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Sorptive removal of cadmium from aqueous solutions by *Delonix regia* derived lignin: effect of amination

Afamefuna Elvis Okoronkwo*, Albert Ojo Adebayo, Oluwatoyin Iyanu Omotunde

Department of Chemistry, The Federal University of Technology, Akure, Nigeria
Email: afamex@yahoo.com

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ABSTRACT

The relative cadmium sorption ability of unmodified and aminated lignins was examined as a function of solution pH, sorbent—sorbate resident time and ratio, concentration and temperature. Experimental results showed that the surface characteristics of both the unmodified and aminated lignins were favourable to effective cadmium ions sorption from aqueous solutions. Sorption of cadmium was dependent on equilibrium solution pH, as maximum removal was attained at pH 5. The Langmuir and Freundlich isotherm models fitted the experimental data. The biosorption of cadmium onto unmodified and aminated lignins was rapid and equilibrium was attained within 120 min. The sorption kinetic data revealed that the biosorption of cadmium onto these biosorbents followed pseudo-second-order model. This was further supported by Elovich and intraparticle diffusion models. The process was endothermic and ΔG° was positive showing non-spontaneity of the process within the studied temperature range.

Keywords: Adsorption isotherms; Cadmium; Lignin; Wastewater; Amination

1. Introduction

Anthropogenic sources of heavy metal pollution have been a major concern in recent years. The deleterious effect of these metals to man such as toxicity, carcinogenicity and mutagenicity cannot be overemphasized.

The contamination of aquatic environments by toxic heavy metals due to the increased activities of metal mining and metal processing industries has become a major source of concern over the last several decades. The removal of these contaminants from industrial effluents is, therefore, a priority both in current environmental research and legislation [1]. Therefore, the imposition of strict regulations increased the demand for innovative treatment technologies to remove metals from wastewater and to attain today's toxicity-driven concentration limits [2].

Cadmium is one of the heavy metals, which is highly toxic to humans, plants and animals. The metal is of special concern because it is non-degradable and therefore persistent.

Cadmium use has been steadily increasing in growing applications such as in electroplating,

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*Corresponding author.

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pigments, paints, plastics, silver cadmium batteries [3], smelting [4], cadmium nickel batteries, stabilizers, phosphate fertilizers, mining and alloy industries [5].

Cadmium can be regarded as an element of high toxicity and mobility in the environment [1]. According to the World Health Organization, Cd(II) ions are among the metals of most immediate concern. It is also one of six substances banned by the European Union's Restriction on Hazardous Substance directive, which bans certain hazardous substances in electrical and electronic equipment but allows for certain exemptions and exclusions from the scope of the Law. Its harmful effects on man include: renal dysfunction, bone degeneration, lung insufficiency, liver damage and hypertension in human [6].

Different treatment techniques for wastewater laden with heavy metals have been developed in recent years both to decrease the amount of wastewater produced and to improve the quality of the treated effluents [7]. Removal and recovery of heavy metals are very important with respect to environmental and economical consideration [8].

Various methods employed for the treatment of contaminated wastewater include: chemical precipitation as sulphides and hydroxides, lime coagulation, evaporation, flotation, ion exchange and membrane filtration [7,9]. In recent years, research attention has been focused on biological methods for the treatment of effluents, some of which are in the process of commercialization [10]. There are three principal advantages of biological technologies for the removal of pollutants: first, biological processes can be carried out *in situ* at the contaminated site; second, bioprocess technologies are usually environmentally benign (no secondary pollution) and third, they are cost-effective [11].

The mechanism of biosorption is generally based on physicochemical interactions between metal ions and the functional groups present on the cell surface, such as electrostatic interactions, ion exchange and metal ion chelation or complexation. Different types of biomass have been investigated for biosorption of cadmium and other heavy metal ions. These included banana peel [12], brown algae [13], yeast [14], sawdust [15], baker's yeast [16], snail (Lymnaea nifescens) shell [17], and kraft lignin [18].

The primary objective of this study was to extract lignin from *Delonix regia*, modify the lignin through amination and apply the obtained ligno-amine material for biosorptive removal of cadmium ions from aqueous solutions.

2. Experimental materials and methods

2.1. Material preparation and characterization

The pods of flame of the forest (*D. regia*) that were used for this research work were obtained from environment of the Federal University of Technology Akure, Ondo State, Nigeria. The pods were cut into small pieces and sun dried. The dried samples were then grinded into powder and sieved using 850 μm mesh screen sieve.

2.2. Extraction of lignin

Sieved biomass 150 g was weighed and added to 1,500 ml of the prepared 15% NaOH solution in a plastic container. The mixture was stirred and immersed inside water bath, whose temperature was set at 80˚C and allowed to stay in the bath for 2 h; thereafter the plastic container was then removed and allowed to cool overnight. The pH of the filtrate (black liquor) was adjusted to 2 using 40% H_2SO_4. The sample was filter and dried in an over at 60˚C.

2.3. Amination of lignin

The obtained lignin (10 g) and 6.0 g of hexamine were dissolved in 100 ml 0.5 mol/L NaOH solution. The pH of the solution was adjusted to 11.5 using hydrochloric acid solution. The solution was added into a three-necked flask. Then 6.0 g of formaldehyde solution (37 wt.%) was added stepwise with stirring. The reaction was carried out at 75˚C for 3 h. After that, the solution was added into three times its volume of i-propanol to precipitate lignin amine. The lignin amine was recovered by filtration, washed by i-propanol several times, vacuum-dried and ground to powder.

2.4. Batch adsorption experiment

Batch experiments were conducted to generate pH-based plots by adding 0.5 g of the lignin materials to 50 ml of 100 mg/l cadmium solution. The experiments were performed at pH values where metal hydroxide precipitation is not expected to occur.

Equilibrium adsorption of Cd(II) ion on the lignin was carried out using 50 ml of various concentrations (25–500 mg L^{-1}) of metal ions at constant metal ions–substrate contact time (2 h) at temperature of 28˚C and at a predetermined pH of 5. At the end of the given contact time, the mixture was filtered rapidly. The metal ion concentration in the filtrate was determined by flame atomic absorption spectrometry model 200A.

The amount of metal ion adsorbed by lignin was obtained as the difference between the initial and final ion concentration of the solutions.

2.5. Characterization of sorbent

To investigate the changes of functional groups during biosorption of cadmium by biosorbent, Fourier transform infrared analysis was employed. Infrared spectra of the biosorbent, aminated and unmodified were acquired. The sample/KBr mass ratio used for the preparation of the disk was 1:100. The samples were scanned 20 times with a wavenumber range from 4,000 to 400 cm^{-1}.

3. Results and discussion

3.1. Effect of pH on biosorption of Cd(II)

The pH of the aqueous solution is an important controlling parameter in the biosorption process [19]. This factor is capable of influencing not only the binding site dissociation state, but also the solution chemistry of the target metal in terms of hydrolysis, complexation by organic and/or inorganic ligands and redox potentials [20]. Most research conducted on heavy metal biosorption indicates that the decrease in ion biosorption at acid pH may be due to the increase in competition with protons for active sites [21]. At alkaline pHs, however, other effects may arise that also alter the process, such as the predominant presence of hydrated species of heavy metal, changes in surface change or the precipitation of the appropriate salt [22]. Effect of solution pH on the biosorption of cadmium ion by using unmodified and aminated lignin was studied and results are shown in Fig. 1.

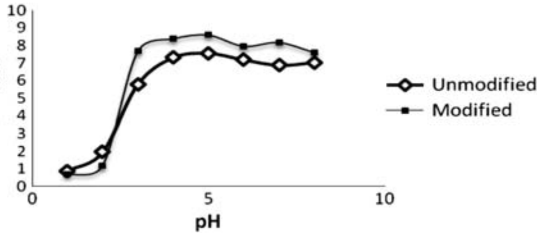

Fig. 1. Effect of pH on cadmium removed by unmodified and aminated lignin.

The influence of the pH value was the same at the different biosorbents but the adsorption capacity for aminated lignin was better than the unmodified lignin. There was an increase in cadmium ion removal with increasing pH from 1 to 5 and the maximum cadmium uptake capacities were 7.56 and 8.60 mg/g for unmodified and aminated lignin, respectively. The cadmium ion removal increased rapidly. At pH of around 5, the cadmium ion removal levelled off at a maximum value. The biosorption of cadmium in a very highly acidic pH (pH 1) was negligible. According to several authors [23,24], the biosorption below pH 2 was little due to the competition of hydrogen ions for the active sites. It is clear that cadmium ion has effectively adsorbed from pH 3 to 6 and the maximum biosorption of cadmium ion onto unmodified and modified lignin occurred at pH 5. The dependence of percentage cadmium removal on pH is similar to the cadmium ion sorption on banana peel and cystine-modified biomass [12,25]. They decreased as the pH continued to increase. Because proton (H^+) vies with the cadmium ion in lower pH, the sorbent surface takes more H^+, consequently reducing cadmium ions binding on the sorbent surface. At higher pH, the sorbent surface takes more negative charges, thus attracting greater cadmium ions.

3.2. Effect on absorbent dosage on biosorption of Cd(II)

Biosorption experiments are performed at different biosorbent dosage namely: 0.25, 0.5, 1.0 and 1.5 g of unmodified and aminated lignin. The sorption efficiency increased with an increase in biosorbent dosage. This is due to an increase in the surface area of the biosorbent which in turn increases the number of binding sites, which resulted in easier penetration of metal ions to the sorption sites. The percentage removal of cadmium was found to increase from 56.7 to 82.9% and 68.6 to 96.5% for both unmodified and aminated lignin, respectively, with an increase of biosorbent dose from 0.2 to 1.5 g/l. Increase in the adsorption with the increase in the adsorbent dosage can be attributed to increased sorbent surface areas of mesopores and the availability of more sorption sites. Modified lignin seems to be better than unmodified lignin in this biosorption experiment (Fig. 2).

3.3. Effect of contact time on biosorption of Cd(II)

The contact time is of great importance in adsorption for the assesement of the suitability of these biomass preparations to serve as biosorbents in a continous flow system. Fig. 3 shows the biosorption time curve of Cd ions on unmodified and aminated lignin at the initial concentration of 100 mg/l.

It can be seen that biosorption consists of two phases: a primary rapid phase that accounts for the major part in the total metal biosorption and a second slow phase that contributes to a relatively small part.

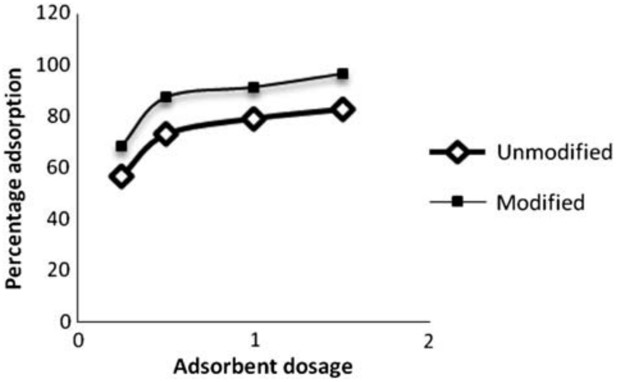

Fig. 2. Effect of absorbent dosage on cadmium removal by unmodified and aminated lignin.

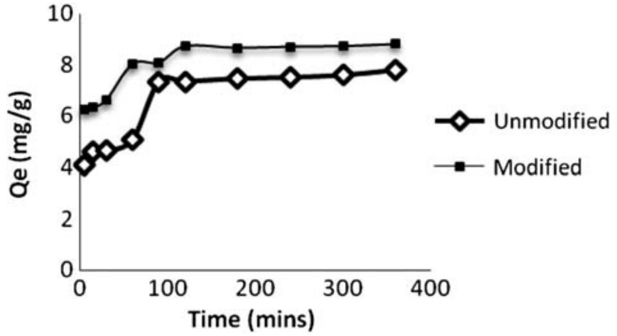

Fig. 3. Effect of contact time on cadmium removal by unmodifed and aminated lignin.

Most of the metal ions are adsorbed from aqueous solution within the first 120 min and there is no more metal uptake after. This trend suggests that the uptake may be due to the interaction with functional groups located on the surface of the biomass at the first rapid stage and intercellular accumulation of the second phase [26]. After attaining the equilibrium, the amount of biosorbed metal ions did not appreciably change with time. Data on the contact time of heavy metal ions by various biosorbents have shown a wide range of adsorption time. The biosorption equilibrium time of Cd(II) on Pleurotus ferulae was 20 min [27]. Cd(II) on pre-treated tridax procumbens reached equilbrium in 100 min at pH 6 [28]. The Cd(II) bisorption rate on Ulmus leaves and their ash reached saturation within 60 min [29]. There are several parameters that determine the biosorption rate such as the stirring rate of the aqueous phase, structural properties both of the support and the biosorbent, amount of sorbent, properties of the ion under study, initial concentration of ionic species, and, of course, existence of other metal ions. Therefore, it is very difficult to compare the biosorption times reported.

3.4. Biosorption kinetic of cadmium onto unmodified and aminated lignin

Several steps can be used to examine the controlling mechanism of adsorption process such as chemical reaction, diffusion control and mass transfer. Kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modelling the adsorption processes. Thus, the kinetics of cadmium adsorption onto unmodified and aminated lignin were analysed using pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion kinetic models. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficient (R^2, values close or equal to 1).

The adsorption kinetic data were described by the Lagergren pseudo-first-order model, which is the earliest known equation describing the adsorption rate based on the adsorption capacity. The differential equation is generally expressed as follows:

$$dq_t/d_t = k_1(q_e - q_t) \tag{1}$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg/g), k_1 is the rate constant of pseudo-first-order adsorption (l/min). Intergrating the above equation for the boundary conditions $t = 0$ to t and $q_t = 0$ to q_t gives:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \tag{2}$$

In order to obtain the rate constants, the values of $\log(q_e - q_t)$ were linearly correlated with t from which k_1 and predicted q_e can be determined from the slope and intercept of the plot, respectively. The first-order-kinetic model presuppose that the rate of adsorption is influenced by the adsorbate concentration and the number of free sites for adsorption.

The differential equation for pseudo-second-order model is generally given as follows:

$$dq_t/d_t = k_2(q_e - q_t)^2 \tag{3}$$

where k_2 (g(mg/min)) is the second-order rate constant of adsorption. Intergrating equation above, for the boundary conditions $q_t = 0$ to q_t at $t = 0$ to t and rearranging gives the following linear form:

$$t/q_t = 1/k_2 q_t^2 + (1/q_e)t \tag{4}$$

if the second-order kinetic is applicable, then the plot of t/q_t vs. t should show a linear relationship. Values of k_2 and q_e were calculated from the intercept and slope of the plot.

The Elovich equation is another rate equation based on the adsorption capacity generally expressed as:

$$dq_t/d_t = B_E \exp(-A_E q_t) \tag{5}$$

where B_E is the initial adsorption rate (mg(g/min)) and A_E is the desorption constant (g/mg) during any experiment. The equation above can be simplified by assuming $A_E B_E t >> t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at t to yield Eq. (6)

$$q_t = 1/A_E \mathrm{In}(B_E A_E) = 1/A_E \mathrm{In}(t) \tag{6}$$

If cadmium adsorption by lignin fits the Elovich model, a plot of q_t vs. In(t) should yield a linear relationship with a slope of $1/A_E$ and intercept of $1/A_E$ In ($B_E A_E$).

The adsorbate species are most probably transported from the bulk of the solution into the solid phase through intraparticle diffusion/transport process, which is often the rate-limiting step in many adsorption processes. Hence, the intraparticle diffusion is another kinetic model that should be used to study the rate of cadmium ion adsorption onto unmodified and aminated lignin. The possibility of intraparticle diffusion was explored by using the intraparticle diffusion model, which is commonly expressed by the equation:

$$q_t = k_{\mathrm{dif}}^{1/2} + C \tag{7}$$

where C (mg/g) is the intercept and k_{dif} is directly evaluated from the slope of the plot. The value of intercept C provides information about the thickness of the boundary layer, the resistance to the external mass transfer increase as the intercept increase.

The expermental data obtained from this study do not correspond with first-order kinetics. Moreover, the q_e values predicited for psuedo-first-order kinetic were far away from the experimental q_e values than the results from pseudo-second-order kinetic. The theoretical $q_{e,\mathrm{cal}}$ values in the case of pseudo-second-order model were closer to the experimental $q_{e,\mathrm{exp}}$ values (Table 1). These observations show that metal sorption by unmodified and aminated lignin followed the second-order reaction, and this suggests that the process-controlling rate maybe a chemical sorption involving valence forces through sharing or exchanging of electrons between sorbent and sorbate. Also, the correlation coefficients of the pseudo-first-order kinetic model obtained for cadmium were small compared to the pseudo-second-order kinectic model and other kinetic models studied in the present investigation. The pseudo-second-order kinectic model provided good correlation for the bisorption of Cd(II) onto the biomass than the other kinetic models used. Therefore, the reaction meachanism is a second-order reaction.

Table 1
Pseudo-first and-second-order parameters for metal sorption onto unmodified and aminated lignin

	Pseudo-first-order		Pseudo-second-order	
	Unmodified	Aminated	Unmodified	Aminated
$Qe_{(\mathrm{expt.})}$ (mg/g)	7.79	8.81	7.79	8.81
$q_{e(\mathrm{cal})}$	2.22	1.17	8.07	9.82
K (I/min)	0.0064	0.0055	32.3	64.7
r^2	0.45	0.27	0.99	0.98

The constant C (Table 2) was found to be 3.75 and 6.12 mg/g for unmodified and aminated lignin, respectively, which indicate the increase in the thickness of the boundary layer of modified lignin compared to that for unmodified lignin.

3.5. *Effect of concentration on biosorption of Cd(II)*

The effect of initial metal concentration on the removal of Cd(II) was conducted using unmodified and aminated lignin at different Cd(II) concentration of 25, 50, 100, 300 and 500 mg/l for different intervals of contact time. It was observed that the amount of removed cadmium initially increased linearly with the Cd(II) concentration and then attained saturation after 120mins (Fig. 4(a) and (b)). The saturation concentration was observed at 100 mg/L of the metal solution for which only 75 and 89% were removed by unmodified and aminated lignins, respectively. At lower concentration, Cd ions in the solution would interact with the binding sites and does facilitate adsorption. At higher concentration, more Cd ions are left unabsorbed in solution due to the saturation of binding site. Aminated lignin showed more absorption capacity for cadmium removal than unmodified lignin.

Table 2
Parameters obtained from Elovich kinetic model using cadmium on unmodified and aminated lignin

	A_E	B_E	R^2
Unmodified lignin	7.79	2.22	0.85
Aminated lignin	8.81	1.17	0.88

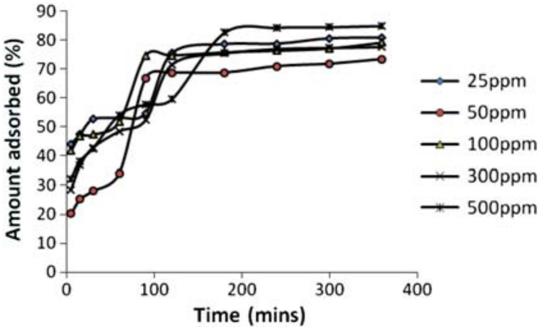

Fig. 4a. Effect of concentration on cadmium removal by unmodified lignin.

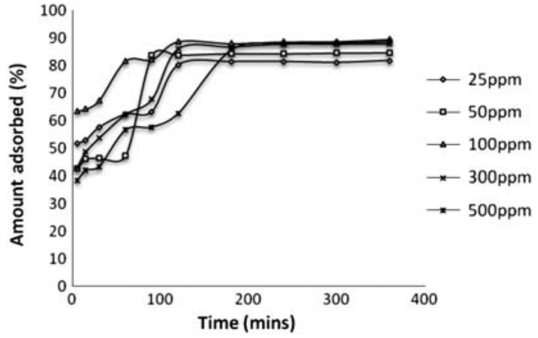

Fig. 4b. Effect of concentration on cadmium removal by aminated lignin.

3.6. Biosorption equilibrium of cadmium onto unmodified and modified lignin

The Langmuir and Freundlich equilibrium models have been applied to this study. The Langmuir isotherms equation is valid for monolayer sorption onto surface containing finite number of identical sorption site which is described by the following equation:

$$q = (q_{\max} b C_{\text{eq}})/(1 + bC_{\text{eq}}) \tag{8}$$

where q (mg/g) and C_{eq} (mg/L) are the amount of adsorption and the residual concentration in solution at equilibrium, respectively; $q_{\max}$ (mg/g) and b are Langmuir constants denoting maximum adsorption capacity and the affinity of the binding sites, respectively, which can be determined by the linearized Langmuir isotherm as below:

$$C_{\text{eq}}/q = C_{\text{eq}}/q_{\max} + 1/bq_{\max} \tag{9}$$

The Freundlich equation is purely empirical based on sorption on a heterogeneous surface, which is commonly presented as:

$$q = k_f C_{\text{eq}}^{1/n} \tag{10}$$

where k_f and n are the Freundlich constant related to adsorption capacity and the adsorption intensity respectively, and linearized form of the model is given as:

$$\text{In}\, q_e = \text{In} k_f + \text{In} C_{\text{eq}} \tag{11}$$

The experimental data (Table 3) shows that the sorption process can be described with both the Langmuir and Freundlich isotherms. The correlation coefficient (R^2) values for Freundlich and for Langmuir model were within the same range lignin materials. The maximum capacity ($q_{\max}$) values obtained from these plots are higher cadmium experimental values. The comparison of maximum biosorption capacities for cadmium ions obtained in this study with some using different low-cost biosorbents shows that biosorption capacity for cadmium using unmodified and aminated lignin was greater than which has been found using other biosorbent (pomelo peel, $q_{\max} = 21.83$ [30]; papaya wood, $q_{\max} = 11.30$ [31]; tea industry waste, $q_{\max} = 11.30$ [32]; cystine-modified biomass, $q_{\max} = 11.63$ [25]). The magnitude of intercept k_f and n were calculated from the plots. The value of n which is related to the distribution of bonded ions on the sorbent surface was greater than unity. The magnitude of Freundlich constant expresses easy separation of metal ions from aqueous medium and indicates favourable adsorption. Also, the higher the k_f valves, the greater the adsorption intensity. Therefore, the k_f value which is higher for modified lignin

Table 3
Isotherm parameters for the adsorption of cadmium ions onto unmodified and modified lignin

	Langmuir (mg/g)			Freundlich		
	$q_{\max}$ (mg/g)	B (dm^3/mg)	R^2	n	k_f (mg/g)(dm^3/mg)$_{1/n}$	R^2
Unmodified lignin	63.6	0.0047	0.80	1.19	0.42	0.97
Modified lignin	43.2	0.016	0.88	1.36	0.99	0.84

confirms that the adsorption capacity of the modified lignin was greater than that of the unmodified lignin.

3.7. Effects of temperature and thermodynamic consideration on biosorption of Cd(II)

Temperature has important effects on the adsorption process. The biosorption of Cd(II) at different temperatures namely: room temperature, 35, 45, 55 and 65°C was studied using unmodified and aminated lignin and results are shown in Fig. 5. There was an increase in cadmium ion removal with increasing temperature from 28 to 35°C before a rapid fall in the cadmium absorption with an increase in temperature from 35 to 65°C, thereby causing biosorption affinity to decrease at higher temperature (i.e.) 65°C. As the temperature increases, rate of diffusion of adsorbate molecules across the external boundary layer and internal pores of adsorbent particles also decreases [33]. Similar results have been reported for the removal of Cd(II) ions by sawdust from aqueous solution at temperature 30–60°C [15] and biosorption of copper II from aqueous solution using teak (*Tectona grandis* L.F) leaves at temperature 20–40°C [34].

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. Gibb's free energy change, ΔG°, is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG° is a negative value. The thermodynamic parameters of Gibb's free energy change, ΔG°, enthalpy change, ΔH° and entropy change, ΔS° for the adsorption processes are calculated using the following equations.

$$\Delta G^\circ = -RT\ \mathrm{In}k_a \tag{12}$$

and

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{13}$$

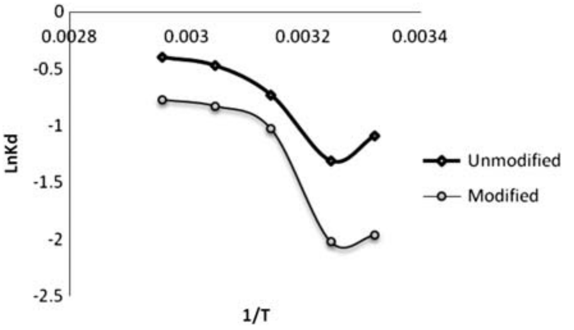

Fig. 5. Effect of temperature on cadmium removed by unmodified and aminated lignin.

Table 4
Thermodynamic parameters for biosorption of cadmium ions onto unmodified and modified lignin

Unmodified lignin			
Temp (°k)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)
301	2.729	2.039	0.057
308	3.357	2.039	0.057
318	1.926	2.039	0.057
328	1.279	2.039	0.057
338	1.117	2.039	0.057
Aminated lignin			
301	4.910	3.240	0.091
308	5.183	3.240	0.091
318	2.723	3.240	0.091
328	2.261	3.240	0.091
338	2.177	3.240	0.091

where R is the universal gas constant (8.314 $\mathrm{J\,mol^{-1}\,k^{-1}}$) and T is the absolute temperature in Kelvin.

The calculated values of ΔH°, ΔS° and ΔG° of biosorption of Cd(II) on unmodified and modified lignin are shown in Table 4. Positive ΔH° (2.04 and 3.24 kJ/mol) values obtained for both adsorbents, respectively, indicated that the biosorption process was endothermic in nature. The positive values of ΔS° (0.057 and 0.091 kJ/mol) obtained reflect the increased randomness of the solid/liquid interface during the biosorption process. The positive values of ΔG° obtained at different temperatures for these lignins indicate the non-spontaneous nature of the biosorption process at the range of temperature being studied.

3.8. Recovery study on biosorption of Cd(II)

Sorbents already loaded with Cd(II) ions were contacted with HCl solutions of different concentration for 120 min. The amount of Cd(II) released back into the HCl solution is expressed as desorption efficiency. The result shows that increasing the concentration of HCl solution decreases the desorption efficiency. This study also revealed that the regeneration of adsorbent was not satisfactory in relation to an increase in the mole concentration of the HCl. Recovery efficiency of Cd(II) ion by unmodified lignin was 69.7% under 0.1 M HCl and 54.6% by aminated lignin (Fig. 6). Reduced performance of 0.1 M HCl for the aminated lignin indicates that the presence of amine group could have influenced complexation with the metal. Hence, the biosorption process could be an interplay of physisorption and chemisorption.

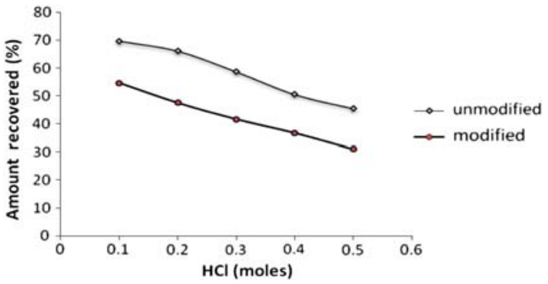

Fig. 6. Effect of HCl on recovery of cadmium from loaded unmodified and modified lignin.

3.9. Charaterization of lignin and lignin amine

Infrared spectra can yield valuable information regarding the chemical groups possesed by the biosorbents. In the present studies, the main effective binding sites have been identified by FTIR in the spectral comparison of lignin and lignin amine. The spectra (not included) displayed several vibrational bands indicating the complex nature of the materials examined. Broad and strong bands at 3,423 and 3,434 cm^{-1} for both biomass were due to free hyroxyl (–OH) groups at the biomass. The peaks observed at 2,923 and 2,928 cm^{-1} for both biomass can be assigned to the –CH group. The peaks at 1,640 and 1,624 cm^{-1} for both biomass were attributed to stretching vibration of carboxyl group (–C=O). Peak position at 1,459 cm^{-1} indicated –NH stretching in lignin amine. Also, the FT-IR spectra of lignin amine showed some characteristic absorption band of amine group: N–H bending band at 1,624 cm^{-1}, N–H out of plane bending band near 812 cm^{-1} and C–N stretching band at 1,237 and 1,108 cm^{-1}. These absorptions bands in the spectra of the aminated lignin indicate that the amino groups were introduced into the lignin macromolecules. N–H stretching band in the range of 3,800–3,500 cm^{-1} was not distinct possibly because it was subsumed by a strong and broad band attributed to hydroxyl group in the range of 3,500–2,500 cm^{-1}.

4. Conclusion

In this study, lignin and lignin amine were used for investigating the effect of pH, contact time, metal concentration, temperature, biosorbent dosage and recovery study on the biosorption of Cd(II) from aqueous sloution. From these variables, kinetic, equilibrium and thermodynamic parameters were dertermined and conclusion drawn. The modification of the adsorbent by amination has been shown to enhance the adsorption capacity during this study. There was an increase in the biosorption metal with increase in pH up to 5.0 and thereafter reaching a plateau. Though removal of Cd(II) was still observed up to pH 8.0, this was strongly assumed to be due to precipitation. There was rapid biosorption of Cd(II) within the first 120 min with biosorption capacity of 7.6 mg/g for unmodified lignin and 8.7 mg/g for modified lignin, and thereafter became very slow. Rapid biosorption was observed up to initial Cd(II) concentration of 100 mg/L, but thereafter did not show appreciable sorption. Increase in temperature leads to decrease in sorption of Cd(II) on to unmodified and modified lignin. There was an increase in sorption of Cd(II) with increase in biosorbent dosage from 0.25 to 1.5 g, showing an increase in the active sites on the biomass. Recovery studies reveals that no satisfactory desorption taking place indicating chemisorptive nature of adsorption. Kinetic analysis using rate expressions of Lagergren showed that the process is pseudo-second-order reaction model. This has been further supported by chemisorptive Elovich model. Equilibrium analysis using Freundlich and Langmuir models showed that the biosorption process partly obeyed both Langmuir and Freundlich models. Evaluation of thermodynamical parameters showed the process as endothermic and non-spontaneous in nature. Intraparticle diffusion studies revealed that pore diffusion plays a major role in the adsorption process. The possible functional groups on lignin and lignin amine responsible for the sorption of Cd(II) are: –OH, –NH, C=O and C–N.

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