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Biosorption of nickel using unmodified and modified lignin extracted from agricultural waste

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ABSTRACT

Adsorption capacity for the removal of nickel (II) ions from aqueous solution using unmodified and modified lignin extracted from *Tithonia diversifolia* was investigated. The lignin was characterized with FT-IR. Parameters like initial pH, initial concentration, and contact time were investigated. The optimum pH for metal removal was found to be 7, while optimum contact time of 360 min was achieved. The modification of the adsorbent by phenol affected the adsorption capacity. The kinetic studies showed that the sorption rates could be described by both pseudo-second-order and intraparticle diffusion models. The pseudo-second-order model showed a better fit with a correlation coefficient of 0.9955 and 0.9958 for both unmodified and modified lignins, respectively. The adsorption isotherm was best fitted using the Freundlich model. The adsorption capacity for Ni(II) on the unmodified and modified lignin was found to be 12.48 and 16.94 mg g^{-1}, respectively.

Keywords: Biosorption; Nickel; Lignin; Modification; *Tithonia diversifolia*; Isotherm

1. Introduction

The increased level of environmental contamination as a consequence of industrial development is posing a very serious problem to the global environment. Industrial processes for extracting metals or, more generally, all processes involving metals in their productive cycle generate significant heavy metal cations [1]. Mine drainage, metal industries, refining, electroplating, dye and leather industries, domestic effluents, land fill leachate, and agricultural run-off all generate wastewater that contain heavy metal ions [2]. These heavy metals have been found to be detrimental to man's existence. Excessive exposure to nickel, for example, can lead to severe damage of lungs, kidneys, skin dermatitis, and cancer [3].

Over the last few decades, several methods have been devised for the treatment and removal of heavy metals including nickel from waste water. The commonly used procedures for removing metal ions from aqueous streams include chemical precipitation, lime coagulation, ion exchange, reverse osmosis, and solvent extraction [4].

In place of these conventional methods, many low-cost biosorbents, such as chitosan, clay, saw dust, peat moss, lignin, pectin, seaweed, zeolite, bark materials, and ironoxide-coated sand, have been previously investigated for metal removal [5,6], in

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addition Mangrove bark [7], oil palm fruit fiber [8], and bamboo [9] had also been used. Lignin, the by-product of paper industry and emerging cellulose ethanol industry, is a potential metal sorbent with abundant supply. The alternative utilization of lignin as potential low cost metal sorbents has been explored by other researchers [10]. This option appears attractive due to the natural abundance of lignin and the availability of appropriate functional groups for metal sorption.

In the present study, lignin extracted from *Tithonia diversifolia*, a bio-based waste material, was modified by phenol treatment and used as biosorbent for the removal of Ni(II) from aqueous solution. Batch experiments were conducted over a range of pH and initial metal concentration.

2. Materials and method

The stock solution of Ni(II) ions used in this study was prepared by dissolving weighed quantities of $NiSO_4 \cdot 6H_2O$ salt in distilled water. Experimental solutions with the desired concentration were prepared by diluting the stock solution with distilled water.

2.1. Lignin extraction and modification

T. diversifolia biomass (150 g) sieved out of a 850 µm mesh screen 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, allowed to stay for 2 h, at 80˚C. The plastic container was then removed and allowed to cool overnight. Muflin cloth was used to filter the mixture. The pH of the filtrate (black liquor) was adjusted to 2 by using 40% H_2SO_4. The precipitated lignin was filter and oven dried at 60˚C. The extracted lignin (100 g) was mixed with 1,000 ml 30% phenol and stirred for five minutes at 60˚C. The mixture was then cooled to 30˚C and 400 ml of 72% sulfuric acid was slowly added with constant stirring. The mixture was further stirred for 1 h at 30˚C and two separate layers of organic and aqueous phases were obtained. The organic layer was retained while the aqueous layer was discarded. The product thus collected was added drop wise to 300 ml diethyl ether in an ice bath, with continuous stirring. After stirring for a few minutes, the mixture was decanted and the lingo-phenol portion settled at the bottom.

2.2. Experimental design

2.2.1. pH effects on the sorption of nickel

The respective biosorbents (0.5 g) were weighed and suspended into different beakers containing 50 ml of 50 ppm of Ni(II), solution whose pH had been adjusted to 1–9, with dilute HCl or NaOH. The mixture of the biosorbent and Ni(II) solution was centrifuged after 6 h of contacting.

2.2.2. Sorption kinetics

Batch adsorption experiments were carried out in a series of Erlenmeyer flasks of 250 ml capacity by agitating 1 g of the adsorbents (unless otherwise stated) with 50 ml of the aqueous Ni(II) solution. Kinetic studies were carried out by suspending treated biomasses in the Ni^{2+} solutions adjusted to pH 7 and stirred for 10, 30, 60, 90, 120, 150, 180, 240, 300, and 360 min at room temperature. They were subsequently filtered at the expiration of each contact time.

2.2.3. Adsorption capacity studies

Sorption capacity study was conducted for 10 capacity cycles using biomass of 0.5 g per 50 ml of the Ni(II) solution at pH 7. The suspension was equilibrated in a rocker for 30 min, centrifuged, and the supernatant collected in sample tubes for analysis marking the end of the first cycle. Fresh metal solution was added to the same biomass and equilibrated for another 30 min, centrifuged and withdrawn for analysis.

2.2.4. Adsorbent dose

Keeping the concentration, contact time, and pH constant, the adsorbent dose was varied to know the effect that increment in the active sites of unmodified and modified lignin will have on the adsorption of Ni (II). The 0.1, 0.5, 0.75, 1.0, and 2.0 g of the respective biomass were weighed into different beakers containing 50 ppm of the metal ion solution. The suspension was centrifuged and supernatants were collected into clean tubes for metal analysis.

2.2.5. Sorption isotherms

Sorption isotherms were obtained by using the extracted and modified lignin samples. Nickel solutions were prepared at concentrations from 10 to 500 mg/l. Aliquots (50 ml) of each solution were added to 0.5 g of the biosorbent samples and the pH of the solutions was adjusted to 7. The mixtures were placed in a shaker bath at room temperature until nickel sorption equilibrium was reached in approximately 6 h. Likewise, the effect of temperature changes on the sorption process was monitored at (30, 40, 50, and 60℃). Experimental data obtained were adjusted to Freundlich, Langmuir isotherm models and thermodynamic parameters were equally deduced.

2.2.6. Recovery studies

Various concentrations of hydrochloric acid and EDTA (disodium) solution and deionized water were used to recover the adsorbed metal ion. The 0.5 g of unmodified and modified lignin were, respectively, weighed and suspended into different beakers containing 50 ml of the metal solution. The mixture was centrifuged and the supernatants were discarded. The 20 ml of 0.1, 0.3, 0.5 M HCl; 2, 5, 10 mM EDTA; and deionized water were added to the used biomass and kept for 1 h. The mixture was centrifuged and supernatant was collected in sample tubes for metal analysis.

2.3. Biosorption data analysis

Characterization of the biosorbents was carried out by FT-IR spectroscopic studies. Metal content analysis was conducted using Atomic absorption spectroscopy. The quantity of nickel adsorbed by the biosorbent (q_e in mg/g) was extrapolated from Eq. (1):

$$q_e = \frac{C_o - C_e}{m} V \tag{1}$$

where C_o and C_e are the Ni(II) concentrations in $\mathrm{mg\,L^{-1}}$ before and after adsorption for time t, V is the volume of adsorbate in liter, and m (g) is the weight of the adsorbent. The efficiency of biosorption ($R\%$) was calculated using Eq. (2)

$$R\% = (C_o - C_e)100/C_o \tag{2}$$

3. Results and discussion

3.1. Characterization of adsorbent

The FTIR technique is an important tool to identify the characteristics of functional groups on the adsorbent surface [7]. The raw and modified lignins show characteristic infrared bands in accordance with the other reported results [11,12]. Differences occasioned by modification are observed in the shift from 3,482 to 3,415 $\mathrm{cm^{-1}}$ region, corresponding to the wave number of –OH group.

3.2. Effect of pH

Studies on the effect of pH on the adsorption of Ni (II) ions on unmodified and modified lignin were carried out over the pH range of 1–9. As illustrated in Fig. 1 a pronounced dependence of metal sorption on solution's pH may be noticed. There is a remarkable sharp increase in sorption of nickel by the modified lignin from the pH of 5. At pH lower than 8, the dominant forms of nickel were Ni^{2+}, while at pH more than 8, $Ni(OH)_2$ was present as precipitate; therefore, the percentage of metal removed cannot be attributed to adsorption alone [13]. The effect of pH can be explained in terms of pHzpc (zero point of charge) of the adsorbent [14]. At pH less than pHzpc, the predominant metal species [M^{n+} and $M(OH)^{(n-1)+}$] are positively charged; therefore, uptake of metals in the pH range of 2–7 is a H^+–M^{n+} exchange process. The possible sites on lignin for sorption are due to the C_6H_5 OH groups. Other sites on the modified lignin can also contribute to the sorption process. With increasing pH, total number of negative groups available for the binding of metal ions increased; therefore, competition between proton and metals ions became less pronounced [15]. Also with increasing pH, more functional groups, such as amino and carbonyl groups, would be exposed leading to attraction between these negative charges and the metals and hence increases in biosorption onto the surface of adsorbent [16].

3.3. Effect of contact time

Kinetics of metal ion sorption governs the rate, which determines the residence time, and it is one of

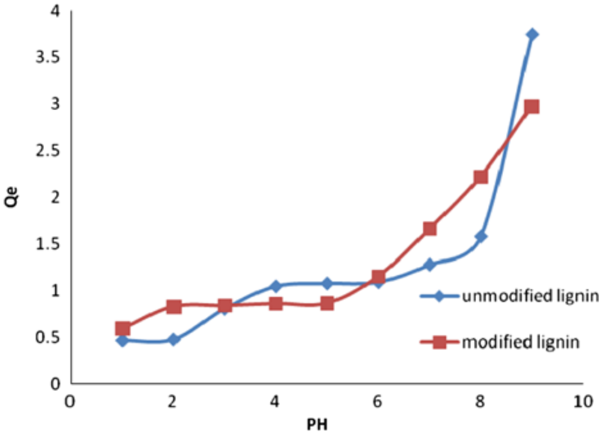

Fig. 1. Effect of initial pH on the adsorption of Ni(II) on unmodified and modified lignin.

the important characteristics defining the efficiency of an adsorbent [17]. The rate at which sorption takes place is of importance especially when designing batch sorption systems. Consequently, it is important to establish the time dependency of such systems for various pollutant removal processes [18].

An ideal biosorbent should rapidly adsorb high concentration of the heavy metals [9]. However, in this study the biosorbent used did not follow this trend. Nonetheless, the modified lignin showed a better result over the unmodified lignin. The adsorption at 30 min was about 4.91% and 4.97% for the unmodified and modified lignin, respectively. The optimum adsorption time for the two biosorbents is at 360 min with an uptake of 24.35% and 33.83% for the unmodified and modified lignin, respectively.

3.4. Adsorption kinetics

Three kinetics models, pseudo-first-order, pseudo-second-order and intraparticle diffusion, were used to investigate and fit the experimental data obtained under the optimized conditions from 30 to 360 min.

There are three common steps involved in adsorption process. The first step is mass transfer across the external boundary layer film of liquid surrounding the outside layer of the particle. The second step is the adsorption process at individual site on the surface (internal or external) and the energy depends on the binding process (physical or chemical adsorption). This step is often assumed to be extremely rapid. The third step is the diffusion of the adsorbate molecules to an adsorption sites either by a pore diffusion process through the liquid filled pores or by a solid diffusion mechanism [19]. One or any combination of these adsorption processes could be the rate-controlling mechanism.

3.4.1. The pseudo-first-order kinetic model of Lagergren

The pseudo-first-order rate model of Lagergren is as expressed in Eq. (3):

$$\log(q_e - q_t) = \log q_e - k_1 t/2.303 \tag{3}$$

where q_e is the amount adsorbed (mg/g) at equilibrium, q_t is the amount adsorbed (mg/g) at any time, and t and k_f are the Largergren adsorption rate constant (min^{-1}). The values of q_e and k_f can be calculated from the slopes and the intercept of the plot of log $(q_e - q_t)$ vs. t (Fig. 2). Linear plots of log $(q_e - q_t)$ vs. t indicate the applicability of this kinetic model. As can be seen from Fig. 2, adsorption process using the two adsorbents does not follow pseudo-first-order kinetic model.

3.4.2. Pseudo-second-order kinetic model

The pseudo-second-order kinetic model is given as follows:

$$t/q_t = 1/k^2 q_e^2 + t/q_e \tag{4}$$

where k^2 is the equilibrium rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}). The plot of t/q_t vs. t gives a linear relationship if this model is obeyed. The estimated parameters obtained along with values of the correlation coefficient (r^2) are listed in Table 1. The ability of the applied model to describe the experimental kinetic data for Ni(II) sorption on the modified and unmodified lignins is shown

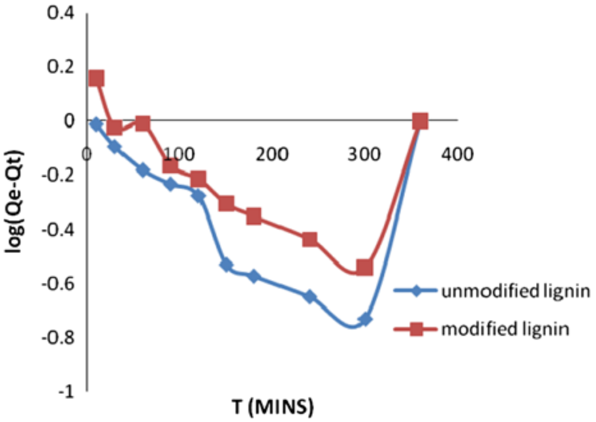

Fig. 2. Pseudo-first-order kinetic plot of Ni(II) adsorption on unmodified and modified lignin.

Table 1
Pseudo-first and -second-order parameters for metal sorption onto *Tithonia diversifolia* lignin

	Pseudo-first-order		Pseudo-second-order	
	Unmodified lignin	Modified	Unmodified lignin	Modified
q_e	1.053	1.217	1.356	1.7035
K	0.006	0.0052	0.019	0.0278
r^2	0.9712	0.9715	0.9956	0.9958

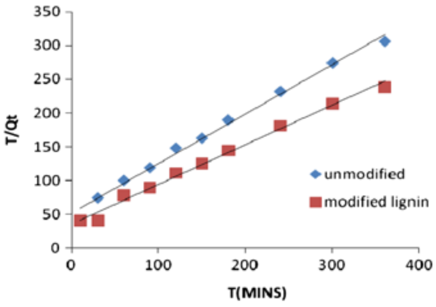

Fig. 3. Pseudo-second-order kinetic plot of Ni(II) adsorption on unmodified and modified lignin.

in Fig. 3. As seen, the pseudo-second-order model succeeds in representing properly the kinetic data obtained for both samples with high r^2 values. In agreement with the results shown in Fig. 2, the estimated q_e values better predicted the metal sorption performance (Table 2).

3.4.3. Intraparticle diffusion model

The sorption kinetics are controlled by different steps, including solute transfer to the sorbent particle surface, transfer from the sorbent particle surface to intraparticle active sites, and retention on these actives sites via sorption, complexation, and intraparticle precipitation phenomena. Intraparticle diffusion is characterized by the relationship between specific sorption (q_t) and the square root of time according to the Weber and Morris relation [20].

$$q_t = K_d t^{1/2} \tag{5}$$

where q_t is the amount of solute adsorbed at time t (mg g^{-1}) and K_d is the initial rate of intraparticle diffusion (mg L^{-1} s$^{-1/2}$). The rate constant of intraparticle diffusion K_d was determined by plotting q (mg g^{-1}) as a function of the square root of the time (Fig. 4). This figure shows a nonlinear distribution of points, indicating intraparticle diffusion in the process. Similar results were obtained for other sorbents [21,22].

3.4.4. Effect of adsorbent dosage

The removal efficiency of unmodified and modified lignin increased as the adsorbent dosage increased from 0.1 to 2.0 g at pH 7 (Fig. 5). The primary factor explaining this characteristic is that adsorption sites remain unsaturated during the adsorption reaction, whereas the number of sites available for adsorption increased by increasing the adsorbent dose. Increasing the amount of adsorbent added into a fixed concentration ions solution will increase the availability of active sites of the adsorbent. Therefore, adsorbent percentage and efficiency will also increase [23].

The critical value of dosage of unmodified and modified lignin was 2.0 g and the equilibrium concentration at this value is 1.92 mg/g and 2.19 mg/g for the unmodified and modified lignin, respectively.

3.4.5. Sorption capacity

The applicability of lignin samples without regeneration was investigated. It is observed that the adsorption capacity decreased as the number of cycles increased (Fig. 6). This is quite reasonable because the cycle time increases under the unchanged total amount of available adsorption sites. Though the adsorption capacity of the modified lignin is better than that of the unmodified, the fact remains that the two lignin samples cannot withstand more than 10 cycles. The adsorption capacity of unmodified lignin at the 10th cycle appeared more than that of the 9th cycle. Though this may be considered abnormal, it is noteworthy to observe that the adsorption capacity of Cu(II) on *Cinnamomum camphora* leaves powder increased as the cycle time increased [24]. It can be concluded, however, that the most meaningful effects were recorded within the first five cycles.

Table 2
Model parameters estimated for Ni(II) ion sorption isortherms

Model	Parameter	Unmodified lignin	Modified lignin
Freundlich	K_F (mg/g)(dm^3/mg)$^{1/n}$	0.3434	0.2934
	n^F	1.2019	1.2257
	r^2	0.8702	0.8134
Langmuir	q_{max} (mg/g)	21.55	24.33
	b (dm^3/mg)	0.0016	0.0022
	r^2	0.9995	0.9968

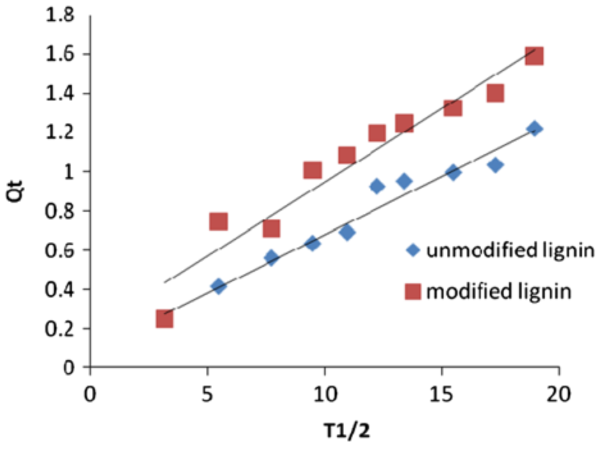

Fig. 4. Intraparticle diffusion kinetic plots of Ni(II) adsorption on unmodified and modified lignin.

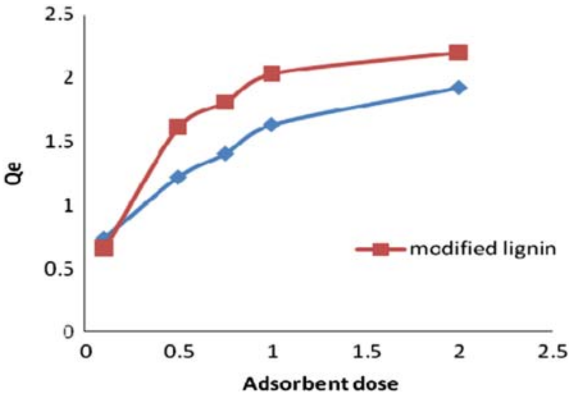

Fig. 5. Adsorbent dosage's plot of Ni(II) adsorption on unmodified and modified lignin.

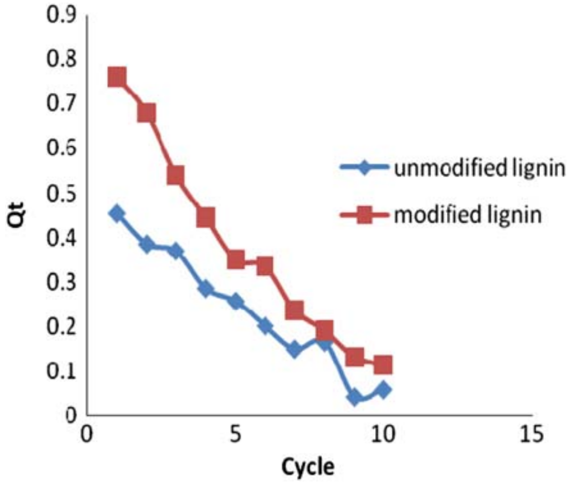

Fig. 6. Effect of sorption capacity on the adsorption of Ni (II) on unmodified and modified lignin.

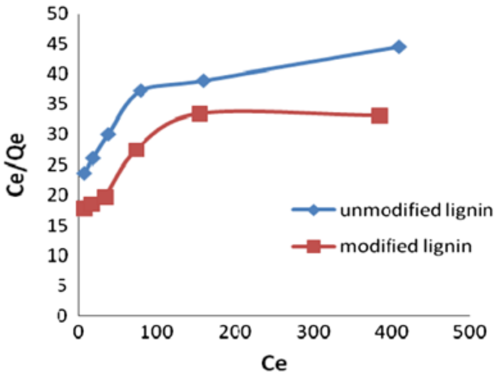

Fig. 7. Langmuir adsorption isotherms of Ni(II) on unmodified and modified lignin.

3.5. Effect of concentration

Initial concentration provides the necessary driving force to overcome resistance of mass transfer between metal ions in the aqueous phase and adsorbents [25]. Adsorption efficiency decreased with the increment of initial heavy metals ion concentration [7]. Increase in initial concentration from 10 to 500 ppm decreased the percent removal for Ni(II) ion on unmodified lignin from 29.75% to 18.34%, while that of modified lignin decreased from 36% to 23.23%.

3.6. Adsorption isotherms

The equilibrium of the biosorption process is often described by fitting the experimental points with models used for the representation of isotherm adsorption equilibrium. Two widely accepted and linearized equilibrium adsorption isotherm models for single solute system are given by the Langmuir and Freundlich Models (Eqs. 6 and 7). The linearized equations of these models relating the molar amount of metal ions sorbed at equilibrium per sample mass unit (q_e) and the equilibrium metal ion concentration (C_e) are given by Langmuir model (Fig. 7):

$$C_e - q_e = 1/q_{\max}b + C_e/q_{\max} \tag{6}$$

where $q_{\max}$ is the monolayer adsorption capacity ($\mathrm{mg\,g^{-1}}$) and b is the Langmuir equilibrium constant ($\mathrm{L\ mg^{-1}}$).

Freundlich model:

$$\log q_e = \log K_F + 1/n \log C_e \tag{7}$$

where K_F is the Freundlich constant and $1/n$ is the heterogeneity factor.

The result obtained showed that adsorption efficiency decreased with the increment of initial Ni(II)

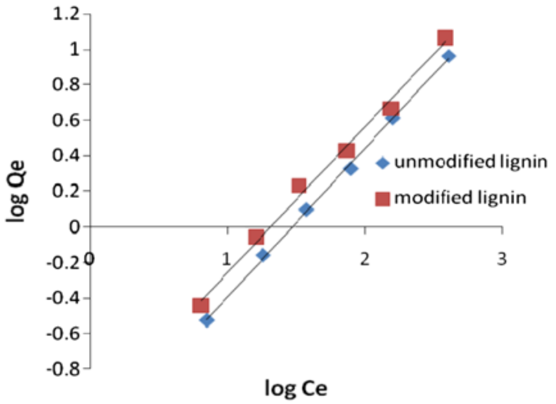

Fig. 8. Freundlich adsorption isotherms of Ni(II) on unmodified and modified lignin.

ions concentration. The correlation coefficient (r^2) of the adsorption isotherm data showed that the adsorption of Ni(II) ions on unmodified and modified lignin was better fitted to Freundlich isotherm model (Fig. 8). This suggests that heterogeneous adsorption of Ni(II) ions on both unmodified and modified lignins. Langmuir and Freundlich correlation values for unmodified lignin are 0.8702 and 0.9995, respectively; while those of modified lignin are 0.8134 and 0.9968, respectively. The $1/n$ value lower than 1.0 confirmed the heterogeneity of the adsorbent and it indicates that the bond between Ni(II) ions and the absorbent is strong.

3.7. Sorption thermodynamics

Thermodynamic parameters of a biosorption process are necessary to conclude about the nature of the process. The Gibbs free energy, ΔG°, gives an indication of the feasibility of a chemical reaction. It has been reported that at a high temperature, the thickness of the boundary layer decreases due to the increased tendency of the metal ion to escape from the biomass surface to the solution phase, which results in decrease in the adsorption as the temperature increases [16].

Contrary to this, the data obtained in this study show a slight increase in the adsorption as the temperature increases. The equilibrium capacity measured increased from 1.24 mg/g at 27˚C to 1.50 mg/g at 60˚C for the unmodified lignin. For the modified lignin, the values obtained were slightly higher from 1.68 mg/g to 1.92 at 27 and 60˚C, respectively. This suggests an endothermic reaction however lignins are biopolymers and biodegradable. As the temperature is increased, a number of bonds in the lignin structure, which are the suggested sorption agents, are weakened. As these bonds are weakened and broken, a more flexible structure is obtained and the groups are exposed. This exposure of more groups to the solvent presumably increases the number of binding sites for enhanced nickel (II) ion sorption. This type of reaction was also observed in [24], where the adsorption capacity of Cu (II) on cinnamomum camphora leaves powder increased as the temperature increased. Themodynamic parameters obtained for this adsorption process are presented in Table 3. The values of equilibrium constants (K_d) were calculated from the relation in Eq. (8):

$$K_d = \frac{C_e}{C_b} \tag{8}$$

where C_e and C_b are the equilibrium concentrations (mg/L) of Ni(II) on the biosorbent and in solution, respectively. The Gibbs free energy is given by Eq. (9):

$$\Delta G^\circ = -RT \ln K_d \tag{9}$$

where T is the absolute temperature, R is the gas constant, and ΔG° is the standard free energy change. The values of enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from the following relation in Eq. (10):

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{10}$$

Table 3
Thermodynamic parameters for biosorption of Ni(II) ions

Temp (K)	Unmodified				Modified			
	K_d	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/Kmol)	K_d	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/K mol)
300	3.08	−2.77	−6.15	−11.36	1.99	−1.72	−4.96	−10.88
303	2.90	−2.68	−6.15	−11.36	1.91	−1.64	−4.96	−10.88
313	2.68	−2.57	−6.15	−11.36	1.79	−1.53	−4.96	−10.88
323	2.55	−2.52	−6.15	−11.36	1.74	−1.48	−4.96	−10.88
333	2.34	−2.35	−6.15	−11.36	1.61	−1.32	−4.96	−10.88

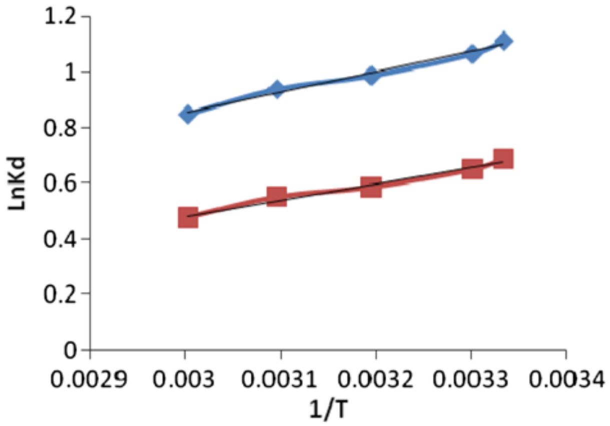

Fig. 9. Plot of K_d against $1/T$.

where ΔH° and ΔS° were calculated from the slope and intercept of Van't Hoff plot of $\ln K_d$ vs. $1/T$ (Fig. 9).

The ΔG° showed negative values indicating that the sorption reaction is feasible. The ΔH° is also negative, indicating that the nickel biosorption reaction is actually exothermic.

3.8. Recovery study

After the filtration procedure, Ni-loaded biosorbents were dried and the dried materials on the average were treated with different concentrations of HCl, EDTA, and deionized water. The results obtained showed that HCl performed better in the recovery of Ni(II) from the modified lignin with 58.25%, 63.07%, and 64.33% at the concentration of 0.1, 0.3, and 0.5 HCl, respectively (Fig. 10). Whereas unmodified lignin had percentage recovery of 11.96%, 59.66%, and 65.31% at the concentration of 0.1, 0.3, and 0.5 HCl. EDTA performed better in the recovery of Ni(II) from the unmodified lignin. The percentage recovered at the concentrations of 2 mM EDTA, 5 mM EDTA, and 10 mM EDTA are 41.93%, 50.16%, and 52.27%, respectively, for unmodified lignin. The modified lignin showed 16.95%, 20.99%, and 25.72% of recovery at the concentrations of 2 mM EDTA, 5 mM EDTA, and 10 mM EDTA, respectively. The percentage of recovery obtained using deionized water is 18.16% and 44.66% from unmodified and modified lignin, respectively. As the concentration of the desorping agents used increases, their efficiency in the release of Ni^{2+} ions increased; nevertheless, a complete desorption could not be achieved. This might be due to entrapment of the Ni^{2+} ions in the intrapores of the lignin materials [26].

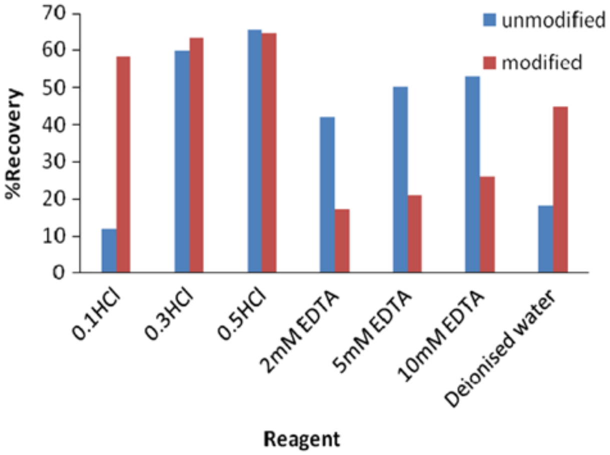

Fig. 10. The plot of recovery study of adsorption of Ni(II) on unmodified and modified lignin.

4. Conclusion

The comparative analyses of unmodified and modified lignin on the adsorption of nickel ions were investigated in this study. The equilibrium data were best fitted into Freundlich isotherm model which connote heterogeneous adsorption of Ni(II) ion on the surface of the unmodified and modified lignin. The adsorption data obtained for the unmodified and modified lignin were best fitted into pseudo-second-order and intraparticle diffusion. The thermodynamics of the reaction suggest an endothermic reaction. The recovery of Ni(II) from the modified lignin was best using dilute HCl and deionized water, whereas EDTA was best for the recovery from unmodified lignin.

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