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Modeling of Cd²⁺ Sorption Kinetics from Aqueous Solutions onto Some Thiolated Agricultural Waste Adsorbents

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Abstract: Batch kinetic studies was conducted to determine the influence of contact time and chemical modification of adsorbent on sorption of Cd²⁺. Results indicate that maximum removal efficiencies of 54.66% and 58.66% was obtained for 0.5 and 1.0 MCF at the end of 30 min. Analysis of kinetic models applied to the sorption of Cd (II) ions on the adsorbents was evaluated for the pseudo-first order, pseudo-second order, Elovich, intraparticle diffusion, mass transfer and intra-particle diffusivity models, respectively. The results indicate that the pseudo-second order kinetic model was found to correlate best with the experimental data with rate constants of 2.34×10^{-1} and $4.64 \times 10^{-1} \text{ g mg}^{-1} \text{ min}^{-1}$ for 0.5 and 1.0 MCF, respectively.

Key words: Heavy metals, cadmium, kinetics, sorption, adsorbent, modeling

INTRODUCTION

The generation of heavy metal ions into the environment has increased in geometrical proportions due to a wide range of industrial activities. The influx of these metal ions into the air, land and water environment has caused a variety of problems to the ecosystem.

In contrast to organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products (Qadeer and Akhtar, 2005). This makes it necessary for heavy metal ions to be eliminated or at least reduced substantially from water and wastewater before discharge into the environment.

Some of the most common heavy metals found in effluents that are significantly toxic to flora and fauna include, cadmium, lead and chromium (Sayilkan *et al.*, 2004). Cadmium which exist in the divalent state has no known beneficial function to the human system. However, Cadmium absorption can entail a decrease in zinc and magnesium ions absorption in the body. It also causes genetic changes and cancer (Hill, 1984).

Due to the toxic effects of heavy metal ions, some methods have been developed to help remove them from effluent systems. These include, chemical precipitation, solvent extraction, ion exchange and cementation. These methods have some limitations in their application due to their high cost and sludge disposal problems both in solid and aqueous discharges.

Due to the above problems, adsorption technique has been examined and found to be a more efficient and economical method in the removal of heavy metal from effluents. This has led to its extensive application in wastewater treatment recently.

To further enhance the cost effectiveness of adsorptive separation method, a great deal of interest has been devoted to the utilization of agricultural by products as adsorbents for the removal of trace amounts of toxic heavy metals from industrial and municipal effluents (Igwe *et al.*, 2005).

In our earlier study (Abia *et al.*, 2003) we investigated the use of chemically modified and unmodified cassava waste for the removal of Cd²⁺, Cu²⁺ and Zn²⁺ from aqueous metal solutions. This present study explores the different kinetic models that can be used to account for the transport of Cd²⁺ from the aqueous metal solution on to the surface of the different thiolated cassava adsorbents. This will assist in elucidating the different diffusion controlled rate mechanisms that influence metal sorption.

MATERIALS AND METHODS

Cassava fibre waste from processing of cassava into the staple food garri was obtained, air dried and ground using a Wiley grinder. The powdered fibre was washed with deionized water and wet sieved through a set of sieves (106 and 150 µm) and further dried in air.

The screened fibre was then soaked in excess 0.3 M trioxonitrate (v) acid (HNO₃) solution for 24 h. It was later filtered, air dried and sieved through the mesh sieves. The powdered cassava fibre was then divided into two portions (A and B) each weighing 20 g. Portion A was soaked in excess 200 mL of 0.5 M thioglycollic acid (HSCH₂COOH) solution while B was soaked in excess 1.0 M thioglycollic acid for 24 h as described by Okieimen *et al.* (1988).

The two mixtures were later filtered, air dried and labeled 0.5 and 1.0 MCF for the 0.5 and 1.0 M thioglycolic acid modified cassava fibres, respectively. To determine the sorption of Cd²⁺ by the two adsorbents, 1000 mg dm⁻³ stock solution of cadmium (II) chloride (CdCl₂.2½ H₂O) [BDH] was prepared using distilled deionized water. All working solutions were prepared by diluting the stock solution with distilled deionized water.

Hundred milliliter of cadmium (II) ion solutions of initial concentration 30 mg dm⁻³ were measured into different conical flasks containing 1 g of each adsorbent (0.5 and 1.0 MCF). The flasks were corked and uniformly agitated at a speed of 25 rpm, temperature of 29°C and pH of 5.0 for 5 min. The experimental set was repeated for various time intervals of 10, 15, 20, 25 and 30 min. Kinetic equilibrium infinity sorption (α) was also carried out for 24 h. At the end of each contact time, the contents of each flask was filtered using a whatman No. 41 filter paper. The concentration of Cd²⁺ in each filtrate was determined using a Buck scientific flame Atomic absorption spectrophotometer [FAAS] model 200A.

DATA ANALYSIS

The metal sorption capacity (qt) of the two thiolated cellulosic materials can be calculated from the relationship in Eq. 1 (Demirbas *et al.*, 2004).

$$qt = \frac{[C_i - C_t]}{M_s} V \tag{1}$$

Also, the percentage of Cd (II) ions removed (%R_E) from solution by each adsorbent was calculated using Eq. 2

$$\%R_E = \frac{(C_i - C_t)}{C_i} \times 100 \tag{2}$$

Whereas the fraction of adsorption of Cd (II) ions by the two thiolated adsorbents was determined from the relationship in Eq. 3 (Karthikeyan *et al.*, 2004):

$$Y_t = \frac{C_i - C_t}{C_i - C_e} \tag{3}$$

Where:

- q_s is the metal sorption capacity of the adsorbent (mg g⁻¹).
- C_i is the initial metal ion concentration
- C_t is the metal ion concentration in solution at time t (mg L⁻¹)
- Y_t is the fraction of the metal adsorbed at time t.

M_s is the weight of the adsorbent (g)

V is the volume of the metal ion solution used for sorption (dm³) and

C_e is the concentration of metal ion

when sorption is complete, i.e., infinity sorption [C_α = C_e]

KINETIC MODELING

The study of sorption kinetics describes the adsorbate uptake rate and evidently this rate controls the residence time of adsorbate at the solid-liquid interface (Demirbas *et al.*, 2004). The kinetics of Cd²⁺ sorption on the two thiolated cassava adsorbents was analysed using different kinetic models, these include: the pseudo-first order (Lagergen, 1898), pseudo-second order (Ho and McKay, 1998), Elovich (Chien and Clayton, 1980; Sparks, 1986), intraparticle diffusion (Weber and Morris, 1963, Srivastava *et al.*, 1989), Mass transfer model (Qadeer and Akhtar, 2005) and the intraparticle diffusivity model (McKay and Poots, 1980). The agreement between experimental data and the model predicted values for each model was expressed by the coefficient of determination (r², values close or equal to 1). A relatively high r² value indicates that the model so examined successfully describes the kinetics of Cd (II) Sorption onto the thiolated cassava adsorbents.

The pseudo-first order equation: The pseudo-first order equation (Lagergren, 1898) is generally expressed as follows:

$$\frac{d_{qt}}{dt} = K_1(q_e - q_t) \tag{4}$$

Where q_e and q_t are the sorption capacities at equilibrium and at time t, respectively (mg g⁻¹) and K₁ is the rate constant of pseudo-first order sorption (L min⁻¹). After integration and applying boundary conditions t = 0 to t = t and q_t = 0 to q_t = q_e, the integrated form of Eq. 4 becomes:

$$\log (q_e - q_t) = \log (q_e) - \frac{k_1}{2.303} t \tag{5}$$

When the values of Log (q_e-q_t) were linearly correlated with t, the plot of Log (q_e-q_t) versus t should give a linear relationship from which K₁ and q_e can be determined from the slope and intercept of the graph, respectively.

The pseudo-second order equation: If the rate of sorption is a second order mechanism, the pseudo second order chemisorption kinetic rate equation (Ho and McKay, 1998) is expressed as Eq. 6:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{6}$$

Where q_e and q_t are the sorption capacity at equilibrium and at time t , respectively ($mg\ g^{-1}$) and K_2 is the rate constant of the pseudo-second order sorption ($g\ mg^{-1}\ min^{-1}$). For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t - q_e$, the integrated form of Eq. (6) becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K_2 t \tag{7}$$

Which is the integrated rate law for a pseudo-second order reaction. Equation 7 can be rearranged to obtain:

$$q_t = \frac{1}{\frac{1}{K_2 q_e^2} + \frac{t}{q_e}} \tag{8}$$

Which has a linear form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{9}$$

Where h ($mg\ g^{-1}\ min^{-1}$) can be regarded as the initial sorption rate as

$$q_t / t \longrightarrow 0, \text{ hence } h = K_2 q_e^2 \tag{10}$$

Further more Eq. 9 can be written as:

$$\frac{1}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \tag{11}$$

If the pseudo-second order-kinetics is applicable to the experimental data, the plot of t/q_t versus t of Eq. 11 should give a linear relationship from which q_e , K and h can be determined from the slope and intercept of the plot, respectively.

The elovich kinetic equation: The Elovich equation is generally expressed as (Chien and Clayton, 1980; Sparks, 1986):

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{12}$$

Where:

q_t is the sorption capacity at time t ($mg\ g^{-1}$) α is the initial adsorption rate ($mg\ g^{-1}\ min^{-1}$) and β is the desorption constant ($g\ mg^{-1}$) during any one experiment

To simplify the Elovich equation, Chien and Clayton (1980) assumed $\alpha\beta t \gg 1$ and by applying the boundary

condition $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. 12 becomes (Sparks, 1986);

$$qt = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \tag{13}$$

Thus, the constants will be determined from the slope and intercept of a plot of q_t versus $\ln t$, which should give a linear relationship if the Elovich equation is applicable in describing the kinetics of Cd^{2+} Sorption.

The intraparticle diffusion model: The intraparticle diffusion model is expressed as (Weber and Morris, 1963, Srivastava *et al.*, 1989) Eq. 14:

$$R = K_{id} (t)^a \tag{14}$$

A linearised form of the equation is Eq. 15:

$$\text{Log } R = \text{Log } K_{id} + a \log t \tag{15}$$

Where:

R is the percent Cd^{2+} adsorbed

t is the contact time

a is the adsorption mechanism

K_{id} is the intraparticle diffusion rate contact (min^{-1}). K_{id} may be taken as a rate factor that is percent Cd^{2+} adsorbed per unit time (Demirbas *et al.*, 2004).

The plot of $\log R$ versus $\log t$ (Eq.15) should give a linear relationship from where the constants a and K_{id} can be determined from the slope and intercept of the plot, respectively.

The mass transfer model: The mass transfer kinetic model is generally expressed as Eq. 16 (Qadeer and Akhtar, 2005)

$$C_o - C_t = D \exp(K_o t) \tag{16}$$

Where:

C_o is the initial metal ion concentration ($mg\ L^{-1}$)

C_t is the metal ion concentration at time t ,

t is the shaking time (min)

D is a fitting parameter

K_o is a constant which is the mass transfer adsorption coefficient

A linearised form of Eq. (16) is:

$$\ln(C_o - C_t) = \ln D + K_o t \tag{17}$$

If the sorption of cadmium (II) ions is depicted by the mass transfer model, then a plot of $\ln(C_o - C_t)$ versus time should give a linear relationship from where $\ln D$ and K_o

can be determined from the intercept and slope of the plot, respectively.

The intraparticle diffusivity equation: The intraparticle diffusivity equation for description of sorption kinetics is expressed as Eq. 18 (Mckay and Poots, 1980)

$$q_t = X_i + K^1 \sqrt{t} \quad (18)$$

Where:

K_1 gives the initial rate of sorption controlled by intraparticle diffusivity ($\text{mg g}^{-1} \text{min}^{-1}$)

X_i depicts the boundary layer thickness.

If the sorption of Cd (II) ions follows the intraparticle diffusivity equation, then a plot of q_t versus \sqrt{t} should give a linear relationship from where K^1 and X_i can be determined from the intercept and slope of the plot, respectively.

RESULTS AND DISCUSSION

The kinetics of Cd^{2+} sorption onto the two thiolated adsorbents (0.5 and 1.0 MCF) was investigated using an initial metal ion concentration of 30 mg L^{-1} at pH 5.0 and temperature 29°C . The percentage of Cd (II) ion removed by each adsorbents with time is shown in Fig. 1 while the variation of sorption capacity with time is presented in Fig. 2. From Fig. 1 and 2, the adsorption of cadmium (II) ion was rapid in the first 5-10 min followed by a continuously relatively slower rate up to a maximum at 30 min where 53.66 and 58.66% of Cd^{2+} was removed by 0.5 and 1.0 MCF, respectively.

The time-dependence of fraction of adsorption of Cd (II) ion is graphically shown in Fig. 3. Where the rate of fraction of adsorption of Cd^{2+} , Y_t is plotted against the square root of time. The curve for both adsorbents show two different stages of sorption transport. The initial stage of the curve relates to the transfer of Cd^{2+} from the bulk of the solution to the boundary film of the adsorbent. While the next stage indicates a transfer of cadmium (II) ions from the surface of the adsorbent to the intraparticle active sites of the adsorbents. Similar result was obtained by the study of sorption of reactive dyes by ChitoSan (Ruey-Shin *et al.*, 1997).

In addition the initial faster rate of adsorption of Cd^{2+} in 5-10 min may be due to the availability of the uncovered surface area of the adsorbents, since adsorption kinetics depends on the surface area of the adsorbent (Smith, 1970). Also the increased amount of Cd^{2+} adsorbed as chemical modification increases, may be due to the increased number of binding sites due to chemical

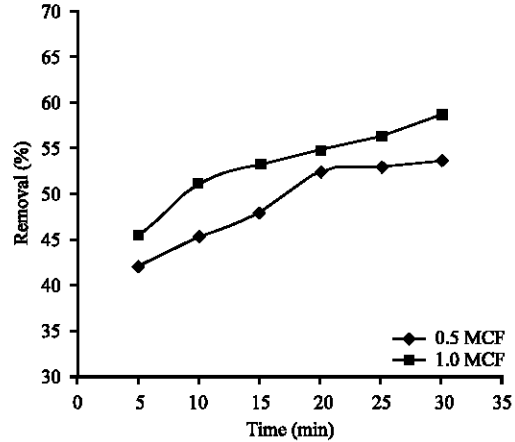


Fig. 1: Percentage removal of Cd^{2+} with time for different adsorbents

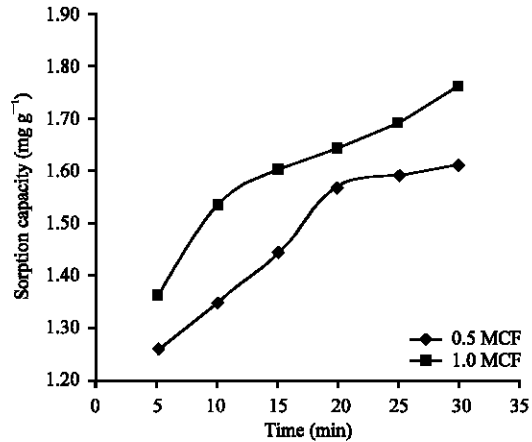


Fig. 2: Cd^{2+} sorption capacity (q_t) variation with contact time for adsorbents

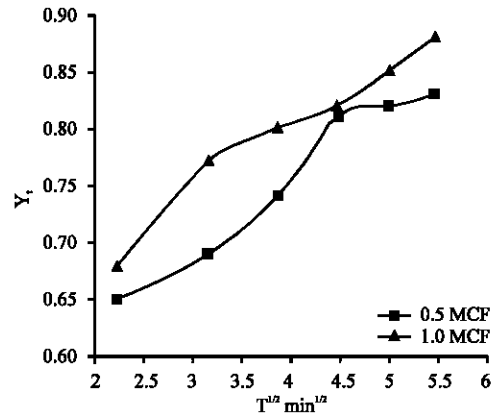


Fig. 3: Time dependence of the fraction of adsorption of Cd^{2+} for various adsorbents

modification. Abia *et al.* (2003) reported that the incorporation of thiol groups on an adsorbent surface enhances the binding capacity of the sorbent by increasing the number of binding sites.

Thus from Fig. 1 and 2 the percentage removal and sorption capacity of Cd²⁺ increased following the order 0.5 MoPF<1.0 MoPF. Thereby confirming that increase in chemical modification of the cassava adsorbents which has cyano, carboxyl and hydroxyl functional groups increased the sorption capacity of the chemically modified adsorbents. This is due to the introduction of the Sulphydryl group (SH) into the adsorbent matrix. This process of chemical modification enlarges the surface area of an adsorbent, by introducing a suitable degree of porosity into the solid matrix (Horsfall *et al.*, 2004). This enhances the percentage removal of Cd²⁺ from the aqueous solution.

Kinetic modeling of cadmium (II) ion sorption:

Adsorption kinetics of metal transport onto an adsorbent can be controlled by several independent processes. These are (i) Bulk diffusion (ii) External mass transfer, (Film diffusion), (iii) Chemical reaction (Chemisorption) and (iv) Intraparticle diffusion. These processes can act in series or parallel to account for the surface transport of a metal unto an adsorbent (Ho *et al.*, 2000).

To investigate the mechanism of adsorption of Cd²⁺ onto the two adsorbents (0.5 and 1.0 MCF), some kinetic models were used to analyse the mechanism of cadmium (II) ion sorption.

These kinetic models include; pseudo-first order, pseudo-second order, Elovich equation, intraparticle diffusion model, mass transfer kinetic model and intraparticle diffusivity equation. To determine which of these mechanisms could account for cadmium ion transport onto the two adsorbents; it is necessary to assume that each one of the concurrent processes dominates over the others at specific time regimes of the sorption process (that is the rate determining step) and so study them independently (Loukidou *et al.*, 2004).

The adsorption kinetic data was analysed in terms of the pseudo-first order kinetics. Figure 4 shows the data linearised to fit the pseudo-first order equation. The pseudo-first order plot should be log (q_e-q_t) against time (min) gave the linear equation parameters of K₁ and q_e and the coefficient of determination r², are presented in Table 1.

Figure 5 shows the plot of the pseudo-second order kinetic model, where t/q_t is plotted against time (min). The kinetic parameters obtained from the linearised pseudo-second order equation, K₂, h, r² and q_e calculated from the plot of Fig. 5 are given in Table 1. From Table 1, the Pseudo-second order rate constant K₂ for the two adsorbents 0.5 and 1.0 MCF increased with chemical modification. Also the sorption capacity (q_e) also increased with chemical modification.

Table 1: Kinetic parameters for pseudo-first order and pseudo-second order equations

Adsorbent	K ₁ (Pseudo-first order rate constant (L min ⁻¹))	q _e (Sorption capacity) (mg g ⁻¹)	r ²	
Pseudo-first order				
0.5 MCF	3.20×10 ⁻²	1.289	0.9493	
1.0 MCF	3.77×10 ⁻²	1.419	0.9747	
Pseudo-second order	K ₂ (Pseudo-second order rate constant) (g mg ⁻¹ min ⁻¹)	h (Initial adsorption rate) (mg g ⁻¹ min ⁻¹)	q _e (Sorption capacity) (mg g ⁻¹)	r ²
0.5 MCF	2.34×10 ⁻¹	0.7082	1.739	0.9976
1.0 MCF	4.64×10 ⁻¹	0.6523	1.852	0.9983

Table 2: Kinetic parameters for elovich equation

Adsorbent	α (Initial adsorption rate) (mg g ⁻¹ min ⁻¹)	β (Desorption constant) (g mg ⁻¹)	r ²
0.5 MCF	2.56×10 ⁻¹	4.716	0.9527
1.0 MCF	2.59×10 ⁻¹	4.775	0.9887

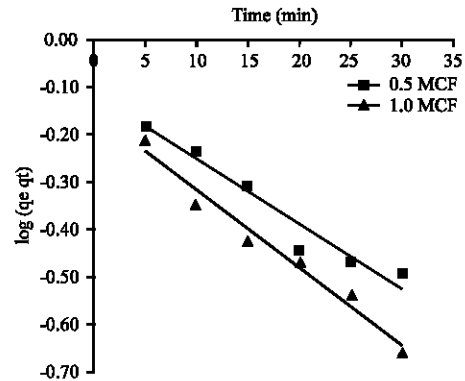


Fig. 4: Pseudo-first order kinetics of Cd²⁺ on different adsorbents

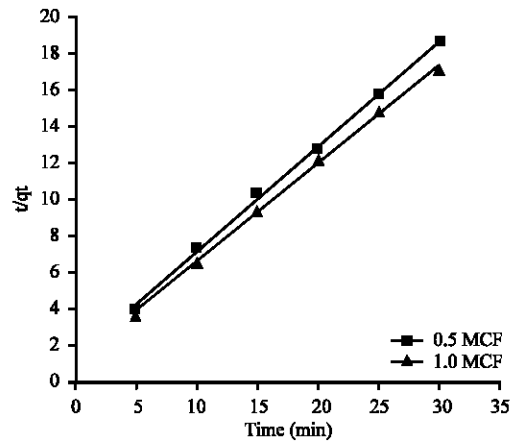


Fig. 5: Pseudo-second order of Cd²⁺ on different adsorbents

Figure 6 presents the plot of the Elovich equation with a plot of sorption capacity (q_t) against Ln time. The calculated parameters from the plot, α (initial adsorption rate), β (desorption constant) and the coefficient of determination, r² are present in Table 2. It can be seen that

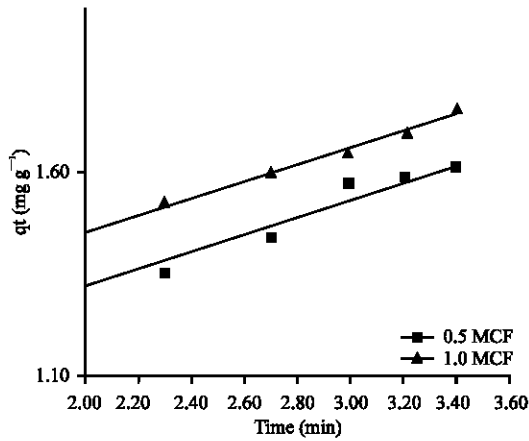


Fig. 6: Elovich sorption model for Cd²⁺ on different adsorbents

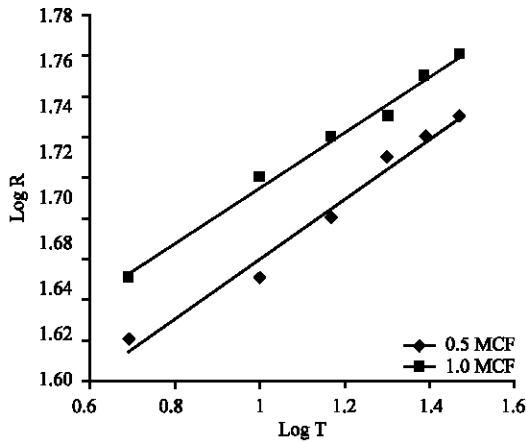


Fig. 7: Intraparticle diffusion kinetics of Cd²⁺ sorption onto different adsorbents

Table 3: Kinetic parameters for intraparticle diffusivity model

Adsorbent	K _{id} (Intraparticle diffusion rate constant (min ⁻¹))	a (adsorption mechanism)	r ²
0.5 MCF	32.44	1.486×10 ⁻¹	0.9789
1.0 MCF	36.12	1.372×10 ⁻¹	0.9906

the initial adsorption rate and desorption constant increased with chemical modification.

The intraparticle diffusion kinetic plot is presented in Fig. 7, with a plot of log R against log T which gave the calculated values of the intraparticle diffusion rate constant K_{id}, adsorption mechanism, a and the coefficient of determination r² are presented in Table 3. The intraparticle diffusion rate constant, K_{id} was seen to increase with chemical modification of the adsorbents.

Figure 8 shows the plot of the mass transfer kinetic equation for the sorption of Cd²⁺. From the plot of ln (C₀-C_t) against time (min), the kinetic constants K₀

Table 4: Kinetic parameters for mass transfer model

Adsorbent	K ₀ (Mass transfer sorption coefficient (min ⁻¹))	InD (Fitting Parameter)	r ²
0.5 MCF	10.1×10 ⁻³	2.5013	0.9193
1.0 MCF	9.00×10 ⁻³	2.6047	0.9103

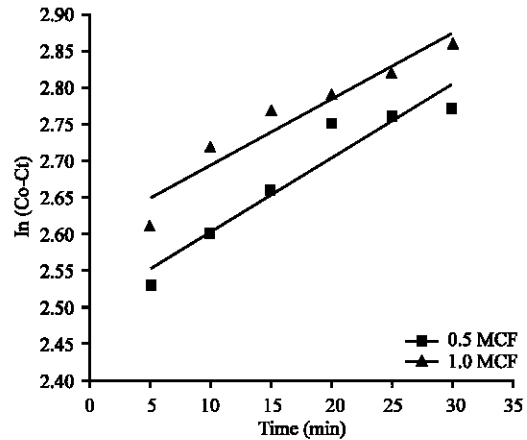


Fig. 8: Mass transfer kinetic model for Cd²⁺ on various adsorbents

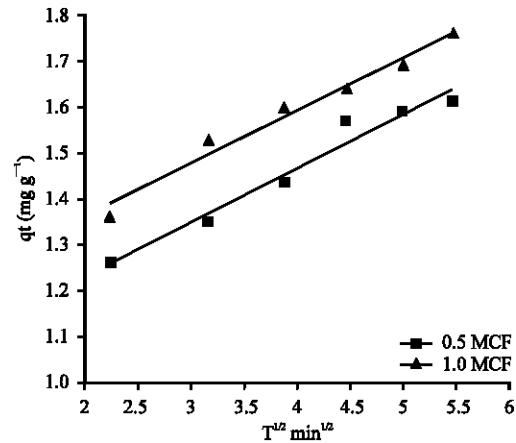


Fig. 9: Intra-particle diffusivity model for Cd²⁺ sorption on various adsorbents

(mass transfer sorption coefficient), InD (fitting parameter) and the coefficient of determination, r² were calculated and presented in Table 4. From Table 4, it can be seen that the mass transfer sorption coefficient, K₀ decreased with increase in chemical modification of the adsorbents.

Finally, analysis of the intraparticle diffusivity model for the sorption of cadmium (II) ions is presented in Fig. 9, with a plot of sorption capacity (q_t) against the square root of time (T^{1/2}). From Fig. 9, the initial sorption rate, K¹ the boundary layer thickness, X_i and the coefficient of determination, r² were calculated and

Table 5: Kinetic parameters for intraparticle diffusivity equation

Adsorbent	K' (Initial sorption rate) ($\text{mg g}^{-1} \text{min}^{-5}$)	X ₁ (Boundary layer thickness)	r ²
0.5 MCF	11.74×10^{-2}	9.963×10^{-1}	0.9646
1.0 MCF	11.46×10^{-2}	11.346×10^{-1}	0.9708

presented in Table 5. Examination of Table 5 indicates that the initial sorption rate decreased with chemical modification while the boundary layer thickness increased with chemical modification.

Analysis of coefficient of determination of kinetic models: Linear regressions are frequently used to determine the best fitting kinetic models. The most common method used is the coefficient of determination, r², since a Kinetic model is concerned with the effect of observable parameters on the overall rate. (Ho, 2006). The best fitting kinetic model for the adsorption of cadmium (II) ion by the two adsorbents is the one with the highest coefficient of determination. That is the kinetic model with r² values closest to unity is deemed as the most appropriate mechanism of sorption.

Examination of the coefficient of determination values for the pseudo first order equation, pseudo-second order equation, Elovich equation, intraparticle diffusion model, mass transfer Kinetic model and intraparticle diffusivity equation indicates that the pseudo-second order Kinetic model is the best fitting kinetic model for the description of Cd²⁺ sorption. Since it has the highest coefficient of determinations (r² = 0.99) for the two adsorbents.

The pseudo-second order model is based on the assumption that sorption of cadmium (II) ions follows a second order mechanism, so the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites (Antunes *et al.*, 2003). In addition, the pseudo-second order model is based on the assumption that the sorption of a metal by an adsorbent may involve a chemical sorption (Chemisorption) which can be the rate controlling step (Ho *et al.*, 2002). In addition the observation that from the pseudo-second order kinetic model, the calculated values of sorption capacity (q_e) agree with the experimental q_e values confirms the pseudo-second order kinetic model as the most applicable model for description of Cd²⁺ sorption.

Furthermore, earlier studies have also confirmed the applicability of the pseudo-second order kinetic model as the most fitting kinetic equation for the explanation of metals sorption kinetics (Demirbas *et al.*, 2004, Krishnan and Anirudhan, 2003; Cordero *et al.*, 2004).

CONCLUSIONS

The kinetic modeling of cadmium (II) ion sorption from aqueous solution using two chemically modified adsorbents was examined in this study. Modeling of

kinetic data is fundamental for the industrial application of adsorption. This is due to the fact that it gives information for comparison among different biomaterials under different operational conditions, designing and operating procedures. Sorption was rapid within the first 5-10 min of contact but later slowed with increase in time up to the maximum at 30 min.

Analysis of experimental data was carried out using the pseudo-second order, pseudo-first order, Elovich equation, intraparticle diffusion, mass transfer model and intraparticle diffusivity equation with the coefficient of determination as fitting parameter.

From the analysis the pseudo second-order kinetic model was the best fitting with r² values of 0.99. Hence, it can be said that the rate determining step for the sorption of Cd²⁺ onto the two adsorbents is chemical sorption of the adsorbate onto the adsorbent.

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