



Studies on the Use of Agricultural By-Product for the Removal of Trace Metals from Aqueous Solutions

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ABSTRACT: The use of pure activated and differentially thiolated cassava waste biomass as adsorbents for the removal of metal ions such as cadmium, copper, and zinc in aqueous solutions were studied by means of equilibrium sorption. The sorption rates of the three metals are 0.2303 min^{-1} (Cd^{2+}), 0.0051 min^{-1} (Cu^{2+}) and 0.0040 min^{-1} (Zn^{2+}) for 0.5M thiolation level and 0.109 min^{-1} (Cd^{2+}), 0.0069 min^{-1} (Cu^{2+}) and 0.0367 min^{-1} (Zn^{2+}) for 1.00M thiolation level respectively. The adsorption rates are quite rapid and within 60 minutes of mixing about 60 - 80 percent of these ions were removed from the solutions by the biomass. The results further showed that increased thiolation led to increased incorporation or availability of more binding groups into the cellulosic matrix, resulting in improved adsorptivity of the cassava waste biomass. The binding capacity study showed that the cassava waste, which is hitherto a serious environmental nuisance due to the fouling odour, released during decomposition has the ability to adsorb trace metals from solutions. @JASEM

Point and non-point source inputs of trace metals into the ecosystem are largely as a result of anthropogenic activities. Once in the environment, metals are difficult to recover and can therefore pose a threat to the ecosystem. Hence, it is necessary to extract these metals from industrial effluents before discharging the aqueous waste into the environment. Technologies currently in use to extract trace metals from wastewater which involve filtration, flocculation, activated charcoal, reverse osmosis, precipitation or coagulation and ion-exchange have many problems associated with their use. Many of these techniques are very expensive, not effectively efficient, and also use toxic chemicals in their preparation, which may increase the environmental load. Although remediation of polluted waters (wastewaters) are necessary, in order to prevent further discharge of contaminants into the environment, simpler cost-effective methods need to be developed for industrial use. In recent times, a great deal of interest has been given to the use of biological systems for the removal of trace metals from polluted sites (Baker *et al* 1994; Lucido and Iwakasi 1991; Gang and Weixing, 1998; Lujan, *et al* 1994; Gardea-Torresdey, *et al* 1990; Gardea-Torresdey, *et al* 1996a, 1996b). It has been found by Mofa (1995) that phytochelatin and proteins within the plant may be produced in large concentrations to bind metals and reduce their toxicity. Therefore plants that grow in contaminated environment should show a greater ability to recover toxic metals and may be a good source for naturally occurring biological compounds that have potential for contaminant remediation. Although live biological systems work well for low concentrations they cannot survive the high concentrations found in seriously contaminated areas and industrial effluents (Vanka

and Tiwari, 2002). The use of non-living biomaterials as metal-binding compounds has the advantage of not being affected by high levels of contamination. Moreover, they require minimum care and maintenance and can be obtained more cheaply. Several studies have shown that non-living plant biomass materials are effective for the removal of trace metals from the environment (Mofa, 1995; Lujan *et al* 1994 and Gardea-Torresdey *et al* 1996a). The unique ability of these plants to bind metals has been attributed to the presence of various functional groups, which can attract and sequester metal ions. The work of Gardea-Torresdey *et al* (1990) demonstrated that carboxyl groups found on the cell walls of dead algal biomass are potentially responsible for copper binding. This phenomenon has spurred interest in other natural materials that may contain similar functional groups. Cellulosic non-reducing carbohydrate polysaccharides found in plant fibre may also be used as cheap materials capable of removing metals from their solutions. This technology is attractive mainly because it is effective, environmentally friendly, and inexpensive. Several dead and inactive plant materials grown in different climatic regions have been studied for this purpose (Madgwick, 1991; Gardea-Torresdey *et al* 1999; Winterbourn *et al* 2000). However, a survey of trace metal studies in Africa by Biney *et al* (1994) did not show any study in this area for the region of Nigeria. The objective of this research is to develop inexpensive and effective metal ion adsorbents from agricultural by-products of the tropical Manihot sp. (Cassava) tuber wastes, which is plentiful in Nigeria. The purpose is to offer these agricultural wastes as adsorbents as a replacement for existing commercial materials.

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In this paper we examine the binding of Cd (II), Cu (II) and Zn (II) ions to cassava biomass in an attempt to remediate metal-contaminated waters.

MATERIALS AND METHODS

Sample Collection

The tropical Manihot wastes are selected for this study for their abundance and availability all season. Cassava as garri, foofo and starch is a major staple food in Eastern Nigeria and therefore produces large volumes of wastes, which has been creating environmental nuisance in the region. The tropical Manihot series TMS 30572 tubers were collected from the controlled agricultural fields at the Rivers State University of Science & Technology, Port Harcourt Agric Farm. The plants were harvested by manually removing the matured crops from the soil, washed thoroughly to remove any debris, and the tubers separated from the stems. The tubers were further washed with deionized water and allowed to air dry. The dried tubers were cut into 5 cm and carefully peeled with a built-in paring edge peeler of a multi-purpose wonder mill to obtain the cassava peel wastes. The peelings were oven dried at 90°C for four days to constant weight. The dried samples were ground using a Wiley Mill and sieved through a 100-mesh Tyler screen to obtain a fine biomass which was used for the various experiments as described below.

Chemical Modification

Cellulose is the most abundant among the polysaccharides and is the chief component of wood and plant fibres. The cellulose in the cassava fibre biomass was chemically modified by thiolation. This was achieved by first activating the cassava fibre by soaking 500g biomass in an excess 0.3M HNO₃ for 24hr, followed by washing with deionized water until a pH of 7.4 was attained and then air-dried. The air-dried biomass was divided into three equal portions. The first portion labeled A was left untreated. The second and third portions labeled B and C respectively were treated with excess 0.50M and 1.00M thioglycollic acid solutions respectively. For the treated biomass samples, 100g was treated with 250mL of thioglycollic acid and stirred for 24hr at 25°C while maintaining a pH of 7.3. This will cause the thiolation of the methylene hydroxyl group of the cellulose pyran ring.

The thiolated biomass was then centrifuged at 3000rpm for five minutes and the supernatants were discarded. The biomass was then washed with de-ionized water, and then re-suspended in 1.0M hydroxylamine to remove all O - acetyl groups. To remove all other soluble materials, the biomass was washed with 0.1M HCl and three times with de-ionized water and centrifuged at 3000rpm for five

minutes and the supernatants were discarded. The sample was placed in liquid nitrogen for 45 minutes until completely frozen and lyophilized.

Effect of Metal ion Concentration on Metal ion - Biomass Binding

A 200 mg of non-thiolated and differentially thiolated (at 0.50M and 1.00M) biomass of cassava wastes was used for this experiment. The non-thiolated, which was the control was labeled as 0.00M - SH, while the differentially thiolated biomass at 0.50M and 1.00M levels were labeled as 0.50M - SH and 1.00M - SH respectively. A 10 mg of each of the non-thiolated and differentially thiolated biomass samples were weighed and placed in pre-cleaned test tubes in triplicates. Several metal ion solutions with standard concentrations of 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, and 0.10M were made from HPLC - analytical grade standards of Cd²⁺ (from Cd(NO₃)₂.4H₂O), Cu²⁺ (from CuSO₄) and Zn²⁺ (from ZnCl₂). These metal solutions 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 24hr by shaking. The biomass suspensions were centrifuged for five minutes at 3000rpm. The supernatants were analyzed by flame atomic absorption spectroscopy.

Effect of pH on Metal ion - Biomass Binding

The experiment on the effect of pH on metal ion binding was carried out based on a procedure previously reported by Gardea-Torresdey *et al* (1996b). A 200 mg non-thiolated and differentially thiolated biomass samples were weighed and washed with 0.1M HCl and twice with de-ionized water to remove any metals or soluble biomolecules present in the biomass. Fifty milliliters of 0.01M HCl were added to the biomass to obtain a biomass concentration of 5mg/mL. The pH of this suspension was adjusted to 2.0. Two milliliters aliquot of the suspension were added to three 5mL clean test tubes. The pH was adjusted to pH 3.0, 4.0, 5.0, and 6.0 by adding a solution of conc. HCl. Three two milliliters aliquot of each suspension were collected and centrifuged at 2800rpm for five minutes and the supernatants were collected in separate tubes. Solutions of 0.10 mol/L metal ion concentration of Cd²⁺ (from Cd(NO₃)₂.4H₂O), Cu²⁺ (from CuSO₄) and Zn²⁺ (from ZnCl₂) from HPLC - analytical grade standards of these metal ions. At each pH, two milliliters of the metal ion solution was added to the respective biomass suspension. All the tubes were reacted on a shaker for one hour. The tubes were then centrifuged at 2800rpm for five minutes, and the supernatants were collected in separate clean test tubes. The metals content were determined using

flame atomic absorption spectroscopy after recording the final pH of the test tubes.

Effect of Contact Time on Metal ion Binding

The experiment on the effect of contact time on metal ion binding was performed according to the previously work of Gardea-Torresdey *et al* (1996b). A 250 mg non-thiolated and differentially thiolated biomass samples were weighed and washed with 0.1M HCl and twice with de-ionized water to remove any metals or soluble biomolecules present in the biomass. Fifty milliliters of de-ionized water were added to the biomass to obtain a biomass concentration of 5mg/mL. The pH of this suspension was adjusted to 5.0. Two milliliters aliquot of the suspension were added to twenty-one 5mL clean test tubes; three for each time interval of 5, 10, 15, 20, 25, 30, and 90 minutes. The test tubes were centrifuged and the supernatants were discarded. Two milliliters of 0.10 mol/L metal ion solutions of Cd²⁺, Cu²⁺ and Zn²⁺ from HPLC-analytical grade standards was added to each pellet. All the tubes were reacted on a shaker for the specified time. The tubes were then centrifuged at 2800rpm for five minutes and the supernatants were analyzed by flame atomic absorption spectroscopy.

Desorption Study of the Adsorbed Metal ions

The dried pellets from metal sorption capacity experiment were reacted with two milliliters of 0.10M HCl for fifteen minutes and centrifuged to remove the bound metals. The supernatants were collected for analysis. The process of acid treatment was repeated thrice and all portions added together. The tubes were then centrifuged at 2800rpm for five minutes and the supernatants were analyzed by flame atomic absorption spectroscopy.

RESULTS AND DISCUSSION

The data on the use of biomass of agricultural by-products of Manihot sp. (cassava) for the removal of three metal ions are presented in this work.

Effect of Metal ion Concentration on Metal ion – Biomass Binding

The adsorption capacities of thiolated and non-thiolated biomass at different metal ion concentrations are given in Table 1. The results indicated that both thiolated and non-thiolated biomass of cassava wastes have the capacity to remove the three metals from aqueous solution. The uptake of the three metals by the biomass from the solution is independent of metal ion concentrations. For cadmium and zinc, non-thiolated biomass had a

Analysis of Metal Content

The metal content in all the experiment was determined by a Buck Scientific Flame Atomic Absorption Spectrometer (FAAS) model 200A. The samples were read in duplicates. The following analytical wavelengths were used for the metals studied: cadmium 228.8nm, copper 327.4nm and zinc 213.9nm. HPLC analytical grade standards were used to calibrate the instrument, which was checked periodically throughout the analysis for instrument's response. The correlation coefficient for the calibration curve was between 0.986 – 0.989.

The batch experiments were performed in duplicates and the mean and were computed for each set of values. All statistical analysis was performed using DATA ANALYSIS TOOLPAK Microsoft Excel for Windows 98 with level of significance maintained at 95% for all tests. One-analysis of variance (ANOVA) without replication was used to test differences between non-thiolated and differentially thiolated biomass sample data.

Equilibrium Sorption Studies

The equilibrium sorption was studied by calculating the fractional attainment, α , of equilibrium for both non-thiolated and differentially thiolated cassava waste biomass for the three metal ions. The fractional attainment, α , of equilibrium, which is the ratio of the amounts of metal ion removed from solution after a certain time, t , to that removed when sorption equilibrium is attained was obtained using the following equation:

$$\alpha = \frac{[M]_t^n}{[M]_e^n}$$

A plot of α versus t enables us to access the rate of adsorption onto the biomass.

maximum observed adsorption capacity at a metal concentration of 0.04 mmol/g, while the maximum adsorption for copper was attained at a metal ion concentration of 0.05 mmol/g. Hence, for non-thiolated cassava waste biomass, the optimum may be obtained between 0.04 mmol/g and 0.05 mmol/g. The differentially thiolated biomass had a maximum cadmium adsorption at a metal ion concentration of 0.10 mmol/g at 0.50M thiolation and 0.04 mmol/g metal ion concentration at 1.00M thiolation. Copper adsorption had similar behaviour to cadmium with respect to metal uptake by 0.5M differentially thiolated biomass at low metal ion concentration. However, at 1.00M thiolation, optimum copper ion uptake was achieved at metal ion concentration of 0.02 mmol/g. Zinc adsorption on thiolated biomass

was observed to behave differently from cadmium and copper. Optimum adsorption capacities for 0.50M and 1.00M biomass thiolation for zinc was observed at 0.07 mmol/g and 0.010 mmol/g metal ion concentrations respectively. This differential behaviour in metal adsorption at low and high metal ion concentrations may be an artifact of the presence of high affinity ligands in or on the cassava biomass. Such ligands may be hydroxyl, sulphur, cyano and/or amino groups. At high metal ion concentrations, the metals may be forced to bind to low-affinity ligands, but at trace levels the binding may occur through high-affinity ligands only. It has been observed by

Parsons *et al* (2000) that such differential behaviour may be due to a charge repulsion of the metal chloro-complexes and the surface of the cassava waste biomass. The chloro-complexes are present as negatively charged species, which would explain the observed reduction in the adsorption of the metals to the cassava waste biomass with increasing metal ion concentration. Although the different metals were adsorbed to the thiolated and non-thiolated biomass at low and high metal ion concentrations, there was no significant difference ($P < 0.05$) observed in the overall adsorption capacities with increase in metal ion concentrations.

Table 1. Concentration of Metal ions (mmol/g bound by each gram of thiolated and non-thiolated cassava waste biomass after equilibration for one hour at 5.0 pH.

Metal ion Conc. (mol/L)	0.00M - SH			0.50M - SH			1.00M - SH		
	Cd ²⁺	Cu ²⁺	Zn ²⁺	Cd ²⁺	Cu ²⁺	Zn ²⁺	Cd ²⁺	Cu ²⁺	Zn ²⁺
0.010	0.0066	0.0086	0.0049	0.0092	0.0093	0.0069	0.0071	0.0082	0.0098
0.020	0.0139	0.0168	0.0158	0.0143	0.0166	0.0162	0.0132	0.0174	0.0151
0.030	0.0233	0.0242	0.0256	0.0216	0.0260	0.0242	0.0226	0.0250	0.0251
0.040	0.0331	0.0394	0.0394	0.0344	0.0346	0.0334	0.0391	0.0322	0.0318
0.050	0.0395	0.0493	0.0345	0.0375	0.0417	0.0427	0.0422	0.0422	0.0418
0.060	0.0400	0.0536	0.0526	0.0454	0.0520	0.0514	0.0476	0.0513	0.0505
0.070	0.0436	0.0612	0.0610	0.0562	0.0608	0.0601	0.0557	0.0598	0.0582
0.080	0.0466	0.0702	0.0721	0.0630	0.0690	0.0694	0.0614	0.0688	0.0680
0.090	0.0506	0.0790	0.0783	0.0685	0.0784	0.0776	0.0718	0.0776	0.0762
0.100	0.0576	0.0890	0.0856	0.0765	0.0874	0.0846	0.0771	0.0852	0.0850

Effect of pH on Metal ion – Biomass Binding

The pH dependency for the adsorption of the three metals under investigation on the thiolated and non-thiolated cassava waste biomass are presented in Table 2. It can be seen from the data that at 0.10 mmol/g metal ion concentration, all the metals binds to the thiolated and non-thiolated biomass in a pH-dependent manner.

At pH 2, increase in cadmium adsorption capacity of the biomass as a function of the level of thiolation was observed. The non-thiolated biomass adsorbed 0.0127 mmol/g cadmium ion in solution, while the 0.50M and 1.00M thiolated adsorbed cadmium ion to the magnitude of 0.0424 mmol/g and 0.0489 mmol/g respectively.

For pH 3, about 0.0143 mmol/g cadmium, 0.0254 mmol/g copper and 0.0410 mmol/g zinc were adsorbed by the non-thiolated biomass. The different level of thiolation increased the adsorption capacities of the biomass for the three metals, each of them binding to a significant amount of metal. At 0.5M

thiolation, biomass bound to 0.0512 mmol/g cadmium, 0.0391 mmol/g copper and 0.0789 mmol/g zinc, while 0.0687 mol/L cadmium, 0.0385 mmol/g copper and 0.0893 mmol/g zinc were sequestered by the biomass at 1.0M thiolation. Thiolated and non-thiolated biomass had similar cadmium adsorption behaviour for cadmium, copper and zinc but different uptake capacities at pH's 4, 5 and 6. In general, for thiolated and non-thiolated biomass, increasing the pH of the solution from 2 – 6, leads to an increase in the amount of metal ions adsorbed by the cassava biomass, with optimum adsorption capacities occurring between 4.0 and 5.0. The overall trend observed in the pH-dependent adsorption behaviour suggests that metal uptake could occur through the ion-exchange mechanistic approach, which further indicates that those metal ions that can be adsorbed by the cassava waste biomass may be desorbed by reducing the pH. This trend was also observed in the alfalfa biomass (Gardea-Torresdey *et al* 1996b).

Table 2. Concentration of Metal ions (mmol/g) bound by each gram of thiolated and non-thiolated cassava waste biomass after equilibration for one hour at different pH using 0.10 mol/L metal ion concentration

pH	0.00M - SH			0.50M - SH			1.00M - SH		
	Cd ²⁺	Cu ²⁺	Zn ²⁺	Cd ²⁺	Cu ²⁺	Zn ²⁺	Cd ²⁺	Cu ²⁺	Zn ²⁺
2.0	0.0127	0.0217	0.0358	0.0424	0.0349	0.0737	0.0489	0.0391	0.0850
3.0	0.0143	0.0254	0.0410	0.0512	0.0391	0.0789	0.0687	0.0385	0.0893
4.0	0.0226	0.0314	0.0601	0.0683	0.0569	0.0890	0.0677	0.0537	0.0893
5.0	0.0576	0.0890	0.0856	0.0765	0.0874	0.0846	0.0771	0.0852	0.0901
6.0	0.0139	0.0339	0.0529	0.0562	0.0338	0.0751	0.0640	0.0345	0.0866

Effect of Contact Time on Metal ion Binding

The data from the time-dependency experiment for the adsorption of the three metal ions to the differentially thiolated biomass of cassava wastes are shown in Table 3. The biomass was shaken with 0.10 mol/L solution of each metal for the time interval of 5, 10, 15, 20, 25, 30 and 90 minutes. The data indicates that the metal adsorption to the biomass is very rapid for all three metals investigated. Although

each metal adsorbed to the biomass at varying degrees, there was no significant difference in the adsorption capacities between the 0.5M and 1.00M thiolated biomass. Optimum adsorption of all the metals were achieved with the first 20 – 30 minutes and remains fairly stable thereafter. The rapid adsorption of the metal ions to the biomass indicates that adsorption may be taking place on the cell wall of the biomass.

Table 3. Concentration of Metal ions (mmol/g) adsorbed by differentially thiolated cassava waste biomass at various time intervals using 0.10 mol/L metal ion concentration

Time (min)	0.00M - SH			0.50M - SH			1.00M - SH		
	Cd ²⁺	Cu ²⁺	Zn ²⁺	Cd ²⁺	Cu ²⁺	Zn ²⁺	Cd ²⁺	Cu ²⁺	Zn ²⁺
5	0.0211	0.0314	0.0484	0.0374	0.0409	0.0721	0.0504	0.0461	0.0849
10	0.0214	0.0329	0.0583	0.0386	0.0442	0.0849	0.0550	0.0508	0.0892
15	0.0266	0.0334	0.0667	0.0451	0.0481	0.0896	0.0804	0.0521	0.0904
20	0.0311	0.0361	0.0679	0.0626	0.0539	0.0924	0.0902	0.0506	0.0906
25	0.0514	0.0398	0.0691	0.0783	0.0513	0.0868	0.0983	0.0633	0.0931
30	0.0556	0.0416	0.0721	0.0899	0.0506	0.0809	0.0883	0.0301	0.0822
90	0.0551	0.0338	0.0633	0.0634	0.0317	0.0833	0.0632	0.0216	0.0816

Desorption Study of the Adsorbed Metal ions

The pH-dependency studies for the adsorption of cadmium, copper and zinc ions to the cassava biomass demonstrates that at lower pH values, metal ions were adsorbed to the biomass, which invariably suggests that the bound metals could be desorbed with by lowering the pH of the solution. Table 4 shows the amount of metal ion that can be desorbed from 0.10 mol/L thiolated biomass by treating it with 0.1M HCl for fifteen minutes. The metal recovery data on Table 4 showed that the amount of cadmium ion desorbed from the biomass varies from 0.0389

mmol/g for non-thiolated biomass and 0.387 mmol/g and 0.0265 mmol/g for 0.50M and 1.00M thiolation respectively. Desorption behaviour for copper and zinc follow similar trend with that of cadmium. This apparent low recovery may be due to the fact that thiolation enhances the binding ability of the biomass by increasing the binding sites and also enable metals to be bound strongly to the biomass. The data indicated non-thiolated biomass desorbed more metal ions than the thiolated biomass leading to a low metal recovery.

Table 4. Concentration of Metal ions (mmol/g) desorbed by thiolated and non-thiolated cassava waste biomass after treating with 0.1M HCl for fifteen minutes using 0.10 mol/L metal ion concentration

	Cd ²⁺	Cu ²⁺	Zn ²⁺
Thiolation condition			
0.00M	0.0389	0.013	0.0535
0.50M	0.0387	0.011	0.0522
0.10M	0.0265	0.011	0.0517

Equilibrium Sorption Studies

In a kinetic study of the adsorption of metal ions on non-thiolated and differentially thiolated cassava waste biomass, the three metal ions Cd²⁺, Cu²⁺ and Zn²⁺ were tested. The adsorption rates of these ions on the cassava waste biomass were very rapid. Figure 1 shows the kinetic adsorption rates of Cd²⁺, Cu²⁺ and Zn²⁺ for non-thiolated and differentially thiolated biomass. Amongst the three level of thiolation, the 1.0M thiolation had the highest adsorption on the biomass for the three metals with more than 80% of the initial Cd²⁺ and Zn²⁺ removed and 45% of Cu²⁺

removed. No significant difference (P < 0.05) in adsorption rates of Cd²⁺ for 0.50M and 1.00M differentially thiolated biomass was observed. Meanwhile, the non-thiolated biomass (0.00M thiolation level) had the lowest adsorption, however, still with more than 50%, 45% and 23% of initial Cd²⁺, Cu²⁺ and Zn²⁺ ion concentrations removed from the solution. The figures further indicated that after 1hr of adsorption the removal rates of these ions by non-thiolated and thiolated biomass slowed due to saturation of binding sites on the biomass.

Table 5. Constants in the Freundlich isotherm

Thiolation condition	Cd ²⁺			Cu ²⁺			Zn ²⁺		
	1/n	log K	r ²	1/n	log K	r ²	1/n	log K	r ²
0.00M	0.632	0.062	0.904	0.762	0.315	0.904	0.885	0.091	0.916
0.50M	0.651	0.104	0.624	1.209	0.357	0.944	1.008	0.152	0.943
0.10M	0.861	0.415	0.686	0.788	0.187	0.974	0.843	0.014	0.974

The adsorption capacities of the non - thiolated and differentially thiolated biomass was further tested by employing the Freundlich adsorption isotherm model. The equation is represented as

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log Ce$$

The constants in the Freundlich isotherms have been determined for the various thiolation conditions of the biomass and are listed in Table 5. The values of 1/n were found to be less than unit except for Cu²⁺ and Zn²⁺ at 0.50M thiolation levels. For those less than unity, significant adsorption took place at low concentration and the increase in the amount with concentration became less significant at higher concentrations. The ultimate adsorption capacity of the biomass can be calculated from the isothermal data by substituting the required equilibrium concentration in the Freundlich equation. Thus for an equilibrium concentration of 10 mol/L, each gram of biomass can remove 6.39, 12.45 and 9.03 mmoles of Cd for non-thiolated, 0.50M thiolated and 1.00M thiolated biomass respectively. The coefficient of

determination, r², for non-thiolated biomass has shown that approximately 90.41% Cd, 90.36% Cu and 91.58% Zn ions adsorption in the biomass can be attributed to the initial metal ion concentrations.

Conclusions: The effect of metal ion concentration on adsorption capacities show that pure activated cellulose adsorbed metal ions from solution, with an increase in adsorptivity of the cellulose with increased thiolation. For the same thiolation level, the three metals studied were adsorbed in the fashion Cd²⁺ > Zn²⁺ > Cu²⁺. The amount of metal adsorbed increased with increase in initial metal ion concentration. The pH profile studies showed that adsorption of the three metals has been shown to be pH dependent, with optimum adsorption occurring between pH 4 and 5. This effect suggests that the adsorption mechanism for the metals investigated may be an ion-exchange type process. Again, the adsorption mechanism for these metals is a stable; rapid process, which implies that adsorption, is taking place on the cell wall surface of the cassava waste biomass. The desorption study to recover the metal

ions from the biomass using a dilute acid demonstrates the potential of recycling the metals. Once the metals are recovered, the cellulosic material, which is biodegradable, will cause no environmental damage and may be utilized as natural soil conditioners or fertilizers. Hence, the dry cassava waste biomass could be used for cleansing the environment and industrial waste effluents from trace metals.

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