KINETIC STUDIES ON THE SORPTION OF LEAD AND CADMIUM IONS FROM AQUEOUS SOLUTIONS BY CALADIUM BICOLOR (WILD COCOYAM) BIOMASS

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ABSTRACT. Kinetic investigations are necessary for determining the rate of reaction and mechanism. The kinetics of the sorption of Pb²⁺ and Cd²⁺ from aqueous solution on to the biomass of *C. bicolor* was studied by batch equilibrium technique. The removal of the two metal ions was found to be > 60% depending on the initial metal ion concentration during the contact time. The maximum sorption was found to be 75.11 mg/g and 25.30 mg/g for Pb²⁺ and Cd²⁺ at an equilibrium contact time of 150 min. The process of uptake is governed by film-diffusion controlled pseudosecond order reversible rate kinetics. The sorption capacity at any contact time has been evaluated and a Langmuir-type model equation has been developed to predict the optimized minimum operating time to determine a specific amount of metal ion sorption.

KEY WORDS: Sorption kinetics, Contact time optimization, Water treatment, Heavy metals removal

INTRODUCTION

Sorption has been described as an effective separation process for a wide variety of applications. Since conventional technologies ranging from granular activated carbon to reverse osmosis are expensive and not economically feasible for small-scale industries prevalent in developing economies due to huge capital investment. It is therefore necessary to search for alternative sorbents, which are inexpensive, often naturally occurring biodegradable products that have good sorbent properties and low value to the inhabitants. A range of products has been examined clay [1], sago waste [2], cassava waste [3], banana pith [4], peanut skin [5], *Medicago sativa* (Alfalfa) [6], and sphagnum moss peat [7] just to mention a few; however, most of these products are materials from agro-wastes. In this investigation, we have employed a non-useful, non-economic plant and readily available plant material — *Caladium bicolor* (wild cocoyam) as an adsorbent for metal ions. The plant is inedible because of the presence of large quantity of calcium oxalate in the corm [8], which produces an intense irritation after eating. The economic use of this plant will provide employment, enhance and improve the economies of local farmers and improve their resource base. The biomaterial is cellulosic and therefore biodegradable and environment friendly.

Kinetics describes the solute uptake rate that controls the residence time of sorbate uptake at the solid-solution interface. Kinetic studies are important in determining the time needed to reach equilibrium and examinations into the rates of adsorption can be used to develop models and an understanding of solutes on adsorbent surface. Kinetics is so important that, it can also be used to predict the rate of pollutant removal from aqueous solutions in the design of appropriate sorption treatment plants. Sorption kinetic models that have been used widely are the Lagergren pseudo-first order rate equation [9, 10] and recently the pseudo-second order kinetic expression developed by Ho [7]. The study of kinetics in wastewater treatment is significant as it provides available insights into the reaction pathways and mechanisms of

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sorption reactions. A screening previously performed [8] to assess the proximate chemical composition, surface characteristics and the effect of pH on the sorption of metal ions by *C. bicolor* has shown that, the biomass from the corm of *C. bicolor* is an excellent sorbent for metal ions in aqueous solution. The aim of this research is to present the sorption kinetics of Pb²⁺ and Cd²⁺ in order to obtain an optimum time required for maximum sorption of these metals in aqueous effluent using *Caladium bicolor* (wild cocoyam) biomass. Secondly, to present a modeling equation to predict the amount of metal ion sorbed at any given contact time.

EXPERIMENTAL

Adsorbent

The adsorbent used in the present study is *C. bicolor* (wild cocoyam) biomass. The plant was harvested in the University of Port Harcourt, Choba – Port Harcourt, Nigeria, where it grows as weed in cassava farms.

Preparation of adsorbent

After harvesting, the corm were washed with deionized water, air-dried, cut into 5 cm pieces and ground using a food processor (Magimix Cuisine System 5000, Great Britain), dried in an oven (GallenKamp, model OV-160, England) at 105 °C to constant weight and then screened through a 100-µm mesh Tyler screen to obtain a fine biomass.

Activation of the biomass

It is often necessary to activate a solid before using it as an adsorbent for sorption studies. The purpose of activation is to increase the surface area of the solid by introducing a suitable degree of porosity into the solid matrix. Again, activation may also produce structural defects in solids, which may be favourable to sorption processes [11]. 500 g of finely divided biomass was activated by soaking in excess 0.3 M HNO_3 for 24 h. After which it was washed thoroughly with deionized water until a pH of 7.1 ± 0.1 was attained and then air-dried. The air-dried activated biomass was then washed with deionized water and re-suspended in 1.0 M hydroxylamine to remove all O-acetyl groups. To remove all other soluble materials, the biomass was washed with deionized water and centrifuged at $3000 \times g$ for five minutes using a Portable Refrigerated test tube centrifuge model PR -2 with 20° diameter stainless solid basket 3/4 HP 1/60/115 volt motor with temperature indicator, timer and speed controls. The supernatants obtained were discarded.

Batch sorption study on the effect of contact time

A 250 mg biomass sample was weighed, washed with 0.1 M HCl and twice with de-ionized water to remove any metals or soluble biomolecules present in the biomass. 50 mL of de-ionized water were added to the biomass to obtain a biomass concentration of 5 mg/mL. The pH of this suspension was adjusted to 5.0. A 2 mL aliquot of the suspension was added to twenty-seven 5 mL clean test tubes; three for each time interval of 5, 10, 20, 30, 40, 60, 80, 100 and 150 min. The test tubes were centrifuged and the supernatants were discarded. Metal ion solutions (Pb²⁺ and Cd²⁺) with initial concentrations 10, 25, 50 and 100 mg/L were prepared and 10 mL of each metal ion solution of Pb²⁺ and Cd²⁺ was added to each pellet. All the tubes were shaken on a shaker for the specified time. The tubes were then centrifuged at 2800 x g for 5 min and the

supernatants were analyzed by flame atomic absorption spectroscopy (FAAS) model 200A (Germany). The following wavelengths were used for the metals studied: Pb - 283.3 nm and Cd - 228.8 nm.

Calculation of metal ion uptake efficiency

The adsorption efficiency of the metal ion by the biomass was calculated using the equation

$$\% R = \left(\frac{C_o - C_e}{C_o}\right) \times 100$$

where R is adsorption efficiency; C₀ is initial concentration (mg/L) and C_e is concentration of metal ion in aqueous phase at equilibrium (mg/L).

RESULTS AND DISCUSSION

Kinetics of metal sorption

The kinetic model applied in the present investigation to describe the reaction rate was based on the assumption that sorption of metal ions onto the *C. bicolor* biomass is a pseudo-first order reversible process. The hypothetical reaction may be expressed as:

$$\begin{array}{ccc}
K_a \\
B & \rightleftharpoons C \\
K_d
\end{array} \tag{2}$$

where K_a and K_d are the adsorption and desorption constants, respectively. The linear driving force concept earlier developed by Vinod and Anirudhan [1] for pseudo-first order rate equation was modified and used to obtain the fractional attainment of equilibrium. The equation is expressed as

$$\ln(1-t) = -K_1 t \tag{3}$$

where f is the fractional attainment of equilibrium, and K_1 is the overall rate constant. The fractional attainment of equilibrium (f) is the ratio of the amounts of metal ion removed from solution after a certain time to that removed when sorption equilibrium is attained.

In order to quantify the changes in sorption as a function of time, the rate of metal ion uptake was applied to the data. A plot of fractional attainment of equilibrium (f) against time of the experimental data for the sorption of Pb^{2+} and Cd^{2+} onto the biomass was made. For the purpose of this plot, f is given as

$$f = \frac{C_o - C_t}{C_o - C_e} \tag{4}$$

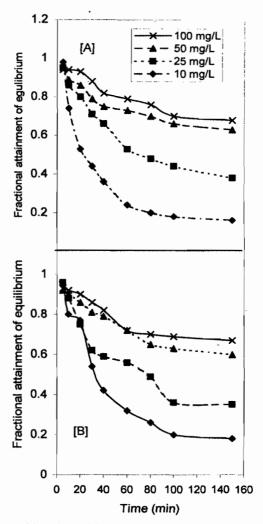


Figure 1. Sorption rates of initial metal ion concentration as a function of time on C. bicolor biomass at pH 5 and 29 °C ([A] = Pb^{2+} and [B] = Cd^{2+}).

A plot of f against time (t) for the two divalent metal ions is shown in Figure 1. The plot shows that the values of f decrease with contact time. This indicates that increasing the contact time above the equilibrium time do not have any significant increased sorption by the biomass. However, most of the metal ions in solution were removed in less than 50 min. The plot further confirms that, the adsorption rates were rapid and that increasing the initial metal ion concentration resulted in a decrease in the initial rate especially for low metal ion concentrations. The data show that the most marked effect occurred when the initial concentration increased from 10 to 20 mg/L and that further increases in the metal ion concentration had little effect. However, the plots show that after this initial period, the rates and

consequently the removal efficiency for metal ions by the biomass became almost constant; probably due to surface saturation of the biomass. A long contact time necessary to reach equilibrium indicates that the predominant mechanism is physical adsorption; consequently the process will be reversible, hence column regeneration is possible. A relatively short contact time indicates that chemisorption is the predominant mechanism. The contact time obtained in this study indicates that both physisorptions and chemisorptions may be involved [7]. From Figure 1, it was observed that fractional attainment of equilibrium value increased for both metal ions as initial metal ion concentration increased. Again, the fractional attainment of equilibrium, f, show that the effectiveness of the C. bicolor biomass towards the removal of the metal ions from aqueous solution was $Cd^{2+} > Pb^{2+}$. The higher f value for Cd^{2+} may be explained in terms of ionic radius of the metal ions ($Pb^{2+} = 1.20 \text{ Å}$; $Cd^{2+} = 0.97 \text{ Å}$). Cd^{2+} with smaller ionic radius will have greater accessibility to the biomass surface of certain pores than the Pb^{2+} , therefore leading to higher extent in the adsorption.

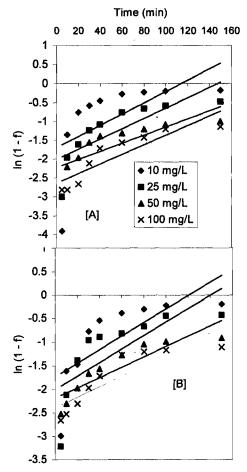


Figure 2. Pseudo-first order sorption kinetics of metal ions onto C. bicolor biomass ([A] = Pb^{2+} and [B] = Cd^{2+}).

The kinetic theory behind the fractional attainment of equilibrium is that it can be used to explain the sorption process in terms of adsorption being controlled by film-diffusion or particle-diffusion [7]. If the plot of $\ln(1-f)$ against t gives a linear relationship, then adsorption is controlled by particle-diffusion and the diffusivity of the metal ions onto the biomass surface is independent of the extent of sorption. However, a non-linear plot indicates that the diffusivity of the ions onto the adsorbent surface is film-diffusion controlled [1].

A plot of $\ln(1-f)$ against t (Figure 2) gave the pseudo-first order kinetics. From the plot (Figure 2), it is observed that the relationship between metal ion diffusivity, $\ln(1-f)$ and time is non-linear, indicating that the diffusivity of metal ions onto the C. bicolor biomass surface is film-diffusion controlled. Hence, the uptake time for Pb^{2+} and Cd^{2+} by C. bicolor biomass is dependent on the initial metal ion concentration. The non-linearity of the diffusivity plot showed that the pseudo-first order equation proposed was not adequate in describing the reactions between the two divalent metal ions on C. bicolor biomass surface.

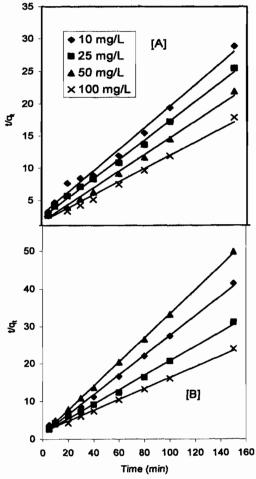


Figure 3. Pseudo-second order sorption kinetics of metal ion onto C. bicolor ([A] = Pb^{2+} and [B] = Cd^{2+}).

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Therefore a pseudo-second order equation based on the sorption capacity on the solid biomass phase was employed. This model predicts the sorption behaviour of Pb²⁺ and Cd²⁺ over all the concentrations of studies and enables the initial sorption rate to be evaluated. If the rate is presumed to be second-order mechanism, the pseudo-second order kinetic rate expression in a linearised form [12] may be expressed as follows:

$$\frac{t}{q_1} = \frac{1}{h_0} + \frac{1}{q_e} t \tag{4}$$

where q_t is the amount of divalent metal ion on the biomass surface (mg/g) at any time(t); q_e is the amount of divalent metal ion sorbed at equilibrium (mg/g); h_o is the initial sorption capacity (mg/g min)

The batch experimental data were fitted into equation 4 and a plot of t/q_t against t was made as shown in Figure 3. The equilibrium sorption capacity, q_e , the pseudo-second order rate constant, k_2 , and the determination coefficient, r_2^2 , were calculated from the slope and intercept of Figure 3. The initial sorption rate, h_0 , was computed using the following expression:

$$h_{\alpha} = k_2 q_{\alpha}^2 \tag{5}$$

where K₂ is the pseudo-second order rate constant (g/mg min)

The results as presented in Table 1 showed that the pseudo-second order rate constants, k₂, were found to decrease from 9.97 x 10⁻³ to 5.99 x 10⁻³ g/mg min for the sorption of Pb²⁺ and decrease from 5.51 x 10⁻² to 1.13 x 10⁻³ g/mg min for Cd²⁺ for an increase in initial metal ion concentration from 10 to 100 mg/L. This characteristic behaviour indicates that surface saturation is dependent on the initial metal ions concentration. The observed decrease in the rate constants with increase in initial metal ion concentration may be that, at high concentration, the average distance between the sorbing species is diminished to a point where each affects the charge distribution of its neighbours. This interaction can alter the ability of the species to sorb on the biomass, hence, high concentration of metal ions may limit the ability of the biomass to adsorb metals and sorption process may require several cycles in order to meet regulatory standards.

Table 1. Values of kinetic parameters for the pseudo-second order rate for the sorption of Pb²⁺ and Cd²⁺ on the biomass

_	Pb ²⁺				
Co, mg/L	h _o , mg g ⁻¹ min ⁻¹	k ₂ , g mg ⁻¹ min ⁻¹	q _c , mg g ⁻¹		
10	0.354	9.97×10^{-3}	5.96		
25	0.438	9.90 x 10 ⁻³	6.96		
50	0.598	5.99 x 10 ⁻³	7.68		
100	0.588	1.01 x 10 ⁻³	9.70		
C _o , mg/L		Cd ²⁺			
10	0.795	5.51 x 10 ⁻²	3.80		
25	0.624	2.31 x 10 ⁻²	5.20		
50	0.796	2.8 x 10 ⁻²	3.11		
100	0.533	1.3 x 10 ⁻²	6.92		

Coefficient of determination

Furthermore, the coefficient of determination, R², for the pseudo-first order and pseudo-second rate laws were used to confirm the sorption mechanism proposed. The R² values for the two rate constants are listed in Table 2. The data show a good compliance with the pseudo-second order equation as the coefficients of determination for metal ions on the biomass were > 0.992 for the two divalent metal ions. The coefficient of determination for the first order kinetic model was smaller than the pseudo-second order, indicative that the pseudo-second order equation is more appropriate in describing the sorption. Furthermore, the initial sorption rates for the sorption of Cd²⁺ were found to be greater than that of Pb²⁺. This suggests that smaller ionic radius has more effect on the initial sorption rate in the case of Cd²⁺ whereas in the case of Pb²⁺, hydration of metal ion has greater effect on the pseudo-second order rate constant.

Table 2. Coefficients of determination, R², for the pseudo-first (K₁) and pseudo-second (K₂) order rate constants at various initial metal ion concentrations

C _o , mg/L	Pb ²⁺		Cd ⁺²		
	K ₁	K ₂	K ₁	K ₂	
10	0.351	0.990	0.546	0.998	
25	0.637	0.996	0.555	0.997	
50	0.637	0.991	0.794	0.9996	
100	0.80	0.980	0.772	0.995	

The internal associations of the data in Table 2 was ascertained using the two-way analysis of variance (ANOVA) (p < 0.05) by considering the metals as objects and the R^2 values as variable. The result is presented in Table 3.

Table 3. Two-way analysis of variance (ANOVA) without replication at $\alpha = 0.05$.

Source of variation	SS	df	MS	P-value	F _{-cal}	F _{-crit}
Metals	0.064	3	0.021	0.184	0.021	3.86
R ²	0.517	3	0.172	0.001	16.25	3.86
Error	0.095	9	0.011			
Total	0.676	5				

SS = sums of square; df = degrees of freedom; MS = mean square; $P_{\text{-value}}$ = probability value; $F_{\text{-cal}}$ = calculated F-ratio value; $F_{\text{-crit}}$ = critical or tabulated F-ratio value.

The data showed no significant difference (as $F_{cal} < F_{crit}$) in the sorption behaviour of the two metal ions on the pseudo-first order rate law as well as on the pseudo-second order rate law. This indicates that Pb^{2+} and Cd^{2+} have similar sorption mechanism on both rate laws. However, it is clear from the result that the pseudo-second order rate law has best described the sorption of Pb^{2+} and Cd^{2+} on C. bicolor biomass at the various reaction conditions, confirming the film-diffusivity of metal ion onto the biomass surface.

Equilibrium sorption

The determination of the equilibrium sorption contact time between dissolved and solid-bound sorbate is important in studying the metal biosorption kinetics. Equilibrium time is a function of many factors, such as type of biomass, size and form of biomass, physiological state of biomass, as well as the metal involved in the sorption process. Reported values for equilibrium time are in

the range from 15 min [13] to ten days [14]. Hence, to quantify the differential sorption characteristics between the metals for the *C. bicolor* biomass as a function of time, the effect of time on the sorption characteristics was applied to the data.

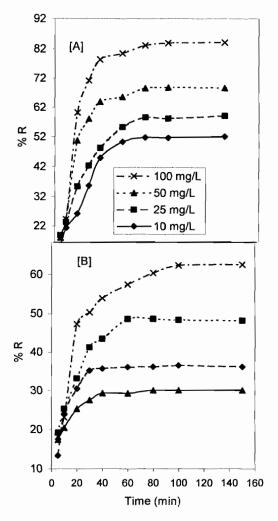


Figure 4. Effect of contact time on the sorption of metal ions in aqueous solution by C. bicolor biomass ($[A] = Pb^{2+}$ and $[B] = Cd^{2+}$)

The effect of contact time on the removal of Pb²⁺ and Cd²⁺ ions by the *C. bicolor* biomass is presented in Figure 4. The sorption characteristic indicates that saturation time is dependent on the metal ion and the initial metal ion concentrations and that maximum sorption was achieved within 60 minutes and equilibrium attained in 90 minutes. This was because the adsorption sites took up the available metal more quickly at low concentrations. The results also show a marked effect of the two divalent metal ions on the biomass caused due to the difference in their ionic

size. The biomass adsorbs more Pb²⁺ than Cd²⁺ in all the contact time range studied. This differential sorption discrepancy was most probably due to the difference in their molecular weight when molar considerations are made. The rapid adsorption of the metal ions to the biomass indicates that adsorption may be taking place on the cell wall of the biomass. It is clear from Figure 4 that removal of Pb²⁺ and Cd²⁺ by the biomass takes place in two different phases. The first phase of metal ion sorption is the immediate solute removal phase, which is achieved relatively quickly. This is followed by the second gradual phase, which extends over a longer period of time.

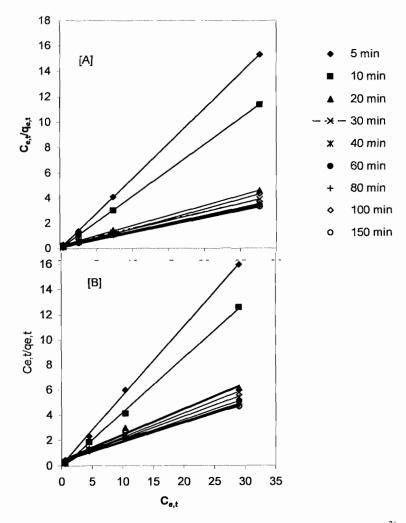


Figure 5. Time-dependent Langmuir-type isotherm plots for the sorption of (A) Pb²⁺ and (B) Cd²⁺ onto *C. bicolor* biomass.

In order to predict the minimum contact time required to remove a fixed percentage of metal ions from a given volume of aqueous effluent of specified metal ion concentration, using a fixed mass of biomass, the Langmuir isotherm model was used to correlate all concentrations at each contact time. The Langmuir equation as a time-dependent equation [15] expressed as in equation (7) was used.

$$q_{e,t} = \frac{X_{m,t} K_{L,t} C_t}{1 + K_{L,t} C_{e,t}} \tag{7}$$

where $q_{e,t}$ = the time-dependent sorption capacity of the biomass at the equilibrium solute concentration, C_e (mg metal ion g^{-1} biomass); $C_{e,t}$ = the time-dependent equilibrium concentration of metal ion in solution (mg metal ion L^{-1}); $X_{m,t}$ = the time-dependent maximum sorption capacity corresponding to complete monolayer coverage (mg metal ion g^{-1} biomass) and $K_{L,t}$ = the time-dependent Langmuir constant related to the energy of sorption (L mg⁻¹).

The time-dependent linearised Langmuir equation is in the form

$$\frac{C_{e,t}}{q_{e,t}} = \frac{1}{X_{m,t} K_{L,t}} + \frac{C_{e,t}}{X_{m,t}}$$
(8)

The capacity of the C. bicolor biomass was then obtained by plotting $C_{e,t}/q_{e,t}$ against $C_{e,t}$ for each contact time (Figure 5). The monolayer surface saturation, which represents the sorption capacity of the biomass for the two metal ions at different fixed contact time was then obtained from the slope of the plot (Figure 5) and are presented in Table 4. Also presented in Table 4 are the values of the effective time-dependent Langmuir equation parameters for the nine samples from 5 to 150 min. Furthermore, the corresponding plots of the values of $X_{m,t}$ and $K_{L,t}$ against time (t) were made (Figure 6 and 7). These linear plots were regressed to obtain expressions in terms of contact times. The regression equation for $X_{m,t}$ and $K_{L,t}$ as a function of time for Pb²⁺ and Cd²⁺ are expressed as in equations (9) and (10), respectively:

$$X_{m,t,pb} = 0.410t + 16.90$$

$$X_{L,t,Cd} = 0.075t + 14.58$$
(9)

$$K_{L,tpb} = 0.0012t + 0.376$$

$$K_{L,tCd} = 0.0021t + 0.169$$
(10)

Substitution of equations 9 and 10 into equation 7 gives the Langmuir type time-dependent sorption capacity prediction equation as given in equation 11 for the sorption of Pb²⁺ and Cd²⁺, respectively.

$$q_{e,t,pb} = \frac{(0.41t + 16.90)(1.2x10^{-3}t + 0.376)C_{e,t}}{(1 + 1.2x10^{-3}t + 0.376)C_{e,t}}$$

$$q_{e,t,cd} = \frac{(0.075t + 14.58)(2.1x10^{-3}t + 0.169)C_{e,t}}{(1 + 2.1x10^{-3}t + 0.169)C_{e,t}}$$
(11)

Equation 11 can then be used to predict the amount of metal ion (Pb²⁺ and Cd²⁺) sorbed from aqueous effluent at any given contact time and the time-dependent Langmuir-type parameters on a fixed time basis. The time-dependent regression equation was then employed to evaluate the sorption capacity of the biomass at a fixed time of 150 min and found to be 78.40 mg/g and 25.83 mg/g for Pb²⁺ and Cd²⁺, respectively. These calculated values are in agreement with the experimentally obtained values (Table 4). This confirms that a minimum time to achieve a fixed percentage of metal removal from aqueous effluent by sorption onto the *C. bicolor* biomass can be readily predicted using the proposed time-dependent Langmuir-type equation. This technique may minimize contact time and may be very useful in industrial scale-up process design. The data (Table 4) further indicated that the coefficients of determinations, R², are extremely high (> 0.99) for both metals, indicative that the proposed optimization equations fit the experimental data appropriately.

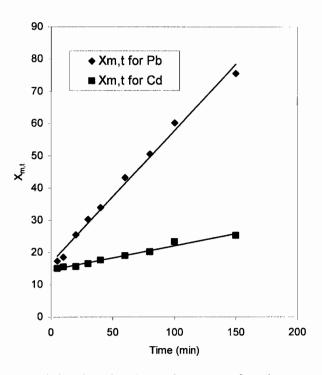


Figure 6. Plot of time-dependent Langmuir constant of maximum sorption for a monolayer coverage, X_{mb} against time.

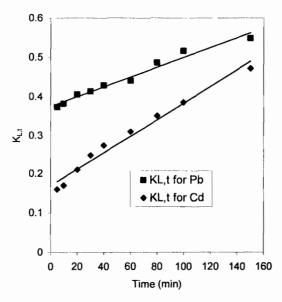


Figure 7. Plot of time-dependent Langmuir adsorption constant, K_{Lt}, as a function of time.

Table 4. Time-dependent Langmuir isotherm parameters and coefficients of determination for Pb²⁺ and Cd²⁺ on *C. bicolor* biomass at varying contact time and fixed initial metal ion concentration (100 mg/L)

Time (min)		Pb ²⁺			Cd ²⁺		
	$X_{m,t}$	$K_{L,t}$	R^2	$X_{m,t}$	$K_{L,t}$	R^2	
5	17.41	0.374	1.000	15.10	0.16	0.9994	
10	18.63	0.382	1.000	15.51	0.17	0.9987	
20	25.53	0.406	0.9976	15.66	0.21	0.985	
30	30.26	0.414	0.9966	16.55	0.25	0.9936	
40	33.89	0.429	0.9965	17.69	0.27	0.9916	
60	43.21	0.441	0.9969	19.07	0.31	0.9923	
80	50.64	0.486	0.9973	20.22	0.35	0.9883	
100	60.22	0.516	0.9993	23.39	0.39	0.985	
150	75.11	0.548	0.9971	25.30	0.47	0.986	

CONCLUSION

The kinetics of Pb^{2+} and Cd^{2+} sorption on to C. bicolor biomass were found to be based on the assumption of a film-diffusion controlled pseudo-second order mechanism with physisorption being the predominant mechanism. An optimization model has been developed to minimize the total contact time for the removal of Pb^{2+} and Cd^{2+} ions in a single stage batch sorber. The minimum time to achieve a fixed percentage of metal sorption from wastewater using C. bicolor can readily be predicted. The contact time obtained in this study indicates that both physisorptions and chemisorptions are involved in the sorption process.

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