Kinetic studies on the use of agricultural wastes for the removal of lead, cadmium and nickel ions from aqueous solutions

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ABSTRACT

The potential of economically cheap cellulosic materials from two different species of cassava-manihot esculenta cranz (ME) and manihot walkarae (MW) was assessed for Cd(II), Ni(II) and Pb(II) adsorption from aqueous solutions. Batch adsorption experiments were carried out as a function of adsorbent mass and exposure time. Results showed that the percentage removal of the metal ions increased with increasing adsorbent dosage. *Kinetic experiments revealed that equilibrium adsorption for the metal ions were reached within 120 min. The pseudo first-order, pseudo second-order mechanism and Elovich equation were applied to examine the kinetics of the adsorption process. Results showed that kinetic data fitted better into pseudo second-order model than the pseudo first-order and Elovich equations. Results generally showed that the metal ions were considerably adsorbed onto the cassava wastes and this could be considered as an economic method for the removal these metal ions from aqueous solutions.*

Keywords: Adsorption, biosorbents, heavy metal ions, Manihot esculenta cranz, manihot walkarae.

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INTRODUCTION

Indiscriminate release of heavy metals into the environment due to industrialization and urbanization poses a great threat to our environment. Unlike organic pollutants in which majority of which are biodegradable, heavy metal ions do not degrade into harmless end products [1]. They are very persistent and can accumulate the food chain in the environment and thus may pose a significant danger to human health. Most of the industries discharge wastewater and their effluents containing toxic materials into rivers without adequate treatment. Heavy metals are major pollutants in marine, ground, industrial and even treated wastewater.

Environmental pollution particularly from heavy metals and minerals in the waste water is one of the most serious problems in industrialized nations.

Some of the point sources of heavy metal pollutants are industrial wastewater from mining, metal processing, tanneries, chloralkali, radiator manufacturing, smelting, alloy industries, storage battery industries, pharmaceuticals, pesticides etc. [2, 3]. The heavy metals are transported by runoff water and contaminate water sources downstream from the industrial site. To avoid health hazards, it is essential to remove these toxic heavy metals from wastewater before its disposal. Most of the heavy metals discharged into the wastewater are found toxic and carcinogenic and cause serious threats to many life forms [4].

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Advanced wastewater treatment methods such as ion-exchange, chemical precipitation, electrolysis, adsorption, reverse osmosis, electrodialysis, ultrafiltration, nanofiltration, coagulation, flocculation, floatation etc. have been used to remove these non-biodegradable wastes [5-7]. Most of these processes are efficient in removing the bulk of metals from solution at high or moderate concentrations and also generate a large amount of metallic sludge, making metal recovery difficult. The sludge also needs further disposal. These chemical processes when applied to dilute metal wastes or lower concentrations of metal ions, are either ineffective or not cost-effective and require high level of expertise; hence they are not applied by many end-users. For these reasons, adsorption technology has gained a wider application due to its inherent low cost, simplicity, versatility and efficiency. Studies on the treatment of effluent bearing heavy metals have revealed adsorption to be a highly effective technique for the removal of heavy metals from waste stream and activated carbon has been widely used as an adsorbent [8,9]. Despite its extensive use in the water and wastewater treatment industries, activated carbon remains an expensive material.

In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives to commercially available activated carbon. The low cost agricultural waste by-products such as saw dust [10-12], sphagnum moss peat[13, 14], modified pine bark [15], husk of Bengal gram [16] sugarcane bagasse pith [17], bagasse fly ash [18]waste acorn of Quercus ithaburensis [19] rice husk [20-22] etc., for the removal of heavy metals from wastewater have been investigated by various researchers. Low cost adsorbents derived from agricultural by-products and other solid agro-wastes can now be used to remove recalcitrant wastes from synthetic wastewater. Conversion of these materials into adsorbents for wastewater treatment would help to reduce the cost of waste disposal. The technical feasibility of various low-cost adsorbents for heavy metal removal from contaminated water has been reviewed [23-25]. Instead of using commercial activated carbon, researchers have worked on inexpensive materials, such as zeolites, chitosan, algae, fungi, yeast, and other biosorbents, which have high adsorption capacity and are locally available.

Therefore, there is an urgent need for all possible sources of agro-based inexpensive adsorbents to be explored and their feasibility for the removal of heavy metals should be studied in detail. The objective of this study is to contribute in the search for less expensive adsorbents and the utilization possibilities for agricultural waste by-products, which in many cases are also pollution sources. Cassava wastes from two different species of cassava viz. *manihot esculenta cranz* and *manihot walkarae* are being evaluated as possible biosorbents for adsorption of lead, nickel and cadmium ions from aqueous solutions. Our goal in the present study is to compare the rate of removal of these metal ions by the adsorbents and to propose a likely mechanism for the adsorption process using different adsorption kinetic models.

EXPERIMENTAL SECTION

Preparation of the adsorbents
The source of 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 30^0C 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.

Adsorption studies
A standard solution of 100 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. 50 mL of each of the standard solutions prepared were transferred 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 at different contact times ranging from 10 min to 120 min. At the end of each exposure time, the

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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 adsorbent dose on the adsorption process, a similar procedure was carried out just as in the case of contact time except that the mass of the adsorbents were varied from 1.0 g/L to 10 g/L while keeping the temperature fixed at 29^0C. 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 different times q_t (mg/g) was determined using the mass balance equation (1).

$$q_t = \frac{C_0 - C_t}{m} \times V \qquad\qquad (1)$$

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

RESULTS AND DISCUSSION

Effect of mass of the adsorbent
The influence of adsorbent mass on the adsorption of the metal ions Cd(II), Ni(II) and Pb(II) onto the adsorbents (*ME* and *MW*) was measured at five different adsorbent concentrations (1, 2, 5, 8 and 10 g L^{-1}) for initial metal ion concentration of 100 mg L^{-1}. The equilibrium amount adsorbed and the removal efficiencies are presented in Figs. 1- 4. From Figures 1 and 2, it can be observed that the amount of these metal ions Ni^{2+}, Cd^{2+} and Pb^{2+} adsorbed decreased as adsorbent concentration increases. This Result shows that more active sites are utilized at lower adsorbent concentration, producing a higher adsorption capacity, while only part of the active sites are occupied by these metal ions at higher adsorbent concentration, leading to a lower adsorption capacity and this is in accordance with earlier observation made by Argun *et al*. [11] in their study of heavy metal adsorption by modified oak sawdust. Also, from Figs. 3 and 4, it is clear that Ni^{2+}, Pb^{2+} and Cd^{2+} percentage removal increases with increasing adsorbent concentration. As the adsorbent mass increases from 1.0 g/L to 10 g/L, the percentage removal of Pb^{2+} increased from 98.85% to 99.30%, Cd^{2+} increased from 96.02% to 96.67% while Ni^{2+} increased from 91.16% to 91.62% for their adsorption onto MW and for ME, Pb^{2+} increased from 99.47% to 99.67%, Cd^{2+} from 96.97% to 97.07% while Ni^{2+} increased from 93.53% to 93.61%. This increase may be due to the presence of more active adsorption sites for these metal ions at higher adsorbent concentrations. A similar observation had been made by Malkoc and Nuhoglu [19] in their study on the determination of kinetic and equilibrium parameters of the batch adsorption of Cr(VI) onto waste acorn of *Quercus ithaburensis*. The plots (Figs. 1- 4) show in general that the percentage removal of these metal ions increased with increasing adsorbent dosage while the amount adsorbed per unit mass decreased and became almost constant at higher dosages. The increase in percent removal of these heavy metals with increase in the dosage of the adsorbent is due to the greater availability of the exchangeable sites or surface area of the adsorbent while the decrease in sorption capacity with increasing adsorbent dosage is mainly due to unsaturation of adsorption sites through the adsorption reaction. It is also worthy to note that there was no significant effect in the removal efficiency of ME for the metal ions as the mass of adsorbent increased beyond 1.0 g/ L and this is reflected in the leveling effect observed with the curves. This shows that there was slight increase in percentage removal as the adsorbent dose increased from 1.0 g/L to 10 g/L.

The increasing adsorption trend for the metal ions generally follows Pb(II) > Cd(II) > Ni(II) for adsorption onto both adsorbents. Comparison of adsorption capacities of the two adsorbents shows that ME adsorbed better than MW.
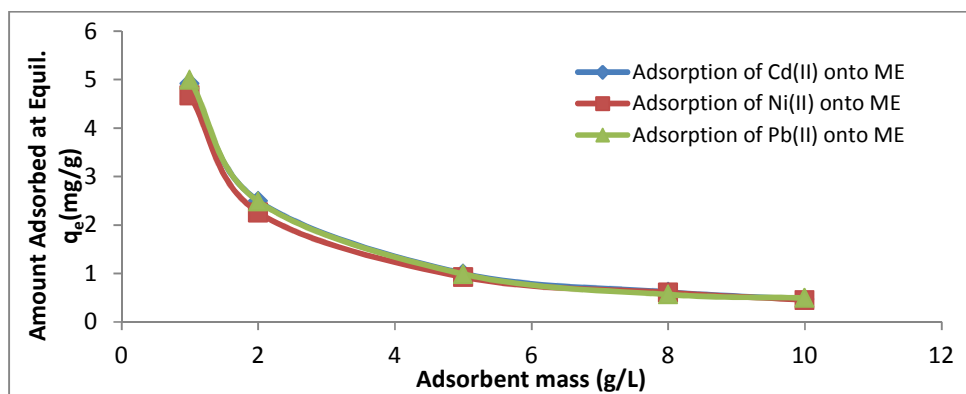
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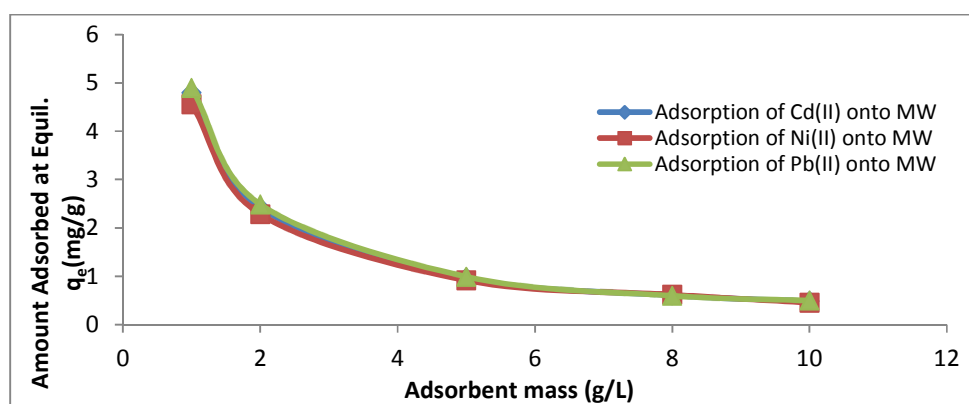**Fig. 1 Effect of adsorbent mass on the amount of metal ion adsorbed onto ME**

Fig. 2 Effect of adsorbent mass on the amount of metal ion adsorbed onto MW
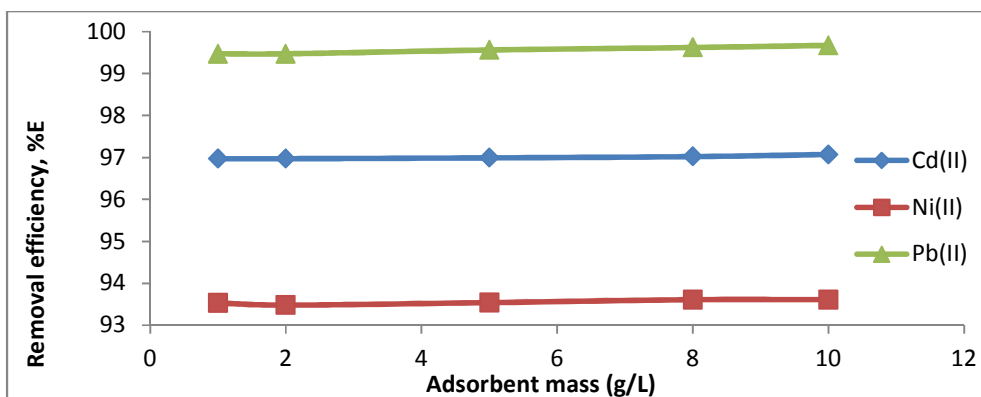

Fig. 3 Effect of adsorbent mass on the metal-removal efficiencies of ME

Effect of Contact time

Results (Figures 5 and 6) indicate that adsorption efficiencies increased with increase in contact time before equilibrium was attained. The amount of metal ion adsorbed by an adsorbent at a particular time is one of the important characteristics defining the efficiencies of an adsorption system. Optimum contact time for adsorption of Cd(II), Ni(II) and Pb(II) by 0.5 g of both adsorbents was 120 min. This result is vital since equilibration time is one of the important parameters to be considered for an economical wastewater treatment system. The figures also indicate that greater amount of the Pb(II), Cd(II) and Ni(II) ions were taken up by the adsorbents within the first 60 min and that equilibrium was attained within 90 min and on the overall, the amount of the metal ions adsorbed onto the ME was higher compared to that adsorbed onto MW.
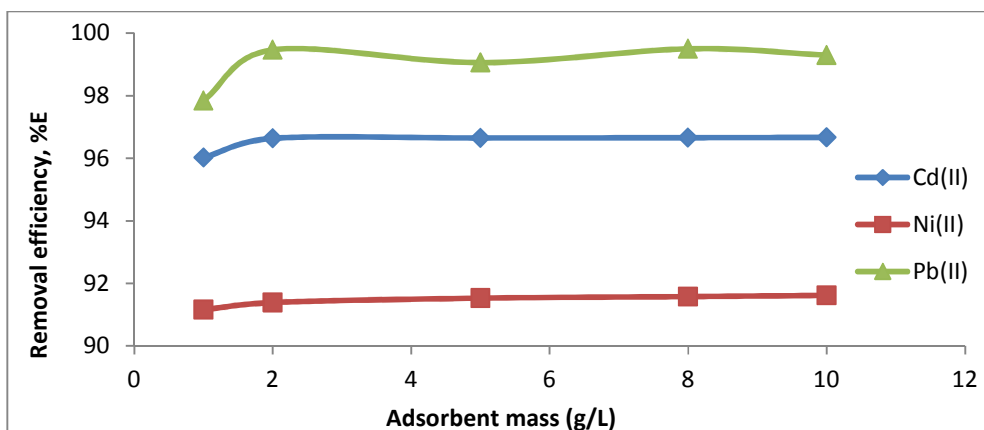
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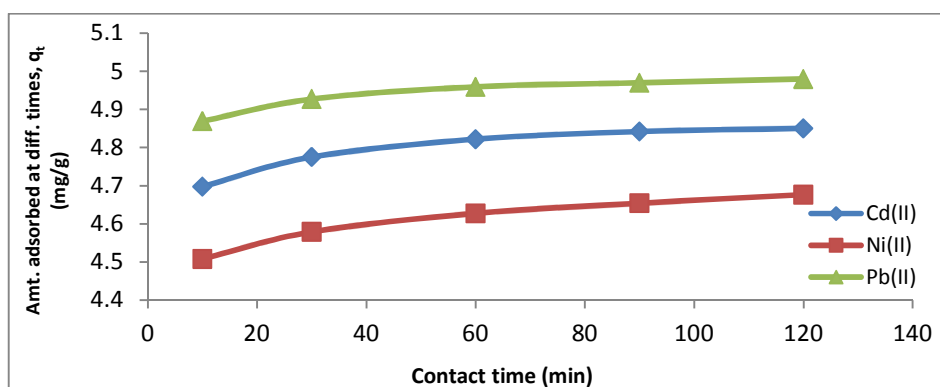**Fig 4. Effect of adsorbent mass on the metal-removal efficiencies of MW**

Fig. 5 Effect of contact time on the adsorption of the metal ions by ME
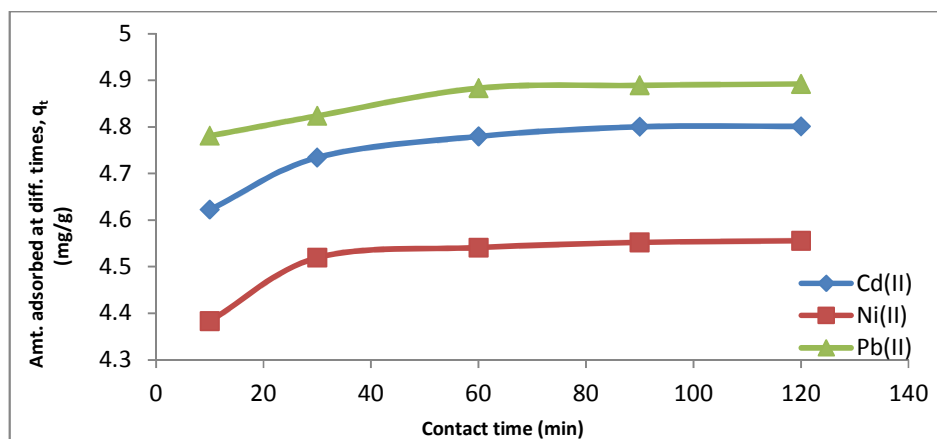

Fig. 6 Effect of contact time on the adsorption of the metal ions by MW

ADSORPTION KINETICS

Adsorption kinetics enables us to measure the rate and mechanism of metal ions adsorption onto the adsorbents. In our present study, three different adsorption kinetic models viz; pseudo first-order, pseudo second-order and Elovich models [26, 27] were applied to analyze the experimental data. The values of correlation coefficients (R^2 values)

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obtained from such plots were used to assess the level of fitting of the experimental data into the applied kinetic models. R^2 values close to or equal to 1 shows that the model describes the kinetics of the metal ion adsorption.

The pseudo first-order model

The integrated pseudo first-order equation is generally given as:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \tag{2}$$

Where q_e and q_t are the adsorption capacities (mg/g) at equilibrium and at a time t, respectively, k_1 is the rate constant of pseudo first-order adsorption (min^{-1}). The plots of ln (q_e - q_t) vs. t yielded straight lines from which k_1 and q_e were determined from the slope and intercept of the linear plots and are presented in Table 1. Figures 7 and 8 show the linear plots for the pseudo first-order model
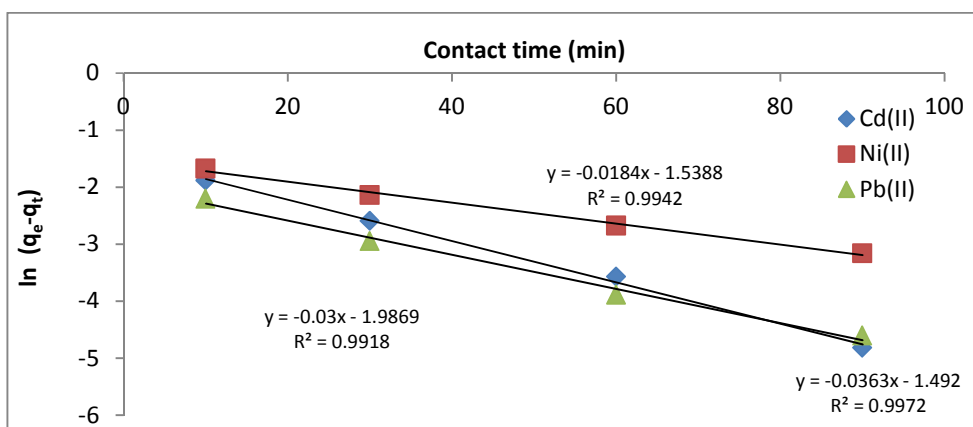

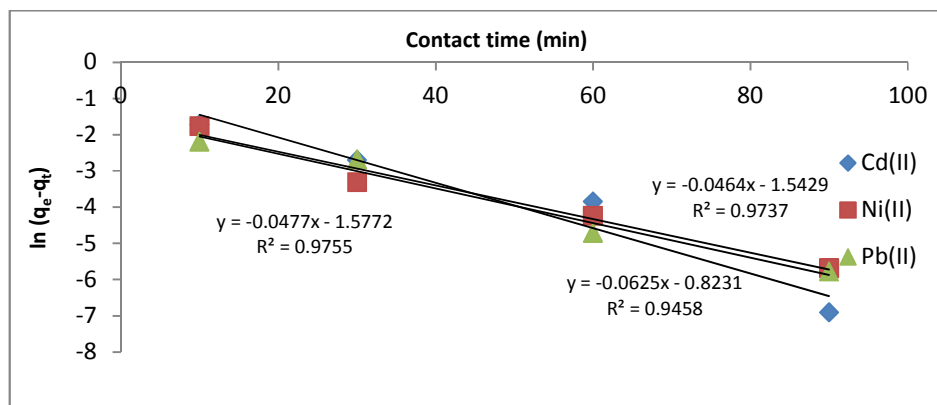**Fig. 7 Pseudo first-order plot for adsorption of the metal ions onto ME**

Fig. 8 Pseudo first-order plot for adsorption of the metal ions onto MW

Table 1. Kinetic rate constants for pseudo first-order reaction

Constants	*ME*			*MW*		
	Cd(II)	**Ni(II)**	**Pb(II)**	**Cd(II)**	**Ni(II)**	**Pb(II)**
q_e (mg g^{-1})	0.225	0.215	0.137	0.439	0.214	0.207
k_1 (min^{-1})	3.63×10^{-2}	1.84×10^{-2}	3.00×10^{-2}	6.25×10^{-2}	4.64×10^{-2}	4.77×10^{-2}
R^2	0.9972	0.9942	0.9918	0.9458	0.9737	0.9755

Pseudo second-order kinetic model

The pseudo second-order is based on the assumption that sorption follows second order chemisorptions. The integrated Pseudo second-order model is usually given as:

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$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad\qquad (3)$$

Where $h_o = k_2 q_e^2$ is usually described as the initial adsorption rate as t approaches zero. The pseudo second-order model was applied in this analysis and a plot of t/q_t vs t gave linear plots, from which the pseudo second-order parameters q_e, k_2 and h_o were evaluated. According to Ho *et al*; [14]; if the plots are linear, then the rate-limiting step for the adsorption process may be described as chemisorption. As shown in Table 2 and Figures 9 and 10, the adsorption data of both adsorbents fitted the pseudo second-order model perfectly judging by the high correlation coefficients ($R^2 > 0.990$), suggesting that the rate-limiting step of Pb^{2+}, Cd^{2+} and Ni^{2+} adsorption by the adsorbents in our study may be chemical reaction.

The rate constant, k_2, the equilibrium adsorption capacity, q_e, the initial sorption rate, h_o and R^2 values are presented in Table 2. These parameters were calculated from the intercept and slope of the linear plots of t/q_t versus t. The equilibrium adsorption capacities, q_e calculated from the pseudo second-order kinetic model agree very closely with the experimental values.
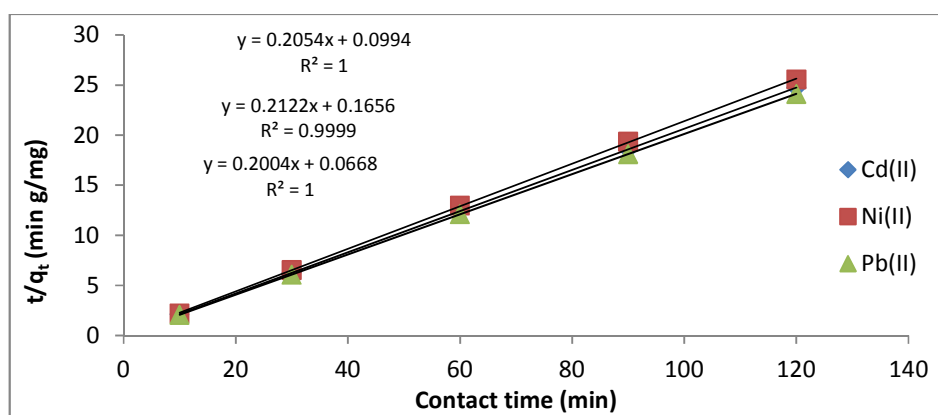

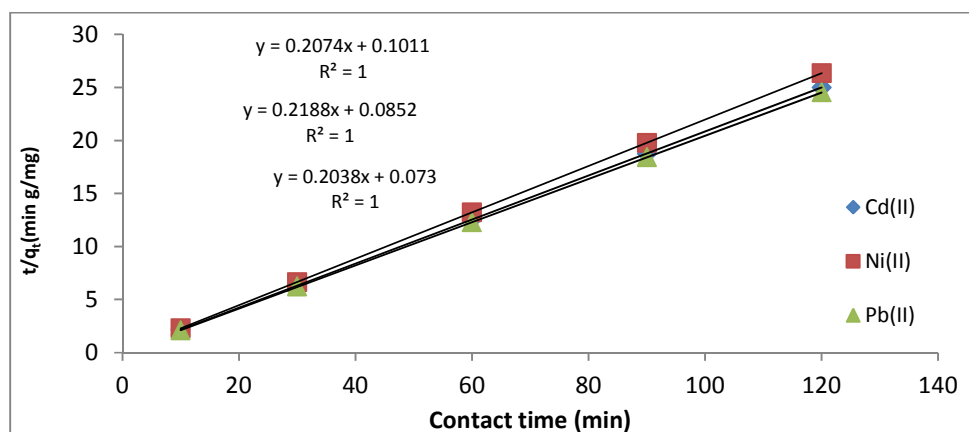**Fig. 9 Pseudo-second order plot of t/qt vs t for adsorption of the metal ions onto ME**

Fig. 10 Pseudo-second order plot of t/qt vs t for adsorption of the metal ions onto MW

Table 2. Kinetic rate constants for pseudo second-order reaction

Constants	*ME*			*MW*		
	Cd(II)	**Ni(II)**	**Pb(II)**	**Cd(II)**	**Ni(II)**	**Pb(II)**
q_e (mg/g)	4.869	4.713	4.990	4.821	4.570	4.907
k_2 (g.mg^{-1}min^{-1})	0.424	0.272	0.601	0.425	0.562	0.569
h_o (mg.g^{-1}min^{-1})	2.356	3.678	1.663	2.35	1.780	1.758
R^2	1.000	0.9999	1.000	1.000	1.000	1.000

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Elovich model

The Elovich equation is used successfully to describe second-order kinetics on assumption that the actual solid surfaces are energetically heterogeneous [19, 28]. The linear form of the equation is given by [29]:

$$q_t = \beta \ln(\alpha\beta) + \beta \ln t \tag{4}$$

Where α and β are known as Elovich coefficients representing the initial sorption rate (mg g^{-1} min^{-1}) and the desorption constant (g mg^{-1}) respectively. The Elovich coefficients are evaluated from the intercept and slope of linear plots of q_t versus ln t and are shown in Figures 11 and 12 while the parameters are presented in Table 3.
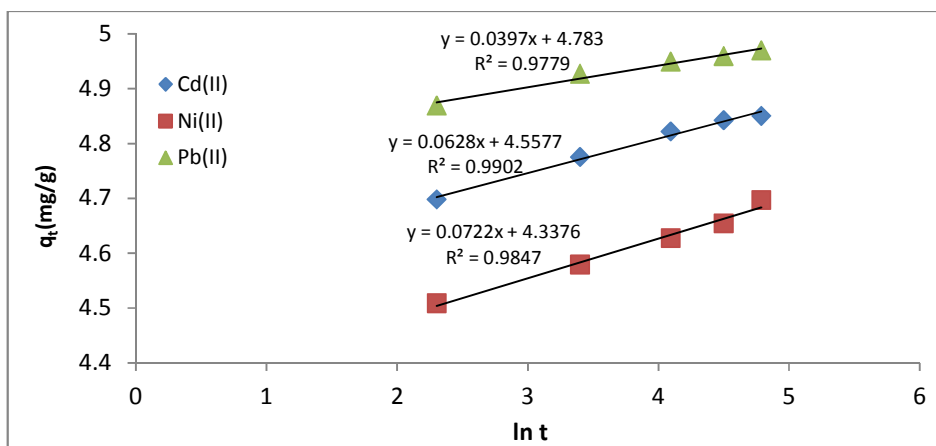

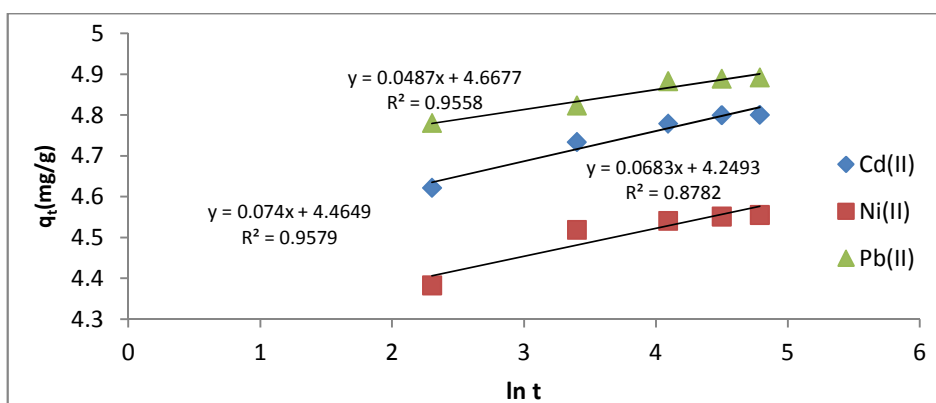**Fig.11 Elovich plot for adsorption of the metal ions onto ME**

Fig. 12 Elovich plot for adsorption of the metal ions onto MW

Table 3 Elovich Kinetic parameters

Constants	ME			MW		
	Cd(II)	Ni(II)	Pb(II)	Cd(II)	Ni(II)	Pb(II)
α	5.259×10^{32}	1.709×10^{27}	5.30×10^{33}	2.161×10^{27}	1.532×10^{28}	8.667×10^{42}
β	6.28×10^{-2}	7.22×10^{-2}	3.97×10^{-2}	7.40×10^{-2}	6.83×10^{-2}	4.87×10^{-2}
R^2	0.9902	0.9847	0.9779	0.9579	0.8782	0.9558

Comparison of the pseudo first-order, pseudo second-order and Elovich rate constants for the two adsorbents.

The validity of the three kinetic models-pseudo first-order, pseudo second- order and Elovich models was tested by the magnitude of the regression coefficients (R^2 values), given in Tables 1, 2 and 3. As shown in the tables, the high correlation coefficients (R^2 values) obtained for pseudo second-order reveals that pseudo second-order provided the best description for the kinetics of the metal adsorption on both adsorbents as compared to pseudo first-order and

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Elovich models. Therefore, the fitting of the adsorption data into pseudo second-order model means that the rate of occupation of active sites is proportional to the square of the number of unoccupied sites [30]. Also, from the tables, it was observed that q_e values obtained from pseudo first-order kinetic model were lower and significantly different compared to experimental values and also R^2 values were found to be fairly lower, indicating that pseudo first-order was not be the best model for the description of the adsorption data.

However, for pseudo second-order, the calculated q_e values agree very much closely with the experimental q_e values and with R^2 values all close or equal to 1, indicating the that kinetics of the adsorption process is best described by pseudo second-order kinetics. The data obtained generally show that lead(ll) ions were better adsorbed than Cadmium(II) and nickel(II) ions onto both adsorbents.

CONCLUSION

The present study evaluates the potential 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 this present study, the following conclusions can be drawn:

1. The adsorbent materials *ME* and *MW* have the potential to adsorb Cd(II), Ni(II) and Pb(II) ions from aqueous solutions. The batch adsorption studies were dependent on adsorbent dosage and exposure time. The equilibrium of the adsorption process was attained within 120 min.

2. The pseudo first-order, pseudo second-order kinetic models and the Elovich equation were used to analyze the adsorption data. Results obtained indicate that pseudo second-order equation provided the best correlation for the adsorption data.

3. The obtained results show that the agricultural wastes from the two species of cassava can adsorb Pb(II), Cd(II) and Ni(II) ions from aqueous solutions and could be an effective alternative method for the economic treatment of wastewater.

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