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
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 though 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 Chatteraj [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'-isopropylidenediphenol (Bis-phenol A) and diphenyldipropylene-4,4'-diosy-acetic 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>
<thead>
<tr>
<th>Sorbent</th>
<th>Solute</th>
<th>Model</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Giridih coal and Coconut shell</td>
<td>Cd(II)</td>
<td>1st order</td>
<td>Bhattacharya and Venkobachar [2]</td>
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<tr>
<td>Fly ash/Wollastonite</td>
<td>Cr(VI)</td>
<td>1st order</td>
<td>Pandey et al. [42]</td>
</tr>
<tr>
<td>Fly ash</td>
<td>Cu(II)</td>
<td>1st order</td>
<td>Panday et al. [43]</td>
</tr>
<tr>
<td>Peat</td>
<td>Cu(II), Cd(II), Ni(II) and Zn(II)</td>
<td>2nd order</td>
<td>Gosset et al. [12]</td>
</tr>
<tr>
<td>Hydrous ferric oxide</td>
<td>Cd(II)</td>
<td>2nd order</td>
<td>Dzombak and Morel [20]</td>
</tr>
<tr>
<td>Fly ash</td>
<td>Victoria Blue</td>
<td>1st order</td>
<td>Khare et al. [34]</td>
</tr>
<tr>
<td>Peat</td>
<td>Pb(II)</td>
<td>2nd order</td>
<td>Ho and McKay [44]</td>
</tr>
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<td>Fe(II)</td>
<td>1st order</td>
<td>Singh et al. [35]</td>
</tr>
<tr>
<td>Fly ash</td>
<td>OCRME</td>
<td>1st order</td>
<td>Gupta et al. [45]</td>
</tr>
<tr>
<td>1:1 Fly ash and coal</td>
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<td>1st order</td>
<td>Gupta et al. [45]</td>
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<td>Fly ash</td>
<td>Fluoride</td>
<td>1st order</td>
<td>Chaturvedi et al. [46]</td>
</tr>
<tr>
<td>Peat</td>
<td>CN⁻</td>
<td>2nd order</td>
<td>Cancela et al. [47]</td>
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<td>Wollastonite</td>
<td>Ni(II)</td>
<td>1st order</td>
<td>Sharma et al. [7]</td>
</tr>
<tr>
<td>China clay</td>
<td>Ni(II)</td>
<td>1st order</td>
<td>Sharma et al. [8]</td>
</tr>
<tr>
<td>Groundnut husk carbon</td>
<td>Cr(VI)</td>
<td>1st order</td>
<td>Periasamy et al. [48]</td>
</tr>
<tr>
<td>Banana pith</td>
<td>Acid violet</td>
<td>1st order</td>
<td>Namasiyavam and Kanchana [49]</td>
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<tr>
<td>Beech leaves</td>
<td>Cd(II)</td>
<td>1st order</td>
<td>Salim et al. [27]</td>
</tr>
<tr>
<td>Coconut shell carbons</td>
<td>Cr(VI)</td>
<td>1st order</td>
<td>Rao et al. [50]</td>
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<td>Biogas residual slurry</td>
<td>Congo Red</td>
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<td>Namasiyavam and Yamuna [51]</td>
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<tr>
<td>Biogas residual slurry</td>
<td>Rhodamine-B</td>
<td>1st order</td>
<td>Namasiyavam and Yamuna [52]</td>
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<td>Biogas residual slurry</td>
<td>Acid Brilliant Blue</td>
<td>1st order</td>
<td>Yamuna and Namasiyavam [53]</td>
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<tr>
<td>Peanut hull carbon</td>
<td>Hg(II)</td>
<td>1st order</td>
<td>Namasiyavam and Periasamy [54]</td>
</tr>
<tr>
<td>Waste tea, Turkish coffee, Exhausted coffee, Nut shell and Walnut shell</td>
<td>Cr(VI), Cd(II), Al(III)</td>
<td>1st order</td>
<td>Orhan and Büyükgün-goğ [55]</td>
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<tr>
<td>Peat</td>
<td>Cr(VI)</td>
<td>2nd order</td>
<td>Sharma and Forster [13]</td>
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<tr>
<td>Silica</td>
<td>Lysozyme, β-Lactoglobulin and Hemoglobin</td>
<td>0.7 order</td>
<td>Sarkar and Chattoraj [23]</td>
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<td>Fe(III)/Cr(III) hydroxide</td>
<td>Cr(VI)</td>
<td>1st order</td>
<td>Namasiyavam and Ranganathan [56]</td>
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<td>Namasiyavam et al. [57]</td>
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<td>Phenol, o-Cresol, m-Cresol, p-Cresol, o-Nitrophenol, m-Nitrophenol and p-Nitrophenol</td>
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<td>Singh and Rawat [38]</td>
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<tr>
<td>Bi₂O₃</td>
<td>Cr(VI)</td>
<td>1st order</td>
<td>Bhutani and Kumari [39]</td>
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<tr>
<td>Peanut hull carbon</td>
<td>Cd(II)</td>
<td>1st order</td>
<td>Periasamy and Namasiyavam [58]</td>
</tr>
<tr>
<td>Leaf mould</td>
<td>Cr(VI)</td>
<td>2nd order</td>
<td>Sharma and Forster [14]</td>
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<td>Cypress leaves</td>
<td>Pb(II)</td>
<td>0.7 order</td>
<td>Salim et al. [28]</td>
</tr>
<tr>
<td>Peat</td>
<td>Cu(II)</td>
<td>2nd order</td>
<td>Ho et al. [16]</td>
</tr>
<tr>
<td>Peanut hull carbon</td>
<td>Pb(II)</td>
<td>1st order</td>
<td>Periasamy and Namasiyavam [59]</td>
</tr>
<tr>
<td>Peanut hull carbon</td>
<td>Ni(II)</td>
<td>1st order</td>
<td>Periasamy and Namasiyavam [60]</td>
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<td>Ni(II)</td>
<td>2nd order</td>
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<td>Fe(III)/Cr(III) hydroxide</td>
<td>Cd(II)</td>
<td>1st order</td>
<td>Namasiyavam and Ranganathan [61]</td>
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<td>Water hyacinth roots</td>
<td>Merthylene Blue</td>
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<td>Low et al. [10]</td>
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<td>Moss and Copper-coated moss</td>
<td>Cr(III) and Cr(VI)</td>
<td>1st order</td>
<td>Lee et al. [62]</td>
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<td>Algae</td>
<td>Lauryl benzyl sulphonate</td>
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<td>Fernandez et al. [63]</td>
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<td>Direct red 12 B</td>
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<td>Namasiyavam and Yamuna [64]</td>
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<tr>
<td>Biogas residual slurry</td>
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Table 1 (Continued)

<table>
<thead>
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<th>Sorbent</th>
<th>Solute</th>
<th>Model</th>
<th>Reference</th>
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<td>Activated carbon</td>
<td>CN−</td>
<td>*1st order</td>
<td>van Deventer and van der Merwe [67]</td>
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<td>Hydrous ceric oxide</td>
<td>Cd(II)</td>
<td>1st order</td>
<td>Mishra and Singh [68]</td>
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<td>Hydrous zirconium oxide</td>
<td>Hg(II)</td>
<td>1st order</td>
<td>Mishra et al. [69]</td>
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<td>Kaolinitic clay</td>
<td>Pb(II)</td>
<td>1st order</td>
<td>Orumwense [70]</td>
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<td>Immobilized bimomass</td>
<td>Cu(I) and Pb(II)</td>
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<td>Ramelow et al. [29]</td>
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<td>Singh et al. [71]</td>
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<td>Haematite</td>
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<td>Dasmahapatra et al. [72]</td>
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<td>Cu(II)</td>
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<td>Periasamy and Namasivayam [73]</td>
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<td>Lanthanum-impregnated silica gel</td>
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<td>Peat</td>
<td>Cu(II) and Ni(II)</td>
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<td>Activated carbon</td>
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<td>Sharma and Forster [15]</td>
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<td>Biopolymers</td>
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<td>Seki and Suzuki [11]</td>
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<td>1st order</td>
<td>Mittal and Gupta [76]</td>
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<td>Kaolinite</td>
<td>Bis Acid A2</td>
<td>1st order</td>
<td>Atun and Sismanogly [24]</td>
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<td>Antimony(V) phosphate cation exchanger</td>
<td>Bisphenol A</td>
<td>*1st order</td>
<td>Varshney et al. [22]</td>
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<td>Pesticide phosphamidon</td>
<td>Pesticide phosphamidon</td>
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<td>Varshney et al. [22]</td>
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<td>Orange peel</td>
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<td>Lee et al. [78]</td>
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<td>Fe(III)/Cr(III) hydroxide</td>
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<td>Namasivayam and Senthilkumar [79]</td>
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<td>Red mud</td>
<td>Congo red</td>
<td>1st order</td>
<td>Namasivayam and Arasi [81]</td>
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<td>Isoprotron</td>
<td>+1st order</td>
<td>Worrall et al.[30]</td>
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<td>Soil</td>
<td>Acifluorfen</td>
<td>*1st order</td>
<td>Locke et al. [31]</td>
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<td>Soil</td>
<td>Hg(II)</td>
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<td>Yin et al. [82]</td>
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<td>Chitin</td>
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<td>2nd order</td>
<td>Kim et al. [83]</td>
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<td>Fly ash</td>
<td>o-xylene</td>
<td>*1st order</td>
<td>Banerjee et al. [84]</td>
</tr>
</tbody>
</table>

* 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.

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 Sinjg et al.
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].

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:

$$\frac{dq_t}{dt} = k_{S1}(q_1 - q_t)$$  \hspace{1cm} (1)

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

$$\log(q_1 - q_t) = \log(q_1) - \frac{k_{S1}}{2.303} t$$  \hspace{1cm} (2)

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

<table>
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<th>Sorbent</th>
<th>Solute</th>
<th>Best fit model</th>
<th>Literature mechanism</th>
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<td>Fly ash</td>
<td>Victoria Blue</td>
<td>Pseudo 2nd order</td>
<td>Pseudo 1st order</td>
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<td>Wollastonite</td>
<td>Ni(II)</td>
<td>Pseudo 2nd order</td>
<td>Pseudo 1st order</td>
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<td>Bi_2O_3</td>
<td>Cr(VI)</td>
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<td>Pseudo 1st order</td>
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<td>Peat</td>
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<td>OCL and PNP</td>
<td>Pseudo 2nd order</td>
<td>Pseudo 1st order</td>
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<td>PHC and GAC</td>
<td>Cu(II)</td>
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<td>Pseudo 1st order</td>
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<td>Beech leaves</td>
<td>Cd(II)</td>
<td>Pseudo 2nd order</td>
<td>*1st Order</td>
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<td>Cypress leaves</td>
<td>Pb(II)</td>
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<td>*0.7 Order</td>
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<td>OCRME</td>
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<td>*1st Order</td>
</tr>
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<td>Bottom ash</td>
<td>Cu(II) and Pb(II)</td>
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<td>Diffusion</td>
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<td>TNSAC</td>
<td>Phosphate</td>
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<td>None</td>
</tr>
<tr>
<td>Reed leaves</td>
<td>Cd(II)</td>
<td>Pseudo 2nd order</td>
<td>None</td>
</tr>
</tbody>
</table>

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

\[
\frac{dC_B}{dt} = -\frac{dC_A}{dt} = C_A^* \frac{dX_A}{dt} = k_1 C_A - k_2 C_B
\]

\[= k_1 (C_A^* - C_A X_A) - k_2 (C_B^* - C_A X_A)\] \(3\)

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

\[
\frac{dC_B}{dt} = \frac{dC_A}{dt} = 0
\] \(4\)

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.

\[ K_c = \frac{C_{B^*}}{C_{A^*}} \]

where

\[ X_{Ac} = \frac{C_{Bc}}{C_{Ac}} \]

\[ K_c = \frac{C_{B^*}X_{Ac}}{C_{A^*} + X_{Ac}} \]

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

\[ K_c = \frac{C_{Bc}}{C_{Ac} - C_{A^*}X_{Ac}} \]

where 

\( C_{Bc} \) and \( C_{Ac} \) are the equilibrium concentrations for soluted sorbate on the sorbent and solution, respectively.
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 $k_2 = k_1/k_3$ in Eq. (3);
2. substituting $K_e$ by Eq. (6).

Now, Eq. (3) becomes:

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

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

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

Integration of Eq. (9) gives:

$$- \ln \left( \frac{1 - X_A}{X_{Ac}} \right) = \frac{1}{k_1} \left( \frac{C_{B^*}}{C_{A^*}} + 1 \right) t$$

Therefore a plot of $- \ln(1 - X_A/X_{Ac})$ 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]:

$$2P^- + Cu^{2+} \leftrightarrow CuP_2$$  \hspace{1cm} (11)

or

$$2HP + Cu^{2+} \leftrightarrow CuP_2 + 2H^+$$  \hspace{1cm} (12)

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

$$\frac{d(P)_t}{dt} = k[(P)_0 - (P)_t]^2$$  \hspace{1cm} (13)

or

$$\frac{d(HP)_t}{dt} = k[(HP)_0 - (HP)_t]^2$$  \hspace{1cm} (14)

where

- $(P)_t$ and $(P)_0$ are the number of active sites occupied on the sorbent at time $t$,
- $(HP)_t$ 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...
follows:

\[
\frac{dq_t}{dt} = k(q_c - q_t)^2
\]

(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).

Integrating this for the boundary conditions \( t = 0 \) to \( t = t \) and \( q_t = 0 \) to \( q_t = q_t \), gives:

\[
\frac{dq_t}{(q_c - q_t)^2} = k \, dt
\]

(16)

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

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

\( q_t \) is amount of soluted sorbate on the surface of the sorbent at any time \( t \) (mg/g).

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.

\[
\frac{1}{q_t} - \frac{1}{q_c} = \frac{1}{q_c} kt
\]

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

Eq. (17) can be rearranged to obtain:

\[
\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_c} t
\]

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 \( \ln(q_t - q) \) 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 $t/q$ 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 $t/q$ 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 $t/q$ 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 $t/q$ 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 Br2O3, 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 reaction 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.

References


