

Full Length Research Paper

A diffusion-chemisorption kinetic model for simulating biosorption using forest macro-fungus, *fomes fasciatus*

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Accepted 12 August 2010

Research into the development of cheaper technologies for the interception and treatment of heavy-metal-laden waste streams continues unabated. Biosorption using low-cost media provides an attractive alternative. The kinetic manner of a forest product, macro-fungus *Fomes fasciatus*, was analysed for the selection of an appropriate kinetic model. All experiments were conducted using Cu(II) as a model cation. The kinetic effect of initial Cu(II) concentration and sorbent size was studied in a batch laboratory-scale reactor. *Fomes fasciatus* exhibited an affinity to Cu(II) ions and approached maximum sorption efficiency as initial concentrations increased beyond 100 mg/l. The sorption process was more complex than that to be scripted by pseudo-first-order kinetics. Pseudo-second-order modelling produced a more defined simulation, however, the precision diminished as sorbent size increased. Intraparticle diffusion modelling showed an increasing conformity to increased sorbent size. The mechanisms of biosorption were found to be controlled by film diffusion or combined with surface adsorption during the initial stages. This was followed by a tangled combination of diffusion and chemisorption for the subsequent 98% of the reaction period. A diffusion-chemisorption model was successfully used to simulate the entire period of biosorption kinetics. Additionally, the model produced a good correlation to the reaction variables which not only advanced the development of predictive models involving *Fomes fasciatus* but can also improve the development of full-scale batch sorption systems.

Keywords: biosorption; kinetics; macro-fungus; heavy metal; chemisorption; copper (II); intraparticle diffusion

INTRODUCTION

Despite the extensively publicised global episodes on heavy metal contamination in rivers and streams, there exists a continuous and ubiquitous presence of metal ions in waters, sediments and marine organisms. These environmentally pertinacious contaminants in drinking water (above permissible limits) may cause possible damage to the ecosystem, to the health of human beings, and places an insuperable burden on treatment plants. Available technologies for removal of metals from waste

streams such as ion exchange, chemical precipitation and adsorption using activated carbon are often viewed by small industries as uneconomical and a financially burdensome option. Kulshreshtha and Venkobachar (2008) described biosorption to involve the use of biological materials, dead or alive, for heavy metal removal and recovery. According to Vieira and Volesky (2000) the origin of biomass is paramount to its selection and can come from: (i) industrial wastes which should be obtained free of charge; (ii) organisms easily available in large amounts in nature; and (iii) organisms of rapid growth, especially cultivated or propagated for biosorption purposes.

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Development of biosorption technologies using low-cost, abundantly available, natural heterogeneous materials continues to gain considerable momentum. This is mainly due to: (i) the low attainable treatment levels; (ii) the ability to remove and recover metal ions; and (iii) the low capital and operating costs. The effective development of such systems requires the biosorption process to be scrutinised and the effect of changing operating conditions, on sorption mechanisms, must be quantified.

The kinetic simulation of batch biosorption processes involving heavy metals is most commonly done using first-order, second-order and intraparticle diffusion models. In 1898 Lagergren presented a kinetic expression (Kannan and Murugavel, 2008) which assumes a first-order rate based on surface reactions. Ho and McKay (1998a) later described the equation as pseudo-first-order. The expression has been successfully applied to biosorbents like green algae (Doshi et al., 2008) and fungal biomass (Bishnoi et al., 2007). Ho and McKay (1998b) presented a pseudo-second-order equation based on chemisorption for heavy metal removal. This model has been successfully applied to biosorbents such as coir (Quek et al., 1998), sago waste (Quek and Wase, 1998), fungus (Fu and Viraraghavan, 2000), bacteria (Aksu and Tezer, 2000), bakers yeast (Padmavathy et al., 2002) and macro-fungus (Pan et al., 2005). However, Wu et al. (2000) highlighted that the equation did not give definite mechanisms while studying dye and metal biosorption by chitosan. Krim et al. (2006) describe fungi sorption of chromium using pseudo-second-order kinetics and showed intraparticle diffusion to be significant at lower concentrations.

A commonality among biosorbents is their inherent complex physical, chemical and biological characteristics, eliciting the need for testing multiple kinetic models to achieve the best possible simulation. The accuracy of fit is paramount in the development of predictive models. In this investigation, the effect of metal concentration and sorbent size on sorption kinetics using a new biosorbent *Fomes fasciatus*, is reported. Kinetic simulation of the biosorption process is examined using four models: Lagergren model (Kannan and Murugavel, 2008); pseudo-second-order model (Ho and McKay, 1998b); Weber and Morris intraparticle model (Weber and Morris, 1962), and a recently developed diffusion-chemisorption model (Sutherland, 2004). Sorption processes were modelled in an attempt to explicate the rate limiting steps in the reaction and select an appropriate kinetic model which can: (i) quantify the effect of changing solution and sorbent parameters; and (ii) aid in the eventual development of predictive models that enable process design of batch treatment systems with minimal experimentation.

MATERIALS AND METHODS

Sampling and Identification of Biosorbent

Batch adsorption studies were carried out using a wood rotting macro-fungus found growing in the central range forest of Trinidad. This evergreen seasonal forest covers 40,136 hectares of natural and cultivated forest. The main species of trees found are crappo (*Carapa guianensis*) and guatecare (*Eschweilera subglandulosa*) as well as extensive teak (*Tectona grandis*) plantations. This macro-fungus, which is not used in Trinidad as a commercially viable mushroom, was found growing on dead tree trunks. Samples were collected and placed in plastic bags in the field along with a sample of the decaying wood substrate. The sample was subsequently identified with the assistance of the Royal Botanical Gardens, Kew, UK, and the Herbarium at the University of the West Indies, Trinidad to be *Fomes fasciatus* (Swartz : Fries) Cooke, belonging to the order Polyporales and family Polyporaceae.

Preparation of Biosorbent

In preparation for biosorption experiments, the hand-picked macro-fungus specimens were separated from the wood substrate, dried at 90 °C for 1 hour, and then pulverized in a mortar and pestle. They were subsequently washed in distilled water and sieved into different sizes.

Analytical Methods

Cu(II), a model cation, was selected for these experiments. Copper stock solution was prepared from copper sulphate in distilled water (prepared by a Corning Mega Pure System MP-1 of pH approximately 7 and conductivity < 10 µmhos/cm) and estimated by the Cuprethol method (APHA, 1971). The intensity of the coloured complex formed was measured at 435 nm using an ultraviolet spectrophotometer (Milton Roy – Spectronic 601). The determination of copper was verified periodically using an Atomic Adsorption Spectrophotometer, (Perkin-Elmer 3030B). Conductivity of the reaction solution was measured using a conductance bridge (YSI Model 31A). A constant pH (of 5.5) was maintained throughout the reaction by a 0.01M acetate buffer and measured using a pH meter (Accumet Research-AR10, Fisher Scientific).

Biosorption Studies

Kinetic studies for metal uptake were carried out in triplicate in a batch reactor with an adsorbent mass of 1.0 g/l and spiked with 50 ml of synthetic Cu(II) solutions in 100 ml conical flasks. Sorbent masses were accurate to ±0.001 g and solution volumes to ±0.5 ml. The study of adsorbent size was carried out by varying particle geometric mean size, (GMS) (0.5, 0.65 and 1.1 mm) while the study of adsorbate was carried out by varying Cu(II) solutions (21.5, 53.6, 98 and 211 mg/l). The reaction mixtures were agitated in a mechanical shaker at 200 rpm and stopped at predetermined time intervals between 1 and 60 minutes. The biosorbent, *Fomes fasciatus*, was then separated by gravity filtration using Whatman No. 2 (8.0 µm) qualitative filter paper. The filtrate was subsequently tested for residual metal ions. A blank comprising distilled water and *Fomes fasciatus* was prepared to monitor and control any interference due to leaching during the test period. To determine the optimum pH, the reactor was influenced by the addition of appropriate amounts of HCl and NaOH to achieve pH within the

range of 2.5 to 10. Maximum biosorption was observed to occur at pH 5.5. The amount of Cu(II) ion adsorbed per unit mass of adsorbent was obtained using the equation:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

Where q_e (mg/g) is the mass of adsorbate adsorbed per mass of adsorbent, C_o (mg/l) is the initial concentration of metal ions in solution, C_e (mg/l) is the final concentration of metal ion in solution, V (l) is the volume metal ion solution and m (g) is the mass of adsorbent.

Kinetic Models

Pseudo-first-order model

The Lagergren model is given by the derivatives:

$$\frac{dq_t}{dt} = K_{PFO} (q_e - q_t) \quad (2)$$

where,

K_{PFO} = rate constant of pseudo-first order adsorption, (min^{-1})

q_t = mg of Cu(II) absorbed/g of sorbent at any time, t (mg/g)

q_e = amount of adsorption at equilibrium, (mg/g)

After definite integration using the conditions $q_t = 0$ at $t = 0$ and $q_t = q_e$ at $t = t$, the linear form after simplification is presented as:

$$\log_{10}(q_e - q_t) = \log_{10} q_e - \frac{K_{PFO}}{2.303} t \quad (3)$$

Pseudo-second-order model

The pseudo-second-order equation by (Ho and McKay, 1998b), was developed for the sorption of divalent metal ions onto peat moss. The pseudo-second-order equation is as follows:

$$\frac{dq_t}{dt} = K_{PSO} (q_e - q_t)^2 \quad (4)$$

where,

q_t = mg of Cu(II) adsorbed / g of sorbent at any time

q_e = amount of adsorption at equilibrium, (mg/g)

K_{PSO} = pseudo-second-order rate, (g/mg-min)

Integrating and applying the boundary conditions $q_t = 0$ at $t = 0$, and $q_t = q_e$ at $t = t$, the resulting equation can be arranged as follows:

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

where K_{PSO} is the pseudo-second-order rate (g/mg-min) and the initial sorption rate, h , as $t \rightarrow 0$ is expressed as:

$$h = (K_{PSO})q_e^2 \quad (6)$$

Intraparticle diffusion model

Weber and Morris (1962) theorized that the rate of intraparticle diffusion varies proportionally with the half power of time and is expressed as:

$$q_t = K_{id} (t^{1/2}) + c \quad (7)$$

where,

q_t = adsorbate uptake at time t , (mg/g)

K_{id} = the rate constant of intraparticle transport, (mg/g \cdot t $^{1/2}$)

The values of intercept, c are related to the boundary layer thickness, i.e., the larger the value of the intercept, the greater is the boundary layer effect (Kannan and Rengasamy, 2005). According to Weber and Morris (1962), if the rate limiting step is intraparticle diffusion, a plot of solute adsorbed against the square root of the contact time should yield a straight line passing through the origin. Also, the rate constant for intraparticle diffusion is obtained from the slope of the curve.

Diffusion-chemisorption model

An empirical diffusion-chemisorption kinetic model was developed by (Sutherland, 2004) to simulate sorption of heavy metals onto heterogeneous media. To obtain the derivatives, a correlation is made, where the rate of change of concentration of the solid phase, (q_t , mg/g) is equated as a function of rate of mass transfer of Cu(II) ions from the fluid phase to the biosorption site (K_{DC} , mg/g \cdot t $^{0.5}$); the equilibrium sorption capacity (q_e , mg/g); and time to the power of $n-1$, t^{n-1} .

$$\frac{dq_t}{dt} = \frac{nK_{DC}t^{n-1}}{q_e^2} (q_e - q_t)^2 \quad (8)$$

Separating the variables in equation (8) gives:

$$\frac{q_e^2 * dq_t}{(q_e - q_t)^2} = nK_{DC} dt * t^{n-1} \quad (9)$$

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ the integrated form of equation (9) becomes:

$$\frac{q_e^2}{(q_e - q_t)} = K_{DC} t^n + q_e \quad (10)$$

To solve equation (10) using simple linear regression, Sutherland (2004) resolved the exponential factor, n , empirically by non-linear regression analysis of twenty (20) kinetic datasets using the Levenberg-Marquardt algorithm (Marquardt 1963). The analysis show the value of n centred around 0.5. Therefore, rearranging equation (10) and substituting this value of n in the above equation produced the following:

$$q_t = \frac{1}{\frac{1}{q_e} + \frac{1}{K_{DC} * t^{0.5}}} \quad (11)$$

equation (11) can be rearranged as follows:

$$\frac{t^{0.5}}{q_t} = \frac{1}{q_e} * t^{0.5} + \frac{1}{K_{DC}} \quad (12)$$

According to Sutherland (2004), the initial slope of the experimental kinetic curve is found empirically to be a function of the diffusion-chemisorption constants K_{DC} and equilibrium sorption capacity, q_e .

Table 1 - Precision of the pseudo-first-order and pseudo-second-order model for uptake of Cu(II) ions by *Fomes fasciatus*

Sorbent	Sorbate	Pseudo-First-Order Model		Pseudo-Second-Order Model	
		r^2	RPE %	r^2	RPE%
GMS (mm)	C_o mg/l				
	21.5	0.914	67.11	0.999	9.05
	53.6	0.901	53.12	0.998	11.17
	98	0.893	58.67	0.999	10.8
0.5 mm	211	0.6181	76.4	0.999	4.35
	21.5	0.901	50.54	0.999	6.15
	53.6	0.923	45.65	0.996	13.8
	98	0.971	37.65	0.996	11.98
0.65 mm	211	0.932	34.99	0.997	12.9
	21.5	0.975	36.51	0.996	13.14
	53.6	0.945	26.44	0.982	17.53
	98	0.947	29.65	0.992	14.33
1.1 mm	211	0.936	34.06	0.994	13.36

The following relationship is obtained by assuming a linear region, as $t \rightarrow 0$. The initial rate is presented by the empirical relationship:

$$k_i = K_{DC}^2/q_e \quad (13)$$

where,
 k_i is the initial sorption rate (mg/g-t)

Error Analysis

The goodness of fit of the various kinetic models to the experimental data was evaluated by the coefficient of determination, r^2 using Microsoft Excel (version 2003) and the Relative Percent Error (RPE) (Marquardt 1963; Sag and Atkay, 2001).

RESULTS AND DISCUSSIONS

Sorption Kinetics

The phenomenon whereby ions are transferred from a liquid phase to a solid phase usually involves the following steps: (i) boundary layer mass transfer across the liquid film surrounding the particle; (ii) internal diffusion/mass transport within the particle boundary as pore and/or solid diffusion; and (iii) adsorption within the particle and on the external surface (Poots et al., 1976).

According to Allard et al. (1986), there are three further pathways by which sorption may occur unto the surface: (i) physical adsorption which is considered rapid and reversible and is due to non-specific forces of attraction (e.g. Van der Waals forces); (ii) electrostatic adsorption due to coulombic forces of attraction between charged solute species and the adsorbing phase - this process is usually rapid and largely reversible; and (iii) specific adsorption due to the action of chemical forces of attraction which leads to surface bonding at a specific site

on the solid phase - this process can be slow and partly irreversible.

Simulation by the pseudo-first-order model

Precision of the pseudo-first-order model

To test the applicability of the Lagergren model to simulate *Fomes fasciatus* biosorption of Cu(II) ions, twelve (12) sets of experimental kinetic data of varying sorbent size and initial Cu(II) concentrations were analysed by linear regression. The value of q_e is determined by isotherm studies (Sutherland, 2004). Linear plots using equation (3) were carried out and the resulting values of K_{PFO} were found to vary with initial Cu(II) concentration. This implies that the biosorption process may not be following pseudo-first-order kinetics (Singh and Pant, 2006). Coefficient of determination, r^2 , from linear plots of each dataset reveals varying correlations within the range 0.61 to 0.975 (Table 1). A further comparison of the primary kinetic curves and theoretical curves generated using values of q_e and K_{PFO} , was performed by calculating the RPE (Table 1). The resulting elevated values indicated a poor simulation by the Lagergren model and again suggested that the sorption process may be more complex than pseudo-first-order kinetics.

Simulation by pseudo-second-order model

Precision of pseudo-second-order model

Table 1 presents the precision of the pseudo-second-order equation in simulating the kinetics of *Fomes fasciatus* sorption of Cu(II) for various sorbent size and

Table 2 : Precision of the intraparticle diffusion model and diffusion-chemisorption model for uptake of Cu(II) ions by *Fomes fasciatus*

Sorbent GMS (mm)	Sorbate C ₀ mg/l	Intraparticle Diffusion Model		Diffusion-Chemisorption Model	
		r ²	RPE %	r ²	RPE%
0.5	21.5	0.892	8.39	0.999	1.17
	53.6	0.933	5.82	0.994	4.25
	98	0.909	5.84	0.995	3.88
	211	0.505	15.5	0.987	8.26
	21.5	0.808	13.15	0.99	3.94
	53.6	0.961	5.09	0.988	5.07
0.65	98	0.945	6.36	0.992	3.87
	211	0.915	6.52	0.996	3.04
	21.5	0.924	18.52	0.978	5.83
	53.6	0.988	2.55	0.911	9.73
1.1	98	0.976	5.19	0.979	5.12
	211	0.948	6.96	0.986	3.94

initial Cu(II) concentrations. Coefficients of determination, r^2 , for the 12 sets of data, were obtained by linear regression of the experimental data using equation (5). Table 1 reveals r^2 values greater than 0.998 for sorbent GMS 0.5 mm. As the sorbent size increase to GMS 1.1 mm, only slight reduction in correlation is observed. The pseudo-second-order equation therefore appears to successfully represent the sorption process over the span of process variables.

The equation parameters obtained from equation (5) were subsequently used to generate theoretical kinetic curves and were compared to the original primary kinetic data by calculating the RPE. These values are also presented in Table 1, which reveals significantly reduced values as compared to simulations by the Lagergren model. These RPEs were still surprisingly high, considering the high r^2 values obtained from linearization. The values also tend to increase as sorbent size is increased from GMS 0.5 to 1.1 mm.

To further elucidate this variance, observation of the non-linear plots of experimental and generated pseudo-second-order curves for sorbent GMS 1.1 mm and varying initial Cu(II) concentrations (21.5 to 211 mg/l) are presented in Figures 1A-D. A close look at the curves show that the pseudo-second-order model deviates during the first 50 % of the reaction time.

Pseudo-second-order equation parameters

To gain insight into the effect of process variable on biosorption, the values of K_{PSO} are plotted against initial Cu(II) concentrations for various sorbent size and are presented in Figure 2. The plot shows that the curves do not present a common trend and the values of K_{PSO}

exhibit an inconsistent behaviour as initial Cu(II) concentration changes. This behaviour would present a challenge when developing a function for correlating process variables.

Mechanisms as elucidated by pseudo-second-order model

The pseudo-second-order model was developed on the premise that chemisorption is the operative reaction mechanism. The pseudo-second-order model produces a good fit to the experiment data for sorbent size GMS 0.5 mm, however, as particle size is increased, the correlation falls off, and continues to change as initial concentration increases (Table 1). Consequently, this infers that *Fomes fasciatus* biosorption of Cu(II) is more complex than pseudo-second-order and chemisorption may not be the only active rate limiting mechanism.

A further understanding of the operative mechanisms may aid in the selection of a more appropriate model which can represent all varying parameters and conditions of *Fomes fasciatus* reaction kinetics. The Weber and Morris (1962) intraparticle model is applied to extricate the influence of intraparticle diffusion.

Simulation by intraparticle diffusion model

Precision of the intraparticle diffusion model

The precision of this model to the experimental data is also analysed by the use of r^2 and calculated RPE values, and is presented in Table 2. It can be ascertained from the table that as the sorbent size increases, there is increased conformity to the model. This

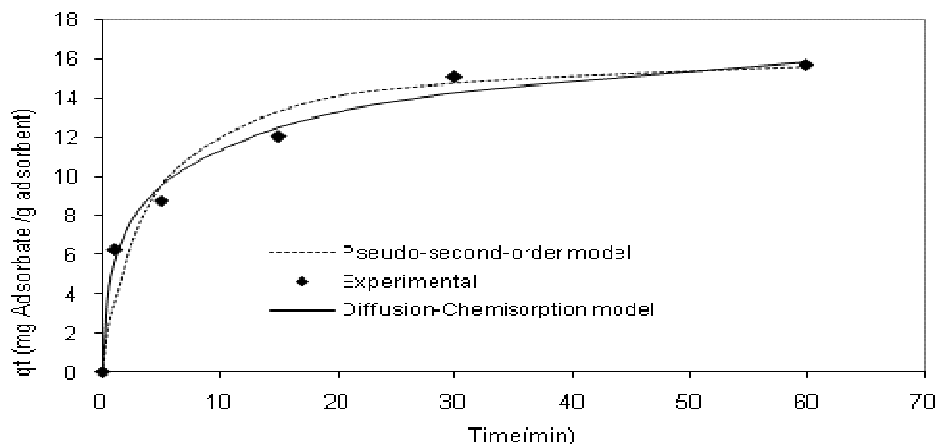


Figure 1A - Non-linear plot showing fit of kinetic models to experimental data for sorbent, GMS 1.10mm and Initial Cu(II) concentration C_o , 21.5 mg/l

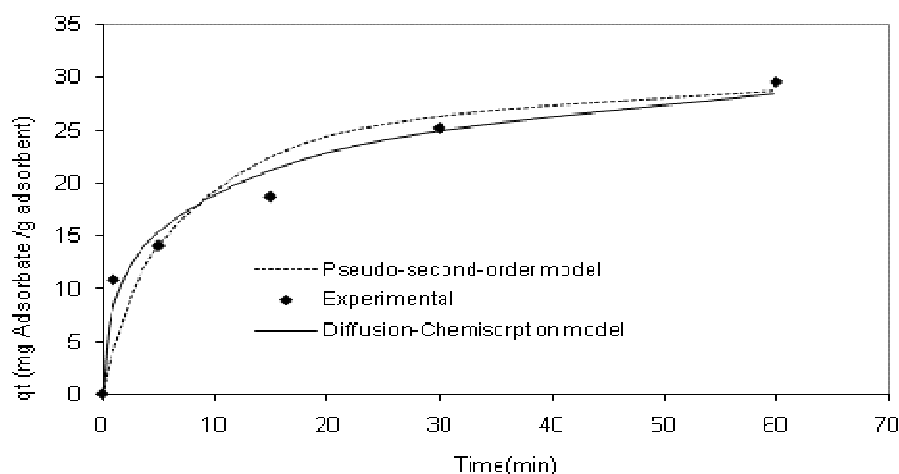


Figure 1B - Non-linear plot showing fit of kinetic models to experimental data for sorbent, GMS 1.10mm and Initial Cu(II) concentration C_o , 53.6 mg/l

infers that as sorbent size increases, the intraparticle diffusion becomes more prominent. The precision of the model also changes with initial concentration, however no discernible trend is observed, indicating that one or more other mechanisms may be influencing the reaction.

Mechanisms as elucidated by the intraparticle diffusion model

Figure 3 shows the plot of q_t versus $t^{0.5}$ for varying sorbent size. The plots did not pass through the origin,

but, the straight line observed confirms the presence of intraparticle diffusion. Badmus et al. (2007) stated that such deviation from the origin shows that intraparticle transport is not the only rate limiting step. The figure also illustrates that with decrease sorbent size (which involves in an increase in surface area and reduction in pore length) the plots moved further from the origin, indicating an increase in intercept c , and by extension, reveals the growing effect of the boundary layer. This behaviour, during the first 2% of the reaction time, may infer the dominance of film diffusion or a combination of

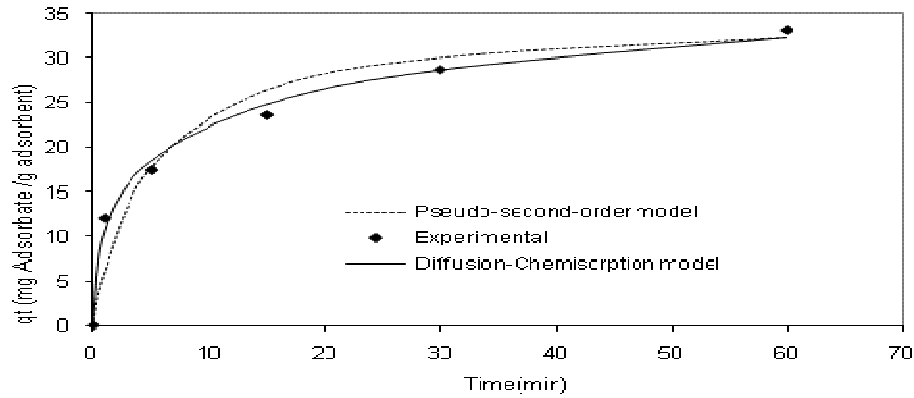


Figure 1C - Non-linear plot showing fit of kinetic models to experimental data for sorbent, GMS 1.10mm and Initial Cu(II) concentration C_0 , 98 mg/l

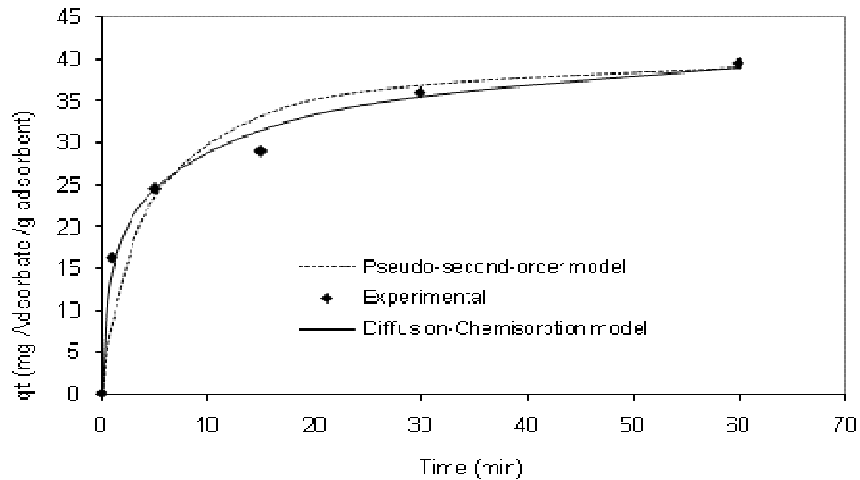


Figure 1D : Non-linear plot showing fit of kinetic models to experimental data for sorbent, GMS 1.10mm and Initial Cu(II) concentration C_0 , 211 mg/l

film diffusion and surface sorption as the initial operative mechanisms.

Analysis of Table 1 and Figures 1A-D revealed that the dominance of chemisorption is influenced by sorbent size and concentration of sorbate over time. As the pseudo-second-order model reduces in conformity, the Weber and Morris (1962) model exhibits increased compliance, inferring the presence of intraparticle diffusion. It is therefore postulated that the sorption of Cu(II) by *Fomes fasciatus* is controlled by a combination of diffusion and chemisorption for 98% of the reaction time. Further, the mechanisms and degree of their influence vary with, as well as, by changing reaction parameters over time. This

behaviour emphasises the inseparability of these mechanisms during the *Fomes fasciatus* biosorption process.

Simulation by diffusion-chemisorption model

Precision of the diffusion-chemisorption model

Equation (12) was reduced to a linear form by a plot of $t^{0.5}/q_t$ vs. $t^{0.5}$, which was used to regress the dataset previously analysed using the pseudo-first-order, pseudo-second-order, and the intraparticle diffusion models. The error analysis presented in Table 2 reveals consistently

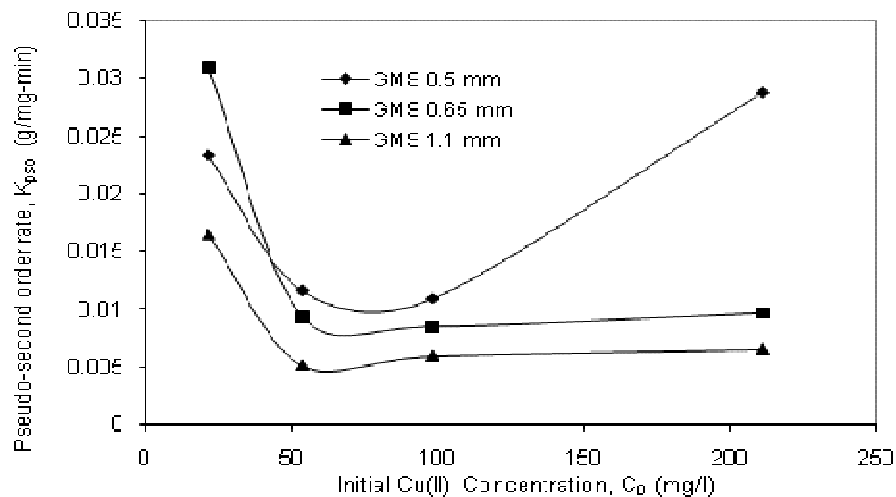


Figure 2 : Plot showing trend of pseudo-second-order rate constant K_{ps0} vs. initial Cu(II) concentration

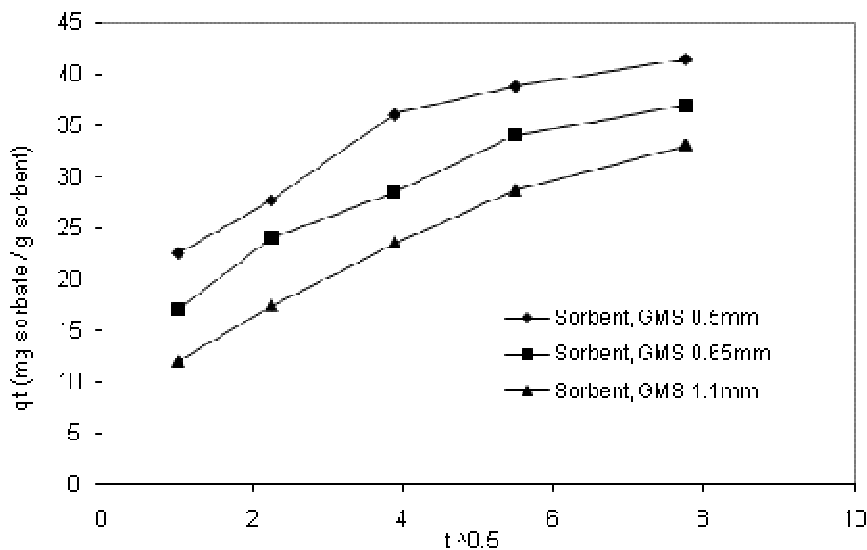


Figure 3 : Kinetic simulation by the Intraparticle diffusion model for various sorbent size

high r^2 values. Additionally, the calculated RPE values are lower than those presented in Tables 1 and 2. Figures 1A-D, show a graphical comparison between the non-linear experimental kinetics and the theoretical curves generated using parameters obtained from the diffusion-chemisorption model. The plots reveal a more precise simulation of the multi-mechanistic reaction of *Fomes fasciatus* uptake of Cu(II). Conformity by the data to the diffusion-chemisorption model tells that the rate of

occupation of biosorption sites by Cu(II) ions is not only a function of unoccupied.

Effect of diffusion-chemisorption rate constant

Figure 4 is a plot of the diffusion-chemisorption rate constant, K_{DC} , versus initial Cu(II) concentration for

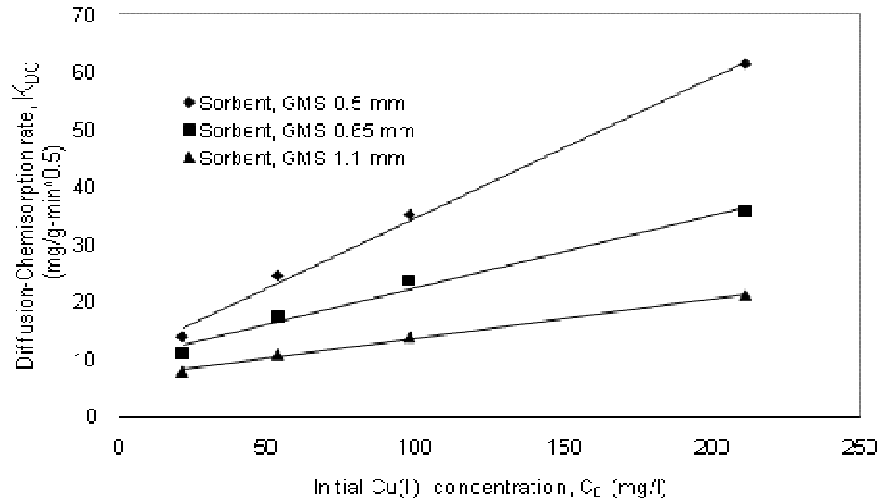


Figure 4 : Plot showing trend of diffusion-chemisorption rate constant K_{DC} vs. initial Cu(II) concentration for various sorbent size

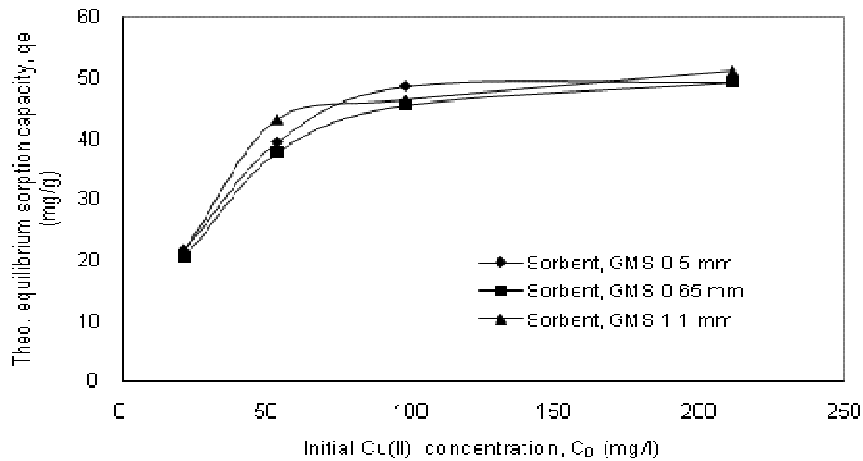


Figure 5 - Plot showing trend of theoretical equilibrium sorption capacity obtained from diffusion-chemisorption model vs. initial Cu(II) concentration

varying sorbent size. A linear relationship is observed within the range of initial concentrations tested. Further, the plot reveals an increase in diffusion-chemisorption rate with increases in initial concentration up to 211 mg/l. This trend is expected due to the increased concentration gradient developed between the inner and outer regions of the sorbent. The plot also depicts an increase rate of change in the value of K_{DC} with decrease sorbent size. This is attributed to the greater available surface area and reduced distance for the sorbate to travel to reach an active sorption site.

Effect of theoretical equilibrium sorption capacity

Figure 5 shows a plot of theoretical equilibrium capacity, q_e , against initial concentrations for varying sorbent size. There is good concurrency among the data, showing the maximum sorption capacity to average around 50 mg/g. This behaviour is expected as it infers that the internal sorbent characteristics are similar to that of its surface. The plot also shows the driving force for biosorption to be greatly influenced by initial concentration. Additionally, available sorption sites become fully occupied for initial

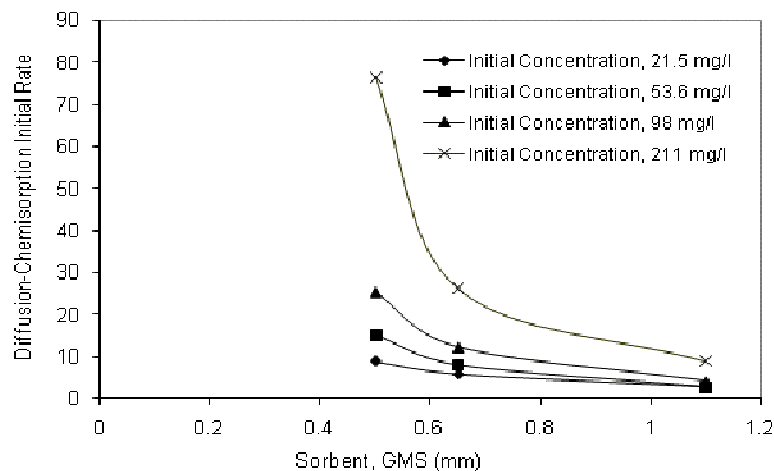


Figure 6. - Plot showing trend of diffusion-chemisorption initial sorption rate, k_i vs. sorbent size

Cu(II) concentration beyond 100 mg/l. As initial concentration drops below 100 mg/l, the efficiency of the biosorption process decreases.

Effect of initial rate constant

The initial rates of reaction, k_i ($mg/g-t$) were calculated using equation 13 and a plot of these initial rates vs. sorbent size is presented in Figure 6. The initial rate increases generally with increase initial solution concentration, and decrease sorbent size. This trend may be attributed to the increased concentration gradient and increased surface area respectively.

CONCLUSIONS

Batch biosorption kinetic experiments were performed using the macro fungus *Fomes fasciatus* as a new biosorbent and Cu(II) as a model adsorbate. Experimental parameters were varied and analysed using theoretical kinetic equations (i) to gain some insight into the mechanisms of biosorption; and (ii) to select an appropriate kinetic model which can advance the development of predictive models. Based on the output of the investigation the following conclusions may be drawn:

1. Film diffusion, or a combination of film diffusion and surface adsorption, dominated the first 2% of the reaction time. Beyond the initial 2%, biosorption involved two mechanisms, viz.: diffusion and chemisorption.

2. The dominance of either diffusion or chemisorption varied according to sorbent size, initial solution concentration and changes in concentration over time.

Consequently, these mechanisms become inseparable and led to the failure of single mechanistic models.

3. The multi-mechanistic kinetic reaction was successfully simulated using the Sutherland (2004) diffusion-chemisorption model. Higher correlation to the linear and non-linear plots was observed over that of the other tested models.

4. The diffusion-chemisorption model was successful in providing a means of correlating model parameters, K_{DC} and q_e , with reaction parameters. This correlation advances the development of predictive models, which consequently, can reduce experimentation and improve the development of full-scale batch treatment systems using *Fomes fasciatus*.

ACKNOWLEDGEMENTS

The authors would like to extend sincere appreciation to Dr. Ian Khan-Kernahan, Dr. Richard Clarke, Mr. Kenneth Bahadoorsingh, Mrs. Zaleena Chin-Yuen-Kee, Mr. Glen Joseph, Mrs. Karima Mohammed, Ms. Donica Mahabir, Mr. Seunarine Persad, Ms. Shalini Ramsaran, Mr. Anand Gayadeen and Mrs. Sintra Ramlal for their kind assistance.

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