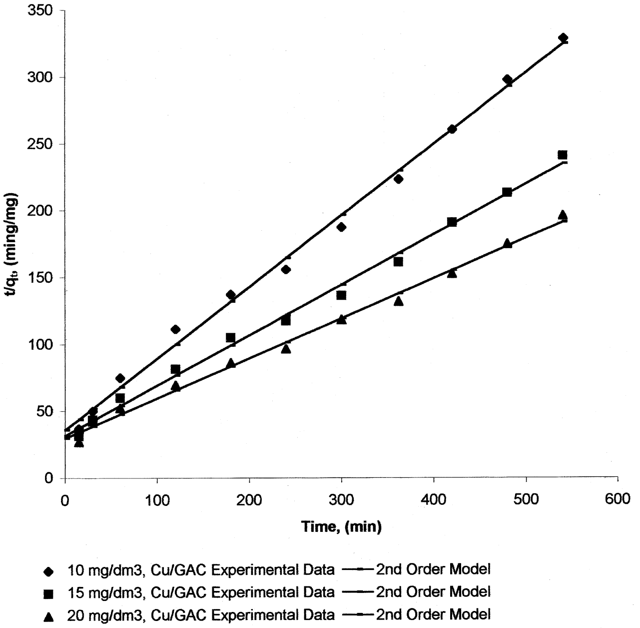

Fig. 12. Pseudo-second order sorption kinetics of copper(II) onto commercial granular activated carbon (GAC) at various initial concentrations.

$$\frac{dX_A}{dt} = \frac{-k_1\left(\frac{C_{B*}}{C_{A*}} - \frac{C_{B*}}{C_{A*}}X_{AE} + X_A - X_AX_{Ac}\right)}{\left(\frac{C_{B*}}{C_{A*}} + X_{Ac}\right)} \qquad (8)$$

By elimination and factorization, Eq. (8) reduces to:

$$\frac{dX_A}{dt} = k_1\frac{\left(\frac{C_{B*}}{C_{A*}} + 1\right)(X_{Ac} - X_A)}{\left(\frac{C_{B*}}{C_{A*}} + X_{Ac}\right)} \qquad (9)$$

Integration of Eq. (9) gives:

$$-\ln\left(1 - \frac{X_A}{X_{Ac}}\right) = \frac{\left(\frac{C_{B*}}{C_{A*}} + 1\right)k_1t}{\left(\frac{C_{B*}}{C_{A*}} + X_{Ac}\right)} \qquad (10)$$

Therefore a plot of $-\ln(1\text{-}X_A/X_{Ac})$ versus time will give a straight line and from the gradient k_1 can be obtained. In effect, Eq. (10) may be regarded as a pseudo-first order irreversible reaction and in this respect is analogous to Eq. (2).

In order to derive the rate constant for the pseudo-second order sorption mechanism:

The peat-copper reaction may be represented in two ways [41]:

$$2P^- + Cu^{2+} \Leftrightarrow CuP_2 \qquad (11)$$

or

$$2HP + Cu^{2+} \Leftrightarrow CuP_2 + 2H^+ \qquad (12)$$

where P^- and HP are polar sites on the peat surface.

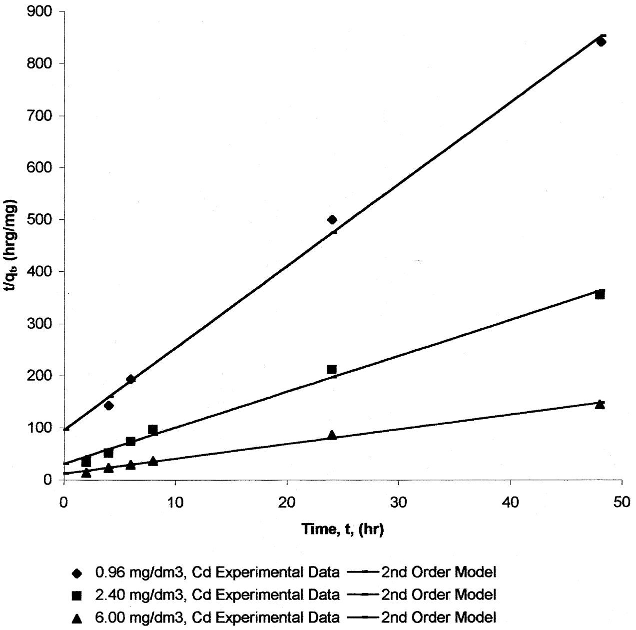

Fig. 13. Pseudo-second order sorption kinetics of cadmium(II) onto beech leaves at various initial concentrations.

A pseudo-second order rate expression based on sorption equilibrium capacity may be derived from Eqs. (11) and (12). If the pseudo-second order kinetic model holds true, the rate law for the reaction is expressed as:

$$\frac{d(P)_t}{dt} = k[(P)_0 - (P)_t]^2 \qquad (13)$$

or

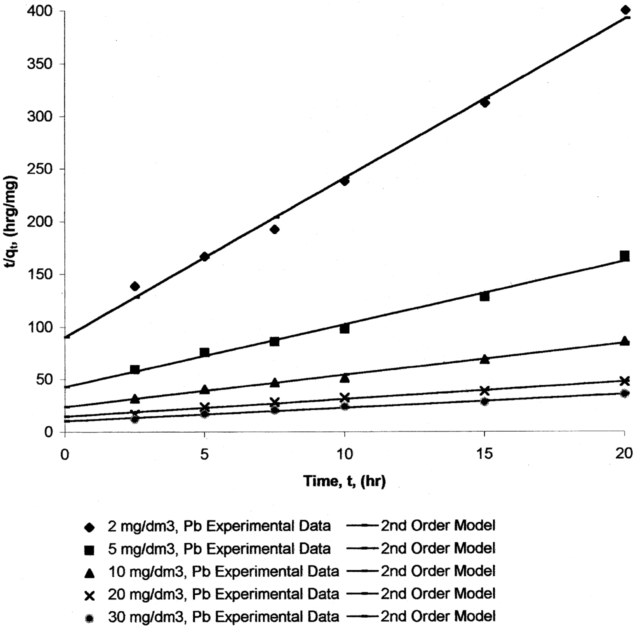

Fig. 14. Pseudo-second order sorption kinetics of lead(II) onto cypress leaves at various initial concentrations.

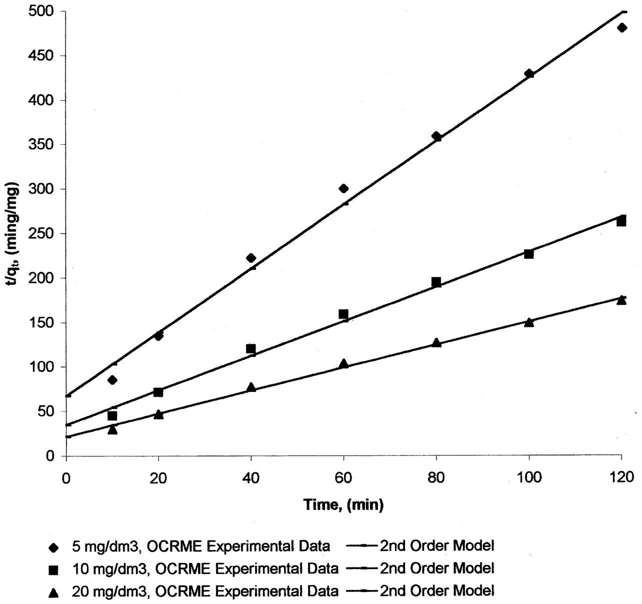

Fig. 15. Pseudo-second order sorption kinetics of Omega Chrome Red ME on fly ash at various initial concentrations.

$$\frac{d(HP)_t}{dt} = k[(HP)_0 - (HP)_t]^2 \qquad (14)$$

where

$(P)_t$ and $(HP)_t$ are the number of active sites occupied on the sorbent at time t,
$(P)_o$ and $(HP)_0$ are the number of equilibrium sites available on the sorbent.

It is assumed that the sorption capacity is proportional to the number of active sites occupied on the sorbent, then the kinetic rate law can be rewritten as

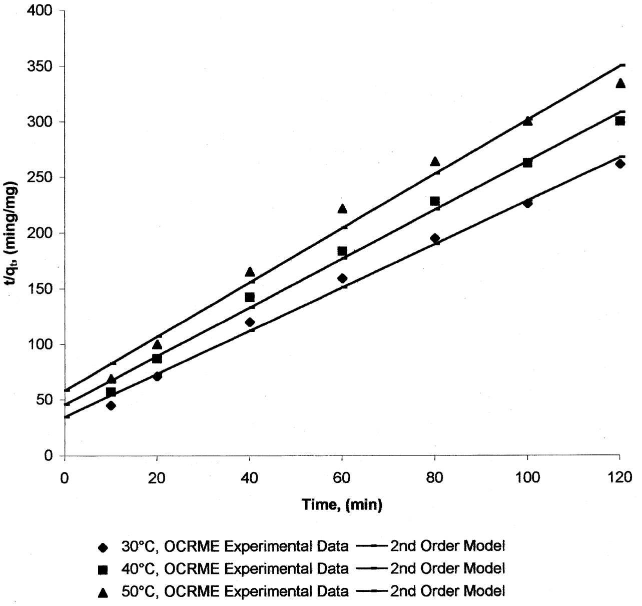

Fig. 16. Pseudo-second order sorption kinetics of Omega Chrome Red ME on fly ash at various temperatures.

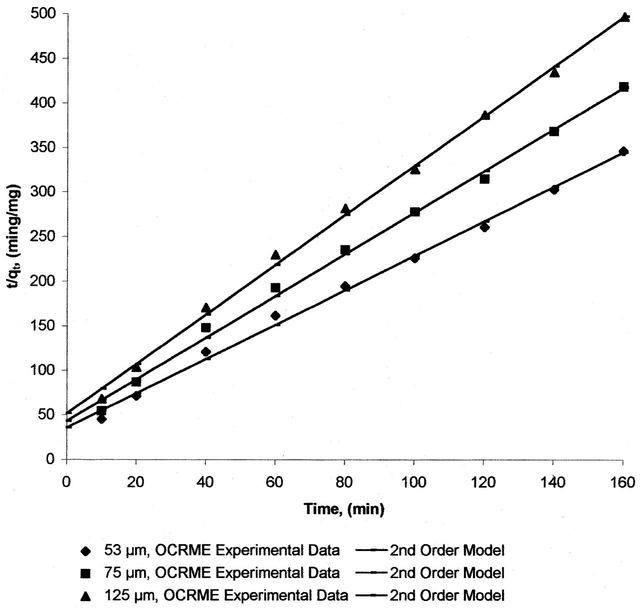

Fig. 17. Pseudo-second order sorption kinetics of Omega Chrome Red ME on fly ash at various particle sizes.

follows:

$$\frac{dq_t}{dt} = k(q_c - q_t)^2 \tag{15}$$

where

k is the rate constant of sorption (g/mg min),
q_c is the amount of soluted sorbate sorbed at equilibrium (mg/g),
q_t is amount of soluted sorbate on the surface of the sorbent at any time t (mg/g).

Separating the variables in Eq. (14) gives:

$$\frac{dq_t}{(q_c - q_t)^2} = k\ dt \tag{16}$$

Integrating this for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, gives:

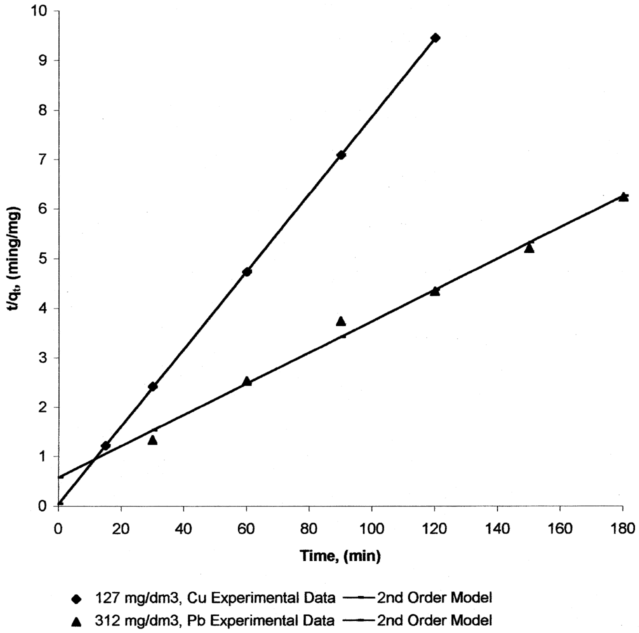

Fig. 19. Pseudo-second order sorption kinetics of copper(II) and lead(II) onto bottom ash.

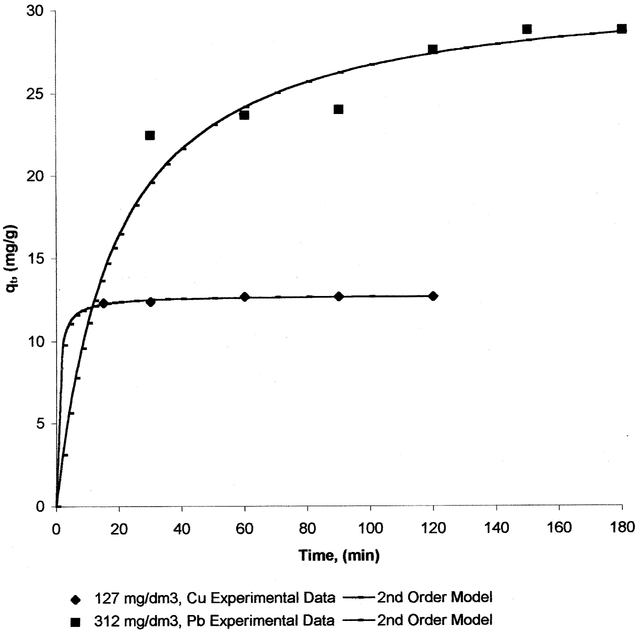

Fig. 18. Plot of sorbed capacity versus time for effect of metal ions on the sorption kinetics of copper(II) and lead(II) onto bottom ash.

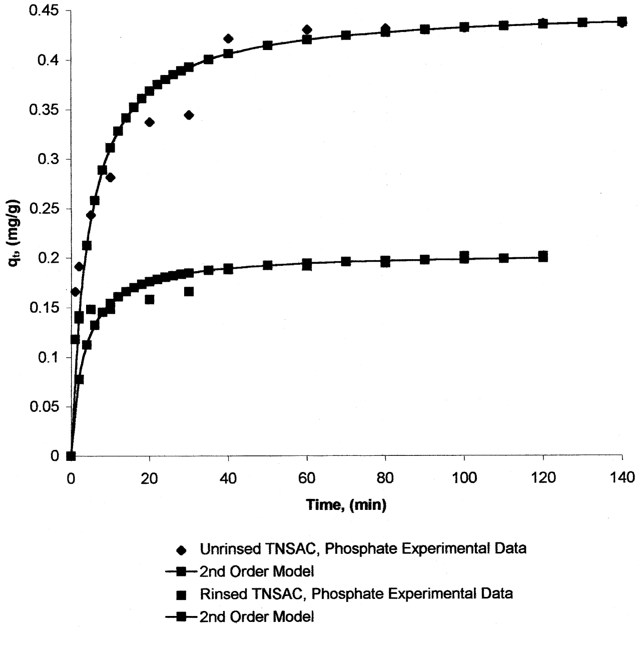

Fig. 20. Plot of sorbed capacity versus time for effect of unrinsed and rinsed TNSAC on the sorption kinetics of phosphate onto TNSAC.

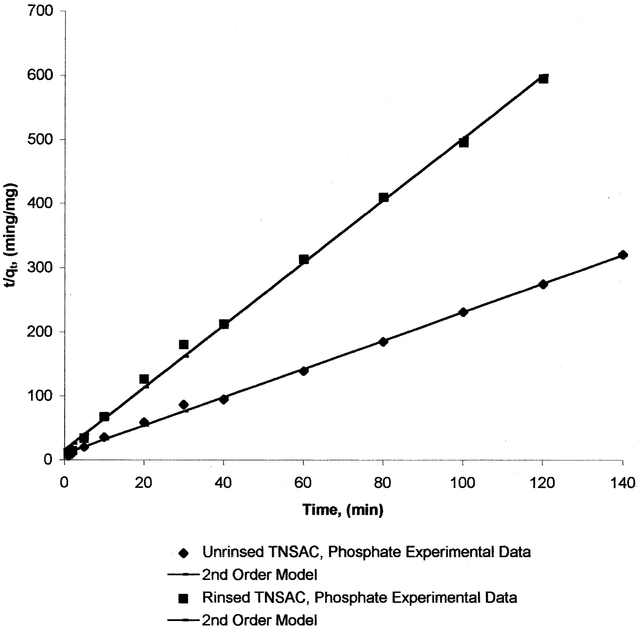

Fig. 21. Pseudo-second order sorption kinetics of phosphate onto TNSAC.

$$\frac{1}{(q_c - q_t)} = \frac{1}{q_c} + kt \tag{17}$$

which is the integrated rate law for a pseudo-second order reaction.

Eq. (17) can be rearranged to obtain:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_c}t \tag{18}$$

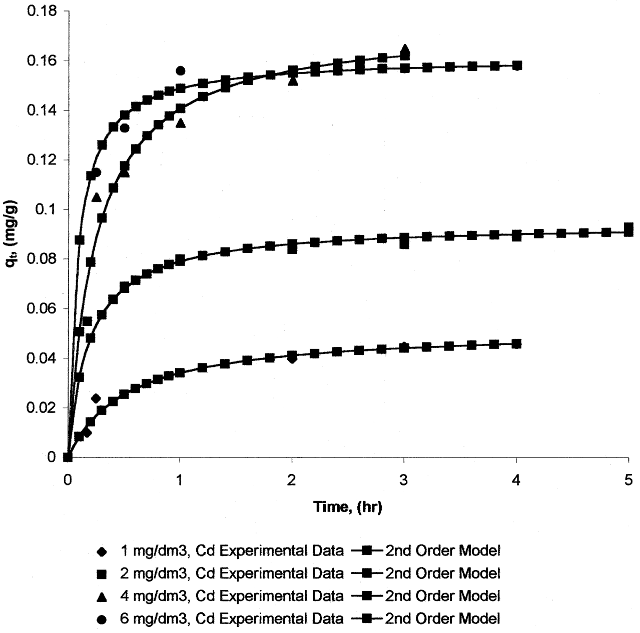

Fig. 22. Plot of sorbed capacity versus time for effect of initial concentration on the sorption kinetics of cadmium(II) onto dry reed leaves.

The constants can be determined by plotting t/q_t against t.

4. Results and discussion

Table 1 shows the mechanism of sorption for various systems reported in the literature since 1984.

Fig. 1 shows a plot of the linearized form of the pseudo-first order model in Eq. (2) for the sorption of copper(II) onto peat at various initial copper(II) concentrations for the initial 20 min. However, the experimental data deviate considerably from the theoretical data after this short period. The rate of sorption was assumed to be proportional to the difference between the maximum capacity, q_c, at equilibrium and the capacity at any time, t, of the sorbed in a first order at the initial reaction stage. Fig. 2 shows a plot of the linearized form of the first order model using liquid phase copper concentration in Eq. (2) for the sorption of copper(II) onto peat at various initial copper(II) concentrations for the initial 20 min. Fig. 3 shows a plot of the linearized form of the pseudo-second order model in Eq. (17) for the sorption of copper(II) onto peat at various initial copper(II) concentrations. The correlation coefficients for the linear plots of t/q_t against time from the pseudo-second order rate law are greater than 0.996 for all systems for contact times of 120 min. This suggests that this sorption system is not a first order reaction and that the pseudo-second order model, based on the assumption that the rate-limiting step may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate, provides the best correlation of the data.

Panday et al. [42] have found that for sorption of chromium(VI) using a homogeneous mixture of fly ash and wollastonites is first governed by diffusion followed by surface compound formation. Multiple pseudo-first order kinetics have been represented in some sorption systems such as proteins/silica [23], mercury(II)/kaolinite [21] and persostent/kaolinite [24]. Basically a multiple pseudo-first order process means that a plot of $\ln(q_1 - q_t)$ versus time can be divided into two or three linear sections, each linear section representing a pseudo-first order reaction mechanism. In the multiple first order kinetics sorption process, one stage corresponds to the initial binding or anchorage of protein molecules with the active spots of the solid surface by removal and reorganization of surface-bound water. The other stage represents the denaturation and reorganization of the bound biopolymer at the interface, leading to the formation of spread films [23]. Atun and Sismanoglu [24] reported that in the case of two kinetic steps, the first step of sorption was more rapid than the

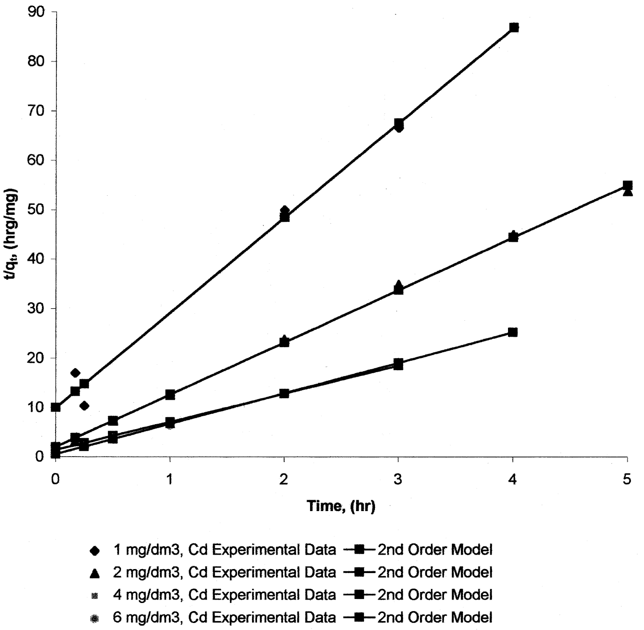

Fig. 23. Pseudo-second order sorption kinetics of cadmium(II) onto dry reed leaves at various initial concentrations.

second one and the sorption rate is controlled by either a film diffusion or an intraparticle diffusion mechanism. This might be because kaolinite is a clay and its macroscopic structure is probably closer to a micro-porous 'honeycomb' than a macroporous 'capillary' system [85]. Furthermore, Varshney et al. [22] reported that the kinetics of sorption of the pesticide phosphamidon on beads of antimony(V) phosphate cation exchanger was completed in two steps. In the first step, the sorbate molecules are sorbed on the surface where there are no other such molecules and consequently the sorbate–sorbate interaction is negligible, leading to the formation of a monolayer. As this monolayer approaches saturation, a process of rearrangement may start with a further increase in the sorbate molecules, which constitutes the second step.

A comparison of the mechanisms from the literature and the pseudo-second order analysis from this study is shown in Table 2. The pseudo-first order sorption rate expression of Lagergren has been widely used. Many studies have been investigated: Khare et al. [34] reported that the sorption of Victoria Blue by fly ash is diffusion controlled and the process follows the pseudo-first order sorption rate expression of Lagergren; the sorption of nickel(II) by wollastonite is diffusion controlled and the process follows the pseudo-first order sorption rate expression of Lagergren [3]; the sorption of low level chromium(VI) from aqueous solution by bismuth trioxide is an exothermic sorption process and follows the pseudo-first order sorption rate expression of Lagergren [39]; and the sorption of *o*-cresol (OCL) and *p*-nitrophenol (PNP) from aqueous solution by fly ash are endothermic sorption processes. Intraparticle diffusion was found to be rate-limiting following the pseudo-first order sorption rate expression of Lagergren [38]. The sorption of copper(II) from water by both peanut hull carbon (PHC) and commercial granular activated carbon (GAC) also follows the pseudo-first order sorption rate expression of Lagergren [3]. In addition, Salim et al. [27] reported that the uptake of cadmium(II) on beech leaves is a first order reaction with respect to cadmium(II) and the rate-limiting step is mainly diffusion. Salim et al. [28] reported that the reaction mechanism process was the sorption of lead(II) on cypress leaves. The rate-limiting step was concluded to be film diffusion, followed by a fractional order kinetic step of 0.7. Gupta et al. [45] reported that the sorption of Omega Chrome Red ME (OCRME) from water by fly ash is a first order exothermic process. A first order rate expression [2], Eq. (9), based on solution concentration has been used to represent the sorption of Omega Chrome Red ME using fly ash. However, the best fit model for all these sorption systems might possibly be the pseudo-second order sorption rate expression. Figs. 4–17 show plots of the linearized form of the pseudo-second order model in Eq. (18) for all 12 of these sorption systems. The correlation coefficients for the linear plots of t/q_t against time from the pseudo-second order rate law are greater than 0.982 for all systems.

Removal of copper(II) and lead (II) from wastewater by sorption on bottom ash has been reported [36]. Fig. 18 shows contact time curves with bottom ash and the results are also shown in Fig. 19 as a plot of t/q_t against time for sorption of copper(II) and lead(II) for the pseudo-second order model. The values of the correlation coefficients are all extremely high (>0.990). The sorption of phosphate using both unrinsed and rinsed tamarind nut shell activated carbon (TNSAC) has been investigated [37]. Fig. 20 shows contact time curves with bottom ash and the results are also shown in Fig. 21 as a plot of t/q_t against time for sorption of phosphate for the pseudo-second order model. The values of the correlation coefficients are all extremely high (>0.998). The removal of cadmium(II) from aqueous solution by reed leaves has been studied [40]. Fig. 22 shows a series of contact time curves with bottom ash and the results are also shown in Fig. 23 as a plot of t/q_t against time for sorption of phosphate for the pseudo-second order model. The values of the correlation coefficients are all extremely high (>0.991).

5. Conclusions

The kinetics of sorption of Victoria Blue, aromatic compounds, *p*-nitrophenol and *o*-cresol, a chrome dye, Omega Chrome Red ME (OCRME) on fly ash, of copper(II) on peat and bottom ash, bicarbonate-treated peanut hulls (PHC) and activated carbon (GAC), of nickel(II) on wollastonite, of chromium(VI) on Bi_2O_3, of cadmium(II) on beech and reed leaves, of lead(II) on cypress leaves and bottom ash and phosphate on tamarind nut shell activated carbon (TNSAC) were analysed on the basis of the pseudo-second order rate mechanism. For all of the systems studied, chemical reaction seems significant in the rate-controlling step and the pseudo-second order chemical reaction kinetics provide the best correlation of the experimental data, whereas the pseudo-first order model proposed fits the experimental data well for an initial period of the first reaction step only. However, over a long period the pseudo-second order model provides the best correlation for all of the systems studied.

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