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Batch and continuous fixed-bed column biosorption of Cd^{2+} and Cu^{2+}

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ABSTRACT

Biosorption of Cd^{2+} and Cu^{2+} by wheat straw (*Triticum sativum*) using a batch system and a continuous up-flow fixed-bed column was studied. For the batch system, the effect of pH over a range from 3.0 to 7.0 and the temperature from 20 to 40 °C on the metal removal was investigated. Various initial metal concentrations from 20 to 150 $mg\,L^{-1}$ were used. Adsorption of metal ions was observed to increase with pH and temperature. By increasing the temperature from 20 to 40 °C at an initial concentration 100 $mg\,L^{-1}$, the metal uptake increased from 12.2 to 15.7 $mg\,g^{-1}$ and 9.1 to 12.2 $mg\,g^{-1}$ for Cd^{2+} and Cu^{2+}, respectively. Similarly, by increasing the solution pH from 3.0 to 7.0, adsorption capacity of Cd^{2+} and Cu^{2+} increased from 2.7 to 14.4 $mg\,g^{-1}$ and 3.4 to 12.4 $mg\,g^{-1}$, respectively. Among the three widely used isotherms, namely the Langmuir, Freundlich and Temkin models, the experimental data better fitted the Langmuir isotherm.

For the continuous up-flow mode in a fixed bed of wheat straw, experiments were performed over a range of flow rates from 1.10×10^{-3} to 3.67×10^{-3} $m^3\,s^{-1}$ (0.3–1.0 LPM) and varied bed heights from 0.5 to 2.0 m. The results obtained agree to the bed-depth service-time (BDST) model well. In addition, for estimations of the parameters necessary for the design of a large-scale fixed-bed adsorber, the experimental data were also fitted to the Thomas, Bohart–Adams and Yan models. The Thomas model appeared to describe the experimental results better. A mass transfer model for adsorption of metal ions in a fixed bed of wheat straw was also developed and found to agree with the experimental data fairly well.

1. Introduction

Contamination of aqueous environment by heavy metals is the driving force behind a great attention towards metal remediation methods. Among heavy metals in wastewaters, cadmium and copper are considered having a high priority due to their toxicity and high disposal rate [1,2]. Conventional technologies for the removal of heavy metals include chemical precipitation, ion exchange, adsorption, evaporation and membrane separation. Those processes require high operational and capital costs [3,4].

Biosorption has been demonstrated as an efficient and economical method for the removal of heavy metals in wastewaters [5]. Several naturally available biomasses, such as seaweeds and wheat straw, can be used as biosorbents. Non-living microorganisms, seaweeds, crab shells and other waste biomasses have also been tested and shown as promising sources of biosorbents [6,7]. The availability of a biomass at a low cost is a key factor dictating its selection for a biosorption process.

Biosorption was earlier considered to follow a mechanism similar to that of adsorption [8]. Several governing mechanisms of metal uptake by a biomaterial have been proposed, including chemisorption, complexation, chelation of metals, ion exchange, adsorption and micro-precipitation [9]. The metal binding depends on the biosorbent type, the metal ion species and concentration, temperature, pH, and ionic interference by other metal ions in the solution. Metal sorption tends to decrease with temperature [10,11]. Among various factors, the solution pH can be considered as the most important parameter influencing the biosorption process [12]. It has been reported that electrostatic repulsion between metal ions and the biomass surface, and the competition of hydronium ions for adsorption sites decreased with pH; hence, the metal uptake increased [13,14,15]. In some cases, the metal uptake increased with pH until an optimum pH was reached, then the uptake decreased with further increases in pH [13]. High dosages of the biomass would obviously lead to more metal binding to the biomass, but could also result in more sorption site interaction [16,17].

The characteristics of a biosorption process are usually evaluated and classified by equilibrium isotherms and biosorption kinetics. The isotherms are also useful tools in interpreting the biosorption mechanism. Many models relating the adsorbate concentration remaining in the fluid phase and the adsorbate amount uptaken by the adsorbent at equilibrium have been developed. Among those, the Langmuir, Freundlich and Temkin

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Nomenclature

C	solute concentration of the effluent of the column (mg L^{-1})
C_b	solute concentration of the effluent of the column at breakthrough (mg L^{-1})
C_i	solute concentration in the influent to the column (mg L^{-1})
C_e	equilibrium concentration of the solute in solution (mg L^{-1})
C_o	initial solute concentration (mg L^{-1})
D	metal ion diffusivity ($m^2\,s^{-1}$)
d_p	particle diameter (m)
F	volumetric flow rate (L min^{-1})
K	adsorption rate constant (L $mg^{-1}\,min^{-1}$)
K_{AB}	the Bohart–Adams model rate constant (L mg^{-1} min)
K_{TH}	the Thomas model rate constant (L $mg^{-1}\,min^{-1}$)
K_Y	the Yan model rate constant (L $mg^{-1}\,min^{-1}$)
Z	length of the bed (m)
M	mass of adsorbent (g)
N_o	adsorption capacity (mg L^{-1})
N_{Re}	the Reynolds number ($N_{Re} = (d_p \rho u)/\mu$)
N_{Sc}	the Schmidt number ($N_{Sc} = \mu/(\rho D)$)
q_e	equilibrium metal uptake (mg g^{-1})
q_{max}	maximum adsorption capacity (mg g^{-1})
q_t	maximum metal uptake (mg g^{-1})
T	absolute solution temperature (K)
t_b	breakthrough time (time at which the metal concentration of the effluent is equal to 10% of the metal concentration of the influent to the bed) (min)
t_e	equilibrium time when column is exhausted ($C = C_i$) (min)
u	superficial velocity of liquid in the column (dm min^{-1})
V	cumulative throughput liquid volume (L)
Z	biosorbent bed depth in the column (dm)

Greek letters

μ	liquid viscosity (Pa s)
ρ	liquid density (kg m^{-3})

and Pyzhev isotherms are the most commonly used models [18,19,20].

Biosorption process can be performed under either a batch or continuous mode. For a continuous process, a fixed-bed adsorber is usually used. The effectiveness of a biomass can be evaluated from the breakthrough curve of the effluent concentration (or the concentration–time profile). A typical S-shaped breakthrough curve is usually observed [21]. In order to predict the breakthrough curve of an adsorption process in a fixed bed, the Bohart–Adams, Thomas and Yans model have been often used [22,23,24]. Moreover, the required bed height is an important parameter in designing an adsorption column. This can be determined from the breakthrough curve and the bed-depth service-time (BDST) model. In the present study, the effectiveness of wheat straw as a biosorbent was evaluated. The effect of the initial metal concentration, temperature, pH and co-adsorption on the metal uptake was studied using a batch system. The adsorption capacity of wheat straw in a continuous fixed-bed column was also determined. For a proper design of an adsorption column, an accurate prediction of the breakthrough curve is needed. Therefore, the experimental results obtained from the continuous system were fitted to the abovementioned models for adsorption. A mass transfer model for the biosorption of metal ions by wheat straw in a fixed-bed column was also developed.

2. Materials and methods

2.1. Sample preparation

Wheat straw obtained from a farm in Vaughan, Ontario, Canada, was used as a biosorbent. Prior to the experiments, the wheat straw was cut into uniform lengths of 1 cm and pretreated using the following steps: (1) washing the wheat straw with distilled water, (2) drying the wheat straw at 60 °C, (3) immersing the sample in a 0.1N solution of H_2SO_4 for one and a half hour, (4) washing the sample with distilled water, (5) immersing the sample in a 0.1N NaOH solution for one and a half hour, (6) washing the sample with distilled water, and (7) drying the sample at 60 °C in a vacuum dryer.

2.2. Batch biosorption system

The experimental setup was basically a temperature-controlled variable-speed agitator water bath (Julabo SW22, Labortechnik GmbH, Germany). A metal solution of a known concentration was prepared by dissolving analytical grade cadmium sulfate octahydrate ($3CdSO_4{\cdot}8H_2O$) and cupric sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$) in distilled water. The chemicals were obtained from VWR (Mississauga, Ontario, Canada). Initial metal concentrations of 20, 50, 75, 100, and 150 mg L^{-1} were used. A 200-mL aliquot of the metal solution was transferred to a 300-mL Erlenmeyer flask. One gram of pretreated biomass was then added to the flask containing the metal solution. The flask was placed in the shaker water bath at a predetermined temperature. The temperature effect on the adsorption of metal was studied over a range from 20 to 40 °C with 5 °C increments, using an initial metal concentration of 100 mg L^{-1} and a shaker speed of 120 rpm. The effect of pH over a range from 3.0 to 7.0 was also tested. The solution pH was adjusted with 0.1N H_2SO_4 or 0.1N NaOH. Each run was performed for 6 h and samples were taken at 5-min intervals in the first 30 min and then at 30-min intervals for the rest of the experiment duration. The concentration of the residual metal in each sample collected was determined using an atomic adsorption spectrophotometer (AAnalyst 800, PerkinElmer, Toronto, Ontario, Canada).

The amount of metal adsorbed by the wheat straw was calculated using the following equation:

$$q = \frac{(C_o - C_t)V}{M} \qquad (1)$$

where q is metal uptake (mg g^{-1}), C_o is initial concentration (mg L^{-1}), C_t is metal concentration at a given time (mg L^{-1}), M is mass of biosorbent (g), and V is volume of the solution (L).

The experimental error of the results obtained in the present study was from water sampling, preparation and analysis. The averaged deviation from the means of the data was determined to be within ±4%, which was used for the error bars in some of the graphs presented below.

2.3. Continuous system

The experimental set-up for a continuous system consisted of four 0.5-m long column sections of a 0.076 m diameter as shown in Fig. 1. Dry wheat straw was cut to 1-in. particles and packed into the columns with plastic meshes installed at both the top and the bottom of the packed bed to hold the wheat straw particles in place. For an even liquid flow across the column's cross-sectional area, a liquid distributor was used to introduce liquid into the packed bed. In order to have a consistent packing porosity, the column was packed at varied bed heights using a constant bulk density of wheat

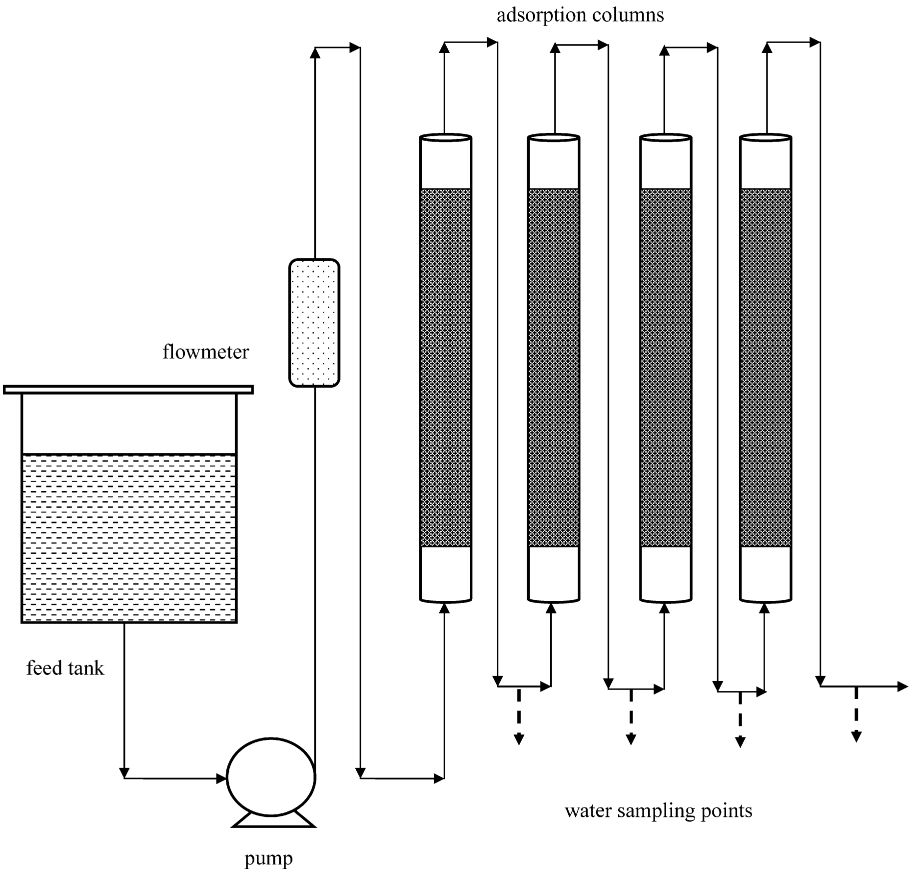

Fig. 1. Schematic diagram of the experimental set up for a continuous process.

straw of 68.5 g L^{-1}, which was determined from the packing bulk density in a 0.5-m high column.

A solution of Cd^{2+} or Cu^{2+} with an initial concentration of 100 mg L^{-1} was pumped from a holding tank to the bottom of the column. The liquid flow rate was monitored using a rotameter (Blue-White F-450, Fabco Inc., Vaughan, Ontario, Canada). All experiments were performed at 25 °C and an initial pH of 6.0. The effect of the bed height was studied using one, two, three or all four column sections at the same time. The equivalent bed heights were 0.5, 1.0, 1.5 and 2.0 m. Liquid flow rates of 0.3, 0.5, 0.8 and 1.0 L min^{-1} (1.10×10^{-3} to 3.67×10^{-3} m^3 s^{-1}) were used for both Cd^{2+} and Cu^{2+} solutions.

In order to ensure the formation of a complete breakthrough curve, each experiment was run for approximately 8 h. Water samples were taken from the sampling points at the same intervals as those used for experiments with the batch system. The breakthrough curves for various bed heights and liquid flow rates were obtained from the measured metal concentrations in the water samples collected. The amount of metal ions adsorbed in the column was determined from the area above the breakthrough curve of the metal concentration in the effluent stream and the liquid flow rate.

3. Results and discussions

3.1. Batch system

3.1.1. Effect of initial $Cd^{2+}$and Cu^{2+}concentration and co-adsorption

The effect of the metal concentration on the adsorption efficiency of Cd^{2+} and Cu^{2+} by wheat straw was investigated over a range from 20 to 150 mg L^{-1}. Figs. 2 and 3 present Cd^{2+} and Cu^{2+} uptakes at 25 °C and the initial pH values of 5.5 and 6.0 for Cu^{2+} and Cd^{2+}, respectively. The metal uptake for both Cd^{2+} and Cu^{2+} increased quickly during the first 30 min. For Cd^{2+} at all initial concentrations, about 90% of the total metal uptake occurred over this period. For example, at an initial concentration of 75 mg L^{-1}, Cd^{2+} uptake was 11.4 mg g^{-1} as compared to the equilibrium uptake of 21.1 mg g^{-1}. For Cu^{2+}, the metal uptake over the same period was about 85%, at an initial concentration lower than 75 mg L^{-1}, and about 70% of the total uptake at higher initial concentrations. As an example, at an initial concentration of 50 mg L^{-1}, the Cu^{2+} uptake after 30 min was 8.6 mg g^{-1}, and the total uptake was 9.8 mg g^{-1}. On the other hand, at an initial concentration of 75 mg L^{-1}, the metal uptake over the same period was 6.1 mg g^{-1} out of the total uptake of 8.3 mg g^{-1}. However, the equilibrium time varied between 60–210 min for Cd^{2+} and 75–210 min for Cu^{2+}, as can be seen in Figs. 2 and 3.

It was found that the percentage metal removal decreased from almost 100% to 54% and 86% to 38% for Cd^{2+} and Cu^{2+}, respectively, with increases in the initial concentration from 20 to 150 mg L^{-1}. This was due to the exhaustion of the sorption sites available on the biomass, for a given biomass dosage, when the metal concentration was increased. A similar trend of concentration dependency of biosorption of metal ions was also observed by Malkoc [25].

The effect of co-adsorption of multiple metals on the biosorption capacity of individual metal ions present in the wastewater was also investigated. Fig. 4 presents the equilibrium uptake of Cd^{2+} and Cu^{2+} on wheat straw with single metal and bimetal solutions. For the single metal system, Cd^{2+} was adsorbed slightly more than Cu^{2+}. On the other hand, the wheat straw appeared to uptake more Cu^{2+} than Cd^{2+} in the bimetal solution as can be seen in Fig. 4. It is

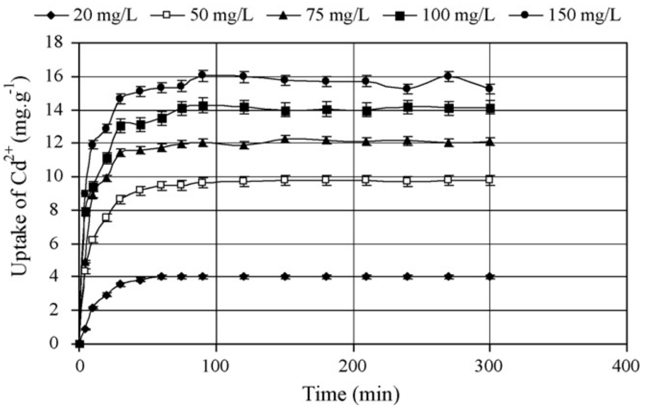

Fig. 2. Cd^{2+} uptake vs. contact time ($T = 25\,^{\circ}C$ and pH 6.0), single-ion solution.

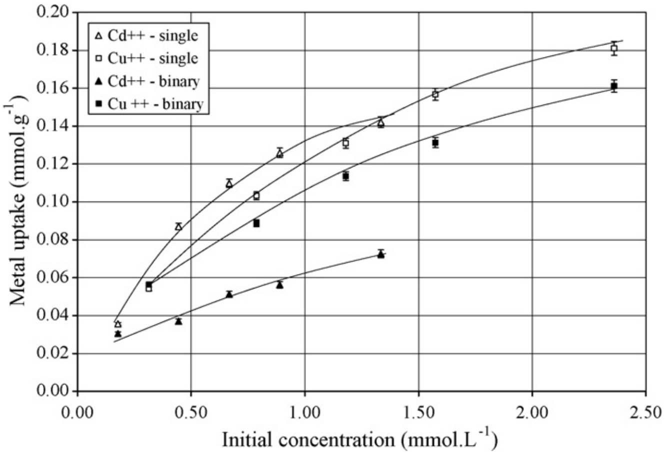

Fig. 4. Effect of co-adsorption on the removal of Cd^{2+} and Cu^{2+}.

relevant to note that the electronegativity of copper is 1.90 while the electronegativity of cadmium is 1.69. The higher electronegativity tends to hinder the biding of metal ions to the negative sites on the wheat straw. However, the atomic weight of cadmium is 112.4 as compared to 63.6 for copper [26]. The mobility of heavier ions from liquid to the adsorbent would be lower than that of lighter ions. This was indeed the case as reflected by the higher diffusivity of Cu^{2+} ($5.355 \times 10^{-8}\,m^2\,s^{-1}$) compared to that of Cd^{2+} ($3.005 \times 10^{-8}\,m^2\,s^{-1}$) [27]. Therefore, when both Cd^{2+} and Cu^{2+} were present in a bimetal solution, the effect of the ion mobility might have outweighed the effect of the electronegativity, resulting in a substantially higher uptake of Cu^{2+}.

3.1.2. Effect of solution temperature and pH

Biosorption of metal ions by wheat straw at varied temperatures of 20, 25, 30, 35 and 40 °C was investigated. The initial metal concentration of $100\,mg\,L^{-1}$ and the liquid pH of 6.0 and 5.5 for Cd^{2+} and Cu^{2+}, respectively, were used in all experiments. A slight increase in metal uptake with temperature was observed. By increasing the temperature from 20 to 40 °C, the metal uptake increased from 12.2 to $15.7\,mg\,g^{-1}$ and 9.1 to $12.2\,mg\,g^{-1}$ for Cd^{2+} and Cu^{2+}, respectively. The increase in the metal uptake with temperature may be attributed to the increase in the active sites available on the surface of the adsorbent for biosorption. This came about by the opening up of the cellulose fibers of the wheat straw when it was soaked in a warmer solution. In an investigation of adsorption of Pb(II) ions by pine bark, Gundogdu et al. reported that a higher metal uptake at high temperature may be attributed to the availability of more active sites on the surface of the bark by expansion of the pores [28]. However, significant variation of the effect of temperature on biosorption has been reported in the literature, even conflicting results at times. Antunes et al. showed that over a range from 25 to 55 °C, temperature did not affect biossorption of copper by brown seaweed, *Sargassum* sp., significantly [29]. This might be due to different types of biosorbents and their interaction with metal ions.

The uptake of Cd^{2+} and Cu^{2+} was also examined over a pH range from 3.0 to 7.0. Fig. 5 shows the variation of the equilibrium uptake of Cd^{2+} and Cu^{2+} with the solution pH at 25 °C. Adsorption of both metal ions increased with pH. Over the range of pH from 3.0 to 7.0, the metal uptake increased by 5.2 and 3.7 times for Cd^{2+} and Cu^{2+}, respectively. It is also noted that, for pH from 3.0 to 4.0, the metal uptake for Cu^{2+} increased at a much greater rate than that of Cd^{2+}. However, at the solution pH higher than 4.0, the uptakes of both Cd^{2+} and Cu^{2+} increased at a similar rate. At a high pH (a low H^+ concentration in the solution), the competition of H^+ with the metal ions for the adsorption sites on the wheat straw was less; hence, the metal ions could be adsorbed more onto the biomass surface. However, Cu^{2+} uptake was consistently higher than Cd^{2+} uptake over the whole range of pH from 3.0 to 6.5. Nevertheless, at pH of 3.0 the difference in the metal uptakes for the two metals was less due to the hindrance to adsorption of both metals by a high concentration of H^+ in the solution. At higher pH values of 4.0 to 6.5, less H^+ was present in the solution; hence, the competition between Cu^{2+} and Cd^{2+} became more predominant, which was more favorable for Cu^{2+}.

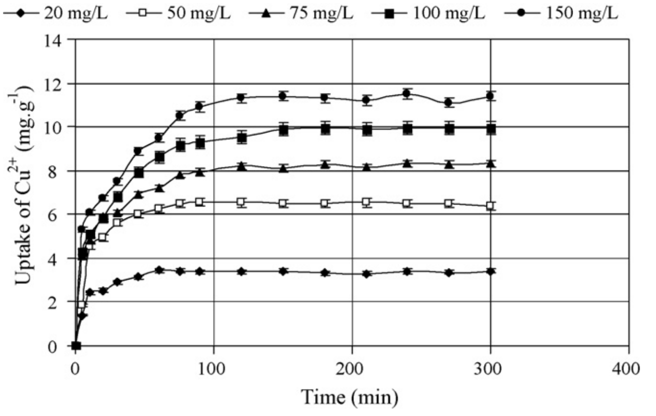

Fig. 3. Cu^{2+} uptake vs. contact time ($T = 25\,^{\circ}C$ and pH 5.5), single-ion solution.

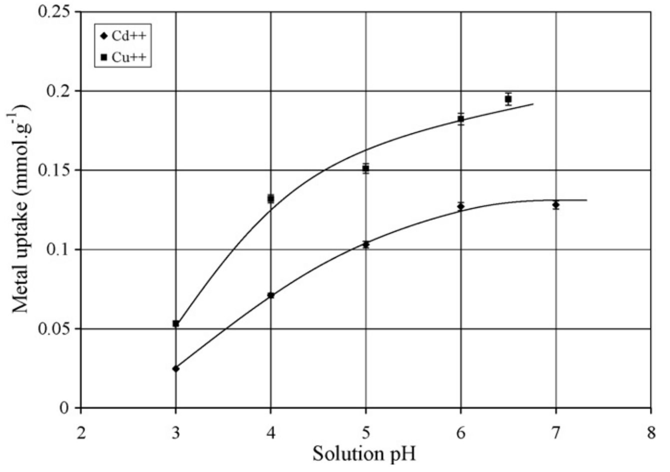

Fig. 5. Effect of pH on the uptake of Cd^{2+} and Cu^{2+} at 25 °C.

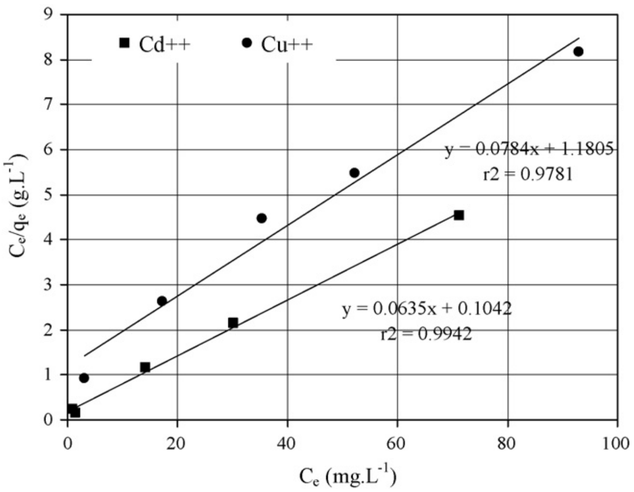

Fig. 6. Langmuir isotherm for Cd^{2+} and Cu^{2+} at 25 °C.

3.1.3. Isotherm models for adsorption of Cd^{2+} and Cu^{2+} on wheat straw

The experimental data for single-ion solutions were fitted to the Langmuir, Freundlich and Temkin isotherm models for both Cd^{2+} and Cu^{2+}. The Langmuir, Freundlich and Temkin models can be expressed as in Eqs. (2)–(4), respectively, below:

$$q_e = \frac{q_{max} b C_e}{(1 + b C_e)} \tag{2}$$

where q_e is the equilibrium amount of metal adsorbed, C_e is the equilibrium concentration of metal ions in the solution, q_{max} is the maximum adsorption capacity or the theoretical monolayer saturation capacity and b is the Langmuir equilibrium constant [18].

$$q_e = K_F C_e^{1/n} \tag{3}$$

For the Freundlich model, K_F is the constant related to the adsorption capacity of the adsorbent, n is the exponent related to adsorption intensity [19].

$$q_e = \left(\frac{RT}{B}\right) \ln(A C_e) \tag{4}$$

In the Temkin model, R is universal gas constant, T is the absolute temperature (K), A and B are constants [20].

The values of q_{max} and b in the Langmuir model can be determined from the slope and the intercept of a plot of C_e/q_e versus C_e. Similarly, K_F and n in the Freundlich model can be obtained from a plot of $\ln(q_e)$ versus C_e. A plot of q_e versus $\ln C_e$ is a linear line that can be used to determinate the constants A and B in the Temkin model.

It was found that Langmuir model best fitted to the experimental data with the values to the coefficient of determination, r^2, of 0.978 and 0.994 for Cd^{2+} and Cu^{2+}, respectively, as shown in Fig. 6. This indicates that wheat straw would provide monolayer and homogeneous adsorption for the metal ions.

3.2. Continuous biosorption system

3.2.1. Effect of bed height and liquid flow rate on biosorption process

The effect of the bed height on adsorption of Cd^{2+} and Cu^{2+} was investigated using various bed heights from 0.5 to 2.0 m. The breakthrough curves of Cd^{2+} and Cu^{2+} for various bed heights were obtained from the variation of the metal concentration in the column effluent with time. Typical breakthrough curves are plotted in Fig. 7(a) and (b) for the case with a liquid flow rate of $1.10 \times 10^{-3}\,m^3\,s^{-1}$ (0.3 LPM).

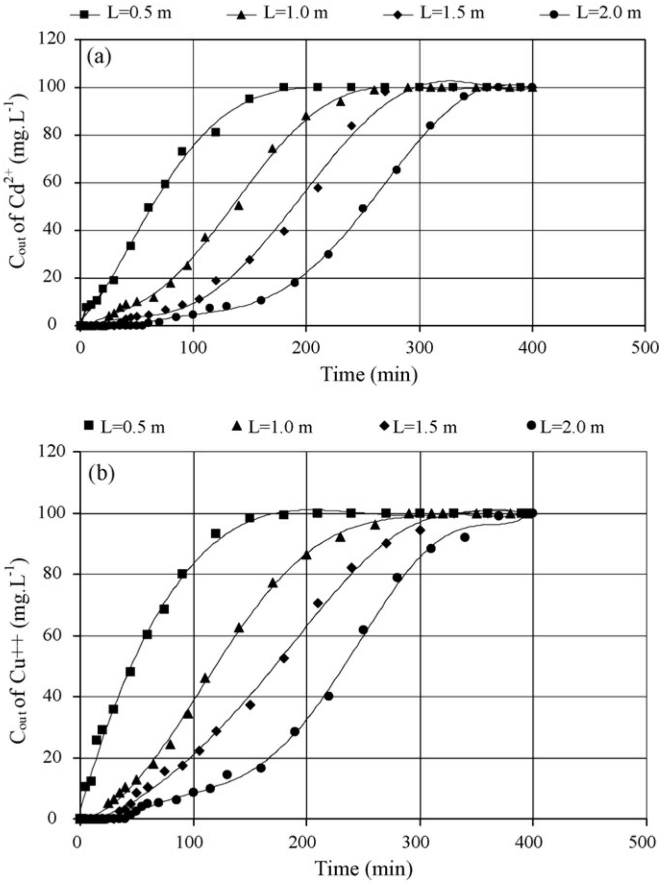

Fig. 7. Effect of the bed height on adsorption of (a) Cd^{2+} and (b) Cu^{2+} at a liquid flow rate of LPM and an influent metal concentration of 100 mg L^{-1}.

The shape and the gradient of the breakthrough curves change significantly with the bed height, as can be seen in Fig. 7(a). The slope of the breakthrough curve of a tall bed of a 2.0-m height is lower than that of a shorter bed, especially at lower liquid flow rates, as expected. For a taller bed, a larger volume of the metal solution could be treated, and a higher percentage metal removal was obtained. However, the metal uptake per unit mass of wheat straw remained relatively constant for different bed heights. This indicates that the metal uptake amount was directly proportional to the amount of adsorbent available in the bed. For Cu^{2+}, a similar trend was observed, as can be seen in Fig. 7(b). It was also found that the 10% breakthrough time, t_b (the time at which the metal concentration in the effluent was equal to 10% of the metal concentration of the influent to the bed) increased with the bed height as shown in Table 1. It is self-evident that a taller bed has more adsorbent available for metal binding; hence, more liquid could be treated and the breakthrough time is longer.

Fig. 8(a) and (b) presents the breakthrough curves for Cd^{2+} and Cu^{2+} at different flow rates from 0.3 to 1.0 LPM through a 2.0-m high column. The breakthrough curves shifted towards a lower time scale with increases in liquid flow rate from 0.3 to 1.0 LPM. This indicates a shorter column active life at a higher liquid flow rate. For the 2.0-m high bed, the percentage Cd^{2+} removal decreased by 32% when the liquid flow rate was increased about 2.7 times from 0.3 to 0.8 LPM. However, a further increase in the liquid flow rate by only 25% from 0.8 to 1.0 LPM, the percentage metal removal decreased at a much faster rate by another 11.4%. A similar trend was also observed for Cu^{2+}. The rapid decrease of the percentage

Table 1
Experimental uptake and breakthrough time for biosorption of Cd^{2+} in a fixed bed of wheat straw with an influent metal concentration of 100 mg L^{-1}.

Flow rate (LPM)	Bed height (m)	Experimental uptake (mg g^{-1})	t_b at 10% (min)	t_e (min)	Cd^{2+} removal (%)
0.3	0.5	16.9	15	180	53.4
	1.0	15.7	45	290	68.8
	1.5	13.5	100	300	76.9
	2.0	13.3	150	370	86.5
0.5	0.5	16.4	10	120	50.9
	1.0	15.1	35	255	51.3
	1.5	14.6	60	295	62.3
	2.0	14.4	90	305	70.1
0.8	0.5	16.1	5	150	34.1
	1.0	14.9	25	190	41.0
	1.5	14.4	35	230	48.3
	2.0	14.1	55	270	54.6
1.0	0.5	16.1	3	150	27.4
	1.0	15.7	15	155	35.7
	1.5	15.6	25	220	41.9
	2.0	14.6	45	230	43.2

metal removal at liquid flow rates higher than 0.8 LPM indicates that there might be a critical flow rate at which flow channeling could become significant, and hence, lead to less metal adsorption. The sensitivity of the adsorption to the liquid flow rate can be explained by the fact that the liquid residence time in the column is critical for the biosorption process. When the flow rate was increased, the liquid residence time in the column decreased resulting in less metal ions adsorbed to the biomass; and hence, the percentage metal removal was decreased. Similar observation was reported by Netpradit et al. in their study using metal hydroxide sludge for adsorption of reactive dye in a fixed-bed column [30]. On the other hand, the metal uptake per unit mass of adsorbent in the bed remained relatively constant with the liquid flow rate, as can be seen in Table 1. This indicates that adsorption was the predominant step of the overall metal removal process, which includes two steps: the mass transfer from the bulk liquid to the solid adsorbent, and the adsorption of metal ions onto the adsorbent surface. It was also noted that the metal uptake decreased slightly with the bed height. This might be due to the effect of liquid maldistribution and channeling in the tall beds.

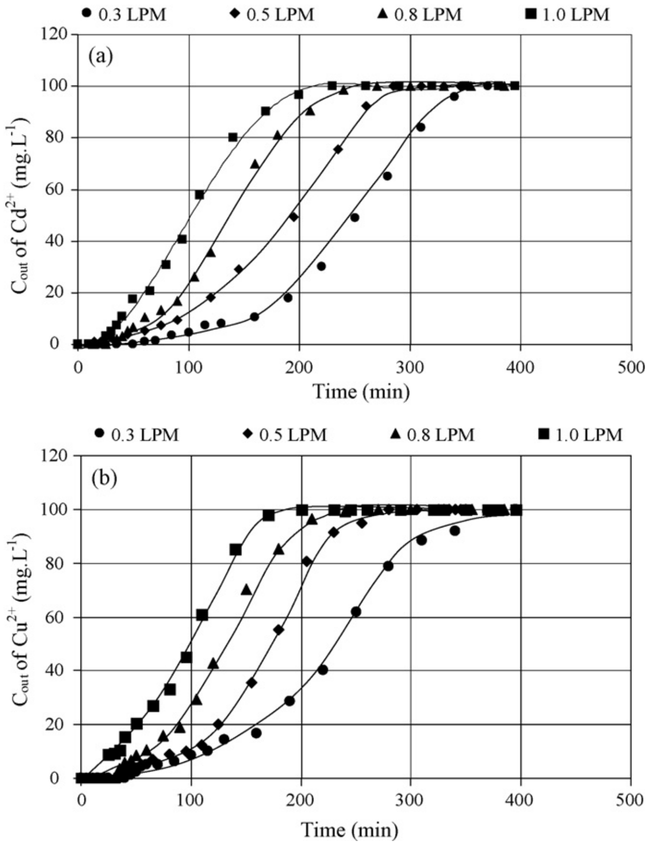

Fig. 8. Effect of the liquid flow rate on adsorption of (a) Cd^{2+} and (b) Cu^{2+} in a 2.0 m bed and an influent concentration of 100 mg L^{-1}.

3.2.2. Models for adsorption in the column of wheat straw

3.2.2.1. Bed-depth service-time model (BDST). Data collected from laboratory and pilot-plant tests serve as the basis for the design of a full-scale adsorption column. Among various parameters, the required bed depth for a specific adsorption time (service-time) before the regeneration of the adsorbent is an important design parameter. The bed-depth service-time model can be used to estimate the required bed depth for a given service-time. The BDTS model can be expressed as below [16]:

$$t_b = \frac{N_o}{C_i u} Z - \frac{1}{C_i K} \ln\left(\frac{C_i}{C_b} - 1\right) \quad (5)$$

where C_b is the solute concentration in the effluent of the column at breakthrough, C_i is the solute concentration in the influent to the column. The adsorption capacity, N_o, can be determined from the slope of the plot of the service-time t_b versus the bed height Z. The rate constant, K, can be obtained from the intercept of the plot, which represents the rate of solute transfer from the liquid phase to the solid phase. Once the constants of the model have been determined from the experimental data, the model can be used to estimate the service-time for a given bed height and specific solute concentrations at the bed inlet and outlet.

Fig. 9(a) and (b) shows the plots of the service-time (t_b) at the 10% breakthrough point (i.e. t_b at C_{out} = 10 mg L^{-1}) versus the bed height at different flow rates and an influent metal concentration of 100 mg L^{-1}. The linear relationship between t_b and the bed height was obtained with the r^2 values mostly close to unity, indicating the suitability of the BDST model to represent the adsorption of Cd^{2+} and Cu^{2+} in a fixed bed of wheat straw. The adsorption capacity, N_o, only slightly decreased with the flow rate while the rate constant K increased significantly with the flow rate, as can be seen in Table 2.

3.2.2.2. Other kinetic models. The experimental data obtained from the continuous biosorption system were also fitted to the most

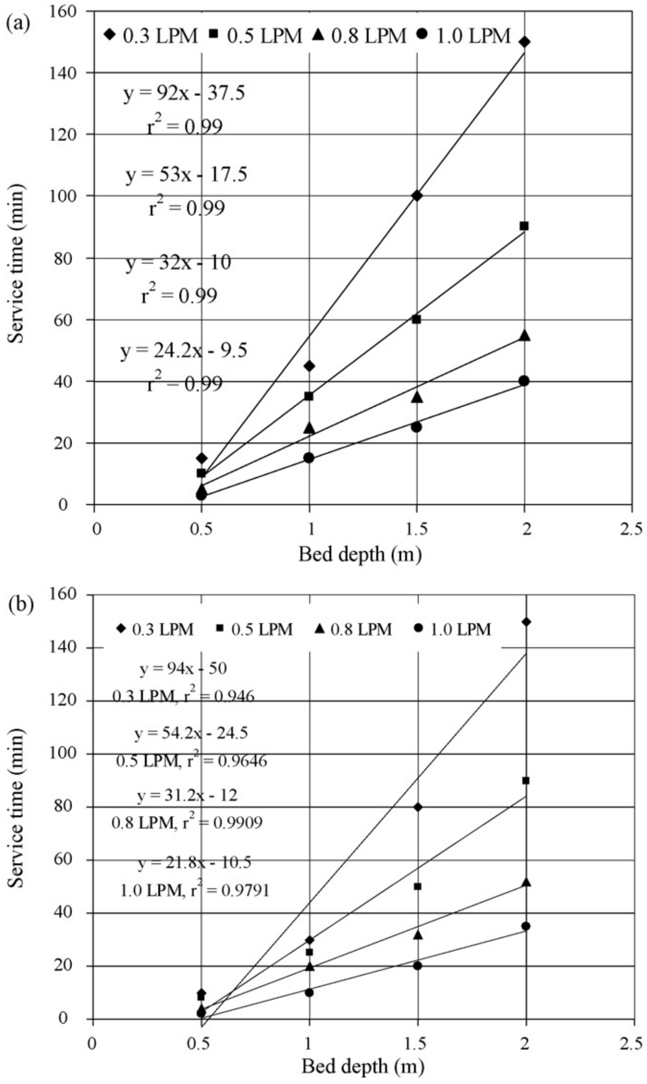

Fig. 9. BDST curve at 10% breakthrough for biosorption of (a) Cd^{2+} and (b) Cu^{2+} on wheat straw.

commonly used kinetic models for adsorption in a fixed bed. Those are the Thomas, Bohart–Adams and Yan models, which can be written respectively as below:

$$\ln\left(\frac{C_i}{C}-1\right)=\frac{K_{TH}q_TM}{F}-\frac{K_{TH}C_iV}{F} \tag{6}$$

$$\ln\left(\frac{C_i}{C}-1\right)=K_{BA}N_o\frac{Z}{V}-K_{BA}C_it \tag{7}$$

$$\ln\left(\frac{C}{C_i-C}\right)=\frac{K_yC_i}{F}\ln(V)-\frac{K_yC_i}{F}\ln\left(\frac{K_yq_tM}{F}\right) \tag{8}$$

where C is the effluent solute concentration, C_i is the influent solute concentration, K_{TH} is the Thomas rate constant, F is the volumetric liquid flow rate, q_t the maximum metal uptake to the solid adsorbent, M mass of adsorbent (g) in the bed, V is the cumulative liquid throughput volume, and K_{BA} is the Bohart–Adams rate constant. Similarly, K_y is the Yan rate constant.

Table 2
Parameters predicted from the BDST model for biosorption of Cd^{2+} and Cu^{2+} on wheat straw.

Flow rate (LPM)	Cd^{2+}		Cu^{2+}	
	N_o (mg L^{-1})	K (L mg^{-1} min^{-1})	N_o (mg L^{-1})	K (L mg^{-1} min^{-1})
0.3	340	0.000586	348	0.000439
0.5	327	0.00126	334	0.000897
0.8	316	0.00220	308	0.00169
1.0	311	0.00231	269	0.00209

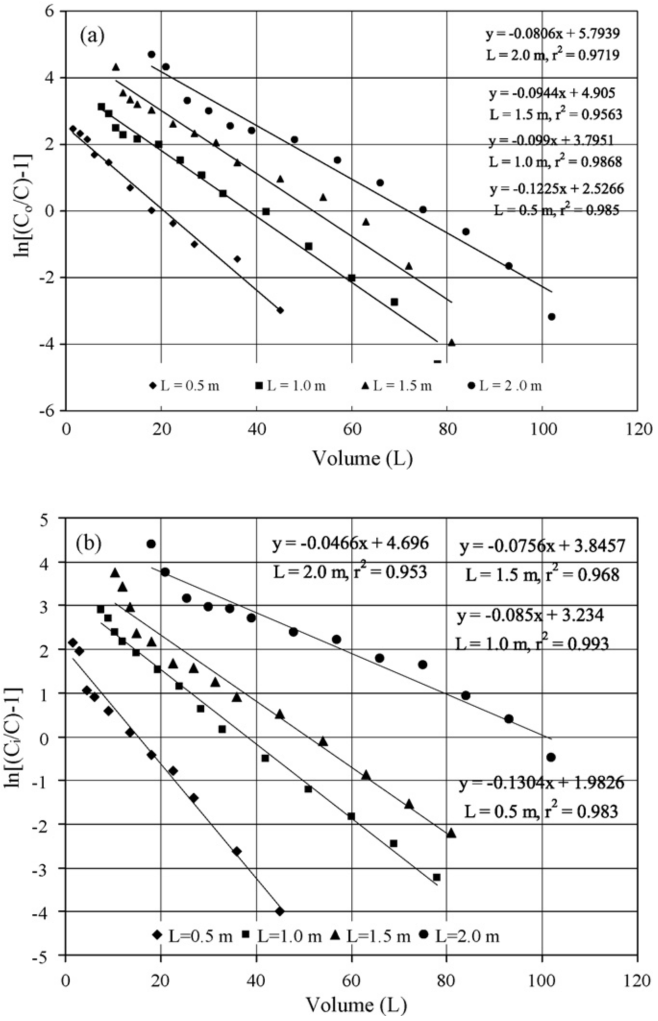

Fig. 10. The Thomas model for metal adsorption in a fixed bed of wheat straw at 0.3 LPM: (a) for Cd^{2+} and (b) for Cu^{2+}.

Among the three models presented above, it was found that the Thomas model best fitted to the experimental data for Cd^{2+} and Cu^{2+} with the r^2 values ranging from 0.96 to 0.99 as can be seen in Fig. 10(a) and (b). However, at the initial stage of adsorption, a large deviation between the model prediction and the experimental data was observed. The Thomas model was derived from the equation of mass conservation in a flow system [23]. In addition, the model also assumes that the rate driving force obeys second-order reversible reaction kinetics, and the adsorption equilibrium follows the Langmuir model with no axial dispersion [31]. The Thomas model is widely used to evaluate the column performance. It can be used to predict the breakthrough curve and the maximum solute uptake by the adsorbent. These parameters are essential for a successful design of an adsorption column [32].

The Thomas rate constant (K_{TH}) and the maximum solid phase concentration (q_t) were determined, respectively, from the slope and the intercept of the plots of $\ln[(C_i/C)-1]$ versus V as shown in Fig. 10(a) and (b). The values obtained are given in Table 3 for Cd^{2+}. The rate constant K_{TH} appear to increase significantly only when the liquid flow rate is increased to 1.0 LPM. The insensitivity of the rate constant with the liquid flow rate lower than 1.0 LPM

Table 3
Predicted parameters from the Thomas model for biosorption of Cd^{2+} on wheat straw.

Flow rate (LPM)	Z (m)	K_{TH} ($L\,mg^{-1}\,min^{-1}$)	q_t ($mg\,g^{-1}$)	Experimental uptake ($mg\,g^{-1}$)	r^2
0.3	0.5	0.000368	12.13	16.9	0.98
	1	0.000297	11.27	15.7	0.99
	1.5	0.000283	10.19	13.5	0.96
	2	0.000242	10.57	13.3	0.97
0.5	0.5	0.000512	14.18	16.4	0.99
	1	0.000295	16.59	15.1	0.99
	1.5	0.000273	16.03	14.6	0.98
	2	0.000263	15.68	14.4	0.98
1.0	0.5	0.00055	19.8	16.1	0.99
	1	0.00048	19.0	15.7	0.98
	1.5	0.00041	16.10	15.6	0.99
	2	0.00036	15.50	14.6	0.98

reinforces the hypothesis of the adsorption-controlled nature of the overall metal adsorption process in a fixed bed of wheat straw. However, the rate constant K_{TH} and the metal uptake q_t appear to decrease with the bed height at all liquid flow rates from 0.3 to 1.0 LPM. The experimental values of the metal uptake also exhibit a similar trend. At a low liquid flow rate of 0.3 LPM, the model underestimates the metal uptake by about 30%. On the other hand, at a high liquid flow rate of 1.0 LPM and short beds of 0.5 m and 1.0 m, the model overestimates the metal uptake by about 20%. However, for all bed heights from 0.5 to 2.0 m, the model prediction agrees quite well with the experimental data at 0.5 LPM. Moreover, when all experimental data at various bed heights from 0.5 to 2.0 m and liquid flow rates from 0.3 to 1.0 LPM are combined, the averaged value of the metal uptake is 15.2 $mg\,g^{-1}$ with a standard deviation of 1.1 $mg\,g^{-1}$. The averaged uptake q_t predicted from the Thomas model is 14.8 $mg\,g^{-1}$ with a standard deviation of 3.2 $mg\,g^{-1}$, which is quite close to the averaged experimental value. A two-tailed "t" test at a 95% confidence level was performed and found that the difference between the averaged experimental metal uptake and the averaged value predicted from the Thomas model was statistically insignificant [33]. Therefore, the Thomas model can be considered as a suitable kinetic model to describe Cd^{2+} and Cu^{2+} adsorption in a fixed bed of wheat straw.

3.2.2.3. *Mass transfer model for adsorption in the column.*

The BDST and Thomas models represent the experimental data fairly well. However, those models are undefined mathematically when the effluent concentration approaches zero during the initial period of the adsorption process. Therefore, in order to overcome this shortfall, a mass transfer model based on the first principle of mass transfer was developed. The following assumptions were used in the model development:

- One dimensional flow and diffusion in the axial direction.
- The fluid temperature, density and velocity are constant.
- Mass diffusivity is independent of the concentration of the solute.
- N_o intraparticle diffusion.

Mass transfer takes place between the bulk liquid at a metal concentration C and the wheat straw surface at a metal concentration C_e. The concentration at the surface of the particle, C_e, is the equilibrium concentration between liquid and wheat straw, which can be calculated from the equilibrium isotherm such as the Langmuir model. By using the differential mass balance, the following model was obtained:

$$\frac{\partial C}{\partial t} = \frac{D}{\varepsilon}\frac{\partial^2 c}{\partial z^2} - \frac{u}{\varepsilon}\frac{\partial C}{\partial z} - \frac{(1-\varepsilon)}{\varepsilon}k_C a(C - C_e) \tag{9}$$

where a is the specific area of the wheat straw particles in the column, D is the diffusivity of metal ions, ε is the bed porosity, k_C is the mass transfer coefficient of metal ions from the bulk liquid to the surface of the wheat straw particles in the column, u is the superficial velocity of liquid in the column, t is time and z is the axial distance in the column.

For mass transfer in liquid in a packed bed, the following correlation of the J_D factor for the Reynolds numbers ranging from 55 to 1500 can be used to estimate k_C [34]:

$$J_D = \frac{0.25}{\varepsilon}N_{Re}^{-0.31} \tag{10}$$

where $J_D = (k_C N_{Sc}{}^{2/3})/u$ and N_{Sc} is the Schmidt number.

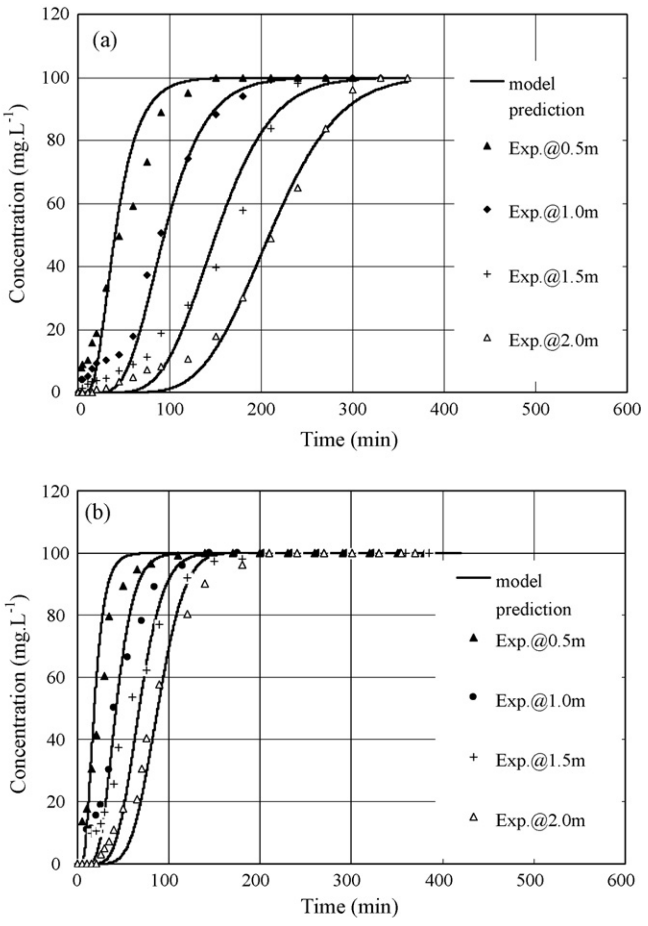

Fig. 11. Experimental and predicted outlet concentration: (a) 0.3 $L\,min^{-1}$ and (b) 1.0 $L\,min^{-1}$, inlet concentration of 100 $mg\,L^{-1}$ Cd^{2+}, T = 25 °C.

Table 4
Parameters used for the mass transfer model simulation.

Parameter	Value
ε	0.37
D [m^2 s^{-1}] of Cd^{2+}	3.005×10^{-8}
D [m^2 s^{-1}] of Cu^{2+}	5.355×10^{-8}
Z [m]	0.5, 1.0, 1.5, 2.0
Liquid flow rate [L min^{-1}]	0.3, 0.5, 0.8, 1.0
k_c of Cd^{2+} [m s^{-1}]	1.62×10^{-5}
k_c of Cu^{2+} [m s^{-1}]	2.3×10^{-5}
C_o [mg L^{-1}]	100
μ of Cd^{2+} [Pa s]	0.941×10^{-3}
μ of Cu^{2+} [Pa s]	0.94×10^{-3}
a [m^2 m^{-3}]	250

The model in Eq. (9) was solved numerically using the finite difference method. The values of the parameters used in solving the model are given in Table 4. The predicted values of Cd^{2+} concentration in the column effluent for various bed heights from 0.5 to 2.0 m, which were obtained from the numerical solution of the model, are plotted in Fig. 11(a) and (b). The metal concentration predicted from the model agrees quite well with the experimental data. The averaged deviation between the experimental data and the predicted values over the entire breakthrough curve was found be in the range of 7.5–15% among different experiments. The predicted values from the mass transfer model appear to agree to the experimental data better than the Thomas model prediction. The mass transfer model can thus be used to predict the breakthrough curve for adsorption of metal ions in a fixed-bed column.

4. Conclusion

Biosorption of Cd^{2+} and Cu^{2+} by wheat straw was studied, using a batch system and a continuous fixed bed. The batch system with an initial metal concentration of 100 mg L^{-1} was used to investigate the effect of temperature and pH on the metal uptake, and the equilibrium isotherms. The metal uptake was found to increase with both temperature and pH. The metal uptake increased from 12.2 to 15.7 mg g^{-1} and 9.1 to 12.2 mg g^{-1} for Cd^{2+} and Cu^{2+}, respectively, when the liquid temperature was increased from 20 to 40 °C. Over a pH range from 3.0 to 7.0, the metal uptake increased by 5.2 and 3.7 times for Cd^{2+} and Cu^{2+}, respectively. It was also found that the adsorption of Cd^{2+} and Cu^{2+} by wheat straw appeared to follow the Langmuir isotherm.

In the continuous system using a fixed-bed adsorber, breakthrough curves were obtained for different bed heights and liquid flow rates. It was found that the adsorption breakthrough was strongly dependent on the liquid flow rate, as expected. The biosorption process was showed to be more effective at a low flow rate (1.10×10^{-3} m^3 s^{-1} or 0.3 LPM) and a tall bed (2.0 m).

The bed-depth service-time model well correlated the bed height and the 10%-breakthrough time for metal adsorption in a fixed bed of wheat straw. Application of other mathematical models such as the Thomas, Bohart–Adams and Yan models to a fixed-bed adsorber was also investigated. Among those models, the Thomas model was found to be most suitable to represent the kinetics of biosorption of Cd^{2+} and Cu^{2+} in a fixed bed of wheat straw.

A mass transfer model for biosorption of metal ions in a fixed bed of wheat straw was also developed. The model predicted the concentration of metal ions in the effluent stream quite well.

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