

Dear Editor,

The response to the reviewer's comments are as follows:

### **Reviewer #1**

General comments:

- line 104-118

A clear objective of the study has been included at the end of the introduction and the way it relates to previous research have been included.

The "therefore" now in line 118 is now well underpinned.

- Tenses have been revised and redundant information have been deleted.

- line 306-340; line 350-418

The results (i.e isotherm and kinetics) have been linked and supported with other research

- line 337-340, Table 3, etc

The kinetics, isotherm and removal efficiency of *D. regia* biomass is now compared with other agro-waste

- The order in which the experiment was conducted was reported. i.e. parameters where optimised at different stages, therefore, rearranging the sequence will distort the manuscript.

Specific comments:

- Batch test has been mentioned in line 14

- pg 1, line 22-26

how well Cu (II) and Ni (II) adsorb on the adsorbents has been mentioned in the abstract.

- pg 1, line 21 -22

The sentence (line 21-22) supports our studies and we have not deleted it. Moreso, the biomass is an agricultural waste and cheap. However, we have avoided the use of the word "economics".

- Grammatical errors where checked and corrected in the entire manuscript.

i.e Line 20: "concentrations" was been corrected

Line 38: "of heavy metals" have been deleted

Line 39: "and cause serious pollution" deleted

Line 43: supply revised to resources

Line 44: "production" ( of glass, textiles, paper etc.) have been added

Line 45: "apart from.. ecosystem" deleted

Line 46: "human" (gills, liver: : :) can not be inserted, as the sentence refers to marine animals and not human

Line 48: during = in the; of animal = in animals; have been revised

Line 52: "also" (reported) has been added

Line 53: "Like most heavy metals" deleted  
Line 54: "," after "health" is added  
Line 55: "," after "compounds" and after "nickel", added  
Line 58-61 have been revised  
Line 64: "," after "value" has been added  
Line 66 and 67: "shells" corrected  
Line 68: "treat" = "remove" have been corrected  
Line 71: "," after "biomass" inserted; "optimum conditions" = "dosage" have been corrected  
"at" was inserted before pH and the stirring speed deleted  
Line 75-78: sentence deleted  
Line 83: "seeds" resvised  
Line 84: "the treatment : : . To" revised; "reduce" = "reducing" revised  
Line 88-90: sentence deleted  
Line 96-98: sentence deleted  
Line 99-:  
The knowledge gap based on previous research have been provided i.e. line 106-118.  
Line 106-108: sentence deleted  
Lin 111: the concentrations of stock solutions was mentioned in line 116  
Line 118-121: pHs to be studied, concentrations that are studied were now given in line 153-162  
Line 129: "use" = "used" revised  
Line 130-131: "is" = "was" (three times) revised  
Line 132: "are" = "were" revised  
Line 129-137: the procedure of the batch tests has been reported in detail.  
The modelling part now explained in the M&M section  
Line 141: "structures, being potentially beneficial for the uptake" revised  
Line 143-144: "is" = "was" (two times) corrected  
Line 144-145 the EDS data represent the composition of the sample. However, It is used for qualitative analysis and not quantitative analysis, therefore there is no need to give a detail discussion of EDS. If it were to be XRF which provides the true quantitative analysis of the samples, a detail discussion might be required.  
Line 156, Line 158-159: The XRD has been replotted and discussed anew. The different peaks and what they correspond to, has been indicated in the new plot  
Line 167: "reveals" has been revised; "significant" deleted  
Line 168: "adsorbents" revised ; "very" (subjective) was deleted; "increased" revised  
Line 169: sentence deleted  
Line 170: "is" = "was" revised; "as the optimum pH and used" deleted  
Line 173: ", thus being in line with our findings" added  
Line 175 lines connecting data have been removed in figures, except the trendline in the isotherm and kinetic plots.  
Line 180: "for Cu(II) ions" has been deleted; "pH 4 was used : : : pods while pH 5 was" = "which were further" has been revised.  
Line 181: "leaves and pods, respectively" revised  
Line 182-184: the results on the effect of pH has been discussed with literature  
Line 184: "Thus: : : studies" deleted; "literatures" = "authors" revised  
Line 187: "Generally: : . Media" deleted  
Line 188: reference given  
Line 189-191: ""when: : .. particles" deleted  
Line 192: "the positive metal ions" added; "decreases" revised  
Line 194: "This will: : : adsorbent" deleted

Line 201: “for” = “of” revised  
Line 203:  
the lines connecting data in Fig 5a have been removed, except the trendlines for the kinetic plot (5b)... the trendline is important for the equations and R<sup>2</sup> values displayed.  
Also the lines connecting data in Fig 6 a, 7 and 8 were also removed  
Line 209: “interacting” = “interaction with” revised  
Line 212: “adsorbents” revised  
Line 213: “to” = “until” revised  
Line 217: how the work of Hansen supports the data has been explained  
Line 221: “is a : : fact” = “indicates” revised; reference for this statement has been given  
Line 223-226: transferred in Materials and methods section  
Line 225: “any” deleted  
Line 235: “decreased” revised; references are given  
Line 246: “higher number” = “high concentration” revised; reference for this statement was given  
Line 248-249: sentence deleted  
Line 250:263: now explained in Materials and methods section  
Line 264- 267 revised  
Line 269: “The fit to the plot of the Langmuir isotherm suggests the possible monolayer: : : revised  
Line 271: “slight” deleted  
Line 272-274: delete sentence  
Line 283: “The Freundlich isotherm is used to describe adsorptions onto..”  
Line 288-293 moved to Materials and methods section  
Line 321: “shows” revised  
Line 322: “biomasses” revised  
Line 322-325: the statement now referenced  
Line 335: “concentrations” revised  
Line 336: “Was” = “were” revised  
Line 348: “application” = “use” revised  
Line 352-354 have been explained in the body of the manuscript  
Line 357-359: We have avoided the use of the word “economics”, however, the fact remains that the biomass is an agricultural waste, the pods and leaves of *D. regia* litters the ground and rot. This has been mentioned in the introduction and concluding section.

## **Reviewer #2**

### General comments

The manuscript has been improved in the way of comparing the results with other literature studies.

The quality of the graphs has been improved.

We have now compared the *D. regia* adsorption capacity with other agro-waste reported in the literature. A new table has been created in this regard (Table 3). However, we have chosen to use percentage as a measure of the capacity based on the suggestion by reviewer #1.

The aim of the study is now well stated at the end of the introduction section.

The conclusions, both the pods and leaves could be used for the removal of Ni and Cu ions. However, the pods performed better in term of the percentage metal ions removed and regeneration of the biosorbent. These have been stated clearly in the concluding section.

We have conducted a batch experiment and our findings have shown that the agro-wastes are effective. We encourage other researchers to build on our studies by conducting the column/filter experiment.

Since an economic study was not performed, we have avoided the use of the term economics.

#### Specific comments

Abstract: the results of the other conditions have been included (line 17-19). The adsorption isotherm i.e. the adsorption capacity of the pods and leaves of *D. regia* in terms of mgMetal/g adsorbent has been stated in the abstract.

#### Introduction:

Newer references have been included

The permissible limit of Cu(II) and Ni(II) in drinking water and wastewater has been included in the manuscript (line 52 and 53; line 62 and 63).

The reason why this research is needed and why we have chosen to use the pods and leaves of *D. regia* have now been detailed in the manuscript (line 106-118)

#### Materials and methods:

The leaves and pods were dried, this has been included in the manuscript (line 113)

The concentrations of metal ions used are now included (line 157).

The sodium and nitric acid concentrations used are now mentioned in the manuscript (line 160).

The procedures used in the adsorption experiment have been detailed in the manuscript (line 153 – 166)

The experiments were performed in triplicate, this was mentioned in the manuscript

All equations regarding kinetics and isotherm are now transferred to the materials and methods.

A subsection on analytical procedure has been included (line 168-179).

#### Results and discussion:

The diffractogram has been replotted and all phases present have been identified.

We have chosen to report the experiment in the order in which the experiment was conducted i.e. pH was optimized, followed by contact time, etc.

We have now mentioned that the pods performed better than leaves for both metals (line 416 - 418), also in the concluding section.

Adsorbent dosage has been included in the experimental conditions mentioned in all of the adsorption plots.

The nature of the precipitates has been included (line 277).

The equipment and time evaluated have been moved to the materials and methods section.

Comments have been made on the fact that the pods are better than leaves (line 309 -310).

Adsorption dosage included in the experimental conditions mentioned in the plot

The uniqueness of 30 min contact time for *D. regia* biomass in comparison to other agro-waste has been detailed in the manuscript (line 312-320)

How Hansen et al. (2010) supports the results on kinetics have been included.

All equations have been transferred to the materials and methods.

The  $Q_e$  and  $k$  values obtained for the pods and the leaves in the literature has been included (line 337-340).

The data obtained on the effect of initial metal ions concentration is often used to model the isotherm. The title now reflects isotherm experiments (line 342).

The authors have chosen to retain the kinetic and isotherm plots, unless the editor insists that the authors remove these plots.

Repeated word “correlation” has been deleted.

The fact that  $1/n$  and  $K_f$  are lower and higher respectively for the pods for both metals confirming that the pods perform better have been included in the manuscript (line 416 -418). The wrong notion of a higher  $R^2$  and a favorable adsorption has been corrected. The adsorbent dose experiment can not be used to determine the isotherm, but the initial adsorbate concentration experiment. Normal scale is now used to plot Fig 7b. All experiments were conducted in triplicate. Section 3.3 has been re-discussed. The isotherm has been detailed in section 3.2.3, a brief of the isotherm study is required in the concluding section and this is what has been done. The desorption study has been revisited and re-discussed. We have avoided the use of the term “economics”

An author (Olayide S Lawal) was initially omitted and has been added, moreover, Olushola S Ayanda is now the last author on the list.

We appreciate the editors and reviewers of this manuscript, the comments and suggestions received have greatly improve the quality of the manuscript.

Thank you.

Dr Olushola S Ayanda.

# 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, adsorbent dosage, 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, an increase in the initial concentration of the adsorbate, pH and adsorbent dosage led to increase in the amount of Ni(II) and Cu(II) ions adsorbed. ~~and the~~ The adsorption process followed the pseudo-second-order kinetic model for all the metal ions sorption, ~~with the exception of Cu(II) sorption on the leaves.~~ The equilibrium data fitted well with both the Langmuir and Freundlich Isotherms, ~~the monolayer adsorption capacity ( $Q^0$  mg/g) of the pods and leaves of *Delonix regia* for Ni(II) ions was 5.88 mg/g and 5.77 mg/g, respectively, and 9.12 mg/g and 9.01 mg/g, respectively for Cu(II) ions. The efficiency of the powdered pods and leaves of *Delonix regia* for Ni(II) and Cu(II) ions removal was  $> 80\%$ , ~~except for the sorption of Ni(II) ions onto the leaves.~~ ~~the~~ The desorption study revealed that the percentage of metal ions recovered from the pods were higher than the leaves at various concentrations 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 wastewateraqueous solution.~~

**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 resources~~ by industrial activities such as electroplating, smelting, production of glass, textile, paper and ceramics, mining, textiles, storage batteries, petroleum, metal finishing, pulp and paper (Dean et al., 1972; Ksakas et al., 2018; Kumar et al., 2019). ~~Apart from the~~ 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 in the metabolism in animal; its excessive intake can result in serious health problems (Paulino et al., 2006). The permissible limit of copper in wastewater and portable water is 0.5 mg/L and 2.5 mg/L, respectively (Zhou et al., 2018; Kumar et al., 2019). 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 also 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 effects on human health, resulting in allergic dermatitis, immunologic urticarial; immediate and delayed hypersensitivity (Festus et al., 2013). 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). Due to its toxicity in minute quantity, 0.05 mg/L was set for the permissible limit of nickel in wastewater (Zhou et al., 2018).

Conventional methods for the ~~treatment-removal~~ of metal ions includes: ~~reverse osmosis,~~ chemical precipitation, oxidation/reduction, ion exchange, electrochemical processes, membrane separation, Fenton process, ozonisation, electrocoagulation, photochemical degradation and evaporation (Okoya et al., 2014). 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 shells, tree bark treated with formaldehyde and sulphuric acid (Guibal et al., 1993; Raji et al., 1997), bone char, tea leaves, wood charcoal (Ajmal et al. 2003), and coconut shells have been used to produce activated carbon to ~~treat remove~~ heavy metal ions from wastewater. Rice hulls (Ajmal et al., 2003), rice bran (Montanher et al., 2005) and pine bark (Nath et al., 1997) have also been used in the raw and treated form to remove 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 dosage~~ for maximum removal of Ni(II) ions from an aqueous solution of 50 mg/L were reported to be ~~at adsorbent dosage of 1500 mg/L adsorbent dosage, and at 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 seeds as alternative adsorbents for the removal of Pb and Cu. The ~~treatment removal~~ of Pb and Cu ~~with by~~ these agricultural wastes was reported to ~~reduce reducing~~ 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.~~

*Delonix regia* also known as flame of forest, is a semi-deciduous tree, native to Madagascar. It 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 and attractive red peacock flowers. Researchers have reported the usefulness of the green leaves and flowers of *Delonix regia* in medicine i.e. *Delonix regia* have a broad spectrum of pharmacological activities in various ailments (Modi et al., 2016). However, it sheds its leaves and flowers in dry areas and seasons, the trees are less attractive after the leaves and flowers are shed, with their pods remaining on the branches until they are dropped by wind, these make *Delonix regia* an agro-waste with limited valuable use.

There are limited studies on the use of *Delonix regia* for the removal of organic and inorganic contaminants from aqueous solution, except for Ponnusami et al. (2009), Onwuka et al. (2016) and Babalola et al. (2019) who have reported the viability of *Delonix regia* for the removal of methylene blue dye, crude oil spill and Pb(II) ions, respectively. Therefore, the objective of this research work is to investigate the capacity of ~~an agro-waste~~ the pods and leaves of *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. The materials were washed with deionised water, sun-dried and milled. 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<sub>3</sub> 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<sub>3</sub>.

### 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<sup>2</sup> 20). X-ray diffractometer (Siemens D8 Advance Bruker XRD) was used for the phase characterization.

### 2.4 Adsorption

Adsorption procedure by Meena et al. (2008) was slightly modified and used in this work. Parameters such as the influence of pH, contact time, initial adsorbate concentration, adsorbent dosage and solution's ionic strength were investigated.

For the influence of pH, a 0.5 g of the biomass was weighed into designated tubes containing 20 mL of 100 mg/L metal ions solution of various pH in the range 1 to 8. The suspensions were shaken on an end-over-end shaker for 300 min at ambient temperature (21±2°C). The influence of contact time was conducted by varying the contact time from 5 - 300 min at optimised pH. The concentration of Ni(II) and Cu(II) ions was varied from 1 - 1000 mg/L for the influence of initial metal ions concentration at optimised pH and contact time. Finally, the influence of adsorbent dosage and solution's ionic strength was achieved using 100 mg/L metal ions concentration, the parameters were varied from 0.25 - 1.0 g and 0.001 - 0.5 M NaNO<sub>3</sub>, respectively at optimised pH and contact time. Each of the experiment was carried out in triplicate and the results were the average values.

At the expiration of each of the experiment, aliquot was taken, centrifuged (twice at 4500 rpm for 15 min and 10300 rpm for 10 min) and diluted with 0.1 M HNO<sub>3</sub> before the residual metal content was analysed by Thermo elemental inductively coupled plasma – mass spectroscopy (ICP-MS; X Series II).~~As soon as each experiment is concluded, an aliquot is withdrawn and diluted with 0.1 M HNO<sub>3</sub> before residual metal content is analysed with ICP-MS (X Series).~~

### 2.5 Analytical procedure

Multi-elements standard solution was used to prepare different concentrations of external calibration standard solutions (1 – 100 µg/L) used for the analysis. After the instrument was switched to the operate mode, the pressure of the nebulizer was checked, and the instrument's sensitivity and stability were checked by running a tuning solution of 1 µg/L multi element standard solution for 10 min. It was ensured that the <sup>115</sup>In counts was less than 20 K counts per second, precision less than 2%. The backgrounds (5BKg and 220BKg) were less than 1 count per second, the oxides cerium oxide (CeO<sup>+</sup>) less than 2.0% and the doubly charged ions (Ba<sup>2+</sup>) less than 6.0%. Therefore, the calibration standard solution and the blank were analysed to obtain a calibration curve where the samples to be analysed will properly fit. The analysis of the samples proceeded after the calibration curve for each of the metal ions was good with R<sup>2</sup> = 0.9999.

~~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<sub>e</sub>) was calculated using Equation 1.

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

where C<sub>o</sub> is the initial metal concentration (mg/L), C<sub>e</sub> is the final metal ion concentration in the solution, ICP-MS reading (mg/L), V is the volume of the metal solution used in litre (L) and m is the mass of the biosorbent (g).

## 2.6 Kinetics and Equilibrium modelling

Further examination of the contact time experiment was carried out by modelling the data with the pseudo-second-order kinetic models to determine the mechanism of the sorption process.

The pseudo-second-order kinetic model can be expressed in Equation 2 where k<sub>2</sub> (g/mg/min) represent the rate constant for the pseudo-second-order kinetics; Q<sub>e</sub> and Q<sub>t</sub> (both in mg/g) being the amount of adsorbate taken up by the adsorbent at equilibrium and at time t, respectively. All parameters in Equation 2 were derived by plotting t/Q<sub>t</sub> against t.

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

The data obtained on the effect of initial metal ions concentration was also modelled using the Langmuir and Freundlich isotherms. 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

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

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.

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

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 Freundlich isotherm 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. The Freundlich isotherm is used to describe adsorption onto heterogeneous surfaces (Equation 5).

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

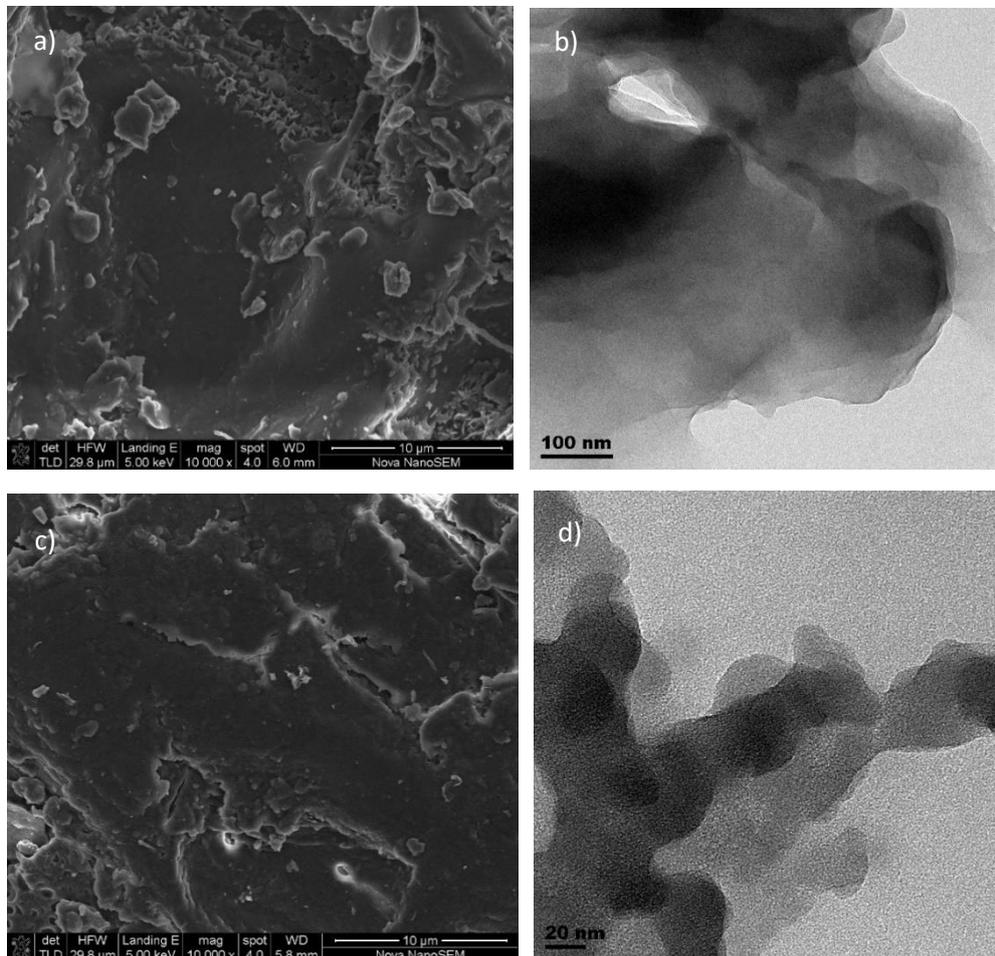
where  $1/n$  is the constant related to the adsorption efficiency,  $K_F$  is the adsorption capacity,  $Q_e$  is the quantity of adsorbate adsorbed per unit weight of the adsorbent and  $C_e$  is the final concentration of metal in the solution. The Freundlich constant  $1/n$  is a factor giving an 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.

### **3. Results and discussion**

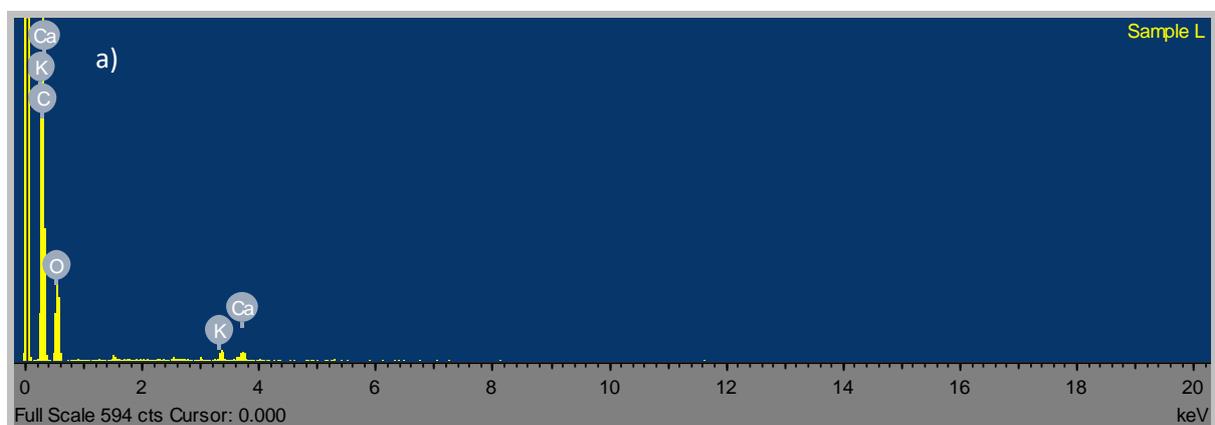
#### **3.1 SEM-EDS, TEM and XRD analyses**

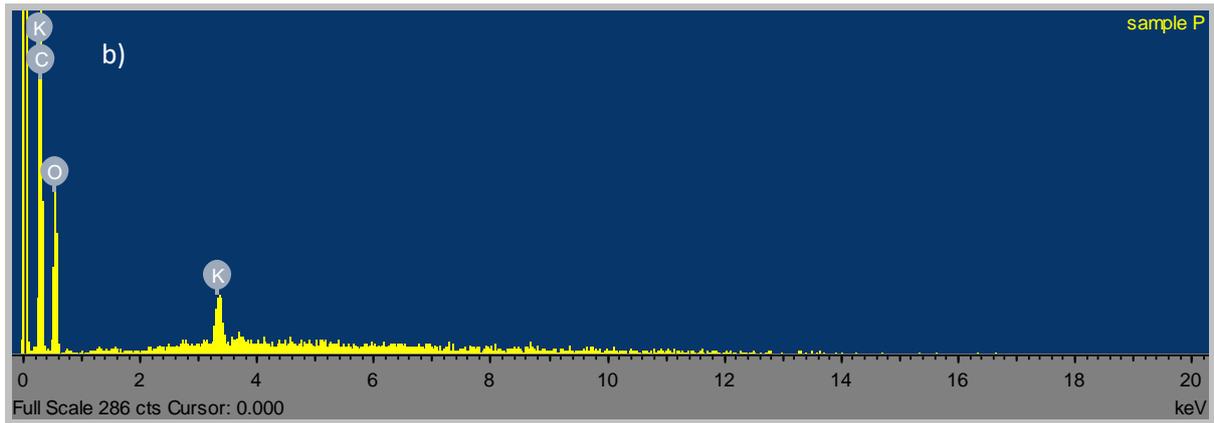
The SEM (at x10 000 magnification) and TEM micrographs of the pods and leaves of *Delonix regia* (Fig. 1) indicated the spongy nature of *Delonix regia* with porous structures. ~~This structural properties might improve, being potentially beneficial for~~ the uptake of the Ni(II)

and Cu(II) ions from aqueous solution. The EDS of *Delonix regia* showed that the surfaces of the leaves ~~is~~was composed of 66.79% C, 32.97% O and traces of Ca and K, while, the pods ~~is~~was composed of 57.61% C, 41.15% O and trace of K.



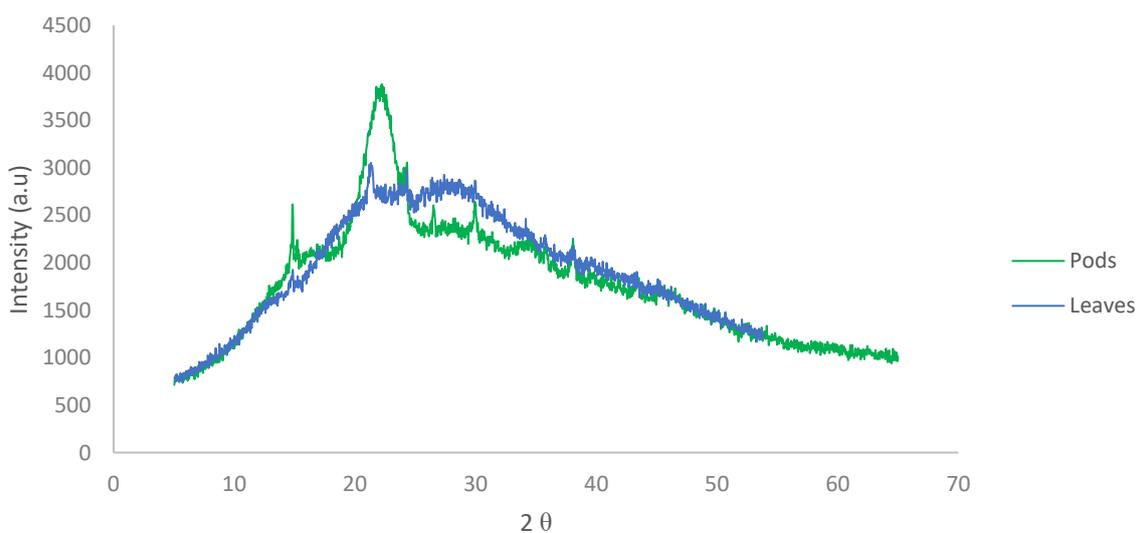
**Figure 1.** SEM (at x10 000 magnification) and TEM micrographs of *Delonix regia* leaves (a & b) and pods (c & d)



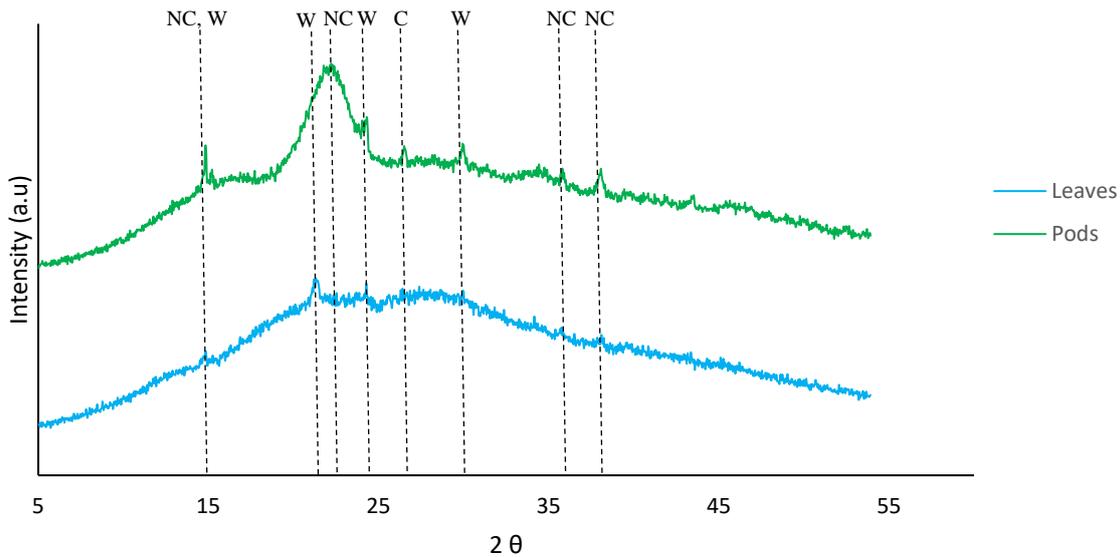


**Figure 2.** EDS of leaves (a) and pods (b) of *Delonix regia*

According to the ICSD Nos. 03-0289, 20-0231 and 26-1077, native cellulose ( $C_6H_{12}O_6$ )<sub>x</sub> and whewellite, syn ( $C_2CaO_4 \cdot H_2O/CaC_2O_4 \cdot H_2O$ ) were identified as major peaks in *Delonix regia* (Fig. 3). The pods were mainly native cellulose, whereas, the leaves were rich in whewellite, syn. The hemicellulosic moieties in the pods and leaves might provide sites ~~was identified in~~ *Delonix regia*, the peak at  $22.15^\circ$  for pods and  $21.36^\circ$  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*



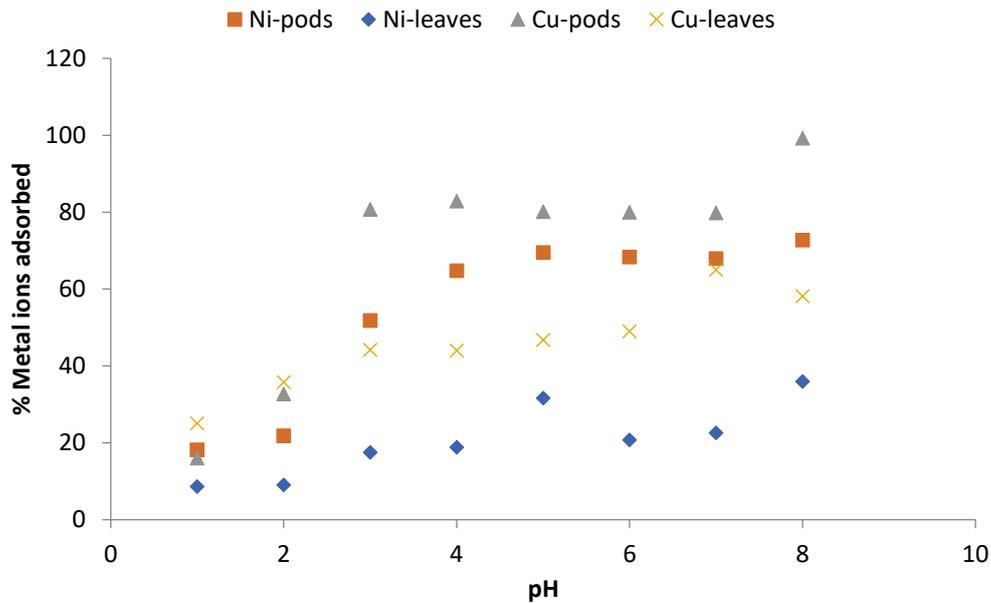
**Figure 3.** X-ray diffractogram of the leaves and pods of *Delonix regia*

(NC – native cellulose ((C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>)<sub>x</sub>); W – whewellite, syn (C<sub>2</sub>CaO<sub>4</sub>·H<sub>2</sub>O/CaC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O); C – carbon)

### 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-reveals~~ that there was no ~~significant-evident~~ nickel uptake by both adsorbents at low pH, but a very noticeable uptake was achieved as pH ~~increases-increased~~. ~~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 was~~ 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), thus being in line with our findings.



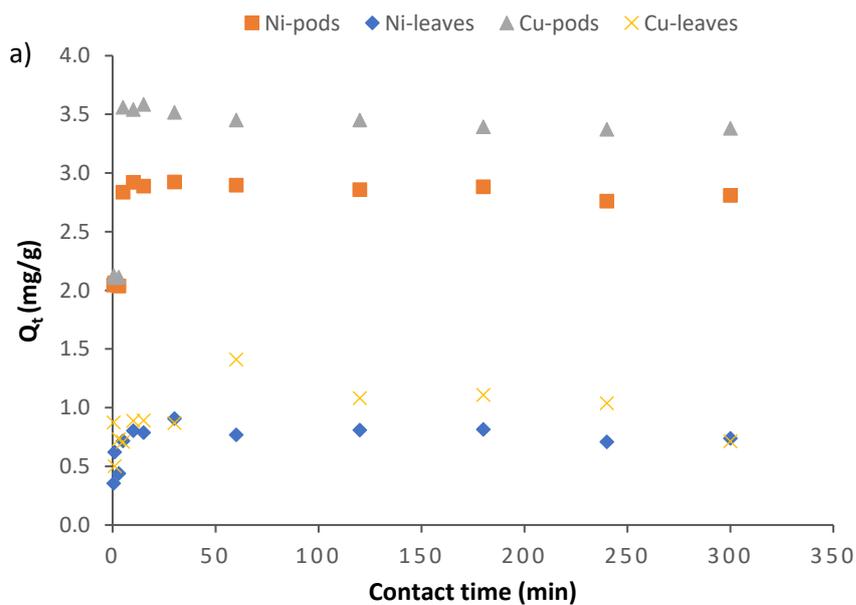
**Figure 4.** Effect of pH on the adsorption of Ni(II) and Cu(II) by *Delonix regia* pods and leaves. *Experimental conditions:* pH 1-8; contact time: 300 min; adsorbent dosage: 0.5; metal ions concentration: 100 mg/L

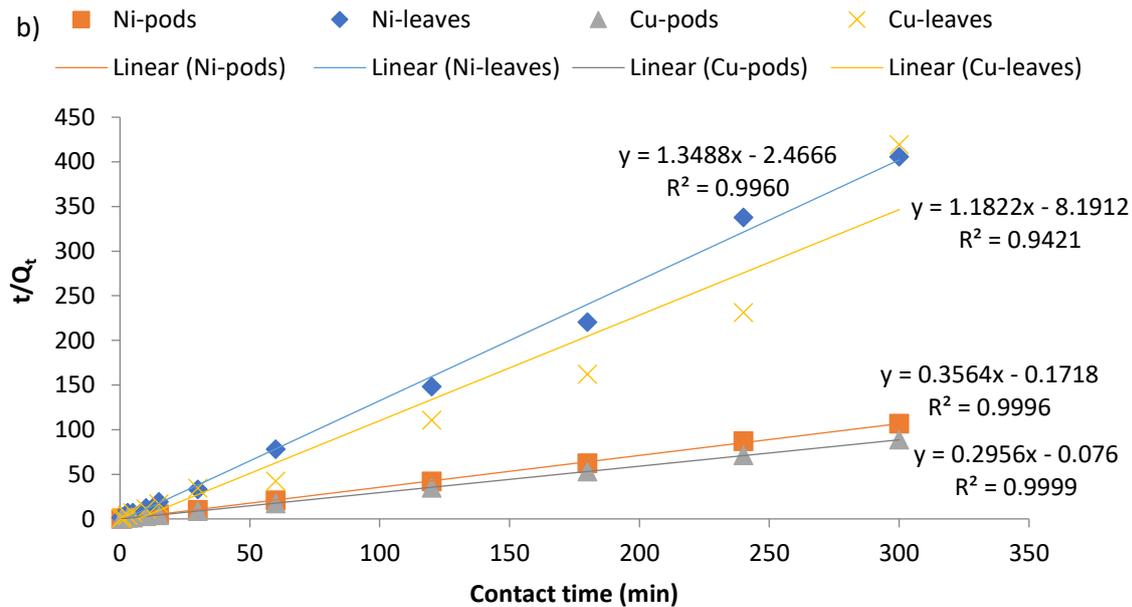
A small increase in the uptake value was achieved between pH 1 to 3, but maximum uptake of 46.7% was recorded at pH 5 for Cu(II) ions sorption onto leaves and maximum uptake of 82.9% at pH 4 onto the pods which were further used for adsorption of Cu(II) onto the leaves and pods, respectively. at pH 4 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 which might be due to the formation of  $\text{Cu}(\text{OH})_2$  or other soluble complexes had been formed in the experimental set up at these pH (Larous and Meniai, 2012). ~~Thus, pH 5 was used for other studies.~~ Some literatures authors 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). This might be as a result of the increased overall negative charge particularly between pH 4 and 6 which would subsequently lead to increase the sorption of the positive metal ions. 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 decreases~~ 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., 2005a).

### 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 investigation of the effect of agitation time performed at different time intervals of 5 min up to 300 min showed that the two adsorbents used in this work had rapid uptake ~~for of~~ the metal ions within short period of interaction (Fig. 5a).





**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; adsorbent dosage: 0.5 g; metal ions concentration: 100 mg/L

A slight desorption and adsorption was observed between 5 to 10 min of interacting interaction of the adsorbent with the metal ions solution. Within 30 min of interaction, maximum uptake has been achieved on both adsorbents irrespective of the metal ions considered, though the uptake recorded on the pods were higher than those on the leaves. The native cellulose, a major component of the pods might be responsible for the enhanced uptake on the pods. Metal uptake by the adsorbents remained fairly constant after 30 min of interaction ~~to~~ until the end of the experiment. Moreover, the maximum uptake at 30 min could be considered to be faster when compared with other biosorbents reported in the literature. Olufemi and Eniodunmo (2017) reported 30 min and 120 min as the optimum time for the removal of Ni(II) ions from aqueous solutions using coconut shell and banana peels, respectively. Ksakas et al. (2018) reported 60 min and 180 min as the optimum contact time for the sorption of Cu(II) ions unto some types of natural clay. Alatabe (2018) reported 120 min as the optimum sorption time for Cu(II) ions onto activated carbon from *Cane papyrus*. However, 30 min was the optimum contact time reported by Kumar et al. (2019) on the removal of Cu(II) ions by groundnut seed cake powder, sesame seed cake powder and coconut cake powder.

~~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~~ The kinetic modelling of

data 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) who reported that the adsorption of Cu(II) ions onto various agriculture waste materials fitted the pseudo-second-order kinetic model, the plots and kinetic parameters ~~for of~~ this model are shown in Fig. 5b and Table 1, respectively. The pseudo-second-order kinetic model ~~is a pointer to the fact~~ indicates that the mechanism involved in the sorption is governed by ion exchange or sharing of electrons (Babalola et al., 2019).

~~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  $t$ .~~

$$\frac{t}{Q_t} = \frac{1}{k_2} + \frac{t}{Q_e} \quad \text{--- 2}$$

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

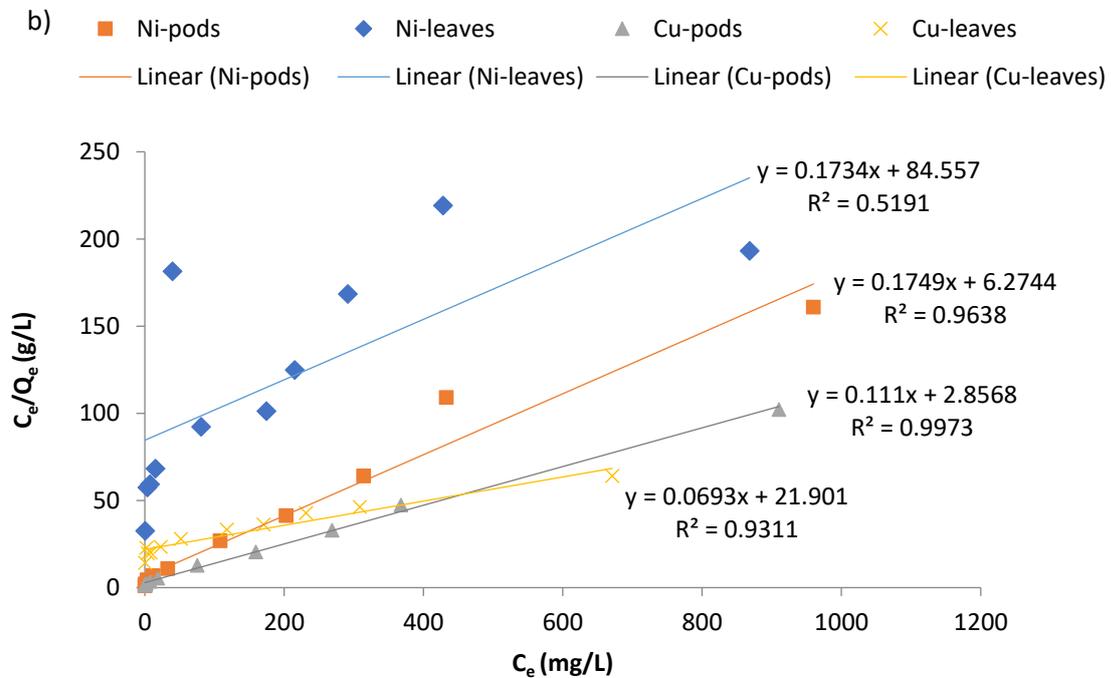
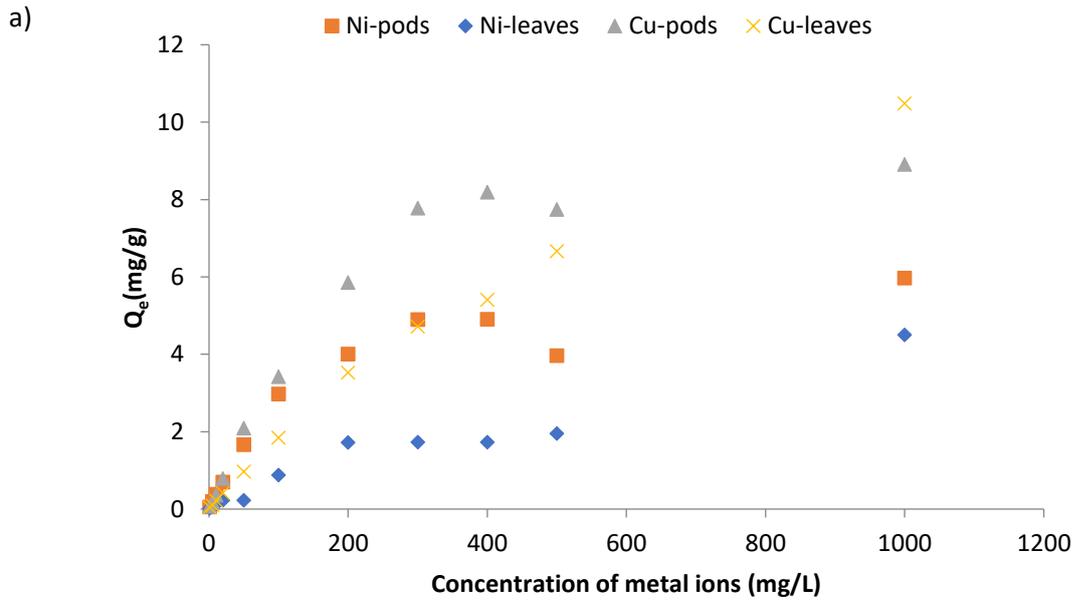
Metal ions	$Q_e$ (mg/g)	$k_2$ (g.mg <sup>-1</sup> min <sup>-1</sup> )	$R^2$
<i>Delonix regia</i> pods			
Ni	2.8	-2.36	0.9996
Cu	3.4	-3.24	0.9999
<i>Delonix regia</i> leaves			
Ni	0.7	-0.25	0.9960
Cu	0.8	-0.09	0.9421

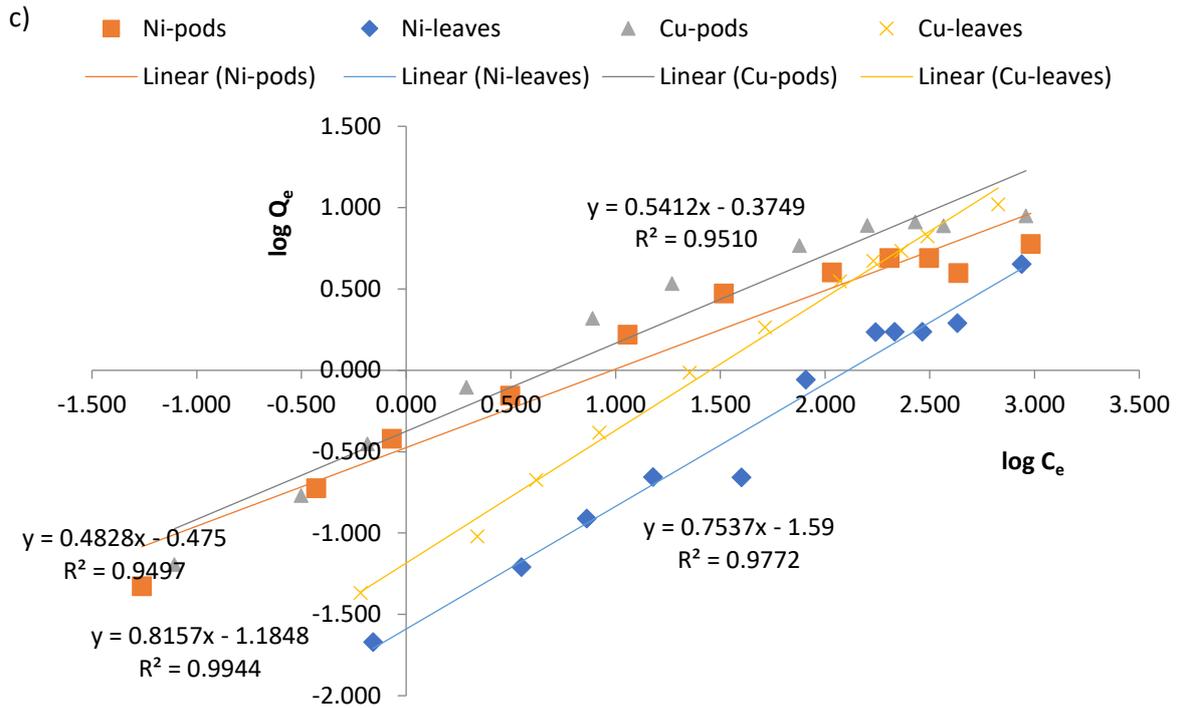
In a similar study by Babalola et al. (2019), the calculated  $Q_e$  value from the pseudo-second-order kinetic model of the adsorption of Pb(II) ions onto *Delonix regia* pods and leaves are 4.12 mg/g and 2.7g mg/g, respectively. Bansal et al. (2009) reported 2.81 mg/g for the sorption of Ni(II) ions onto rice husks.

### 3.2.3 Initial adsorbate concentration and isotherm experiment

The experiment conducted to study the effect of the initial concentration of adsorbate on the uptake of Ni(II) and Cu(II) ions by the pods and leaves of *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 metal ions to the binding sites of the adsorbents and thus increased uptake is recorded. Though, the uptake per unit gram of the adsorbent increased, the

opposite which is a decrease was observed in the percentage of metal removed from the solution as the adsorbate concentration increased. This is because as the ratio of the metal ions to the adsorbent increases, the exchangeable sites in the adsorbent structure are saturated, resulting in a decrease in the percentage removed (Man et al., 2012). The data obtained in Figs. 5a and 6a also suggested that the pods are better than the leaves and the adsorption is more favourable onto the pods at all concentrations used in this study.





**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; adsorbent dosage: 0.5 g; metal ions concentration: 1 - 1000 mg/L

The relatively ~~higher number~~ high concentration of metal ions compared to the adsorbent available binding surfaces as concentration is increased could be responsible for the decrease observed in percentage removal (Meena et al., 2005b; Hamza et al., 2013). ~~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

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

~~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.~~

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

~~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 onto the leaves is more favourable than that of Ni(II) ions. The fit to the plot of the Langmuir isotherm suggests ~~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~~ observed. 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*

Metal ions	Langmuir Isotherm				Freundlich Isotherm		
	$Q^0$ (mg/g)	b (L/mg)	$R^2$	$K_R$	$K_F$ (mg/g)	1/n	$R^2$
<b>Pods</b>							
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
<b>Leaves</b>							
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.

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

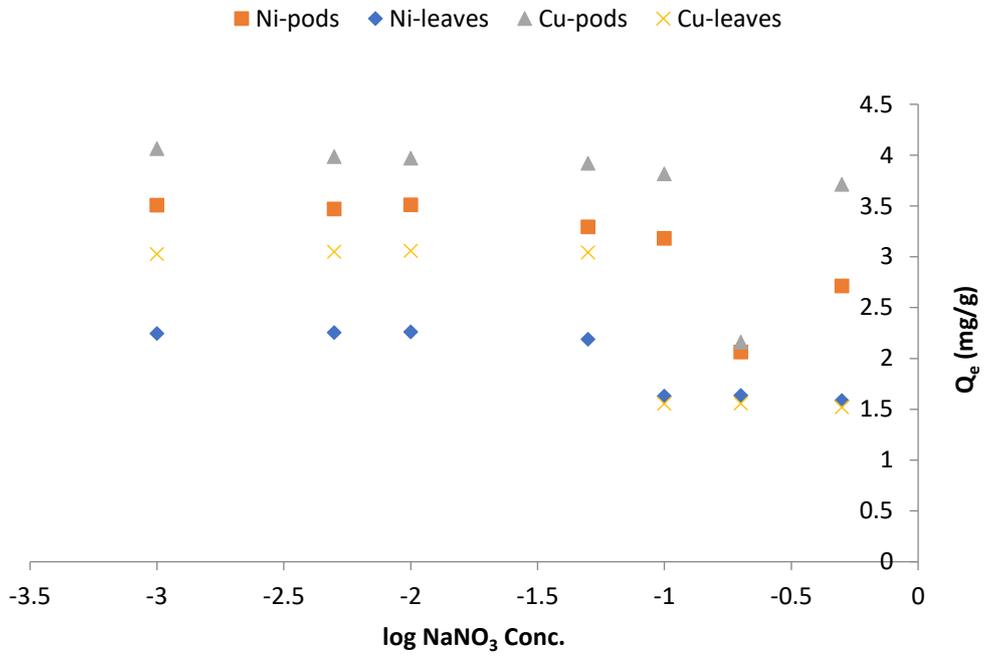
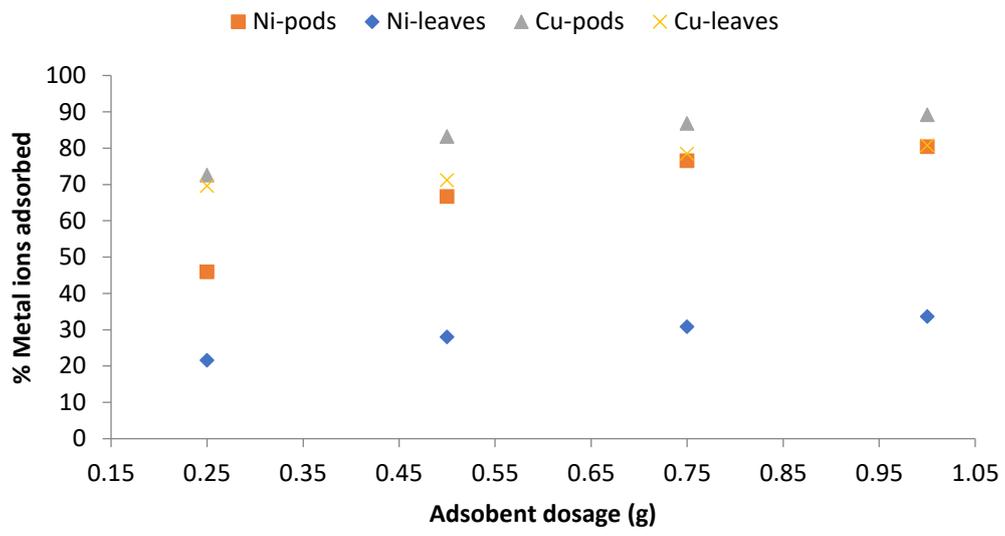
where  $1/n$  is the constant related to the adsorption efficiency,  $K_F$  is the adsorption capacity,  $Q_e$  is the quantity of adsorbate adsorbed per unit weight of the adsorbent and  $C_e$  is the final concentration of metal in the solution. The Freundlich constant  $1/n$  is a factor giving an 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 further 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. The values of the Freundlich constant  $1/n$  which are lower for the pods and a higher adsorption capacity,  $K_F$  for the pods are further confirmation that the pods adsorb better than the leaves.

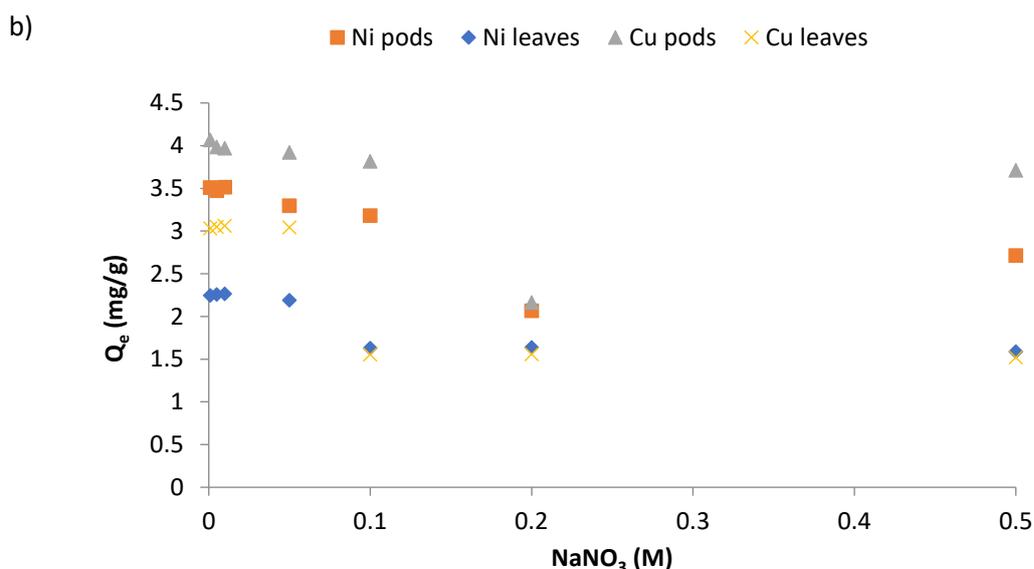
~~To support this observation, the~~ The values obtained for the Freundlich isotherm correlation coefficient ( $R^2$ ) during the adsorption of Ni(II) and Cu(II) ions onto the leaves are higher than those obtained for the adsorption onto the pods. Thus, the Freundlich isotherm is a better isotherm to describe the adsorption of Ni(II) and Cu(II) ions onto *Delonix regia* leaves, while, the Langmuir isotherm is better fitted to describe adsorption onto the pods.

#### 3.2.4 Adsorbent dose-dosage 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.

a)





**Figure 7.** Effect of adsorbent ~~dose~~ dosage (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; adsorbent dosage: 0.5 g; 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~~ shows a reduction in the uptake of both metal ions by each of the biomasses. 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 (Alegbe et al., 2019). Thus, as the concentration of sodium ion is increased metal uptake by the adsorbent was observed to be lower.

A comparison of the adsorption efficiency of different agricultural waste for Ni(II) and Cu(II) ions is presented in Table 3.

**Table 3.** Comparison of the amount of Ni(II) and Cu(II) ions removed by some agro-waste with the pods and leaves of *Delonix regia*

<u>Agricultural waste</u>	<u>Metal ion</u>	<u>Efficiency</u>	<u>References</u>
<u>Tea waste</u>	<u>Ni(II)</u>	<u>86%</u>	<u>Malkoc and Nuhoglu, 2005</u>
<u>Maple saw dust</u>	<u>Ni(II)</u>	<u>75%</u>	<u>Shukla et al., 2005</u>
<u>Sugarcane bagasse</u>	<u>Ni(II)</u>	<u>&gt; 80%</u>	<u>Garg et al., 2008</u>
<u>Banana peel</u>	<u>Ni(II)</u>	<u>78%</u>	<u>Olufemi and Eniolaodunmo 2018</u>
<u>Coconut shell</u>	<u>Ni(II)</u>	<u>75%</u>	
<u>Papaya wood</u>	<u>Cu(II)</u>	<u>95%</u>	<u>Saeed et al., 2005</u>
<u>Rice bran</u>	<u>Cu(II)</u>	<u>&gt;80%</u>	<u>Montanher et al., 2005</u>

### Groundnut seed cake

Sesame seed cake      Cu(II)      99.7%      Kumar et al., 2019

### Coconut cake

Spruce Sawdust      Cu(II)      >85%      Kovacova et al., 2019.

Delonix regia pods      Ni(II)      >80%

Delonix regia leaves      Ni(II)      >30%

Delonix regia pods      Cu(II)      >85%      This study

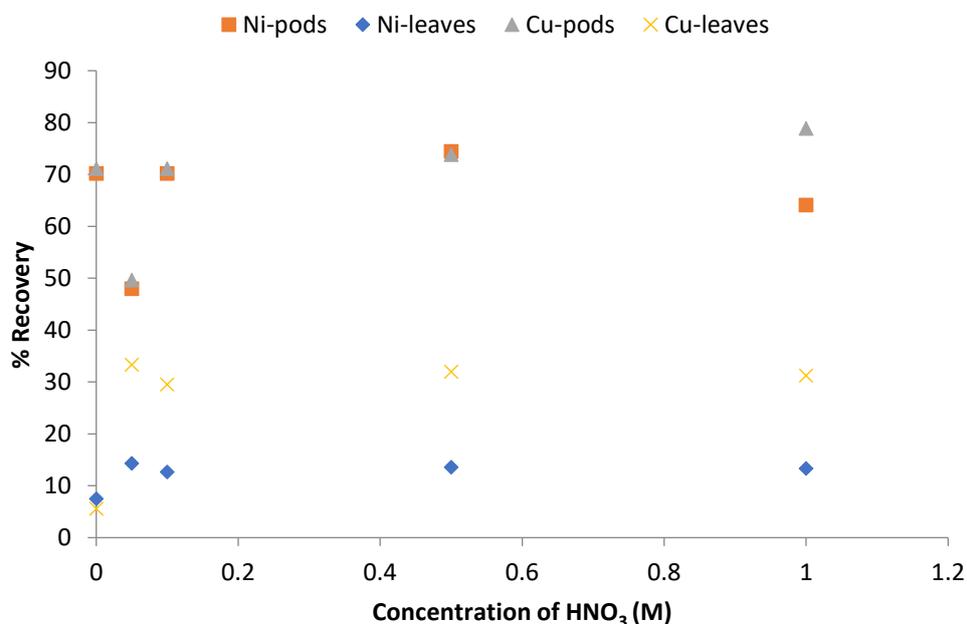
Delonix regia leaves      Cu(II)      >80%

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The results obtained from this study have shown that *Delonix regia* biomass compete favourably with other agricultural waste used in previous studies and hence, could be useful in removing Ni(II) and Cu(II) ions from aqueous solution.

### 3.3 Desorption Study

The regeneration of adsorbents after adsorption is of utmost importance, metal ions adsorbed should be easily desorbed under suitable conditions and the adsorbents should be repeatedly use to reduce the cost of the material. Thus, ~~The~~ recovery experiment was carried out to investigate the possibility of recovering the adsorbed metal ions from the biomasses. 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~~ showed that different percentages of metal ions were recovered at different concentrations of the desorbing ~~solution, medium.~~ The results also revealed that relatively low concentration of nitric acid (0.1 M) could be used to recover more than 50% of the metal ions from the pods. ~~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 was~~ 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 ~~were recovered from *Delonix regia* pods with 1.0 M nitric acid concentration, 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~~ ~~whereas~~, 14.3% Ni(II) ions and 33.3% Cu(II) ions ~~was were~~ recovered from the *Delonix regia* leaves with ~~the same concentration of 0.05 M~~ nitric acid (1.0 M). The recovery experiment showed that metal ions recovery increased with increasing concentration of nitric acid. ~~Moreover, *Delonix regia* biomass, most especially the pods could be repeatedly used in the removal of heavy metal without losing its adsorption properties.~~

#### 4. Conclusion

The study concerns the ~~application-use~~ 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-dosage~~ 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 ~~metal ions could be desorbed from spent *Delonix regia* and could be repeatedly used in the removal of heavy metal without losing its adsorption properties~~ ~~the recovery of the metal ions from the spend pods and leaves increased with increasing concentration of nitric acid. The pods performed better than the leaves in terms of the amount of metal ions removed and regeneration of the spent adsorbent.~~ ~~Thus~~ In conclusion, the powdered pods and leaves of *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. AOB and EOO were involved in the characterization of the adsorbent. COA, OSL and SFA were involved in the adsorption studies. OSA was involved in the modelling of the adsorption data and 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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