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Adsorption and Desorption studies of *Delonix regia* pods and leaves: Removal and recovery of Ni(II) and Cu(II) ions from aqueous solution

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Abstract

In this study, the adsorption of Ni(II) and Cu(II) ions from aqueous solutions by powdered pods and leaves of *Delonix regia* was investigated by batch adsorption techniques. The effects of operating conditions such as pH, contact time, metal ions concentration and the presence of sodium ions interfering on the sorption process were investigated. The results obtained showed that the equilibrium sorption was attained within 30 min of interaction and the adsorption process followed the pseudo-second-order kinetic model for all the metal sorption with the exception of Cu(II) sorption on the leaves. The equilibrium data fitted well with both the Langmiur and Freundlich Isotherms; the desorption study revealed that the percentage of metal ions recovered from the pods were higher than the leaves at various concentration of nitric acid. This study has proven that *Delonix regia* biomass, an agro-waste could be used for removing Ni(II) and Cu(II) ions from wastewater

Keywords: *Delonix regia*, low-cost adsorbent, Ni(II) ions, Cu(II) ions, equilibrium, kinetics

1. Introduction

The persistent nature, non-biodegradability, toxicity and ability of heavy metals to bio-accumulate in the environment and cause serious pollution have made heavy metals priority pollutants (Hamza et al., 2013). Various health effects are caused by anthropogenic pollutants in water; which are majorly heavy metals such as mercury, nickel, lead, cadmium copper, zinc and cobalt (Hamza et al., 2013; Singh et al., 2011). Heavy metals gain entrance into water supply by industrial activities such as electroplating, smelting, glass and ceramics, mining, textiles, storage batteries, petroleum, metal finishing, pulp and paper (Dean et al., 1972). Apart from the damage to the marine ecosystem, damage caused by copper to the marine life include damage of gills, liver, nervous system, kidneys and changing the sexual life of fishes (Flemming and Trevors, 1989; Ho et al., 2002; Van Genderen et al., 2005). Although, copper is known to play a vital role during metabolism in animal; its excessive intake can result in serious health problems (Paulino et al., 2006). Reactive free oxygen species which damage lipids, proteins and DNA are released when copper is present in the blood system (Brewer, 2010). Wilson's and Alzheimer's diseases, mental illness, Indian childhood cirrhosis and schizophrenia are reported to be caused by excess copper in the blood (Brewer, 2007; Faller, 2009; Hurean and Faller, 2009). Like most heavy metals, nickel has its detrimental effect on human health resulting in allergic dermatitis, immunologic urticarial; immediate and delayed hypersensitivity. All nickel compounds except for the metallic nickel have been classified as human carcinogens by the International Agency for Research on Cancer (IARC) (IARC, 1990) and the U.S. Department of Health and Human Services (DHHS, 1994).

Conventional methods for the treatment of metal ions includes: reverse osmosis, chemical precipitation, oxidation/reduction, ion exchange, electrochemical processes, membrane separation and evaporation. These techniques require high operational costs and yield minimal removal efficiencies, they have been reported to be expensive and inadequate. Therefore, there is the need to investigate alternative techniques that are cheaper, efficient and easy to handle. One of such techniques is biosorption, that is, the use of low-cost adsorbent like agricultural materials of no economic value and industrial by-products (Jeme, 1968; Inoue and Munemori, 1979) for the removal of heavy metal ions from polluted water.

Almond shell tree bark treated with formaldehye and sulphuric acid (Guibal et al., 1993; Raji et al., 1997), bone char, tea leaves, wood charcoal (Ajmal et al. 2003), coconut shell have been used to produce activated carbon to treat heavy metal ions from wastewater. Rice hulls, rice bran and pine bark (Nath et al., 1997) have also been used in the raw and treated form to remove

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heavy metal ions. The removal of Ni(II) ions from aqueous solution using sugarcane bagasse, an agricultural waste biomass has been investigated by Garg et al. (2008). The optimum conditions for maximum removal of Ni(II) ions from an aqueous solution of 50 mg/L were reported to be adsorbent dosage of 1500 mg/L, pH 7.5 and a stirring speed of 150 rpm. Moodley et al. (2011) investigated the adsorption capacity of pine sawdust by treating wastewater containing Ni (II), and other metal ions (Co(II) and Fe(III) ions). The authors reported that the Freundlich isotherm fitted the experimental data better than the Langmuir isotherm and that the use of pine sawdust could be a promising solution to the elimination of Ni(II) ions from multi-component aqueous solutions. The adsorption and desorption of Ni(II) Ions from aqueous solution by a lignocellulose/montmorillonite nanocomposite was reported by Zhang and Wang (2015). Their report indicated that the maximum adsorption capacity of Ni(II) ions reached 94.86 mg/g at an initial Ni(II) ions concentration of 0.0032 mol/L, a solution pH of 6.8, temperature of 70°C, and contact time of 40 min. Kahraman et al. (2008) examined the use of cotton stalk and apricot seed as alternative adsorbents for the removal of Pb and Cu. The treatment of Pb and Cu with these agricultural wastes was reported to reduce their toxic effects on *P. aeruginosa*. The sorption capacity of Cu(II), kinetics and isotherms of different low-cost residual agricultural materials including peanut shells, nut shells, plum seeds, eucalyptus bark, olive pips, peach stones, and pine sawdust was studied by Hansen et al. (2010). It was found that the pseudo-second-order model described the sorption kinetics satisfactorily, while, the Langmuir and Freundlich models described the equilibrium sorption isotherms well for the biosorbents. Moreover, Abdel-Tawwab et al. (2017) used rice straw, sugarcane bagasse, and maize stalks for the removal of Pb, Cd, Cu, and Zn from aqueous solution. All the biosorbents were reported to be effective and cheap for the removal of the metal ions from polluted water, with rice straw showing a higher adsorption efficiency than the others. The application of treated pumpkin husk as an excellent adsorbent for removing Cu(II) and Ni(II) ions has been reported by Samuel et al. (2016). The adsorption of Cu(II) and Ni(II) ions was found to be suitable at pH 5. The Langmuir isotherm data fitted well the equilibrium data, whereas, the kinetic experimental data correlated well with the pseudo-second-order kinetic model.

Therefore, the objective of this research work is to investigate the capacity of an agro-waste *Delonix regia* pods and leaves in the removal of Ni(II) and Cu(II) ions from aqueous solutions. The desorption of bound metals from spent *Delonix regia* pods and leaves using various concentrations of nitric acid was also considered. *Delonix regia* is popularly grown in Africa and Hong Kong as a shade tree and for ornamental purpose. The tree has pods that can be as long as 60 cm in length and 5 cm wide, with a distinct bright green fern-like compound leaves. It belongs to the flowering plant family *Fabaceae* and commonly called the flame of the forest tree. The outcome of this research would be of great benefit to most industries in the developing countries of the world, the adsorbent would serve as cheaper adsorbent for the removal of heavy metals from wastewater.

2. Materials and methods

2.1 *Delonix regia* sample

Leaves and pods of *Delonix regia* collected from Ekiti State University, Ado-Ekiti, Nigeria were used as adsorbent for the sorption study. After milling, the adsorbents were sieved through a 250µm mesh nylon sieve and kept in air tight containers until required for use.

2.2 Chemicals and reagents

Diammonium nickel hexahydrate and copper chloride dihydrate salts supplied by Merck, Germany were dissolved in high purity milli-Q water to prepare 1000 mg/L stock solutions of Ni(II) and Cu(II) ions, respectively. Working standard solutions were prepared from the stock solutions and pH adjustment was done with 0.1 M HNO_3 and 0.1 M NaOH when necessary. The effect of solution ionic strength on sorption was studied using different concentrations of sodium nitrate salt and desorption of bound metal from spent biomass was achieved with different concentrations of HNO_3.

2.3 Characterization

The elemental composition of the pods and leaves of *Delonix regia* was achieved by energy dispersive spectroscopy (EDS). The morphological study was by the scanning electron microscope (Nova Nano SEM 230) and the transmission electron microscope (FEI Tecnai G^2 20). X-ray diffractometer (Siemens D8 Advance Bruker XRD) was used for phase characterization.

2.4 Adsorption

Adsorption procedure by Meena et al. (2008) was slightly modified and use in this work. As soon as each experiment is concluded, an aliquot is withdrawn and diluted with 0.1 M HNO_3 before residual metal content is analysed with ICP-MS (X Series). Each experiment was carried out in triplicate and the results are the average values. The amount of Ni(II) and Cu(II) ions sorbed on the pods and leaves of *Delonix regia* (Q_e) was calculated using Equation 1.

$$Q_e = (C_o - C_e)V/m \qquad 1$$

where C_o is the initial metal concentration (mg/L), C_e is the final metal ion concentration in the solution, ICPMS reading (mg/L), V is the volume of the metal solution used in litre (L) and m is the mass of the biosorbent (g).

3. Results and discussion

3.1 SEM-EDS, TEM and XRD analyses

The SEM (at x10 000 magnification) and TEM micrographs of the pods and leaves of *Delonix regia* (Fig. 1) indicated the spongy nature of *Delonix regia* with porous structures. This structural properties might improve the uptake of the Ni(II) and Cu(II) ions from aqueous solution. The EDS of *Delonix regia* showed that the surfaces of the leaves is composed of 66.79% C, 32.97% O and traces of Ca and K, while, the pods is composed of 57.61% C, 41.15% O and trace of K.

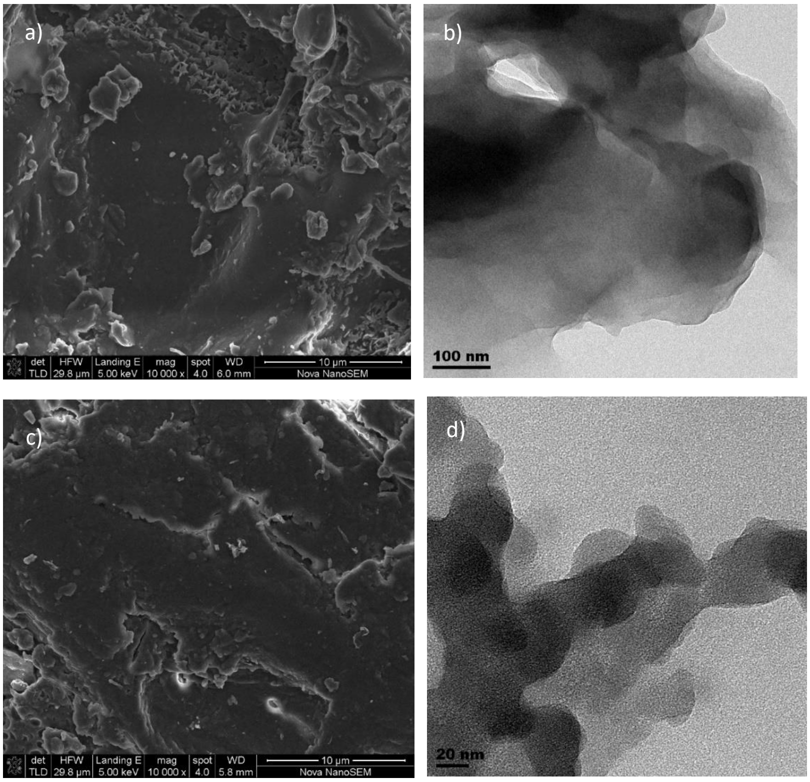

Figure 1. SEM (at x10 000 magnification) and TEM micrographs of *Delonix regia* leaves (a & b) and pods (c & d)

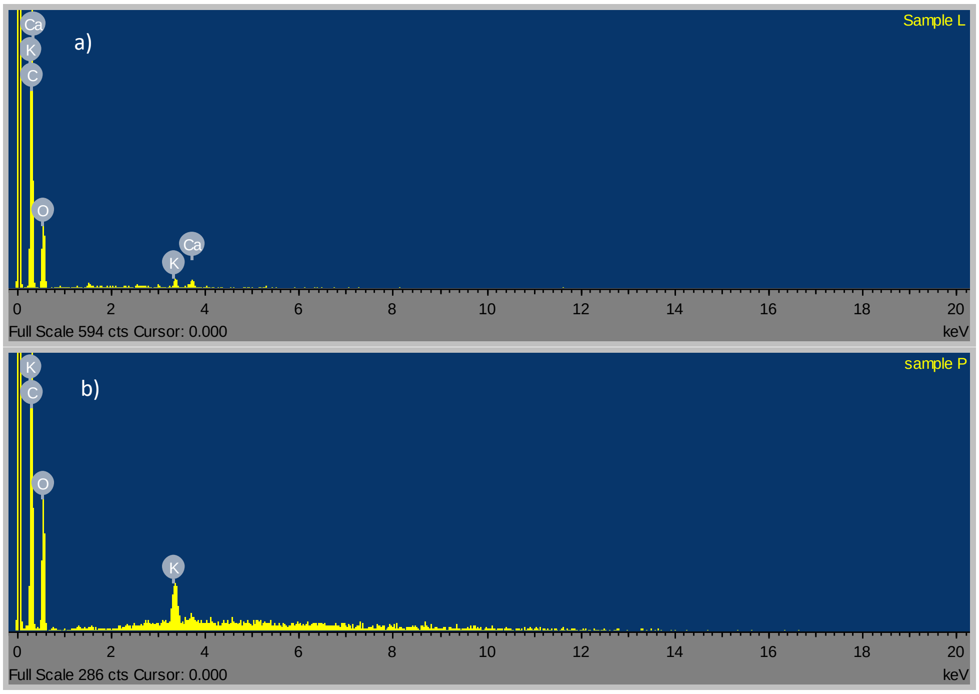

Figure 2. EDS of leaves (a) and pods (b) of *Delonix regia*

Native cellulose ($(C_6H_{12}O_6)_x$) was identified in *Delonix regia*, the peak at 22.15° for pods and 21.36° for the leaves may be due to the amine, hydroxyl, aldehydic and ketonic groups of the hemicellulosic moieties. Thus, the pods and leaves are rich in cellulosic material which may provide sites for the binding of Ni(II) and Cu(II) ions.

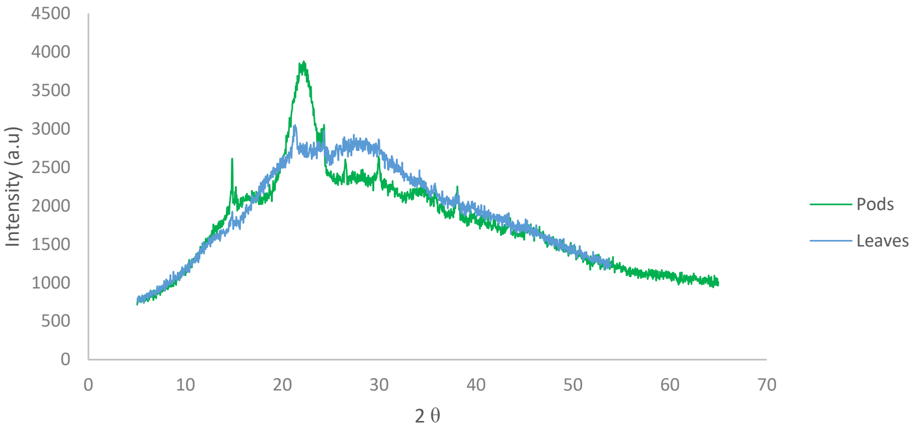

Figure 3. X-ray diffractogram of the leaves and pods of *Delonix regia*

3.2 Adsorption studies

3.2.1 pH

The result of the study of pH on the adsorption of Ni(II) and Cu(II) ions onto *Delonix regia* is shown in Fig. 4. The figure revealed that there was no significant nickel uptake by both adsorbent at low pH, but a very noticeable uptake was achieved as pH increases. This showed that the sorption of Ni(II) on *Delonix regia* pods and leaves is pH dependent. pH 5 at which maximum sorption was recorded is used as the optimum pH and used in subsequent experiments. Saeed et al. (2005) reported an optimum sorption pH of 6 for Ni(II) on crop milling waste while pH 5 was reported for its sorption onto natural neem sawdust and almond husk (Hasar, 2003; Rao et al., 2007).

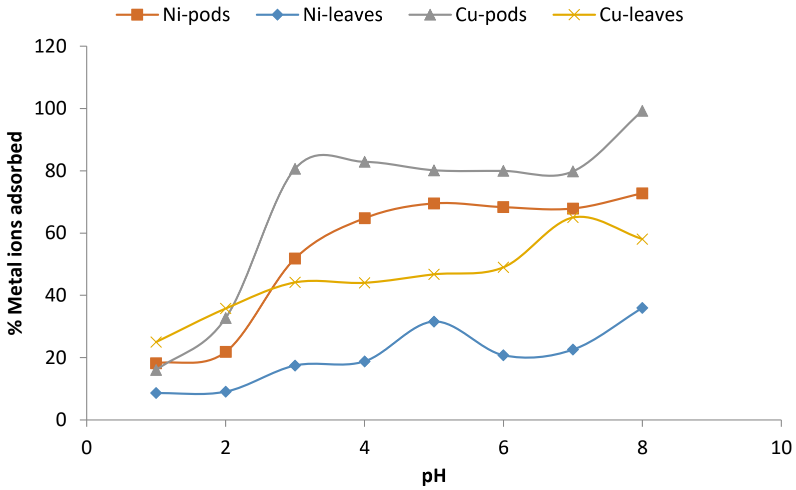

Figure 4. Effect of pH on the adsorption of Ni(II) and Cu(II) by *Delonix regia* pods and leaves. *Experimental conditions:* pH 1-8; contact time: 300 min; metal ions concentration: 100 mg/L

A small increase in uptake value was achieved between pH 1 to 3, but maximum uptake of 46.7% was recorded at pH 5 for Cu(II) ions sorption onto leaves and maximum uptake of 82.9% at pH 4 for Cu(II) ions onto the pods. pH 4 was used for sorption experiment of Cu(II) ions to *Delonix regia* pods while pH 5 was used for adsorption of Cu(II) onto the leaves. The increase recorded at pH 6 and 7 were not considered in choosing the optimum pH at which Cu(II) ions sorption onto the leaves occurred because visible precipitate had been formed in the experimental set up at these pH. Thus, pH 5 was used for other studies. Some literatures reported pH 5 and 5.8 as the optimum for the uptake of Cu(II) ions by some modified natural wastes (Shukla and Pai, 2005; Witek-Krowiak et al., 2011; Anantha and Kota, 2016). Generally, the result pointed to the fact that enhanced metal uptake is possible by increasing the pH of the sorption media, this might be a result of the increased overall negative charge particularly between pH 4 and 6. When this happened, there is increased negative charge on the adsorbent surface; this will lead to an increasing electrostatic attraction between positive ionic species and adsorbent particles which would subsequently lead to increase sorption of metal ions. The increase of pH definitely decrease the concentration of hydrogen ions and therefore the competition between metal ions and hydrogen ions for active sites on the adsorbent is reduced. This will lead to increase sorption of metal ions to the adsorbent (Kadirvelu et al., 2000; Kadirvelu et al., 2001; Sánchez-Polo and Rivera-Utrilla, 2002; Kadirvelu et al., 2003; Meena et al., 2005).

3.2.2 Contact time

The result shown in Fig. 5a was obtained from time of agitation of the biomass and adsorbate on an end-over-end shaker. Investigating the effect of agitation time performed at time intervals of 5 min up to 300 min showed that the two adsorbents used in this work had rapid uptake for the metal ions within short period of interaction.

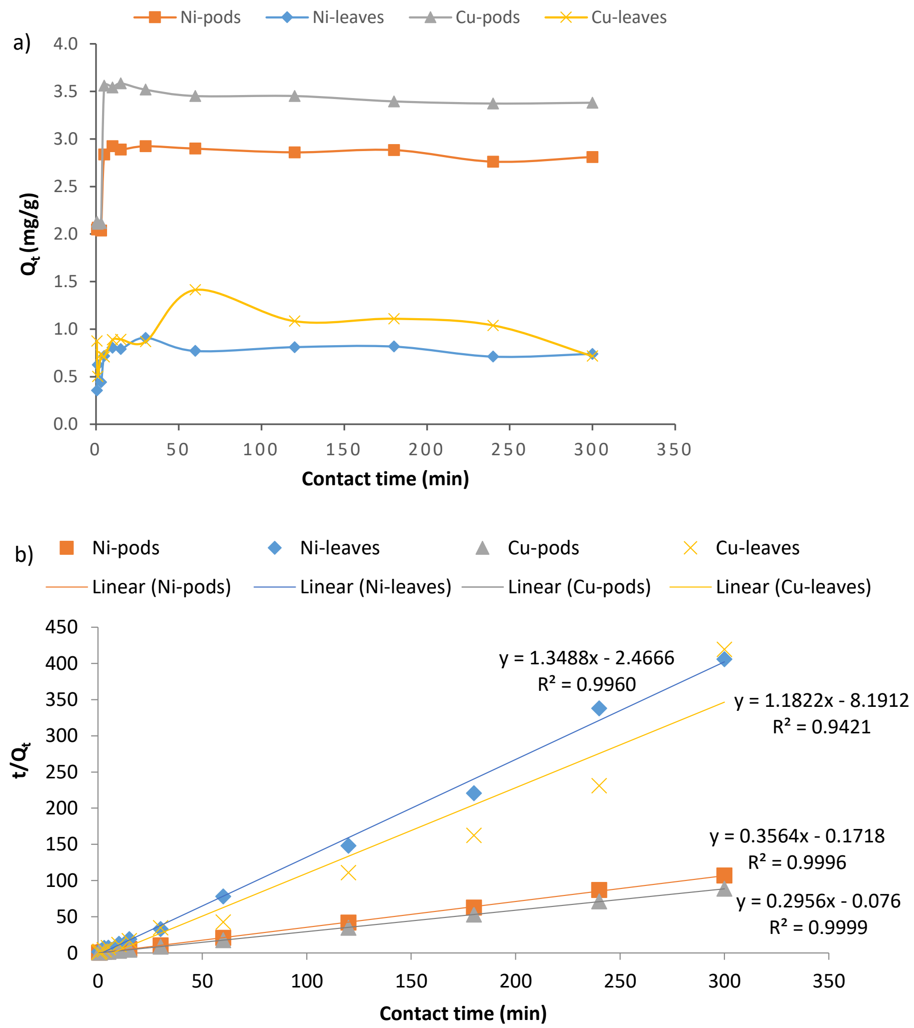

Figure 5. Effect of contact time (a) and pseudo-second-order kinetics (b) of the adsorption of Ni(II) and Cu(II) ions by *Delonix regia* pods and leaves. *Experimental conditions:* pH 4 and 5; contact time: 5-300 min; metal ions concentration: 100 mg/L

A slight desorption and adsorption was observed between 5 to 10 min of interacting the adsorbent with the metal ion solution. Within 30 min of interaction, maximum uptake has been achieved on both adsorbents irrespective of the metal considered, though the uptake recorded on the pods were higher than those on the leaves. Metal uptake by the adsorbent remained fairly constant after 30 min of interaction to the end of the experiment.

Further examination of the contact time experiment was carried out by modelling the data with the pseudo-first-order, pseudo-second-order kinetic models and intra particle diffusion models, to determine the mechanism of the sorption process. Results obtained showed that the process was well fitted to the pseudo-second-order kinetic model. This is supported by the work of Hansen et al. (2010), the plots and kinetic parameters for this model are shown in Fig. 5b and Table 1, respectively.

The pseudo-second-order kinetic model is a pointer to the fact that the mechanism involved in the sorption is governed by ion exchange or sharing of electrons.

The pseudo-second-order kinetic model is well expressed in Equation 2 where k_2 (g/mg/min) represent the rate constant for the pseudo-second-order kinetics; Q_e and Q_t (both in mg/g) being the amount of adsorbate taken up by the adsorbent at equilibrium and at any time t, respectively. All parameters in Equation 2 were derived by plotting t/Q_t against t.

$$t/Q_t = 1/k_2 + t/Q_e \qquad 2$$

Table 1. Parameters obtained from the pseudo-second-order kinetic model

Metal ions	**Q_e (mg/g)**	**k_2 (g.mg^{-1}min^{-1})**	**r^2**
Delonix regia pods			
Ni	2.8	-2.36	0.9996
Cu	3.4	-3.24	0.9999
Delonix regia leaves			
Ni	0.7	-0.25	0.9960
Cu	0.8	-0.09	0.9421

3.2.3 Initial adsorbate concentration

The experiment conducted to study the effect of the initial concentration of adsorbate on the uptake of Ni(II) and Cu(II) ions by *Delonix regia* pods and leaves showed that the uptake of both metal ions on the two types of adsorbent increased with increasing adsorbate concentration (Fig. 6a). When adsorbate concentration is increased, there is increased driving force of the

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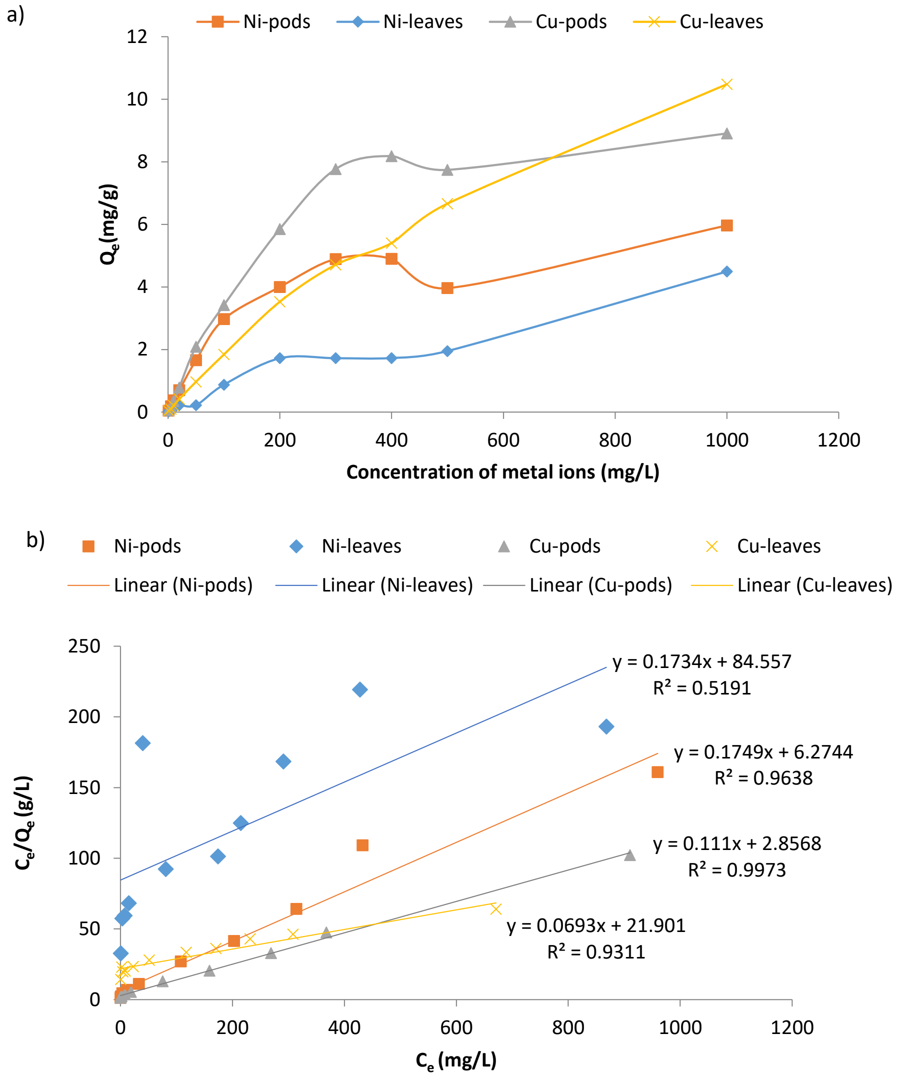
metal ions to the binding sites of the adsorbents and thus increase uptake is recorded. Though, the uptake per unit gram of adsorbent increased, the opposite which is a decrease was observed in the percentage of metal removed from the solution as adsorbate concentration increased.



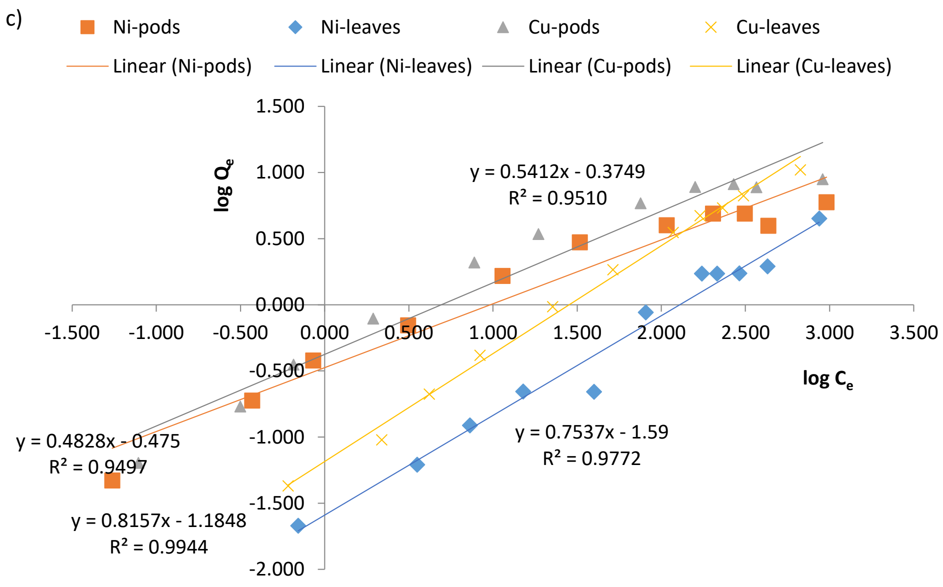


Figure 6. Effect of initial metal ions concentration (a), plots of Langmuir (b) and Freundlich isotherm (c) isotherms for the adsorption of Ni(II) and Cu(II) ions by *Delonix regia* pods and leaves. *Experimental conditions:* pH 4 and 5; contact time: 30 min; metal ions concentration: 1 - 1000 mg/L

The relatively higher number of metal ions compared to the adsorbent available binding surfaces as concentration is increased could be responsible for the decrease observed in percentage removal. Thus, it could be said that the uptake of metal ions depends on the initial concentration of the adsorbate (Meena et al., 2005).

The data obtained from this experiment was modelled using the Langmuir and Freundlich isotherm models. Monolayer surface coverage, availability of equal number of adsorption sites on the adsorbent and no interaction between adsorbed species were assumptions of the Langmuir model (Liu and Wang, 2014). The Langmuir Isotherm is represented in Equation 3

$$\frac{C_e}{Q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \qquad 3$$

where Q_e (mg/g), is the amount of solute adsorbed per unit mass of adsorbent; C_e (mg/L) is the equilibrium concentration of solute in the bulk solution, Q^0 (mg/g) represent the monolayer adsorption capacity of the adsorbent and *b* (L/mg) represents the constant related to the energy of adsorption. The Langmuir equation could be further expressed using a dimensionless constant separation factor K_R shown in Equation 4. K_R is a relationship containing all the essential features of the Langmuir isotherm.

$$K_R = \frac{1}{1+K_a C_i} \qquad 4$$

where C_i is the initial concentration of metal ions in solution (mg/L) and K_a stands for the Langmuir constant (L/mg). This dimensionless separation factor is interpreted to imply that the isotherm is favourable if $0<K_R<1$. The results presented in Fig. 6b for the Langmuir Isotherm model showed that for the pods the Langmuir isotherm is favourable for its adsorption of Ni(II) and Cu(II) ions. The values obtained for the adsorption of the metal ions onto the leaves showed that adsorption of Cu(II) ions unto the leaves is more favourable than that of Ni(II) ions.

The plot of the Langmuir isotherm also revealed that the curves are continuous leading to saturation thus suggesting the possible monolayer coverage of the metal ions on the adsorbent surface except for the sorption of Ni(II) ions to the leaves where slight fluctuations were noticed. The high correlation correlation coefficient (R^2) obtained for the isotherm when sorption was carried out using the pods of *Delonix regia* is also an indication of its applicability in the sorption reaction. The correlation correlation coefficient obtained using *Delonix regia* leaves as adsorbent were not as high as those obtained as the correlation for the pods, implying that Langmuir Isotherm is not the best model to explain the sorption of Ni(II) and Cu(II) onto the leaves. The parameters obtained for the Langmuir isotherm modelling are shown in Table 2.

Table 2. Isotherm models adsorption parameters for the adsorption of Ni(II) and Cu(II) onto *Delonix regia*

	Langmuir Isotherm				Freundlich Isotherm		
Metal ions	Q^0 (mg/g)	b (L/mg)	R^2	K_R	K_F (mg/g)	1/n	R^2
Pods							
Ni	5.88	0.02	0.9638	0.32	0.66	0.34	0.9497
Cu	9.12	0.03	0.9973	0.24	0.86	0.39	0.9510
Leaves							
Ni	5.77	0.0021	0.5191	0.83	0.03	0.75	0.9772
Cu	9.01	0.0389	0.9311	0.21	0.07	0.81	0.9944

The Freundlich isotherm represented in Equation 5 states that the ratio of the amount of solute adsorbed onto a given mass of the adsorbent to the concentration of the solute in the solution is not constant at different concentration. It is an isotherm used to describe adsorption onto heterogeneous surfaces.

$$log Q_e = log K_F + \frac{1}{n} log C_e \qquad 5$$

where 1/n is the constant related to the adsorption efficiency, K_F is the adsorption capacity, Q_e is the quantity of adsorbate adsorbed per unit weight of the adsorbent and C_e is the final concentration of metal in the solution. The Freundlich constant 1/n is a factor giving an indication of how favourable the adsorption of the adsorbate onto the sorbent is, $0 < 1/n < 1$ imply favourable adsorption. It is also related to the heterogeneity of the adsorbent surface. The plot of the Freundlich isotherm is presented in Fig. 6c.

Using the Freundlich isotherm model on the data obtained from the concentration study, it was discovered from the values of the adsorption parameters shown in Table 2 that the adsorption of Ni(II) and Cu(II) ions onto *Delonix regia* leaves is more favourable than the adsorption of these metal ions onto the pods. Values obtained for 1/n are 0.75 and 0.81 for the adsorption of Ni(II) and Cu(II) ions, respectively for the leaves while the values for their respective sorption onto the pod are 0.34 and 0.39, respectively. To support this observation, the values obtained for the correlation coefficient (R^2) during the adsorption onto the leaves are higher than those obtained for the adsorption onto the pods. Thus, the Freundlich isotherm is a better isotherm to describe the adsorption of Ni(II) and Cu(II) ions onto *Delonix regia* leaves while Langmuir isotherm is better fitted to describe adsorption onto the pods.

3.2.4 Adsorbent dose and solution's ionic strength

Fig. 7a revealed the results of the effect of changing the adsorbent doses on the adsorption of Ni(II) and Cu(II) ions by *Delonix regia* biomass. It was observed that the percentage adsorption of Ni(II) ions increased from 45.9% to 80.4% and from 21.6% to 33.7% onto the pods and leaves, respectively, whereas, the percentage adsorption of Cu(II) ions onto both adsorbent increased from 72.6% to 89.2% and from 69.6% to 80.8% onto the pods and leaves, respectively. The observed increase in the percentage Ni(II) and Cu(II) ions adsorption might be due to the availability of more binding sites as adsorbent doses are increased.

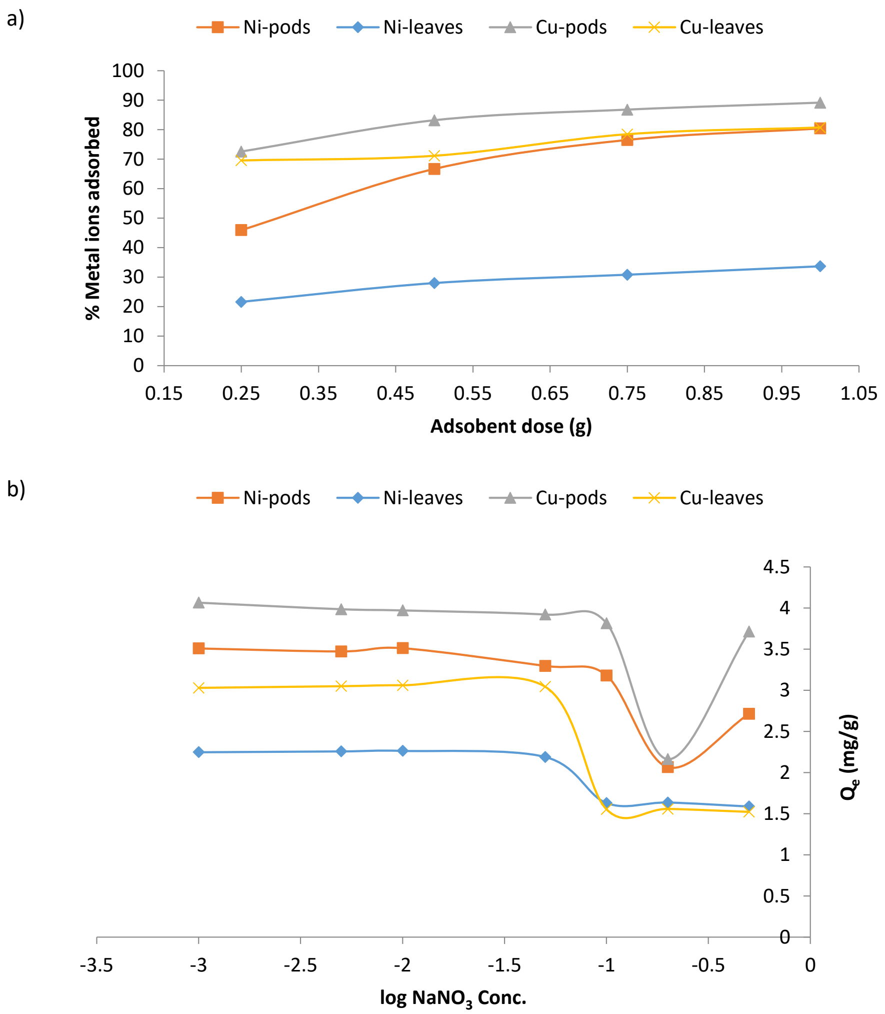


Figure 7. Effect of adsorbent dose (a) and ionic strength (b) on the adsorption of Ni(II) and Cu(II) ions by *Delonix regia* pods and leaves. *Experimental conditions:* pH 4 and 5; contact time: 30min; metal ions concentration: 100 mg/L

The result of the effect of sodium ion on the adsorption of Ni(II) and Cu(II) ions by *Delonix regia* biomass is shown in Fig. 7b. The figure showed a reduction in the uptake of both metal ions by each of the biomass. It could be explained that there was competition for the available binding sites on the adsorbents by the positive sodium ions present in the adsorption medium. Thus, as the concentration of sodium ion is increased metal uptake by the adsorbent was observed to be lower.

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3.3 Desorption Study

The recovery experiment was carried out to investigate the possibility of recovering the adsorbed metal ions from the biomass. The result obtained from the recovery study is shown in Fig. 8.

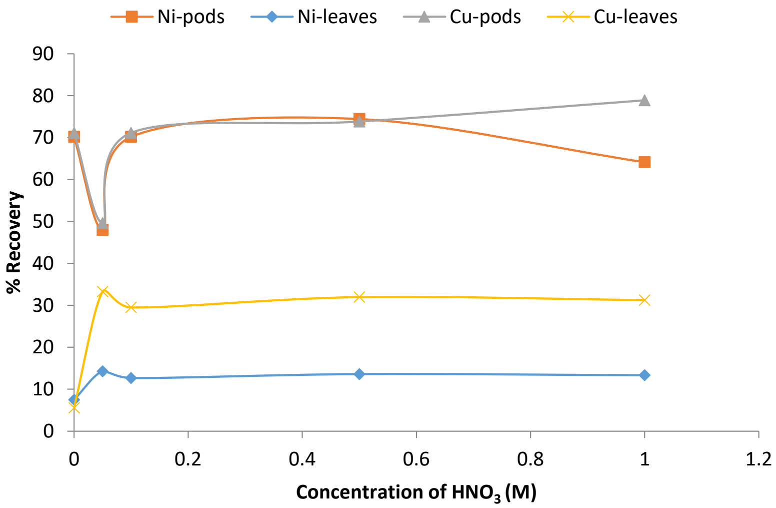

Figure 8. Recovery study of the adsorbed Ni(II) and Cu(II) ions from the pods and leaves of *Delonix regia*

From Fig. 8, the values obtained for the percentage recovery of Ni(II) and Cu(II) ions from the pods of *Delonix regia* were very similar at different concentration of the desorbing solution, whereas, when the leaves was considered, different percentages were recovered at different concentration of the desorbing medium. The figure also revealed that the percentage of metal ions recovered from the pods were higher than what was recovered from the leaves at various concentration of nitric acid except at 0.0 M when the percentage obtained were very close to each other. At this concentration (0.0 M) level, ultra-pure water (milli Q water) was used for desorbing the metal ions from the adsorbent. Approx. 74.4% Ni(II) ions and 78.9% Cu(II) ions was recovered from *Delonix regia* pods when the concentration of nitric acid used for desorbing the metal ions was 0.5 M and 1.0 M, respectively. Moreover, 14.3% Ni(II) ions and 33.3% Cu(II) ions was recovered from the *Delonix regia* leaves with 0.05 M nitric acid. The recovery experiment showed that metal ions recovery increased with increasing concentration of nitric acid.

4. Conclusion

The study concerns the application of powdered *Delonix regia* pods and leaves for the removal of Ni(II) and Cu(II) ions from aqueous solutions. The results obtained indicated that the pH of the solution, contact time, initial metal ion concentrations, adsorbent dose and ionic strength affect the uptake of the metal ions by the biosorbent. It was observed that the Freundlich isotherm is a better isotherm to describe the adsorption of Ni(II) and Cu(II) ions onto *Delonix regia* leaves, while, Langmuir isotherm is better fitted to describe the adsorption onto the pods. The pseudo-second-order kinetic model agrees with the sorption of Ni(II) and Cu(II) ions onto *Delonix regia* pods and leaves. The desorption study also showed that the recovery of the metal ions from the spend pods and leaves increased with increasing concentration of nitric acid. Thus, powdered *Delonix regia* pods and leaves could be used as an eco-friendly, economically cheap and effective adsorbents for the removal of Ni(II) ions, Cu(II) ions and other environmental contaminants from aqueous solution.

Data availability

The data generated and/or analysed during the current research are available with the authors upon reasonable request.

Author contributions

BMB was the investigator and contributed to writing the paper. AOB was involved in the characterization of the adsorbent. COA and OSA were involved in the adsorption studies and modelling of the adsorption data. SFA and EOO contributed to the writing of the paper.

Conflict of Interest

On behalf of the authors, the corresponding author states that there is no conflict of interest.

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