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# Equilibrium studies on biosorption of lead, cadmium and nickel ions using cassava waste biomass

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**ABSTRACT**

*The efficiencies of agricultural wastes from two different species of cassava-manihot esculenta cranz (ME) and manihot walkarae (MW) as adsorbents in removing Cd(II), Ni(II) and Pb(II) from aqueous solutions were compared. Batch adsorption experiments were carried out as a function of pH and concentration. The adsorption results were analyzed by the Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, Harkins Jura and Halsey isotherm models using linearized correlation coefficient values. The characteristic isotherm parameters for each isotherm were determined and results obtained showed that Freundlich and Halsey best represented the equilibrium data for the metal ions-adsorbents systems. This was followed by the Langmuir model. The optimum pH for adsorption of Pb(II) and Ni(ll) on both adsorbents (ME and MW) occurred at 4.5 having maximum removal efficiencies of 98.94% and 93.05% respectively for Pb(II) and Ni(II) adsorption onto ME and 96.79% and 91.04% for adsorption onto MW following the initial order. Cd(II) exhibited a different pH dependence having maximum removal at pH 6.5 on both adsorbents and with removal efficiencies of 96.74% for ME and 96.23% for MW.*

**Keywords:** Adsorption isotherms, biosorbents, heavy metal ions, *Manihot esculenta cranz* and *manihot walkarae*

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## INTRODUCTION

Continuous discharges of industrial, domestic and agricultural wastes into rivers and lakes deposit toxic heavy metals into these water bodies. These heavy metals endanger public health due to their poisonous or toxic nature and constitute threats to our environment. Lead is classified as one of the priority metals from the point of view of potential health hazards to humans and has been included in a list by Environmental Protection Agency (EPA) as one of the 129 priority pollutants [1, 2]. Exposure to cadmium causes severe health effects to human ranging from renal dysfunction, liver damage, bone degradation and hypertension [3]. Due to its toxicity, cadmium has been included in the list of priority pollutants by Department of Environment, UK [4]. Cadmium is also a potent neuro toxic metal with a permissible limit of 0.003 mg/L in drinking water and has been classified by USEPA as a group B1 carcinogen [2, 5].

Dermatitis (Ni itch) remains the most frequent effect of exposure to nickel(II) [6]. High concentrations of nickel(II) in ingested water may cause severe damages to lungs, kidneys and gastro intestinal distress such as nausea, vomiting, diarrhea, pulmonary fibrosis, renal edema and skin dermatitis [7].

The removal of these metal ions from water bodies constitutes big problem due to their trace quantities and formation of complexes with natural organic matter [8]. Strict regulations on the discharge of toxic metals particularly in highly industrial nations make it imperative to develop various technologies for the removal of pollutants from industrial effluents. Different technologies and processes are currently in use and include: Membrane processes [9, 10], Advanced oxidation processes [11, 12], Biological treatments [13, 14], Chemical and Electrical techniques [13, 15] and Adsorption Processes [16-18].

However, problems with some of the aforementioned techniques such as high cost of equipment, ineffective and inefficient metal removal particularly when low concentrations of the metal ions are involved, make it necessary to develop easily available, inexpensive and effective alternatives for wastewater treatment. Biosorption, which involves use of biological materials, both living as well as dead (metabolically inactive) biomass to sequester metal ions from solutions, has offered an effective, eco-friendly and a competitive alternative to the conventional techniques for heavy metal removal from solutions. It has been found that various functional groups present on the surface of the cell wall of the biomass confer on them certain forces of attractions that adsorb the metal ions onto the surface of the biosorbent. A number of materials derived from plants and animals have been employed for metal removal and these include: Sago waste[19], Black tea leaves [20], *Shorea dasyphylla* sawdust [21], waste acorn of *Quercus ithaburensis* [22], husk of Bengal gram (*Cicer arientinum*) [23] Rice husk [6, 24], chitosan [25-27], seaweed [28], pseudomonas sp.[29, 30], algae[31-33], fungus[34] and yeast[35, 36].

Cassava wastes are being evaluated as possible substrates (materials) for adsorption of metal ions from solutions in this study because they are produced in large quantities. Our goal in the present study is to compare the efficiencies of agricultural wastes from two species of cassava viz. *manihot esculenta cranz* and *manihot walkarae* in removing lead, nickel and cadmium ions from aqueous solutions. Experimental conditions such as pH and metal ion concentration, which affect biosorption process, were investigated and the equilibrium adsorption data evaluated using different isotherm models.

## EXPERIMENTAL SECTION

**Preparation of the adsorbents**

The adsorbents, *Manihot esculenta cranz* and *manihot walkarae cassava* were collected from a cassava experimental site at National Root Crops Research Institute, Umudike Abia State, Nigeria. Their peels were washed extensively in running tap water to remove dirt and other particulate matter. They were subjected to further washing with distilled water repeatedly. Subsequently, the peels were air-dried and later oven-dried for 12 hours at a temperature of 90 $^0$C. The dried samples were crushed using grinding mill fitted with sieves to obtain a particle size of 500 µm. The samples were labelled and stored in tight plastic containers and kept for the adsorption analysis.

100 g of each of the sample size of the two species of the cassava were soaked in excess of 0.5 M $HNO_3$ solution in a beaker, stirred for 30 min at a temperature of 30$^0$C and then left undisturbed for 24 h. They were then filtered through a whatman filter paper and rinsed severally with deionised water until a pH 7 was obtained. The adsorbents were finally air-dried. The treatment with acid opens up the pores of the adsorbent samples in preparation for the adsorption analysis and to destroy any debris or soluble biomolecules that might interfere with the metal ions during the adsorption process.

**Adsorbates Preparation**

Stock solutions of 1000 mg/L of each of the metal ions, cadmium, lead and nickel were prepared from their salts, $CdSO_4.8H_2O$, $(CH_3COO)_2Pb.3H_2O$ and $NiSO_4.6H_2O$ respectively. From the stock solutions, different working concentrations ranging from 20 - 100 mg $L^{-1}$ of each of the metal ions were prepared by serial dilution. The effect of concentration on the adsorption of the metal ions was studied by transferring 50 mL of the different concentrations of the metal ions into different 250 mL conical flasks while maintaining the pH of the solutions at 5.5. Thereafter, 1.0 g of each of the adsorbents (ME and MW) was weighed into the flasks, corked and labeled and agitated in a rotary shaker for 2 h. At the end of the adsorption process, the content of each flask was filtered, centrifuged and the residual metal ion concentrations ($C_e$) analyzed. The concentrations of the standards and the test solutions were confirmed using buck scientific Atomic Absorption Spectrophotometer (AAS) model 210. The pH of the adsorbate solutions was kept at 5.5 using pH meter (model: pHS-25). For the study on influence of pH on the adsorption process, a similar procedure was carried out just as in the case of initial metal concentration except that a fixed initial metal ion concentration of 100 mg/L was used and the pH of the solutions adjusted from pH 2.5 to 10.5 using either 0.1 M HCl or 0.1 M NaOH solution and at a fixed temperature of $29^0$C. The amount of the metal ions adsorbed was calculated by difference. The analysis was carried out in triplicates and mean residual concentrations analyzed. The amount of metal ions adsorbed at equilibrium, $q_e$ (mg/g) was determined using the mass balance equation (1).

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (1)$$

The percentage of metal ions adsorbed (% R) was also computed using the expression:

Percent adsorption: $$\% R = \frac{C_0 - C_e}{100} \times 100 \quad (2)$$

where $C_o$ and $C_e$ are the initial and equilibrium concentrations (mg/L), *V* is the volume of solution (L) and *m* the dry weight of the adsorbents (g).

## RESULTS AND DISCUSSION

### Effect of pH

The amount of lead, nickel and cadmium ions adsorbed onto the adsorbents at various pH values are shown in Figs.1 and 2. The pH of an aqueous solution is a vital parameter that affects both the availability of metal ions in solution as well as the number of binding sites on the adsorbent [37, 38]. This means that the dependence of heavy metal adsorption on pH is linked to both the metal solution chemistry and the ionization state of the functional groups of the adsorbent which will in turn affect the availability of the active binding sites. The biosorption capacity increased with increasing pH and optimum pH for removal of $Pb^{2+}$ and $Ni^{2+}$ by both adsorbents occurred at pH 4.5 with adsorption capacities of 4.8395 mg/g (96.79%) and 4.5520 mg/g (91.04%) respectively for $Pb^{2+}$ and $Ni^{2+}$ removal by MW and 4.9470 mg/g (98.94%) and 4.6525 mg/g (93.05%) for adsorption onto ME. That of $Cd^{2+}$ removal has optimum removal at a pH 6.5 with values of 4.8115 mg/g (96.23%) for adsorption onto MW and 4.8370 mg/g (96.74%) for adsorption onto ME. The trend of heavy metal removal followed Pb > Cd > Ni. The effect of pH on the biosorption capacity can be interpreted by the competition of the hydronium ions [$H_3O^+$] and metal ions for binding sites. At low pH values (< 4.5), the ligands on the cell walls of the adsorbents may have been closely associated with the hydroxonium ions leading to a decreased removal efficiency due to the competition of positive metal ions with the hydroxonium ions for the free binding sites, but when the pH is increased, the hydroxonium ions are gradually dissociated and the positively charged metal ions are associated with the free binding sites. Similar findings have been reported by other researchers [39, 40]. The adsorbents generally show a preferred affinity for $Pb^{2+}$ than for $Cd^{2+}$ and $Ni^{2+}$ at the initial concentration of 100 mg $L^{-1}$ used.

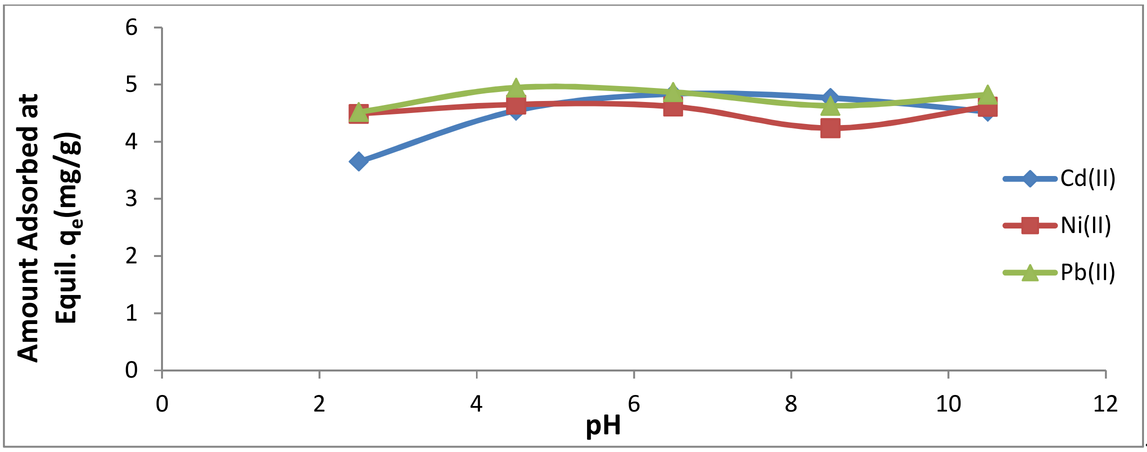


**Fig. 1. Effect of pH on the biosorption of the metal ions onto ME ($C_o$: 100 mg/L, biomass conc.: 1.0 g/L, 29 $^oC$)**

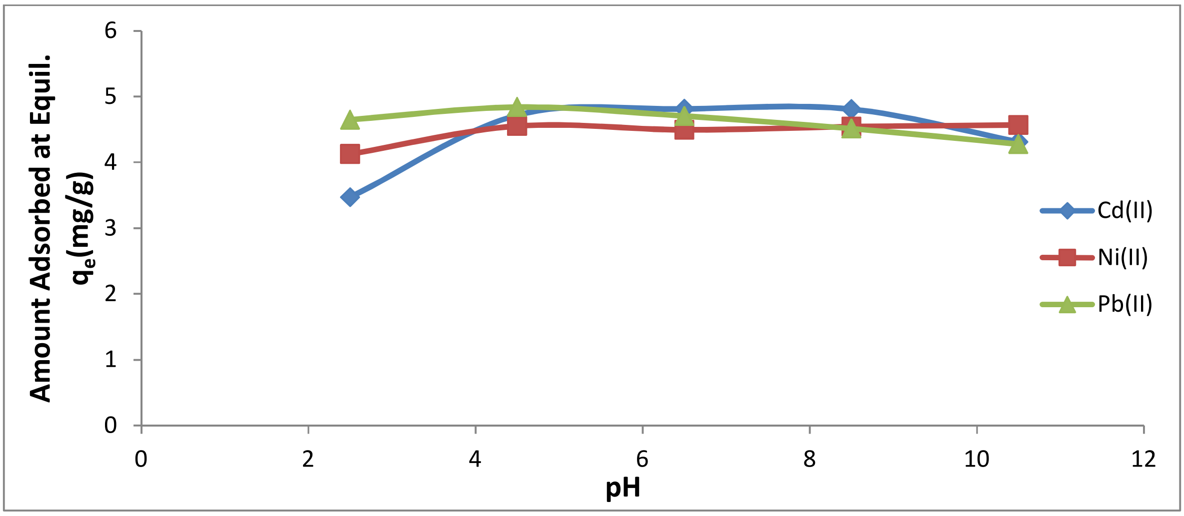


**Fig. 2. Effect of pH on the biosorption of the metal ions onto MW ($C_o$: 100 mg/L, biomass conc.: 1.0 g/L, 29 °C)**

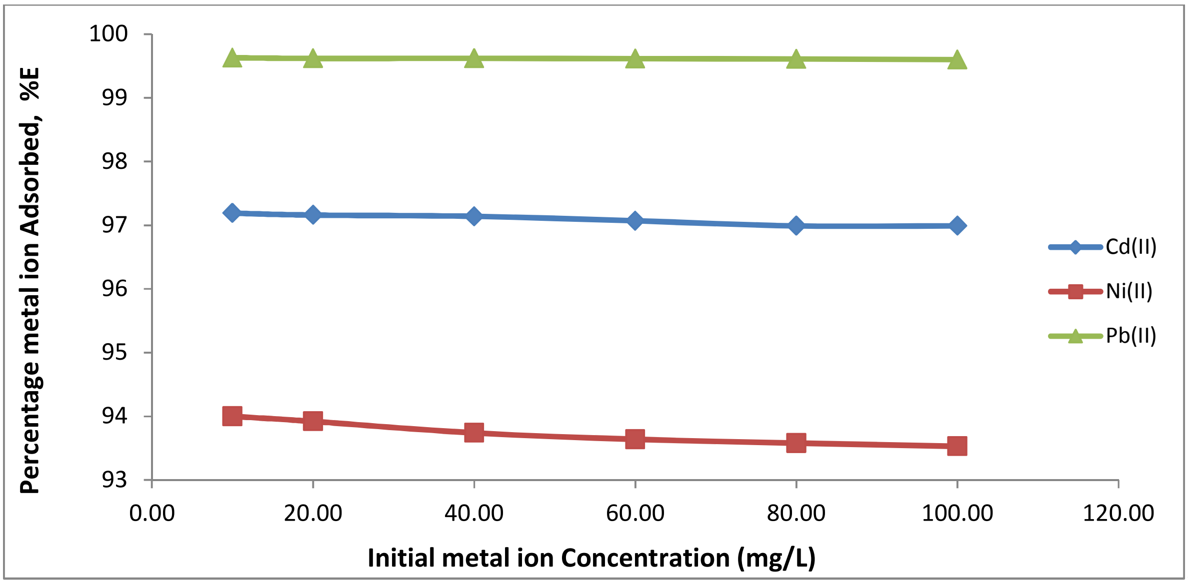


**Fig. 3 Effect of initial metal ion concentration on the percentage metal ion adsorbed onto ME**

**Effect of metal ion concentration**

Figures 3 and 4 show the variation of removal efficiencies with initial metal ion concentrations while Figs. 5 and 6 show the variation of the amount of metal ions adsorbed with initial metal ion concentrations. The heavy metal concentrations chosen in our study ranged from 10 mg $L^{-1}$ to 100 mg $L^{-1}$ and pH 5.5. For the fixed adsorbent mass of 1.0 g/L used, it was observed that as metal ion concentrations increased from 10 mg/L to 100 mg/L, the removal efficiencies of the adsorbents decreased from 99.63% to 99.60% for Pb(II), 97.19% to 96.99 for Cd(II) and 94.00% to 93.52% for Ni(II) in their adsorption onto ME while that of MW decreased from 98.01% to 97.85% for Pb(II), 96.23% to 96.22% for Cd(II) and 91.80% to 91.16% for Ni(II). This result shows that increasing the initial heavy metal concentrations in the solutions decreased the percentage metal removal. It is very pertinent here to observe that a given mass of an adsorbent material has a finite number of adsorption sites, and that as metal concentrations increase, these sites become saturated. This explains that there is a certain metal concentration that should produce the maximum adsorption capacity for a given adsorbent mass, and thereafter, further increase in metal concentration produces no further increase in adsorption because there will be no more adsorption sites available: all sites would have already been occupied. This may have been the possible cause of decrease in percentage of adsorption with increasing metal ion concentrations. It is also observed here that the amount of the metal ions adsorbed increased with increase in initial metal ion concentrations (Figs. 5 and 6). Assessment of level of metal ion removal shows that Pb(ll) ions were better adsorbed than Cd(ll) and Ni(II) ions on both adsorbents.

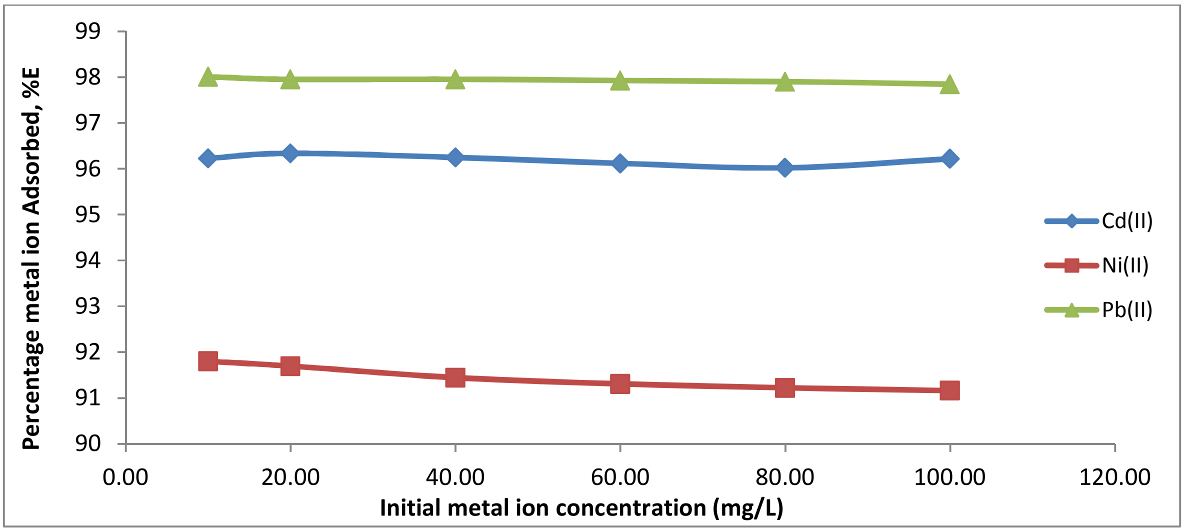


**Fig. 4 Effect of initial metal ion concentration on the percentage metal ion adsorbed onto MW**

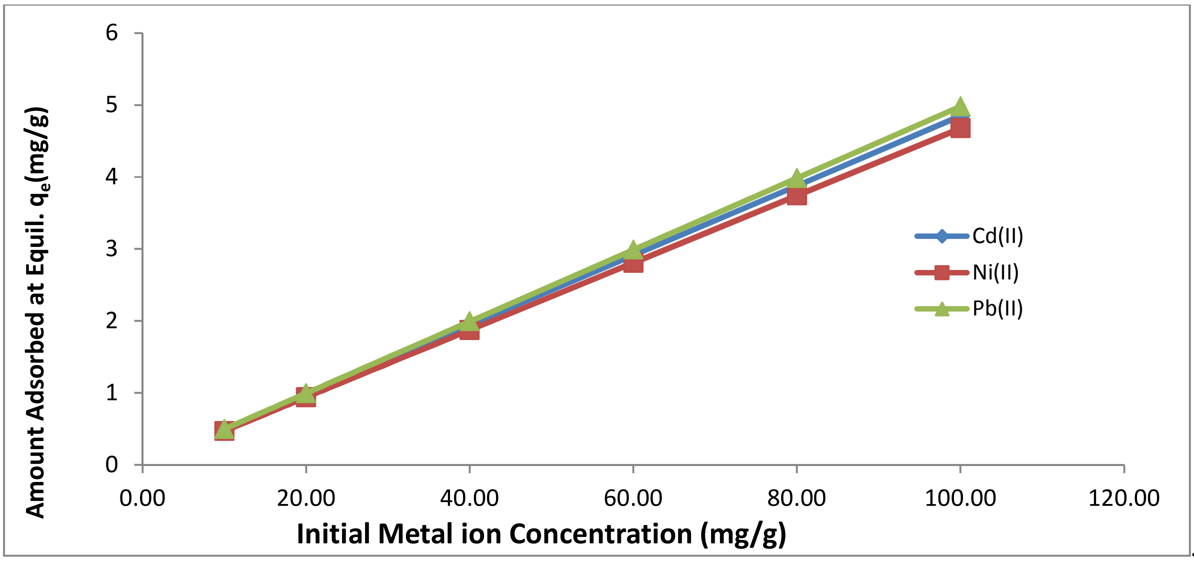


**Fig. 5 Effect of initial metal ion concentration on the amount adsorbed onto ME**

**Adsorption Isotherms**

A clear representation of the dynamic adsorptive separation of solute from solution onto an adsorbent depends upon a good description of the equilibrium separation between the two phases [41]. Equilibrium adsorption isotherms are of great importance in the design of adsorption systems since they show how metal ions are distributed/ or partitioned between the adsorbent and the bulk (liquid) phases at equilibrium as a function of metal ion concentration and at a given temperature.

In order to quantity the amount of metal ions adsorbed by the adsorbents and to determine the mechanism of the adsorption process onto the adsorbents, the experimental data were applied to Langmuir, Freundlich, Dubinin–Radushkevich (D-R), Temkin, Halsey and Harkins–Jura isotherm equations. The constant parameters of the isotherm equations for the adsorption process were calculated by regression using linear form of the isotherm equations.

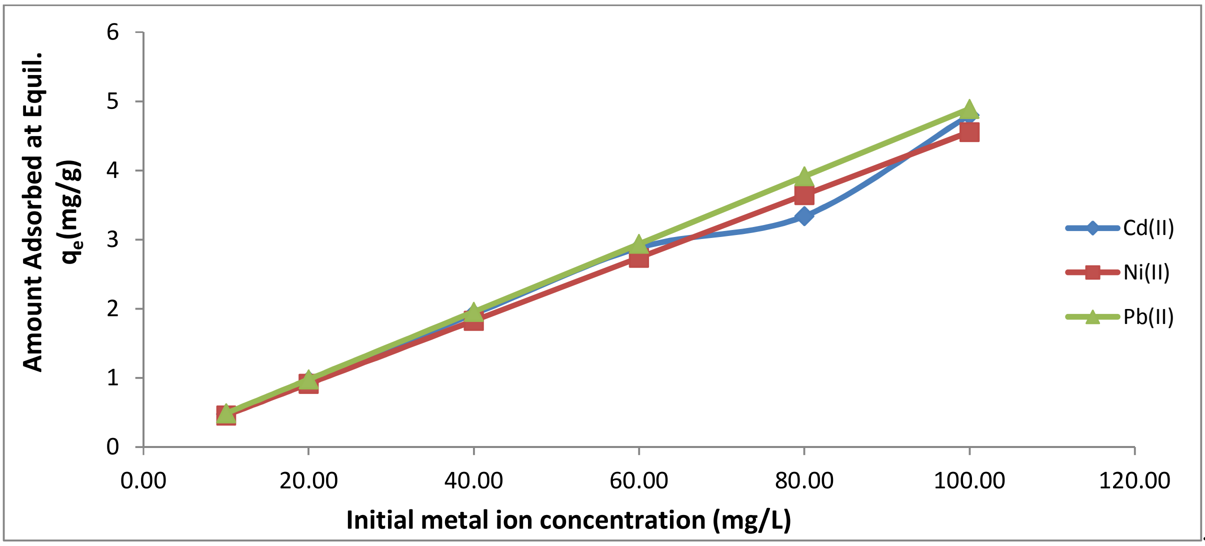


**Fig. 6 Effect of initial metal ion concentration on the amount adsorbed onto MW**

**The Langmuir Isotherm model**

The Langmuir isotherm predicts monolayer coverage of the adsorbates (metal ions) on the active reaction sites of the adsorbent surface and assumes that there is no lateral interaction between the adsorbed molecules. The isotherm is generally expressed as [42]:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \qquad (3)$$

Where $q_e$ is the adsorption capacity in mg of adsorbate per gram of adsorbent, $C_e$ is the equilibrium metal ion concentration in solution (mg/L), $q_{max}$ is the maximum adsorption capacity corresponding to monolayer coverage and $K_L$ is the Langmuir isotherm constant, which expresses the intensity of the adsorption process. Plots of $C_e/q_e$ vs $C_e$ were all linear as shown in Figures 7 and 8 and this shows that the adsorption study follows the Langmuir adsorption isotherm model. The applicability of the Langmuir isotherm indicates good monolayer coverage of the metal ions on the surface of the biomass. The Langmuir parameters, $q_{max}$ and $K_L$ were evaluated from the slope and intercept of the linear plots of $C_e/q_e$ vs $C_e$ and are presented in Table 1. The Langmuir capacity corresponding to sites saturation, $q_{max}$ is used to make a comparison of the efficiencies of the adsorbents under study (i.e., ME and MW) with other adsorbents, which have been employed for the adsorption of these metal ions from aqueous solutions. The $q_{max}$ values obtained from our results indicate high removal for $Pb^{2+}$ followed by $Cd^{2+}$ and lastly $Ni^{2+}$ for adsorption onto both biosorbents (MW and ME) and generally, ME displayed higher removal efficiency for the heavy metal ions compared to MW. Also, the values of the linear regression coefficient ($R^2$) as shown in Table 1 are all greater than 0.950, suggesting a good fitting of the experimental data into the Langmuir isotherm equation.

The essential features of the Langmuir isotherm are expressed in terms of a dimensionless constant, termed separation factor or equilibrium parameter, $R_L$, which is used to predict whether an adsorption system is “favorable” or “unfavorable”. The separation factor, $R_L$ is defined as [22]:

$$R_L = \frac{1}{(1+K_L C_o)} \qquad (4)$$

where $C_o$ is the initial Pb(II), Cd(II) and Ni(II) ions concentration (mg/L) and $K_L$ is the Langmuir adsorption equilibrium constant (L/g) which expresses the ratio of the adsorption to the desorption process. The isotherm is described as: unfavorable when $R_L > 1$, linear when $R_L = 1$, favorable when $0 < R_L < 1$ and irreversible when $R_L = 0$. The $R_L$ values obtained for the adsorption of the three metal ions by the adsorbents were all less than unity (Table 1) at the initial concentrations studied, indicating that the isotherm was favourable under the conditions of the present study

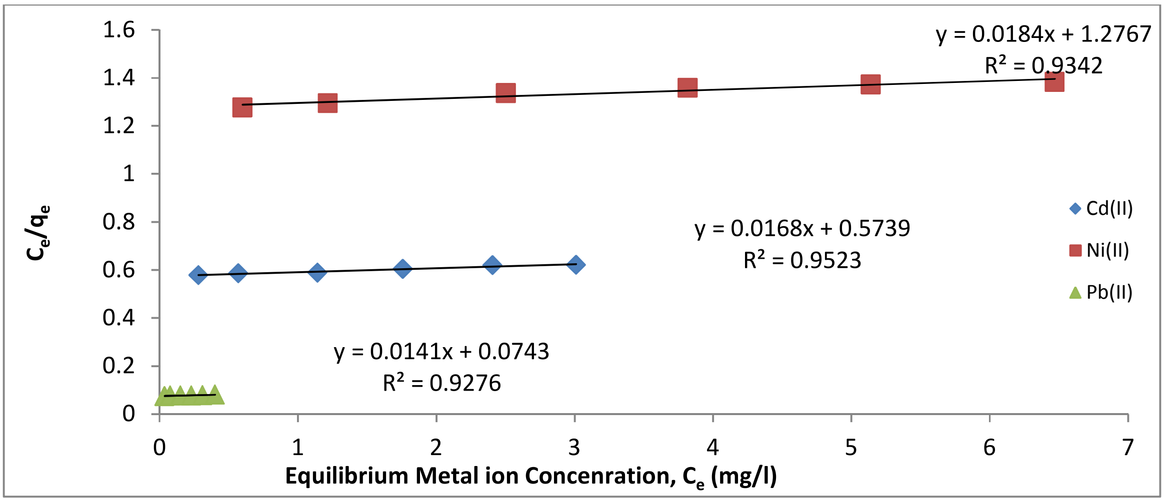


**Fig. 7. Langmuir isotherm plots for adsorption of the metal ions onto ME**

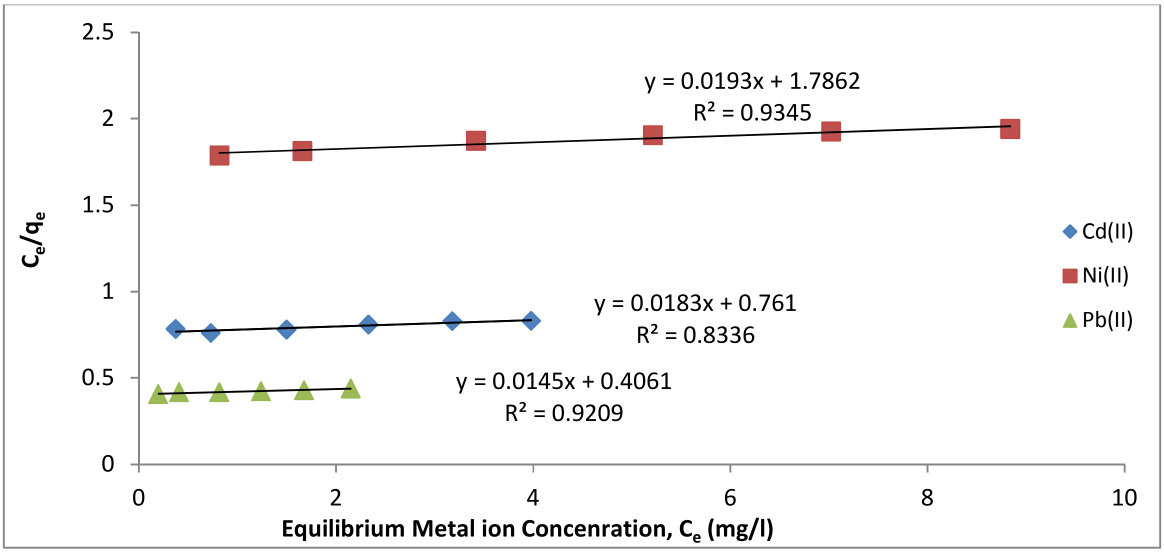


**Fig. 8. Langmuir isotherm plots for adsorption of the metal ions onto MW**

**Equilibrium Freundlich Isotherm**

The Freundlich model is derived to model the multilayer adsorption, applicable to a highly heterogeneous surface and is represented as [21]:

$$\ln q_e = \ln k_F + \frac{1}{n}\ln C_e \qquad (5)$$

where $K_F$ represents maximum adsorption capacity and n is related to the adsorption intensity and both constants were calculated from the intercept and slope of linear plots of ln $q_e$ vs ln $C_e$ according to equation 5. Figures 9 and 10 are linear Freundlich plots for the adsorption process while the constants and the $R^2$ values are presented in Table 2. $K_F$ shows the ease of removal and separation of the heavy metal ions from aqueous solutions. The 'n' values were greater than 1 and less than 10, indicating that the adsorption of the metal ions onto the adsorbents was favourable. The high $R^2$ values observed in Table 2 suggest an excellent fitting of experimental data into the Freundlich model.

**Table 1. Langmuir Isotherm Constants for adsorption of Pb(II) and Ni(II) ions by the adsorbents**

| Constants | ME | | | MW | | |
|---|---|---|---|---|---|---|
| | **Cd(II)** | **Ni(II)** | **Pb(II)** | **Cd(II)** | **Ni(II)** | **Pb(II)** |
| $K_L$ (L/mg) | 2.93 x $10^{-2}$ | 1.44 x $10^{-2}$ | 18.98 x $10^{-2}$ | 2.40 x $10^{-2}$ | 1.08 x $10^{-2}$ | 3.57 x $10^{-2}$ |
| $q_{max}$ (mg/g) | 59.52 | 54.35 | 70.92 | 54.64 | 51.81 | 68.97 |
| $R_L$ at diff. conc. | | | | | | |
| 10 | 0.773 | 0.874 | 0.345 | 0.806 | 0.903 | 0.734 |
| 20 | 0.631 | 0.776 | 0.209 | 0.676 | 0.822 | 0.583 |
| 40 | 0.460 | 0.635 | 0.116 | 0.510 | 0.698 | 0.412 |
| 60 | 0.363 | 0.536 | 0.081 | 0.410 | 0.607 | 0.318 |
| 80 | 0.299 | 0.465 | 0.062 | 0.342 | 0.536 | 0.259 |
| 100 | 0.254 | 0.410 | 0.050 | 0.294 | 0.481 | 0.219 |
| $R^2$ | 0.9523 | 0.9340 | 0.9276 | 0.8336 | 0.9345 | 0.9209 |

**Table 2. Freundlich Isotherm Constants for adsorption of Pb(II) and Ni(II) ions by the adsorbents**

| Constants | ME | | | MW | | |
|---|---|---|---|---|---|---|
| | Cd(II) | Ni(II) | Pb(II) | Cd(II) | Ni(II) | Pb(II) |
| $K_F$ | 1.676 | 1.294 | 12.32 | 1.270 | 0.558 | 2.358 |
| n | 1.032 | 1.037 | 1.028 | 1.033 | 1.038 | 1.028 |
| $R^2$ | 0.9998 | 1.0000 | 0.9999 | 0.9995 | 1.0000 | 0.9999 |

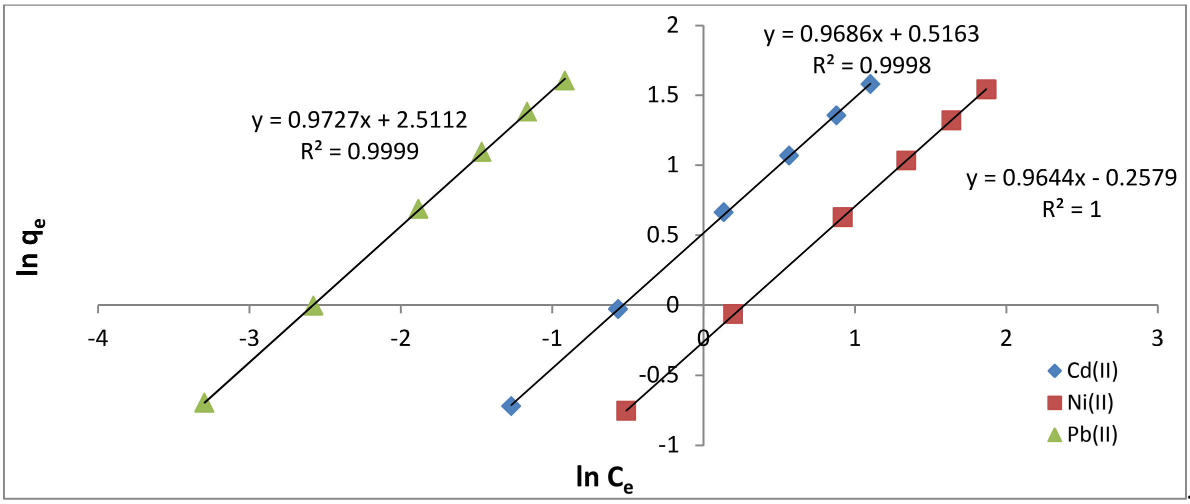


**Fig. 9. Freundlich isotherm plot of ln $q_e$ vs ln $C_e$ for adsorption of the metal ions onto ME**

## Dubinin-Radushkevich Isotherm

The Dubinin-Radushkevich (D-R) model was applied to the equilibrium data to assess the nature of the adsorption process, *i.e.* whether it is physical or chemical adsorption. The linearized D-R adsorption isotherm is represented as [20, 43]:

$$\ln q_e = \ln q_D - B_D \varepsilon^2 \quad (6)$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (7)$$

Where $q_D$ is the theoretical saturation value (mg/g), $q_e$ is the amount adsorbed at equilibrium (mg/g), $B_D$ is a constant related to adsorption energy ($mol^2$ $kJ^{-2}$), R is the gas constant (8.3145 J $mol^{-1}$ $K^{-1}$), T is the temperature (K) and $\varepsilon$ is the Polanyi potential which is related to the equilibrium concentration as expressed in equation (7). The linear plots obtained (Figs. 11 and 12) show the fit of the isotherm to the experimental adsorption data. The values of $B_D$ and $q_D$ were obtained from the slope and intercept of the linear plots and are presented in Table 3. Examination of the data shows that the Dubinin-Radushkevish isotherm also provides a good description of the data for the metal ions over the range of concentrations studied. The coefficients of correlation ($R^2$ values) were all high for the three adsorbents indicating that the model to a large extent gave a good interpretation to the experimental adsorption data.

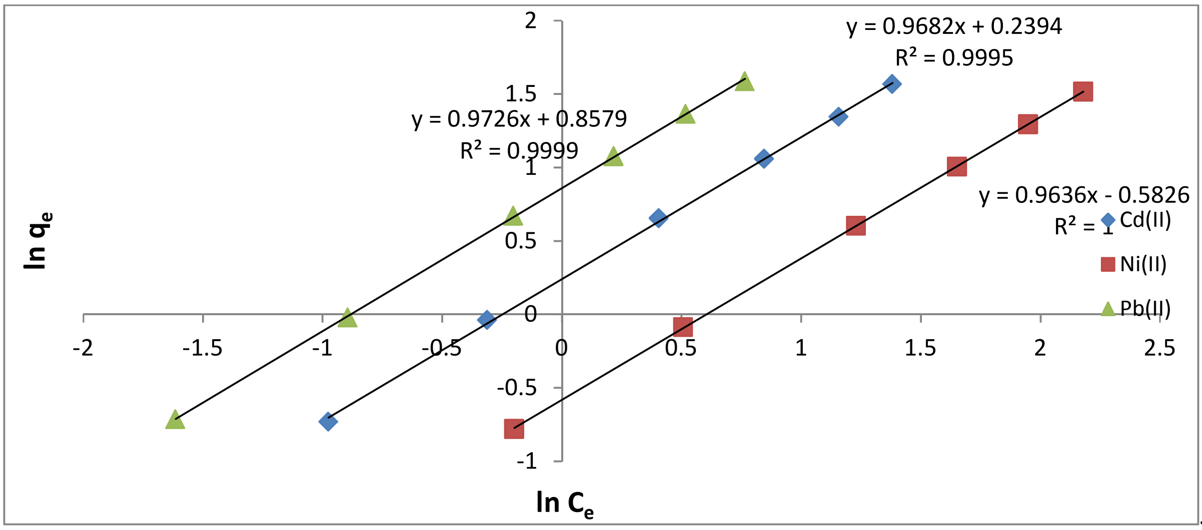


**Fig. 10. Freundlich isotherm plot of ln $q_e$ vs ln $C_e$ for adsorption of the metal ions onto the MW**

The constant $B_D$ gives an idea of the mean energy, E (kJ $mol^{-1}$) of adsorption per mole of the adsorbate as it is transferred to the surface of the solid from infinite distance in the solution and this energy is usually evaluated from the relation in eqn.(8).

$$E = \frac{1}{\sqrt{2B_D}} \quad (8)$$

Some researchers [43, 44] had reported that when the value of $E_D$ is below 8 kJ $mol^{-1}$, the adsorption process could be considered as physical adsorption and when it is within the range of 9–16 kJ $mol^{-1}$, it is chemical adsorption. From Table 3, it can be observed that the obtained values of mean D-R energy, $E_D$ are within the range of 2.178 - 4.560 kJ $mol^{-1}$, indicating that physisorption may have played a dominant role in the adsorption of Pb(II), Cd(II) and Ni(II) ions onto the biosorbents.

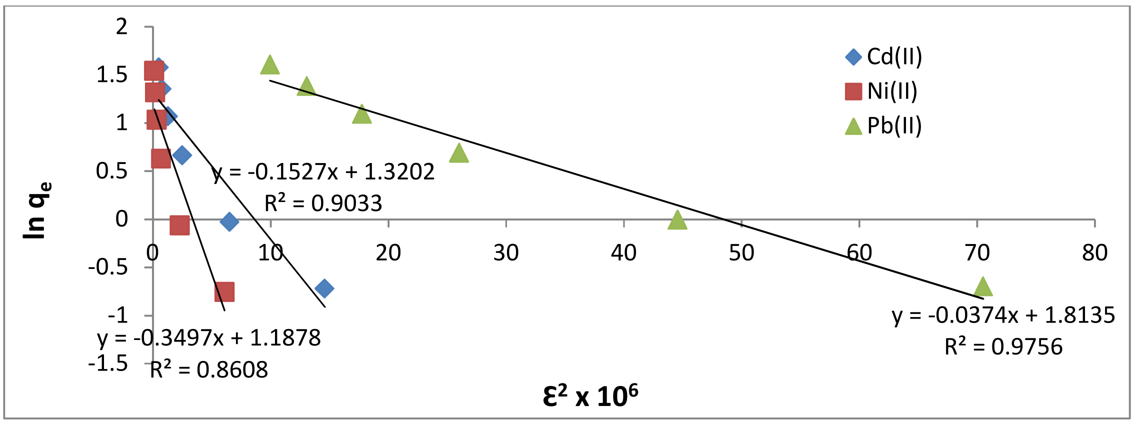


**Fig. 11. Dubinin-Radushkevich isotherm plot of ln qe vs $\varepsilon^2$ for adsorption of the metal ions onto ME**

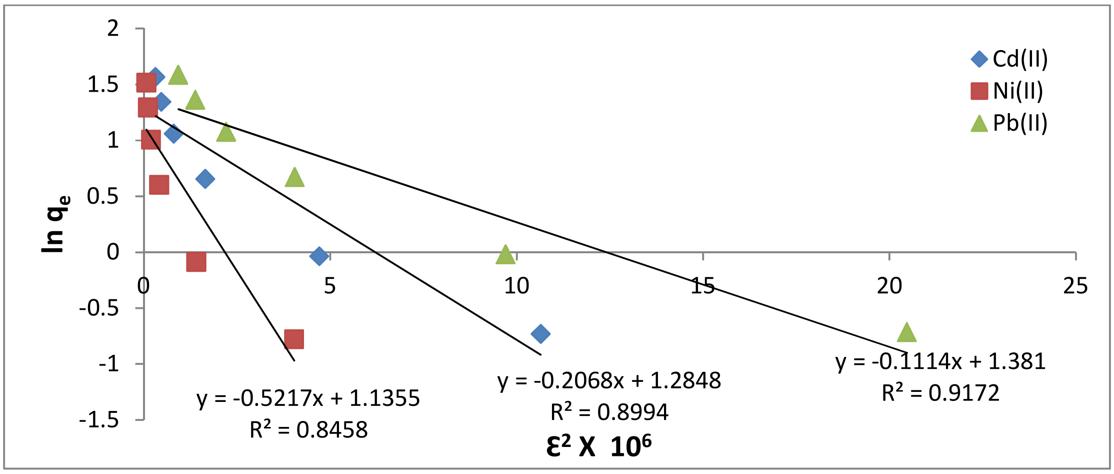


**Fig. 12. Dubinin-Radushkevich isotherm plot of ln qe vs $\varepsilon^2$ for adsorption of the metal ions onto MW**

### The equilibrium Temkin Isotherm

The Temkin isotherm describes the characteristic adsorption potential of the cassava wastes for the metal ions. The derivation of the Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation [22]. The linearized form of the isotherm model is given as [45]:

$$q_e = \frac{RT}{b_T} \ln k_T + \frac{RT}{b_T} \ln C_e \quad (9)$$

Where $q_e$ (mg/g) and $C_e$ (mg/L) are the amount adsorbed at equilibrium and the equilibrium concentration, respectively. T the absolute temperature in K and R is the universal gas constant, 8.314 J $mol^{-1}$ $K^{-1}$. According to Akkaya and Ozer [46], the constant *b* is related to the heat of adsorption. A linear plot of adsorption capacity, $q_e$ vs ln $C_e$ describes the isotherm for the adsorption of the metal ions (Figures 13 and 14). The Temkin constants $b_T$ and $k_T$ were determined from the slope and intercept of the linear plots and are displayed in Table 4. Assessment of the values of coefficient of determination ($R^2$) showed that Temkin isotherm is another good model for the description of the adsorption of the metal ions by the adsorbents. Their $R^2$ values are all high but lower than those of Freundlich and Langmuir isotherm models.

**Table 3. Dubinin-Radushkevich Isotherm Constants for adsorption of Pb(II) and Ni(II) ions by the adsorbents**

| Constants | ME | | | MW | | |
|---|---|---|---|---|---|---|
| | Cd(II) | Ni(II) | Pb(II) | Cd(II) | Ni(II) | Pb(II) |
| $q_D$ (mg $g^{-1}$) | 3.744 | 3.280 | 6.130 | 3.614 | 3.113 | 3.979 |
| $B_D$($mol^2kJ^{-2}$) | 1.527 X $10^{-7}$ | 3.497 X $10^{-7}$ | 3.47X$10^{-8}$ | 2.068X$10^{-7}$ | 5.217X$10^{-7}$ | 1.114X$10^{-7}$ |
| E (kJ $mol^{-1}$) | 1.810 | 1.196 | 3.790 | 1.555 | 0.979 | 2.119 |
| $R^2$ | 0.9033 | 0.8608 | 0.9756 | 0.8994 | 0.8458 | 0.9172 |

**Table 4. Temkin Isotherm Constants**

| Constants | ME | | | MW | | |
|---|---|---|---|---|---|---|
| | Cd(II) | Ni(II) | Pb(II) | Cd(II) | Ni(II) | Pb(II) |
| $K_T$ | 3.540 | 1.660 | 26.688 | 2.747 | 1.215 | 4.965 |
| $b_T$ (kJ/mol) | 1.412 | 1.473 | 1.371 | 1.499 | 1.511 | 1.395 |
| $R^2$ | 0.9197 | 0.9157 | 0.9185 | 0.9077 | 0.9159 | 0.9186 |

### Harkins-Jura Isotherm model

Harkins-Jura isotherm model mainly describes the multilayer adsorption and the existence of the heterogeneous pore distribution in the surface of adsorbents.

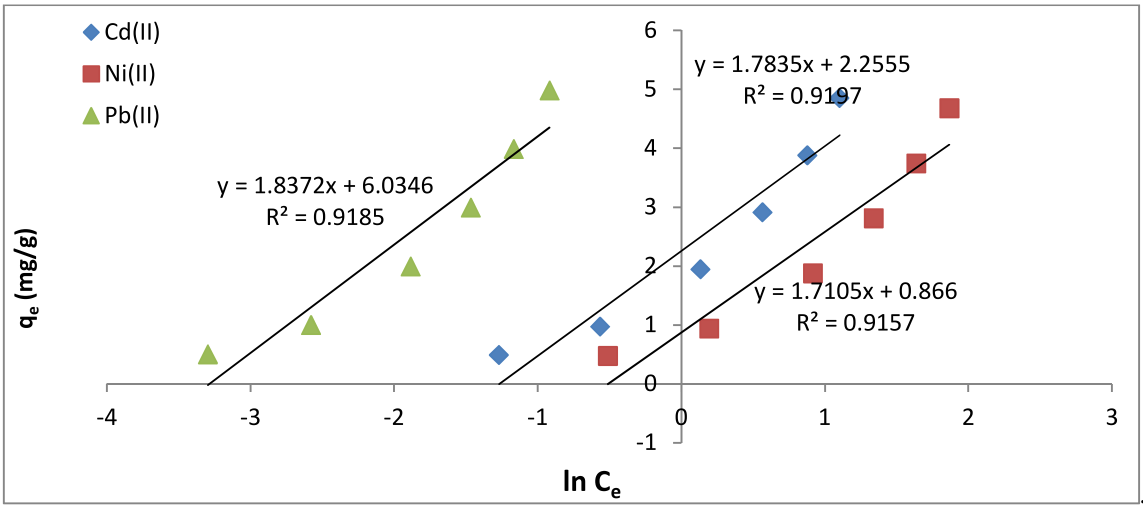


**Fig. 13 Temkin isotherm plot of $q_e$ vs ln Ce for adsorption of the metal ions onto ME**

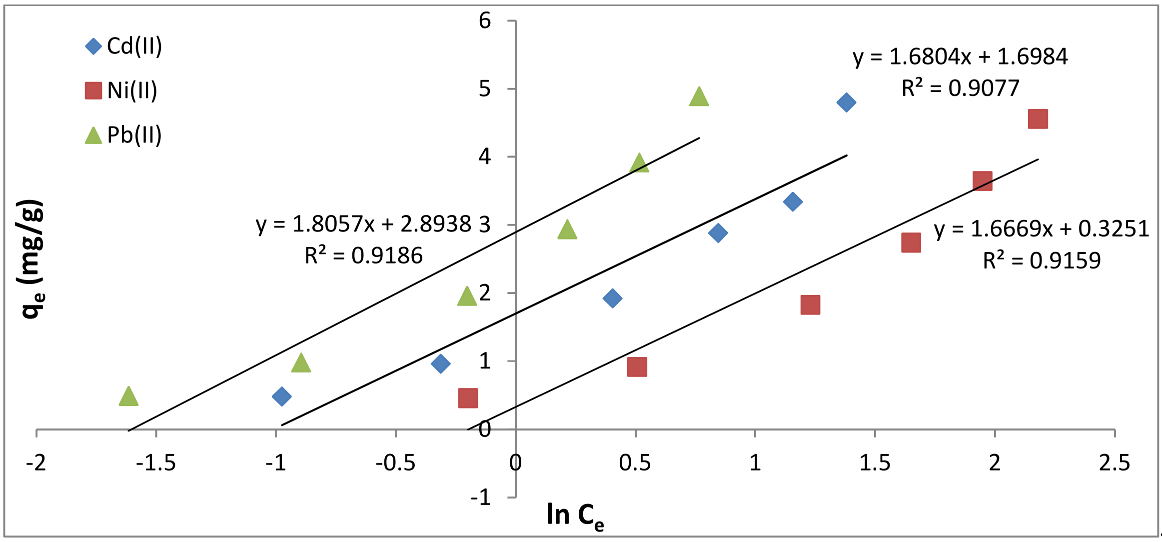


**Fig. 14 Temkin isotherm plot of $q_e$ vs ln Ce for adsorption of the metal ions onto MW**

The Harkins-Jura isotherm equation is usually expressed as [22]:

$$\left[\frac{1}{q_e^2}\right] = \left[\frac{B_{HJ}}{A_{HJ}}\right] - \left[\frac{1}{A_{HJ}}\right] log(C_e) \qquad (7)$$

where $B_{HJ}$ and $A_{HJ}$ are the Harkins-Jura constants. Both $A_{HJ}$ and $B_{HJ}$ can be achieved from the slope and the intercept of the linear plots of $\left[\frac{1}{q_e^2}\right]$ versus $log(C_e)$ respectively. The Harkins-Jura isotherm plots for the Cd (II), Ni(II) and Pb(II) adsorption onto the adsorbents are presented in Figs. 15 and 16 and the relevant isotherm constants are calculated and presented in Table 5. It can be observed from Table 5 that the low $R^2$ values signify a poor fit of the isotherm model to the experimental adsorption data. This result reveals that the adsorption of the metal ions on both adsorbents did not involve a multilayer adsorption.

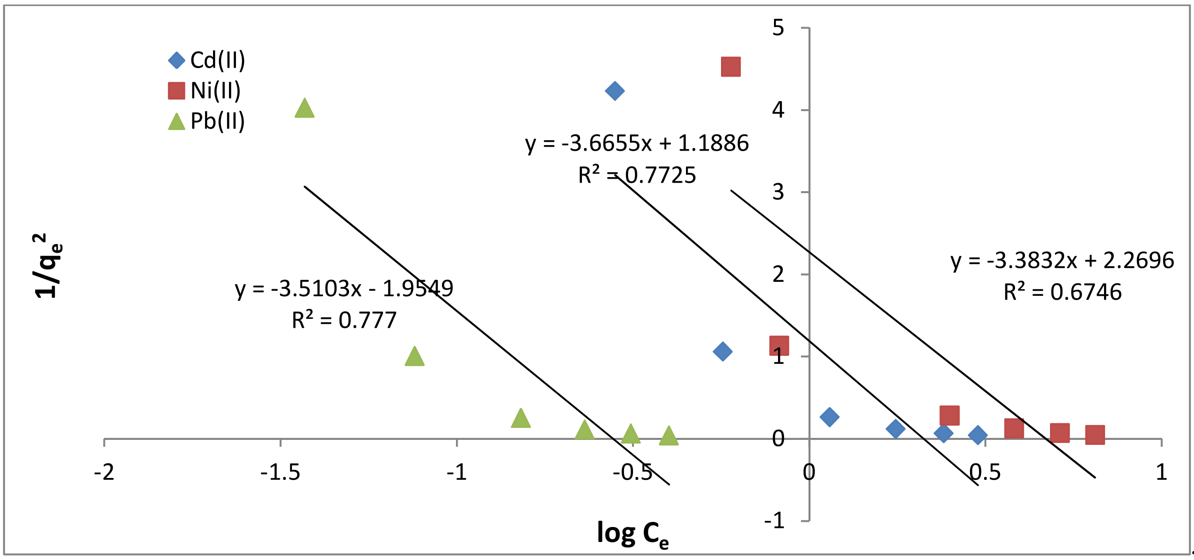


**Fig. 15: Plot of the Harkins-Jura isotherm model for adsorption of the metal ions onto ME**

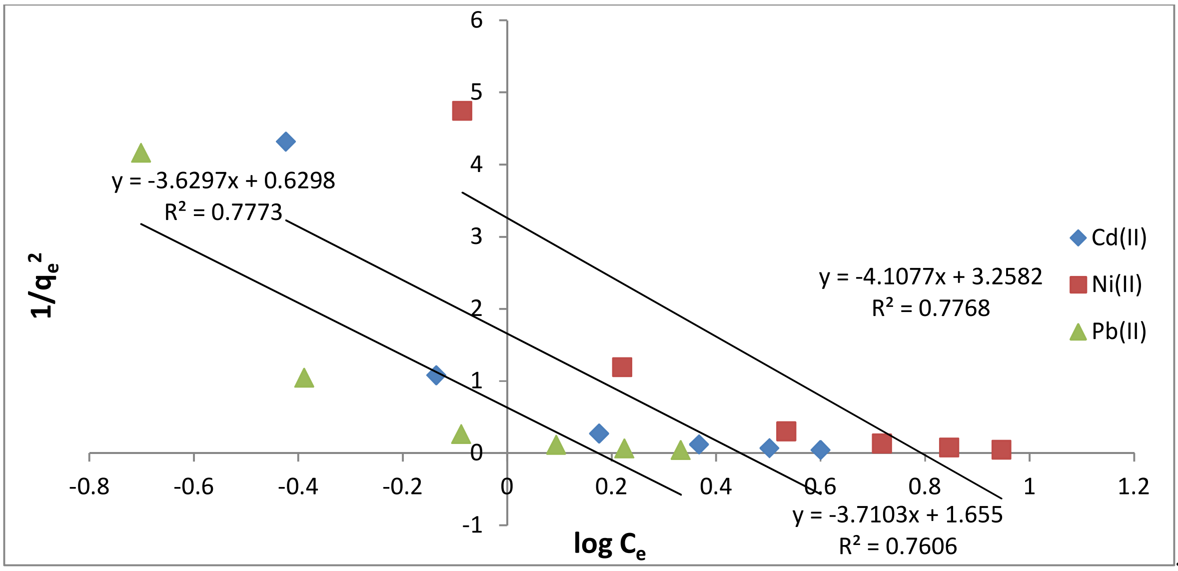


**Fig. 16: Plot of the Harkins-Jura isotherm model for adsorption of the metal ions onto MW**

**TABLE 5. Harkins-Jura Isotherm Constants**

| Constants | ME | | | MW | | |
|---|---|---|---|---|---|---|
| | Cd(II) | Ni(II) | Pb(II) | Cd(II) | Ni(II) | Pb(II) |
| $A_{HJ}$ | 0.2728 | 0.2956 | 0.2849 | 0.2695 | 0.2434 | 0.2755 |
| $B_{HJ}$ | 0.5333 | 0.6709 | 0.5570 | 0.4462 | 0.7930 | 0.1735 |
| $R^2$ | 0.7725 | 0.6746 | 0.7770 | 0.7606 | 0.7768 | 0.7773 |

**Halsey Isotherm Model.**
Halsey isotherm model can be used to evaluate the multilayer adsorption system for metal ions adsorption at a relatively large distance from the surface and is expressed as [47]:

$$ln(q_e) = \left[\left(\frac{1}{n_H}\right)\ln(K_H)\right] - \left(\frac{1}{n_H}\right) ln\left(\frac{1}{C_e}\right) \quad (8)$$

Where $K_H$ and $n_H$ are the Halsey constants, which can be evaluated from the intercept and slope of the linear plot of $ln(q_e)$ versus $ln\left(\frac{1}{C_e}\right)$, respectively. The related Halsey isotherm constants and coefficient of determination ($R^2$ values) were calculated and presented in Table 6. The high $R^2$ values as observed from Table 6 show an excellent fit of the isotherm for the experimental adsorption data. This finding implies that Cd(II), Ni(II) and Pb(II) adsorption on both ME and MW obeys the Halsey isotherm model (Figs. 17 and 18). Comparison of the values of linear regression coefficient ($R^2$) of the examined six isotherm models, revealed that the Freundlich and Halsey isotherm models gave much better fitting than the other four isotherm models (i.e., Langmuir, D-R, Temkin and Harkins-Jura isotherms). Consequently, the adsorption behaviour of these metal ions on both surfaces could be well described using these two isotherm models.

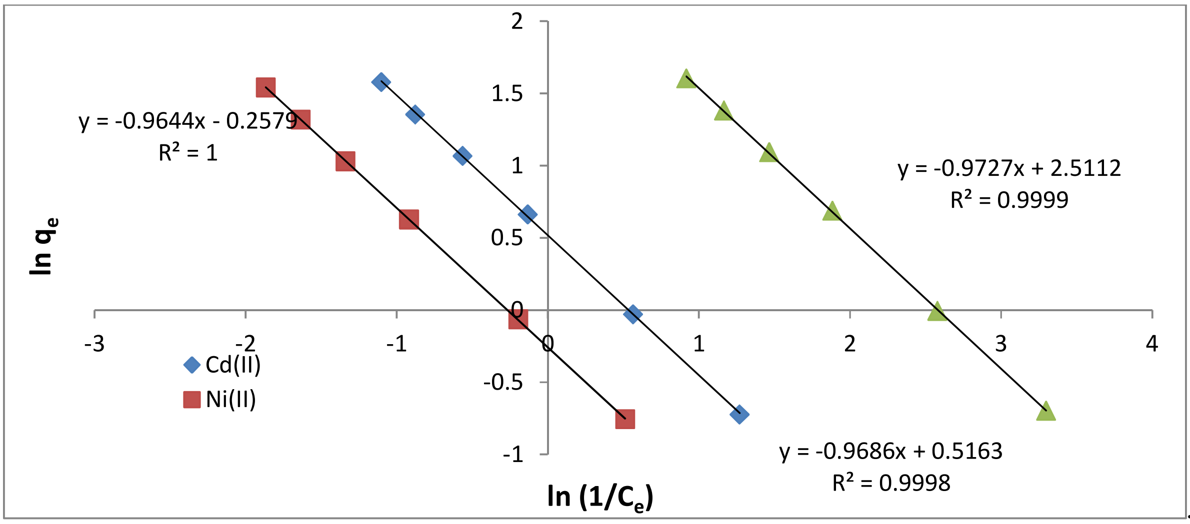


**Fig. 17 Halsey isotherm model for adsorption of the metal ions on ME**

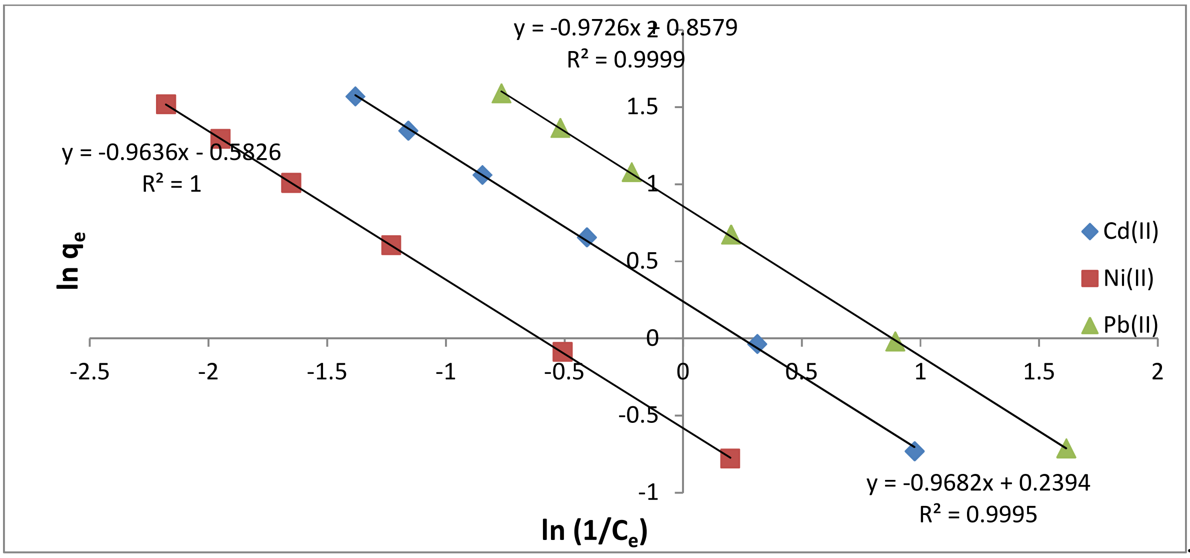


**Fig. 18 Halsey isotherm model for adsorption of the metal ions on MW**

**TABLE 6. Halsey Isotherm Constants**

| Constants | ME | | | MW | | |
|---|---|---|---|---|---|---|
| | Cd(II) | Ni(II) | Pb(II) | Cd(II) | Ni(II) | Pb(II) |
| $K_H$ | 1.704 | 0.765 | 13.217 | 1.281 | 0.546 | 2.416 |
| $n_H$ | 1.032 | 1.037 | 1.028 | 1.033 | 1.038 | 1.028 |
| $R^2$ | 0.9998 | 1.000 | 0.9999 | 0.9995 | 1.000 | 0.9999 |

## CONCLUSION

The present study evaluates the efficiency of agricultural wastes from two different species of cassava viz: *manihot esculenta cranz* (ME) and *manihot walkarae* (MW) in removing Cd(II), Ni(II) and Pb(II) ions from aqueous solutions. Based on the findings of the present study and information obtained from Chemical literature, the following conclusions can be drawn:

1. The adsorbent materials ME and MW are capable of removing Cd(II), Ni(II) and Pb(II) ions from aqueous solutions. The batch adsorption studies were dependent on initial metal ion concentration and pH. The optimum pH for removal of Pb(II) and Ni(II) by both adsorbents occurred at a pH 4.5 while that of Cd(II) at occurred at pH 6.5 on both adsorbents.

2. Among the six isotherm model equations viz. Langmuir, Freundlich, Dubinin-Radushkevich (D-R), Temkin, Harkins-Jura and Halsey applied to the equilibrium adsorption data, the Freundlich and Halsey models provided the best description to the adsorption process based on their high correlation coefficients. The Langmuir model also gave a fairly good interpretation to the adsorption data.

3. The energy values obtained from Dubinin-Radushkevich model were all less than 8.00 kJ $mol^{-1}$ suggesting that physisorption may have been the predominant mode of the adsorption process.

4. The obtained results are indication that the wastes from the two species of cassava could be applied as an adsorbent for heavy metal removal from aqueous solutions and could be employed as an effective alternative method for the economic treatment of wastewater.

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