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## Decontamination of Ni(II) and Co(II) ions from Aqueous Medium using the Cola *Lepidota* Pericarp

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### Cover Page Footnote

The authors would like to sincerely acknowledge Chemical Engineering Laboratories, Ahmadu Bello University, Zaria, for providing laboratory facilities, and the Department of Pure and Industrial Chemistry, University of Port Harcourt for the laboratory equipment used during this research work.

## Decontamination of Ni(II) and Co(II) ions from Aqueous Medium using the *Cola lepidota* Pericarp

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### Abstract

In this study, the batch adsorption of Ni(II) and Co(II) ions was investigated by using the pericarp of *Cola lepidota* as the adsorbent. The pulverized sample was modified using sodium hydroxide. In addition, the effects of pH, particle size, contact time, temperature, and initial concentration on adsorption were investigated. Results revealed that maximum adsorption of metal ions are observed at pH of 6, a contact time of 60 min, and a temperature of 70 °C. In addition, modification was to considerably impact the effectiveness of the adsorbent. The percentage removal of the metal ions on the modified (MCLR) and unmodified adsorbents (UCLR) followed increasing order of Co(II) ion on UCLR < Ni(II) ion on UCLR < Co(II) ion on the NaOH-modified adsorbent < Ni(II) ion on the NaOH-modified adsorbent. Equilibrium data were analyzed by the Langmuir and Freundlich isotherm models, and kinetic studies were carried out using pseudo-first-order and pseudo-second-order models. The adsorption data were well fitted to the Freundlich isotherm model equation, with correlation coefficient ( $R^2$ ) values greater than 0.950, and the pseudo-second-order kinetic model, with correlation coefficient ( $R^2$ ) values greater than 0.990. The monolayer adsorption capacities for modified *C. lepidota* residue and unmodified *C. lepidota* residue were 5.890 mg/g and 5.627 mg/g, respectively.

**Keywords:** Adsorption parameters, cobalt, *Cola lepidota*, modeling, nickel, decontamination

### Introduction

Population increase and urbanization are typically accompanied by a rapid increase in energy utilization and waste generation from industrial and domestic sources. If these wastes are not treated appropriately, they contribute to the contamination of the ecosystem. In areas in which marginal adherence to stringent environmental protection regulations is observed, humans do not comply with waste management practices. Industries discharge untreated or insufficiently treated sewage (effluents) into the surroundings. As a result of human negligence, aquatic surroundings are contaminated, making them unfit or hazardous for consumption.

The disposal of wastewater introduces pollutants to surroundings, which mostly exceeds the permissible sanitary level [1]. A previous study has revealed that some of these pollutants include aromatic hydrocarbons, synthetic materials, and heavy metals. Phenols and aromatic compounds are known to lead to unpleasant in water, and some heavy metals such as lead contribute to stunted growth and low intelligence quotient in children, mental retardation, and kidney problems [2].

As a result of pollution, industries are placed under strict regulations to check or mitigate the release of hazardous substances into the surrounding to a minimal level. These regulations have encouraged the development of antiseptic, energy-efficient, holistic, and intrinsically safe methods for the treatment of waste before discharge.

According to Sharma *et al.* [3], the global awareness on environmental deterioration has received immense attention. Nevertheless, various treatment techniques must be selected on the basis of the properties of wastewater

Over the years, researchers have made appreciable efforts to develop remediation procedures for polluted water bodies. Denis *et al.* [4], have reported that some undesirable metals and organic pollutants can be removed from aqueous surroundings by ion exchange, electrodeposition, reverse osmosis, and adsorption. Adsorption, which involves the use of cost-effective adsorbents that can be easily used and regenerated, is very interesting topic. Numerous materials such as carbonized maize tassels, banana pitch, and cassava waste have been investigated for the removal of metal ions and organic pollutants from an aqueous solution [5].



Figure 1. *Cola lepidota* Fruit

As an underutilized fruit, monkey kola is dominant in South-Eastern Nigeria. It is a member of the family Sterculiaceae and genus *Cola*. It has three species: red (*Cola laleritia*), white (*Cola pachycarpa*), and yellow (*Cola lepidota*) [6]. Figure 1 shows the types of monkey kola used.

Several physicochemical and phytochemical analyses of different species of monkey kola fruit have been carried out, and the result revealed that monkey kola fruit is highly nutritious, with medicinal properties, and it can be used to produce different beverages [7, 8].

Several agro-wastes have been used for the dislodgement of metals from aquatic surroundings, but marginal or no information has been reported on the use of *C. lepidota* pericarp as an adsorbent for decontamination.

Hence, to examine the metal binding affinity for remediation, the possibility of using the modified and unmodified forms of a pulverized *C. lepidota* pericarp residue is investigated.

## Methods

**Collection of sample and Preparation.** Fruits of *C. lepidota* were purchased from Igwuruta and Oil Mill markets in Port Harcourt, River state, Nigeria. The fruits were sorted and washed with deionized (DI) water to remove undesirable particles attached to the pericarp. The pericarp was peeled off and dried in the oven at 40 °C for 5 days. The dried *C. lepidota* pericarp was pulverized to a powder and sieved through a 150 µm sieving mesh.

**Extraction Procedure.** First, an average mass of 50 g of the 150-µm pulverized *C. lepidota* pericarp was added in the thimble of Soxhlet extractor, and 750 mL of acetone was added in a 1000-mL round bottom flask. The Soxhlet extraction set-up was completed with a condenser attached to the thimble, which was fixed on

the round-bottom flask and then placed in a water bath. The Hose pipes were connected to the inlet and outlet of the condenser to ensure a steady, continuous flow of water through the condenser for the condensation of acetone vapor. Extraction was continued until the acetone in the thimble became colorless, indicative of the process completion. An average time of 5 h was used for complete sample extraction. The residue was removed from the thimble, dried, and weighed, and the fresh sample was loaded; this process was repeated for 1000 g of the sample. The residue (raffinate) collected from each extraction was collected together, dried at 50 °C for 12 h, and stored in a corked container. A part of the dried residue was crushed and sieved through a 150-µm sieving mesh and referred to as the unmodified *C. lepidota* pericarp (UCLR).

**Modification of Residue.** The residue was modified using sodium hydroxide. First, 100 mL of 0.1 M NaOH was added in a round-bottom flask containing 10 g of the residue. Second, the flask was placed on a stirrer and heated at 60 °C for 5 h. The modified adsorbent was allowed to cool and washed with DI water to remove residual reactants present in the adsorbent. The washed adsorbent was dried at 50 °C. Then, the resultant product of the Na-modified *C. lepidota* pericarp was referred to as MCLR.

**Preparation of Metal Ion Solution.** First, 0.283 g of a NiCl<sub>2</sub>·6H<sub>2</sub>O sample was added into a 250-mL beaker, and 100 mL of DI water was added to dissolve the salt. Second, the dissolved Ni(II) ion was transferred to a 1000-mL volumetric flask, and the solution diluted up to the mark to prepare a 59.5 mg/L Ni(II) ion stock solution. In addition, 0.2826 g of CoCl<sub>2</sub>·6H<sub>2</sub>O was dissolved in a 250-mL beaker, and 100 mL of DI water was added to dissolve the salt. The dissolved cobalt(II) chloride salt was transferred into a 1000-mL volumetric flask, and the solution was diluted up to the mark to prepare a 59.5 mg/L Co(II) ion stock solution. The working solutions were prepared using the serial dilution formula in equation 1.

$$C_1V_1 = C_2V_2 \quad (1)$$

where  $C_1$  and  $C_2$  represent the concentrations of the stock and working solutions and  $V_1$  and  $V_2$  represent the volumes of stock and working solutions, respectively.

**Determination of Zero-Point Charge (pH<sub>zpc</sub>).** The zero-point charges of UCLR and MCLR were determined by the addition of a 0.01M NaCl (0.5 mL) solution in 14 conical flasks (100 mL), and the pH of the solutions were adjusted in duplicates to 2.0, 4.0, 6.0, 8.0, 10.0, 12.0, and 13.0 using 0.1M NaOH or 0.1M HCl. First, 0.5 g each of UCLR and MCLR was added into a flask and the flask was appropriately corked and agitated by using a mechanical shaker, followed by

standing for 48 h [9]. After 48 h, the mixtures were subjected to filtration using a filter paper. The pH of the filtrates was recorded and various changes in the pH value between the initial ( $pH_{i0}$ ) and final ( $pH_{t1}$ ) were noted. Plots of the changes between the initial and final pH against the initial pH were recorded. The points on the pH-axis were recorded as the zero-point charge [10].

**Gas Chromatography – Mass Spectrophotometry (GC – MS) Characterization.** The *C. lepidota* pericarp extract and particularly the residue were subjected to digestion using a 3:1 mixture of HCl and  $HNO_3$  prior to GC – MS analysis.

**Adsorption Tests.** Adsorption tests were performed at various times, concentrations, and temperatures. The resultant mixtures were filtered using an 18-cm filter paper. The filtrates were collected, and metal-ion concentrations were analyzed by atomic absorption spectrophotometry (AAS).

The percentage removal of Ni(II) and Co(II) ions and the adsorption amount ( $q_e$ ) in mg/g were calculated by equations 2 and 3, respectively.

$$\text{Percentage metal-ion removal} = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

$$\text{Adsorption amount } (q_e) = \frac{C_o - C_e}{M} \times V \quad (3)$$

where  $C_o$  is the initial metal-ion concentration (mg/L),  $C_e$  is metal-ion concentration (mg/L) at any time  $t$ ,  $V$  is the volume (L), and  $M$  is the mass (g) of the adsorbent.

**Effect of pH.** The effect of pH was determined by the adjustment of the pH values of a metal solution using 0.1 M NaOH and 0.1 M HCl solutions. This test was carried out at a constant temperature, concentration, and contact time. First, 0.5 g of UCLR and MCLR was weighed into separate 150 mL beakers containing 50 mL of 59.5 mg/L Ni(II) and Co(II) ions. The pH of the samples was adjusted using 0.1 M NaOH or 0.1 M HCl to 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0. The mixtures were mechanically shaken at 180 revolutions per minutes (rpm) for 1 h, and the mixtures were filtered using a Whatman filter paper. The concentration of metal ions in the filtrate was determined by AAS analysis, and equations 2 and 3 were utilized to estimate the percentage removal and adsorption amount, respectively.

**Effect of Temperature.** At a constant pH and time, 0.5 g of UCLR and MCLR sorbents was weighed into separate 150-mL beakers containing 50 mL of 4.25 mg/L each of Ni(II) and Co(II) ions. The solutions were heated in a water bath at 29, 40, 50, 60, and 70 °C for 1 h, and the filtrates were analyzed to quantify the equilibrium metal ions by AAS, and equations 2 and 3 were utilized to estimate the percentage removal and

adsorption amount, respectively. Thermodynamic parameters were determined by using equations 4 and 5.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (5)$$

Where  $\Delta G^\circ$  represents the standard free-energy change,  $\Delta S^\circ$  represents the standard entropy change,  $\Delta H^\circ$  represents the standard enthalpy change, and  $K_c$  represents the equilibrium adsorption constant. The constant,  $K_c$  was generated by the relationship proposed by Tran et al. [11] as shown in equation 6.

$$K_c = 10^6 \times K_L \quad (6)$$

The plot of  $\ln K_c$  against  $1/T$  should exhibit a linear plot, and  $\Delta S^\circ$ ,  $\Delta H^\circ$ , and  $\Delta G^\circ$  can be estimated from the slope and intercept.

**Effect of Time.** First, 0.5 g of UCLR and MCLR with a particle size of 150  $\mu\text{m}$  and a constant metal concentration of 59.5 mg/L were used. Samples were removed at 5, 10, 20, 30, 40, 50, 60, and 70 min. Supernatants were analyzed according to the above-mentioned procedures. Kinetic studies were performed using the linearized form of the pseudo-first and second-order models as shown in equations 7 and 8, respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

where  $q_e$  and  $q_t$  are the amounts adsorbed at equilibrium and at time  $t$  (mg/g), respectively.  $k_1$  is the rate constant, and  $k_1$  and  $q_e$  values are obtained from the slope of the plot shown in equation 7.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

where  $k_2$  is the second-order rate constant (g/mg/min). A plot of  $t/q_t$  against  $t$  afforded a straight-line graph with a slope equal to  $1/q_e$ . Hence,  $k_2$  and  $q_e$  are calculated from the slope and intercept, respectively.

**Effect of Concentration.** The effect of concentration on adsorption was investigated at a pH of 6. In this test, 0.5 g of UCLR and MCLR (150  $\mu\text{m}$ ) were first weighed into different plastic bottles, and Ni(II) and Co(II) ion solutions with concentrations of 4.25, 8.50, 17.0, 25.5, 42.5, and 59.5 mg/L were added into the bottles. Second, mixtures were agitated for 1h using a JP Selecta vibrator at 29 °C. Next, the mixture was filtered, and the metal-ion concentration of the filtrate determined by AAS. The percentage removal and adsorption amount were estimated from equations 2 and 3, respectively. The obtained equilibrium data were analyzed by Langmuir and Freundlich linearized adsorption models as shown in equations 9 and 10, respectively

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m} \quad (9)$$

where  $C_e$  is the equilibrium liquid-phase concentration,  $q_e$  is the amount of heavy metal ions (mg/g) adsorbed at equilibrium,  $q_m$  (mg/g) is the monolayer adsorption capacity, and  $K_L$  is the Langmuir constant. The  $q_m$  and  $k_L$  values were determined from the intercept and slope of the line obtained by plotting  $C_e/q_e$  against  $C_e$ , respectively.

Predicting whether adsorption by the *C. lepidota* adsorbent is favorable or unfavorable for Langmuir-type adsorption, the isotherm shape was categorized by a variable  $R_L$ , which is a dimensionless constant and a separation factor defined in equation 10 as follows:

$$R_L = \frac{1}{1 + k_L C_o} \quad (10)$$

For  $R_L > 1$ , it is unfavorable. For  $R_L = 1$ , adsorption is linear, and for  $0 < R_L < 1$ , adsorption is favorable [12].

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (11)$$

where  $K_F$  and  $n$  are constants obtained from the slope and intercept of a plot of  $\log q_e$  against  $C_e$ .

**Effect of Adsorbent Size.** Adsorbent with particle sizes of 250, 425, 150, and 65  $\mu\text{m}$  were used to quantify the effect of adsorbent size on the adsorption amount. A 70 mg/L metal solution was used to perform the test following the above-mentioned procedures. Each procedure was repeated for the different adsorbent sizes.

## Results and Discussion

**Zero-Point Charge ( $\text{pH}_{\text{zpc}}$ ).** From the plots of MCLR and UCLR shown in Figure 2, the zero-point charge of UCLR is observed at a pH of approximately 5.0, while that of MCLR is observed at a pH of 7.0. The adsorption of Ni(II) and Co(II) ions was considerably favored at pH higher than  $\text{pH}_{\text{zpc}}$  due to a large amount of negative charge on the adsorbent surface.

The adsorbent surface exhibits neither a positive nor a negative charge at the zero-point charge. Hence, at the zero-point charge, the sorbent is said to be electrically neutral [9].

**GC-MS Analysis.** The results of the investigation carried out on the extract and residue of the *C. lepidota* pericarp are as follows (Figure 3).

Figures 3 and 4 show the GC – MS analysis of the acetone extract and residue of the *C. lepidota* preicarp, re-

spectively, and Tables 1 and 2 show their corresponding compositions.

**Effect of pH.** Figure 5 shows the effect of pH on the adsorption amount. Equilibrium data obtained from the adsorption tests revealed that the process is dependent on pH.

According to previously reported studies [13, 14], at low pH, strong competition is clearly observed between the metal ions and net positive charge on the adsorbent surface, which invariably decreases the adsorption rate. However, the maximum adsorption for the modified *C. lepidota* resin was observed at a pH of 6.0, and the maximum adsorption for unmodified *C. lepidota* resin was observed at a pH of 5.0. Subsequently, at a pH greater than 6.0, Ni(II) and Co(II) adsorption gradually decreased. The reduction in adsorption was possibly related to the saturation of pores. Furthermore, the uniformity of the adsorption amount at a pH greater than 6.0 revealed the formation of Ni(OH)<sub>2</sub> and Co(OH)<sub>2</sub> precipitates. The solubility product constant ( $K_{\text{sp}}$ ) for these metal hydroxides at a pH of 6.0 on the adsorbents were as follows: MCLR Ni(OH)<sub>2</sub> ( $1.02 \times 10^{-5} \text{ mol}^3\text{L}^{-3}$ ), MCLR Co(OH)<sub>2</sub> ( $9.72 \times 10^{-10} \text{ mol}^3\text{L}^{-3}$ ), UCLR Ni(OH)<sub>2</sub> ( $8.90 \times 10^{-10} \text{ mol}^3\text{L}^{-3}$ ) and UCLR Co(OH)<sub>2</sub> ( $8.86 \times 10^{-10} \text{ mol}^3\text{L}^{-3}$ ).

**Effect of Temperature.** Results revealed that adsorption decreases with increasing temperature (Figure 6). The optimum temperature for this process was 312.5 K.

**Thermodynamics.** Table 3 summarizes the thermodynamic parameters, and Figure 7 shows the plot of  $\ln K$  versus  $1/T$ . The thermodynamic parameters constitute parts of the pre-requisites for characterizing adsorption [15-16]. The values obtained revealed that the adsorption of Ni(II) and Co(II) ions on MCLR and UCLR is exothermic. The negative value for the entropy change revealed that the adsorption of Ni(II) and Co(II) ions on MCLR and UCLR occurs via an associative mechanism. In other words, adsorption leads to order via the formation of an activated complex between the adsorbate and adsorbent. The negative  $\Delta G$  values revealed the feasibility and spontaneity of the process.

Results revealed that significant changes do not occur in the internal structure of the adsorbent during adsorption.

**Effect of Time.** The concentration of heavy metals in the solution decreases with increasing time [17]. Figure 8 shows the plots of the effect of contact time on the adsorption of Ni(II) and Co(II) ions. The optimum percentage removal values for Ni(II) and Co(II) ions on MCLR were 97.01% and 96.94%, respectively, and adsorption was completed in 60 min. The corresponding values were 96.56% and 95.64% on UCLR in 60 min.

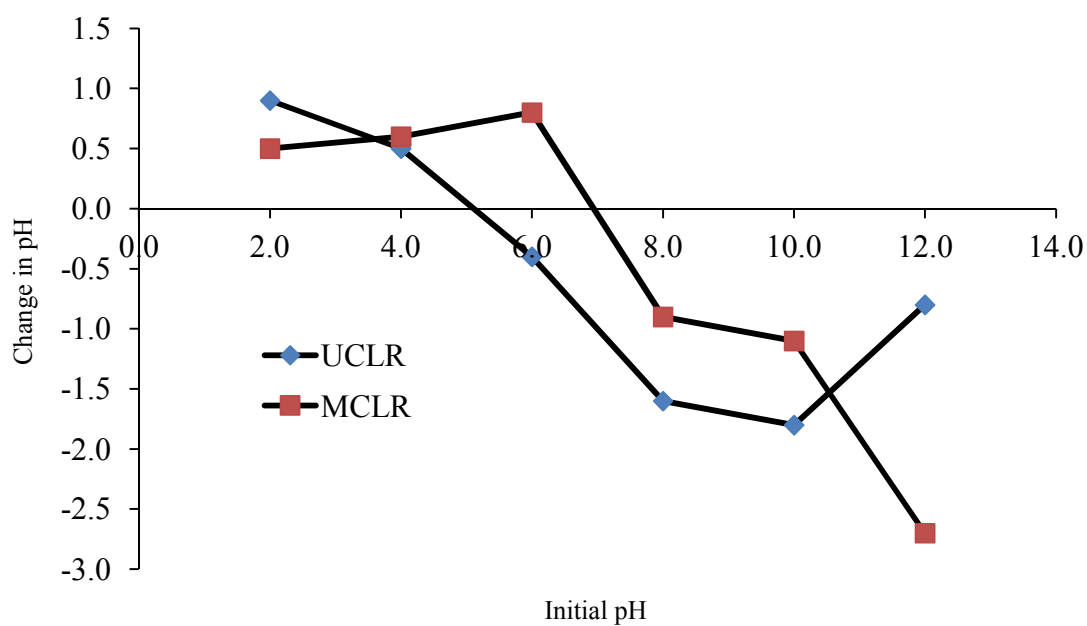


Figure 2. Plot of  $\Delta$ pH against Initial pH for MCLR and UCLR

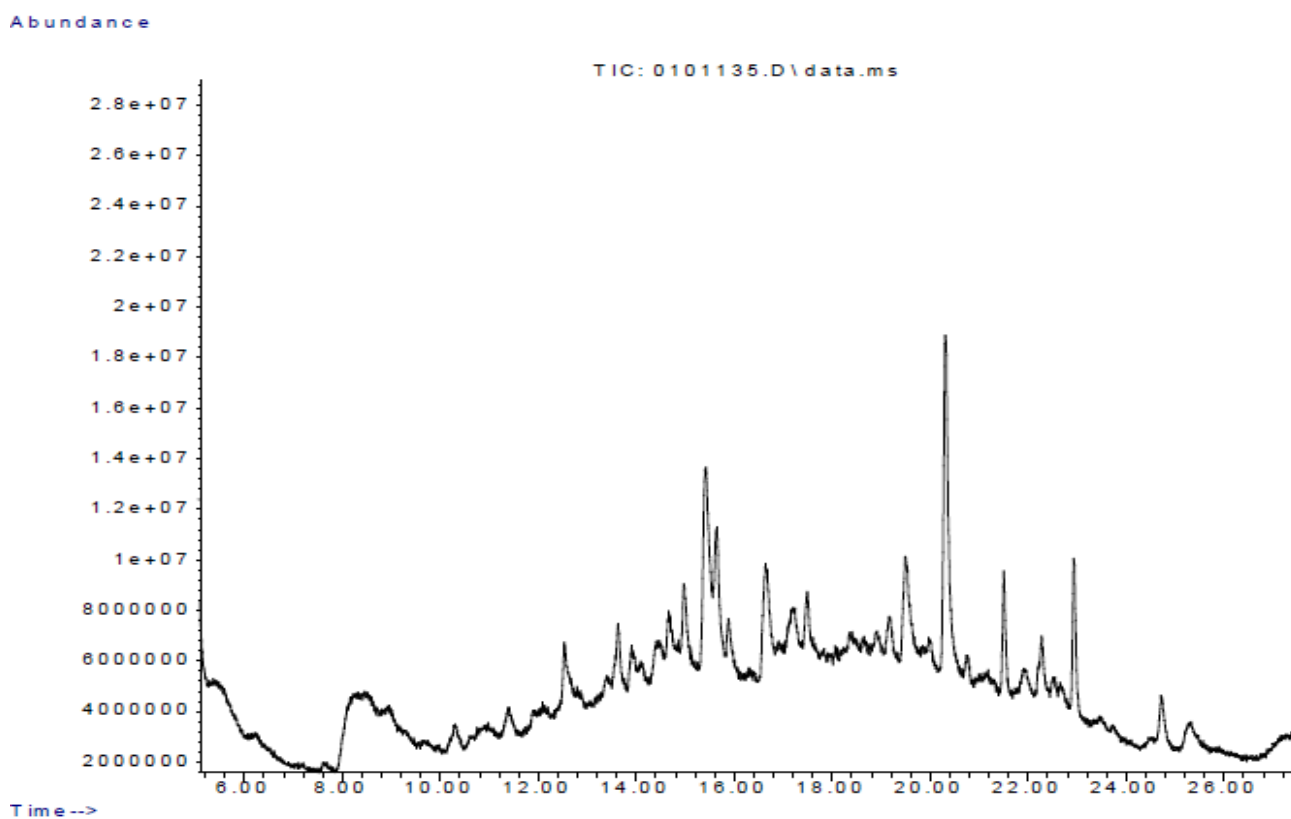


Figure 3. GC-MS Chromatogram of the *C. lepidota* Extract

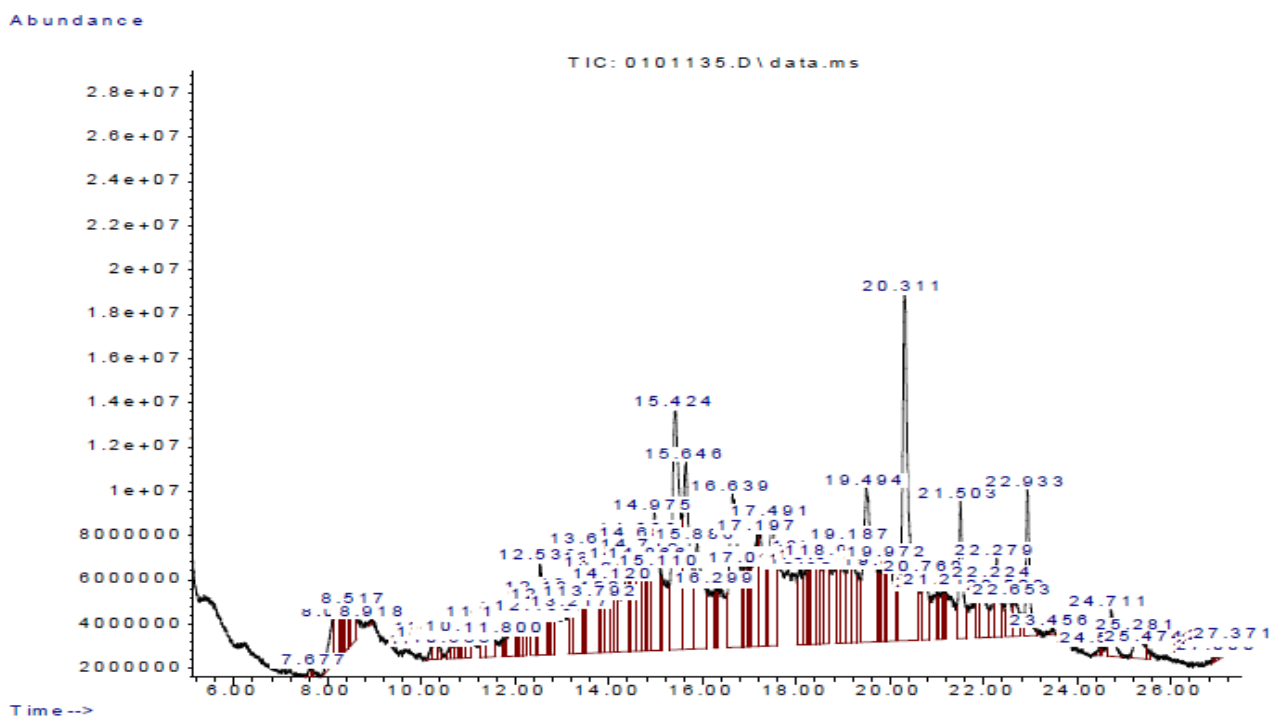


Figure 4. GC – MS Chromatogram of the *C. lepidota* Residue

Table 1. Compounds Observed in the *C. lepidota* Extract

S/N	Compounds	Retention time (Mins)	m/z
1.	6-Methylenebicyclo (3, 2, 0) hept-3-en-2-one	8.154	120
2.	1-Heptatriacotanol	14.661	285
3.	Cyclopropan ebutanoic acid	14.984	298
4.	1,2-Benzenedicarboxylic acid	15.413	205
5.	Cholesta-5,7,9 (11)-trien-3-ol acetate	15.879	424
6.	Cyclopropane dodecanoic acid	17.479	366
7.	Cholesta-8,24-dien-3-ol	19.185	398
8.	2,2-Methylenebis-6-(1,1-dimethylethyl)-4-phenol	19.493	340
9.	Di-n-octyl phthalate	20.320	399
10.	Ethyl iso-allocholate	21.507	430
11.	2,2,4-Trimethyl-3(3,8,12,16-tetramethyl-heptadeca-3,7,11,15-tetraethyl)-cyclohexane	22.274	428
12.	3-Ethyl-5-(2-ethylbutyl)-octadecane	22.927	364
13.	17-(1,5-dimethylhexyl)-2,3-dihydroxyl-10,13-dimethyl-1,2,3,7,8,9,10,11,12,13,14,15-octadecane	24.738	420

Table 2. Compounds Observed in the *C. lepidota* Residue

S/N	Compounds	Retention time (Mins)	m/z
1.	1,1-(1,2-cyclobutanediyl)bis-,trans-benzene	13.489	208
2.	Alpha-phenyl-alpha-tropylacetaldehydetosylhydrazone	19.763	375
3.	N,N-dimethyl,S-1,3-diphenyl-2-butenylester	20.658	311
4.	$\alpha$ -N-Normethadol	21.642	300



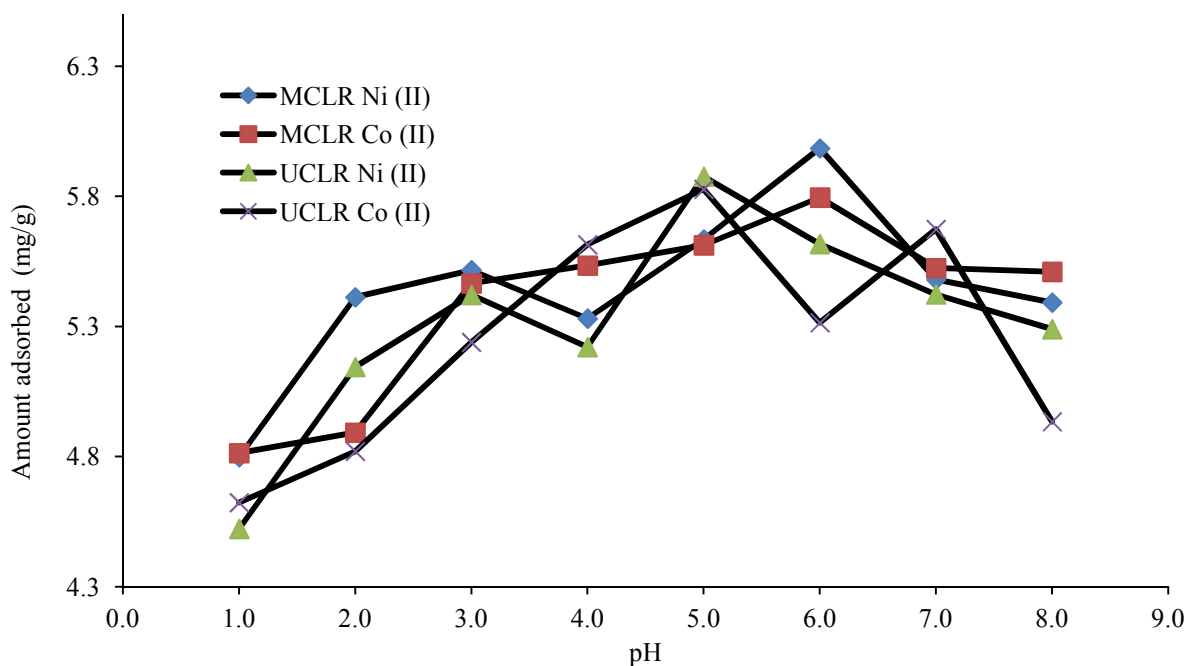


Figure 5. Plot of the Amount Adsorbed against pH

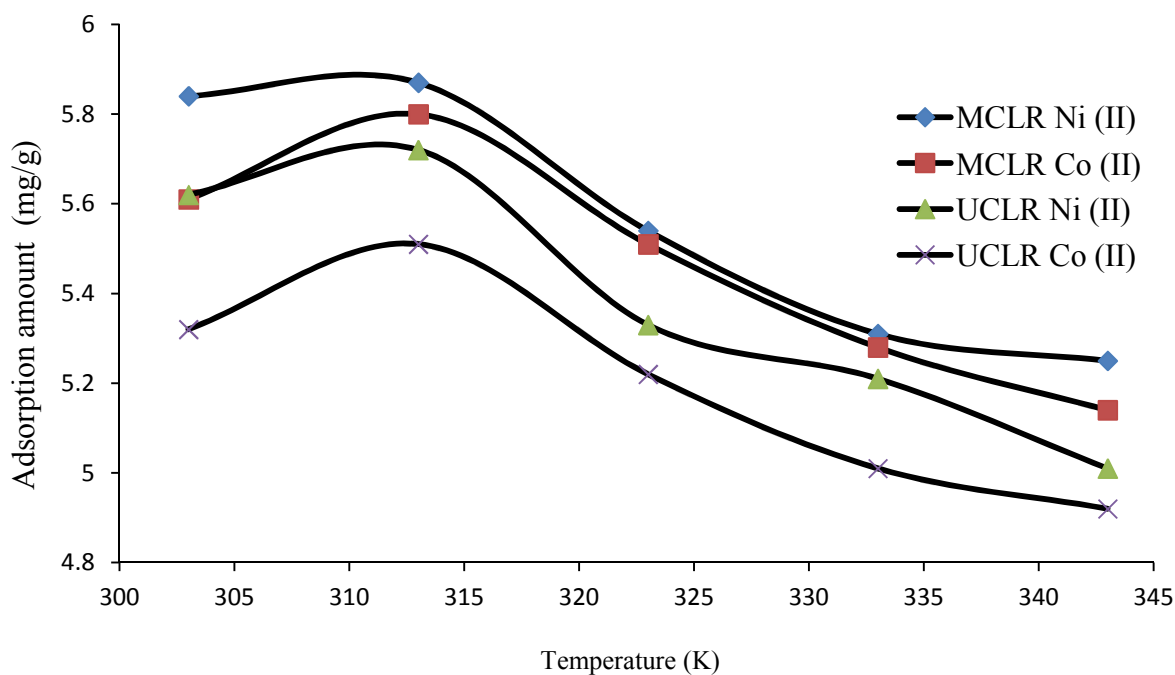


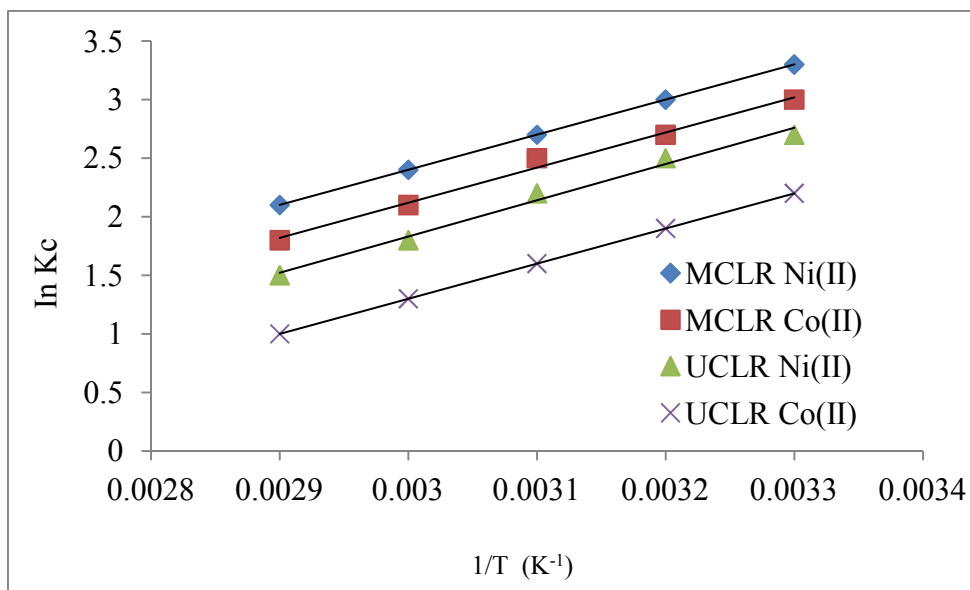
Figure 6. Plot of the Adsorption Amount against Temperature

Table 3. Enthalpy and Entropy Values for Ni(II) and Co(II) Ions on MCLR and UCLR

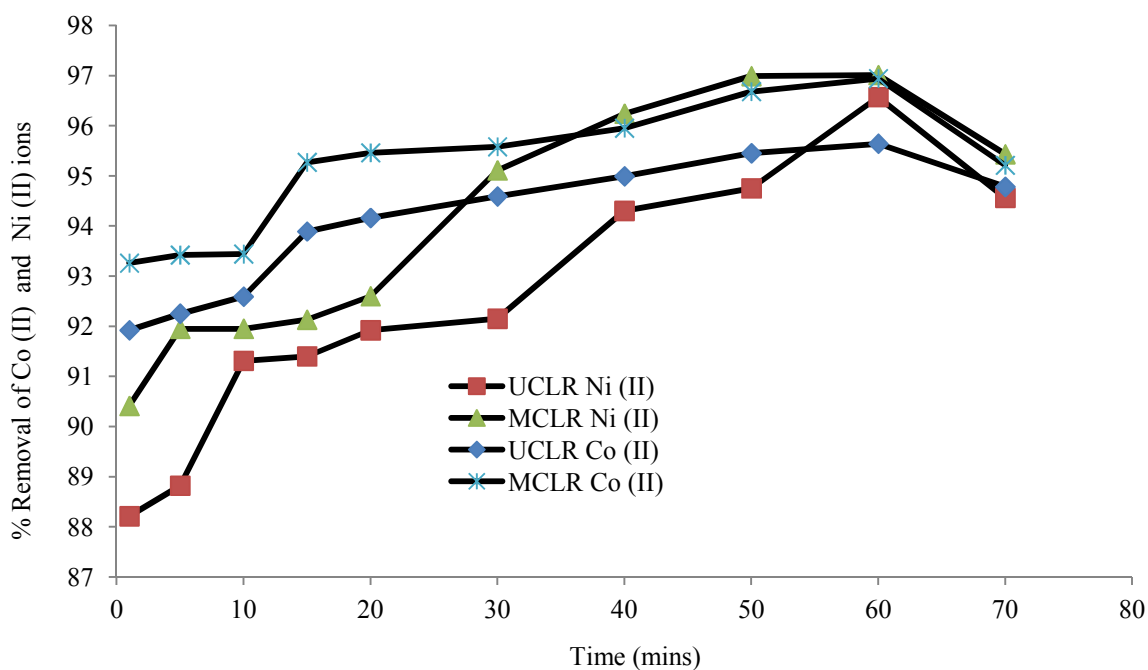
Parameter	MCLR Ni(II)	MCLR Co(II)	UCLR Ni(II)	UCLR Co(II)
$\Delta H^\circ$ kJmol <sup>-1</sup>	-24.94	-24.94	-25.77	-23.28
$\Delta S^\circ$ JK <sup>-1</sup>	-54.87	-56.54	-62.11	-58.70
R <sup>2</sup>	1.000	0.991	0.988	0.994

**Table 4. Gibbs Free-energy Values at Various Temperatures for Ni(II) and Co(II) Ions on MCLR and UCLR**

T (K)	$\Delta G^\circ$ (kJ/mol)			
	MCLR Ni(II)	MCLR Co(II)	UCLR Ni(II)	UCLR Co(II)
303	-3.00	-2.77	-2.50	-1.99
313	-2.86	-2.58	-2.38	-1.67
323	-2.67	-2.46	-2.12	-1.26
333	-2.42	-2.05	-1.63	-0.73
343	-2.11	-1.68	-1.16	-0.27



**Figure 7. Plot of ln K against the Inverse of Temperature**



**Figure 8. Effect of Time on the Adsorption of Co(II) and Ni(II) Ions on UCLR and MCLR**

**Adsorption Kinetics.** Kinetic models were applied to determine the mechanism of adsorption of Ni(II) and Co(II) ions on UCLR and MCLR [18]. To holistically comprehend this mechanism, the generated equilibrium data were used to investigate the pseudo-first-order and pseudo-second-order kinetics. Figures 9 and 10 show the experimental plots. Notably, with increasing time, the adsorption of Ni(II) and Co(II) ions on the adsorbent increased.

Netai *et al.* [19] have reported that the increased adsorption is probably related to the increased number of empty sites on the adsorbent. However, with the increase in time to greater than 60 min, the percentage removal decreased, literally indicating that all of the available adsorbent sites are already occupied. Notably, the adsorption amount increased to 5.5202 mg/g and 5.2513 mg/g for Ni(II) and Co(II) ions, corresponding to 97.01% and 96.94% removal percentages, respectively. At greater than 60 min, the adsorption amount decreased. Greater than 90% adsorption within 60 min corresponded to the initial accumulation of the metal ion on the *C. lepidota* pericarp surface, thereby using the large surface area as the binding sites are increasingly occupied; hence, adsorption consequently slowed down [20].

Experimental data were analyzed by using pseudo-first-order and pseudo-second-order model equations. Table 5 summarizes the parameters of the pseudo-first-order kinetics, with correlation coefficients ( $R^2$ ) of 0.669 for Ni on MCLR, 0.449 for Co on MCLR, 0.729 for Ni on

UCLR, and 0.778 for Co onto UCLR. Table 6 summarizes the parameters of the pseudo-second-order, with correlation coefficient ( $R^2$ ) of 0.998 for Ni on MCLR, 0.996 for Co on MCLR, 0.990 for Ni on UCLR, and 0.980 for Co on UCLR. The result revealed good agreement between the equilibrium data and pseudo-second-order kinetic model at different times. The pseudo-second-order rate constant revealed that the adsorption of Ni(II) ion is more rapid than Co(II) ion. This mechanism showed that adsorption involves valence forces via the sharing of electrons between the adsorbent and adsorbate in the rate-limiting step [15]. The removal of Ni(II) and Co(II) ions by the adsorbent followed chemical adsorption. However, from the adsorption tests, the uptake of Ni(II) and Co(II) ions by the adsorbent clearly involved two steps. The first step was more rapid in the first 30 min, and the second step was slower, which was the rate-determining step, as evident from the kinetic evaluation.

**Effect of Concentration.** Figure 11 shows the plot of the effect of concentration on the adsorption efficiency. At concentrations of 4.25, 8.50, 17.0, 25.5, 42.5, and 59.5 mg/L, the percentage removal values for Ni(II) ion were 78.49%, 87.41%, 88.01%, 93.26%, 95.70%, and 96.73 % for MCLR and 83.93%, 87.39%, 87.07%, 92.36%, 94.77%, and 95.56% for UCLR, indicating that these adsorbents (modified and unmodified) are effective at the high concentration range of heavy metal ions. The percentage removal of Ni(II) and Co(II) ions varied for the same concentration.

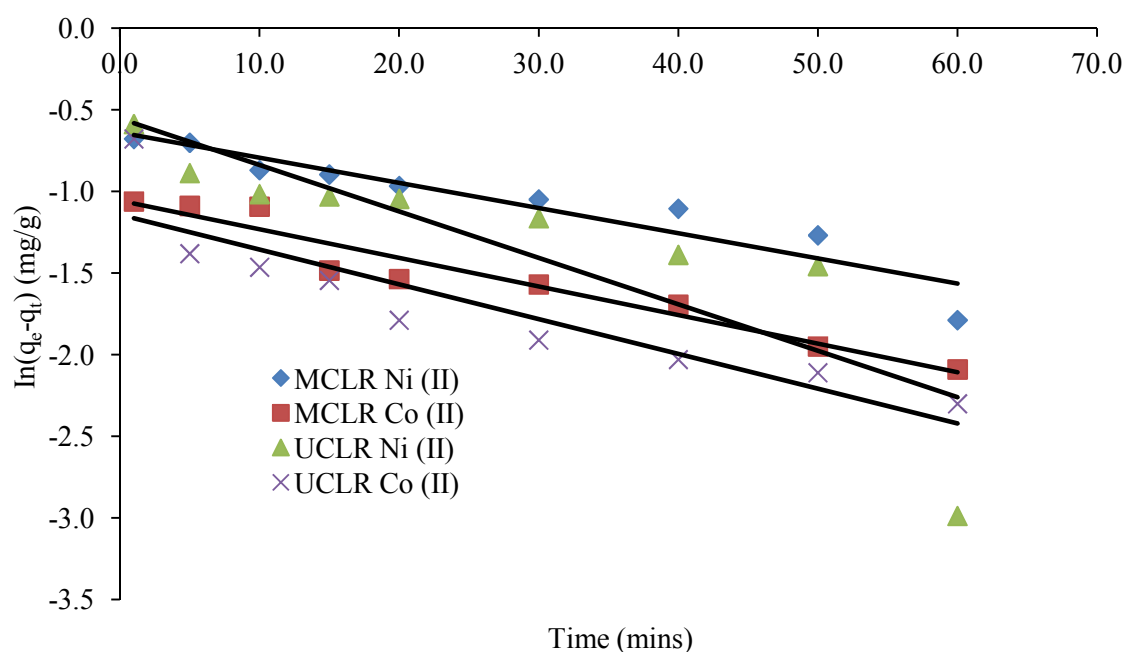
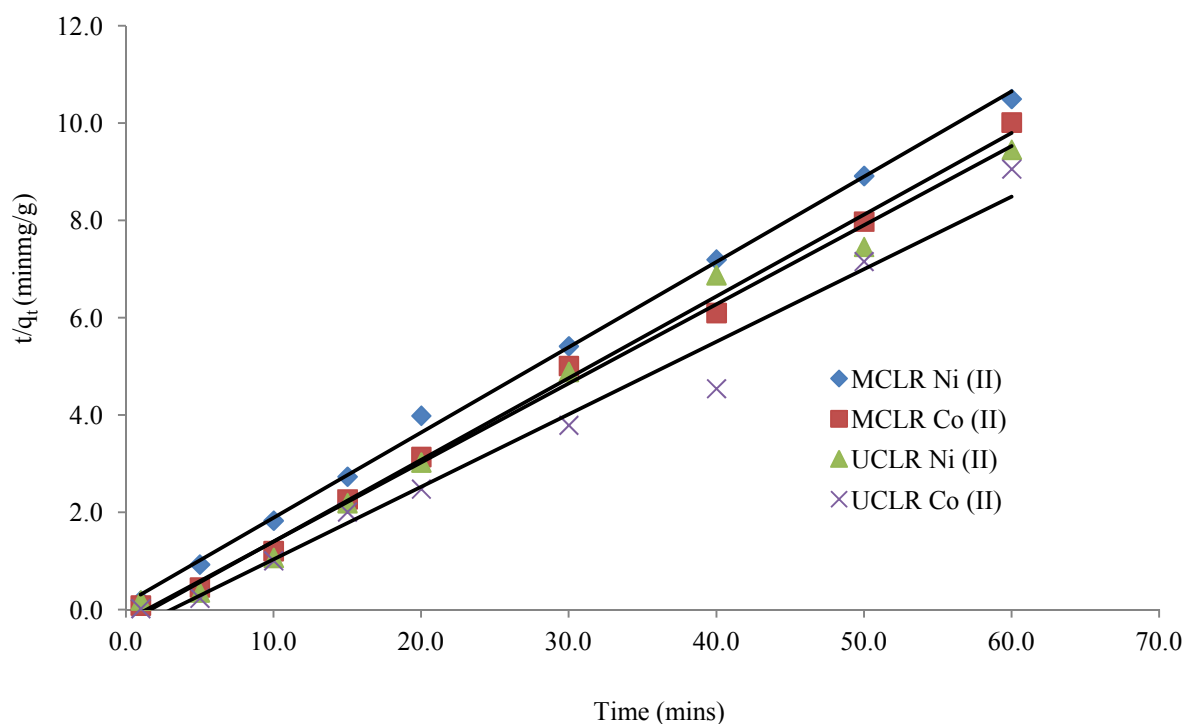


Figure 9. Pseudo-first-order Plot for MCLR and UCLR



**Figure 10. Pseudo-second-order Plot for MCLR and UCLR**

**Table 5. Pseudo-first-order Kinetic Model Parameters**

Parameter	MCLR Ni(II)	MCLR Co(II)	UCLR NI(II)	UCLR Co(II)
$k_1$	- 0.025	- 0.017	- 0.028	- 0.020
$q_e$	0.614	0.347	1.732	0.895
$R^2$	0.669	0.936	0.729	0.778

**Table 6. Pseudo-second-order Kinetic Model Parameters**

Parameter	MCLR Ni(II)	MCLR Co(II)	UCLR NI(II)	UCLR Co(II)
$k_2$	0.232	0.111	0.145	0.073
$q_e$	5.714	5.649	5.495	5.464
$R^2$	0.998	0.996	0.990	0.980

**Adsorption Isotherms.** To describe the correlation between the amounts of Ni(II) and Co(II) ions adsorbed on UCLR and MCLR, the Langmuir and Freundlich adsorption models were employed. Figures 12 and 13 show their corresponding plots. Correlation coefficient ( $R^2$ ) of 0.981 and 0.979 obtained for Ni(II) and Co(II) ions indicated that adsorption well fits the Freundlich isotherm model equation. The result revealed that weak chemical interactions exist between the surface charges of the adsorbents and Ni(II) and Co(II) ions. Hence, Ni(II) ion is preferentially removed from an aqueous solution compared to Co(II) ion. Tables 7 and 8 summarize the adsorption parameters of the Langmuir and

Freundlich model equations, respectively. However,  $R_L$  values revealed favorable interactions between the adsorbents and metal ions i.e.  $0 < R_L < 1$ .

**Effect of Adsorbent Particle Size on Adsorption Amount.** Figure 14 shows the effect of adsorbent particle sizes on the percentage removal of Ni(II) and Co(II) ions. With the increase in the particle size from 65  $\mu\text{m}$  to 425  $\mu\text{m}$ , the percentage removal of Ni(II) and Co(II) ions decreased. This is indicative of the fact that the lower the particle size, the higher the percentage of heavy metal ions removed [21].

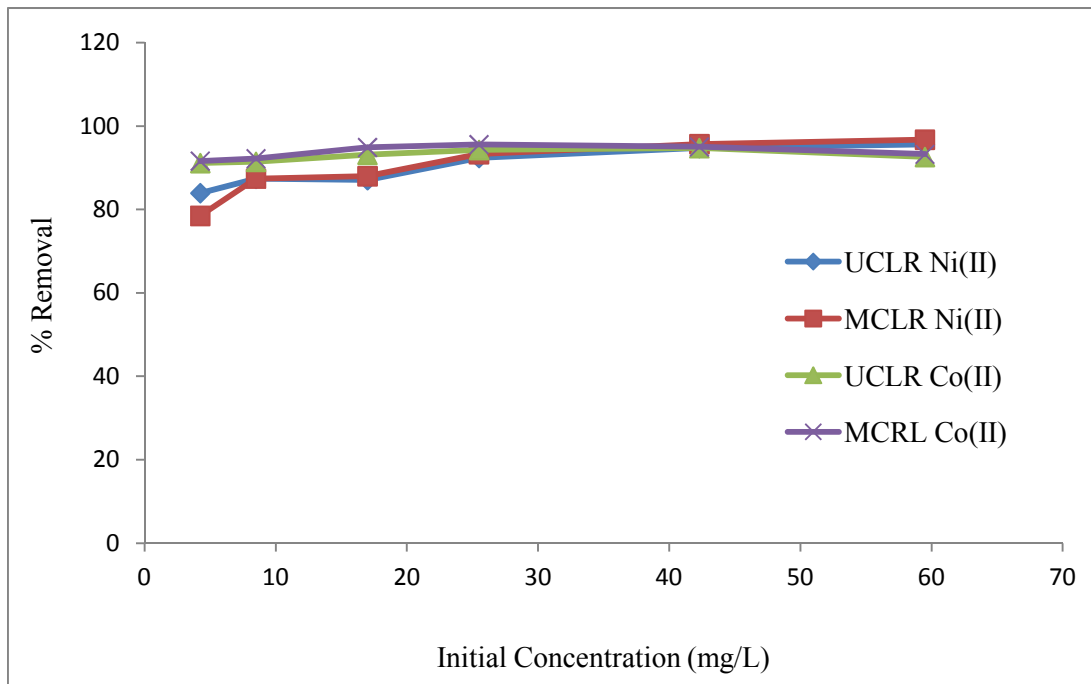


Figure 11. Concentration Plot of Ni(II) and Co(II) Ions on MCLR and UCLR

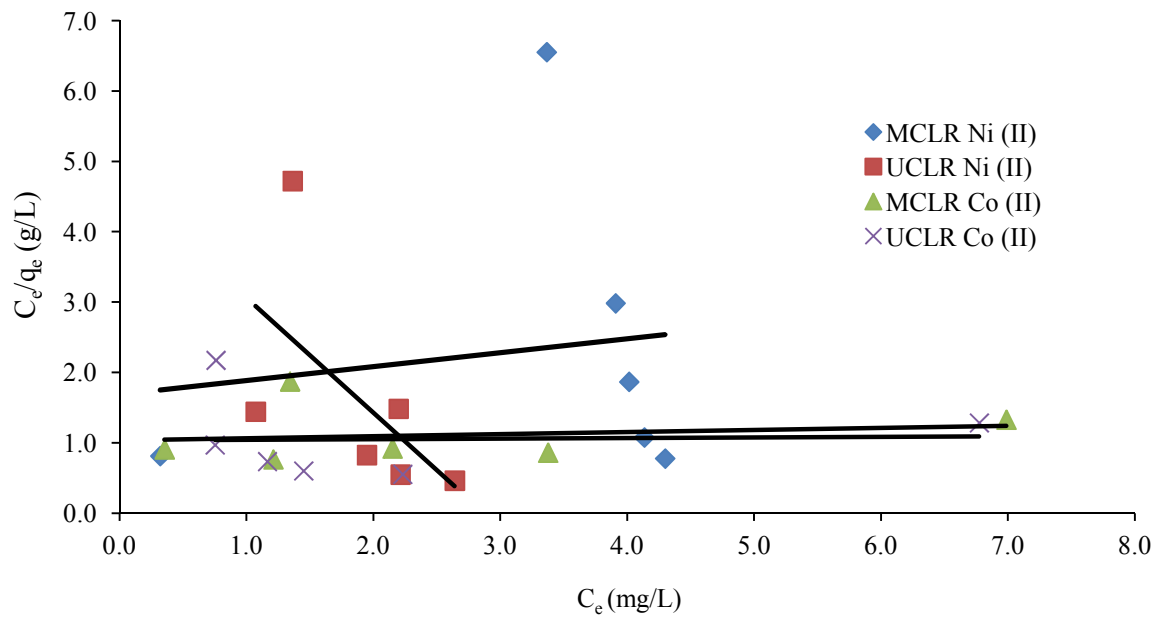


Figure 12. Langmuir Plot for MCLR and UCLR

Table 7. Langmuir Model Equation Parameters

Parameter	MCLR Ni(II)	MCLR Co(II)	UCLR Ni(II)	UCLR Co(II)
$K_L$	0.958	0.040	0.070	0.030
$R_L$	0.020	0.300	0.190	0.360
$q_m$ (mg/g)	5.080	4.614	12.500	5.010
$R^2$	0.018	0.026	0.355	0.000

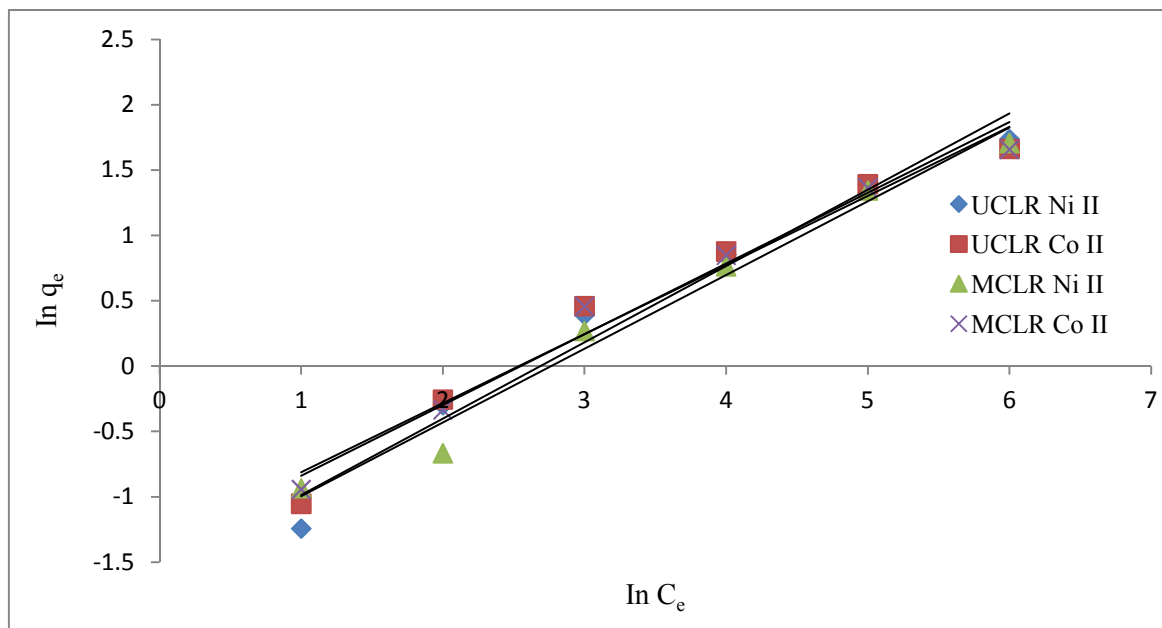


Figure 13. Freundlich Plot for MCLR and UCLR

Table 8. Freundlich Model Equation Parameters

Parameter	MCLR Ni(II)	MCLR Co(II)	UCLR Ni(II)	UCLR Co(II)
$K_F$	1.11	0.91	0.74	0.33
$n$	0.37	0.93	1.08	0.71
$R^2$	0.981	0.979	0.972	0.971

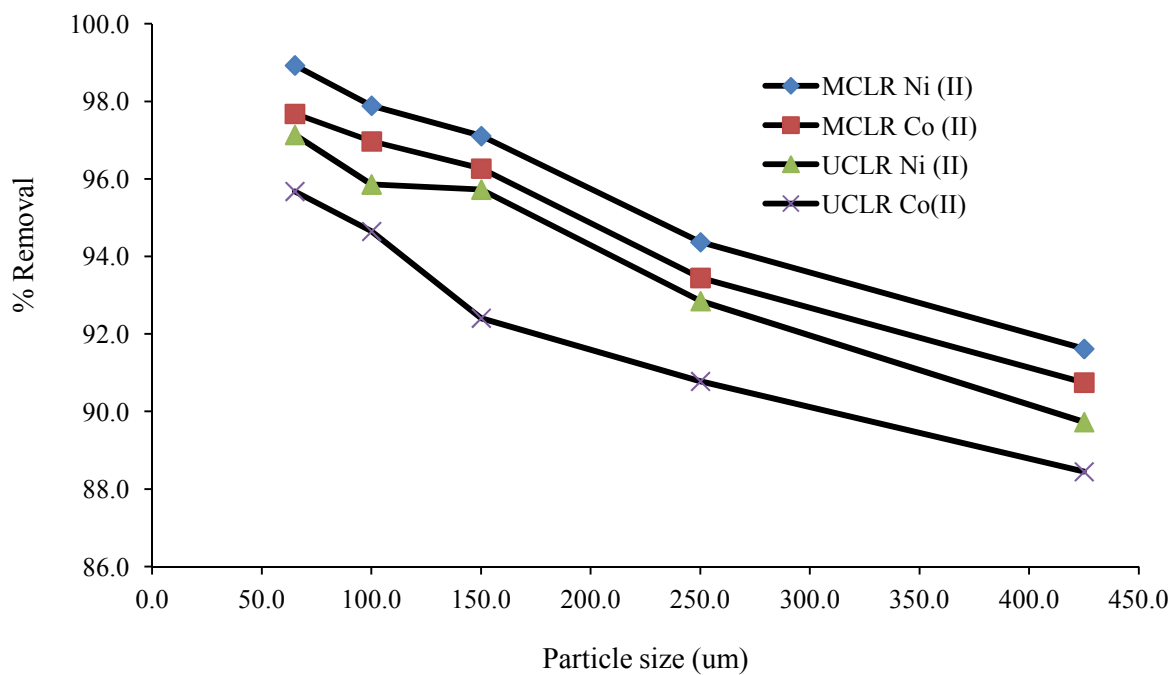


Figure 14. Effect of the Adsorbent Size on the Percentage Removal of Ni(II) and Co(II) Ions

## Conclusion

In this study, the pulverized pericarp of *Cola lepidota* was used to investigate its adsorption efficiency for the removal of Ni(II) and Co(II) ions from an aqueous medium. The GC – MS analysis of the milled *C. lepidota* pericarp extract and residue revealed that the sample is structurally composed of diesters and dicarboxylic acids. The result obtained at various particle sizes indicated that the adsorbent exhibits a high percentage metal-ion removal at reduced particle size. The modified and unmodified *C. lepidota* adsorbents exhibited immense potential as an adsorbent for the removal of Ni(II) and Co(II) ions from an aqueous medium. In addition, the batch adsorption system revealed that the maximum adsorption of Ni(II) ion is observed at a pH of 6.0, while the maximum adsorption of Co(II) ion is observed at a pH of 5.0. Equilibrium data showed reasonable agreement with the pseudo-second-order kinetics, with a correlation coefficient ( $R^2$ ) greater than 0.990 for the adsorption of Ni(II) and Co(II) ions on UCLR and MCLR. Moreso, equilibrium data analysis revealed that the adsorption follows the Freundlich isotherm model, with a correlation coefficient ( $R^2$ ) greater than 0.950 for the adsorption of Ni(II) and Co(II) ions on UCLR and MCLR, indicative of multilayer adsorption.

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## References

- [1] Obi, C., Woke, J. 2014. The removal of phenol from aqueous solution by *Colocacia esculenta araesia Linnschott*. J. Soil Sci. Environ. Manage. 3(6): 59-66. <http://www.skyjournals.org/SJSSEM>.
- [2] Maret, W., Moulis, J-M. 2013. The bioinorganic chemistry of cadmium in the context of its toxicity. Toxicol. Essen. 11: 1-29. doi.org/10.1007/978-94-007-5179-8\_1.
- [3] Sharma, P.K., Ayub, S., Tripathi, C.N. 2016. Removal of Chromium (VI) from aqueous solutions using discarded *Solanum tuberosum* as adsorbent. Inter. J. Eng. Sci. 6(11): 05-15. [www.researchinventy.com](http://www.researchinventy.com).
- [4] Denis, L.G., Rubia, R.V., Claudio, A. 2009. Adsorption of Thorium (IV) on chemically modified Amazon Clay. J. Braz. Chem. Soc. 20(6): 1164-1174. doi.org/10.1590/S0103-50532009000600023.
- [5] Okoro, I.A., Abii, T. 2011. Sorption models of Cadmium (II) ion onto edible fruit waste. Amer. J. Scient. Ind. Res. 2(3): 386-390. doi:10.5251/ajsir.2011.2.3.381.385.
- [6] Singh, B., Gupta, V., Bansal, P., Singh, R., Kumer, D. 2010. Pharmacological potential of plant used as asphrodisiacs. Inter. J. Pharm. Sci. Rev. Res. 5(1): 104-113. [www.globalresearchonline.net](http://www.globalresearchonline.net).
- [7] Osabor, V.N., Bassey, F.I., Ibe, K.A. 2015. Chemical profile of the endocarp and exocarp of yellow monkey cola (*Cola lepidota*). Global J. Pure Appl. Sci. 21(1): 33-39. doi.org/10.4314/qipas.v21i1.6.
- [8] Ene-Obong, H., Asumugha, U.V., Okudu, H.O. 2015. Nutrients and phytochemical composition of two varieties of monkey kola (*Cola parchycarpa* and *Cola lepidota*): An underutilized fruit. Food Chem. 193: 154-159. doi.org/10.1016/j.foodchem.2014.11.045.
- [9] Aki, M.A., Abou-Elanwar, A.M., Badri, M.D., Youssef, A-F. M. 2015. Comparative adsorption studies of Cd(II) on EDTA and acid treated activated carbons from aqueous solutions. J. Anal. Bioanal. Tech. 6(6): 1-9. doi.org/10.4172/2155-9872.1000288.
- [10] Vieira, A.P., Santana, S.A., Bezerra, W.B., Silva, H.S., Santos, K.A., Melo, J.P., Airoldi, C. 2014. High performance maleated lignocelluloses epicarp fibers for copper ion removal. Braz. J. Chem. Eng., 31(21): 183-193. doi.org/10.1590/S0104-66322014000100017.
- [11] Tran, H.N., You, S.J., Hosseini-Bandegharai, A., Chao, H.P. 2017. Mistakes and Inconsistencies regarding adsorption of contaminants from aqueous solutions: A critical review. Water Res. doi:10.1016/j.watres.2017.04.014.
- [12] Georg, J.L., Martin, H.G., Georg, H., Michael, J., Holger, K. 2014. Response of the sorption behavior of Cu, Cd, and Zn to different soil management. J. Plant Nutri. Soil Sci. 169(1): 60-68. doi.org/10.1002/jpln.200521752.
- [13] Georg, J.L., Martin, H.G., Georg, H., Michael, J., Holger, K. 2014. Response of the sorption behavior of Cu, Cd, and Zn to different soil management. J. Plant Nutri. Soil Sci. 169(1): 60-68. doi.org/10.1002/jpln.200521752.
- [14] Akar, T., Tunali, S., Cabuk, A. 2007. Study on the characterization of lead (II) biosorption by fungus *Aspergillus parasiticus*. Appl. Biochem. Biotechnol. 136(3): 389-405. doi.org/10.1007/s12010-007-9032-8.
- [15] Babarinde, A., Babalola, O.J., Ashidi, J. 2013. Batch equilibrium biosorption of Ni (II), Cr (III) and Co (II) from solution using Bitter leaf (*Vernonia amygdalina*): kinetics, isotherm, and thermodynamics. Inter. J. Chem. Biochem. Sci. 3: 101-109. [www.iscientific.org/Journal.html](http://www.iscientific.org/Journal.html).
- [16] Piccin, J.S., Dotto, G.L., Pinto, L.A. 2011. Adsorption isotherms and thermodynamical data of FD and C red n 40 binding by Chitosan. Braz. J. Chem. Eng. 28(2): 1-9. doi.org/10.1590/S0104-66322011000200014.

- [17] Ibezim-Ezeani, M.U., Akaranta, O. 2016. Thermodynamic feasibility of Mn (II), Fe(II) and Pb (II) ions exchange in aqueous medium by red onion (*Allium Cepa*) skin extract resin. *Inter. J. Chem. Technol. Res.* 9(9): 550-562. [www.sphinxesai.com](http://www.sphinxesai.com).
- [18] Baldez, E.E., Robaina, N.F., Cassella, R.J. 1998. Employment of polyurethane foam for the adsorption of Methylene Blue in aqueous medium. *J. Hazard. Mater.* 159(2-3): 580-586. doi: 10.1016/j.jhazmat.2008.02.055.
- [19] Ho, Y.S., Mackay G. 1999. Pseudo second-order model for sorption processes. *Proc. Biochem.* 34(5): 451-465. doi.org/10.1016/S0032-9592(98)00112-5.
- [20] Netai, M., Lydia, C., David, S., Matthew, M. 2013. Adsorption of phenol from aqueous solution using Carbonized Maize Tassels. *Brit. J. Appl. Sci. Technol.* 3(3): 649-661. [www.sciencedomain.org](http://www.sciencedomain.org).
- [21] Iman, M., Esmail, S., Ali, L. 2014. Batch and fixed bed column performance of red mud for lead removal. *Canad. Chem. Trans.* 2(1): 83-96. doi.org/10.13179/canchemtrans.2014.02.01.0059.
- [22] Kadirvalu, K., Namasivayam, C. 2010. Activated carbon from coconut coir pith as metal adsorbent: adsorption of Cd (II) ions from aqueous solution. *Adv. Environ. Res.* 7(4): 471-475. doi.org/10.1016/S1093-0191(02)00018-7.