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Full Length Research Paper

Effect of metal ion concentration on the biosorption of Pb^{2+} and Cd^{2+} by *Caladium bicolor* (wild cocoyam)

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The influence of initial metal ion concentration of the batch sorption of Pb^{2+} and Cd^{2+} onto a low -cost biosorbent was investigated. The experimental results were analysed in terms of Langmuir and Freundlich isotherms. According to the evaluation using Langmuir equation, the monolayer sorption capacity obtained were 49.53 and 65.50 mM/g for Pb^{2+} and Cd^{2+}, respectively The data further showed that, sorption of the two divalent metals onto the biomass increased with increase in initial metal ion concentration until monolayer coverage is attained. The thermodynamic assessment of the metal ion – *Caladium bicolor* biomass system indicates the feasibility and spontaneous nature of the process and Go was evaluated as ranging from –4.55 to –6.63 KJ mol^{-1} and –4.02 to –6.09 KJ mol^{-1} for Pb^{2+} and Cd^{2+} sorption, respectively. The order of magnitude of the G^{o} values indicates an ion-exchange physisorption process.

Keywords: Phytoremediation, cocoyam, adsorption, water treatment, heavy metals removal.

INTRODUCTION

Environmental protection must require the use of natural products instead of chemicals to minimize pollution. Thus, this investigation studies the use of a non-useful plant material as naturally occurring biosorbents for the removal of lead and cadmium ions in aqueous solution. Lead is a toxic element, which is conservative and has cumulative characteristics (Ho et al., 1996). The majority of lead discharged into the environment comes from atmospheric and particulate sources. However, there are a range of industries which generate waste waters containing significant concentrations of lead; for example, the lead-acid battery industry, smelting, printed wiring board manufacture and paper mills. Mine drainage can also give rise to inputs of lead to the aquatic environment. Excessive amounts of lead in the human body can cause hypertension and brain damage. Cadmium is a highly toxic metal that is rather ubiquitous in its distribution in 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, (Kefala et al., 1999) over the years. Large dosage of cadmium in human can result in tubular and glomerula damage and causes proteinura and anaemia.

The presence of Cd^{2+} and Pb^{2+} and other heavy metals in the environment has become a major threat to plant, animal and human life due to their bioaccumulating tendency and toxicity and therefore must be removed from municipal and industrial effluents before discharge. It is therefore necessary that there are technologies for controlling the concentrations of these metals in aqueous discharges/effluents. The conventional technologies, which have been used, ranged from granular activated carbon to reverse osmosis. However, these processes are not economically feasible for small-scale industries prevalent in developing economies due to huge capital investment. As such, it is necessary to search for alternative adsorbents, which are low-cost, often naturally occurring biodegradable products that have good

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adsorbent properties and low value to the inhabitants. A range of products has been examined. 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), peanut skins (Randall et al., 1974), Medicago sativa (Alfalfa) (Gardea- Torresdey et al., 1998) and Spagnum Moss Peat. (Ho et al.,1995), just to mention a few.

The adsorbent used in the present study is *Caladium bicolor* (Wild Cocoyam) biomass. The plant is a tuberous perennial plant with brightly coloured foliage found in warm, shady areas. It grows to a height of 20 cm. The presence of calcium oxalate in the corm produces an intense irritation if eaten, and therefore makes the plant unedible. The gainful use of this crop will not only bring about the practical exploitation of this non-edible abundant natural resource because of their low cost and availability but would also encourage local farmers. In addition, the anticipated use of the biomass from this plant as a biosorbent for trace metals in water and waste effluents will solve environmental problems. The principal aim of the present work is to asses the potential use of the biomass of *C. bicolor* as a novel biosorbent for the sorption of valuable and toxic metal ions from aqueous media.

The purpose of this paper is to report the effect of initial metal ion concentration and thermodynamics on the sorption of Pb^{2+} and Cd^{2+} ions from aqueous effluents by *C. bicolor* biomass.

MATERIALS AND METHODS

Materials

The *C. bicolor* corm used in this study was harvested in Choba – Port Harcourt, Nigeria, were it grows as weed in cassava farms. The corm was washed with deionized water, air- dried, cut into 5 cm pieces and ground using a food processor (Magimix Cuisine System 5000), dried in an oven (GallenKamp, model OV -160, England) at 105^0C for 24 h and then screened through a 100- m 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, followed by washing thoroughly with deionized water until a pH of 7.1 was attained and then air-dried. The air-dried activated biomass was then washed with deionized water and re-suspended in 1.0 M hydroxylamine to remove all O–acetyl groups. To remove all other soluble materials, the biomass was further washed with deionized water and centrifuged at 3000 x g for 5 min 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 and the paste air – dried and grounded to a finely divided powdered biomass.

Batch sorption experiment

The batch experimental procedure to determine the effect of metal ion concentration is described below. An equilibrium contact time of 2 h was used for metal ion-*C . bicolor* biomass. A 10 mg of the biomass samples was 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 Pb^{2+} (from $Pb(NO_3)_2$ and Cd^{2+} (from $Cd(NO_3)_2.4H_2O$). The two sets of metal solutions made separately were adjusted to pH 5.0 with concentrated HCl. 2 mL of each metal solution were added to each tube containing the biomass and equilibrated for 2 h by shaking at 29°C. The supernatants were analyzed for Pb^{2+} and Cd^{2+} using flame atomic absorption spectrometer model 300A.

RESULTS AND DISCUSSION

The percent removal of metal ion by *C. bicolor* biomass was calculated using the equation:

$$\%R = \frac{C_o - C_w}{C_o} x100 \qquad (1)$$

where R is removal and Co and Cw are the initial and equilibrium metal ion concentrations in solution. The maximum adsorption efficiency of the C. bicolor was 96.4 and 92.4% for Pb^{2+} and Cd^{2+}, respectively.

The apparent capacity of the biomass for metal ions was further determined at the different concentrations. The capacity in m mole/g was calculated from the following relationship:

$$Capacity\ (\text{mM/g}) = \frac{\%\ \text{R}}{100}\ \text{x}\ \text{C}_\text{o}\ \ \text{x}\,\frac{\text{v}}{\text{m}} \qquad (2)$$

where, Co = initial concentration of metal ion solution (M), v = volume of metal ion solution used (L), and m = weight of biomass used (g) . The plot of initial metal ion concentration and the capacity of the biomass were then made. Figure 1 clarifies the relation between capacities and metal ion concentrations, which shows that as the metal ion concentration increases, the capacity increases for both metal ions until 5.2 x 10^{-3} M and 6.5 x 10^{-3} M Pb^{2+} and $Cd^{2+,}$ respectively, and it remained nearly constant after this value. The selectivity order for metal ion towards the studied biomass matrices is $Pb^{2+} > Cd^{2+}$.

For a given initial metal ion concentration, the amount of Pb^{2+} ions sorbed by the biomass was greater than the corresponding amount of Cd^{2+} ions. This differential soption of the two ions may be ascribed to the difference in their ionic radii. The ionic radius of Pb^{2+} is 1.20 while that of Cd^{2+} is 0.97 . The smaller the ionic radius, the greater its tendency to hydrolysed leading to reduced sorption. The biomass exhibited adsorption isotherms of mixed type I – type IV, which is a characteristic of the biomass substrate containing both micropores and mesopores (Vinod and Anirudhan, 2001).

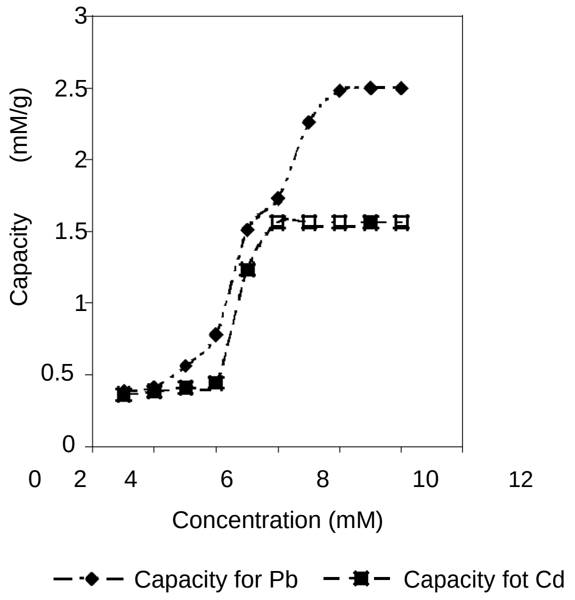

Figure 1. The effect of metal ion concentration on the capacity of Cladium bicolor biomass.

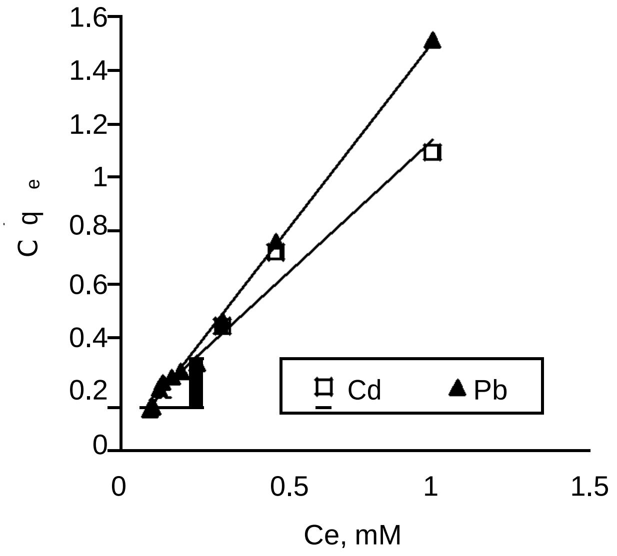

Figure 2. The Langmuir plot.

In general, the data indicates that sorption capacity increased with increase in initial metal ion concentration for both metals on the biomass. This sorption characteristic indicates that surface saturation is dependent on the initial metal ion concentrations. At low concentrations, adsorption sites took up the available metal more quickly. However, at higher concentrations, metals need to diffuse to the biomass surface by intra-particle diffusion and greatly hydrolyzed ions will diffuse at a slower rate.

The maximum metal ion sorption of an adsorbent may be determined from column experiments, by the use of a large excess of the adsorbate. If, however, the metal ions are taken up independently on a single type of binding site in such a way that the uptake of the first metal ion does not affect the sorption of the next ion, then the sorption process would follow the Langmuir adsorption isotherm equation, which was linealized to the form:

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

where X_m and K_L are the Langmuir constants.

Table 1. Langmuir isotherm parameters.

Metal ions	X_m mM g^{-1}	K_L	R^2
Pb^{2+}	49.53	2.09×10^{-3}	0.975
Cd^{2+}	48.20	5.7×10^{-3}	0.995

The capacity of *C. bicolor* biomass in binding with Pb^{2+} and Cd^{2+} was determined by plotting Ce/qe against Ce, using the Langmuir equation. Figure 2 shows the data linearised to fit the Langmuir equation. The plots of specific sorption (Ce/qe) against equilibrium concentration (Ce) gave the linear isotherm parameters of Xm, KL and the coefficient of determination and these are presented in Table 1.

The R^2 values suggested that the Langmuir isotherm provides a good model of the sorption system. The sorption capacity, X_m, which is a measure of the maximum adsorption capacity corresponding to complete monolayer coverage showed that the *C. bicolor* biomass had a slightly higher mass capacity for Pb^{2+} (49.53 mM g^{-1}) than for Cd^{2+} (48.20 mM g^{-1}).

The adsorption coefficient, K_L, which is related to the apparent energy of adsorption for Cd^{2+} (5.7×10^{-3} dm^3 g^{-1}), was greater than that of Pb^{2+} (2.07×10^{-3}) and this could mean that the energy of adsorption is more feavourable for Pb^{2+} than Cd^{2+} . This indicates that not all binding sites may be available for Cd^{2+} binding due to its relatively larger hydration energy.

The shape of the Langmuir isotherm can be used to predict whether a sorption system is favourable or unfavourable in a batch adsorption process (Poots et al., 1978). Accordingly, the essential features of the Langmuir isotherm was expressed in terms of a dimensionless constant called the equilibrium parameter, E_p, which is defined by the following relationship:

$$Ep = = \frac{1}{1+K_L C_0} \qquad (4)$$

Where E_p = is a dimensionless equilibrium parameter or separation factor

K_L = constant from Langmuir equation
C_o = initial metal ion concentration of 10mg/l.

The parameter, *Ep*, indicates the shape of the isotherm and nature of the sorption process as given below:

Values of *Ep*	Type of isotherm
$E_p > 1$	Unfavourable isotherm
$E_p = 1$	Linear isotherm
$E_p = 0$	Irreversible Isotherm
$0 < E_p < 1$	Favourable isotherm

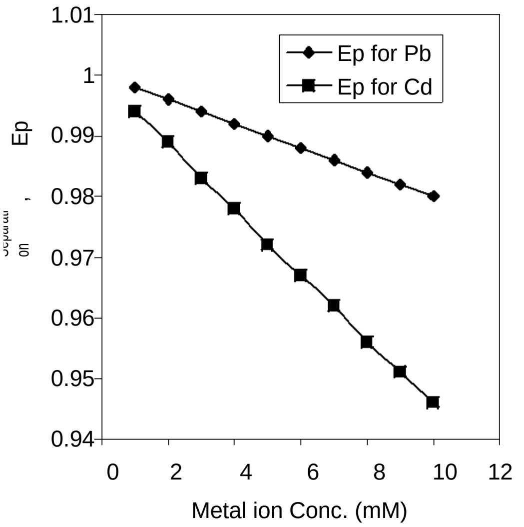

Figure 3. The calculated separation factor profile for the two metal ions as a function of metal ion concentration.

The values of *Ep* for Pb^{2+} and Cd^{2+} were calculated from equation 4 and plotted against initial metal ion concentration. The data (Figure 3) showed that, the sorption of Pb^{2+} and Cd^{2+} on the C. bicolor biomass increased as the initial metal ion concentration increased from 1.0 to 10 mM, indicating that adsorption is even favourable for the higher initial metal ion concentrations. The sorption process was favourable for Pb^{2+} and Cd^{2+} removal at all concentrations investigated. According to this classification, removal ability tends to be in the order Pb > Cd and that the *C. bicolor* biomass is an excellent adsorbent for the two divalent metal ions.

Adsorption-partition constants were determined for Pb^{2+} and Cd^{2+} using the following log form of the Freundlich isotherm:

$$\log N = \frac{1}{n} \log C_e + \log K \qquad (5)$$

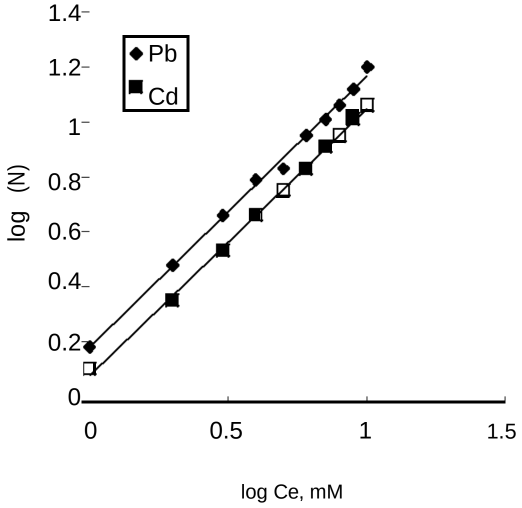

Figure 4. Freudlich isotherm plot.

where N is metal ion sorbed (mM/g), Ce is the equilibrium concentration of metal ion solution, mM, K is a constant and 1/n is a constant. The constants K and 1/n were determined by linear regression from the plot of log N against log Ce (Figure 4). K is a measure of the degree or strength of adsorption, while 1/n is used as an indication of whether adsorption remains constant (at 1/n = 1) or decreases with increasing adsorbate concentrations (with 1/n 1). The Freundlich isotherm data as in Table 2 suggest that the biomass sorbed increasing concentrations of the metal ions as 1/n values approach unity in a linear fashion. However, the small K values for Cd^{2+} indicate minimal sorption while more sorption was observed for Pb^{2+} because of larger K values.

To account for the adsorption behaviour of the metal ions on the *C. bicolor* biomass, the Langmuir type equation related to surface coverage was used. The equation is expressed as follows:

$$\frac{\theta}{1-\theta} = KC \qquad (6)$$

Where K is the adsorption coefficient and is surface coverage.

Table 2. Freudlich isotherm parameters.

Metal ions	1/n	K	R^2
Pb^{2+}	0.973	0.838	0.998
Cd^{2+}	0.990	0.663	0.996

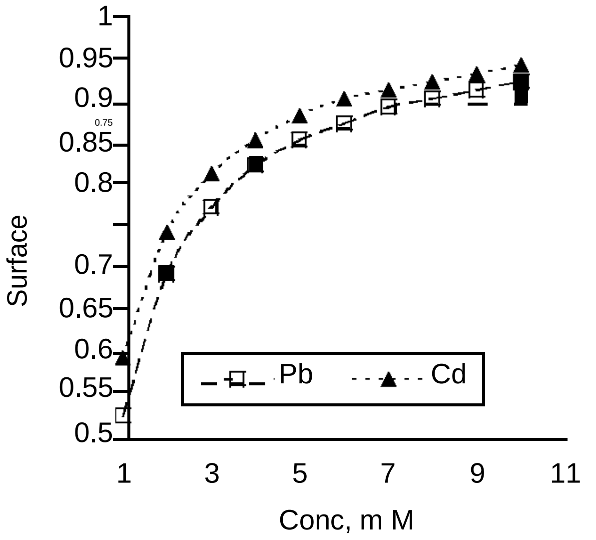

Figure 5. A plot of surface coverage ( ) against concentration (mM).

The fraction of biomass surface covered by metal ion was studied by plotting the surface coverage values ( ) against metal ions concentration. The data is presented in Figure 5. The figure shows that, increase in initial metal ion concentration for both metals increases the surface coverage on the biomass until the surface is nearly fully covered with a monomolecular layer. Further examination of Figure 5 reveals that the surface coverage ceases to vary significantly with concentration of metal ion at high concentrations and the reaction rate becomes independent of the metal ion concentration. The overall adsorption process indicate that, the reaction is first order at lower metal ion concentration and zero order at higher concentration, indicative that the biomass will be highly effective in removing trace amounts of Pb^{2+} and Cd^{2+} ion in aqueous effluent.

Since the displacement of water molecules from aquo ion is the crux in adsorption dynamics, the stability of aquo ion is very essential in the adsorption process. The aquo complex is in the form $[M(H2O)x]n^{+}$; its stability can be estimated from the hydration energy of the metal ion and found to be dependent on the size of metal ion.

Again, the surface of the biomass in aqueous media is considered to be covered with water dipoles. Therefore, for adsorption to occur, these water dipoles must be replaced by metal ions in a reaction of the type:

$$Mn^{+}{}_{sol} + nH_2O_{ads} \rightleftarrows nH_2O_{sol} + M_{ads}$$

Table 3. Distribution ratios, D, and apparent Gibbs free energy $\Delta G_{ads}{}^{o}$, (KJ mol-1) of the metal ions between the *C. bicolor* biomass and aqueous phase.

C_o (mM)	Pb^{2+}		Cd^{2+}	
	D	$\Delta G_{ads}{}^{o}$	D	$\Delta G_{ads}{}^{o}$
1.0	0.53	-6.10	0.45	-6.09
2.0	0.53	-5.16	0.48	-4.66
3.0	0.57	-4.55	0.52	-4.044
4.0	0.68	-5.01	0.63	-4.56
5.0	0.69	-5.57	0.64	-4.01
6.0	0.80	-5.58	0.72	-4.47
7.0	0.85	-6.07	0.74	-4.34
8.0	0.87	-6.15	0.76	-4.28
9.0	0.90	-6.60	0.80	-4.57
10.0	0.91	-6.63	0.89	-6.07

The relativeness of the biomass in removing the metal ions from aqueous solution was again evaluated in terms of the distribution coefficient, D, which can be defined as the ratio of the metal ion concentration in the adsorbent phase, Mads to the concentration in the aqueous phase, Mn+sol. Table 3 shows the value of D for a range of metal ion concentrations. The results show that the concentration of metal ions at the sorbent-water interface is higher than the concentration in the continuous aqueous phase. This suggests that the biomass is effective in the removal of metal ions from aqueous systems. The nature of the sorbed species may be deduced from the fact that the metal ions are divalent. This indicates that two (2) molecules of biomass were associated with metals. Hence the composition of the sorbed complex and the probable mechanism may be given as follows:

$$M^{2+} + 2B - OH = M\,(BO\,-)_2 + 2H^{+}$$

The sorption occurs by an ion-exchange mechanism.

The thermodynamics of the exchange process depends on the number of water molecules (n) replaced by the metal ions. Since the most probable value of n is 2, the apparent Gibbs free energy of the adsorption processes (G^o_{ads}) corresponding to Pb^{2+} and Cd^{2+} ion on the biomass are evaluated using the Bockris – Swinkel's adsorption isotherm equation as reported by Rudresh and Mayanna (1977) with n = 2 and – values. The equation is expressed as:

$$G^{o}_{ads} = -2.303RT \log \frac{55.4\theta}{C_o(1-\theta)} x \frac{\theta + n(1-\theta)^{n-1}}{n^{n}} \qquad (7)$$

where C_o is the initial concentration of Cd^{2+} ion in the solution. The values of G^o_{ads} were then evaluated with n = 2 at various initial metal ion concentrations. The data are presented in Table 3.

The negative values of G^o indicate the spontaneous adsorption nature of Cd^{2+} ion by the *C. bicolor* adsorbents and suggest strong adsorption of Cd^{2+} ions on the biomass surface. In general, it is of note that up to –20 KJ mol^{-1} are consistent with electrostatic interaction between charged molecules and surface indicative of physisorption while more negative than –40 KJ mol^{-1} involve chemisorption. The order of magnitude of the values indicates a physical mechanism for the adsorption of metal ions on to the *C. bicolor* biomass.

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