Effect of pH on cadmium biosorption by coconut copra meal

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Abstract

Biosorption of cadmium ion by coconut copra meal, an agricultural waste product was investigated as a function of initial solution pH and initial cadmium concentration. Pseudo-second-order kinetic analyses were performed to determine the rate constant of biosorption, the equilibrium capacity, and initial biosorption rate. Cadmium biosorption by copra meal was found to be dependent on the initial solution pH and initial cadmium concentration. Ion exchange occurred in the initial biosorption period. In addition, mathematical relationships were drawn to relate the change in the solution hydrogen ion concentration with equilibrium biosorption capacity, initial cadmium concentration, and equilibrium biosorption capacity.
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1. Introduction

Processing of agricultural products oftentimes yield large amounts of by-products. These by-products usually are produced in an excess of 320,000,000 kg/year [1] and are considered to be of low value. Agricultural by-products usually are composed of lignin and cellulose as major constituents and may also include other polar functional groups of lignin, which includes alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups. These groups have the ability to bind heavy metals by the replacement of hydrogen ions for metal ions in solution or by donation of an electron pair from these groups to form complexes with the metal ions in solution.

Several studies have shown that in metal biosorption by biological materials, pH is an important factor [2–4]. There is an observed relationship between the metal biosorption and the magnitude of negative charge on the surface of the biosorbent, which is related to the surface functional groups [5]. Availability of negatively charged groups at the biosorbent surface is necessary for the biosorption of metals to proceed [6].

The ionic form of the metal in solution and the electrical charge on the biological material depends on solution pH. Ionization of the polar functional groups on most agricultural by-products is therefore pH dependent. For pH values greater than the pK_a of these groups, the sites are mainly in dissociated from and can exchange H^+ with metal ions in solution. At pH values lower than pK_a of these groups complexation phenomenon can occur, especially for carboxylic groups [7]. pH is an environmental factor that dose not affect only site dissociation, but also the solution chemistry of the heavy metal ions: hydrolysis, complexation, by organic/or inorganic ligand, redox reactions, precipitation are strongly influenced by pH and on the other side strongly influences the speciation and biosorption availability of the metal ions in solution [8–10].

Coconut copra meal is a by-product of coconut production and it is characterized by functional groups such as alcohols, hydroxyl, and carboxylic acids, etc. on its surface. Its effective use as a biosorbent for the removal of heavy metals such as cadmium from wastewater will be affected by the pH of the wastewater. The focus of this work is to study the possible use of coconut copra meal as an efficient biosorbent for cadmium from aqueous solution. Kinetic experiments were performed to study the effect of the initial pH value and initial cadmium ion concentration. Kinetics analyses were carried out to correlate

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the experimental data, based on a pseudo-second-order and ion exchange model.

2. Materials and methods

2.1. Materials

Coconut was obtained from the open market in Benin City. The fruits were dehusked, split, and sun dried until the meat (endosperm) reaches 5% moisture content. The copra was blendered in a food processing blender and the oil extracted with hot water. The copra meal was then washed several times with hot water to remove excess oil, sun dried and sieved to obtain particles of size less than 250 μm. The sieved copra meal was soaked in 0.02 mol/dm^3 HCl overnight. The acid solution was filtered off, and the copra meal was washed with distilled water until the pH of the wash became neutral. The copra meal was dried at 373 K for 24 h and stored in an air-tight container. Proximate analysis was carried out on the copra meal sample. The IR spectra of the copra meal sample were recorded using KBr wafers in conjunction with a Perkin-Elmer infrared spectrophotometer. KBr wafers were prepared by mixing a given sample with KBr crystals, the resulting mixture being ground to a fine powder and heated for 1 h at 373 K. Finally, the mixture was pressed into a KBr wafer under vacuum conditions and used as such for IR studies. The stock solution of cadmium(II) (1000 mg/dm^3) was prepared in distilled water using cadmium nitrate salt (BDH); all working solutions were prepared by diluting the stock solution with distilled water.

2.2. Methods

2.2.1. Point of zero charge

One gram of the copra meal prepared above was suspended in 10^{-3} mol/dm^3 NaNO$_3$ solution for 24 h. 60 ml of the suspension was measured into eight plastic containers. The content of the plastics were adjusted to different pHs (2.23, 3.14, 4.02, 5.12, 6.2, 7.13, 8.02, and 9.11). The suspension in each of the container was divided into four equal parts with the aid of a pipette. 0.3 g of NaNO$_3$ was added to two sets while the other pair contained no added nitrate. They were left for 6 h and after this the pH of the reference and the test suspensions were taken as initial and final pHs respectively. The pairs containing no added nitrate were taken as the reference while those with added nitrate were taken as test samples. The results were plotted as ΔpH against initial pH (pH$_i$).

2.2.2. Influence of pH on biosorption kinetics at 120 mg/dm^3

Two grams of copra meal were added to five 250 ml beakers containing 100 ml of 120 mg/dm^3 of cadmium solution each having pH of 3.53, 4.06, 4.52, 5.04, and 5.53. The solutions were stirred at 150 rpm for 2 h at 24 °C. Two millilitres of sample was withdrawn at suitable time intervals and analyzed for the residual cadmium content by atomic absorption spectrophotometer (AAS). Blank experiments were also carried out under similar experimental conditions with the same volume of distilled water

(no cadmium ions added) and the initial and final solution pH determined after 120 min.

2.2.3. Influence of initial cadmium concentration on biosorption kinetics at pH 5.53

Two grams of copra meal were added to five beakers containing 100 ml of 30, 60, 90, 120, and 150 mg/dm^3. All solutions were set at pH 5.53. The solutions were stirred at 150 rpm for 2 h at 24 °C. 2 ml of sample was withdrawn at suitable time intervals and analyzed for the residual cadmium content by atomic absorption spectrophotometer (AAS).

3. Results and discussion

3.1. Composition of copra meal

The percentage proximate composition of copra meal on dry weight basis was: moisture 8.90%, protein 26.7%, crude fibre 10.0%, ash 3.90% lipid 12.2% and carbohydrate 38.4%. The IR measurement of the copra meal revealing the presence of the following groups: –OH (3600–3300 cm^{-1}), R–NH$_3{}^+$ (2250–3000 cm^{-1}), –C–O (1300–1000 cm^{-1}) and C=O (1650–1800 cm^{-1}) and C–C (1150–1225 cm^{-1}).

3.2. Point of zero charge

The value of the pH necessary to affect a net zero charge on a solid surface in the absence of specific biosorption is called the point of zero charge, pH$_{pzc}$. This is a convenient index of a surface when the latter becomes either positively or negatively charged as a function of pH. Both positive and negative ΔpH values recorded for the copra meal are plotted against the initial pH, pH$_i$, values to yield the pH$_{pzc}$ at the pH where ΔpH 0. When the solution pH is greater than the pH$_{pzc}$ of the sample, a decrease in pH would be observed on sample addition and the surface would possess a negative charge. However, if the pH value of the solution is lower than the pH$_{pzc}$ of the sample, an increase in pH value would occur on sample addition and the surface would possess a positive charge.

On addition of NaNO$_3$ to the copra meal in solution, the ΔpH became negative after initial pH of 3.07 (Fig. 1). Below this pH$_{pzc}$, ΔpH had a positive value. Extrapolation of the plot of ΔpH versus pH$_i$ to the ΔpH 0 line indicated that the pH$_{pzc}$ of the copra meal is 3.07. The surface of the copra meal becomes negatively charged at pHs extending from 3.07 to 9.11 and acquires a net positive charge at pH value less than 3.07. Point zero charge determination has been used to study the charge properties in the sorption of Pb, Zn and Cd on to kaolinite clay [11] and the sorption of simple aromatic compounds on activated carbon [12].

3.3. Influence of pH on biosorption kinetics at 120 mg/dm^3

The mechanism of biosorption often involves chemical reaction between functional groups present on the biosorbent surface and the metal ions. This involves, in most cases, formation of metal–organic complexes or cation exchange reactions due to high cation exchange capacity of the biosorbents [13,14]. Other
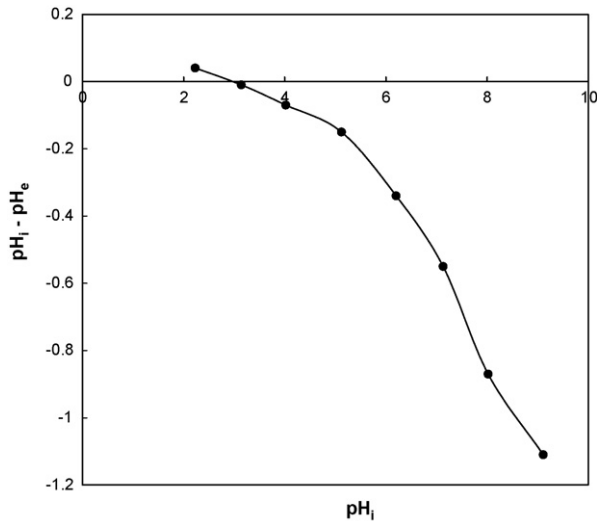
Fig. 1. Relationship between ΔpH (pH$_i$ − pH$_e$) and pH$_i$.

possible mechanisms involve mass-transport processes, bulk transport in the liquid phase, diffusion across the liquid film surrounding the solid particles, and diffusion into micropores and macropores [15]. System parameters such as temperature and pH can also markedly influence biosorption as they affect one or more of the above parameters [16]. The kinetic reaction order of biosorbate–sorbent interactions has been described by using various kinetic models. Traditionally, the pseudo-first-order model derived by Lagergren [17] has found wide application [18]. On the other hand, many authors have shown that pseudo-second-order kinetics can also very well describe these interactions in certain specific cases such as the biosorption of metal ions, dyes, herbicides, oil, and organic substances from aqueous solutions [19–21]. In the case of biosorption preceded by diffusion through a boundary, the kinetics in most cases follows the pseudo-first-order rate equation of Lagergren [4,22]:

$$\frac{dq_t}{dt} = k_{ad}(q_e - q_t) \tag{1}$$

where q_t and q_e are the amount sorbed at time t and at equilibrium, and k_{ad} is the rate constant of the pseudo-first-order biosorption process. The integrated rate law, after applying the initial condition of $q_t = 0$ at $t = 0$, is

$$\log(q_e - q_t) = \log(q_e) - \frac{k_{ad}}{2.303}t \tag{2}$$

Plot of $\log(q_e - q_t)$ versus t gives a straight line for first-order kinetics, which allows computation of the biosorption rate constant, k_{ad}. If the experimental results do not follow Eq. (1), they differ in two important aspects: (i) $k_{ad}(q_e - q_t)$ then does not represent the number of available biosorption sites, and (ii) $\log q_e$ is not equal to the intercept of the plot of $\log(q_e - q_t)$ against t [23]. In such cases, pseudo-second-order kinetics [24–26] given by

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{3}$$

where k is the second-order rate constant is applicable. For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the

integrated form of the equation is

$$q_t = \frac{q_e^2 kt}{1 + q_e kt} \tag{4}$$

or, in the linear form,

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t. \tag{5}$$

When t approaches 0 the biosorption rate q_t/t becomes the initial biosorption rate $h = kq_e^2$. If the pseudo-second-order kinetics is applicable, the plot of t/q_t versus t gives a linear relationship, which allows computation of q_e, k and h without having to know any parameter beforehand [23].

The possibility of coconut copra meal acting as an effective biosorbent for the removal of metal pollutant from aqueous solution in this study depends on the formation of active sites by the surface functional groups on the copra meal. Since ion exchange is one possible biosorption process by which cadmium ion may be removed from solution, the rate of cadmium ion biosorption onto copra meal is expected to vary with the initial pH values of the solution. Therefore experiments were conducted using a given weight of copra meal in contact with 120 mg/dm^3 of cadmium ion solution at different initial solution pH.

The results of the experiment showed that indeed the initial pH of solution affected the uptake of cadmium onto copra meal. Fig. 2 shows the rate of uptake of cadmium ion onto copra meal as a function of time. This trend has generally been observed in biosorption studies such as the biosorption of Cd(II) onto tree fern [27], and fucus spialis [28]. As the initial solution pH is reduced from 5.53 to 3.53, the equilibrium biosorption of cadmium ions on copra meal is reduced. For all initial solution pH investigated, an initial rapid uptake of cadmium ions from solution occurs in the first few minutes which gave way to a slow reaction as time progressed.

The reaction order of the uptake of cadmium onto copra meal was investigated using the pseudo-second-order rate kinetics. Fig. 3 shows the plot of the linear representation when cadmium
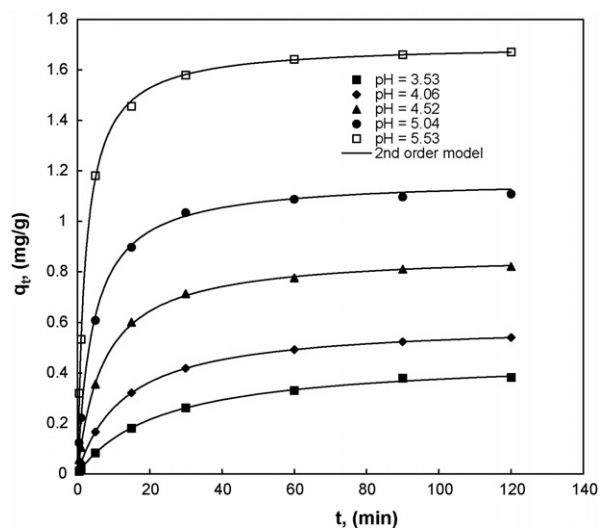

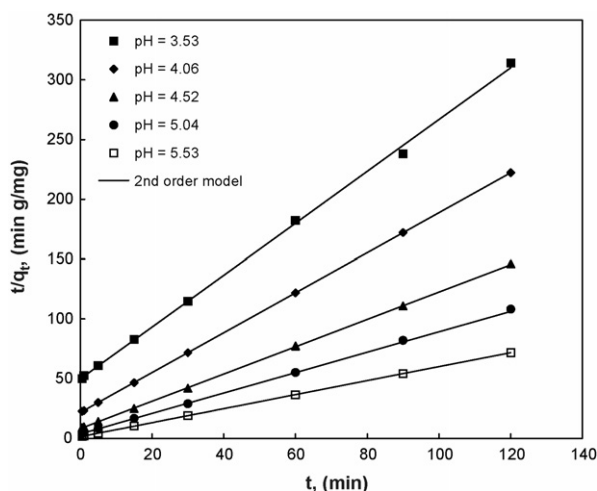Fig. 2. Uptake of cadmium with time at different solution pH.

Fig. 3. Pseudo-second-order plot of cadmium uptake on coconut copra.

Table 2
pH changes in blank experiment test

pH_i	pH_e	ΔH^+ (mmol/dm^3)
5.53	4.58	0.0234
5.04	4.25	0.0471
4.52	4.25	0.0260
4.06	3.97	0.0201
3.53	3.52	0.00687

uptake is plotted via the pseudo-second-order Eq. (5) with the initial solution pH value of the cadmium solution ranging from 3.53 to 5.53. The pseudo-second-order rate parameters, k, h, and q_e, as well as the coefficient of determination, r^2, are shown in Table 1. The equilibrium biosorption capacity increased from 0.461 to 1.70 mg/g, when the initial solution pH is value of the system is changed from pH 3.53 to 5.53. Again, the initial biosorption rate increased rapidly as the pH increased from 0.0201 to 0.784 mg/g min, and rate constant from 0.0945 to 0.258 mg/g min as initial solution pH is increased from pH 3.53 to 5.53. The increase in sorption capacity is attributed to changes in the surface properties of the sorbent and the chemical nature of the cadmium ions. At low initial solution pH, the functional groups on the copra meal tend to acquire a net positive charge due to its association with hydronium ions (H_3O^+). As the initial solution pH increases, dissociation of surface functional groups occurs with the surface causing the surface to acquire a net negative charge with subsequent attraction of positively charged cadmium ions and sorption onto copra meal surface [29]. Thus, at a lower initial solution pH, the sorption of cadmium should be low because of the higher dissociation of the cadmium salt, as well as the positively charged copra meal surface [4].

The role of ion exchange as a biosorption process in this study is revealed by the fact that when the initial solution pH was varied between pH 3.53 and 5.53, the biosorption capacity was influenced by changes in the solution hydrogen ion concentration, ΔH^+. Higher capacities result in higher ΔH^+ values (Table 1). This suggests that as more cadmium ions are sorbed

onto the copra meal surface, more hydrogen ions are released from the copra meal into the solution. Consequently, the pH of the reaction mixture decreases. There are two sources that may contribute to an increase in the hydrogen ion concentration during the biosorption process [4,29]. The first source of pH variation could originate from the acidic groups of copra meal surface. This is confirmed from results of the blank experiment shown in Table 2. The result reveals that there was a decrease in the solution pH after 120 min of agitation, which was found to increase with increasing initial solution pH. The release of protons was suppressed by reducing pH. The resulting negative charge is believed to be responsible for the cation exchange capacity of the copra meal. The second source of pH variation is from ion exchange reactions, such as proton release when cadmium cations bind to the copra meal [4]. At higher initial pH values of the solution, ion exchange ability of the sorbent are improved and the biosorption rate is largely controlled by ion exchange reactions rather than by complexation reactions [30]. Clearly, the resulting equilibrium pH is governed by the factor of the initial pH value of the cadmium solution and the initial hydrogen ion concentration in solution when the temperature, initial cadmium concentration, and copra meal dose is fixed. This was also observed when lead(II) is sorbed on tree fern under similar conditions [4].

The corresponding linear plots of ΔH^+ against q_e were regressed to obtain an expression for these values in terms of ion exchange, with a high coefficient of determination (0.996). Therefore it is further considered that q_e can be expressed as a function of ΔH^+ as follows [4]:

$$q_e = 0.518 \, \Delta H^+ + 0.430 \tag{6}$$

When the biosorption system of initial and equilibrium hydrogen ion concentration showed no changes ($\Delta H^+ = 0$), the equilibrium capacity obtained from the intercept of Eq. (6) was 0.430 mg/g. The ion exchange rate can be determined from the slope of the straight line in Eq. (6) and was 0.518 mg/g mM of hydrogen ion concentration.

Table 1
Pseudo-second-order model parameters for various initial solution pH

pH_i	q_e (mg/g)	k (g/mg min)	h (mg/g min)	r^2	pH_{120}	ΔH^+ (mmol/dm^3)
3.53	0.461	0.0945	0.0201	0.999	3.55	−0.0200
4.06	0.599	0.129	0.0460	1.000	3.29	0.770
4.52	0.875	0.159	0.122	1.000	3.05	1.47
5.04	1.17	0.197	0.269	1.000	2.85	2.19
5.53	1.70	0.258	0.748	1.000	2.61	2.92

Table 3
Pseudo-second-order model parameters for various initial concentration of cadmium solution

C_0 (mg/dm^3)	q_e (mg/g)	k (g/mg min)	h (mg/g min)	r^2	pH_{120}	pH_i	ΔH^+ (mmol/dm^3)
30	1.21	0.630	0.924	1.000	3.09	5.53	0.813
60	1.38	0.389	0.739	1.000	2.87	5.53	1.35
90	1.62	0.305	0.798	1.000	2.69	5.53	2.04
120	1.70	0.259	0.750	1.000	2.61	5.53	2.45
140	1.84	0.191	0.649	1.000	2.52	5.53	3.02

3.4. Effect of initial concentration on biosorption kinetics and final solution pH

The effect of increasing initial cadmium concentration on the kinetics of cadmium biosorption and the accompany change in hydrogen ion concentration, ΔH^+, was investigated so as to establish the contribution of ion exchange process in the biosorption of cadmium onto copra meal. The pseudo-second-order kinetic model was again employed to study the order of the biosorption process. The plots of amount of cadmium sorbed per gram of copra meal versus time showed an initial fast reaction, which gradually slowed down as the reaction progresses (Fig. 4). The pseudo-second-order rate parameters, k, h, and q_e as well as the coefficient of determination, r^2, are presented in Table 3. The data showed good compliance with the pseudo-second-order model, and the regression coefficient for the linear plots were extremely high (1.000) for all systems in this study. From the results obtained, the equilibrium biosorption capacity increased from 1.21 to 1.84 mg/g as the initial cadmium ion concentration was increased from 30 to 140 mg/dm^3. The biosorption rate constant of the process was found to decrease from 0.630 to 0.191 g/mg min as the initial cadmium ion concentration was increased from 30 to 140 mg/dm^3.

The contribution of ion exchange mechanism to the biosorption of cadmium ions onto copra meal can also be observed from the variation of initial cadmium ion concentration with a fixed dose of copra meal at a given temperature and solution pH of 5.53. As the initial cadmium concentration is increased the final solution pH (at 120 min) decreases. A decrease in solution pH occurred as a result of replacement of H$^+$ ions on of functional groups on copra meal surface for cadmium ion by cadmium ions in the bulk solution. To investigation the relationship between initial cadmium ion concentration and the amount of H$^+$ ions released into solution (Table 3), the initial cadmium ion concentration was plotted against the change in hydrogen ion concentration of the solution (ΔH^+ mmol/dm^3). The linear plot of ΔH^+ versus initial cadmium concentration, C_0, was regressed to obtain an expression of these values in terms of ion exchange, with a high coefficient of determination (0.993). Therefore, it is further considered that C_0 can be expressed as a function of ΔH^+ as follows:

$$C_0 = 50.6 \, \Delta H^+ - 9.85 \tag{7}$$

The ion exchange rate with respect to initial cadmium concentration can be determined from the slope of the straight line in Eq. (7) and was 50.6 mg/g mM of hydrogen concentration.

An expression was also derived to relate the equilibrium capacity with the change in pH, ΔH^+ of the reaction. The linear plot of ΔH^+ versus equilibrium capacity, q_e, was regressed to obtain an expression of these values in terms of ion exchange, with a high coefficient of determination (0.992). Therefore, it is further considered that q_e can be expressed as a function of ΔH^+ as follows:

$$q_e = 0.289 \, \Delta H^+ + 0.991. \tag{8}$$

3.5. Ion exchange model

Boyd et al. developed a rate equation, which considered rates of ion exchange adsorption in the exchange adsorption of ions from aqueous solutions by organic zeolites [32]. An application of the ion exchange model was presented for sorption of lead using tree fern [4]. Boyd et al. consider the case of two monovalent ions, the mass law applies to the exchange when written as:

$$A^+ + BR \leftrightarrow B^+ + AR \tag{9}$$

If m_{A^+} and m_{B^+} denote the concentrations of the ions A$^+$ and B$^+$ in solution, and n_{AR} and n_{BR} the moles of A$^+$ and B$^+$ in the adsorbent, then the net reaction rate can be written as follows:

$$\frac{dn_{AR}}{dt} = k_1 m_{A^+} n_{BR} - k_2 m_{B^+} n_{AB}$$

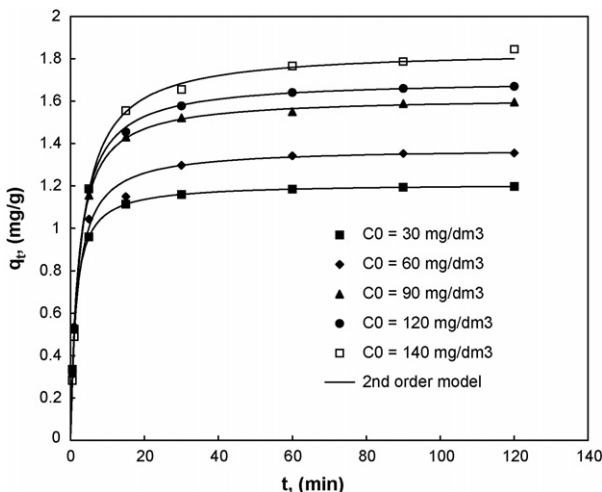$$= -n_{AR}(k_1 m_{A^+} + k_2 m_{B^+}) + k_1 m_{A^+} E \tag{10}$$

Fig. 4. Uptake of cadmium with time at various initial concentrations.

where k_1 and k_2 are the forward and backward specific rates constant and E is a constant defined by

$$E = n_{AB} + n_{BR} \tag{11}$$

When the concentrations of A^+ and B^+ in solution are kept constant, then, on integration, Eq. (10) becomes

$$n_{AR} = \frac{k_1 m_{A^+} E}{k_1 m_{A^+} + k_2 m_{B^+}} (1 - e^{-St}) = q \tag{12}$$

where q is the adsorption capacity at time t. $S = k_1 m_{A^+} + k_2 m_{B^+}$, and Eq. (12) can be rewritten as

$$q_e - q = q_e \, e^{-St} \tag{13}$$

where q_e is the equilibrium capacity. Thus,

$$\log(1 - F) = -\left(\frac{S}{2.303}\right) t \tag{14}$$

where F is the fractional attainment of equilibrium, $F = q_t/q_e$ and $S \ (\mathrm{min}^{-1})$ is a constant.

The predominance of ion exchange phenomenon in the adsorption of cadmium onto copra meal was investigated by the model of Boyd et al. [31]. The model was used to show the dependence of the rate of biosorption on pH exhibited high coefficients of determination. The high coefficients of determination shows the variation in the in the pH value of the cadmium solution with good agreement existing between the experimental and theoretical curves of predicted by Eq. (14) in the initial 5-min period of the biosorption process, and the overall line is not straight (Fig. 5) with high coefficient of determination (>0.996). Values of the constant, S, were calculated from the slope of respective linear plots and are listed in Table 4. It is clear from the high coefficient of determination that Boyd et al. ion exchange biosorption rate descript the biosorption of cadmium onto copra meal well in the beginning stage of biosorption. In addition the pseudo-first-order would also apply for this period as the equation is in the same structure as Boyd et al. rate equation.

The dominance of ion exchange mechanism on the biosorption of cadmium onto copra meal is further seen through the IR

Table 4
Ion exchange model parameter for various initial solution pH at beginning 5 min

pH_i	$S \ (\mathrm{min}^{-1})$	r^2
3.53	0.0386	1.000
4.06	0.0634	1.000
4.52	0.100	0.999
5.04	0.136	0.998
5.53	0.211	0.996

spectra of the copra meal before and after metal cation biosorption. The spectra were identical to each other, indicating that no other solid phases were present in the residues on the surface after the biosorption reactions. Similar results were also shown by Xu et al. [32] and Mustafa et al. [16] who argued that identical IR spectra for biosorbent before and after metal cation biosorption reveals that precipitation/co-precipitation were not dominant in the biosorption process. Thus, the uptake of cadmium ions on the copra meal surface occurred via a cation exchange mechanism.

4. Conclusions

The use of coconut copra meal, a waste product of coconut oil production as biosorbent for cadmium from aqueous solution was found to be a function of the initial solution pH and the initial cadmium concentration of the solution. The pH at point zero charge of the copra meal was found to be pH 3.07. At pHs above the zero point charge cadmium biosorption increased. At pH 5.53 equilibrium sorption capacity increased with increasing initial concentration of cadmium ion in solution. The order of the reaction for the biosorption process of cadmium onto copra meal followed the pseudo-second-order rate expression. In addition, Infrared analyses of the copra meal before and after cadmium biosorption suggest that the biosorption process included ion-exchange mechanism, which occurred in the initial biosorption period.

References

[1] R.E. Wing, Starch-Stärke 48 (1996) 275.
[2] L. Zhang, L. Zhao, Y.T. Yu, C.Z. Chen, Water Res. 32 (1998) 1437.
[3] A. Kapoor, T. Viraraghavan, D.R. Cullimore, Bioresour. Technol. 70 (1999) 95.
[4] Y.S. Ho, Bioresour. Technol. 96 (2005) 1292.
[5] A. Selatnia, M.Z. Bakhti, A. Madani, L. Kertous, Y. Mansouri, Hydrometallurgy 75 (2004) 11.
[6] E. Luef, T. Prey, C.P. Kubicek, Appl. Microbiol. Biotechnol. 34 (1991) 688.
[7] E. Fourest, B. Volesky, Environ. Sci. Technol. 30 (1996) 277.
[8] L.A. Warren, F.G. Ferris, Environ. Sci. Technol. 32 (1998) 2331.
[9] M.O. Corapcioglu, C.P. Huang, Water Res. 21 (1987) 1031.
[10] J. Yang, B. Volesky, Environ. Sci. Technol. 33 (1999) 4079.
[11] J.C. Miranda-Trevino, C.A. Coles, Appl. Clay Sci. 23 (2003) 133.
[12] F. Villacanas, M.F. Pereira, J.J.M. Órfão, J.L. Figueiredo, J. Colloid Interf. Sci. 293 (2006) 128.
[13] W. Ma, J.M. Tobin, Biochem. Eng. J. 18 (2004) 33.
[14] P.A. Brown, S.A. Gill, S.J. Allen, Water Res. 34 (2000) 3907.
[15] N. Kannan, M.M. Sundaram, Dyes Pigments 51 (2001) 25.
[16] S. Mustafa, B. Dilara, A. Naeem, N. Rehana, K. Nargis, Adsorp. Sci. Technol. 21 (2003) 297.
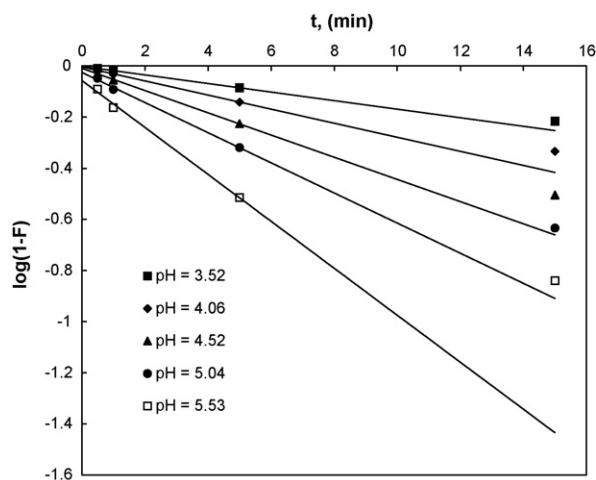[17] S. Lagergren, K. Sven. Vetenskapsakad. Handl. 24 (1898) 1.

Fig. 5. Ion exchange sorption kinetics of lead onto coconut copra meal at various initial pH values.

[18] Y.S. Ho, Scientometrics 59 (2004) 171.

[19] Y.S. Ho, G. McKay, Chem. Eng. J. 70 (1998) 115.

[20] S.K. Zheng, Z.F. Yang, D.H. Jo, Y.H. Park, Y.S. Ho, Water Res. 39 (2005) 264.

[21] Y.S. Ho, J. Colloid Interf. Sci. 283 (2005) 274.

[22] K.G. Bhattacharyya, A. Sharma, J. Environ. Manage. 71 (2004) 217.

[23] Y.S. Ho, G. McKay, Process Saf. Environ. Protect. B 76 (1998) 332.

[24] Y.S. Ho, G. McKay, Process Biochem. 34 (1999) 451.

[25] Y.S. Ho, G. McKay, Process Saf. Environ. Protect. B 77 (1999) 165.

[26] Y.S. Ho, G. McKay, Water Res. 34 (2000) 735.

[27] Y.S. Ho, C.C. Wang, Process Biochem. 39 (2004) 759.

[28] B. Cordero, P. Lodeiro, R. Herrero, M.E. Sastre de Vicente, Environ. Chem. 1 (2004) 180.

[29] G.Ç. Dönmez, Z. Aksu, A. Öztürk, T. Kutsal, Process Biochem. 34 (1999) 885.

[30] D. McNevin, J. Barford, Water Res. 35 (2001) 736.

[31] G.E. Boyd, J. Schubert, A.W. Adamson, J. Am. Chem. Soc. 69 (1947) 2818.

[32] Y.P. Xu, F.W. Schwartz, S.J. Traina, Environ. Sci. Technol. 28 (1994) 1472.