

Studies on the Influence of Mercaptoacetic Acid (MAA) Modification of Cassava (*Manihot sculenta* Cranz) Waste Biomass on the Adsorption of Cu^{2+} and Cd^{2+} from Aqueous Solution

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Cassava peelings waste, which is both a waste and pollutant, was chemically modified using mercaptoacetic acid (MAA) and used to adsorb Cu^{2+} and Cd^{2+} from aqueous solution over a wide range of reaction conditions at 30 °C. Acid modification produced a larger surface area, which significantly enhanced the metal ion binding capacity of the biomass. An adsorption model based on the $\text{Cu}^{2+}/\text{Cd}^{2+}$ adsorption differences was developed to predict the competition of the two metal ions towards binding sites for a mixed metal ion system. The phytosorption process was examined in terms of Langmuir, Freundlich and Dubinin-Radushkevich models. The models indicate that the cassava waste biomass had a greater phytosorption capacity, higher affinity and greater sorption intensity for Cu^{2+} than Cd^{2+} . According to the evaluation using Langmuir equation, the monolayer binding capacity obtained was 127.3 mg/g Cu^{2+} and 119.6 mg/g Cd^{2+} . The kinetic studies showed that the phytosorption rates could be described better by a pseudo-second order process and the rate coefficients was determined to be $2.04 \times 10^{-3} \text{ min}^{-1}$ and $1.98 \times 10^{-3} \text{ min}^{-1}$ for Cu^{2+} and Cd^{2+} respectively. The results from these studies indicated that acid treated cassava waste biomass could be an efficient sorbent for the removal of toxic and valuable metals from industrial effluents.

Key Words : Biosorption, Cassava waste, Heavy metal removal

Introduction

Cadmium is a toxic metal that is rather omnipresent in its distribution around the ecosystem. There has been an increasing use of cadmium for electroplating, batteries, alloys, pigments, stabilizers for catalysts and in semiconductors and TV tube phosphors,¹ over the years. Copper is required by certain enzymes in plants in minute quantities to activate oxidative processes and is an essential element for animals. However, copper in excess can be harmful. Copper is used in jewelry, paints, pharmaceutical products, wood preservatives, pigments, metal works, petroleum refinery, motor vehicle and aircraft plating and finishing. The uses of copper and cadmium can represent a great potential hazard to humans and the environment; hence, removal of these metals from industrial wastewater before discharge is mandatory.

Most conventional wastewater treatment techniques for removal of metals such as filtration, flocculation, activated charcoal, reverse osmosis, chemical precipitation or coagulation and ion-exchange, ultra-filtration or electrochemical deposition are not economically viable for small scale industries due to huge capital investment. It is therefore necessary to search for low-cost techniques that may be effective, less environmentally degrading and economical, which may be used by these industries. The use of agricultural by-products for the removal of toxic and

valuable metals from wastewater has continued to attract considerable attention in recent years because they are cheap, simple, sludge free and involve small initial cost and land investment.²⁻⁸

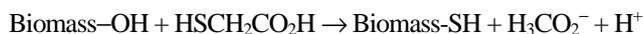
In this paper, we report the ability of mercaptoacetic acid (MAA) modified cassava waste as an adsorbent for the sorption of Cu^{2+} and Cd^{2+} from aqueous solution.

Experimental Procedure

Biomass Preparation: The plants were harvested and carefully prepared, activated and modified using mercaptoacetic acid as previously described in our work elsewhere.⁸ The cassava tubers obtained were washed with deionized water, air-dried, cut into 5 cm pieces and carefully peeled to obtain the cassava peeling wastes which was ground using a food processor (Magimix Cuisine System 5000), dried in an oven (GallenKamp, model OV -160, England) at 105°C for 24 h and then screened through a 100-mesh Tyler screen to obtain a fine biomass. The finely divided biomass was activated by soaking 500 g biomass in excess 0.3 M HNO_3 for 24 h to remove any debris or soluble biomolecules that might interact with metal ions, followed by washing thoroughly with deionized water until a pH of 7.1 was attained and then dried in the air. The air dried activated biomass was divided into two parts. The first portion was left untreated while 1.00 g of the other portions was acid treated with 250 mL excess 0.50 M and 1.00 M mercaptoacetic acid solution and stirred for 24 h at 30 °C while maintaining a pH of 7.1. This mercaptoacetic acid modification process led to

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the thiolation of the hydroxyl groups of the cellulosic biomass by the following reaction:



The degree of incorporation of -SH groups was further determined by reacting 0.5 g of acid treated biomass with 20 mL of iodine solution at pH 7.2 ± 0.2 , followed by back titration of the unreacted iodine with standard thiosulphate solution. The degree of thiolation was calculated to be 93%.

Characterization of Physical Properties of Cassava Waste Biomass: The unmodified and mercaptoacetic acid modified cassava waste biomass samples were characterized in terms of surface area, particle density, porosity, pore volume, cation exchange capacity (CEC) and the surface charge density (SCD) as previously described elsewhere.⁸ The surface area of the biomass was measured by the Brunauer-Emmett-Teller (BET) Nitrogen adsorption technique using a Quantasorb surface area analyzer (Model-05). The porosity and particle density were determined by mercury intrusion porosimeter (Micrometrics model-9310) and specific gravity bottle respectively. Pore volume was obtained as the inverse relation of particle density. While the cation exchange capacity (CEC) of the biomass samples were determined by the ammonium acetate saturation procedure. In this method, a 1.0 g of untreated and acid treated biomass samples were dispersed in 1.00 M sodium acetate solution. The resulting suspension was mixed with 1.00 M-ammonium acetate and mechanically stirred at room temperature for 1 h and centrifuged at 2800-x g for 5 minutes to extract the Na⁺ ions. The extracted Na⁺ concentration of the solution was determined by flame atomic adsorption spectroscopy (FASS). The SCD was calculated as the ratio of CEC and surface area (CEC/surface area).⁸

Phytosorption Experiments: The detailed batch experimental procedure to determine the contact time required for equilibrium sorption, effect of metal ion concentration, effect of biomass dose are previously described elsewhere.⁸ A 10 mg of each of the unmodified and MAA modified biomass samples were weighed and placed in pre-cleaned test tubes in triplicates. Several metal ion solutions with standard concentrations of 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 mM were made from HPLC-analytical grade standards of Cu²⁺ (from CuSO₄) and Cd²⁺ (from Cd(NO₃)₂·4H₂O). The two metal solutions made separately were adjusted to pH 5.0 with conc. HCl. Two milliliters of each metal solution were added to each tube containing the biomass and equilibrated for 2 h by shaking. The biomass suspensions were centrifuged for five minutes at 3000 × g. The supernatants were analyzed by flame atomic absorption spectroscopy.

The determination of the effect of biomass loading weight on the phytosorption of the two metal ions were made as follows: Several weights of 100 mg, 200 mg, 300 mg, 400 mg and 500 mg of 100 μm mesh particle size of unmodified and MAA modified biomass of cassava waste biomass were suspended in fifty milliliters of 0.01 M HCl to obtain biomass concentrations of 2.0 mg/mL, 4.0 mg/mL, 6.0 mg/mL, 8.0 mg/mL and 10.0 mg/mL. Two milliliters aliquots of

10 mg/L Cu²⁺ and Cd²⁺ standard solutions were separately added to each tube containing the different biomass concentrations and equilibrated for 2 h by shaking. The biomass suspensions were centrifuged for five minutes at 3000 × g. The supernatants were analyzed by flame atomic absorption spectroscopy

Theory and Data Evaluation. The mean metal sorption coefficient (q_e ; in mg/g biomass) was calculated from the initial metal ion concentration (C_o ; in mg/dm³) and the final or equilibrium concentration (C_e ; in mg/dm³) in every test tube as follows:

$$q_e = \frac{v}{m}(C_o - C_e) \quad (1)$$

where v is the volume of initial metal ion solution used (dm³) and m is dry mass of biomass used (g).

Sorption equilibria provides fundamental physicochemical data for evaluating the applicability of phytosorption processes as a unit operation usually described by isotherm models whose parameters express the surface properties and affinity of the sorbent, at a fixed temperature and pH.

Three models were used to fit the experimental data: Langmuir model, the Freundlich model and the Dubinin-Radushkevich model.

The Langmuir equation was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surface and expressed by

$$q_e = \frac{q_{\max}K_L C_e}{1 + K_L C_e} \quad (2)$$

where K_L (dm³ g⁻¹) is a constant related to the adsorption/desorption energy, and q_{\max} is the maximum sorption upon complete saturation of the biomass surface. The linearised form of the above equation after rearrangement is given below:

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

The experimental data were fitted into equation (3) for linearisation by plotting C_e/q_e against C_e .

The Freundlich model was chosen to estimate the adsorption intensity of the sorbent towards the biomass and is represented in equation (4):

$$q_e = K_F C_e^{\frac{1}{n}} \quad (4)$$

where; q_e = the adsorption density (mg of metal ion adsorbed/g biomass); C_e = Conc. of metal ion in solution at equilibrium (mg dm⁻³); K_F and n are the Freundlich constants. The value of n indicates the affinity of the sorbent towards the biomass.

Equation 4 is conveniently used in linear form by taking logarithm of both sides as

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

A plot of $\ln C_e$ against $\ln q_e$ (in equation 5) yielding a straight line indicates the confirmation of the Freundlich adsorption isotherm. The constants $1/n$ and $\ln K_L$ can be determined from the slope and intercept respectively.

The Dubinin-Radushkevich model was chosen to estimate the characteristic porosity of the biomass and the apparent energy of adsorption. The model is represented by equation 6.

$$q_e = q_D \exp\left(-B_D \left[RT \ln\left(1 + \frac{1}{C_e}\right)\right]^2\right) \quad (6)$$

where B_D is related to the free energy of sorption per mole of the sorbate as it migrates to the surface of the biomass from infinite distance in the solution and q_D is the Dubinin-Radushkevich isotherm constants related to the degree of sorbate sorption by the sorbent surface. The linear form of equation 6 is given as

$$\ln q_e = \ln q_D - 2B_D RT \ln\left(1 + \frac{1}{C_e}\right) \quad (7)$$

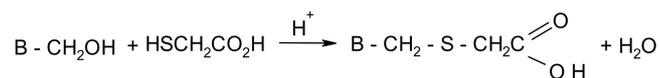
A plot of $\ln q_e$ against $RT \ln\left(1 + \frac{1}{C_e}\right)$ yielding a straight line

was made to confirm the model. The apparent energy of adsorption from Dubinin-Radushkevich isotherm model can be computed using the relationship⁹ (equation 8).

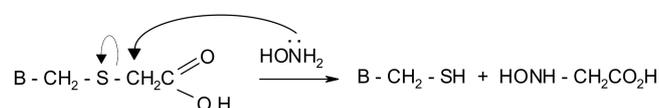
$$E = \frac{1}{\sqrt{2B_D}} \quad (8)$$

Results and Discussion

Cassava Waste Biomass Characterization. The native cassava (*Manihot sculenta* Cranz) waste biomass has been studied for its potential as a phytosorbent for metal ions in aqueous solution and in wastewater.¹⁰ The sorption mechanism was observed to be an ion-exchange type process. The major functional group in the cassava waste biomass is the polar hydroxyl group; others are aldehydes, carboxylic and cyano groups. These groups could be involved in chemical bonding. Thus, the chemical modification of the hydroxyl groups on the phytosorption of Cu^{2+} and Cd^{2+} was studied. The modification of the cassava waste biomass produced changes in the physical and surface properties of the biomass. The process resulted in the exchange of hydroxyl groups by sulphhydryl groups.



The acetate group was released upon treatment with hydroxylamine



The equation for the metal ion M^{n+} and the sulphhydryl

group on the biomass is thus proposed as



The reactions above modified the physicochemical and surface characteristics of the native cassava waste biomass and changed its chemical behaviours. The modification enlarged the surface area of the biomass by introducing a suitable degree of porosity into the solid matrix. The influence of surface modification was further tested by measuring the surface area, particle density, porosity, pore volume, cation exchange capacity and surface charge density for unmodified and MAA modified biomass. The BET (Brunnauer, Emmelt and Teller, nitrogen isotherm) surface area was determined to be $50.98 \text{ m}^2 \text{ g}^{-1}$ and $124.40 \text{ m}^2 \text{ g}^{-1}$ for unmodified and MAA modified biomass respectively. The particle density measured in paraffin oil, were found to be 1.78 g cm^{-3} and 2.16 g cm^{-3} for unmodified and MAA modified biomass respectively. Furthermore, the porosity (34.6% for unmodified; 55.7% for MAA modified), pore volume ($0.56 \text{ cm}^3 \text{ g}^{-1}$ for unmodified; $0.46 \text{ cm}^3 \text{ g}^{-1}$ for MAA modified), cation exchange capacity (CEC) (32.60 meq g^{-1} for unmodified; $100.76 \text{ meq g}^{-1}$ for MAA modified) and the surface-charge density (SCD) (0.64 meq m^{-2} for unmodified; and 0.81 meq m^{-2} for MAA modified) were determined. The result showed that, acid modification presents the biomass with larger surface area and provides the biomass with an enhanced porosity so that phytosorption reaction between metal ion and the biomass may occur at the surface. In general, acid modification enhanced the removal of metal ion from the aqueous solution.

In order to predict the level of competition of the two

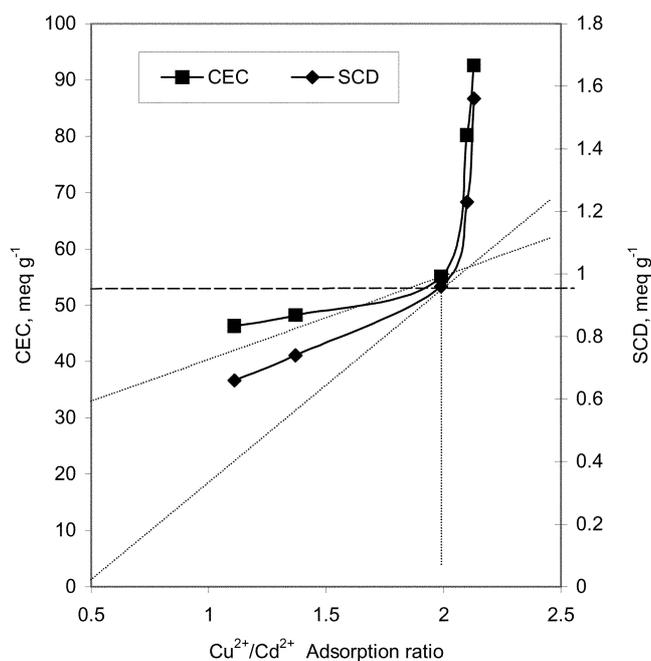


Figure 1. Variation of $\text{Cu}^{2+}/\text{Cd}^{2+}$ Adsorption ratio against cation exchange capacity (CEC) (meq g^{-1}) and Surface charge density (SCD) (meq m^{-2}) of mercaptoacetic acid (MAA) modified cassava waste biomass.

divalent metal ions on the modified cassava waste biomass during phytosorption process, the ratio of $\text{Cu}^{2+}/\text{Cd}^{2+}$ adsorption differences was correlated with the ionic sizes of the metal ions. The data showed that adsorption differences increased in the substrate with stronger bond for small size metal ions, indicative that the competition of Cu^{2+} for binding sites is higher than that of Cd^{2+} . This may be related to the ionic radius of the metal ions ($\text{Cu}^{2+} = 0.71 \text{ \AA}$; $\text{Cd}^{2+} = 0.97 \text{ \AA}$). The elements with lower ionic radius will compete better for exchange sites at high CEC values. Increase in SCD, brought about by acid modification enhanced the capacity of metal ion uptake by the biomass supporting an ion exchange process. Bernal and Lopez-Real¹¹ while investigating adsorption of ammonium and ammonia on natural zeolites and sepiolites as adsorbent materials has shown that ion-exchange process prevailed in materials with high surface-charge density. The analysis of the $\text{Cu}^{2+}/\text{Cd}^{2+}$ adsorption differences-which is based on the ionic radius of the competing metals is important in predicting the extent of competition between the metal ions in a mixed metal ion system, which could be applied to sorption design processes. Cu^{2+} and Cd^{2+} adsorption isosteres was further correlated with operating lines determined by the point of intersection of the data points for SCD and CEC as shown in Figure 1. The operating line is the line, which predicts and controls the selective adsorption of Cu^{2+} and Cd^{2+} in a mixed metal ion solution system, which could control the reaction rate. The prediction further confirmed that Cu^{2+} would have a better sorption affinity for the biomass than Cd^{2+} . The experimental results of the uptake of Cu^{2+} and Cd^{2+} ions on the unmodified and mercaptoacetic acid modified cassava waste biomass are at various initial metal ion concentrations are shown in Table 1. The sorption capacity increases from 8.6 to 49.0 mM and 17.4 to 89.0 mM (Cu^{2+}) and 3.7 to 27.6 and 13.9 to 77.1 mM (Cd^{2+}) for unmodified and modified biomass with an increase in the concentration of metal ion from 2 to 10 mg/dm³ and a biomass dose of 5.0 mg/dm³. However, the actual percent removal of the metal ions from solution was found to decrease with increase in initial metal ion concentration (Fig. 2). This was due to the fact that at lower concentrations almost all the ions were adsorbed. In terms of affinity for the biomass, Cu^{2+} showed to be the most removable as is seen on Table 1. However, a discrepancy between the results on

Table 1. Mean equilibrium sorption (q_e) of Cu^{2+} and Cd^{2+} from aqueous solutions at pH 5.0 by unmodified and 1.0 M-mercaptoacetic acid modified cassava waste biomass at different initial metal ion concentrations (C_o) at 30 °C*

C_o , mg/dm ³	Amount of metal ions adsorbed, (mM), q_e			
	Unmodified biomass		Modified biomass	
	Cu^{2+}	Cd^{2+}	Cu^{2+}	Cd^{2+}
2.0	8.6	3.7	17.4	13.9
4.0	9.4	7.33	19.4	19.1
6.0	13.6	10.0	31.6	27.6
8.0	27.2	16.6	70.2	61.4
10.0	49.0	27.6	89.0	77.1

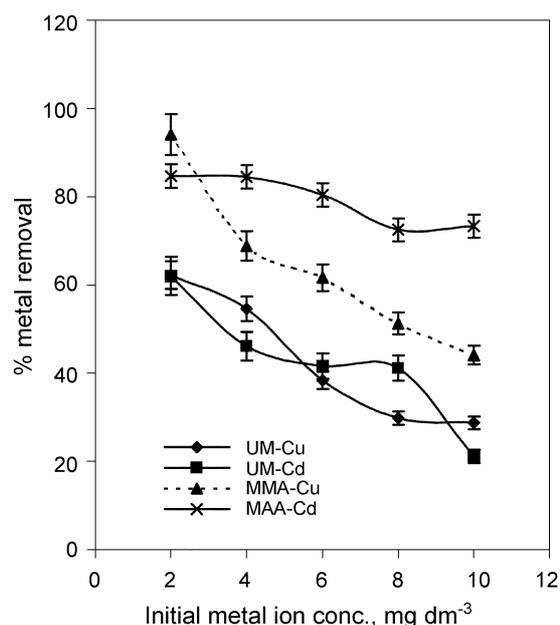


Figure 2. Effect of initial metal ion concentration on Cu^{2+} and Cd^{2+} binding by unmodified (UM) and acid modified (MAA) cassava waste biomass. Error bars display one standard deviation unit.

the molaric and percent basis occurred, which was due to the difference in atomic weights of the metals. On percent basis, Cd^{2+} seemed to be more or easily removable, this was actually because of its high atomic weight. On the whole, acid modification increased the sorption capacity of the biomass.

Further examination of Table 1 indicates that, the amounts of metal ions sorbed by acid modified biomass are much higher than that of unmodified biomass. The improved levels of metal ions sorption by acid modified biomass is thought to result from the relative ease of exchanging hydrogen atoms of the -SH groups on mercaptoacetic acid with heavy metal ions. Similar observations have been reported for maize cobs³.

Kinetics of Metal Sorption. The kinetic behaviour of metal ions on the biomass was further investigated by studying the effect of contact time on the sorption of Cu^{2+} and Cd^{2+} on to the cassava waste biomass. In an attempt to understand the sorption process of divalent metals on to the acid modified cassava waste biomass in a batch adsorption process, the linear form of the kinetic rate expression model for a pseudo-second order reaction developed by Ho¹² was applied to the experimental data. The equation is expressed as

$$\frac{t}{q_t} = \frac{1}{h_o} + \frac{1}{q_e} t \quad (9)$$

where q_t is the amount of divalent metal ion on the biomass surface (mM/g) at any time, t

q_e is the amount of divalent metal ion sorbed at equilibrium (mM/g)

h_o is the initial sorption capacity, (mM/min)

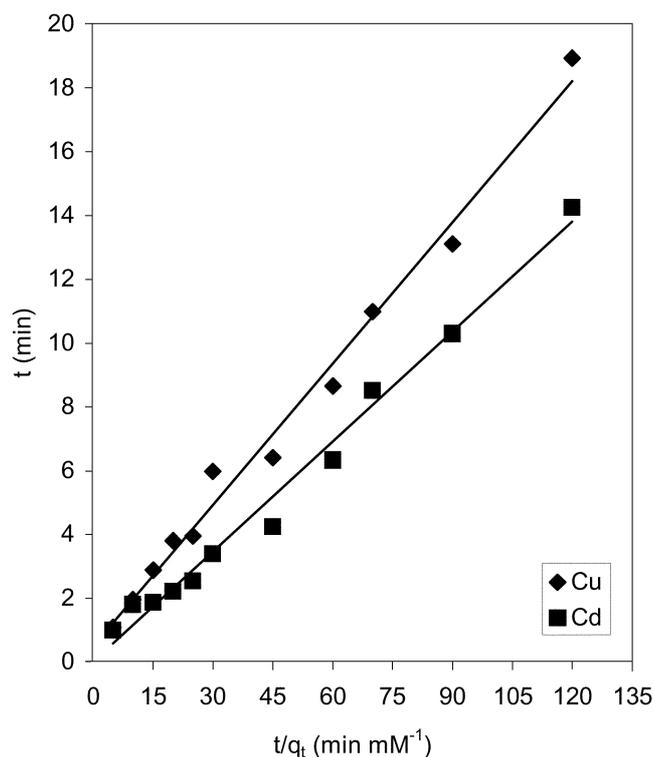


Figure 3. Pseudo-second order phytosorption kinetics of Cu^{2+} and Cd^{2+} onto MAA modified cassava waste biomass.

The initial sorption rate, h_o , as $t \rightarrow 0$ is defined as

$$h = k_2 q_e^2 \quad (10)$$

where K_2 is the Pseudo-second order rate constant (g/mg min)

The initial sorption rate, h_o , the equilibrium sorption capacity, and the pseudo-second order rate constant, k_2 , was determined experimentally from the slope and intercept of a plot of t/q_t against t (Fig. 3). The data showed that the sorption process was rapid, being complete in 30 to 40 min. However, an effective equilibrium was reached at about 90 min. The rapid adsorption of the metal ions to the biomass indicates that adsorption may be taking place on the cell wall of the biomass. This could well suggest that intra-particle diffusion is the limiting factor in this latter portion of the process. The k_2 , q_e , h_o and r_2^2 values were calculated from the plots and are given in Table 2. The results as presented in Table 2 showed that Cu^{2+} had a higher initial rate than Cd^{2+} . This implies that in a mixed metal ion system of both metals, Cu^{2+} may adsorb better than Cd^{2+} .

Phytosorption Equilibria and Adsorption Isotherms.

The adsorption data were analyzed in terms of a Langmuir

Table 2. Kinetic Constants of the Phytosorption process

Metal ions	k_2 (mM min^{-1})	q_e (mg g^{-1})	h_o $\text{mM}^{-1} \text{min}^{-1}$
Cu^{2+}	2.04×10^{-3}	73.3	5.58
Cd^{2+}	1.98×10^{-3}	69.6	3.94

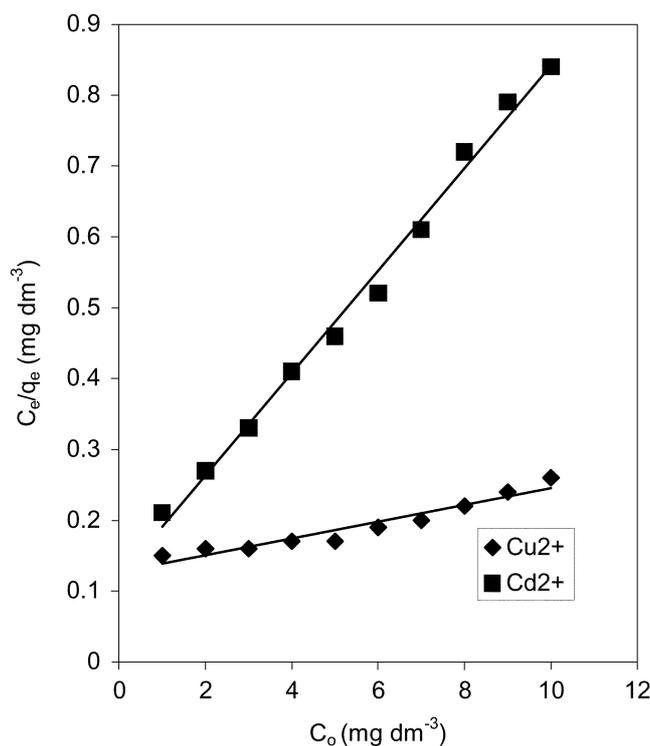


Figure 4. Langmuir equation isotherms of Cu^{2+} and Cd^{2+} ions sorbed on biomass.

Table 3. Langmuir isotherm parameters

Metal ions	q_{\max}	K_L	R^2	S_F
Cu^{2+}	127.3	116.68	0.993	0.009
Cd^{2+}	119.6	256.63	0.972	0.057

model, the Freundlich model and the Dubinin-Radushkevich model. Figure 4 shows the data linearised to fit the Langmuir equation. The plots of specific sorption (C_e/q_e) against equilibrium concentration (C_e) gave the linear isotherm parameters of q_{\max} , K_L and the coefficient of determination are presented in Table 3.

The R^2 values suggested that the Langmuir isotherm provides a good model of the sorption system. The sorption capacity, q_{\max} , which is a measure of the maximum adsorption capacity corresponding to complete monolayer coverage showed that the cassava waste had a mass capacity for Cu^{2+} ($127.3 \text{ mg}\cdot\text{g}^{-1}$) than Cd^{2+} ($119.6 \text{ mg}\cdot\text{g}^{-1}$). The adsorption coefficient, K_L , which is related to the apparent energy of adsorption for Cd^{2+} ($256.63 \text{ dm}^3\cdot\text{g}^{-1}$) was greater and this could mean that the energy of adsorption is not very favourable, hence not all binding sites may be available for Cd^{2+} binding due to its large ionic radius. The same capacity order have been reported by Ho⁷ for metal cation sorption on tree fern.

Furthermore, the favourability of adsorption of the two divalent metal ions onto the MAA modified cassava waste biomass was tested using the essential features of the Langmuir isotherm, expressed in terms of a dimensionless

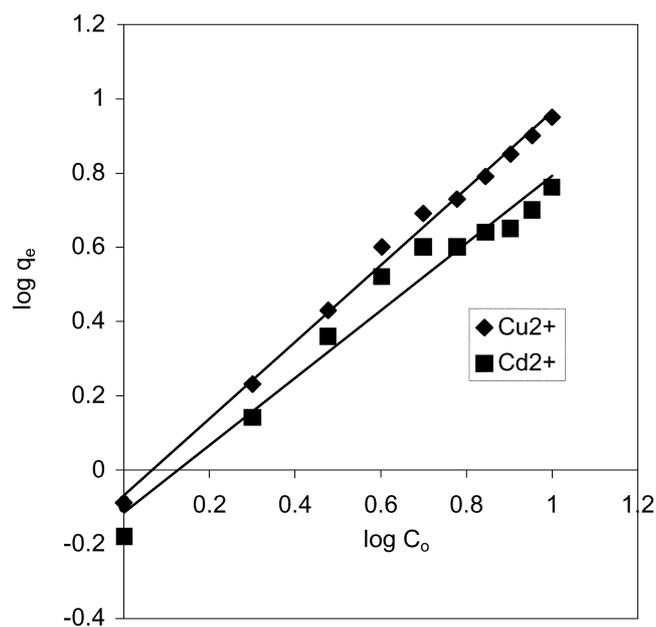


Figure 5. Freundlich equation isotherms of Cu^{2+} and Cd^{2+} sorbed on biomass.

constant called separation factor, S_F , proposed by Poots.¹³ The separation factor, S_F , is defined by the following relationship:

$$S_F = \frac{1}{1 + K_L C_o} \quad (11)$$

Where

K_L = constant from Langmuir equation

C_o = initial metal ion concentration of 10 mg/L.

The parameter indicates the shape of the isotherm as follows:

$S_F > 1$	Unfavourable isotherm
$S_F = 1$	Linear isotherm
$S_F = 0$	Irreversible Isotherm
$0 < S_F < 1$	Favourable isotherm

The values of S_F (Table 3) shows that phytosorption of Cu^{2+} and Cd^{2+} onto the MAA modified cassava waste biomass was favourable, indicative that mercaptocacetic acid modified cassava waste biomass is an excellent phytosorbent for the two metals.

The linear Freundlich isotherm plots for the phytosorption of the two divalent metals onto the MAA modified cassava waste biomass are presented in Figure 5. Examination of the plot suggests that the Freundlich isotherm is also an

Table 4. The Linear Freundlich isotherm parameters for the Cu^{2+} , and Cd^{2+} onto MAA modified cassava waste biomass

Metal ions	K	$1/n$	R^2
Cu^{2+}	5.62	0.971	0.995
Cd^{2+}	1.85	0.907	0.967

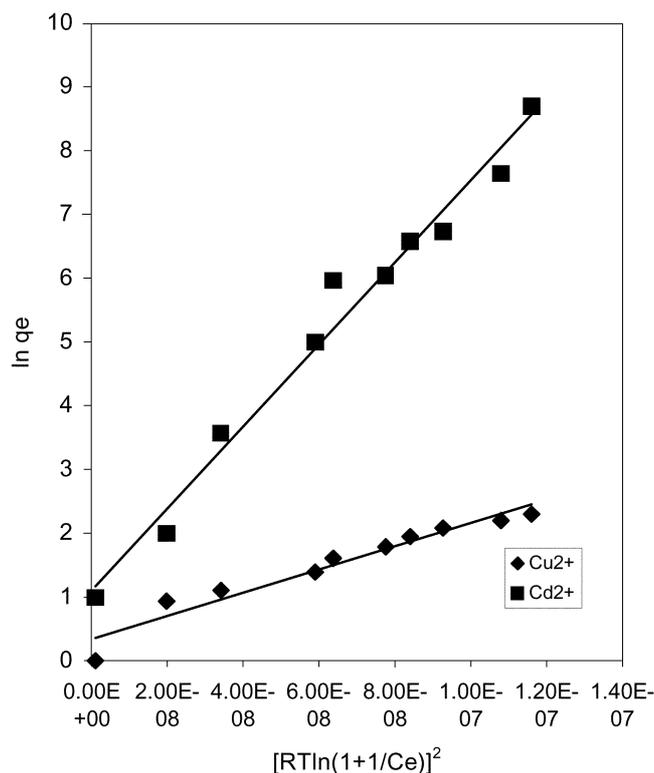


Figure 6. Dubinin-Radushkevich isotherm of Cu^{2+} and Cd^{2+} ions on cassava waste biomass.

appropriate model for the sorption study of Cu^{2+} and Cd^{2+} . Table 4 shows the linear Freundlich sorption isotherm constants and the coefficients of determination (R^2).

Based on the R^2 values, the linear form of the Freundlich isotherm appears to produce a reasonable model for the sorption in the two metals, with Cu^{2+} seeming to fit the data better than Cd^{2+} . The K -value of Cu^{2+} (5.62) is greater than that of Cd^{2+} (1.85), suggesting that Cu^{2+} has greater adsorption tendency towards the cassava waste biomass than Cd^{2+} . Again, the smaller ionic radius of Cu^{2+} might be responsible for its greater adsorptivity. It has been reported³ that the smaller the ionic size, the greater its affinity to active groups of biomaterials. The Freundlich equation parameter $1/n$, which is a measure of the adsorption intensity, ranged between 0.97 to 0.91 for Cu^{2+} and Cd^{2+} respectively. Values of $1/n$ for Cu^{2+} (0.971) are higher than that of Cd^{2+} (0.907), indicating a preferential sorption for Cu^{2+} by the modified cassava waste biomass.

The linear Dubinin-Radushkevich isotherm plot for the phytosorption of the two divalent metal ions onto the modified cassava waste biomass are presented in Figure 6 and examination of the data shows that the Dubinin-Radushkevich isotherm also provides an accurate description of the data for the two metal ions over the concentration range studied. Phytosorption processes usually have adsorption energies less than 40 kJ mol^{-1} and the energy values of 4.47 and 7.75 kJ mol^{-1} for Cu^{2+} and Cd^{2+} respectively indicates physical sorption processes for the adsorption of the two divalent metal ions onto the cassava

Table 5. Dubinin-Radushkevich isotherm parameters for the Cu^{2+} and Cd^{2+} onto the MAA modified biomass

Metal ions	q_D	B_D	R^2	E (KJ mol ⁻¹)
Cu^{2+}	0.343	1.00E - 07	0.98	4.47
Cd^{2+}	1.096	3.30E - 08	0.94	7.75

Table 6. A comparison of coefficients of determination, R^2 , for the three isotherms

Metal ions	Langmuir	Freundlich	Dubinin-Radushkevich
Cu^{2+}	0.993	0.995	0.943
Cd^{2+}	0.927	0.965	0.979

waste biomass. Again, Ho¹² has earlier reported that the typical range of bonding energy for ion-exchange mechanisms is 8-16 KJ mol⁻¹. The low values in this study (Table 5) indicate ion exchange mechanisms.

Coefficient of Determination. The coefficient of determination, R^2 , for the three isotherms is listed in Table 6.

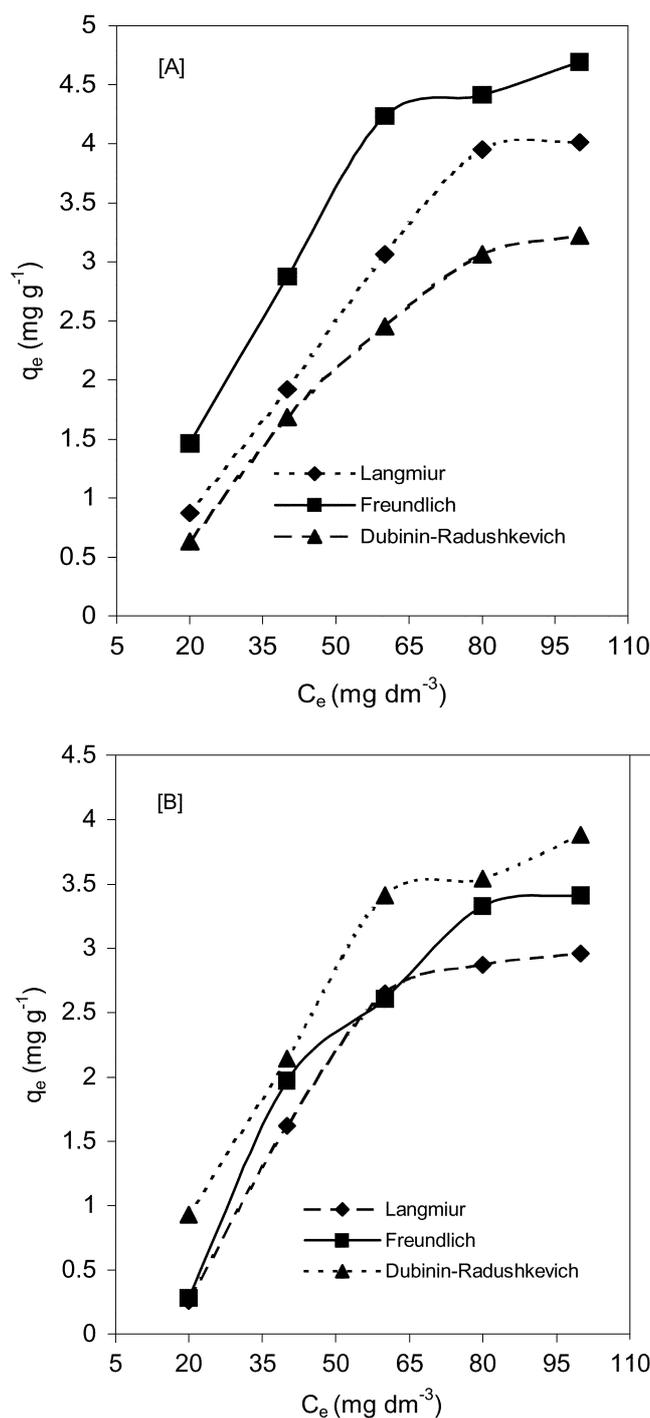
An internal structure not accessible at first glance of the data in Table 5, was obtained by considering the metals as objects and the R^2 as variable. The internal associations was then ascertained using the two-way analysis of variance (ANOVA) without replication ($P < 0.05$) to describe the relationships (1) between the three isotherms in describing the adsorption of the two divalent metals on the biomass and (2) between the two divalent metal ions for binding sites on the biomass. The result is presented in Table 7.

The data (Table 7) showed no significant difference between the three isotherms in describing the adsorption of the two divalent metals onto the cassava waste biomass. This indicates and confirms the three different isotherms as appropriate in their own merits in describing the potential of cassava waste biomass for the removal of Cu^{2+} and Cd^{2+} from aqueous solutions. However, it is clear from the result that Langmuir have best fitted for phytosorption of Cu^{2+} and Dubinin-Radushkevich for Cd^{2+} , while Freundlich isotherm fits the two metal ions on MAA modified cassava waste biomass at various reaction conditions.

The ability of the three isotherm models to correlate with experimental data was further assessed by using the various sorption constants and theoretical equilibrium metal ion concentrations. The theoretical plots from each isotherm with the experimental data for the phytosorption of Cu^{2+} and Cd^{2+} on the cassava waste biomass is shown in Figure 7. The

Table 7. Two-way Analysis of Variance (ANOVA) without replication at $\infty = 0.05$

Source of variation	SS	df	MS	F	P-value	F-crit
Metals	0.0006	1	0.0006	0.45	0.57	18.51
R^2	0.0005	2	0.0003	0.19	0.84	19.00
Error	0.0024	2	0.0013			
Total	0.0038	5				

**Figure 7.** The three isotherms for the phytosorption of Cu^{2+} and Cd^{2+} using cassava waste biomass [A] = Phytosorption of Cu^{2+} ; [B] = Phytosorption of Cd^{2+} .

graph is plotted in the form of metal ion sorbed per unit mass of biomass, q_e , against the equilibrium concentration of metal ion C_e . This data further confirms the essentiality of the three isotherms during the phytosorption process.

Effect of Biomass Dose. The effect of variation of biomass dose for initial metal ion concentration of 10 mg dm⁻³ is shown in Figure 8. The data showed that the equilibrium concentration decreases with increasing adsorb-

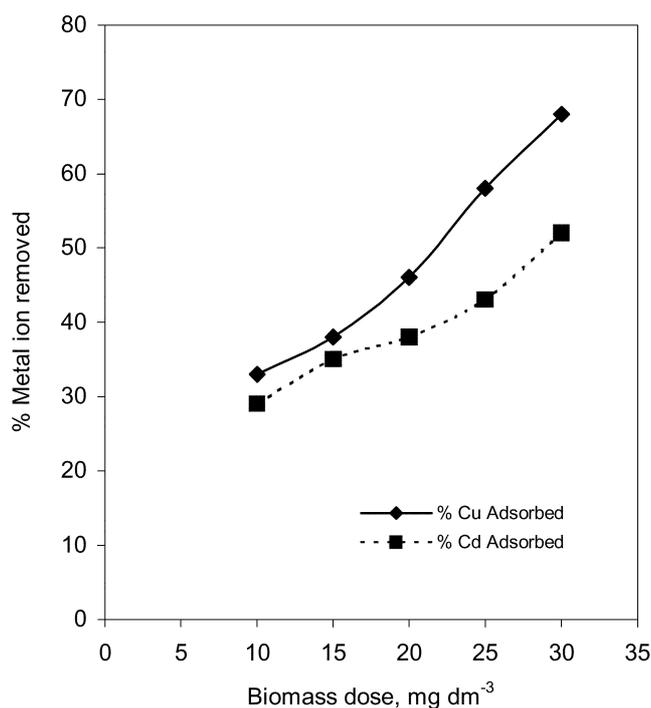


Figure 8. Variation of percent metal ion removed against biomass dose.

ent doses for a given initial metal ion concentration. This is to be expected, because for a fixed initial metal solution concentration, increasing adsorbent doses provides greater surface area or adsorption sites. From the determination coefficient (R^2), 98% of Cu^{2+} and 97% of Cd^{2+} removed by the biomass is attributable to the biomass dose.

Conclusion

The kinetics of the sorption of Cu^{2+} and Cd^{2+} on the modified cassava waste biomass was studied on the basis of the pseudo-second-order rate mechanism. The sorption capacity of Cu^{2+} is higher than Cd^{2+} because of the smaller ionic radius of Cu^{2+} . The rapid but not relatively short contact time for the adsorption of the metal ions to the biomass indicates that the predominant mechanism is physiosorption and binding sites are cell wall components. The low values of the bonding energy in this study an

indicate ion exchange mechanisms. The separation factor or equilibrium parameter obtained from the Langmuir isotherm showed adsorption of metal ions on to the acid modified cassava waste biomass is favourable. On the whole the data showed that, both modified and unmodified cassava waste biomass were successful as biosorbent for treating heavy metal contaminated wastewater and may serve as an alternative adsorbent to conventional means. The $\text{Cu}^{2+}/\text{Cd}^{2+}$ adsorption differences which was developed to predict the competition of the two metal ions towards binding sites in a mixed metal ion system shows that Cu^{2+} competes faster towards binding sites than Cd^{2+} attributable to the differences in ionic size.

References

1. Kefala, M. I.; Zouboulis, A. I.; Matis, K. A. *Environmental Pollution* **1999**, *104*, 283-293.
2. Quek, S. Y.; Wase, D. A. J.; Forster, C. F. *Water S. A.* **1998**, *24*(3), 251-256.
3. Okiemen, F. E.; Maya, A. O.; Oriakhi, C. O. *Inter. J. Environ. Anal. Chem.* **1988**, *32*, 23-27.
4. Parsons, J. G.; Gamez, G.; Tiemann, K. L.; Gardea-Torresdey, J. L. *Determination of Trace Level Gold (III) Binding to Alfalfa Biomass Using GFASS with Zeeman Background Correction*, Proceedings of the Symposium on Harzadous Waste Research; Erickson, L. E., Ed.; Environmental Solutions to Resources Development, Production, and Use: Kansas State University, Manhattan, 2000; KS pp 2-12.
5. Madgwick, J. C. *Australian Biotechnology* **1991**, *4*, 292-297.
6. Lucido, S. P.; Iwasaki, I. *The Removal of Cu^{2+} from the Mine Effluents Using a Fresh Water Green Alga, Cyanidium Caldarium*, *Environmental Management for 1990's*, Proceedings of the Symposium on Environmental Management for the 1990s; Denver, Colorado, 1991, February 25-28; p 143.
7. Ho, Y. S.; Huang, C. T.; Huang, H. W. *Biochem.* **2002**, *37*(5), 1421-1430.
8. Abia, A. A.; Horsfall, M. Jnr; Didi, O. J. *Bioresource Technology* **2003**, *90*(3), 345-348.
9. Hasany, S. M.; Chaudhary, M. H. *Appl. Rad. Isot.* **1996**, *47*, 467-471.
10. Horsfall, M. Jnr; Abia, A. A.; Spiff, A. I. *African J. Biotechnol.* **2003**, *2*(10), 360-364.
11. Bernal, M. P.; Lopez-Real, J. M. *Bioresource Technol.* **1993**, *43*, 27-33.
12. Ho, Y. S.; John Wase, D. A.; Forster, C. F. *Wat. Res.* **1995**, *29*(5), 1327-1332.
13. Poots, V. J. P.; MckKay, G.; Healy, J. J. *J. Wat. Pollut. Control. Federation* **1978**, *May*, 926-934.