

# Adsorption of Nickel (II) from Aqueous Solution Using *Leucaena leucocephala* Shells

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**ABSTRACT:** Water pollution, as a result of industrial development, has detrimental effects on aquatic organisms and human beings. In this research, *Leucaena leucocephala* biomass was modified using Fenton's reagent and sodium hydroxide, and the performances of the native, Fenton-treated, and NaOH-activated adsorbents for removal of Ni(II) from aqueous solution were evaluated under various experimental conditions such as initial pH, contact time, initial concentration of Ni(II), adsorbent dosage, and temperature. The adsorbents were characterized using Fourier transform infrared spectroscopy and pH of the point of zero charge. Kinetic and equilibrium adsorption data were well described by Elovich and Liu models, respectively. The maximum adsorption capacities are 50.66, 56.72, and 75.17 mg/g for the native, Fenton-treated, and NaOH-activated *L. leucocephala* adsorbents, respectively. Desorption of Ni(II) from the surface of the adsorbents was done effectively with 0.03 mol/L of hydrochloric acid. Thermodynamic calculations show that the adsorption process was spontaneous, feasible, and favorable because the values of  $\Delta G^\circ$  were negative. Adsorption of Ni(II) onto the adsorbents was exothermic ( $\Delta H^\circ$  values were negative) and there was also a decrease in the randomness of the liquid-solid interface ( $\Delta G^\circ$  values were negative). Overall, the three adsorbents can be used for the treatment of water that is contaminated with Ni(II).

**KEYWORDS:** *Leucaena leucocephala*; Fenton-treated; Sodium hydroxide-activated; Nickel(II); Adsorption.

## INTRODUCTION

Heavy metal ions are continuously being released into the environment as a result of incessant increases in industrial activities and technological advancement [1,2]. The anthropogenic sources of heavy metals include waste from metallurgical, electroplating, and metal finishing industries, mine drainage, pigment manufacturing, battery industries, tannery operations, chemical manufacturing, manufacturing of leather, fertilizer industries, and

leachates from contaminated groundwater [3,4]. Degradation of recalcitrant heavy metal ions is practically impossible and the accumulation, non-biodegradability and persistent nature of these metal ions in the environment can cause a number of ecological and environmental problems [5]. For instance, water pollution had caused the death of a large number of fish and other aquatic organisms.

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Water is an inevitable constituent of living things, hence there is a need for potable water to be free of pollutants [2]. In modern societies, different measures are taken to prevent the disasters of water pollution that have happened in the past. The Clean Water Acts (CWA) of 1972 defines water pollution, as the man-made or man-induced alteration of the physical, biological, chemical, and radiological integrity of water. The introduction of substances into water affects the quality of water and makes water to be polluted. The intense and inadequate use of fertilizers and pesticides in the soil, coupled with the increase in industrial and mining activities is the main reason for the contamination of soil, waterways, and the water table by heavy metals [6]. A drinking water quality guideline value represents the concentration of a constituent that does not result in any significant health risk to the consumer over a lifetime of consumption. Therefore, drinking water should be suitable for human consumption and for all basic domestic purposes [7].

Nickel is mostly present in water in low concentrations and therefore its removal from water has not been attentively focused on by adsorption researchers [8]. Nickel is also present in a minute amount in foodstuffs and has other useful applications in industries such as electroplating, tanneries, and mining industries, however, accumulation and high concentration of nickel has a lot of environmental implications including health issues such as metal poisoning, dermatitis (eczema), asthma, cancer of the lung, nose, and larynx as well as retardation of spermatogenesis, amylase enzymes, and insulin [8–10]. Nickel must be eliminated from industrial aqueous effluents before the effluents are released into the environment or water bodies. Therefore, the concentrations of Ni(II) must be reduced to the threshold levels (0.01 mg/L for drinking water and 2.0 mg/L for industrial wastewater) that meet environmental regulations and specifications of various water bodies before being discharged into our invaluable environment [11].

Conventional techniques for water treatment include ion exchange, adsorption or biosorption, chemical precipitation, solvent extraction, membrane filtration, ion exchange, reverse osmosis, electrodialysis, and electrochemical technologies [12–14]. The most efficient method, among the conventional technique, for water treatment, is adsorption. The adsorption technique is simple, effective, and economical coupled with the availability of various low-cost adsorbent materials and the ease of adsorbent recycling [15,16].

The adsorption method had been used by a number of adsorption researchers for the removal of Ni(II) from aqueous solutions and a search for abundant biomass for water treatment is on the increase. Among the variety of biomass materials that have been utilized for Ni(II) removal from water include pistachio hull waste [4], watermelon rind [8], *Punica granatum* peel [17], *Litchi chinensis* seeds [18], *Aloe barbadensis* Miller leaves [19,20], *Moringa oleifera* bark [21], and *Trichoderma viride* [22]. Reddy et al. [21] investigated the biosorption of Ni(II) from aqueous solutions using *Moringa oleifera* bark and the report showed that isotherm and kinetic data were best fitted with Langmuir and pseudo-second-order models, respectively. The maximum adsorption capacity of *Moringa oleifera* biosorbent for Ni(II) obtained at pH 6 and 323 K was 30.38 mg/g. The thermodynamic data indicated that the biosorption process was endothermic and spontaneous. The spent biosorbent was successfully regenerated using 0.2 M HCl. Gupta and Kumar [19] investigated the removal of Ni(II) from aqueous solutions using the leaf of *Aloe barbadensis* Miller. The report indicated that the biosorbent could remove up to 60.2% of 100 mg/L of Ni(II) solution. The kinetic and equilibrium data obeyed pseudo-second-order and Freundlich models, respectively. The value of maximum adsorption capacity, obtained from the Langmuir model, was 10 mg/g. The thermodynamic data showed that the biosorption process was spontaneous, feasible, and exothermic. In another report by Babarinde and co-workers [23], Ni(II) was adsorbed from aqueous solutions onto the leaf of *Acalypha hispida*, pseudo-second-order, and Freundlich models described the kinetic and equilibrium data better than other models used in the study. The data from the thermodynamic study revealed that the biosorption process was spontaneous and endothermic, and there was an increase in randomness during the biosorption process for Ni(II).

*Leucaena leucocephala* is a leguminous plant that belongs to *Fabaceae*'s family. The plant, which is popularly known as the white lead tree [24], has small, green, and flat leaves as well as green beans shell or pods. The plant can grow up to 20 m tall. The shell of the *L. leucocephala* turns brown when completely dried. The shell has necklace-like rows of seeds. The seeds of *L. leucocephala* have medicinal values and can be used as a remedy for stomach ache [25]. The *L. leucocephala* shells are mostly and indiscriminately discarded in the environment, however,

the shells could serve as a source of adsorbent because the shells are abundant [26].

The majority of cities cannot afford the use of sophisticated and expensive techniques for water treatment; this has necessitated the usage of adsorption which is a low-cost water treatment technique. The shell of *L. leucocephala* is hard and could therefore serve as a good source of biomass for water treatment. *Leucaena leucocephala* shell constitutes a waste that has no economic value and conversion of the waste into an efficient adsorbent for removal of Ni(II) from the solution is a commendable idea. Most biomass is not good adsorbent material, however, the chemical modification could make biomass better adsorbent material than the native forms for wastewater remediation. In this research work, the removal of nickel(II) from the solution by native *L. leucocephala* shell, Fenton treated *L. leucocephala* shell, and sodium hydroxide-treated *L. leucocephala* shell were examined. Parameters such as initial pH, initial concentration of Ni(II) solution, adsorbent dosage, contact time, and temperature were investigated. A desorption study was also investigated.

## EXPERIMENTAL SECTION

Analytical grade reagents, such as  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ , NaOH, HCl,  $\text{H}_2\text{O}_2$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and  $\text{HNO}_3$ , were used as supplied without further purification. Deionized water was used for the preparation of solutions. A 1.0 g/L of Ni(II) was prepared and used as a stock solution.

### Preparation and characterization of adsorbents

The *L. leucocephala* shells were collected within the campus of The Federal University of Technology, Akure, Nigeria. The matured and dried shells of *L. leucocephala* were split-opened, washed, sun-dried for 72 h, oven-dried at 105 °C for 8 h, chopped into pieces, ground with Victoria grinder and fine particles were obtained using 100  $\mu\text{m}$  mesh sieve size. The fine powder of *L. leucocephala* was divided into three equal parts; a portion was activated with 0.1 mol/L of NaOH, another portion was treated with Fenton solution (20 mg/L of Fe(II) and 25 mg/L of  $\text{H}_2\text{O}_2$ ) while the third portion was left untreated (native *L. leucocephala*). For treated portions, known weights of the sample were added to known volumes of the solution of NaOH and Fenton, and the mixtures were left for 24 h in a fume cupboard for proper equilibration. After equilibration,

the samples were washed with deionized water until neutrality and subsequently oven-dried at 80 °C for 24 h. After cooling, the samples were separately stored in airtight glass bottles prior to usage.

The adsorbents were characterized using  $pH_{pzc}$  (pH of point of zero charges) and Fourier transform infrared (FTIR) spectroscopy. The values of the pH of the point of zero charge ( $pH_{pzc}$ ) of the three adsorbents were determined using pH drift method as described elsewhere [27,28]. The FTIR spectra of native *L. leucocephala* and treated samples were recorded on an FT-IR spectrometer (Agilent Technologies, Germany) in the range 4000 – 500  $\text{cm}^{-1}$ .

### Adsorption study

Working Ni(II) solutions (50 mg/L – 800 mg/L) were prepared by diluting the stock metal solution of 1.0 g/L using deionized water. Different adsorbents (native, Fenton-treated, and NaOH-activated) of known weights (0.25 g – 1.5 g) were separately weighed into different 25 mL sample bottles. Metal solutions of various pH values (pH 1 – 8) were used, and the pH of the solution was adjusted using 0.1 mol/L HCl or 0.1 mol/L NaOH. A 20 mL of Ni(II) solution of a particular pH was measured and transferred into appropriately labeled sample bottles containing the adsorbent. The mixtures were agitated on a thermostatic shaker between 0 and 360 min at temperature ranges 30 – 65 °C. At the end of each experiment, the spent adsorbent was separated from the mixture by centrifugation. 10 mL of the supernatant solution was taken for metal analysis using a Flame Atomic Absorption spectrophotometer. The equilibrium amount ( $q_e$ ) of Ni(II) adsorbed onto each adsorbent was evaluated with the aid of Eq. (1). All the adsorption experiments were repeated three times.

$$q_e = \frac{(C_o - C_e)v}{m} \quad (1)$$

where  $C_o$  = initial concentration of Ni(II) in mg/L;  $C_e$  = final concentration of Ni(II) left in the solution after the adsorption experiment in mg/L;  $v$  = volume of Ni(II) solution in contact with the adsorbent in L; and  $m$  = mass of adsorbent used for each adsorption experiment in g.

For Ni(II) recovery study, 250 mg/L of nickel solution was prepared and the pH was adjusted to the optimum value. Subsequently, 0.25 g of each adsorbent was weighed separately into each of the 25 mL sample bottles and 20 mL

of 250 mg/L Ni(II) solution was added. The mixtures were agitated for 6 h at 30 °C. Immediately after agitation, the sample bottles that contained the mixtures of adsorbent and adsorbate were removed from the thermostatic shaker and the bottles were left to stand for 240 min for the adsorbent to settle down and the clear solution on top of the tubes were removed using a Pasteur pipette. Hydrochloric acid solutions (0.1, 0.2, 0.3, 0.4, and 0.5 mol/L) were prepared as eluants and 20 mL of each solution was added to each of the residues. The mixtures were agitated 2 h at 30 °C, the mixtures were centrifuged and 10 mL of each supernatant was taken for metal analysis using a Flame Atomic Absorption spectrophotometer. The amounts of Ni(II) desorbed by each eluant solution were evaluated. All the experiments were repeated two more times.

#### Adsorption modeling and thermodynamic calculations

The kinetic data were subjected to four non-linear kinetic models; pseudo-first order, pseudo-second order, Elovich, and intraparticle diffusion mechanism. The corresponding equations of these models are presented in Eqs. (2 – 5).

$$q_t = q_e \{1 - \exp(-k_f t)\} \quad (2)$$

$$q_t = q_e - \frac{q_e}{k_s q_e t + 1} \quad (3)$$

$$\frac{dq_t}{dt} = A_E e^{-B_E q_t} \quad (4)$$

$$q_t = k_{id} t^{0.5} + C \quad (5)$$

Where  $q_t$  = experimental amount of metal ion adsorbed at the time,  $t$  (min) in mg/g;  $k_f$  = pseudo-first-order rate constant in 1/min;  $k_s$  = pseudo-second-order rate constant in (g/mg min);  $B_E$  = a desorption constant, which is related to the extent of surface coverage in g/mg;  $A_E$  = initial adsorption rate in mg/g min;  $k_{id}$  = intraparticle diffusion constant in mg/g min<sup>0.5</sup>; and  $C$  = boundary layer in mg/g.

The equilibrium (concentration-dependent) data were also subjected to four non-linear equilibrium models; Langmuir, Freundlich, Liu, and Temkin models. The respective mathematical expressions for the models are presented in Eqs. (6 – 9).

$$Q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \quad (6)$$

$$Q_e = K_F C_e^{\frac{1}{n_F}} \quad (7)$$

$$Q_e = \frac{Q_{max} (K_g C_e)^{n_g}}{1 + (K_g C_e)^{n_g}} \quad (8)$$

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \quad (9)$$

Where  $C_e$  = metal ion concentration at equilibrium in mg/L;  $Q_{max}$  = maximum adsorption capacity of the adsorbent in mg/g;  $K_L$  = Langmuir equilibrium constant in L/mg;  $K_F$  = Freundlich equilibrium constant in mg/g (mg/L)<sup>-1/n<sub>F</sub></sup>;  $n_F$  = heterogeneity factor;  $K_g$  represents the Liu equilibrium constant in L/mg;  $n_g$  = the dimensionless exponent of the Liu model;  $b_T$  = Temkin constant related to heat of adsorption in J/mol;  $A_T$  = equilibrium binding constant corresponding to the maximum binding energy in L/mg;  $R$  = universal gas constant, which is 8.314 J/mol K;  $T$  = Absolute temperature in K.

The thermodynamic equations, used for the calculation of thermodynamic parameters such as standard Gibbs free energy ( $\Delta G^\circ$ ) in kJ/mol, standard enthalpy change ( $\Delta H^\circ$ ) in kJ/mol, and standard entropy change ( $\Delta S^\circ$ ) in J/mol K, are shown in Eqs (10 – 11).

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (10)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \cdot \frac{1}{T} \quad (11)$$

Where  $K$  is the equilibrium constant obtained from the best equilibrium model.

To adjudge the fitting of each model or equation, the values of the determination coefficient ( $R^2$ ) and Standard Deviation (SD) were used. The expressions of the  $R^2$  and SD are presented in Eqs (12 – 13), respectively.

$$R^2 = \left( \frac{\sum_{i=1}^n (q_{i,exp} - \bar{q}_{exp})^2 - \sum_{i=1}^n (q_{i,exp} - q_{i,model})^2}{\sum_{i=1}^n (q_{i,exp} - \bar{q}_{exp})^2} \right) \quad (12)$$

$$SD = \sqrt{\left\{ \frac{1}{n-p} \right\} \sum_i^n (q_{i,exp} - q_{i,model})^2} \quad (13)$$

Where  $i^{th}$  is the individual data;  $n$  is the number of experiments performed;  $q_{i,exp}$  = the individual value of  $q$  measured experimentally;  $q_{i,model}$  = the individual theoretical value of  $q$  predicted by the model;  $\bar{q}_{exp}$  = mean of  $q$  measured experimentally, and  $p$  is the number of parameters in the model. All the graphs were plotted using OriginPro 9.8. The modeling of kinetic and equilibrium data was done nonlinearly with successive interactions calculated by the Levenberg-Marquardt and Simplex methods, using the nonlinear fitting facilities of the software OriginPro 9.8 [29].

## RESULTS AND DISCUSSION

Fenton- and NaOH-treated adsorbents were prepared from *Leucaena leucocephala* pods. Native *L. leucocephala*, Fenton-treated, and NaOH-treated adsorbents were used for the decontamination of Ni(II) from an aqueous solution using a batch adsorption study. Effects of initial pH, adsorbent dosage, agitation time, initial concentration of Ni(II), and temperature on the adsorption capacities of the three adsorbent materials were investigated. Desorption efficiencies of HCl solutions to leach the adsorbed Ni(II) were also probed in the present study. The prepared adsorbents were characterized using FT-IR, and the FT-IR spectra are shown in Fig. 1. The bands at 3394, 3345, and 3363  $\text{cm}^{-1}$  resulted from  $-\text{OH}$  stretching vibrations. The peaks at 1611, 1649, and 1603  $\text{cm}^{-1}$  are assigned to  $\text{C}=\text{O}$  vibrations while the absorption bands at 1459, 1393, and 1350  $\text{cm}^{-1}$  are from the deformation vibration  $\text{C}-\text{H}$  from hemicelluloses and celluloses [1]. The peaks at 879, 894, and 851  $\text{cm}^{-1}$  are assigned to di- or tri-substitution of aromatic rings [1].

### Variation of pH

Fig. 2A shows the effect of the variation of pH on the adsorption of Ni(II) using *L. leucocephala*, Fenton-treated *L. leucocephala*, and NaOH-activated *L. leucocephala*. The pH study of the adsorption of Ni(II) by the adsorbents was significant in establishing the optimum adsorption of the metal ions at a solid/liquid interface. It is known that the initial pH of the medium affects the solubility of metal ions and the concentration of the counter ions on the functional group of the biomass [30]. The pH study is important because it is one of the factors which influence the site dissociation and solution chemistry of heavy

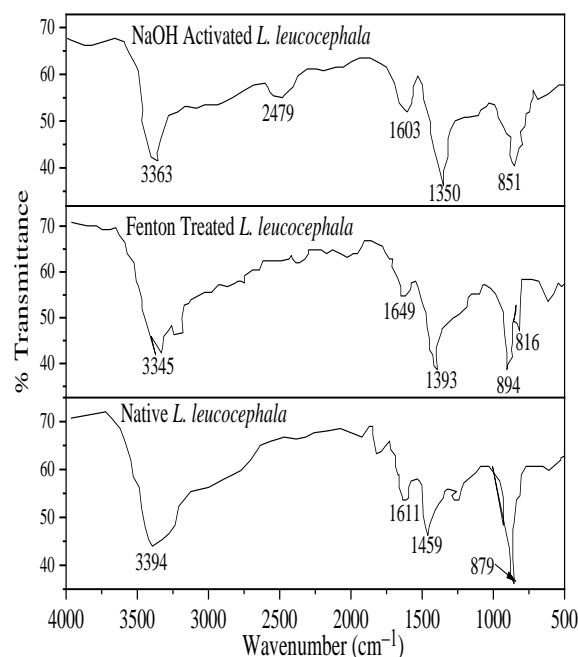
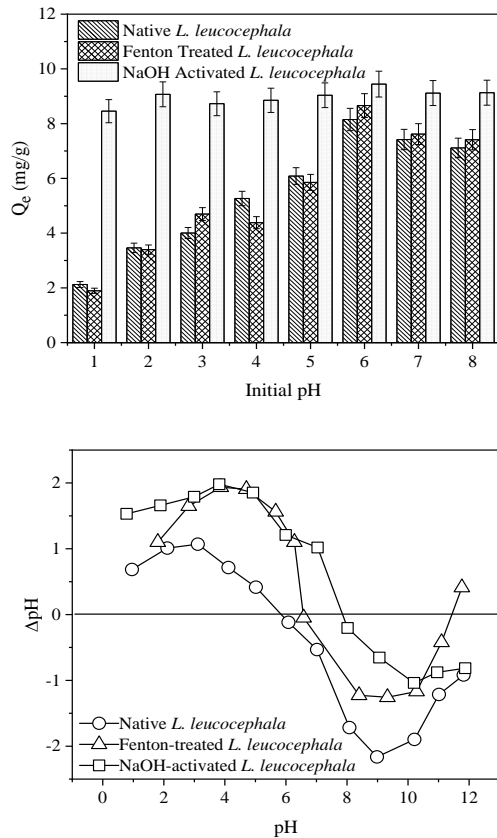


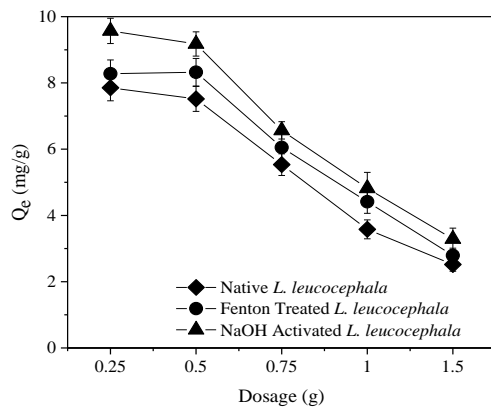
Fig. 1: FT-IR spectra of *L. leucocephala*, Fenton-treated *L. leucocephala*, and NaOH activated *L. leucocephala*.

metals [1,31]. As shown in Fig. 1, although NaOH-treated adsorbent has a tendency to adsorb Ni(II) at all pH ranges, however, the optimum binding pH for Ni(II) in this study using native and modified adsorbents is 6. This result is in agreement with the previous reports [21,32]. The metal adsorbed decreased in the pH range of 7 – 8. Reddy *et al.* [21] and Dermentzis *et al.* [33] reported similar results. The effect of initial pH on nickel adsorption showed that there was an increase in adsorption as pH of the solution increased for the native and Fenton-treated *L. leucocephala* adsorbents.

With an increase in pH, the total number of negative groups available for the binding of metal ions increased and therefore competition between proton and metal ions became less pronounced [34]. At a high pH, nickel ions will bind with  $\text{OH}^-$  to form insoluble nickel hydroxides that reduce the adsorption of Ni(II) onto adsorbents [22,31]. The pH study shows that NaOH-treated *L. leucocephala* adsorbent exhibited the greatest absorption at pH 6, while Fenton-treated adsorbent was slightly better than the native biomass. For experiments on the effects of adsorbent dosage, agitation time, and initial concentration of Ni(II) on the adsorption efficiency of the three adsorbents were performed at pH 6.



**Fig. 2:** (A) Variation of initial pH with adsorption of Ni(II) onto native, Fenton treated and NaOH treated *L. leucocephala* adsorbents; and (B)  $pH_{pzc}$  of the adsorbents; conditions for pH study: 250 mg/L of Ni(II), the mass of adsorbent was 0.25 g, agitation time of 360 min, initial pH of 1 – 8, and a temperature of 30 °C



**Fig. 3:** The profiles of the variation of the amount of Ni(II) adsorbed with adsorbent dosage; conditions: 250 mg/L of Ni(II), the mass of adsorbent was 0.25 g – 1.5 g, agitation time of 360 min, initial pH of 6, and a temperature of 30 °C.

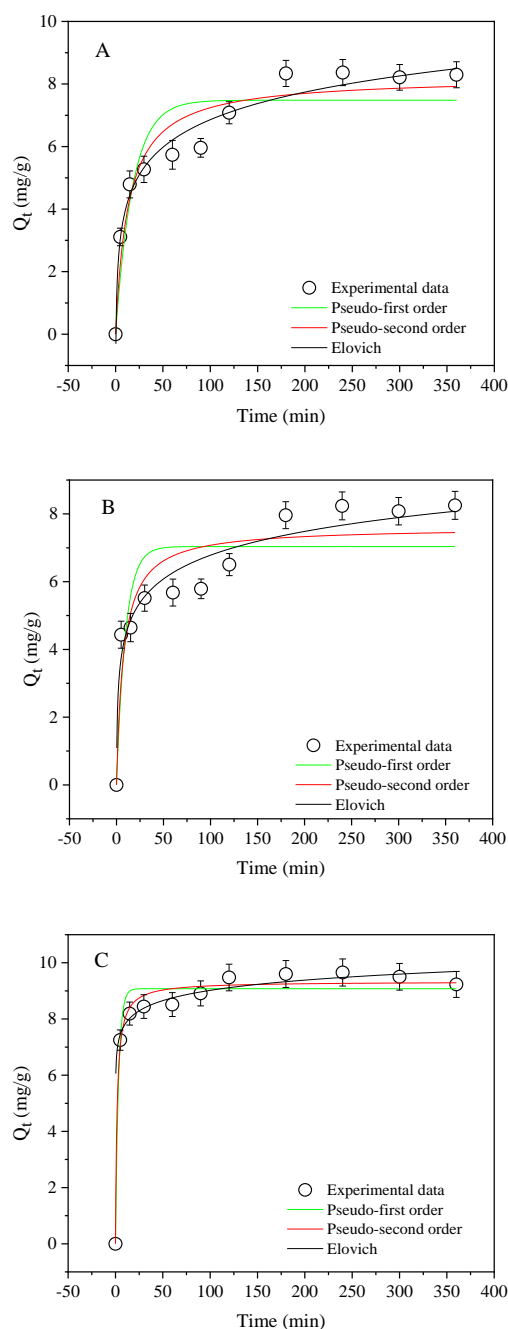
The  $pH_{pzc}$  value is regarded as the pH at which the surface of the adsorbent material has a net charge of zero [28]. Fig. 2B presents the  $pH_{pzc}$  of the three adsorbents. The values of the  $pH_{pzc}$  for native, Fenton-treated, and NaOH-activated *L. leucocephala* are 5.89, 6.52, and 7.98, respectively. When the  $pH > pH_{pzc}$ , the adsorbent surface will be negatively charged, and when  $pH < pH_{pzc}$ , the adsorbent surface will be positively charged [27,28]. pH 6 was the optimum value for the removal of Ni(II) from aqueous solutions by the three adsorbents, hence, the surface of *L. leucocephala* is negatively charged while the surfaces of Fenton treated *L. leucocephala* and NaOH-activated *L. leucocephala* adsorbents are positively charged.

#### The influence of adsorbent dosage on adsorption capacity

Fig. 3 shows the variation in adsorbent dosage with Ni(II) removal using native, Fenton treated *L. leucocephala* and NaOH-activated *L. leucocephala*. Adsorption of Ni(II) was studied using various dosages of the three adsorbents under study. For the three adsorbents, the amounts of Ni(II) adsorbed remained relatively constant as the dosages of adsorbents were increased from 0.25 g to 0.5 g. After 0.5 g, the amounts adsorbed decreased. Although, the amounts of Ni(II) adsorbed by the adsorbents decreased the removal percentages increased. In practice, there will be high adsorption of metal ions onto the adsorbent surface when the dosage of the adsorbent is increased until the amount adsorbed is independent of the dosage of the adsorbent, at this point, the threshold dosage is reached [21,35].

#### Kinetic analysis and modeling

Fig. 4 presents the results of the influence of contact time on the adsorption of Ni(II) by unmodified, Fenton-treated and NaOH-activated *L. leucocephala*. As shown in the figure, adsorption efficiency was directly proportional to the agitation time until a threshold point was reached when the adsorption efficiency was independent of the agitation time. Homayon et al. [36] and Ferhat et al. [37] reported similar observations for the adsorption of Ni(II) from aqueous solutions. The uptakes of Ni(II) ion from aqueous solutions by unmodified and unmodified *L. leucocephala* attained equilibrium at 180 min. The rate of metal removal was high at the beginning of the adsorption process due to the large surface area of the adsorbent initially



**Fig. 4:** Effect of agitation time and kinetic modeling of adsorption of Ni(II) onto (A) native, (B) Fenton treated and (C) NaOH-treated *L. leucocephala* adsorbents; conditions: 250 mg/L of Ni(II), the mass of adsorbent was 0.25 g, agitation time of 0 – 360 min, pH of 6, and a temperature of 30 °C.

available or the adsorption of the metal ions until equilibrium was reached [38]. It is also germane to

reiterate that since active binding sites in the adsorption system were fixed and there was just one ion in a monolayer, the metal uptake by the adsorbent surface was rapid at the start, but as the progression of the reaction, the amount adsorbed slowed down because the competition for binding sites decreased the availability of active sites for metal ions that remained in the solution.

The time-dependent data were subjected to four nonlinear kinetic models (pseudo-first order, pseudo-second order, Elovich, and intraparticle diffusion models) to obtain the values of the rate constants as well as to determine the mechanism of the adsorption process. The curves of the pseudo-first order, pseudo-second order, and Elovich are shown in Fig. 4. The  $SD$  and  $R^2$  values were used to determine how well each kinetic model fits the kinetic data [39–41]. When the value of  $R^2$  is high (tends to unity) the data are well-fitted to the model, however, a small value of  $SD$  signifies an excellent fit of a model [39–41]. The parameters of all the kinetic models used are presented in Table 1. An evaluation of the two fitting determinants shows that the Elovich model has the highest  $R^2$  value and the lowest  $SD$  value, hence, the Elovich model is the best model that described the adsorption of Ni(II) onto the adsorbents. The discussion of the parameters of the Elovich model will therefore be relevant to this study.

The Elovich model is one of the widely used models for the description of the characteristics of chemical adsorption and is mostly used for adsorption systems in which adsorbent has a heterogeneous surface [42,43]. The model was originally developed for gaseous systems, however, the model is now being meaningfully applied to the adsorption process in wastewater remediation. The values of initial adsorption rate ( $A_E$ ) for native, Fenton-treated, and NaOH-treated *L. leucocephala* adsorbents are 0.7851, 0.9883, and 1.901 mg/g min, respectively. As shown in Table 1, the values of the extent of surface coverage or desorption constant,  $B_E$ , are 2.777, 8.238, and  $1.464 \times 10^5$  g/mg for native, Fenton-treated, and NaOH-treated *L. leucocephala* adsorbents, respectively. Sodium hydroxide-treated *L. leucocephala* adsorbent has the highest surface coverage. The large coverage of NaOH-treated adsorbent will enable the adsorbent to adsorb more toxic metal ions from solutions than the native

**Table 1: Kinetic modeling of adsorption of Ni(II) onto native, Fenton treated, and NaOH-treated *L. leucocephala* adsorbents; conditions: 250 mg/L of Ni(II), the mass of adsorbent was 0.25 g, agitation time of 0 – 360 min, pH of 6, and a temperature of 30 °C.**

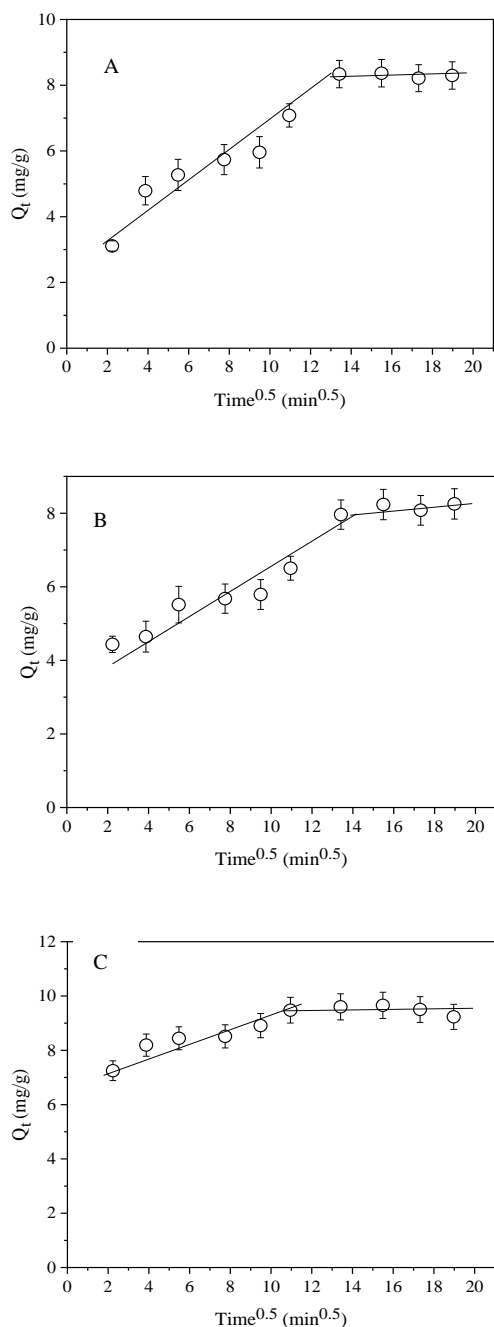
Model	Native <i>L. leucocephala</i>	Fenton treated <i>L. leucocephala</i>	NaOH-treated <i>L. leucocephala</i>
Pseudo-first order			
$k_f$ (1/min)	0.05548	0.1049	0.3086
$Q_{e,exp}$ (mg/g)	8.340	8.080	9.210
$Q_{e,cal}$ (mg/g)	7.482	7.036	9.079
$R^2$	0.8568	0.7748	0.9693
SD (mg/g)	1.046	1.216	0.5130
Pseudo-second order			
$k_s$ (g/mg min)	0.009010	0.01757	0.06424
$Q_{e,cal}$ (mg/g)	8.219	7.605	9.331
$R^2$	0.9317	0.9320	0.9864
SD (mg/g)	0.7222	0.8677	0.3419
Elovich			
$A_E$ (mg/g min)	0.7851	0.9883	1.901
$B_E$ (g/mg)	2.777	8.238	$1.464 \times 10^5$
$R^2$	0.9758	0.9562	0.9924
SD (mg/g)	0.4298	0.5366	0.2556
Intraparticle diffusion			
$k_{id,1}$ (mg/g min <sup>0.5</sup> )	0.3752	0.2199	0.2099
C (mg/g)	2.838	3.970	7.072
$R^2$	0.8958	0.9208	0.8932

and Fenton-treated adsorbents. It is believed that the adsorption of Ni(II) onto *L. leucocephala* adsorbents followed chemisorption kinetics.

The mechanism of adsorption of Ni(II) onto the adsorbents was assessed using the intraparticle diffusion model [44]. This model assumes that the plot of adsorbate uptake ( $q_t$ ) against  $\sqrt{t}$  should be linear if intraparticle diffusion was involved during the adsorption process. The lines will pass through the origin if intraparticle diffusion is the sole rate-controlling step of the adsorption process. In reality, most intraparticle diffusion plots usually exhibit multiple linear segments. There are generally three diffusion processes for the adsorption of adsorbate in a solution onto solid materials. The three diffusion processes are film diffusion (bulk movement or mass migration of adsorbate), surface diffusion, and pore diffusion. As shown in Fig. 5 and Table 1, the intraparticle

diffusion model is not the sole controlling mechanism of the removal of Ni(II) by the three adsorbents because there exist appreciable intercepts from the intraparticle diffusion plots [39,40]. It is also visible from Fig. 5 that there are two stages (two different mechanisms) of the adsorption process because there are two linear segments in each plot. The first segment represents the fast adsorption of Ni(II) onto *L. leucocephala* adsorbents. In the first segment, the molecules of Ni(II) rapidly migrated from aqueous solutions onto the surface of adsorbents. The second part (second linear segment) of the adsorption process is a slow type, which is the diffusion through small pores of the adsorbents. The values of  $k_{pd}$  (intraparticle diffusion constant) are 0.3752, 0.2199, and 0.2099 mg/g min<sup>0.5</sup> for native, Fenton treated and NaOH-treated *L. leucocephala* adsorbents, respectively. Although intraparticle diffusion the mechanism is not the sole controlling mechanism





**Fig. 5:** Intraparticle diffusion plots of the adsorption of Ni(II) onto (A) native, (B) Fenton-treated, and (C) NaOH-treated *L. leucocephala* adsorbents; conditions: 250 mg/L of Ni(II), the mass of the adsorbent was 0.25 g, agitation time of 0–360 min, pH of 6, and a temperature of 30 °C

of adsorption systems in this study, however, the model was able to predict that the adsorption of Ni(II) onto the adsorbents followed two stages. The higher the value

of the boundary layer (C), the greater the effect of the boundary layer. The values of C obtained are low (2.838 mg/g for native adsorbent, 3.970 mg/g for Fenton-treated adsorbent, and 7.072 mg/g for NaOH-treated adsorbent), hence, the effect of the boundary layer on adsorption was not so strong. However, NaOH-treated *L. leucocephala* adsorbent exhibited the strongest boundary layer.

### Equilibrium modeling

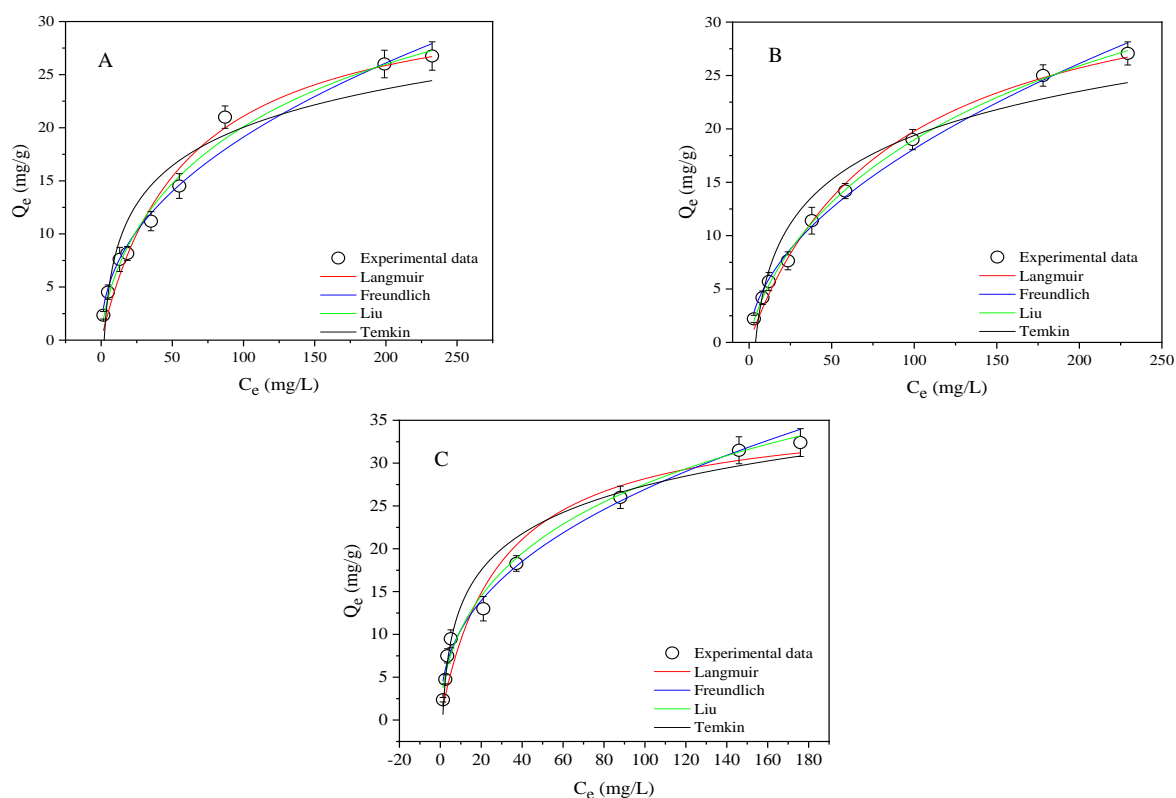
The data from concentration-dependent experiments are presented in Fig. 6. According to the figure, the removal of nickel(II) by the three adsorbents was dependent on the initial concentration of nickel. Similar results were earlier reported [45,46]. At higher concentrations of Ni(II), there are more molecules of Ni(II) in the solution, but the number of active sites is fixed. When the initial concentration of the Ni(II) was high, the amount of Ni(II) removed remained constant because the surface of the adsorbent was saturated. It is also known that a high initial concentration of metal ions will result in a high concentration gradient, which provides a large driving force to overcome the resistance of metal ions from the aqueous phase to the solid phase, leading to a high collision rate of the metal ions and subsequently resulting in high adsorption capacity [18].

Adsorption models are regarded as mathematical equations that provide the distribution of the adsorbate on the adsorbent. The adsorbent-adsorbate relationship is dictated by a set of assumptions, such as the homogeneity or heterogeneity of the adsorbent, the coverage type, and the possibility of interaction between the adsorbate molecules. To obtain equilibrium parameters of adsorption, equilibrium data are usually subjected to isotherm models. Non-linear forms of Langmuir, Freundlich, Liu, and Temkin isotherms were used to describe the adsorption data in this study. The representation of each model for fitting the experimental data is shown in Fig. 6 while the parameters of the equilibrium models are presented in Table 2.

Using the values of  $SD$  and  $R^2$  of the equilibrium models in Table 2, the Liu isotherm model is the best model for the description of the equilibrium data [29,47]. One of the major assumptions of Liu model is that the active sites on the surface of the adsorbent possess varying values of energy [48]. The  $Q_{max}$  values at 30 °C for native, Fenton-treated, and NaOH-treated *L. leucocephala* adsorbents

**Table 2: Equilibrium parameters for adsorption of Ni(II) onto native, Fenton-treated, and NaOH-treated *L. leucocephala* adsorbents; conditions: 50 – 800 mg/L of Ni(II), the mass of adsorbent was 0.25 g, agitation time of 360 min, pH of 6 and a temperature of 30 °C.**

Model	Native <i>L. leucocephala</i>	Fenton treated <i>L. leucocephala</i>	NaOH treated <i>L. leucocephala</i>
Langmuir			
$K_L$ (L/mg)	0.01707	0.01169	0.03464
$Q_{max}$ (mg/g)	33.43	36.69	36.32
$R^2$	0.9789	0.9930	0.9537
$SD$ (mg/g)	1.415	0.8114	2.635
Freundlich			
$K_F$ (mg/g (mg/L) <sup>-1/n<sub>F</sub></sup> )	2.418	1.602	4.097
$n_F$	2.227	1.898	2.445
$R^2$	0.9814	0.9936	0.9829
$SD$ (mg/g)	1.326	0.7737	1.634
Liu			
$K_g$ (L/mg)	0.005390	0.003950	0.003700
$Q_{max}$ (mg/g)	50.66	56.72	75.17
$n_g$	0.6793	0.7405	0.5499
$R^2$	0.9905	0.9987	0.9969
$SD$ (mg/g)	1.029	0.3818	1.146
Temkin			
$B$ (J/mol)	5.215	5.968	6.126
$A_T$ (L/mg)	0.4663	0.2573	0.8713
$R^2$	0.9115	0.9280	0.9599
$SD$ (mg/g)	2.896	2.602	2.505



**Fig. 6: Equilibrium modeling for adsorption of Ni(II) onto (A) native, (B) Fenton treated, and (C) NaOH treated *L. leucocephala* adsorbents; conditions: 50 – 800 mg/L of Ni(II), the mass of adsorbent was 0.25 g, agitation time of 360 min, pH of 6 and a temperature of 30 °C.**

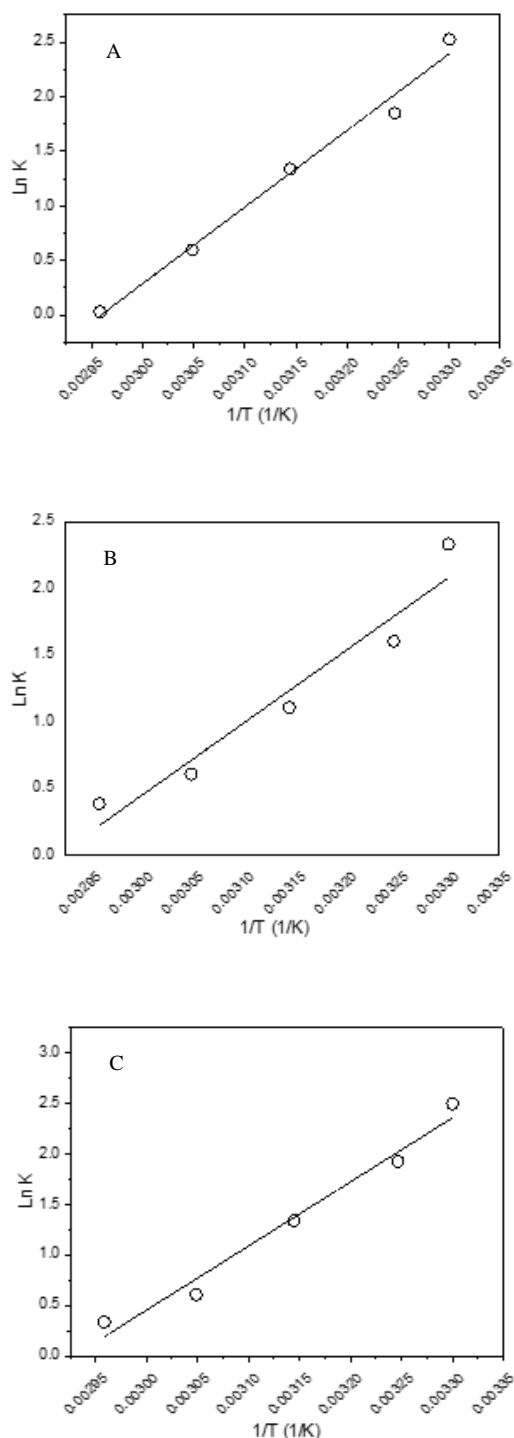


Fig. 7: van't Hoff plots for adsorption of Ni(II) onto (A) native, (B) Fenton treated and (C) NaOH treated *Leucaena leucocephala* adsorbents.

are 50.66 mg/g, 56.72 mg/g and 75.17 mg/g, respectively. The adsorbent-treated NaOH was the best for the removal of Ni(II) from aqueous solutions. The three adsorbents possess different values of energy [29,48].

#### Thermodynamic studies

In most cases, changes in temperature values have a significant effect on the removal of heavy metals from the solution because adsorption is a reversible process. The values of thermodynamic parameters are important determinants of the practical application of adsorption and changes in the reaction or process [1,29,49]. Adsorption of Ni(II) onto *L. leucocephala* adsorbents was investigated as a function of temperature in the ranges of 303 K and 338 K at pH 6 using 0.25 g of adsorbent and 250 mg/L of Ni(II) solution. From the temperature-dependent study, the values of the thermodynamic parameters such as the standard Gibbs free energy change ( $\Delta G^\circ$ ), standard enthalpy change ( $\Delta H^\circ$ ), and standard entropy change ( $\Delta S^\circ$ ) were evaluated. The van't Hoff plots and the values of thermodynamic parameters are presented in Fig. 7 and Table 3, respectively. The values of  $\Delta G^\circ$  for the three adsorbents at all experimental temperature ranges are negative, which indicates that the adsorption process is spontaneous, feasible, and energetically favorable. The values of  $\Delta H^\circ$  are negative for the three adsorbents, an indication that the adsorption Ni(II) occurred exothermically. Similarly, the  $\Delta S^\circ$  values ( $-154.4$  J/mol K for native *L. leucocephala* adsorbent), ( $-172.8$  J/mol K for Fenton treated *L. leucocephala* adsorbent), and ( $-131.9$  J/mol K for NaOH activated *L. leucocephala* adsorbent) indicate that the degree of randomness decreased at the solid-liquid interface during the adsorption process.

#### Adsorption capacities of selected biomass for Ni(II)

Table 4 presents the adsorption capacities of various biomass adsorbents for the removal of Ni(II) from aqueous solutions. It is evident that the maximum Ni(II) adsorption capacities of *L. leucocephala* adsorbents at pH 6.0 (optimum pH) are higher than most of the values listed for other adsorbents earlier reported. *Leucaena leucocephala* can therefore be used as a low-cost, green, and alternative source of material for the preparation of efficient adsorbents for the removal of Ni(II) and generally for the removal of toxic heavy metals from aqueous effluents.

**Table 3: Thermodynamic data for adsorption of Ni(II) onto native, Fenton treated and NaOH treated *L. leucocephala* adsorbents.**

Temperature (K)	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol K)	$R^2$
Native		-5.272	-154.4	0.9771
303	-6.288			
308	-4.931			
318	-3.531			
328	-1.657			
338	-0.9438			
Fenton		-5.838	-172.8	0.9875
303	-6.364			
308	-4.739			
318	-3.536			
328	-1.625			
338	-0.08358			
NaOH		-4.521	-131.9	0.9384
303	-5.878			
308	-4.107			
318	-2.928			
328	-1.6578			
338	-1.084			

**Table 4: Comparison table of maximum adsorption capacities of some adsorbents.**

Biomass	Adsorption capacity (mg/g)	References
Native <i>L. leucocephala</i>	50.66	<i>This study</i>
Fenton-treated <i>L. leucocephala</i>	56.72	<i>This study</i>
NaOH-treated <i>L. leucocephala</i>	75.17	<i>This study</i>
Pistachio hull waste	14.00	[4]
Watermelon rind	18.43	[8]
<i>Punica granatum</i> peel	52.00	[17]
<i>Litchi chinensis</i> seeds	66.62	[18]
<i>Aloe barbadensis</i> Miller leaves	10.00	[19]
Modified <i>Aloe barbadensis</i> Miller leaves	28.99	[20]
<i>Moringa oleifera</i> bark	30.38	[21]
<i>Trichoderma viride</i>	47.60	[22]

**Metal recovery**

Regeneration of spent adsorbent is an important study for evaluation of the ease of recycling adsorbent. Regeneration study is invaluable for industrial applications, especially for expensive adsorptive

materials. One of the solvents for good recovery of metals from spent adsorbent is HCl [21,50]. The Ni(II)-loaded *L. leucocephala* adsorbents were treated with varying concentrations of HCl to assess the desorption of Ni(II) from Ni(II)-loaded *L. leucocephala* adsorbents. The results)

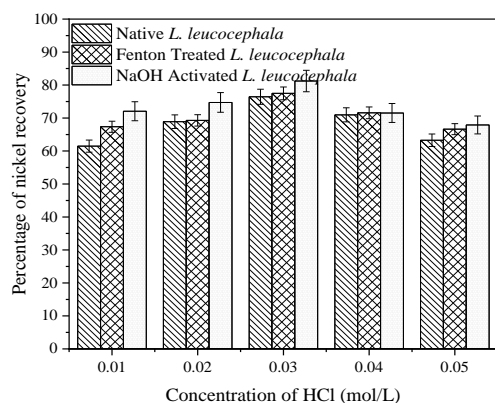


Fig. 8: Recovery of nickel(II) from *L. leucocephala* adsorbents.

of the Ni(II) desorption or recovery are summarised in Fig. 8. Desorption of Ni(II) was most pronounced with 0.03 mol/L HCl with a percentage recovery of 76.43% for native, 77.48% for Fenton-treated adsorbent, and 81.21% for NaOH-treated *Leucaena leucocephala*. The results in Fig. 8 show that an initial increase in hydrochloric acid concentration (up to 0.03 mol/L) resulted in an increase in the desorption of Ni(II) from the surface of the adsorbents, however, the percentage of the metal desorption decreased after 0.03 mol/L HCl solution. A similar finding was earlier reported [51]. Various adsorption-desorption cycles were not investigated in this study, desorption experiments were carried out, after the adsorption experiment, to investigate the method by which the adsorbed Ni(II) could be effectively desorbed from the surface of the spent adsorbents.

## CONCLUSIONS

Removal of nickel onto *Leucaena leucocephala* adsorbents (native, Fenton treated and NaOH activated) was carried out using a batch adsorption process. Adsorption capacities of *L. leucocephala* adsorbents for Ni(II) under different conditions (initial pH, adsorbent dosage, contact time, initial concentrations of Ni(II), and temperature) were evaluated. The kinetic and equilibrium data were best described by Elovich and Liu models, respectively. The maximum adsorption capacities for the native, Fenton-treated, and NaOH-activated *L. leucocephala* adsorbents are 50.66 mg/g, 56.72 mg/g, and 75.17 mg/g, respectively. There are two adsorption processes for the removal of Ni(II) as shown by the intraparticle diffusion mechanism. The thermodynamic parameters proved that the adsorption process was spontaneous, feasible, favorable, and exothermic. The randomness at the

adsorbent-adsorbate interface decreased. The spent adsorbents were regenerated using 0.03 mol/L of hydrochloric acid. Though NaOH-treated *L. leucocephala* adsorbent had the highest performance, the three adsorbents could be used for the treatment of Ni(II) contaminated water.

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