Electronic Journal of Biotechnology ISSN: 0717-3458
© 2004 by Pontificia Universidad Católica de Valparaíso -- Chile
Vol.7 No.3, Issue of December 15, 2004
Received April 7, 2004 / Accepted September 21, 2004
RESEARCH ARTICLE

Studies on the effect of pH on the sorption of Pb^{2+} and Cd^{2+} ions from aqueous solutions by *Caladium bicolor* (Wild Cocoyam) biomass

Michael Horsfall Jnr.*
Department of Pure and Industrial Chemistry
University of Port Harcourt
Uniport P.O. Box 402, Choba
Port Harcourt
Nigeria
Tel: 234 803 507 9595
E-mail: horsfalljnr@yahoo.com

Ayebaemi I. Spiff
Department of Pure and Industrial Chemistry
University of Port Harcourt
Uniport P. O. Box 402, Choba
Port Harcourt, Nigeria
Tel: 234 803 507 9595
E-mail: emisipiff@yahoo.com

http://biomol.ciad.mx

Financial support: This project was supported by a research grant from the International Foundation for Science, IFS, Sweden with grant No W-3624-1.

Keywords: adsorption, Cocoyam, heavy metals removal, phytoremediation, water treatment.

Environmental protection requires the use of natural products instead of chemicals to minimize pollution. This investigation studies the use of a non-useful plant material as naturally occurring biosorbents for the removal of cationic pollutants in wastewater. The effect of pH on the sorption of Pb^{2+} and Cd^{2+} ion onto *Caladium bicolor* corm biomass was investigated. The experimental results have been analysed in terms of Langmuir, Freundlich and Flory-Huggins isotherms. The data showed that the maximum pH (pH_{max}) for efficient sorption of Pb^{2+} was 7.0 and for Cd^{2+} 5.0. Evaluation using Langmuir equation gave the monolayer sorption capacity as 88.50 mg/g and 65.50 mg/g at the respective pH_{max} for Pb^{2+} and Cd^{2+}. Surface characterization of acid and base treated *C. bicolor* biomass indicates a physiosorption as the predominant mechanism for the sorption process. The thermodynamic assessment of the metal ion – *Caladium bicolor* biomass system indicates the feasibility and spontaneous nature of the process.

The presence of Pb^{2+} and Cd^{2+} and other heavy metals in the environment has become a major threat to plant, animal and human life due to their bio accumulating tendency and toxicity and therefore must be removed from municipal and and industrial effluents before discharge. Resultantly, it is necessary that there are technologies for controlling the concentrations of these metals in aqueous emissions.

The conventional technologies for effluent treatment are not economically feasible for small-scale industries prevalent in developing economies due to huge capital investment. It is therefore necessary to search for alternative adsorbents, which are low-cost, often naturally occurring products that have good sorbent properties and no value to the people. A range of products has been examined. Few of these include pillared clay (Vinod and Anirudhan, 2001), Sago waste (Quek et al. 1998), Cassava Waste (Abia et al. 2003) banana pith (Low et al. 1995), *Medicago sativa* (Alfalfa) (Gardea-Torresdey, et al. 1998) and Spagnum Moss Peat, (Ho et al. 1995).

The adsorbent used in this study is *Caladium bicolor* (Wild Cocoyam) Biomass. The *C. bicolor* is a tuberous perennial plant with brightly coloured foliage in warm, shady areas. Eating of the corm produces an intense irritation in the throat, which makes the corm inedible. The gainful uses of the corm of this crop will not only bring about the practical exploitation of this inedible abundant natural resource, which is wild and available; but also will encourage local farmers and boost their economies. In addition, the use of the biomass as a biosorbent for trace metals in water and waste effluents will solve environmental problems.

---

*Corresponding author

Table 1. Mean values of proximate composition of the corm of *C. bicolor* (Wild Cocoyam) which has not been treated with acid.

Parameters	Values
Cellulose, %	85.31 ± 0.18
Moisture, %	29.44 ± 0.22
Crude lipid, %	11.90 ± 0.10
Ash, %	10.40 ± 0.15
Crude protein, %	20.43 ± 0.10
Total carbohydrate, %	20.85 ± 0.10
Phytate, mg/g	3.89 ± 0.05
Tannin, mg/g	0.11 ± 0.01
Total oxalate, mg/g	1.49 ± 0.03
Calcium, mg/g	10.21 ± 0.62

The equilibrium distribution of metal ions between the sorbent and the solution is important in determining the maximum sorption capacity. Several isotherm models are available to describe this equilibrium sorption distribution. Three sorption models (the Langmuir, Freundlich and Flory-Huggins) will be used to assess the different isotherms and their ability to correlate experimental data. The Langmuir equation was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surface. The Freundlich model was chosen to estimate the adsorption intensity of the sorbent towards the biomass. The Flory-Huggins model was chosen to estimate the degree of surface coverage characteristic of the biomass. The principal aim of the present work is to investigate the potential use of the biomass of *Caladium bicolor* (Wild Cocoyam) as a novel biosorbent for the sorption of valuable and toxic metal ions from aqueous media.

This paper reports the effect of pH on the ability of the biomass of the corm of *Caladium bicolor* (Wild Cocoyam) to remove Pb^{2+} and Cd^{2+} ions from single metal ion solutions. The effect of varying initial metal ion concentration, initial pH and equilibrium sorption on the potential ability of the *C. bicolor* in removing these two metal ions from solution was investigated.

MATERIALS AND METHODS

Materials

The *Caladium bicolor* (Wild Cocoyam) plant used in this study was harvested in Choba – Port Harcourt, Nigeria, were it grows as a weed in a cassava farm. After harvesting, the corm were washed with deionized water, cut into 5 cm pieces, air-dried and ground using a food processor (Magimix Cuisine System 5000), dried in an oven (GallenKamp, model OV -160, England) to constant weight. The oven-dried material was screened through a 100 µm-mesh Tyler screen to obtain a fine biomass.

Chemical analysis

All reagents used were of analytical grade. The proximate composition of the *C. bicolor* biomass was determined using the Association of Official Analytical Chemist (AOAC) (1990).

To obtain the pure cellulose, the non-cellulose materials in the *C. bicolor* biomass were removed by extracting with an aqueous solution of sodium hydroxide. 250 g fine biomass in triplicate was soaked in one litre of 0.125 mol dm^{-3} NaOH solution and heated at 80ºC for 2 hrs. The mixture obtained was filtered and the residue washed several times with distilled deionized water until all the alkaline soluble components of the biomass were removed. The alkali-cellulose obtained was then treated with 0.2 M H_2SO_4 in a shaker for 6 hrs and finally heated in a water-bath for 1 hr at 80ºC. The cellulose was filtered, washed to free acid,

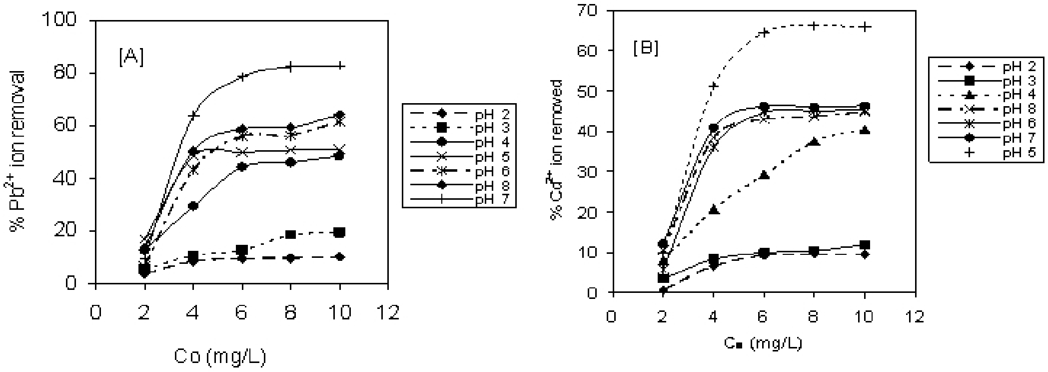

Figure 1. Effect of initial pH (pH_{in}) on Pb^{2+} (A) and Cd^{2+} (B) removal from aqueous solution by *Caladium bicolor* biomass.

Table 2. Surface properties of pure and treated *C. bicolor* using particle size (μm) of 100.

Surface properties	Pure	Acid treated	Base treated
Density, g cm^{-3}	1.63 ± 0.11	1.88 ± 0.14	1.85 ± 0.03
Specific surface area, m^2 g^{-1}	32.91 ± 1.22	45.27 ± 0.96	41.65 ± 1.02
Porosity, %	59.31 ± 1.14	76.44 ± 1.26	68.72 ± 1.16
Pore volume, cm^3 g^{-1}	0.61 ± 0.03	0.54 ± 0.05	0.54 ± 0.03
CEC, meq g^{-1}	25.69 ± 0.58	25.69 ± 0.58	34.79 ± 0.86
SCD, meq m^{-2}	0.78 ± 0.04	0.88 ± 0.03	0.84 ± 0.03

CEC: cation exchange capacity;
SCD: surface charge density.

bleached with sodium hypochlorite and oven-dried at 50ºC to constant weight. The amount of cellulose was determined by gravimetric method.

Thermal drying method was used in the determination of moisture content of the samples. 1.0 g of dried biomass sample was weighed in triplicate and placed in washed, dried and weighed crucible. The crucible was placed in an oven and dried at 105ºC to constant weight. The percentage moisture content (%MC) was computed as follows:

$$\mathrm{MC}\ (\%) = \frac{W_o}{W_i} \times 100 \qquad (1)$$

where W_o = loss in weight (g) on drying and W_i = initial weight of sample (g).

The ash content was determined using the ignition method. The crucibles used were thoroughly washed and pre-heated in a muffle furnace to about 500ºC. 1.0 g of the oven-dried biomass sample used in moisture determination were weighed in triplicate and placed in the pre-heated crucible. The crucible was covered with its lid and placed in a cold muffle furnace. The temperature of the muffle furnace was allowed to rise to 500ºC and the ashing carried on for three hours at this temperature. The crucible was removed and cool in a desiccator and reweighed. The percentage ash content was calculated using the formula:

$$\mathrm{Ash}\ (\%) = \frac{M_a}{M_s} \times 100 \qquad (2)$$

where M_a = Mass of ash (g) and M_s = Mass of sample used (g).

Determination of crude protein was done by first all determining the total organic nitrogen using the macro-Kjeldhal method. One gram of the finely divided biomass was weighed in triplicate and placed in digestion flasks. Few granules of anti-bumps and 3.0 g of copper catalyst mixture (96% anhydrous sodium sulphate, 3.5% copper sulphate and 0.5% selenium dioxide) were added to each of the flasks, followed by the addition of 20 cm^3 concentrated sulphuric acid and heating on a heating mantle. Digestion was continued until a clear solution was obtained. The digest was cooled, filtered and made up to 100 cm^3 with distilled water. 20 cm^3 of the diluted digest was pipetted into round-bottomed flasks containing 30 cm^3 of 40%

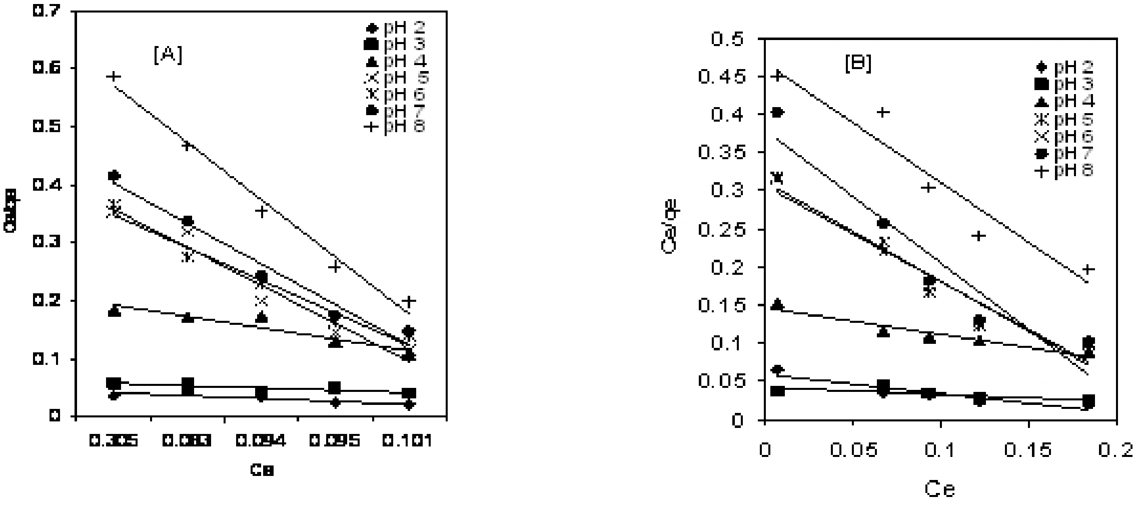

Figure 2. Langmiur isotherms for the sorption pf Pb^{2+} (A) and Cd^{2+} (B) ions on *Caladium bicolor* biomass.

Table 3. Mean equilibrium pH (pH_{fin}) at various initial metal ion concentrations (C_o, mg/L). Values are average of triplicate measurement as indicated in the procedure.

Initial pH	Final pH (pH_{fin})									
	Pb^{2+}					Cd^{2+}				
	2mg/L	4mg/L	6mg/L	8mg/L	10mg/L	2mg/L	4mg/L	6mg/L	8mg/L	10mg/L
2	1.98	1.93	1.94	1.85	1.83	1.94	1.90	1.90	1.87	1.88
3	2.78	2.77	2.75	2.75	2.76	2.63	2.42	2.41	2.38	2.38
4	3.65	3.50	3.48	3.45	3.33	3.52	3.44	3.37	3.30	3.24
5	3.53	3.48	3.45	3.40	3.28	3.75	3.59	3.48	3.36	3.29
6	4.69	4.54	4.54	4.53	4.51	4.91	4.88	4.80	4.78	4.79
7	5.96	5.91	5.91	5.78	5.66	5.91	5.78	5.76	5.65	5.52
8	6.36	6.87	6.75	6.73	6.59	6.94	6.88	6.81	6.79	6.83

sodium hydroxide. The content of the flask was distilled into 20 cm^3 of 2% boric acid with screened methyl red indicator. The distillation was continued until the boric acid solution completely changed from purple to greenish – yellow. The boric acid mixture (containing the ammonium borate complex formed) was then titrated with 0.1 M HCl to colourless end point and the titre noted. The total organic nitrogen (TON) was calculated equation 3.

$$\%\,TON = \frac{TV \times NE \times TV_d}{M_s \times V_d} \times 100 \qquad (3)$$

where TV = Titre value, NE = mg nitrogen equivalent to molarity of acid, TV_d = total volume to which digest was diluted, M_s = mass of sample (g) and V_d = volume of digest distilled.

% crude protein = % TON x 6.25   (4)

(6.25 is a general factor suitable for products in which the proportions of specific proteins are not well defined).

Determination of crude lipid content of the biomass was done using the direct solvent extraction method. The solvent used was petroleum ether (boiling range 40ºC-60ºC). 3.0g of the dried sample was weighed in triplicate and secured in soxhlet extraction thimble. 60 cm^3 of the 40-60ºC boiling range petroleum ether added to the biomass and extracted for four hours. At the end of extraction, the solvent was evaporated and the flask dried in the oven (at 60ºC). The percentage crude lipid (CL) was calculated using the formula:

$$CL\ (\%) = \frac{M_{ex}}{M_s} \times 100 \qquad (5)$$

where M_{ex} = mass of extract (g) and M_s = Mass of sample used (g).

Total carbohydrate content of the biomass was estimated by ‘difference’. In this method, the sum of the percentages of

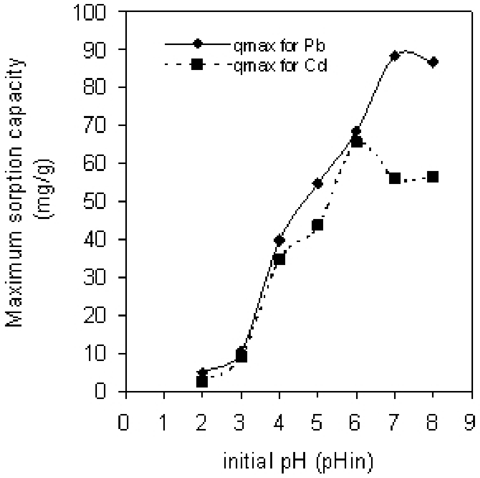

Figure 3. Variation in the Langmuir sorption constaant, q_{max}, with initial pH.

Table 4. Langmuir isotherm parameters.

pH	Pb^{2+}			Cd^{2+}		
	q_{max} (mg/g)	K_L (L/g)	R^2	q_{max} (mg/g)	K_L (L/g)	R^2
2	5.01	0.097	0.760	2.51	0.067	0.849
3	10.40	2.39	0.789	9.0	1.66	0.845
4	39.71	6.32	0.880	34.8	1.96	0.916
5	54.80	8.41	0.955	43.7	2.46	0.921
6	68.50	10.18	0.964	65.5	2.60	0.938
7	88.50	15.62	0.986	56.1	1.51	0.901
8	86.8	14.96	0.970	56.5	1.37	0.923

all the other proximate components was subtracted from 100 *i.e.* total carbohydrate (%) = 100 – (% moisture + % crude protein + % crude lipid + % ash).

The method described by Munro and Bassir (1969) was used for the determination of oxalate in the samples. In this method, 1.0 g of each sample powder were extracted thrice by warming (40ºC-50ºC) and stirring with a magnetic stirrer for 1 hr with 20 cm^3 of 0.3N HCl. The combined extracts were diluted to 100 cm^3 with water and used for the total oxalate estimation.

For oxalate estimation, 5.0 cm^3 of each extract was made alkaline with 1.0 cm^3 of 5.0 N NH_4OH. This was then made acid to phenolphthalein (2 or 3 drops of this indicator added, excess decolourizes solution) by drop wise addition of glacial acetic acid. 1.0 cm^3 of 5% calcium chloride was added and the mixture allowed to stand for 3 hrs and centrifuged at 3000 x g for 15 min. The supernatant was discarded and precipitates washed thrice with hot water with thorough mixing and centrifuging each time. 2.0 cm^3 of 1.5 M H_2SO_4 was added to the precipitate dissolved in a water bath (70ºC-80ºC). The content of each tube was titrated with freshly prepared 0.01 M potassium permanganate solution room temperature (29ºC) until the first pink colour appeared throughout the solution and allowed to stand until the solution was colourless. The solution was then warmed to 70ºC-80ºC and titration continued until a prink colour persisted for 30 seconds. Oxalate content (OC) was estimated as follows:

$$\%\,OC = \frac{W\,100}{5} \qquad (6)$$

where w = mass of oxalate in 100 cm^3 of extract.

Tannin was estimated by the method of Burns (1971). 0.5 g of the finely divided biomass sample was weighed into a conical flask containing 100 cm^3 of distilled water added. The suspension was gently boiled for one hour and then filtered using Whatman No 44 filter paper and the filtrate diluted to the 100 cm^3 mark and then cooled. To develop a greenish-blue colour, 50 cm^3 aliquot of the suspension was placed in a flask, followed by addition of 5 cm^3 Folin – Dennis reagent, 10 cm^3 saturated sodium carbonate solution and then diluted to the 100 cm^3 mark with distilled water and mixed thorough. The flasks were allowed to stand in a water bath at 25ºC for 20 min and the optical density measured at 700 nm. Distilled water was used as blank regarding the calibration curve. Standard tannic acid solution were prepared from which a standard curve was made (absorbance versus concentration in mg/cm^3). From this curve, the concentrations for each sample was obtained

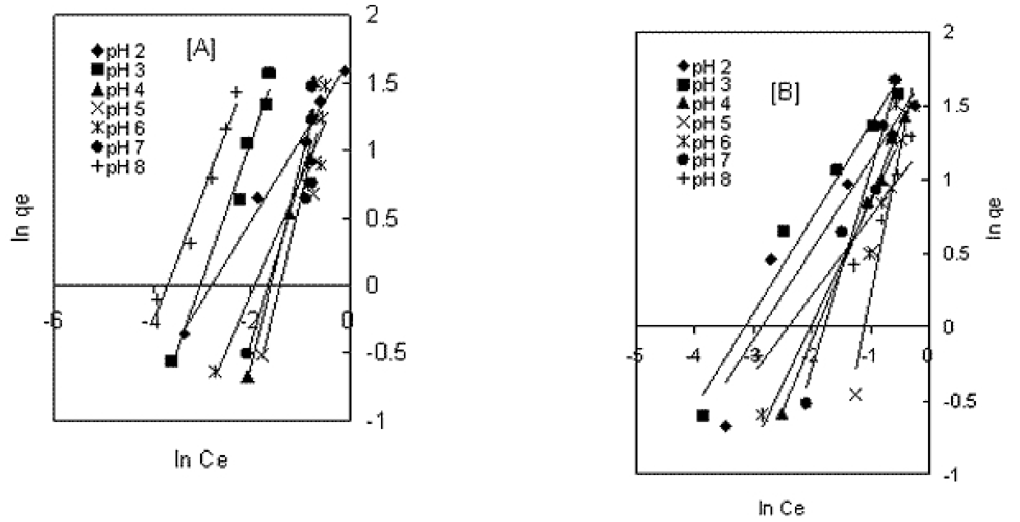

Figure 4. Freundlich isotherms for the sorption of Pb^{2+} (A) and Cd^{2+} (B) ion on *Caladium bilocor* biomass.

and used for the tannin content (TC) calculation.

$$\mathrm{TC}\ (\mathrm{g}/100\mathrm{g}) = \frac{\mathrm{C(mg)} \times V_{ex}}{A \times M_s} \qquad (7)$$

where C (mg) = concentration from standard curve; Vex = extract volume (cm^3), A = aliquot (cm^3) and Ms = mass of sample (mg).

Table 5. The Linear Freundlich isotherm parameters for the Pb^{2+}, and Cd^{2+} onto the biomass.

	Pb^{2+}			Cd^{2+}		
pH	1/n	K_F	R^2	1/n	K_F	R^2
2	1.15	0.04	0.638	1.61	0.51	0.924
3	1.03	0.67	0.908	1.04	0.64	0.971
4	1.09	1.64	0.731	0.97	0.72	0.915
5	0.90	1.70	0.677	0.97	1.60	0.957
6	0.59	1.67	0.971	0.83	0.32	0.905
7	0.56	2.05	0.993	1.06	0.53	0.955
8	0.96	1.83	0.980	1.53	0.72	0.936

Activation of biomass

The surface properties were tested using three media with different pH conditions to activate the biomass. 500 g finely divided biomass was soaked in excess HNO3 solutionof pH 3, NaOH solution of pH 8 and deionized water of pH 7.0 ± 0.01 for 24 hrs. The suspensions were filtered and washed thoroughly until a pH of 7.0 ± 0.01 was attained and then air-dried. The air – dried activated biomass was re-suspended in 1.0 M hydroxylamine to remove all O–acetyl groups and washed with deionized water in order to remove all other soluble materials. The suspension was centrifuged at 3000 x g for five minutes using a Portable Refrigerated test tube centrifuge model PR – 2 with 20" diameter stainless solid basket 3/4HP 1/60/115 volt motor with temperature indicator, timer and speed controls. The supernatants obtained were discarded.

The surface properties of the activated and pure biomasses of the *C. bicolor* pellets were then determined.

Determination of surface properties of biomass

The surface characteristics of the *C. bicolor* biomass samples were determined (Miguel et al. 2001; Horsfall and Abia, 2003) as follows: 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 biomass samples was 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 hr and centrifuged at 2800 x g for 5 min to extract the Na^+ ions. The extracted Na^+ concentration of the solution was determined as the CEC by flame atomic absorption spectroscopy (FASS). The surface charge density (SCD) was evaluated (Horsfall and Abia, 2003) as follows:

$$\mathrm{SCD}\ (\mathrm{meq\ m^{-2}}) = \frac{\mathrm{CEC}\ (\mathrm{meq\ g^{-1}})}{\mathrm{SA}\ (\mathrm{m^2\ g^{-1}})} \qquad (8)$$

where CEC = cation exchange capacity and SA = surface area.

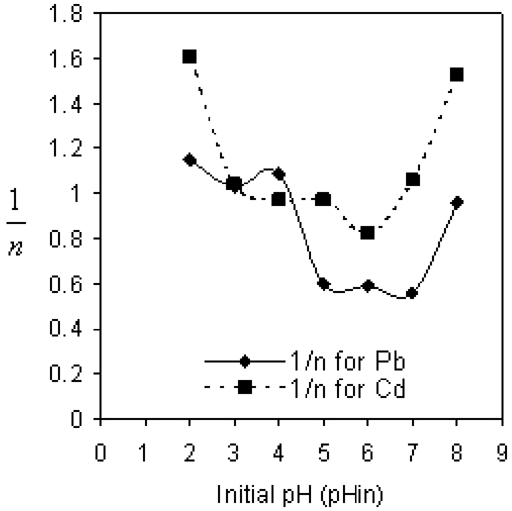

Figure 5. Variation in the Freundlich sorption constant, 1/n, with initial pH.

Determination of Pb^{2+} and Cd^{2+} uptake as a function of pH

1.0 ± 0.01 g *C. bicolor* biomass was weighed into several flasks. Standard solutions of initial metal ion concentrations ranging from 2 to 10 mg/L of Pb^{2+} and Cd^{2+} were prepared from stock solutions of $PbSO_4$ and $Cd(NO_3)_2.4H_2O$ respectively. Fifty millilitres of the metal ion solutions in triplicate were added to the biomass. The pH of these suspensions was adjusted to 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0. The pH adjustments were made either by 2 M HCl or 2 M NaOH solution and the pH recorded as initial pH (pH_{in}). The flasks were tightly stopped and the mixtures gently agitated on a Staurt shaker for 1 hr at 30ºC. At the end of shaking, the pH of the suspension was measured and recorded as the final pH (pH_f) of each solution. The suspension was then filtered through Whatman No 45 filter paper and centrifuged at 2800 x g for five minutes. The

Table 6. Florry-Huggins isotherm parameters for the Cd^{2+} and Pb^{2+} onto the biomass.

pH	Pb^{2+}		Cd^{2+}	
	Ka	ΔG° (KJ mol^{-1} K^{-1})	Ka	ΔG° (KJ mol^{-1} K^{-1})
2	0.732	-0.786	0.467	-0.476
3	0.614	-1.229	0.828	-0.656
4	0.549	-1.511	0.771	-1.390
5	0.548	-1.516	0.583	-1.920
6	0.567	-1.430	0.628	-1.172
7	0.544	-1.534	0.553	-1.493
8	0.553	-1.493	0.651	-1.082

metal content at each pH_f was determined using flame atomic absorption spectroscopy.

Analysis of metal content

The Pb^{2+} content at each pH were determined with a Buck Scientific Flame Atomic Absorption Spectrometer (FAAS) model 300A. Analytical grade standards were used to calibrate the instrument, which was checked periodically throughout the analysis for instrument's response. The batch experiments were performed in triplicates and the averages were computed for each set of values.

DATA EVALUATION

Calculation of Pb^{2+} and Cd^{2+} removed by biomass

The amount of Pb^{2+} and Cd^{2+} sorbet by the biomass during the series of batch investigations were determined using a mass balance equation (Chu and Hashim, 2001) expressed as

$$q_e = \frac{v}{m}(C_o - C_e) \qquad (9)$$

where q_e = metal concentration on the biomass (mg/g biomass) at equilibrium; C_e = metal concentration in solution (mg/dm^3) at equilibrium; C_o = initial metal concentration in solution (mg/ dm^3); ν = volume of initial metal solution used (dm^3); *m* = mass of biomass used (g).

Equilibrium sorption

The sorption data was tested against the Langmuir, Freundlich and Flory-Huggins adsorption isotherm models. The linear form of the Langmuir model as shown below was used.

$$\frac{C_e}{q_e} = \frac{1}{X_m K} + \frac{C_e}{X_m} \qquad (10)$$

where X_m (mg g^{-1}) is the maximum sorption upon complete saturation of the biomass surface and K (dm^3 g^{-1}) is a constant related to the adsorption/desorption energy. The constants were obtained from the slope and intercepts of the plots of C_e/q_e against C_e.

Plotting $\ln C_e$ against $\ln q_e$ using the linear equation below tested the Freundlich model:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (11)$$

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

The Florry-Huggins model is represented by equation 12.

$$\log\frac{\theta}{C} = \log K_a + n\log(1-\theta) \qquad (12)$$

where θ is the degree of surface coverage, n is the number of metal ions occupying sorption sites, K_a is equilibrium constant of adsorption and C is equilibrium metal ion concentrations. A plot of $\log \theta/C$ against $\log(1-\theta)$ yielding a straight line was made to confirm the model.

Statistical analysis

Means and standard deviations were calculated for three independent determinations for each variable except for total carbohydrate, which was simply obtained by difference.

RESULTS AND DISCUSSION

The proximate compositions of the corm of *C. bicolor* based on the chemical analysis are shown in Table 1. The data showed that, the corm of *C. bicolor* (Wild Cocoyam) is a complex material containing mainly organic residues made of several polar functional groups. These groups in biomaterials can be involved in chemical bonding and are responsible for the cation exchange capacity. Exchange sorption between the biomass and the metal ions reaction may be represented in two ways as shown in the following equation:

$$2B^- + Mn^{2+} = Mn(B)_2$$

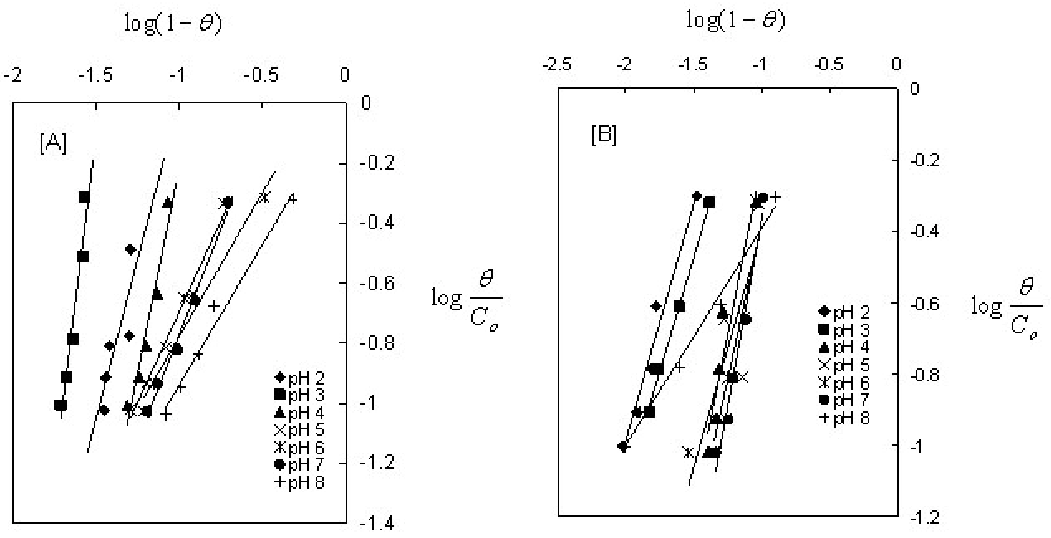

Figure 6. Flory-Huggins isotherm plot for the sorption of Pb^{2+} (A) and Cd^{2+} (B) ions on *Caladium bicolor* biomass.

and

$$2HB + Mn^{2+} = Mn(B)_2 + 2H^+$$

where B^- and B are polar sites on the biomass surface.

Such reactions are highly pH-dependent. According to Gardea-Torresday (1996), pH-dependent binding suggests that metal ions are sorbed by biomass through carboxyl, carbonyl or hydroxyl ligands. The addition of NaOH to raise the pH before equilibration enhanced sorption of metal ions by the biomass, suggesting that metal ion binding was occurring as carboxyl or hydoxyl ligands.

Effect of surface characteristics on metal ion sorption at different pH

The effect of surface characteristics of the sorption of Pb^{2+} and Cd^{2+} ions from aqueous solution was correlated to the pH of the solution, as this affects the surface charge of the adsorbents, the degree of ionization and the species of the adsorbate. The effects of pH treatment on the *C. bicolor* biomass's basic properties were determined to assess the extent of incorporation of surface charges on the biomass matrix and its attendant effect on the sorption of metal ions. The influence of pH treatment on the surface properties of the pure inactivated *C. bicolor* biomass was investigated using three pH treatment conditions. They are pH 7.0, pH 3 and pH 8. The influence on the surface properties was evaluated by measuring the surface area, particle density, porosity, pore volume, cation exchange capacity (CEC) and surface charge density (SCD) (Table 2). The results showed that treatment of the pure biomass with either acid or base presents the biomass with larger surface and enhanced the porosity on the biomass surface. However, the pore volume was observed to decrease when the biomass was treated with either acid or base, indicating that pH treatment enhances the occurrence of physisorption so that cationic reaction may take place on the biomass surface. pH treatment of the biomass increases the cation exchange capacity (CEC) of the biomass. This enhanced CEC indicates improvement of the biomass surface towards the sorption of cationic and anionic species in solution. Furthermore, the surface-charge density, (SCD), which gives an overall intensity of charges on the solid matrix surface was evaluated and was observed to increase with pH treatment. This is an indication of an increase in the number of surface charges as the biomass is being treated with acid or base. Increase in SCD is an indication of enhanced sorption sites as a result of greater surface charges, indicating ion exchange process between the biomass and the metal ion. Investigations (Bernal and Lopez-Real, 1993; Horsfall and Abia, 2003) have shown that ion – exchange mechanism prevails in high SCD materials during the sorption of cationic species on natural and acid modified biomaterials.

The data further showed that acid treated biomass had enhanced surface properties than base treated biomass. This differential behaviour in acidic and basic treatment may be an artefact of the presence of high affinity ligands in the biomass such as cyano and amino groups on the biomass surface. At high pH, metal ion may be forced to bind to low affinity ligands such as hydoxyl and carboxyl groups but at low pH, the binding may occur through high affinity ligands only. This is an indication that the degree of ionization on the biomass surface is pH dependent. Hence, complexation and ion exchange processes are both playing a part in the sorption mechanism.

Effect of pH

The efficiency of metal ion sorption by the biomass is controlled by the initial pH of the reaction mixture. Measurements of the equilibrium pH showed that the reactions that occurred during the sorption process caused slight increases in the pH. Table 3 shows that as the initial metal ion concentration (Co) increases, the resultant equilibrium final pH (pH_{fin}) decreases for all concentrations. The more metal ion added, the greater the effect.

The simple hydrolysis of most divalent metal ions especially Pb^{2+} and Cd^{2+} can be written as follows (Cotton and Wilkinson, 1979)

$$\rightleftarrows M^{2+} (aq) + H_2O (l) \qquad M(OH)^{+} (aq) + H^{+} (aq)$$

where M^{2+} is either Pb^{2+} or Cd^{2+}.

This reaction generates monovalent cations $M(OH)^{+}$ and protons which contribute to the increased acidity of M^{2+} solutions. If M^{2+} is being taken up by the biomass, the reaction above shifts to the left, leading to the depletion of protons and hence a rise in pH. In contrast, if $M(OH)^{+}$ species sorbs onto the biomass, the above reaction naturally shifts to the right and the solution becomes more acidic. The pH_{max} was used to predict the predominant metal ion species taken up by the biomass. The pH_{max} for lead ions was found to be 7.0, indicative that approximately 50% of the overall lead ion content in the system will be in the form $Pb(OH)^{+}$ while the other 50% remains as Pb^{2+}, indicating that the predominant sorbing form will be the two species $Pb(OH)^{+}$ and Pb^{2+} present in solution. This is an indication of quantitative removal of lead ions by *C. bicolor* biomass. It also shows an interaction of lead ions with the biomass by complexation in addition to ion exchange. The pH_{max} for cadmium ion is on the acidic side (pH = 5.0), indicating that the predominant form adsorbing onto the biomass is $Cd(OH)^{+}$ releasing more protons into the solution. It is thought that the presence of a relatively high concentration of hydrogen ions in the medium would influence the exchange of hydrogen ions on the substrate. The observed reduction in the levels of Cd^{2+} ions removed from solution by the biomass indicates that the interaction between the cadmium ion and the biomass is an ion exchange process.

The dependence of sorption of Pb^{2+} and Cd^{2+} onto *C. bicolor* biomass on pH is shown in Figure 1A and 1B respectively. Using 10.0 mg/L initial metal ion concentration, the data revealed that at pH 2, no significant sorption of both metal ions was observed. Only 10.1% of Pb^{2+} and 9.5% of Cd^{2+} were sorbed by the biomass. As pH increased to 3, the sorption of Pb^{2+} and Cd^{2+} also increased to 19.4% and 11.9% respectively. The biomaterial sorbed approximately 48.3% and 40.5% of Pb^{2+} and Cd^{2+} at pH 4. At pH 5, a differential in the metal ion removal was observed. The percent of Cd^{2+} removed was greater than that of Pb^{2+}. While the percent removal for Cd^{2+} increased to 65.9%, that of Pb^{2+} was 50.9% at the 10.0 mg/L initial concentration. Approximately 45% of Cd^{2+} ions were removed by the biomass between pH 6 – 8. The sharpest increase in removal efficiency with pH_{in} was noticed as pH_{in} was raised from 5.00 to 7.00 for Pb^{2+} and 4 - 5 for Cd^{2+}. However, when the pH_{in} of the reaction mixture was raised between 6.00 and 8.00 the efficiency increased only marginally for Cd^{2+}. The optimal binding by *C. bicolor* occurred at pH 7 for Pb^{2+} with 82.9% sorption and pH 5.0 for Cd^{2+} with 65.9% sorption.

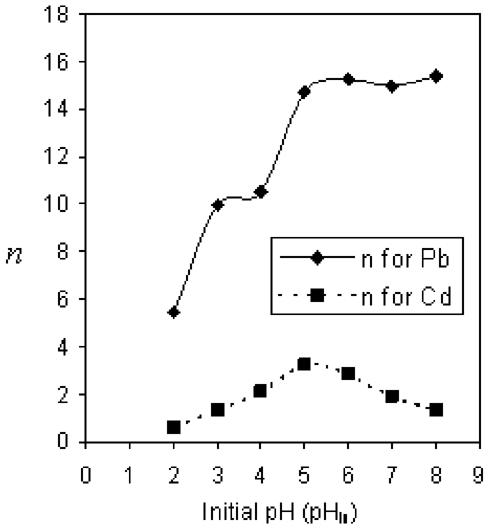

Figure 7. Variation in the Flory-Huggins sorption constant, n, witg initial pH.

This trend in pH-dependence suggests that the removal of both metal ions is favoured by high pH values and lower metal ion concentrations. With low pH, the metal ions bound to *C. bicolor* biomass could be desorbed and the spent biomass regenerated.

The binding behaviour suggests that to some extent carboxyl groups (-COOH) may be responsible for the binding of Pb^{2+} and Cd^{2+}, since the ionization constants for a number of carboxyl groups range between 4 and 5. At lower pHs, the carboxyl groups retain their protons reducing the probability of binding to any positively charged ions. Whereas at higher pHs (above 4.0), the carboxylate ($-COO^{-}$) ligands attract the positively charged Pb^{2+} and Cd^{2+} and binding occurs, indicating that the binding process is an ion-exchange mechanism that involves an electrostatic interaction between the negatively charged groups in the cell walls and the metallic cations. According to Low et al. (1995), at low pH values the surface of the adsorbent, would be closely associated with hydronium ions (H_3O^+) which hinder the access of the metal ions to the surface functional groups. Consequently, the percentage of metal ion removal may decrease at low pH.

Sorption equilibrium

The applicability of sorption processes as a unit operation can be evaluated using isotherm models. The equilibrium sorption data obtained were analysed in terms of the Langmuir, Freundlich and Florry-Huggins equations. Figure 2A and B shows the data linearised to fit the Langmuir equation and Table 4 presents the constants derived by regression analysis for the equation. A comparison of the Langmuir monolayer sorption capacity at various initial pH was made by plotting q_{max} (mg/g) against pH_{in} (Figure 3). The results confirmed that at pH 2 and 3, the sorption of Pb^{2+} and Cd^{2+} on *C. bicolor* biomass was much less than at pH 4 and above, indicating that the *C. bicolor* biomass is a less effective sorbent at lower pH values. Hence, lowering the pH may aid the regeneration and recycling of spent biomass. The R^2 values suggested that the Langmuir isotherm provides a good model of the sorption system. The sorption coefficient, K_L, which is related to the apparent energy of sorption, was greater for Pb^{2+} than for Cd^{2+} at all pH_{in}. The high values of K_L for Pb^{2+} and Cd^{2+} at pH 7 and 5 respectively, indicate that the energy of sorption is more favourable at these pH maxima than other pH values.

The linear Freundlich isotherm plots for the sorption of the two divalent metals (Pb^{2+} and Cd^{2+}) onto the *C. bicolor* biomass are presented in Figure 4A and 4B. Examination of the plot suggests that the Freundlich isotherm is also an appropriate model for the sorption study of Pb^{2+} and Cd^{2+}. Table 5 shows the linear Freundlich sorption isotherm constants and the coefficients of determination (R^2). Values of 1/n for Pb^{2+} and Cd^{2+} were found to be less than unity at initial pH of 5, 6, 7, 8 and 4, 5, 6 respectively, indicating that significant sorption could take place at these initial pH values. Confirmation of the pH_{max} was made by plotting the Freundlich equation parameter, $1/n$, which is a measure of the sorption intensity against pH_{in} (Figure 5). The plot further confirmed that, the pH maxima for the sorption of Pb^{2+} and Cd^{2+} onto *C. bicolor* biomass are 7.0 and 5.0 respectively. Based on the coefficient of determination (R^2) values, the linear form of the Freundlich isotherm appears to produce a reasonable model for the sorption of the two metals, with Pb^{2+} fitting the data better than Cd^{2+}. The K-values suggests that Pb^{2+} has greater sorption tendency towards the *C. bicolor* biomass in neutral solutions. However, for Cd^{2+} the greater affinity towards active groups on the biomaterials was observed at pH 5.0.

To account for the sorption surface behaviour of the metal ions on the *C. bicolor* biomass, the fraction of biomass surface covered by metal ion was also studied at the different pH values using the Flory-Huggins isotherm. The plot of $\log \theta/C$ against $\log(1-\theta)$ was made (Figure 6A and B) and regression lines were obtained. The data shows that, Flory-Huggins adsorption is obeyed at higher pH. The Flory-Huggins model was chosen to estimate the degree of surface coverage on the *C. bicolor* biomass. The number of metal ions occupying sorption sites, n, was plotted against the pH_{in} (Figure 7). The overall coverage process indicate that, increase in initial pH increases the surface coverage on the biomass until the surface is nearly fully covered with a monomolecular layer at pH 5.0 for Cd^{2+} and 7.0 for Pb^{2+}.

Furthermore, the equilibrium constant, K_a, obtained from the Flory-Huggins isotherm was used to compute the apparent Gibbs free energy of change. The apparent Gibbs free energy of sorption, ΔG^o, is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG^o is negative quantity. ΔG^o (KJ mol^{-1} K^{-1}) was evaluated using the following equation:

$$\Delta G^o = -RT \ln K_a \qquad (13)$$

where R is the universal gas constant, 8.314 J/mol K and T is absolute temperature.

The negative values of ΔG^o (Table 6) confirm the feasibility of the process and the spontaneous nature of sorption with high preference at pH values of 7.0 and 5.0 for Pb^{2+} and Cd^{2+} respectively.

In conclusion, the data has shown that, the sorption process of Pb^{2+} and Cd^{2+} ions on to *C. bicolor* biomass is feasible and spontaneous in nature. The metal ions binding capacity of the biomass was shown as a function of initial pH of the aqueous solution. The equilibrium data fitted the Langmuir, Freundlich and the Flory-Huggins isotherms very well. The three models confirmed that maximum sorption capacity onto the biomass occurred at pH 7.0 for Pb^{2+} and pH 5.0 for Cd^{2+}. Thus efficient removal of the two metal ions in an effluent using *C. bicolor* biomass may require pH adjustment between 7.0 and 5.0. The equilibrium sorption of the two metal ions at their pH_{max} was determined from the Langmuir equation and found to be 88.50 mg/g and 65.50 mg/g for Pb^{2+} and Cd^{2+} respectively. The data showed that, *C. bicolor* is a successful biosorbent for treating heavy metal contaminated wastewater and may serve as an alternative adsorbent to conventional means. Hence, not only is *C. bicolor* readily available, it also has the potential for metal removal and recovery from contaminated waters. This process will be environment friendly and convert the non-useful plant into an economic crop for local farmers. It may also provide an affordable technology for small and medium-scale industries. The pH study is particularly important for determining the ligands that may be involved in the reaction for optimization in the design of sorption process units.

REFERENCES

ABIA, A.A.; HORSFALL, M. Jnr. and DIDI, O. The use of chemically modified and unmodified cassava waste for the removal of Cd, Cu and Zn ions from aqueous solution. *Bioresource Technology*, 2003, vol. 90, no. 3, p. 345-348.

ASSOCIATION OF OFFICIAL ANALYTICAL CHEMISTS (AOAC). Official Methods of Analysis, 15th ed., Arlington, VA. 1990, p. 331. ISBN 0-85226-141-1.

BERNAL, M.P. and LOPEZ-REAL, J.M. Natural zeolites and sepiolite as ammonium and ammonia adsorbent materials. *Bioresource Technology*, 1993, vol. 43, no. 1, p. 27-33.

BURNS, R.B. Methods of estimation of tannin in the grain Sorghum. *Journal of Agronomy*, 1971, vol. 63, p. 511.

CHU, K.H. and HASHIM, M.A. Desorption of copper from polyvinyl alcohol-immobilized seaweed biomass. *Acta Biotechnologia*, 2001, vol. 21, no. 4, p. 295-306.

COTTON, F.A. and WILKINSON, G. Advanced inorganic chemistry. *A comprehensive text.* 3rd ed. Wiley Eastern Limited, New Delhi, India. 1979. p. 331-332; p. 504. ISBN 0-85990-704-X.

GARDEA-TORRESDEY, J.L.; GONZALEZ, J.H.; TIEMANN, K.J.; RODRIGUEZ, O. and GAMEZ, G. Phytofiltration of hazardous cadmium, chromium, lead and zinc ions by biomass of *Medicago sativa* (Alfalfa). *Journal of Hazardous Materials*, 1998, vol. 57, no. 1-3, p. 29-39.

GARDEA-TORRESDEY, J.L.; TIEMANN, K.J.; GONZALEZ, J.H.; HENNING, J.A. and TOWNSEND, M.S. Ability of silica-immobilized *Medicago sativa* (alfalfa) to remove copper ions from solution. *Journal of Hazardous Materials*, 1996, vol. 48, no. 1-3, p. 29-39.

HO, Y.S.; JOHN WASE, D.A. and FORSTER, C.F. Batch nickel removal from aqueous solution by Spagnum Moss Peat. *Water Research*, 1995, vol. 29, no. 5, p. 1327-1332.

HORSFALL, M. Jnr and ABIA, A.A. Sorption of Cd(II) and Zn(II) ions from aqueous solutions by cassava waste biomass (*Manihot sculenta* Cranz). *Water Research*, 2003, vol. 37, no. 20, p. 4913-4923.

LOW, K.S., LEE, C.K. and LEO, A.C. Removal of metals from electroplating wastes using banana pith. *Bioresource Technology,* 1995, vol. 51, no. 2-3, p. 227-231.

MIGUEL, G.S.; FOWLER, G.D.; DALL'ORSO, M. and SOLLARS, C.J. Porosity and surface characteristics of activated carbons from waste tyre rubber. *Journal of Chemical Technology and Biotechnology*, 2001, vol. 77, p. 1-8.

MUNRO, A. and BASSIR, O. Oxalate in Nigerian vegetables. *West African Journal of Biology and Applied Chemistry*, 1969, vol. 12, p. 14-18.

QUEK, S.Y.; WASE, D.A.J. and Forster, C.F. The use of Sago waste for the sorption of lead and copper. *Water S.A.*,1998, vol.24, no. 3, p. 251-256.

VINOD, V.P. and ANIRUDHAN, T.S. Sorption of Tanic acid on zirconium pillared clay. *J. Journal of Chemical Technology and Biotechnology*, 2001, vol. 77, p. 92-101.