

Article

Kinetic, Equilibrium and Thermodynamics Study of the Adsorption of Pb(II), Cu(II) and Ni(II) from Aqueous Solution using *Mangifera indica* Leaves

Nasiru Pindiga Yahaya , Aliyu Ahmad Deedat, Yakong David Madugu, Adamu Abubakar

Department of Chemistry, Faculty of Science Gombe State University, Nigeria

* Correspondence: Nasiru Pindiga Yahaya (npy500@gsu.edu.ng)

Abstract: The kinetics, equilibrium and thermodynamic study of the adsorption of Ni²⁺, Pb²⁺ and Cu²⁺ ions from aqueous solution by the leaf of *Mangifera indica* were investigated at different experimental conditions. Optimum conditions of initial metal ion concentration, pH, adsorbent dose, contact time and temperature were determined. The kinetics studies indicate that the adsorption process of the metals ions followed the pseudo second-order model with R² value of 0.9938, 1.00 and 1.00 respectively. Equilibrium studies showed that the adsorption of Ni²⁺, Pb²⁺ and Cu²⁺ ions are well represented by both Langmuir and Freundlich isotherm but the Langmuir model gave a better fit for Pb²⁺ ions with R² value of 0.9950 and Langmuir constant K_L of 4.3383 while Freundlich isotherm model best fit the experimental data of lead(II) and nickel(II) with a R² value of 0.976 and 0.9973 and Freundlich constant K_F value of 4.2677 and 0.0874. The calculated thermodynamics parameters of Ni²⁺, Pb²⁺ and Cu²⁺ ions are (ΔG° -1182.49, -5479.1 and 613.48 KJ/mol) showed that the adsorption of Ni²⁺ and Pb²⁺ are spontaneous while Cu²⁺ non-spontaneous. The findings indicate that the leaf of *Mangifera indica* could be used for the adsorption of Ni²⁺, Pb²⁺ and Cu²⁺ ions from industrial effluents.

How to cite this paper: Yahaya, N. P., Aliyu, A. D., David, Y. M., & Abubakar, A. (2022). Kinetic, Equilibrium and Thermodynamics Study of the Adsorption of Pb(II), Cu(II) and Ni(II) from Aqueous Solution using *Mangifera indica* Leaves. *Online Journal of Materials Science*, 1(1), 16–29. Retrieved from <https://www.scipublications.com/journal/index.php/materials/article/view/262>

Keywords: *Mangifera indica* Leaves; Adsorption of metal ions; Thermodynamics study

1. Introduction

Heavy metals are naturally occurring elements that have a high atomic weight and a density at least 5 times greater than that of water. Their multiple industrial, domestic, agricultural, medical and technological applications have led to their wide distribution in the environment; raising concerns over their potential effects on human health and the environment [1]. Their toxicity depends on several factors including the dose, route of exposure, and chemical species, as well as the age, gender, genetics, and nutritional status of exposed individuals. Because of their high degree of toxicity, arsenic, cadmium, chromium, lead, and mercury rank among the priority metals that are of public health significance [2]. These metallic elements are considered systemic toxicants that are known to induce multiple organ damage, even at lower levels of exposure. They are also classified as human carcinogens (known or probable) according to the U.S. Environmental Protection Agency, and the International Agency for Research on Cancer [3]. This review provides an analysis of their environmental occurrence, production and use, potential for human exposure, and molecular mechanisms of toxicity, genotoxicity, and carcinogenicity [4].

The aim of this research is to prepare and characterize new adsorbent from biomass *Mangifera indica* leaf using AAS and FT-IR analysis in order to removed Ni(II), Pb(II) and Cu(II) ions from aqueous solution.

Received: March 18, 2022

Accepted: April 25, 2022

Published: April 27, 2022



Copyright: © 2022 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).

Heavy metals are among the most investigated environmental pollutants. Almost any heavy metal and metalloid may be potentially toxic to biota depending upon the dose and duration of exposure. Many elements are classified into the category of heavy metals, but some are relevant in the environmental context [5]. List of the environmentally relevant most toxic heavy metals and metalloids contains Cr, Ni, Cu, Zn, Cd, Pb, Hg, and As [2]. Heavy metal pollutants most common in the environment are Cr, Mn, Ni, Cu, Zn, Cd, and Pb [6], China has suggested four metals, i.e., Cr, Cd, Pb, Hg, and the metalloid As, as the highest priority pollutants for control in the "12th 5-year plan for comprehensive prevention and control of heavy metal pollution. Some other heavy metals are also hazardous to living organisms depending upon dose and duration of exposure [7]. Now days, the contamination of water resources by heavy metals has result serious health issues. Heavy metals in their elemental as well as chemically combined form are toxic, non-degradable and persistence in nature. The presence of heavy metal in aquatic environment is major health concern due to their hazardous nature since they can cause severe health problem for both animal and human being [8].

Hence there is need to develop a simple, efficient, inexpensive and economical method for removing dissolved heavy metals from waste water.

2. Materials and Methods

The main material used in this research is *Mangifera indica* (mango) leaf biomass. $\text{Pb}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, NaOH and HNO_3 were used as received. All solutions were prepared in de-ionized water prepared using a water purification system.

2.1. Preparation of adsorbent and aqueous solutions

The leaves of *Mangifera indica* (mango) was use for this research work. The leaf was collected within the Gombe state university in Gombe, Nigeria. The leaves biomass was washed with tap water to remove dirtied and other particulate matter and rinsed with distilled water. The sample leaves was oven dry at about 120°C for 24 hrs. The dried leaves was graded and then sieved to uniform the particles (140 μ m). The prepared adsorbent was stored in clean air-tight glass bottle until the time of usage. 1000g/L stock solution of $\text{Pb}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were prepared according to standard procedure by dissolving 1.5980g, 4.9530g and 3.935g each in 1L distilled water and serial dilution method from the stock solution to obtain different concentration and atomic absorption spectroscopy(AAS) was used to measure the solutions which was used for further experiments.

The adsorbent surface functional group loaded with adsorbent and unloaded was identified with Fourier Transform Infrared (FTIR) spectroscopy, KBr was used as background material.

2.2. Batch adsorption experiments

2.2.1. Effect of Initial metal ion concentration

The effect of initial metal concentration adsorption of Pb^{2+} , Ni^{2+} and Cu^{2+} ions on *Mangifera indica* was determined at different concentration of 10ppm, 15ppm, 20ppm, 35ppm, and 40ppm keeping the pH at 6, room temperature (~25°C). 50ml solution of pb^{2+} , Ni^{2+} and Cu^{2+} ions were transferred into 100ml conical flask, 0.6g of *Mangifera indica* sample were added and the solution was shaken for 40min at 150rpm. The solutions were filtered using whatman No1 filter paper and the filtrate was analyzed with AAS (Buck of scientific 205).

2.2.2. Effect of pH on the adsorption

The effect of pH on the process of adsorption pb^{2+} , Ni^{2+} and Cu^{2+} ions with *Mangifera indica* was determined at different pH value of 2, 4, 6, 8, and 10 optimum initial concentration of metal ions of 15ppm pb, 40ppm Ni and 40ppm Cu at room temperature

(~25°C). 50ml solution of pb²⁺, Ni²⁺ and Cu²⁺ ions were transferred into 100ml conical flask, 0.6g of *Mangifera indica* samples were added and the solutions was shaken for 40min at 150rpm. The solutions were filtered using whatman No1 filter paper and the filtrate was analyzed with AAS (Buck of scientific 205).

2.2.3. Effect on the adsorbent dose on the adsorption

Effect of adsorbent dose pb²⁺, Ni²⁺ and Cu²⁺ ions with *Mangifera indica* was determined at different amount of dosage of 0.2, 0.4, 0.6, 0.8, and 1.0g under optimum initial concentration of metal ions of 15ppm Pb²⁺, 40ppm Ni²⁺ and 40ppm Cu, pH of 4 pb²⁺, 10 Ni²⁺ and 4 Cu²⁺ was suspended in 50ml of pb²⁺, Ni²⁺ and Cu²⁺ ions at room temperature (~25°C). The pb²⁺, Ni²⁺ and Cu²⁺ ions were transferred into 100ml conical flask, and left to shake for 40min at 150rpm. The solutions were filtered using whatman No1 filter paper and the filtrate was analyzed with AAS (Buck of scientific 205).

2.2.4. Effect of contact time on the adsorption

Effect of contact time on the adsorption process of pb²⁺, Ni²⁺ and Cu²⁺ ions by *Mangifera indica* was studied at the following time intervals 20, 40, 60, 80, and 100mins at optimum concentration of 15ppm Pb, 40ppm Ni and 40ppm Cu pH of 4 Pb, 10 Ni and Cu, pH of 4 Pb, 10 Ni and 4 Cu, adsorbent dose 0.4 Pb, 0.2 Ni and 0.8 Cu, at room temperature (~25°C). 50ml of solution pb²⁺, Ni²⁺ and Cu²⁺ ions were transferred into 100ml conical flasks. The solutions were shaken at 150rpm at different time intervals. The solutions were filtered using whatman No1 filter paper and the filtrate was analyzed with AAS (Buck of scientific 205).

2.2.5. Effect of temperature on the adsorption

Effect of temperature on the adsorption process of pb²⁺, Ni²⁺ and Cu²⁺ ions was studied at the following temperature 25, 35, 45, 55 and 65°C at the optimum pH of 4 pb²⁺, 10 Ni²⁺ and 4 Cu²⁺, were transferred into 100ml conical flasks, 0.4 pb²⁺, 0.2 Ni²⁺ and 0.8 Cu²⁺, adsorbent was added to pb²⁺, Ni²⁺ and Cu²⁺. The solutions were shaken at 150rpm at different temperatures, contact time of 100min for pb²⁺, Ni²⁺ for 20min and 60min Cu²⁺. The solutions were filtered using whatman No1 filter paper and the filtrate was analyzed with AAS (Buck of scientific 205).

Calculation of metal uptake: metal uptake by *Mangifera indica* was calculated using the mass balance equation which is shown in

$$q = \frac{(C_0 - C_e)v}{s} \quad (1)$$

Where q is the metal uptake (mg metal g⁻¹ dry weight); v (L) is the volume of metal solution contacted with adsorbent; C₀ is the initial concentration of metal in solution (mg L⁻¹); C_e is the final concentration of metal in solution (mg L⁻¹); S in the dry weight (g) of biosorbent used.

3. Results and Discussion

3.1. FT-IR Analysis of unloaded and Ni²⁺, Pb²⁺, and Cu²⁺ ions-loaded leaf of *Mangifera indica*

In order to ascertain the functional group that are responsible for the adsorption of the metals ions in this study and possibly to explain the mechanism of the adsorption, FT-IR study was carried out on the unloaded and the metal loaded adsorbent at the optimum pH. The FT-IR spectrum (Figure 1) of unloaded biomass shows a number of distinct absorption bands indicating the complex nature of the leaves. Several distinct and adsorption around 3421 cm⁻¹ are indicative of O-H groups. Weak bands around 2920cm⁻¹ in both indicate presence of C-H stretch of alkane. The absorption bands around 1633cm⁻¹ in the spectra indicate the presence of C=C stretch while the bands around 1450 and 1384

cm^{-1} could be attributed to $\text{CH}_2\text{-CH}_2$ and $\text{CH}_2\text{-CH}_3$ bending bands. Band around 1080cm^{-1} could be due to C-O stretch. [1]. have reported similar band in loaded and unloaded husk of *Oryza sativa* shows the characteristic absorption band at $3,400\text{--}3,200\text{cm}^{-1}$ is assigned for surface O-H stretching whereas C-H stretching had a broad band at $2,921\text{--}2,851\text{cm}^{-1}$. Moreover, the peak at 1074.0 cm^{-1} corresponds to anti-symmetric stretching vibration of Si-O, whereas at 476.2cm^{-1} representing the bending vibration of Si-O-Si bond.

Using the metal ions as case of study comparing (Figure 2, Figure 3 and Figure 4) the spectra of Pb^{2+} , Ni^{2+} and Cu^{2+} ions loaded biomass with that of the unloaded, it is observed that the band at 3457 , 4359 and 3477cm^{-1} broadens and its intensity is reduced and the band shift to a higher wave number after metal adsorption. Also the band at 1632cm^{-1} became slight intense. An ion-exchange process occurred when the metal in the solution was transferred from solution to adsorbent leading to the formation of chemical band.

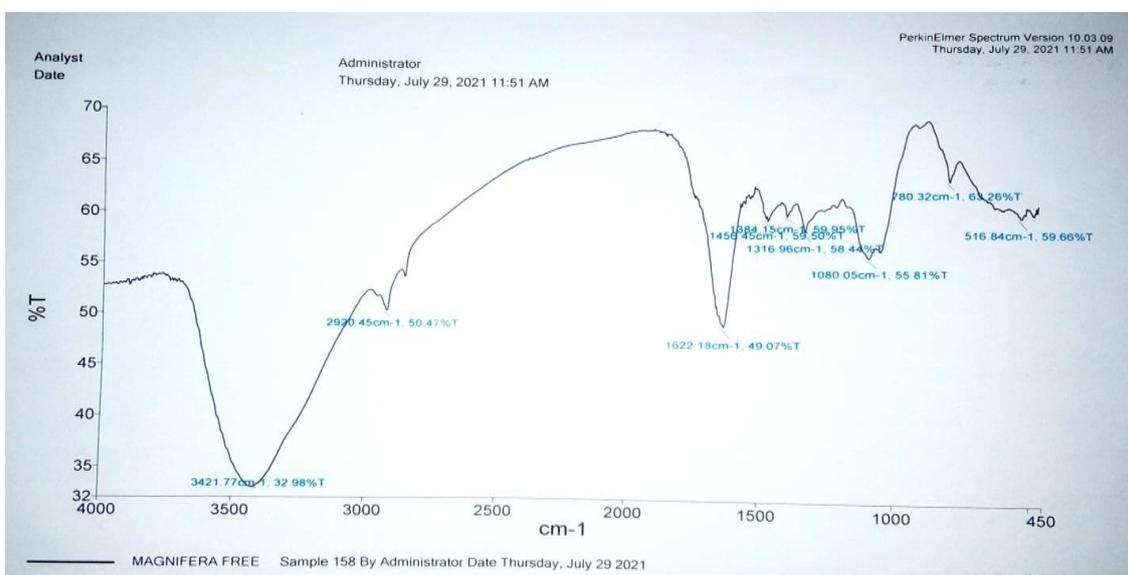


Figure 1. FT-IR spectra unloaded sample

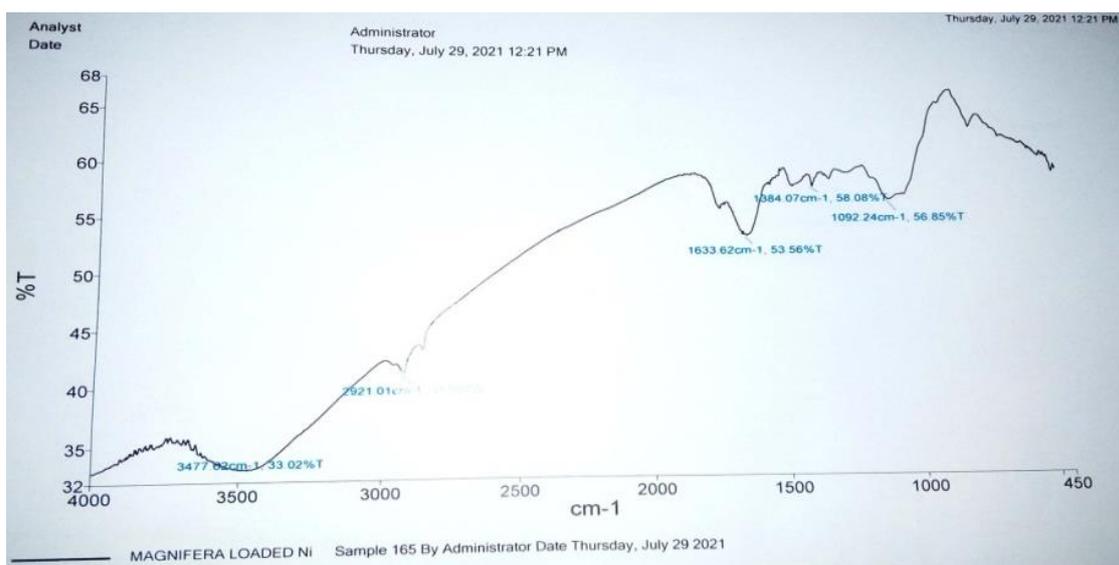


Figure 2. FT-IR spectra unloaded with Ni^{2+} ions

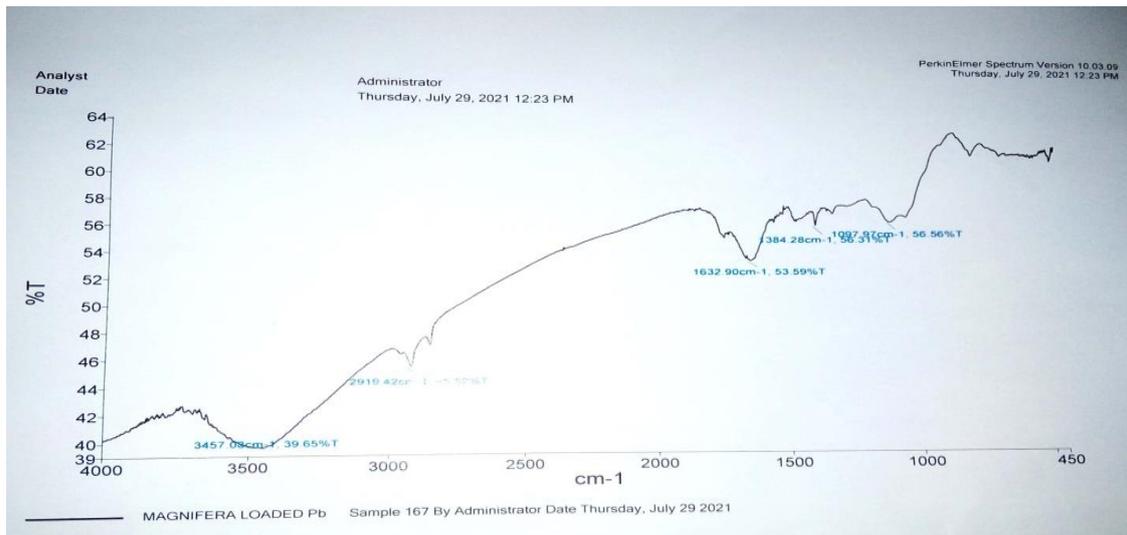


Figure 3. FT-IR loaded with Pb^{2+} ions.

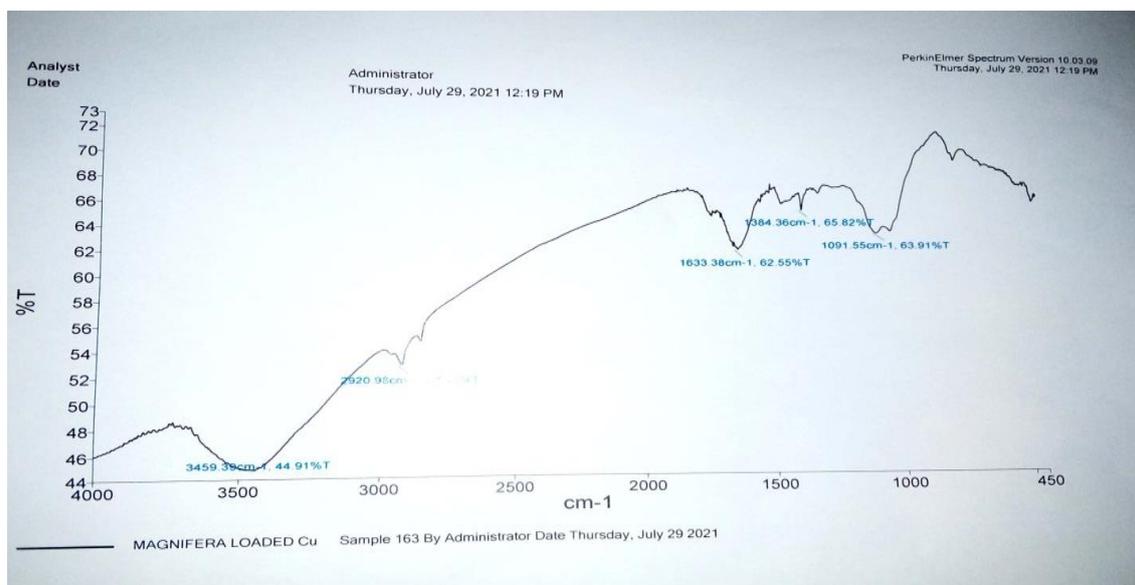


Figure 4. FT-IR loaded with Cu^{2+} ions

3.2. Effect on initial metal concentration

The amount of Ni^{2+} , Pb^{2+} and Cu^{2+} ions adsorbed by *Mangifera indica* leaf at equilibrium (q_e). Figure 5 indicate the Ni^{2+} ions removal efficiency increased from 65.03 to 75.92% at the concentration of 10 to 40ppm after which the optimum was reached. This shows the optimum adsorption capacity of 2.53mg/g at the concentration 40ppm for nickel (II), lead(II) the percentage removal increased from 98.35 to 99.35% at the concentration of 10 to 40ppm with the optimum adsorption capacity at 3.27mg/g at the concentration 10ppm for lead(II). And the percentage removal of copper (II) ions increase from 67.52 to 78.25% at the concentration of 10 to 40ppm which shows that the optimum adsorption capacity is 2.60mg/g at the concentration 40ppm for copper(II) [9].

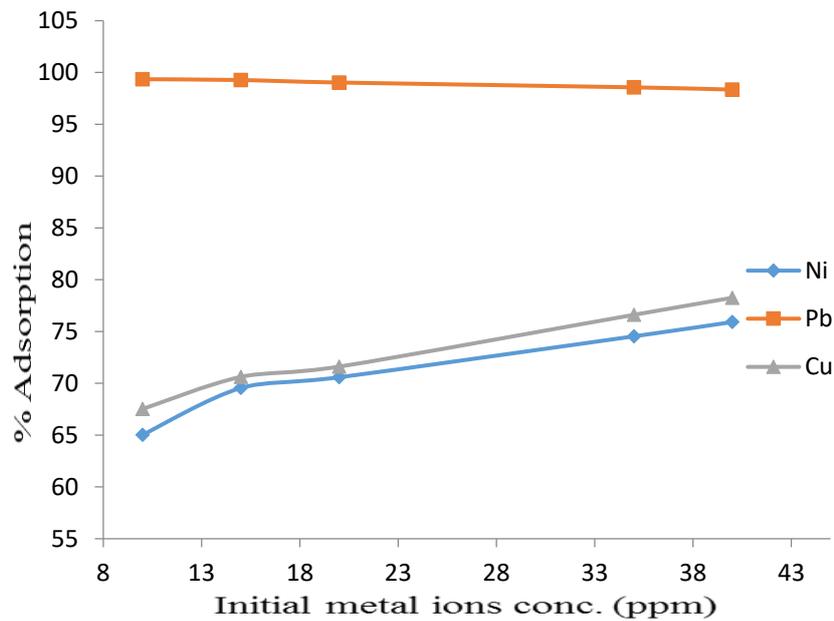


Figure 5. Plots of percentage adsorption against initial metal concentration of Ni^{2+} , Pb^{2+} , and Cu^{2+} ions by *Mangifera indica* leaf at fixed (adsorbent dose of 0.5g, pH 6.0, contact time = 60 min and temp of 25°C)

3.3. Effect of pH

The effect on the adsorption capacity of *Mangifera indica* leaf was investigate on Ni^{2+} , Pb^{2+} , and Cu^{2+} ions at different pH value of 2, 4, 6, 8 and 10 at optimum concentration of metal ion nickel(II) 40ppm, lead(II) 10ppm and copper(II) 40ppm, at a fixed adsorbent dose 0.6g, contact time of 40mins and temperature 25°C.

Low percentage of adsorption was observed at pH 2 for Ni^{2+} and Pb^{2+} , pH 8 Cu^{2+} ions. The optimum percentage adsorption was observed at pH 10 for Ni^{2+} with percentage adsorption of 76.49%, pH 8 for Pb^{2+} with percentage adsorption of 99.11% and pH 4 for Cu^{2+} ions with percentage adsorption of 86.02% as shown in Figure 6. The adsorption of metal ions dependent of pH, adsorption of heavy metal from aqueous solutions depends on the properties of adsorbent and molecule of adsorbate transfer from the solution to the solid phase (Adebayo *et al.*, 2012). It has also being observed that the capacities for the heavy metals are depending on pH. The result shows that high pH favor Ni^{2+} and Pb^{2+} as compare with copper by *Mangifera indica* leaf.

At very high pH, the metal ions get precipitated due to hydroxide anion forming a metal hydroxide precipitates for this reason; the optimum pH value was selected to be 6.0 for other subsequent experiment carried out [7].

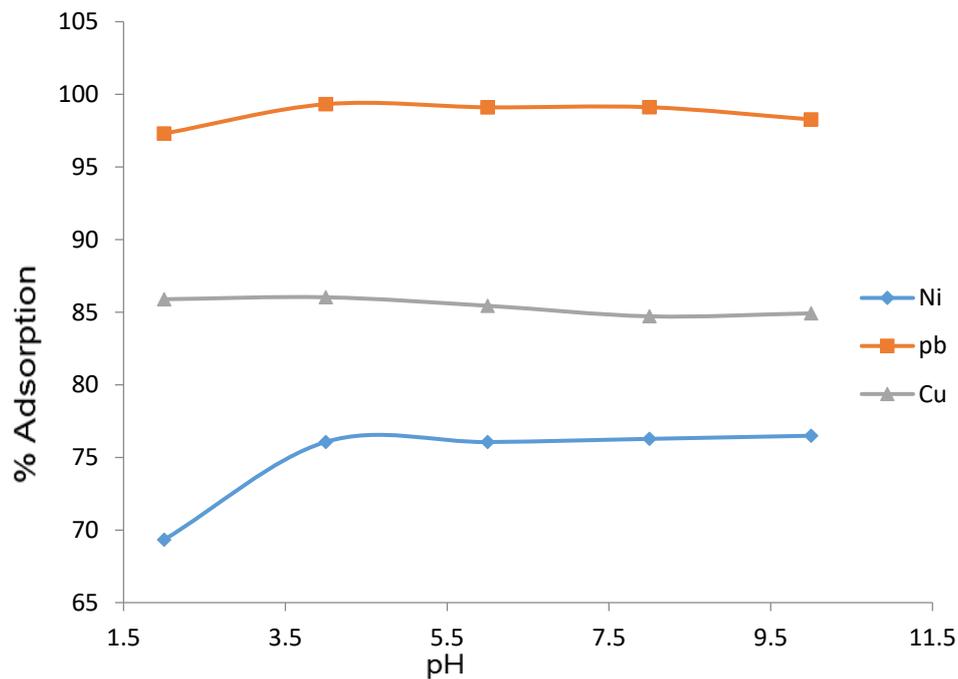


Figure 6. Plots of percentage adsorbed against pH of Ni^{2+} , Pb^{2+} , and Cu^{2+} ions by *Mangifera indica* leaf.

3.4. Effect of adsorbent dose on adsorption

The influence of adsorbent dose on the adsorption capacity of *Mangifera indica* leaves was investigated on Ni^{2+} , Pb^{2+} , and Cu^{2+} ions by varying the adsorbent dosage of 0.2, 0.4, 0.6, 0.8 and 1.0g. optimum condition of metal concentration of 40ppm for Ni^{2+} and Cu^{2+} and 10ppm for Pb^{2+} , pH of 10 for Ni^{2+} pH of 8 for Cu^{2+} pH of 4 for Cu^{2+} , agitation time for 40mins at a temperature 25°C. The result shows that the percentage removal decrease with the increase in amount of adsorbent dose in case of Ni^{2+} and Pb^{2+} , but Cu^{2+} percentage removal increase with increase in amount of adsorbent dose. The percentage adsorption of increase from 97.72 to 99.53% at optimum dose 0.2g for Ni^{2+} , 98.53 to 98.94% at optimum dose 0.2g for Pb^{2+} and 89.23 to 90.97% at optimum dose 1.0g for Cu^{2+} as shown in Figure 7.

Decreased with increase in adsorbent dosage, this result attributed to the metal ions can easily access the adsorption sites when the adsorbent amount is small. With increasing adsorbent content, the corresponding increase in adsorption per unit mass is less because the metal ions find it difficult to approach the adsorption sites due to overcrowding of adsorbent termed as a kind of solid concentration effect [1].

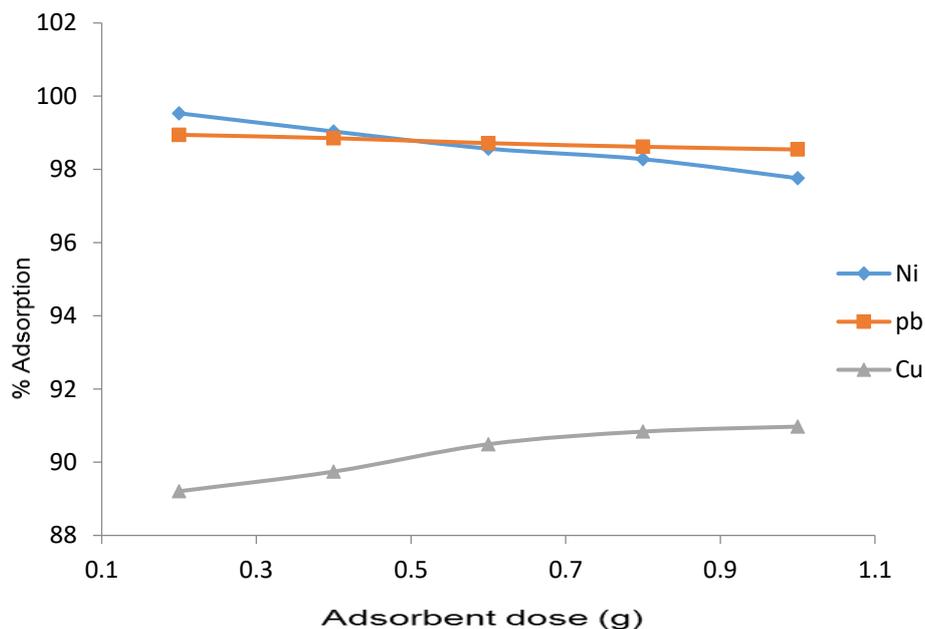


Figure 7. Plots of percentage adsorbed against dose on adsorption of Ni^{2+} , Pb^{2+} , and Cu^{2+} ions by *Mangifera indica* leaf.

3.5. Effect of adsorbent dose on adsorption

The influence of adsorbent dose on the adsorption capacity of *Mangifera indica* leaves was investigated on Ni^{2+} , Pb^{2+} , and Cu^{2+} ions by varying the adsorbent dosage of 0.2, 0.4, 0.6, 0.8 and 1.0g. optimum condition of metal concentration of 40ppm for Ni^{2+} and Cu^{2+} and 10ppm for Pb^{2+} , pH of 10 for Ni^{2+} pH of 8 for Cu^{2+} pH of 4 for Cu^{2+} , agitation time for 40mins at a temperature 25°C. The result shows that the percentage removal decrease with the increase in amount of adsorbent dose in case of Ni^{2+} and Pb^{2+} , but Cu^{2+} percentage removal increase with increase in amount of adsorbent dose. The percentage adsorption of increase from 97.72 to 99.53% at optimum dose 0.2g for Ni^{2+} , 98.53 to 98.94% at optimum dose 0.2g for Pb^{2+} and 89.23 to 90.97% at optimum dose 1.0g for Cu^{2+} as shown in Figure 8.

Decreased with increase in adsorbent dosage, this result attributed to the metal ions can easily access the adsorption sites when the adsorbent amount is small. With increasing adsorbent content, the corresponding increase in adsorption per unit mass is less because the metal ions find it difficult to approach the adsorption sites due to overcrowding of adsorbent termed as a kind of solid concentration effect [10].

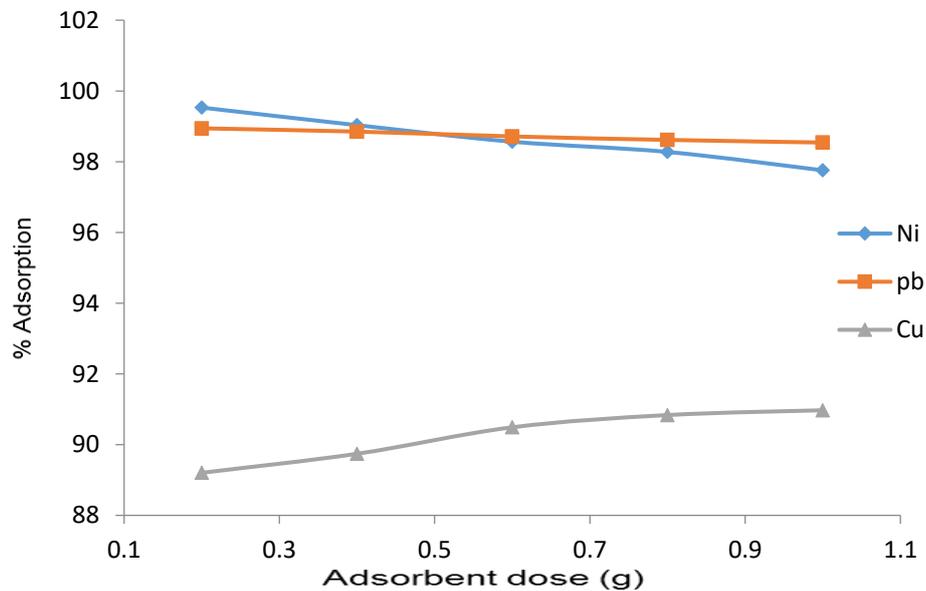


Figure 8. Plots of percentage adsorbed against dose on adsorption of Ni^{2+} , Pb^{2+} , and Cu^{2+} ions by *Mangifera indica* leaf.

3.6. Effect of contact time on adsorption

The effect of agitation time on adsorption capacity of *Mangifera indica* leaf was investigated on Ni^{2+} , Pb^{2+} , and Cu^{2+} ions solution at different contact time of 20, 40, 60, 100 and 120 min at optimum conditions of metal concentration of 40 ppm for Ni^{2+} and Cu^{2+} , 10 ppm for Pb^{2+} , pH of 10 for Ni^{2+} , pH of 8 for Cu^{2+} , pH of 4 for Pb^{2+} , adsorbent dose of 0.2 g for Ni^{2+} and Pb^{2+} , 1.0 g for Cu^{2+} , at temperature of 25°C. The result that was observed in Figure 9, shows that the percentage removal of all metal ions increases with an increase in contact time, until it reaches equilibrium at 100 min. From 100 min to 120 min, no increase in adsorption was observed. The percentage adsorption increases from 88.24 to 90.84% for nickel, 99.58 to 99.96% for lead, and 87.92 to 90.15% for copper, all at equilibrium time 100 min. In the early stage of adsorption, a large number of vacant sites is available for adsorption to proceed. As constant time increases, the adsorption capacity increases until it reaches optimum, the maximum number of sites that got adsorbed to the metal ions increases, which becomes difficult for lead (II) ions to search for the very few remaining sites, thus the rate of adsorption remains constant as agitation [9].

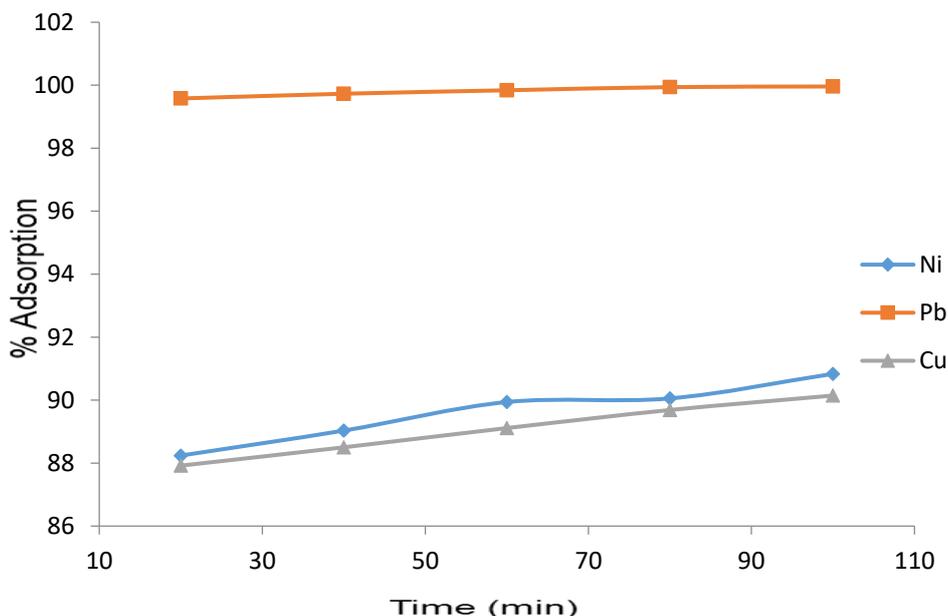


Figure 9. Plots of percentage adsorption against contact time on adsorption of Ni^{2+} , Pb^{2+} , and Cu^{2+} ions by *Mangifera indica* leaf.

3.7. Effect of temperature on adsorption

The equilibrium uptake of Ni^{2+} , Pb^{2+} , and Cu^{2+} ions by *Mangifera indica* leaf was determined at different temperature of 25, 35, 45, 55 and 65°C, at optimum conditions of metal concentration of 40ppm for Ni^{2+} and Cu^{2+} , 10ppm for Pb^{2+} , pH of 10 for Ni^{2+} pH of 8 for Cu^{2+} pH of 4 for Cu^{2+} , adsorbent of dose 0.2g Ni^{2+} and Pb^{2+} , 1.0g for Cu^{2+} , agitation times of 100min Ni^{2+} , Pb^{2+} , and Cu^{2+} ions. The rate of adsorption was affected by temperature as shown in Figure 100.

The percentage adsorption of nickel(II) decrease with increase in temperature from 89.04 to 84.47% at temperature of 25°C to 65°C. Percentage adsorption of lead(II) increase from 98.72 to 98.73% at temperature 25°C to 35°C and further decrease to 98.24% at 65°C while percentage adsorption of Copper was observed increase from 91.41 to 93.14% at temperature of 25 to 45°C and further decrease to 93.01% at temperature 65°C. These shows that adsorption is endothermic up to the optimum temperature because the extend of adsorption decrease with increase in temperature [10].

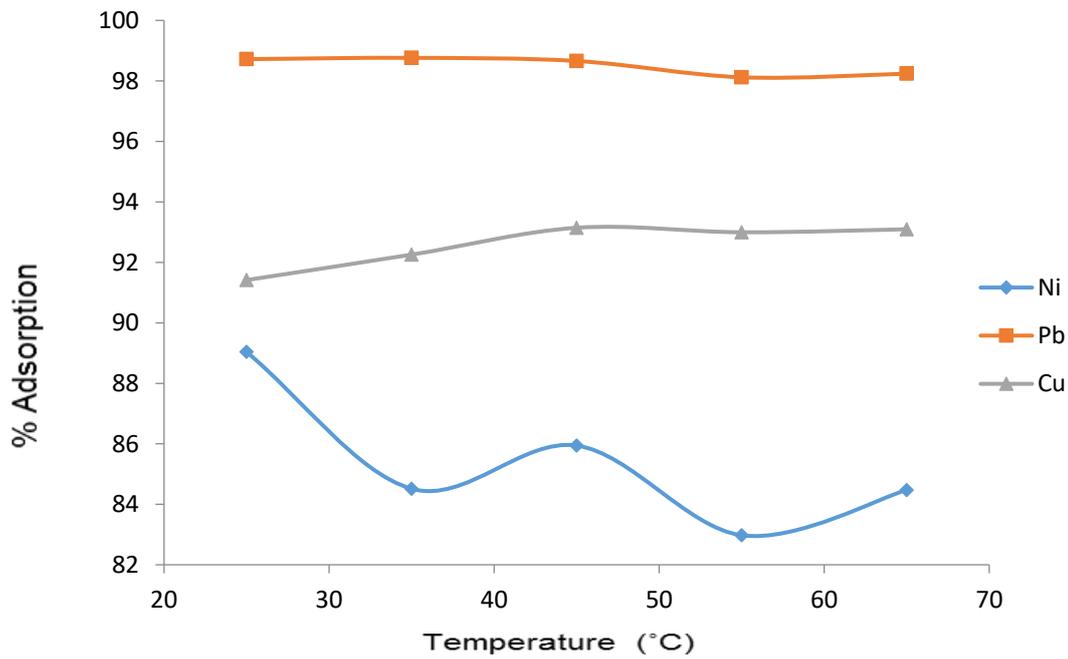


Figure 10. Plots of percentage adsorption against temperature on adsorption of Ni²⁺, Pb²⁺, and Cu²⁺ ions by *Mangifera indica* leaf at optimum conditions

3.8. Adsorption isotherms

Analysis of isotherm is very important for designing the adsorption process. The experimental data were analyzed with Langmuir and Freundlich as the two most commonly use isotherms models.

Langmuir adsorption isotherm models the monolayer coverage of the adsorption surfaces and assumes that sorption take place on a structurally homogeneous surface of adsorbent. Freundlich adsorption isotherm models the multilayer adsorption for the sorption on heterogeneous surface [10].

Freundlich and Langmuir isotherm model were used to describe the equilibrium data. The Langmuir isotherm constant K_L and Q_m were calculated from the slope and intercept of the plot between $1/q_e$ and $1/C_e$. The Langmuir isotherm showed good fit to the experimental data with high correlation coefficient in case of Pb²⁺ ions with R² value of 0.9950 over Ni²⁺ and Cu²⁺ ions with R² Value 0.9214 and 0.9908, as is shown in (Table 1). Q_m and K_L were calculated from the slope and intercept respectively.

Table 1. Isotherm Parameters of Various Adsorbent

Isotherm models	Adsorbates (Metal ions)		
	Ni ²⁺ ions	Pb ²⁺ ions	Cu ²⁺ ions
Langmuir			
R ²	0.9214	0.9950	0.9908
Q _m	-0.3874	3.5523	-0.0603
K _L	-7.1890	4.3383	-2.2470
Freundlich			
R ²	0.9973	0.9976	0.9942
N	0.6762	1.6998	0.6524
K _f	0.0874	4.2677	0.0900

Freundlich isotherm best fit the experimental data of lead(II) and nickel(II) and with R^2 value 0.9976 and 0.9937 when compare with that of copper(II) which has R^2 value 0.9942. Freundlich isotherm constants K_f and $1/n$ were calculated from the slope and intercept of the straight line of $\log q_e$ versus $\log C_e$. The magnitude of n between 1 and 10 ($1/n$ less than 1) represents a favorable adsorption. All information's are represented in (Table 1). Similar findings reported by [11], when determined the adsorption of zinc and copper ions from aqueous solution by thermally treated Quail Eggshell.

3.9. Adsorption kinetics

Kinetic model were applied to test for the experimental data in order to check the mechanism of the adsorption of the metals ions by *Mangifera indica* leaf and the potential rate controlling step mass transport and chemical reactions. Pseudo first-order and Pseudo second-order kinetics model were tested.

3.9.1. Pseudo first-order equation

The adsorption kinetics described by a Pseudo first-order equation. From the studied initial concentration, the rate constant (K_1) and theoretical equilibrium of adsorption capacities (q_e) was calculated from the slope and intercept of the linearized plot of $\log(q_e - q_t)$ against t as shown in the (Table:2). The correlation coefficient (R^2) for nickel(II), lead(II) and copper(II) of the linear graph are 0.9058, 0.9059 and 0.6511 as shown in (Table 2). which indicate the data fit well to pseudo first-order model. The calculated value of K_1 and q_e for the nickel(II), lead(II) and copper(II) are 0.031, 0.0598, 0.1681 min^{-1} and 1.3313, 30.8810, 21.463 mg g^{-1} . Therefore it could be suggested that the adsorption of all the metals ions did not fit; pseudo first-order model when compare with the R^2 value of the pseudo second-order model and the calculated value of q_e .

Table 2. Kinetic parameter of various adsorbates

Isotherm models	Adsorbates (Metal ions)		
	Ni ²⁺ ions	Pb ²⁺ ions	Cu ²⁺ ions
Pseudo-first order			
K_1	0.0310	0.0598	0.1681
q_e	1.3313	30.8810	21.4634
R^2	0.9098	0.9059	0.6511
Pseudo-second order			
K_2	10.248	0.00006	416.66
q_e	3.0931	-1666.7	0.00012
R^2	0.9938	1	1

3.9.2. Pseudo second-order model given in equation

The experimental data was also applied to the pseudo second-order model given in kinetics model. The fit of this model was controlled by each plot of t/q_t versus t respectively. The constant q_e and k_2 was calculated from the slope and intercept of the shown in (Table 2). It can be seen from the result R^2 value obtained for Ni²⁺, Pb²⁺ and Cu²⁺ ions are higher than those obtained from pseudo first-order kinetic model, which are 0.9938, 1.00 and 1.00. These suggest that pseudo second-order model best fit adsorption of nickel(II), lead(II) and copper(II) respectively, the calculated k_2 and q_e are 10.248, 0.00006, 0.00012 min^{-1} and 3.093, -1666.7, 416.66 mg g^{-1} . Pseudo second-order model is based on the capacity of phase and indicating that the rate limiting step is chemical adsorption process [12].

3.10. Thermodynamics Studies

Thermodynamics parameter of the adsorption process such as change in Gibbs free energy ΔG (KJ/mol), change in enthalpy ΔH (KJ/mol) and change in entropy ΔS (KJ/molK), were determined at different temperature. The plot of $\log k$ against $1/T$ gives a linear graph, ΔH and ΔS are determined from the slope and intercept of the graph. The result shows a good R^2 value 0.9795 for Ni^{2+} but less R^2 value 0.6734 and 0.6184. Change in Gibbs free energy of the adsorption Ni^{2+} , Pb^{2+} and Cu^{2+} ions at different temperature are presented in (Table 3). The negative value of ΔG in case of Ni^{2+} , Pb^{2+} ions implies that the process is feasible and spontaneous in nature while the positive value of ΔG for Cu^{2+} ions implies is unfeasible and non-spontaneous [9]. The value of change in enthalpy ΔH , and change entropy ΔS , of Ni^{2+} , Pb^{2+} and Cu^{2+} ions adsorbed by *Mangifera indica* leaf obtained are also present in (Table 3), the positive value of ΔH suggest the endothermic nature of the adsorption and a possible bond which occur between the metals and the adsorbent while the negative suggested exothermic nature [13]. The positive value of ΔS indicate increased In degree of randomness at solid solution interface during the adsorption of the metals ions the *Mangifera indica* leaf. Similar finding was observed by researchers [1].

Table 3. Thermodynamic parameter for the adsorption of Ni^{2+} , Pb^{2+} and Cu^{2+} ions on *Mangifera indica* leaf

Parameters	ΔH° (KJ/mol)	ΔS° (KJ/mol/K)	ΔG KJ/mol					R^2
			298	308	318	328	338	
Temperature (K)								
Ni^{2+}	-8893.84	-1.3515	-1182.49	-923.72	-664.95	-406.18	-147.41	0.9795
Pb^{2+}	-5710.25	-0.7051	-5486.6	-5479.1	-5471.6	-5464.1	-5456.6	0.6734
Cu^{2+}	2994.03	7.486	763.20	688.61	613.48	538.62	463.76	0.6184

4. Conclusion

Removal of Ni^{2+} , Pb^{2+} and Cu^{2+} ions from aqueous solution using *Mangifera indica* leaf as adsorbent; has been investigated. From the investigation it was observed the experimental parameters at optimum condition of initial metal ion concentration, pH, adsorbent dosage, contact time and temperature was determined for their potential effect on the efficiency of Ni^{2+} , Pb^{2+} and Cu^{2+} ions adsorption.

Based on the detailed experimental investigations it was determined to be 40ppm for Ni^{2+} and Cu^{2+} and 10ppm for Pb^{2+} ions, 10 for Ni^{2+} 8 for Cu^{2+} 4 for Cu^{2+} , 0.2g for Ni^{2+} and Pb^{2+} , 1.0g for Cu^{2+} , 100min Ni^{2+} , Pb^{2+} , and Cu^{2+} ions, and 25°C, 35°C and 45°C respectively. The kinetics studies indicate that the adsorption process of the metals ions followed the pseudo second-order model with R^2 value of 0.9938, 1.00 and 1.00 respectively. Equilibrium studies showed that the adsorption of Ni^{2+} , Pb^{2+} and Cu^{2+} ions are well represented by both Langmuir and Freundlich isotherm but the Langmuir model gave a better fit for Pb^{2+} ions with R^2 value of 0.9950 and Langmuir constant K_L of 4.3383 while Freundlich isotherm model best fit the experimental data of lead(II) and nickel(II) with a R^2 value of 0.976 and 0.9973 and Freundlich constant K_F value of 4.2677 and 0.0874. The calculated thermodynamics parameters of Ni^{2+} , Pb^{2+} and Cu^{2+} ions are; ΔG° -1182.49, -5479.1 and 613.48 KJ/mol, ΔH° -8893.84, -5710.25 and 2994.03KJ/mol, and ΔS° -1.3515, -0.7051 and 7.486KJ/molK. The FT-IR analysis suggested alcohol and alkene groups combine intensively with Ni^{2+} , Pb^{2+} and Cu^{2+} ions. The advantage of high metal adsorption, the biomass leaf of *Mangifera indica* has the potential to be used as a simple, efficient, ef-

fective methods and economical adsorbent material for the adsorption Ni²⁺, Pb²⁺ and Cu²⁺ ions from waste water.

Acknowledgments

We Acknowledged Technica staff of the Department of Chemistry, Biochemistry, pharmacy and Geology of Gombe state University .Gombe State and the University for the Equipment's and Laboratory space.

References

- [1] Hagufta, Z. b., Muhammad, I. K., Majeda, K., Mushtaq, H. L., Shabnam, S. M., Farooq, A., Prasert, P., Muhammad, L. M. and Nasir, K. "Kinetic, equilibrium and thermodynamic studies for adsorption of nickel ions onto husk of *Oryza sativa*" *Journal of Desalination and Water Treatment* 2019, 167: 277–290. DOI: 10.5004/dwt.2019.24646.
- [2] Barakat, M. A. (1). "New trends in removing heavy metals from industrial waste water." *Arabian Journal of Chemistry* 2014 (4): 361-377. <https://doi.org/10.1016/j.arabjc.2010.07.019>.
- [3] Mohammed, A. A., Mohd, N. Mohd, H., Abd Wahid, H. M., Yusuf, M. S. and Mohd A. R. "The detrimental effects of lead on human and animal health." *Journal of Veterinary World* 2016, 9(6): 660-671. doi: 10.14202/vetworld.2016.660-671.
- [4] A. Ksakas, K. Tanji, B. El Bali1, M. Taleb, A. Kherbeche. Removal of Cu (II) Ions from Aqueous Solution by Adsorption Using Natural Clays: Kinetic and Thermodynamic Studies. *J. Mater. Environ. Sci.*, 2018, 9(3), 1075-1085. <https://doi.org/10.26872/jmes.2017.9.3.119>.
- [5] Abdel-Moneum M. Ahmed, Alaa E. Ali, Ahmed H. Ghazy. "Adsorption Separation of Nickel from Wastewater by using Olive Stones." *Advanced Journal of Chemistry-Section A* 2019, 2(1), 79-93. <http://ajchem-a.com>.
- [6] Samuel, B., Emily G., Katherine E. H., Tara L. D., Christian E. S., Michael D. T., and Adriana R. O. "Concise Review of Nickel Human Health Toxicology and Ecotoxicology, MDIP" *Journal of inorganic* 2019, 7(6): 35-89. <https://doi.org/10.3390/inorganics7070089>
- [7] Adebayo, M. A., Adediji, J. F., Adebayo, A. A. and Adebayo, O. T. "Equilibrium, Kinetic and Thermodynamic Parameters of Biosorption Ni²⁺". *Journal of Applied Sciences* 2012, 12(1): 71-77. DOI: 10.3923/jas.2012.71.77.
- [8] Amuda O.S., Ibrahim A.O. "Industrial wastewater treatment using natural materials adsorbent"; *African Journal of Biotechnology* 2006, 5 (16), 1483-1487. <http://www.academicjournals.org/AJB>
- [9] Nyoni, S. S. E., Mukaratiwa, M. N. and Shumba, M. "Comparative biosorption of Pd ions from solution using *Moringa Oleifera* plant part equilibrium kinetics and thermodynamic studies." *African Journal of Biotechnology* 2017, 16(48): 2215-2231. DOI:10.5897/AJB2017.16066
- [10] Aroke, U. O, Ibrahim M. and Okoroma L. A. "Parametric studies on sulphate ion sorption at different pH on HDTMA-Br modification kaolin clay." *International journal of emerging trends in engineering and development* 2015, 3(5): 250-259.
- [11] Adeyinka, S. Y., Idowu, I. O. and Emmanuel S. E. "Kinetic and Thermodynamic Studies of the Adsorption of Heavy Metals from Aqueous Solution by Thermally Treated Quail Eggshell." *Journal of Environmental Science and Technology* 2017, 10(5): 245-257. DOI: 10.3923/jest.2017.245.257.
- [12] A.A. Seolatto, T. D. Martins, R. Bergamasco, C. R. G. Tavares, E. S. Cossich and E. A. da Silva "Biosorption study of Ni²⁺ and Cr³⁺ by *sargassum filipendula*: kinetics and equilibrium" *Brazilian Journal of Chemical Engineering* 2014, 31 (1) 211 – 227. DOI:10.1590/S0104-66322014000100020.
- [13] Babalola, J. O., Overah, L. C., Adesola B., Vincent O. O. and Olatunde, A. "Kinetic, Equilibrium and thermodynamic studies on the biosorption of Cd(II) from aqueous solutions by the leaf biomass of *Calotropis Procera* – 'Sodom apple.'" *Journal of Applied Science Environmental and Management* 2011, 15(4): 607 – 615.