

# Sequestering of Ni (II) and Co (II) from Aqueous Solution Using Spines of *Bombax buonopozense* as Low-Cost Adsorbent

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**Abstract:** The release of potentially toxic elements either by anthropogenic or industrial activities has deteriorated water quality rendering water bodies unsuitable. It was on this basis that readily available agricultural waste was used to treat simulated wastewater containing the potentially toxic element (Ni and Co). Adsorption studies of Co and Ni from aqueous solution were performed using spines of *Bombax buonopozense* (raw), carbon prepared from *Bombax buonopozense* (AC<sub>1</sub>) and activated carbon prepared from modification of spines of cotton silk tree (AC<sub>2</sub>). Batch adsorption techniques were carried out as a function of contact time, pH, initial concentration, temperature, and dosage. The respective optimum contact times required for adsorption Co and Ni were 90 min. Characterizations of adsorbents were carried out which include: bulk density, hardness, electrical conductivity, ash contents, percentage moisture, and yield. Fourier transform infra-red spectroscopy (FTIR) showed that functional groups in the sorbents were responsible for the adsorption process. The adsorption isotherms data were tested for Langmuir, Temkin and Freundlich equations. The pseudo-first-order, pseudo-second-order, Elovich and diffusion (intra-particle) models were investigated on the adsorption kinetic data. This could be as a result of ion exchange involved in the sequestration of metal ions by the adsorbents. Therefore, sorption using spines of *Bombax buonopozense* has been adjudged as one of the best tools for replacing conventional methods for the removal of these metals because of its efficiency, cost-effectiveness and the availability of the adsorbents.

**Keywords:** Adsorption, Modification, Characterizations, FTIR, Elovich

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## 1. Introduction

Potentially toxic elements are individual metals and metal compounds that affect human when present in the environment at low levels. The rapid growth in human population and industries have led to the deterioration in water bodies of most under-developed and developing countries due to the unlawful discharged of industrial wastes and human anthropogenic activities. Thus, discharge of these pollutants into the aquatic environment damage the ecosystem making the water bodies

unsuitable for drinking purposes. This in effect, poses a severe health threat to the populace since most of them are toxic to living organisms due to their non-degradable nature [1]. Therefore, in industrial activities such as the discharge of industrial effluents, mining, and metallurgical operations have intensified environmental pollution problems with deterioration of several ecosystems [2]. The immense environmental impact of heavy metal pollution has been reported by Zouboulis *et al.* [3] that these metals are capable of causing both ecological and health damages. Due to their accumulation and transportation down the food chain, these

metals have caused problems such as dysfunction in the renal, reproductive and central nervous system [4]. They are also known for their ability to cause diseases and disorder [5].

Remediation of heavy metals in wastewater is very important with respect to environmental considerations [6]. Various approaches have been developed to remove these potentially toxic elements from industrial wastewater and these include precipitation, electrodialysis, membrane processes, ionic exchange and floatation [7]. Adsorption has emerged as a promising alternative to conventional technologies in water treatment plants (WTP). It is advantageous in terms of cost, flexibility, simplicity of design and ease of operation. It also does not result in the establishment of detrimental substances [8]. However, biosorption mechanisms remain unclear and hence required further studies. It was on this basis that this readily available and affordable agricultural waste known as the spine of *Bombax buonopozense* was used to treat wastewater containing the potentially toxic elements (Ni and Co), in

order to remedy our environment from the effect of these metals as well as improve the quality of water.

Recent studies on biosorption have shown that spines of *Bombax buonopozense* can be used in the removal of copper and zinc from wastewater [9]. In an effort to develop a useful user-friendly, eco-friendly and low cost-effective, the present study was taken up. This study examined the adsorption of Co (II) and Ni (II) ions using spines of this plant.

## 2. Materials and Methods

### 2.1. Preparation and Characterization of Biosorbent

The low-cost adsorbents used in this study were derived from the spines of *Bombax buonopozense* (silk cotton tree). The samples obtained from farms in Bosso Local Government, Niger State, Nigeria, where they are generated as primary agricultural waste. Figure 1 described the sample trees of silk cotton trees.



Figure 1. Diagrams of *Bombax buonopozense* (red flower silk cotton trees).

These were washed to remove debris and other particulate matter that might interact with sorbed metal ions. They were washed with distilled water, sun-dried, ground and they sieved to a particle size of 200  $\mu\text{m}$ . The materials after sieving were divided into: the first part was labeled 'Raw', the second portion was charred in a muffle furnace for 15 min at 500°C ( $\text{AC}_1$ ). This was cooled and washed with deionized water. The third portion was carbonized as mentioned above and then washed with benzoic acid ( $\text{AC}_2$ ). The percentage yield of the adsorbent was calculated using:

$$\% \text{ Yield} = \frac{W_o - W_c}{W_o} \times 100 \quad (1)$$

Where  $W_o$  is the mass of material before carbonization and  $W_c$  is the mass of material after carbonization. The physicochemical characteristics of the adsorbents were measured using standard procedures.

### 2.2. Preparation of Metal ion Concentration

A stock solution of 1000  $\text{mg/dm}^3$  concentration were prepared by dissolving appropriate amounts of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  in distilled water to obtain standard Co and Ni respectively. Standard solutions concentration were prepared by serial dilution of the respective stock solutions.

### 2.3. Batch Adsorption Studied

Effect of four parameters on the adsorption of the metal ions in solutions was considered and these were contact time, dosage, metal ion concentration and pH. The experiments were performed at constant shaking for the optimum time. The solutions were filtered and the filtrates were analyzed by atomic absorption spectroscopy (AAS) for residual metal concentrations. The percentage removal and adsorption capacity were calculated as follows:

$$\text{Adsorption (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

$$q_e = \frac{C_i - C_e}{M} \times V \quad (3)$$

Where  $C_i$  is initial concentration of metal ions in the solution ( $\text{mg/dm}^3$ ),  $C_e$  is the final concentration of metal ions in the solution ( $\text{mg/dm}^3$ ),  $V$  is the initial volume of metal ion solution used ( $\text{dm}^3$ ) and  $M$  is the mass of adsorbent (g).

## 2.4. Adsorption Isotherms

Adsorption isotherms were used to describe the equilibrium adsorptive behaviours and to investigate the adsorption mechanism using Langmuir and Freundlich isotherm equations.

$$\text{Langmuir: } \frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{1}{Q_m} C_e \quad (4)$$

$$\text{Freundlich: } \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

Where  $C_e$  is the equilibrium concentration ( $\text{mg/dm}^3$ ),  $q_e$  is the amount ( $\text{mg/g}$ ) adsorbed at equilibrium time,  $Q_m$  and  $K_L$  are Langmuir constants related to adsorption capacity ( $\text{mg/g}$ ) and energy of adsorption ( $\text{L/mg}$ ) respectively.  $K_F$  and  $n$  are Freundlich constants describing the adsorbent and favourability of adsorption respectively.

The Temkin isotherm model predicts that the heat of sorption decreases with the coverage as a result of the adsorbate-adsorbent interaction and the equation is expressed as:

$$q_e = a + B_T \ln C_e \quad (6)$$

$$B_T = \frac{RT}{b_T} \quad (7)$$

Where  $a$  is the Temkin isotherm constant,  $b_T$  ( $\text{kJmol}^{-1}$ ) is a constant related to the heat of sorption and  $R$  ( $8.314 \text{ Jmol}^{-1}\text{K}^{-1}$ ) is the gas constant.

## 2.5. Adsorption Kinetics

The kinetic models applied for the adsorption of the adsorbents in this study were:

$$\text{Pseudo - first - order: } \ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

$$\text{Pseudo - second - order: } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

Where  $q_e$  and  $q_t$  are the amount adsorbed at equilibrium at a time,  $t$ , while  $k_1$  and  $k_2$  are the pseudo-first-order rate constant ( $\text{min}^{-1}$ ) and the second-order reaction rate equilibrium constant ( $\text{g/mgmin}$ ) respectively.

The kinetic data were analyzed by an intra-particle diffusion model to explain the diffusion mechanism using the equation stated below:

$$q_t = K_{id} \sqrt{t} + I \quad (10)$$

Where  $K_{id}$  ( $\text{mg/gmin}^{1/2}$ ) is the intra-particle diffusion rate constant and  $I$  ( $\text{mg/g}$ ) is the constant that gives the thickness of the boundary layer.

The Elovich kinetic equation which is as given below was

also employed to explain the adsorption pattern in this study. i.e

$$q_t = \alpha + \beta \ln t \quad (11)$$

Where  $q_t$  is the sorption capacity ( $\text{mg/g}$ ) at time  $t$ ,  $\alpha$  and  $\beta$  were constant during the study all through. The  $\alpha$  was regarded as the initial rate.

## 2.6. Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

The finely powdered adsorbents were encapsulated with potassium bromide to prepare translucent sample disk, and the spectra were recorded using FTIR (Shimadzu, Japan 2010).

## 3. Results and Discussion

### Physicochemical properties of the adsorbents

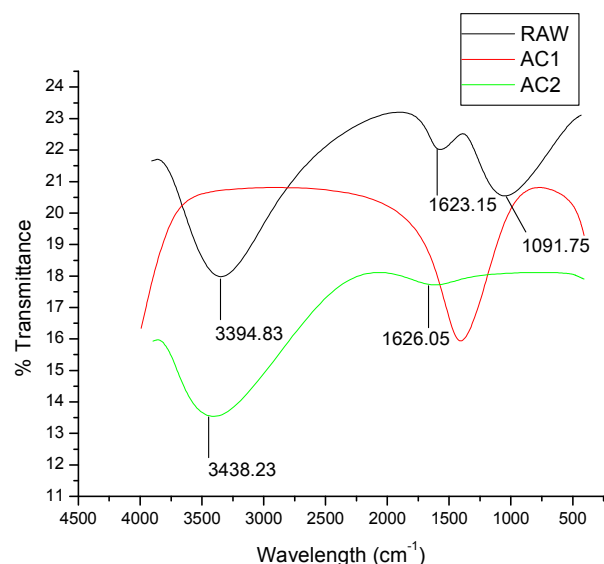
The electrical conductivity (EC), bulk density, moisture, ash, percentage yield and hardness of the raw, activated and modified adsorbents were recorded and are presented in 'Table 1'. The carbonized sample ( $AC_1$ ) recorded the highest bulk density ( $0.94 \text{ g/cm}^3$ ) which is an important characteristic adsorbent. The EC of the raw sample was the highest followed by carbonized ( $AC_1$ ) and activated ( $AC_2$ ). The low conductivity value of the acid activated adsorbent is an indication that the adsorbent removal by the adsorbent could be predominantly by physisorption rather than chemisorption. The hardness of the adsorbent is a significant feature for understanding the relative loss during transportation, regeneration and handling of sorbent. The raw adsorbent had the highest hardness followed by  $AC_2$  while  $AC_1$  had the lowest value. This observation conformed to the finding made by Seshadri *et al.* [10]. The percentage of hardness observed for a particular adsorbent depends on its density [11]. The lower yield of the acid activated adsorbent than the carbonized form might have been as a result of the release of the volatile compounds to the surroundings and the release of these volatile materials might have been the probable reason for pore size development. The ash content which is the mass of incombustible material remaining after burning a given substance as a percentage the original mass for the adsorbents indicated that the acid treated sample had the highest value followed by that of the carbonized sample while the raw sample had the lowest. The acid treated sample, however, had the lowest moisture content while the raw sample had the highest.

Table 1. Physicochemical properties of the adsorbents.

Parameter	Adsorbent		
	Raw	$AC_1$	$AC_2$
Bulk density ( $\text{g/cm}^3$ )	0.48	0.94	0.80
Moisture (%)	7.00	2.50	2.20
Ash (%)	3.20	4.45	7.20
Yield (%)	-	89.00	74.00
Conductivity ( $\mu\text{S/cm}$ )	320.56	172.23	160.11
Hardness (%)	10.30	8.14	9.20

### Infra-red spectroscopy (FT-IR)

The infra-red spectra for raw, carbonized (AC<sub>1</sub>) and activated (AC<sub>2</sub>) adsorbents are shown in Figure 2. The large and intense peaks around 3000-3800 cm<sup>-1</sup> can be attributed to the hydroxyl -OH and NH groups deformation. This shows that these groups are present in these adsorbents. The broad and intense -OH absorption band in the raw adsorbent might be due to the presence of water. Other possible functional groups in the adsorbents are the ketone, aldehyde or carboxylic acid group as indicated by the C=O stretching, the C≡N stretching at bandwidth 2350-2365 cm<sup>-1</sup> and the aromatic or carbonyl C=C bonds that showed absorption between 1623-1626 cm<sup>-1</sup> for the raw and activated samples. For also, the ester, ether or phenolic groups could be present in the raw and activated sample since absorption due C-O-C twist were observed between 1050 and 1091 cm<sup>-1</sup>. These could also contain the OH or phenolic groups since absorption were observed between 407 and 479 cm<sup>-1</sup> which could be due to C-O-H bond twisting. Similar results were recorded by Hu *et al.* [12]; Seshadri *et al.* [10].



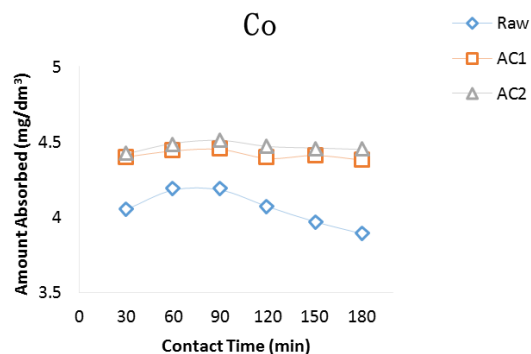
**Figure 2.** FT-IR spectra of raw, carbonized and activated adsorbent of spines of *Bombax. buonopozense* before adsorption.

### Batch Studies

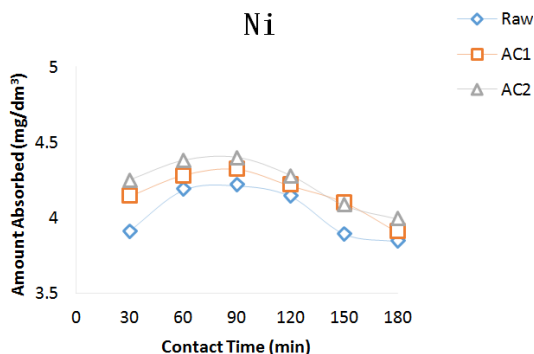
#### Effect of contact time

The rate of adsorption is significant to establish the time dependence under various conditions designing batch adsorption experiments. In this study, the adsorption of cobalt and nickel increased with contact time until it attained the maximum adsorption equilibrium at 90 min for the raw, carbonized and activated adsorbents as shown in Figure 3 and 4. These results showed that the adsorption process was fast due to large amounts of metal ions attached to the adsorbents within the first 90 min. The initial fast adsorption rate could be as a result of sufficient surface vacant sites on the substrates. The optimum time for cobalt and nickel obtained in this study corresponded to the findings of Muthusamy *et al.* [13]. The higher and the

decrease below the optimum time in the removal of metal ions could be due to the availability of large surface area of the adsorbents and repulsive forces between the solute molecules and the bulk phase respectively [14]. The decreased in the rate of adsorption could be due to the longer diffusion process of these ions into the inner cavities of the solutions [15]. Furthermore, an increase in the contact time resulted in the desorption of the metal ions from the adsorbent surfaces.



**Figure 3.** Effect of contact time on the removal of cobalt ions using 0.5 g adsorbent's weight, pH 6 at temperature 28°C±1 and a 5 mg/dm<sup>3</sup> cobalt solution.



**Figure 4.** Effect of contact time on the removal of nickel ions using 0.5 g adsorbent's weight, pH. 6.9 at temperature 28°C±1 and a nickel standard solution of 5 mg/dm<sup>3</sup> cobalt.

#### Effect of initial concentration

Studies were performed with cobalt and nickel concentrations ranging from 10 to 50 mg/dm<sup>3</sup>. Figure 5 and 6 show that the removal of cobalt and nickel initially depended on the initial concentrations of metal ions which decreased with increase in the initial concentration. According to Arief *et al.* [16], the initial concentration acts as driving force that transport metal ions between the adsorbate and the surface of the adsorbents. Hence, at higher concentration, the metal ions are left unabsorbed due to saturation of adsorption site which leaves the amount of sorbate concentration constant [17]. This is as a result of an increase in a number of ions competing for the available binding site or inadequate availability of adsorption sites on the adsorbent at high concentrations. This means that there are more adsorption sites on the sorbent at low concentration of the metal ion than at higher concentration. As the surface of adsorption to metal ion concentration decrease with a rise in metal ion



concentration, the amount of metal ion removed is reduced and this is what was observed in this study. This could be as a result of the aggregation of the adsorbent particle at higher concentrations which led to an increase in the diffusional path length and decrease in the surface area of the adsorbent particle available for adsorption [18].

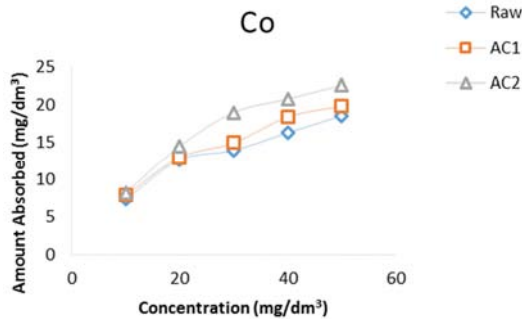


Figure 5. Effect of metal ion concentrations on the removal of cobalt ions at 90 min contact time, pH 6.9 and adsorbent dosage of 0.5 g.

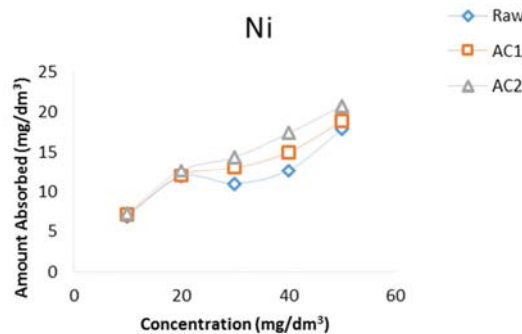


Figure 6. Effect of metal ion concentrations on the removal of nickel ions at 90 min contact time, pH 6.9 and adsorbent dosage of 0.5 g.

#### Effect of pH

The effect of solution pH on Co (II) and Ni (II) ions removal are presented in Figures 7 and 8. The pH of an aqueous solution is a parameter that has a great effect in the adsorption process. This is due to the fact that hydrogen ion ( $H^+$ ) are strong competing ions which impact the chemical speciation of the functional groups onto the adsorbent surface. At low pH, low adsorption rate was observed since high concentration of  $H^+$  ions compete with the free metal cations in aqueous solution for the surface sites. The strong function of the pH is as a result of surface charges on the adsorbents. Therefore, heavy metal cations are completely released in acidic conditions. Low electrostatic repulsion interaction between the metal ions and the surface of adsorbents due to the deprotonation of the functional groups on the adsorbents gave an insight of reduction in positive surface charges [19]. The high sorption levels at high pH values (high percentage removal) indicated that strong affinity for metal ions occurred in this pH region. The complete removal of positively charged metal ions increases as a result of the availability of more ligands having negative charges. Similar trends have been reported by Rozaini *et al.* [20] who stated that rise in pH usually results in increased metal ions sorption and decrease in their solubilities.

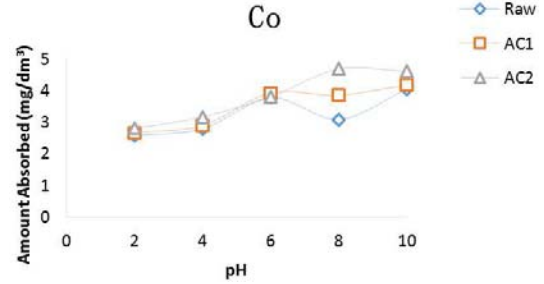


Figure 7. Effect of pH on the removal of cobalt ions from 5 mg/dm³ standard solution and 0.5g. adsorbent's weight.

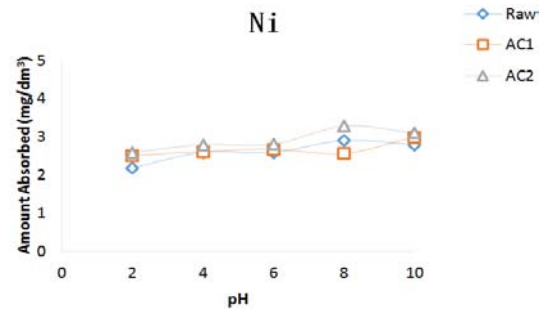


Figure 8. Effect of pH on the removal of nickel ions from 5 mg/dm³ standard solution and 0.5g adsorbent's weight.

#### Effect of adsorbent dosage

Effect of adsorbent doses on amounts of metal absorbed are shown in Figure 9 and 10. Amounts of metal ions removal increased when the adsorbent dose increase from 1 to 3.5 g. The availability of large surface area due to the presence of functional groups on the adsorbent with which the metal ions interacted caused an increase in adsorption with an increase in sorbent dosage. These functional groups are important in the formation of London Vander Waals bonding since they play major roles in binding the metal ions to the adsorbents [21]. According to Aksu and Cagatay [22] who stated that lower sorbent dosages yield higher uptake but lower percentage removal efficiencies. This is applicable to this study which showed that higher percentage removal of metal ions at different dosages increased with increase in adsorbent dosage. This is as a result of the increase in the remains unsaturated as the available adsorption sites. These observations are in line with the report made by Khosravan and Lashkari [23].

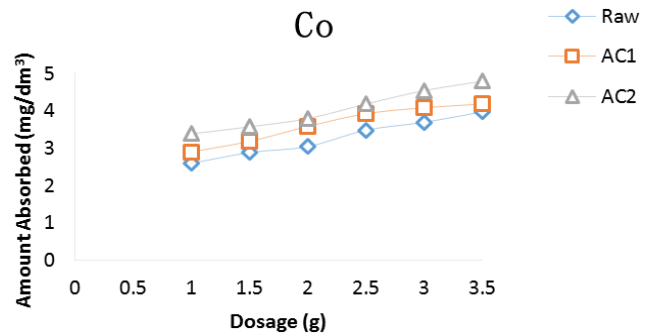
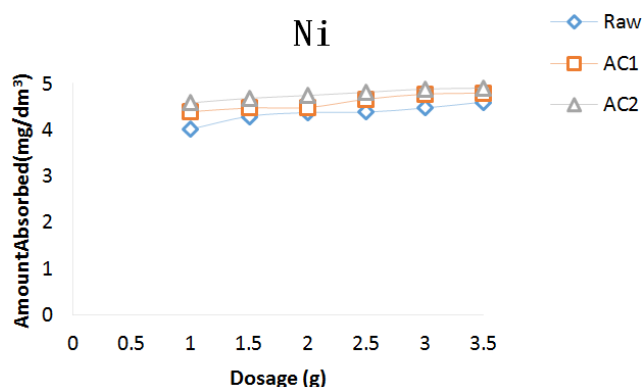


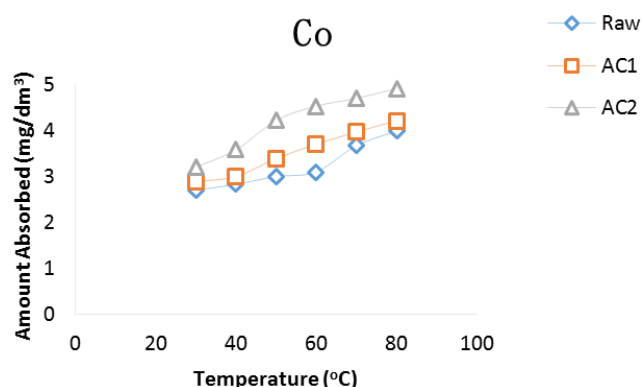
Figure 9. Effect of adsorbent dose on the removal of cobalt ions from 5mg/dm³ standard solution at contact time 90 min and pH 6.9.



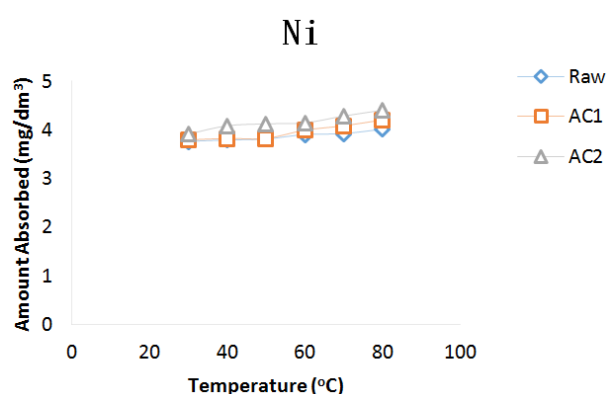
**Figure 10.** Effect of adsorbent dose on the removal of nickel ions from 5 mg/dm<sup>3</sup> standard solution at contact time 90 min and pH 6.9.

#### Effect of temperature

Figures 11 and 12 show that there is a gradual increase in the removal of the metal ions. The results show that the adsorption process is considered to be endothermic when an increase in temperature leads to increase in both adsorption sites and amounts of adsorbed samples. The increase in absorption with temperature could be attributed to the desolvation of the adsorbing species and decrease in the mass transfer resistance of the adsorbent in the boundary layer surrounding the adsorbent with temperature. High temperature augments sorption due to increased surface activities and kinetic energy of the solutes [24]. Since the adsorbent used were permeable in nature and there are possibilities of diffusion of the sorbates, increase in the removal of metal ions in the sorption rate with rising in temperature could be as a result of diffusion controlled sorption process which is endothermic in nature. Thus, the increase in temperature would favour the transportation of the adsorbate during the sorption process. The strong adsorption could also be attributed to a strong adsorptive force among the available sites of the sorbents, adsorbates, and adjacent molecules on the adsorbed phases. This is in concordance to the study of Buasri *et al.* [25] that worked on water hyacinth as a low-cost sorbent.



**Figure 11.** Effect of temperature on the removal of cobalt ions at 90 min contact time and pH value of 6.9 using 5 mg/dm<sup>3</sup> standard solution.



**Figure 12.** Effect of temperature on the removal of nickel ions at 90 min contact time and pH value of 6.9 using 5 mg/dm<sup>3</sup> standard solution.

#### Adsorption isotherms

##### Freundlich

Equilibrium isotherm studies were piloted for the removal of cobalt and nickel ions from the solution of concentrations ranging from 10 to 50 mg/dm<sup>3</sup> by raw, carbonized and activated adsorbents. The isotherm parameters shown in Table 2 reveals that the Freundlich isotherm coefficient and constant,  $n$  and  $K_F$  respectively. The Freundlich constant,  $K_F$ , for the adsorbents, were in the range of 0.40 to 0.56 which are lower than the values reported by Ahalya *et al.* [26] and Krishna [27]. The biosorption intensity  $n$  is indicative of the bond energies between the metal ions and the adsorbents which showed a possibility of physisorption and slight chemisorption. The values of  $n$  were between 2 and 10 which are indications of good adsorption of cobalt and nickel by the spines of *Bombax buonopozense* which correlates with the findings of Nagarajan *et al.* [28]. These high correlation coefficients suggest that this model is the best that describes these equilibria obtained in this study.

##### Langmuir

The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases that describe the formation of a monolayer of adsorbate on the outer surface of the adsorbent. The maximum adsorption capacity,  $Q_m$ , values for the investigated metal ions were in the range of 1.90 to 2.91 mg/g which are slightly higher than the values reported by Jimoh *et al.* [29], Selvarani and Prema [30] and Li *et al.* [31] for akee apple seed, starch and modified areca waste respectively.

**Table 2.** Adsorption isotherm parameters for Co (II) and Ni (II) removal by spines *Bombax buonopozense*.

Isotherm	Parameter	Co (II)			Ni (II)		
		Raw	AC <sub>1</sub>	AC <sub>2</sub>	Raw	AC <sub>1</sub>	AC <sub>2</sub>
Freundlich	$K_F$ (mg/g)	0.56	0.50	0.44	0.41	0.4	0.4
	$n$	2.67	2.91	2.87	3.24	2.75	2.42
	$R^2$	0.959	0.984	0.955	0.774	0.94	0.965
Langmuir	$Q_m$ (mg/g)	2.26	2.56	3.18	1.90	2.30	2.91
	$K_L$ (L/mg)	2.24	0.89	0.27	0.46	0.36	0.23
	$R^2$	0.979	0.985	0.917	0.775	0.915	0.946
Temkin	$a$	0.279	0.343	0.42	0.143	0.201	0.362
	$B_T$	0.33	0.354	0.426	0.415	0.338	0.27
	$b_T$ (kJ/mol)	6.876	6.41	5.327	5.469	6.715	8.406
	$R^2$	0.962	0.975	0.99	0.942	0.901	0.697

The calculated Langmuir separation factors ( $R_L$ ) at different initial Co (II) and Ni (II) concentrations as shown in Fig. 13 and 14 respectively were in the range of 0 to 1 in the experimental isotherm, which confirms the favourable uptake of the two metal ions and lower  $R_L$  values at higher initial metal ion concentrations showed that the adsorption processes were more favourable at higher concentrations [32]. A similar report was made by Yao *et al.* [33] on the adsorption of Cu (II) onto the chestnut shell.

$$R_L = \frac{1}{1 + K_L C_0} \quad (12)$$

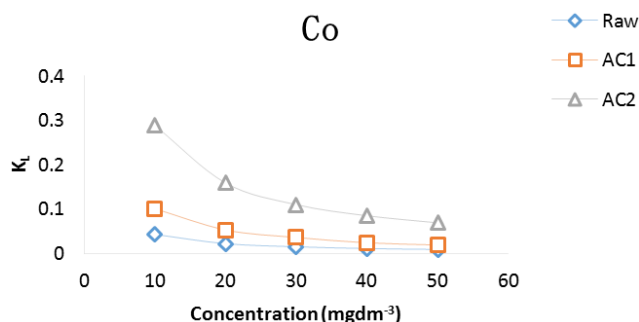


Figure 13. The separation factors of Co (II) ions on the sorbent (0.5 g adsorbent) at pH of 6.9.

#### Kinetic studies

##### First-order

The values of first-order rate constant  $k_1$  and adsorption capacity  $q_e$  for the metal ions are shown in Table 3. The correlation coefficient for the sorption of these ions ranged from 0.02-0.685 which does not fit the adsorption pattern of Co (II) and Ni (II) ions. According to Ho and Mackay [35], the major drawback with the first-order model is that in most cases, the equations does not fit well with experimental data over the entire range of contact times.

Table 3. Kinetic parameter for Co (II) and Ni (II) adsorption onto spines of *Bombax buonopozense*.

Kinetic	Parameter	Co (II)			Ni (II)		
		Raw	AC <sub>1</sub>	AC <sub>2</sub>	Raw	AC <sub>1</sub>	AC <sub>2</sub>
First-order	$q_e$ (mg/g)	0.314	0.314	0.276	0.266	0.297	0.262
	$k_1$	0.0001	0.001	0.001	0.001	0.001	0.001
	$R^2$	0.08	0.685	0.498	0.188	0.429	0.02
Second-order	$q_e$ (mg/g)	0.044	0.058	0.095	0.099	0.092	0.093
	$k_2$	5.584	1.054	0.444	0.362	0.309	0.222
	$R^2$	0.993	0.975	0.946	0.882	0.858	0.819
Elovich	$\alpha$	0.007	0.004	0.001	0.003	0.008	0.011
	$B$	0.042	0.031	0.047	0.001	0.030	0.010
	$R^2$	0.251	0.351	0.077	0.037	0.194	0.321
Intra-particle	$K_{id}$ (mg/gmin <sup>1/2</sup> )	0.002	0.001	0.001	0.001	0.002	0.003
	$I$	0.055	0.038	0.043	0.064	0.044	0.31
	$R^2$	0.371	0.481	0.021	0.093	0.31	0.453

##### Second-order

The rate constant,  $k_2$ , the  $R^2$  and  $q_e$  values for the study are given in Table 3, showing that the correlation coefficient,  $R^2$ , values from the second order kinetics for these cobalt and nickel ions are high indicating that the pseudo-second-order-kinetic model provides a good correlation for their biosorption onto the spines of *Bombax buonopozense*. This corresponds to the studies of Ramachandra and Surya [36] and Ejikeme *et al.* [37] on the adsorption of heavy metal onto shorea Robustus leaf litter and fluted pumpkin shell

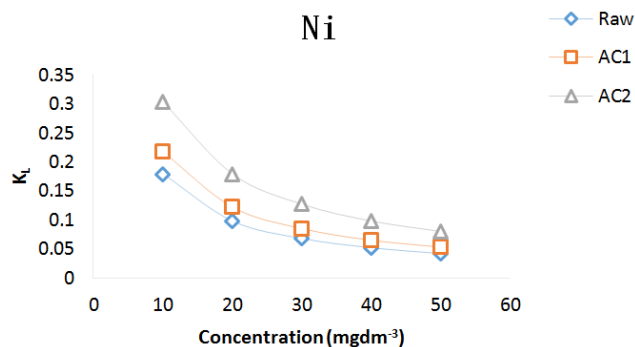


Figure 14. The separation factors of Ni (II) ions on the sorbent (0.5 g adsorbent) at pH of 6.9 Temkin isotherm.

The constant  $b_T$  indicates the heat of adsorption and  $a$  is the Temkin constant which represents the maximum binding energy. The Temkin constant,  $t$ ,  $b_T$ , relate to the heat of sorption for the metal ions range from 5.33 kJmol<sup>-1</sup> to 6.88 kJmol<sup>-1</sup> and 5.50 to 8.41 kJmol<sup>-1</sup> for cobalt and nickel respectively. According to Ho *et al.* [34] the typical range of binding energy for an ion-exchange mechanism is 8-16 kJmol<sup>-1</sup> which indicates a weak interaction between the adsorbate and adsorbent.

respectively.

##### Elovich equation

The  $\alpha$  and  $\beta$  constants in the Elovich equation are obtained from the intercept and slope respectively. The  $\alpha$  is related to the rate of chemisorption while  $\beta$  is related to the surface coverage. The correlation coefficient  $R^2$  of Elovich equation for the raw, activated and modified adsorbent range from 0.077 to 0.352 which are found to be the least when compared to the pseudo-first-order and second-order kinetic equations. The obtained experimental values show that

Elovich equation is not the model fit for the kinetics of the adsorption of these metals to the adsorbents in this study since the application of Elovich equation in adsorption process is only an alternative for the kinetic study of adsorption of gases onto solids [38].

#### Intraparticle diffusion

The intraparticle diffusion coefficient for the adsorption of Co (II) and Ni (II) on the raw, carbonized (AC<sub>1</sub>) and modified (AC<sub>2</sub>) samples were calculated from the plots of  $q_e$  against  $t^{1/2}$  (min<sup>1/2</sup>). In this study, film, intraparticle and pore diffusion are involved in which intraparticle diffusion controlled the batch experiment for the contact time employed. According to Badmus *et al.* [39], intraparticle transport is not the only limiting step but also differentiate rates of mass transfer in the initial from final mechanisms of the adsorption. The value of  $K_{id}$  at zero (0) shows that there is a possibility of pore diffusion.

## 4. Conclusion

The ability of spines of *Bombax buonopozense* adsorbents to remove Co (II) and Ni (II) from aqueous solution were investigated using equilibrium and kinetics studies. The percentage removals of two ions were found to depend on pH, adsorbent dosage, contact time, concentration and temperature. The equilibrium data agreed well with Freundlich isotherm which is suitable for a highly heterogeneous surface indicating a multi-layer adsorption. The kinetic data were found to follow the pseudo-second-order model and the low values of intraparticle diffusion obtained are likely due to the size of the metal ions involved and the nature of the modifying agent. This investigation showed that the spines of this plant are promising sorbent for the removal of Co (II) and Ni (II) from aqueous solutions. Hence, *Bombax buonopozense* commonly known as silk cotton tree will be of low cost but high economic value when employed as a natural product for adsorption of pollutants from aqueous solutions.

## References

- [1] Abowei JFN, Sikoki FD. Water Pollution Management and Control. Double trust Publication Company, 2005. p. 236 Port Harcourt.
- [2] Mustapha, S, Dauda, BEN, Ndamitso, MM, Mathew, TJ, Bassey U Muhammed S.S (2014). Biosorption of Copper from Aqueous Solutions by Raw and Activated Spines of *Bombax buonopozense*: Equilibrium, Kinetics and Thermodynamic Studies. *International Res J Pure Appl Chem* 2014;4(6):886-903.
- [3] Zouboulis AI, Loukidou MX, Matis KA. Biosorption of toxic metals from aqueous solutions by bacteria strain isolated from metal polluted soils. *Proc Biochem* 2004; 39: 909-916.
- [4] Manaham SE. Environmental Chemistry. CRC Press India. 8<sup>th</sup> edition. p. 71.
- [5] Ozer, A., and Pirincci, H. B. The adsorption of Cd (II) ions on sulphuric acid-treated wheat bran. *J Hazardous Mater* 2006; 137 (2): 849-855.
- [6] Nourbakhsh, M., Kilic, S., Arslan, I. S., and Ozdag, H. Biosorption of Cr<sup>+6</sup>, Pb<sup>2+</sup> and Cu<sup>2+</sup> ions in industrial wastewater on *Bacillus* sp. *Chem Eng J* 2002; 85: 352-355.
- [7] Xiaomin L, Yanru T, Zhexian X. Study on the preparation of orange peels cellulose adsorbents and biosorption of Cd<sup>2+</sup> from aqueous solution. *J Separat Purif Tech* 2004; 55: 69-75.
- [8] Rafattullah M, Sulaiman O, Hashim R, Ahmad A. Adsorption of methylene blue on low-cost adsorbents: a review. *J Hazardous Mater* 2010; 177: 70-80.
- [9] Mustapha S, Dauda BEN, Iyaka YA, Mathew TJ, Aliyu IA, Shaba EY. "Removal of Heavy Metals from Aqueous Solutions by Modified Activated Carbon from *Bombax buonopozense*." *Inter J Eng Sci Invention* 2014; 3 (8): 17-24.
- [10] Seshadri S, Sugumaran P, Susan PV, Ravichandran P. Production and characterization of activated carbon from banana empty fruit bunch and Delonix regia fruit pod. *J Sust Energy Envi* 2012; 3: 125-132.
- [11] Bansode RR, Losso JN, Marshall WE, Rao RM, Portier RJ. Adsorption of metal ions by pecan shell-based granular activated carbons. *Bioresour Techn* 2003; 89 (2): 115-119.
- [12] Hu YS, Malarvizhi R, Sulochana N. Equilibrium isotherm studies of methylene blue adsorption activated carbon prepared from Delonix regia pods. *J Environ Prep Sci* 2009; 3: 111-116.
- [13] Muthusamy P, Murugan S, Manothi, S. Removal of Nickel ion from industrial wastewater using maize cob. *J Biol Sci* 2012; 1 (1): 7-11.
- [14] Saravanane R, Sundararajan T, Sivamurthyreddy S. Efficiency of chemically modified low cost adsorbents for the removal of heavy metals from wastewater. A comparative study. *Indian J Environ Health* 2002; 44: 78-81.
- [15] Li X, Zheng W, Wang D, Yang Q, Cao J, Yue X, Shen T, Zheng G. Removal of Pb (II) from aqueous solution by adsorption onto modified areca waste: kinetic and thermodynamic studies. *Desalination* 2010; 258: 143-153.
- [16] Arief VO, Trilestari K, Sunarso J, Indraswati N, Ismadji S. Recent Progress on Biosorption of Heavy Metals from Liquids Using Low Cost Biosorbent Characterization, Biosorption Parameter and Mechanism Studies. *CLEAN-Soil, Air, Water* 2008; 36: 937-962.
- [17] Krishnan KA, Anirudhan TS. Removal of cadmium (II) from aqueous solution by steam activated sulphurised carbon prepared from sugar-cane bagasse pith: kinetic and equilibrium studied. *Water S. A (Pretoria)* 2003; 29 (2).
- [18] Yasemin B, Tez Z. Adsorption studies on groundshells of hazelnut and almond. *J Hazardous Mater* 2007; 149 (1): 35-41.
- [19] El-Said AG. Biosorption of Pb (II) ions from aqueous solution onto rice Husk and its Ash. *J American Sci* 2010; 6 (10): 143-150.
- [20] Rozaini CA, Jain K, Oo CW, Tan KW, Tan LS, Azraa A, Tong KS. Optimization of nickel and copper ions removal by modified Mangrove Barks. *International J Chem Eng Appl* 2010; 1: 84-88.



- [21] Malik R, Ramteke DS, Wate SR. Adsorption of malachite green on groundnut shell waste based powdered activated carbon. *Waste Manag* 2007; 27: 1129-1138.
- [22] Aksu Z, Catgatay SS. Investigation of biosorption of Gemazol Turquoise blue-G reactive dye by dried *Rhizopus arrhizus* in batch and continuous system. *Sep Purif Technol* 2006; 48: 24-35.
- [23] Khosravan A, Lashkari B. Adsorption of Cd (II) by dried activated sludge. *Iranian J Chem Eng* 2011; 8 (2): 41-56.
- [24] Meulepas MA, Lens RJ Removal of heavy metals and cyanide from gold mine wastewater. *J Chem Technol Biotechnol* 2010; 85: 590-613.
- [25] Buasri A, Chaikut N, Tapang K, Jaroensin S, Panphrom S. Biosorption of heavy metals from aqueous solutions using water Hyacinth as a low cost biosorbent. *Civil Environ Res* 2012; 2 (2): 17-24.
- [26] Ahalya N, Ramachandra TV, Kanamadi RD. Biosorption of Heavy Metals. *Res J Chem Environ* 2004; 7 (4): 71-79.
- [27] Krishna RH. Comparative Studies of isotherm and kinetics on the adsorption of Cr (VI) and Ni (II) from Aqueous Solutions by Powder of Mosambi Fruit Peelings. *Inter Res J Pure Appl Chem* 2014; 4: 26-45.
- [28] Nagarajan P, Elezabeth DV, Isaiah S. Removal of chromium (VI) using *pitchellobium dulce* benth-A kinetic study. *Indian J. Environ Protection* 2006; 26 (1): 30-38.
- [29] Jimoh OT, Ndamitso MM, Aliyu IB, Olakunle OS. Equilibrium and Isotherm studies of the biosorption of potentially toxic elements from aqueous solution by *Blighia sapida* (Akee apple) seeds. *Inter J Advan Res Technol* 2013; 2 (3): 1-12.
- [30] Selvarani M, Prema P. Removal of toxic metal Hexavalent Chromium from aqueous solution using starch – stabilized nanoscale zerovalent iron as adsorbent: Equilibrium and kinetics. *Inter J Environ Sci* 2012; 2 (4): 1962-1975.
- [31] Li X, Zheng W, Wang D, Yang Q, Cao J, Yue X, Shen T, Zeng G. Removal of Pb (II) from aqueous solution by adsorption onto modified areca waste: kinetic and thermodynamic studies. *Desalination* 2010; 258: 143-153.
- [32] Hall KR, Eagleton LC, Acrivos A, Vermeulen T. Pore and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. *Ind. Eng. Chem. Fund* 1966; 5 (2): 212-223.
- [33] Yao B, Gueu S, Adouby K, Ado G. Kinetic and thermodynamic study of lead adsorption on to activated carbons from coconut and seed hull of the palm tree. *Inter J Environ Sci Technol* 2007; 4 (1): 11-17.
- [34] Ho YS, Wase DAJ, Forster CFT. 'Batch Nickel Removal from Aqueous Solution by Sphagnum Moss Peat'. *Water Res* 1995; 29: 1327-1332.
- [35] Ho YS, Mckay G. Pseudo-second order model for sorption processes. *Proc Biochem* 1999; 34: 451-465.
- [36] Narayan SD, Ramachandra MV. Preparation of Carbonaceous Heavy Metal Adsorbent from Shorea Robusta Leaf Litter Using Phosphoric Acid Impregnation. *Inter J Environ Sci* 2010; 1 (3): 296-313.
- [37] Ejikeme PM, Okoye AI, Onukwuli OD. Kinetic and isotherm studies of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions removal from simulated wastewater by Gambeya albida seed shell activated carbon. *Afr. Rev. Phy* 2011; 6: 143-152.
- [38] Ritchie AG. Alternative to the Elovich equation for the kinetics of adsorption of gases on solids. *J Chem Soci, Faraday Trans.* 1977; 73: 650-1653.
- [39] Badmus O, Audu K, Anyata U. Removal of Lead Ion from Industrial Wastewater by activated Carbon Prepared from Periwinkle Shells (*Typanotonus fuscatus*). *Turkish J Eng Environ Sci* 2007; 31: 251-263.