Full Length Research Paper

Biosorption of cadmium (ii) ion from aqueous solution by *Afzelia africana*

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The batch adsorption of cadmium (II) ion from aqueous solution using low-cost adsorbent of biological origin, *Afzelia africana* shell under different experimental conditions was investigated in this study. The influences of initial Cd (II) ion concentration, initial pH, contact times and temperature were reported. Adsorption of Cd (II) was found to be pH dependent and the results indicate that the optimum pH for its removal from aqueous solution was 5. No marginal effect on the biosorption of cadmium was detected for temperatures between 298 and 313K as observed from their Langmuir isotherm constants (q_{max}) at different temperatures. q_{max} values obtained at the different temperatures of 298, 303 and 313K were 13.59, 14.04 and 14.27 mg g^{-1}, respectively. The adsorption equilibrium shows that the process followed both Freundlich and Langmuir models with Freundlich giving a better fit for the adsorption data in comparison to the Langmuir model. The fit of the adsorption data into Freundlich model shows that the adsorption process was predominantly a physisorption. The results reveal that cadmium (II) was considerably adsorbed on the *A. africana* shell and could serve as an economical method for the removal of cadmium from aqueous solutions.

Key words: Adsorption isotherms, adsorption kinetics, *Afzelia africana,* biosorbent, biosorption.

INTRODUCTION

The presence of considerable amounts of heavy metals in industrial wastewaters poses serious environmental threats. The physico-chemical methods such as precipitation, filteration, evaporation, ion-exchange, membrane technologies and electrochemical methods, which have been employed in the sequestration of these metal ions, have been found to be capital intensive (Matheickal and Yu, 1999). These conventional methods in addition have been found to be less efficient and ineffective, especially when low concentrations of these heavy metal ions (in the range of 1- 100 mg L^{-1}) are involved (Volesky, 1990). Some of these techniques sometimes generate sludge and other toxic waste products that require secondary treatment and when released into the environment culminates into increased environmental pollution load
Researches into the use of agricultural by-products as

biosorbents for the removal of heavy metals from aqueous solutions have been on the increase. The increased interest in the use of biomass is their abundant occurrence in nature, which makes them less costly as compared with conventional adsorbents like activated carbon. Some of the major advantages of biosorbents include: Competitive performance, heavy metal selectivity, cheapness, ease of regeneration, known process equipment, possible metal recovery and no sludge generation. These merits in the use of biosorbents have led numerous researches into the use of various plants/agricultural by-products in the removal of heavy metals from industrial effluents. The binding mechanisms of heavy metals by biosorption have been explained to result from different physical and chemical interactions between cell wall ligands (active sites) and the adsor-

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bates (metal ions) by ion-exchange, complexation, coordination and microprecipitation (Gardea-Terresdey et al., 1996; Gang and Weixing, 1998). The diffusion of metals from the bulk solution to active sites of biosorbents occurs predominantly by passive transport mechanism (Veglio and Beolchini, 1997) and various functional groups such as carboxyl, hydroxyl, amino and phosphate present on the cell wall of biosorbents can bind the heavy metals (Avery and Tobin, 1993). The use of various plant biomass for adsorption of heavy metals in solution has been reported in literature and some of these include: African white star apple shell (Anusiem et al., 2010), maize leaf (Babarinde et al., 2006); unmodified and modified maize cob (Igwe and Abia, 2007), rice husk (Ong et al., 2007), shear butter seed husks (Eromosele and Otitolaye, 1994), sago waste (Quek et al., 1998), pomelo peel (Saikaew et al., 2009), husk of bengal gram (Ahalya et al., 2005), groundnut husks (Okieimen et al., 1991), brown seaweed (Antunes et al., 2003), cassava waste biomass (Horsfall et al., 2004), tobacco stems (Wei et al., 2008), chemically modified *Rhizopus nigrigans* (Bai and Abraham, 2002), cone biomass of *Thuja orientalis* (Nuhoglu and Oguz, 2003), use of submerged aquatic plant *Ceratophyllum demersum*, (Keskinkam et al., 2004), modified pine tree (Argun et al., 2005) among others.

The current work focused on the use of an economically cheaper adsorbent of natural origin, *Afzelia africana* in the adsorption of cadmium (II) ion from aqueous solutions. Cadmium which is a widely used material in the industries is extremely toxic even in relatively low dosages and is one of the major heavy metals responsible for causing kidney damage, renal disorder, high blood pressure, bone fraction and destruction of red blood cells (Drash, 1993). In this work, the influence of different parameters on adsorption of cadmium such as initial pH, initial cadmium concentration, contact time and temperature were investigated. The kinetic and equilibrium of the biosorption process were evaluated and maximum adsorption capacity of the adsorbent was determined using the Langmuir isotherm model.

MATERIALS AND METHODS

Adsorbent preparation

The *A. africana* seeds used in this work were basically sourced from local market in Abakaliki in Ebonyi State of Nigeria. The shells were extensively washed with distilled water to remove particulate material from their surface. They were cut into small pieces and air-dried and finally oven-dried at 80°C for 12 h in preparation for the adsorption analysis. The oven-dried shells were crushed with manual blender to smaller particles and sieve analysis was performed using the sieve screen to obtain final sample size of 180 μm. Thereafter, 200 g of the screened (180 μm size) adsorbent was further soaked in 500 mL of 0.3 M HNO_3 solution, stirred for 30 min and allowed to stay for 24 h. It was then filtered through a filter paper and washed with excess deionised water. The rinsed biosorbent was later air-dried for 6 h. The treatment of the adsorbent with 0.3 M HNO_3 solution was to remove any soluble biomolecules that might interact with the metal ions during the

adsorption process and to open-up the micropores of the adsorbent in readiness for the adsorption process.

Biosorption studies

All reagents used were of analytical reagent grades and double distilled deionized water was used in the sample preparation. 100 mg L^{-1} stock solution of cadmium (II) from $CdSO_4.8H_2O$ were prepared at a pH 5.0 and temperature of 30°C. From the stock solutions, working solutions of 10 - 60 mg L^{-1} of each of the adsorbates was obtained by serial dilution.

The effect of concen-tration on the adsorption of the metal ion was studied by transferring 100 mL of the different concentrations of the adsorbate (cadmium ion) into different 250 mL Erlenmeyer flasks while maintaining the pH of the solutions at 5.0. Thereafter, 0.4 g of the adsorbent was added into the flasks, corked and labelled. The flasks were placed in a rotary shaker and agitated for 120 min to attain equilibrium.

At the end of the adsorption process, the content of each flask was filtered, centrifuged and the residual metal ion concentrations (C_e) analyzed using buck scientific atomic absorption spectrophotometer (AAS) model 210 VGP. The concen-trations of the metal ions adsorbed at the different concentrations were calculated by difference.

The effect of pH on the adsorption of the metal ion was carried out by adding 0.4 g of the adsorbent into different 250 mL Erlenmeyer flasks containing 100 mL of the 60 mg L^{-1} solutions of the metal ion and then adjusting the pH of the solutions to different pH ranging from 1.0 to 6.0 using 0.1M HCl or 0.1 M NaOH. The flasks were placed in a rotary shaker and agitated for 120 min to attain equilibrium. The concentrations of the metal ions adsorbed at the different pH were calculated by difference.

Kinetic studies were also carried out by adding 0.4 g of the adsorbent into different 250 mL Erlenmeyer flasks containing 100 mL of the 60 mg L^{-1} solutions of the metal ion and agitated in a thermostated versal shaker at different contact times (10, 20, 30, 40, 50, 60, 70, 90, and 120 min). At the end of agitation time, the content of each flask was filtered with a filter paper, centrifuged and the residual concentration of the metal ions at the different contact times analyzed using AAS. The amount of metal ion adsorbed was then calculated by difference. Each of these analysis was carried out in triplicates and mean residual concentration analyzed. Blank solutions were also prepared and analyzed.

Metal uptake

The initial metal ion concentration and metal concentration at any given time and at equilibrium, respectively, were measured and the metal uptake (amount of Cd (II) ion adsorbed in mg g^{-1}) was evaluated from the mass balance expression as shown:

$$q_e = \left(C_o - C_e \right) \frac{V}{m} \tag{1}$$

Where, V is the volume of the solution in dm^3, m the dry mass of the adsorbent in g while C_o and C_e are the initial and equilibrium concentrations of the cadmium ion in mg L^{-1}.

RESULTS AND DISCUSSION

The results of the experimental investigations for the adsorption of Cd (II) ion on the adsorbent *A. africana* are thus presented. These results are presented as amount
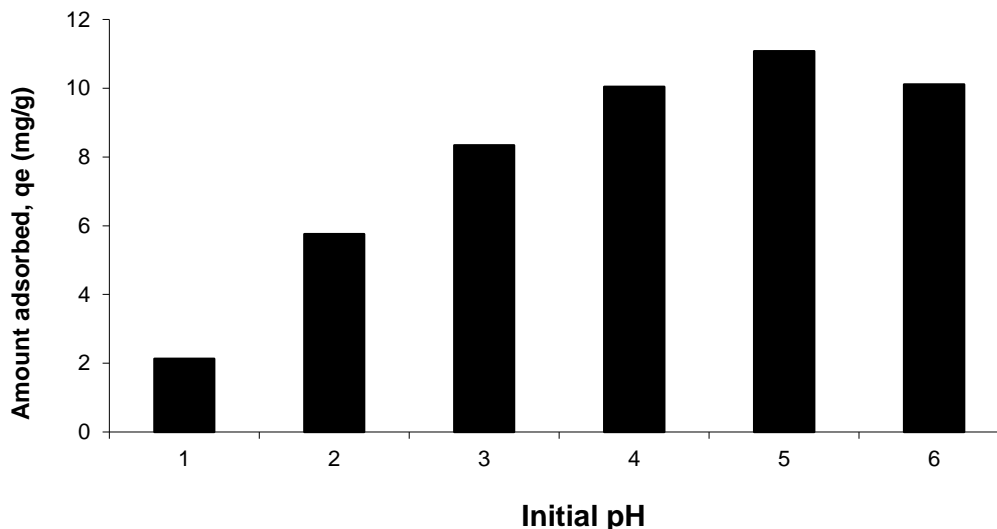
Figure 1. Effect of the initial pH on equilibrium cadmium ions adsorption by the adsorbent.

cadmium (II) ion adsorbed against the various experimental conditions which include initial concentration, initial pH, temperature and time employed.

Influence of Initial pH

pH is an important parameter in the biosorption of metal ions from aqueous solutions since the pH of a medium affects the solubility of metal ions and the concentration of the counter ions on the functional groups of the biomass cell walls. The effect of initial pH on the adsorption of Cd (II) by the adsorbent is shown in Figure 1. The experiments were not conducted beyond pH 6.0 to avoid possible hydroxide precipitation. The amount adsorbed increased with increasing initial pH showing a plateau in the range of 4.0 to 6.0 and having a peak at pH 5.0. This shows that the optimum pH in the removal of Cd (II) from the aqueous solution using the adsorbent is 5.0. The lower uptake at pH below 4.0 may possibly result from competition between hydroxonium ions and Cd (II) ions on the active sites of the adsorbent. The increased presence of these hydroxonium ions (H_3O^+) at lower pH restrict the access of the adsorbates (Cd^{2+} ions) due to repulsive forces to the adsorbent active sites and thereby leading to decreased uptake. Therefore, at lower pH values, the functional groups on the cell walls of the adsorbents are closely associated with hydroxonium ions, but when the pH is increased, the hydroxonium ions are gradually dissociated and the positively charged cadmium ions will be associated with the free binding sites. This may have led to the decreased adsorption at low pH values. Similar findings have been reported by other researchers (Antunes et al. 2003, Benguella and Benaissa, 2002).

Effect of initial metal ion concentration

The effect of concentration on the adsorption of the cadmium (II) ion is displayed as a variation of amount adsorbed with initial cadmium ion concentration (Figure 2). Results show that the equilibrium sorption capacity of the adsorbent increased with increase in initial concentration of the metal ions. The increased amount adsorbed resulting from increase in initial concentration is supported by the distribution coefficients shown in Table 1. The distribution coefficient is the concentration of cadmium in the adsorbent phase divided by the concentration in the continuous (bulk) phase. It expresses the relative effectiveness of the adsorbent in binding the metal ion. It is observed (Table 1) that for all the initial metal ion concentrations used, the distribution coefficients were all greater than unity, thus indicating an uptake of more than 50%. Results generally show that the amount adsorbed increased with initial cadmium ion concentration.

Adsorption isotherms

To study the relationship between the amounts of metal ions adsorbed (q_e, mg g^{-1}) and the equilibrium concentrations left after adsorption, adsorption isotherm models are generally applied for fitting the data. Equilibrium adsorption isotherm is fundamental for the industrial application of biosorption. This is because it gives information for comparison among different biomaterials under different operational conditions and for designing and optimizing operating procedures (Benguella and Benaissa, 2002). In this study, the Langmuir and Freundlich isotherm models were applied
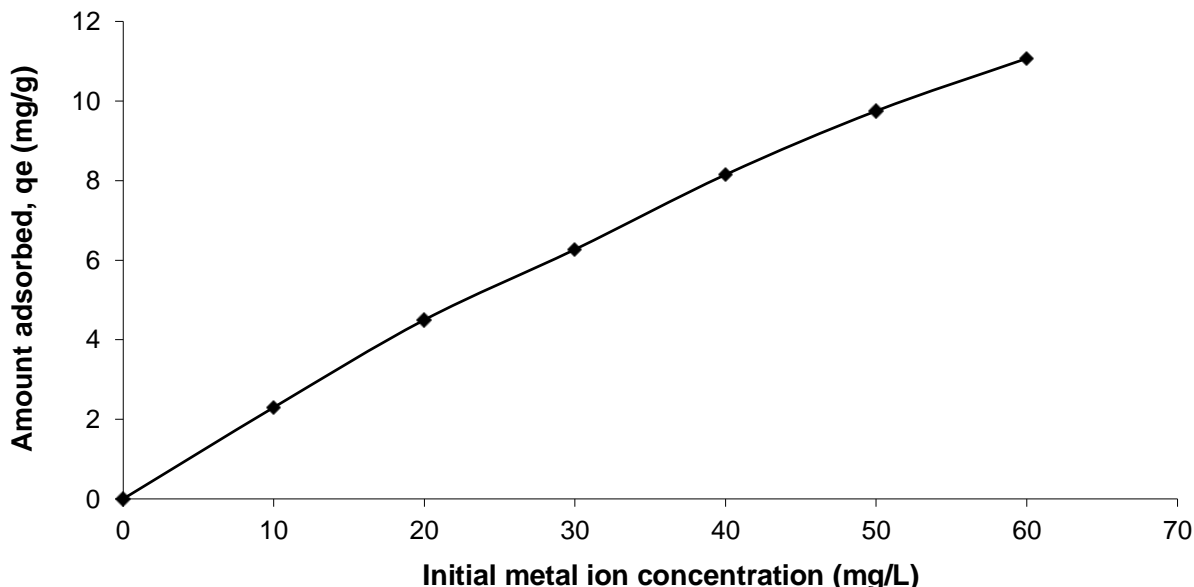
Figure 2. Effect of concentration on the biosorption of cadmium (II) ion by the adsorbent.

Table 1. Distribution coefficients for adsorption of the cadmium (II) ions by the adsorbent.

Initial concentration, C_o (mg L^{-1})	Distribution coefficient
10	11.5000
20	9.0000
30	5.0852
40	4.3908
50	3.5455
60	2.8168

to correlate our experimental data. The linear form of Langmuir adsorption isotherm is represented as:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \tag{2}$$

Where, C_e is the equilibrium concentration of the metal ion (mg L^{-1}), q_{max} (mg g^{-1} adsorbent) is the maximum adsorption capacity of the adsorbent corresponding to monolayer coverage or sites saturation, K_L is the equilibrium Langmuir isotherm constant, which is related to the affinity of the binding sites. K_L represents the ratio of the adsorption to desorption constants and gives information about the intensity of the adsorption process while q_{max} allows the comparison of adsorption performance, especially in the cases where the adsorbent did not attain its full saturation in experimental processes. The values of q_{max} and K_L were calculated from the slope and intercept of the Langmuir plot of C_e versus C_e/q_e (Figure 3).

On the other hand, the Freundlich equation is given as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{3}$$

Where, K_F and n are the Freundlich constants characteristic of the systems, which expresses the adsorption capacity and adsorption intensity, respectively. Values of these constants were calculated from the intercept and slope of the plot (Figure 4) and are presented in Table 2. Parameters, K_F and n affect the adsorption process. Larger values of K_F and n indicate higher adsorption capacity.

The Langmuir and Freundlich constants and their corresponding coefficients of correlation (R^2) values are presented in Table 2. The high coefficients of correlation obtained from both isotherms show that both isotherms could correlate the experimental data with Freundlich giving a better fit since it presents a higher correlation coefficient. According to Karthikeyan et al. (2004), the fit of experimental data to Freundlich isotherm model indicates that the forces of adsorption by the adsorbents are governed by physical adsorption (physisorption). Therefore, the fit of the experimental data into the Freundlich model suggests that the mode of bonding of the cadmium (II) ions onto the adsorbent was by physisorption. Furthermore, the Langmuir isotherm constants were also evaluated at different temperatures ranging from 298 to 313 K and results obtained show that increase in temperature in the range studied did not significantly affect the biosorption of cadmium (II) on the adsorbent employed. Figure 5 shows the Langmuir plots at different temperatures.
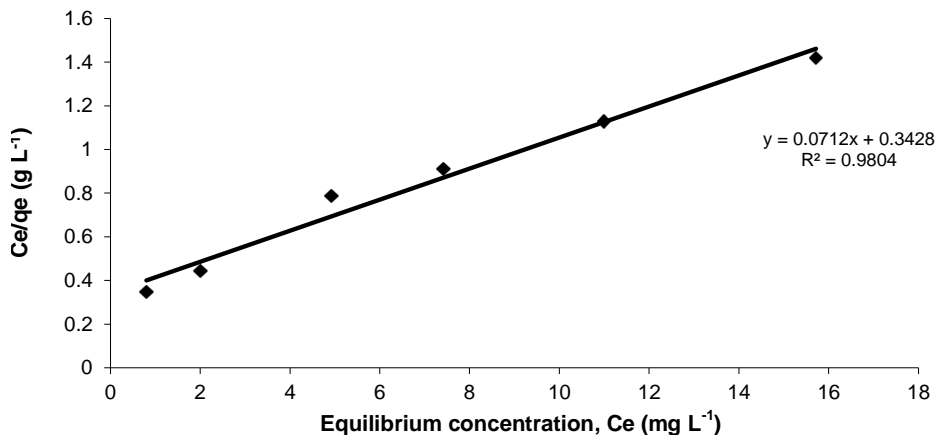
Figure 3. Langmuir isotherm for the adsorption of Cadmium (II) ion from the aqueous solution by the adsorbent at 30°C.
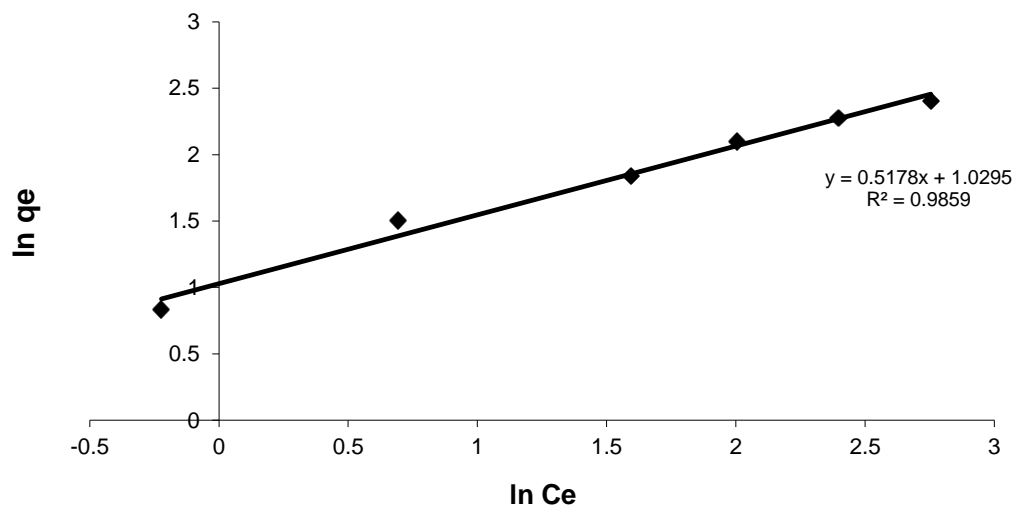

Figure 4. Freundlich isotherm for the adsorption of Cadmium (II) ion from the aqueous solution by the adsorbent at 30°C.

Table 2. Langmuir and Feundlich model's regression constants for the adsorbent at 30°C.

Type of Isotherm	Parameter	Value
Langmuir isotherm	q_{max} (mg g^{-1})	14.04
	K_L (L mg^{-1})	2.078 x 10^{-1}
	R^2	0.980
Freundlich isotherm	K_F	2.800
	N	1.932
	R^2	0.986

Heat of adsorption

The heat of adsorption was evaluated using the Langmuir parameter, K_L, and this parameter can be expressed as a function of temperature using the Arrhenius type relationship:

$$K_L = K_0 \exp\left[-\frac{\Delta H}{RT}\right] \qquad (4)$$

Where, K_0 is a constant, ΔH heat of adsorption (kcal mol^{-1}), R is the gas constant and T is the absolute temperature (K). If K_L values are known for various temperatures, the heat of adsorption can be calculated from the plots of log K_L versus 1/T (Ozer and Ozer, 2003). The variation of ln K_L with reciprocal of temperature, (1/T), is shown in Figure 6 and the value of biosorption heat of adsorption obtained was 4.163 kcal mol^{-1} (17.419 kJ mol^{-1}), while the regression coefficient
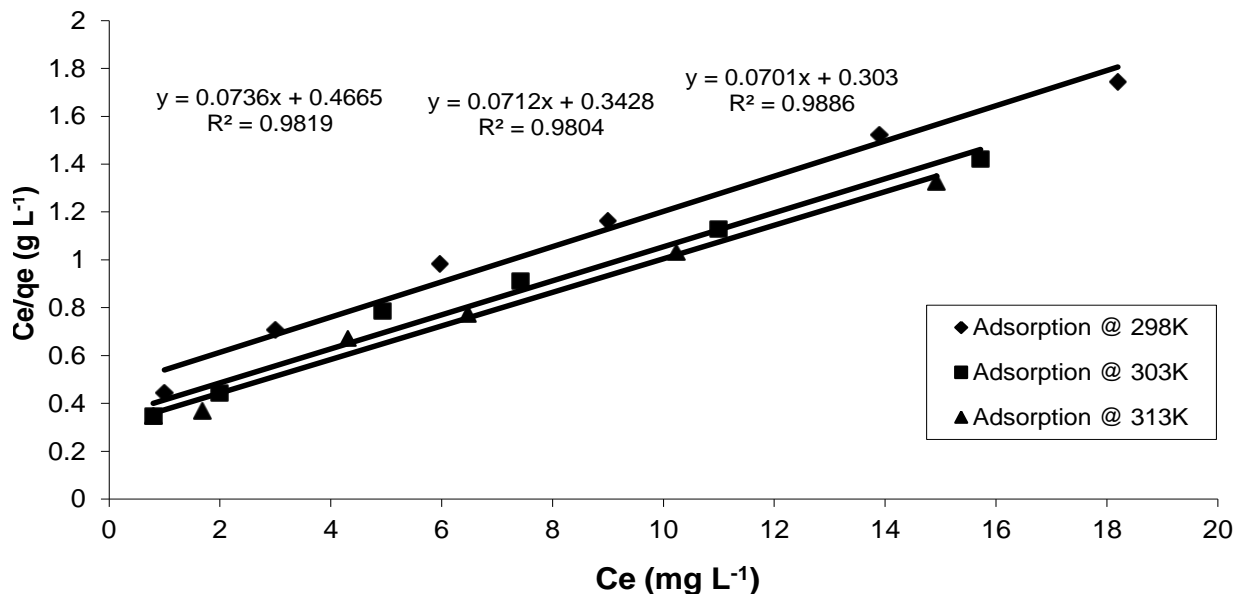
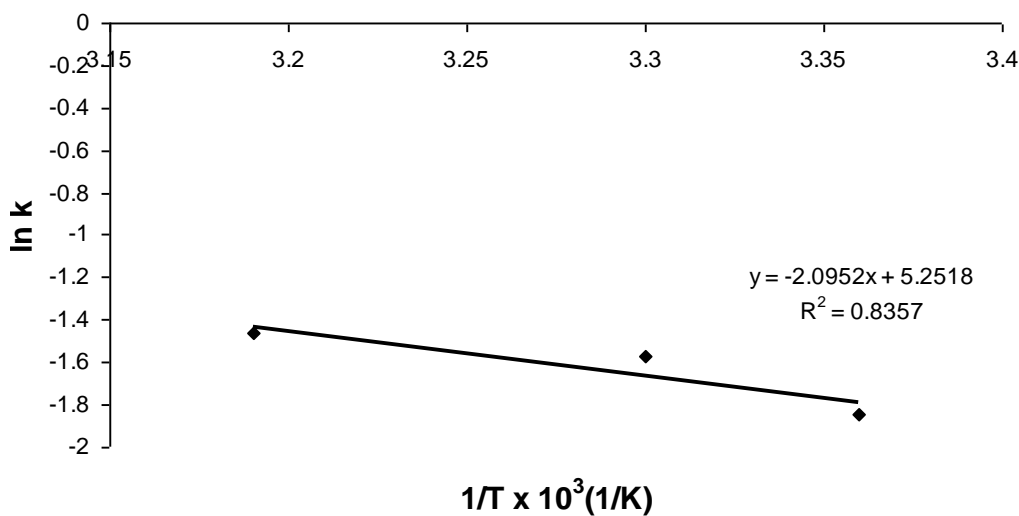**Figure 5.** Langmuir isotherm plots at different temperatures.

Figure 6. Variation of Langmuir constant, K_L with temperature (Arrhenius type plot) for the adsorption of the cadmium (ll) ion by the adsorbent.

obtained is 0.8357. The value of biosorption heat for the cadmium (ll) ion onto the biosorbent shows that the reaction is endothermic. Similar results were reported for biosorption of cadmium and lead by spent grain (Low et al., 2000).

Maron and Lando (1974) had stated in general, that the heat of physical adsorption is of the order of 10 kcal mol^{-1} or less and that of chemical adsorption is in the range of 20-100 kcal mol^{-1}. Since the heat of adsorption in our study is 4.163 kcalmol^{-1}, we could conclude that the mode of adsorption of cadmium (ll) ion by the adsorbent

is physisorption. Kim et al., 2005, had reported that the biosorption of lead, copper and cadmium by waste brewery yeast was an endothermic reaction and heat of biosorption values obtained showed that the mode of adsorption was between physisorption and chemisorption.

Effect of contact time

Figure 7 shows the effect of contact time on the degree of adsorption of cadmium (II) ions by the adsorbent. The
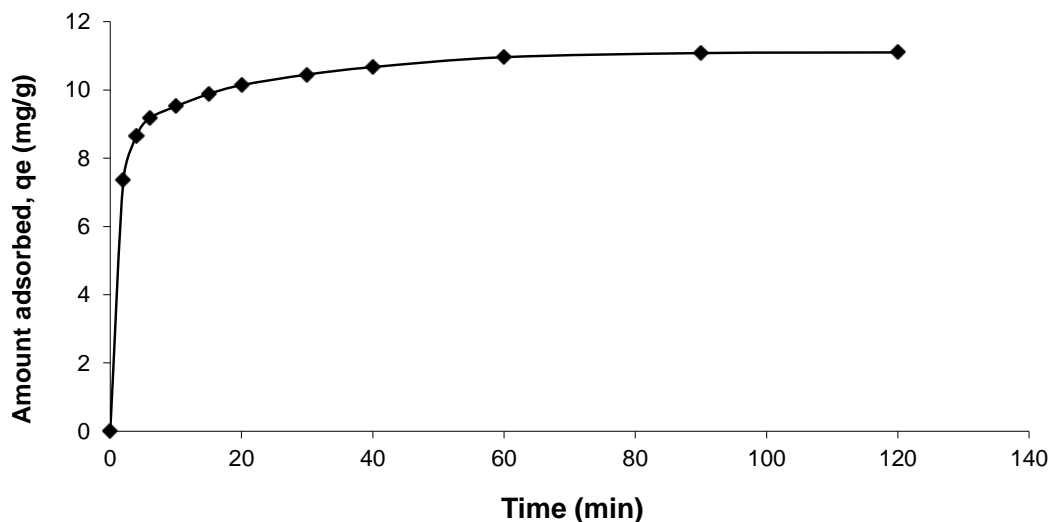
Figure 7. Effect of contact time on cadmium (II) ion adsorption from solution by the adsorbent.

rate of adsorption of the cadmium (II) ions was extremely fast in the first 20 min, but decreased afterward and attained equilibrium in about 60 min. Maximum Cd (II) removal was achieved within 60 min after which Cd (II) concentration in the test solution became constant. This may be explained by the fact that the initial rapid biosorption was due to the availability of a large number of vacant sites, which slowed down later due to saturation of remaining surface sites and repulsive force between solute molecule and bulk phase. The rapid adsorption kinetics observed is also typical for biosorption of metals involving no energy-mediated reactions, where metal adsorption from solution is due to purely physico-chemical interactions between biomass and metal solution (Aksu, 2001).

Sorption kinetic

To investigate the internal diffusion mechanism in the adsorption of cadmium ions onto the biosorbent, the intra-particle diffusion equation has been used. Gerente et al. (2007) stated that adsorption is usually controlled by an external film resistance and/or mass transfer which is controlled by internal or intra-particle diffusion. The intra-particle diffusivity model was employed in our kinetic study. The intra-particle diffusion is characterized by the relationship between specific sorption (q_t) and the square root of time ($t^{1/2}$) and is represented as:

$$q_t = k_{id} \, t^{1/2} \tag{5}$$

Where, k_{id} is the intra-particle rate constant (mg g^{-1} min$^{-1/2}$), t is the time (min), q_t is the specific sorption that is amount of cadmium adsorbed per unit mass of the adsorbent (mg g^{-1}) at a given time.

According to Weber and Morris (1963), if the intra-particle diffusion is the rate-limiting step in the adsorption process, then the graph of q_t vs. $t^{1/2}$ should yield a straight line and particle diffusion would be the only rate controlling mechanism if this line passed through the origin. McKay and Allen (1980) suggested that three linear sections on the plot q_t vs. $t^{1/2}$ can be identified. This means that two or three (multilinear) steps can occur. The first portion represents external surface adsorption or an instantaneous adsorption stage. The second portion is a gradual adsorption stage, where the intra-particle diffusion is the controlling factor. The third portion is a final equilibrium stage where the intra-particle diffusion starts to decelerate due to extremely low solute concentrations in the solution (Wu et al., 2000). Figure 7 shows the intra-particle diffusivity plot for the adsorption of cadmium (II) ion by the adsorbent. A deviation of straight lines from the origin indicates that intra-particle transport may not be the only rate-limiting step. From Figure 8, it can be seen that the intra-particle diffusion of the cadmium (II) ion on the adsorbent occurred in 2 stages. The linear portion in phase 1 is attributed to the macropore diffusion and the second linear portion due to micro-pore diffusion (phase II) (Allen et al., 1989). The intra-particle diffusion constants for these 2 stages are presented as $kid_1 = 0.949$ and $kid_2 = 0.171$. The results indicate that the cadmium (II) ion diffused quickly among the particles at the beginning of the adsorption process, and then intra-particle diffusion slowed down and stabilized. In the two stages observed, kid_1 was found to be greater than kid_2.

Conclusion

The results obtained in this study reveal that initial cadmium (II) ion concentrations, initial pH, contact time
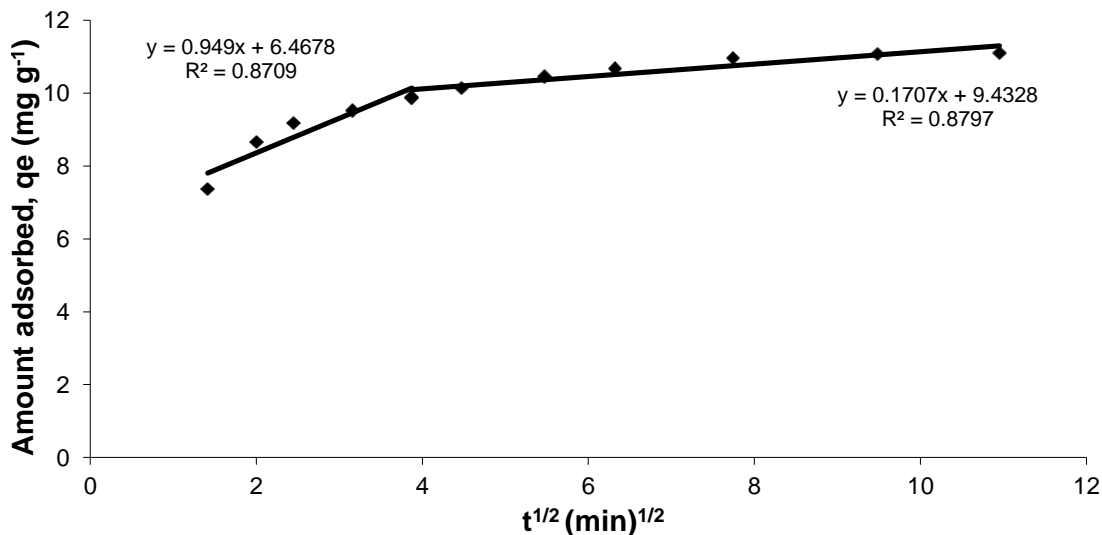
Figure 8. Weber-Morris intra-particle diffusion plot for the adsorption of the cadmium (II) ion by the adsorbent.

and temperature influenced the adsorption capacity of the biosorbent, *A. africana.* Maximum cadmium (II) removal from the solution occurred at a pH 5.0. The equilibrium adsorption showed that the system followed both Freundlich and Langmuir models, with Freundlich giving a better fit for the adsorption data in comparison to the Langmuir model. The temperature did not affect the equilibrium adsorption significantly, since q_{max} values obtained from Langmuir plots vary only slightly at the different temperatures studied. The results revealed that the biosorbent could be a potential biomaterial for the removal of cadmium (II) ions from aqueous solutions having q_{max} values of 14.04 mg g^{-1}.

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