

Recovery of lead and cadmium ions from metal-loaded biomass of wild cocoyam (*Caladium bicolor*) using acidic, basic and neutral eluent solutions

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The effects of acidic, basic and neutral reagents on the recovery of Pb^{2+} and Cd^{2+} from metal-loaded biomass of wild cocoyam (*C. bicolor*) were investigated by eluting the biomass in five successive cycles using 0.01 M HCl, 0.1 M HCl, 0.01 M NaOH, 0.1 M NaOH and distilled water at different contact times. The data showed that the ease of metal ion recovery from metal -loaded biomass by the eluent solutions is of the order 0.01 M HCl > 0.1 M HCl > 0.01 M NaOH > 0.1 M NaOH > distilled water. Over 94% Pb^{2+} and 74% Cd^{2+} of the initially adsorbed metals were recovered by 0.01 M HCl, while < 20% of both metals was recovered by basic reagent. Distilled water recovered less than 9% of both metal ions from the biomass. Macroscopic changes were also observed as the concentration of recovery reagent increased. This study has demonstrated that the selection of a recovery reagent for metal ions on a biomaterial should give consideration to the reusability of the biomass.

Metal ion recovery studies from spent biomass are an important aspect of the waste management and

environmental remediation goals. These studies may help to elucidate the nature of recovery of metal ions from wastewater and the recycling of adsorbent. The possibility of regeneration of spent biosorbent is crucially important to keeping the process costs of remediation down and to opening the possibility of recovering the metal(s) extracted from the liquid phase. The deposited metals are washed out (recovered) and biosorbent regenerated for another cycle of application. The recovery process should result in (1) -high-concentration metal effluent; (2) -undiminished metal uptake upon re-use; (3) -no biosorbent physico-chemical damage. The recovery of metal ions and sorbent regeneration studies might require somewhat different methodologies. Screening for the most effective regenerating solution is the beginning. Different affinities of metal ions for the biosorbent result in certain degree of metal selectivity on the uptake. Similarly, selectivity may be achieved upon the elution-recovery operation which may serve as another means of eventually separating metals from one another if desirable.

A number of studies have demonstrated the feasibility of

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Table 1. Surface properties of pure *C. bicolor* biomass using particle size (μm) of 100.

Surface properties	Amount
Bulk density, g cm^{-3}	1.63 ± 0.11
Specific surface area, $\text{m}^2 \text{g}^{-1}$	32.91 ± 1.22
Porosity, %	59.31 ± 1.14
Pore volume, $\text{cm}^3 \text{g}^{-1}$	0.61 ± 0.03
Cation exchange capacity, meq g^{-1}	25.69 ± 0.58
Surface charge density, meq m^{-2}	0.78 ± 0.04

using plant biomass to remove heavy metal ions from aqueous solutions (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) just to mention a few. Each of these studies have also mentioned the importance of recovery of metal ions from the biomass and eventual regeneration of the spent biomass. However, very little has appeared in the literature as a major study on the recovery of adsorbed metals from the biomass (Gardea-Torresdey et al. 1998; Zhou et al. 1998; Chu and Hashim, 2001). *C. bicolor* biomass has been used as an effective adsorbent for metal ions from aqueous solution (Horsfall and Spiff, 2004a; Horsfall and Spiff, 2004b; Horsfall and Spiff, 2005a; Horsfall and Spiff, 2005b). However, most biomass in its native form may not be suitable for process applications as they may disintegrate under the harsh conditions of wastewater processing, especially in cases where the biomass is exposed to a stronger reagent to recover the adsorbed metal ions and regenerate the biomass for reuse. It is because of this reason we have used several desorption reagent with different strength in order to assess the reusability of the biomass after recovery. The purpose of this study is therefore to examine the effect of acidic, basic and neutral eluents in the recovery of Pb^{2+} and Cd^{2+} from biomass of wild cocoyam (*C. bicolor*).

MATERIALS AND METHODS

Materials

Biomass preparation and surface characterization. *C. bicolor* (wild cocoyam) biomass was used in this study. The preparation and estimation of the surface characteristics of the biomass has been reported elsewhere (Horsfall and Spiff, 2004a; Horsfall and Spiff, 2004b; Horsfall and Spiff, 2005a; Horsfall and Spiff, 2005b), which are outlined below. Before the batch adsorption experiment, the wild cocoyam corms were washed with deionised water, cut into small pieces, air-dried for two days in the laboratory temperature and then dried in an oven (Gallen Kamp, model OV-160, England) at 105°C to constant weight. The oven dried materials were grounded and screened through $100 \mu\text{m}$ Tyler screen sieve to obtain a finely divided biomass. The biomass was activated by soaking in excess 0.3 M HNO_3 for 24 hrs. This was followed by washing the activated biomass thoroughly with deionised water until a

pH of 7.1 ± 0.1 was attained and then dried in the air. The air dried activated biomass was further dried in the oven at 45°C with occasional mixing to constant weight. The activation process removes any debris or soluble biomolecules that might interact with metal ions, and also all biogenic metal ions in the biomass. The activated biomass samples were characterized in terms of bulk density, surface area, porosity, pore volume, cation exchange capacity, and surface charge density. The procedures for characterizing these parameters have been previously described and reported elsewhere (Horsfall and Spiff, 2004a). The surface properties of the pure wild cocoyam biomass are presented in Table 1.

FTIR characterization of biomass. The finely divided biomass was analyzed to determine their functional groups using a Fourier Transform Infrared Spectroscopy (Shimadzu IR Prestige - 21, FTIR - 84005) using KBr as the rock salt. The finely divided solid biomass was mixed with a disc using a hydraulic press and mould. The mixture on the disc was inserted in the path of the IR beam and held in position.

Methods

Batch adsorption experiment. Batch experiments were first conducted to load the *Caladium bicolor* biomass with metal ions separately. In this experiment 500 mg of the biomass samples with particle size $100 \mu\text{m}$ was weighed and placed in pre-cleaned test tubes in triplicates. An initial metal ion concentration of 100 mg/L were made from spectroscopic grade standards of Pb^{2+} obtained from $\text{Pb}(\text{NO}_3)_2$ and Cd^{2+} obtained from $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. The two metal solutions made separately were adjusted to pH 5.0 with concentrated HCl solution. Fifty millilitres of each metal solution were added to each tube containing the biomass and equilibrated for 2 hrs by shaking at 29°C . The biomass suspensions were centrifuged for five minutes at $3000 \times g$, gently washed with deionised water to remove unabsorbed metal ions and centrifuged again. The levels of Pb^{2+} and Cd^{2+} were analysed by digesting some portion of the biomass using HNO_3 and HClO_4 and the metals content measured by Flame Atomic Absorption Spectrometry (FAAS) Varian-Techron AA-6, and found to be 49.53 mg/g and 48.20 mg/g respectively.

Batch recovery experiment. 250 mg of metal-laden *C. bicolor* biomass were placed in several flasks containing 50

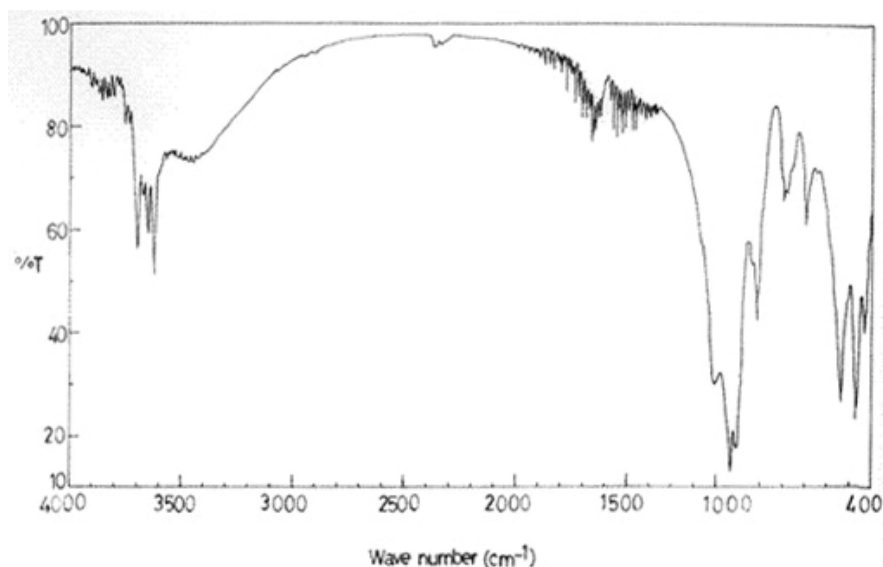


Figure 1. FTIR Spectra of the biomass sample.

mL of 0.01 M HCl, 0.1 M HCl, 0.01 M NaOH, 0.1 M NaOH or pure water. The flasks were shaken for 20, 40, 60, 80, 100, 120 and 140 min at 29°C and agitated on a mechanical shaker at 150 rpm. At the end of each contact time the suspensions were centrifuged at 2500 x g for 5 min. For each fixed time interval, five cycles of recovery equilibrium experiments were conducted to assess the reusability of the biomass. The solutions from the five cycles were combined and evaporated gently to decrease the final volume to 10 mL and digested using 1.0 M HNO₃ and made up to 50 mL. The metal content (Pb²⁺ and Cd²⁺) in the digest were measured in triplicates by FAAS.

Data evaluation

The amounts of metal ion remaining on the biomass as a function of time (q_t) were estimated after determining the amount of metal ion in the recovery reagents and subtracting from the initial amount of metal ion on the biomass (q_e) by using a mass balance equation (Equation 1):

$$q_t = q_e - \frac{v}{m} C_t \quad [1]$$

where q_t is the actual metal ion concentration recovered from the biomass (mg/g) and C_t is concentration of metal ion remaining in solution after recovery (mg/L) at time t (min), respectively, m is mass of biomass used (g) and v is the volume of eluent solution used (mL).

RESULTS AND DISCUSSION

Biomass characterization

The surface area was determined to be 32.91 ± 1.22 (m² g⁻¹), while the bulk density, porosity and pore volume were

1.63 ± 0.11 (g cm⁻³), 59.31 ± 1.14 (%) and 0.61 ± 0.03 (cm³ g⁻¹) respectively. Furthermore, the cation exchange capacity (25.69 ± 0.58 ; meq g⁻¹) and surface charge density (0.78 ± 0.04 ; meq m⁻²) were also determined. The FTIR spectra of the investigated *C. bicolor* biomass are shown in Figure 1. Inspection of these spectra reveals the presence of the following peaks at wave no. 3400 cm⁻¹ representing - OH stretching frequency; several peaks at wave no 1650 cm⁻¹ and 1050 cm⁻¹ representing - C = N of amides and C - O of alcohol, and peak at 1709 cm⁻¹ for C = O group of ketones. The peak at 2300 cm⁻¹ represents a C - H saturated hydrocarbon of chain. On the overall the spectra indicated the presence of hydroxyl, carboxyl, amide and possibly carbonyl group.

The applicability of plant biomass for metal ion recovery from waste stream requires that the biomass be regenerated efficiently so that the bound metal can be recovered in concentrated form and the biomass reused. The data as presented in Figure 2 gives the percent recovery of Pb²⁺ and Cd²⁺ as a function of time. It is apparent from the figure that recovery in the acidic media was quite rapid with equilibrium recovery achieved within the first 15 - 25 min of contact time. It is also noticeable from the figure that increased contact time does not significantly increase recovery after 25 min. From the metal-laden biomass, over 90% and 75% of Pb²⁺ sorbed were recovered by acidic media concentrations of 0.01 M HCl and 0.1 M HCl respectively, while the amount of Cd²⁺ recovered at the same acidic media concentrations were 80.52 and 78.15% respectively. In the case of recovery in basic media, a rapid phase of recovery was observed followed by a relatively slow phase before apparent recovery equilibrium was reached. The fast region occurred during the first 20 min of contact time. However, at the end of the 20 min recovery, only about 12.11% (Pb²⁺); 23.44% (Cd²⁺) and 13.64%

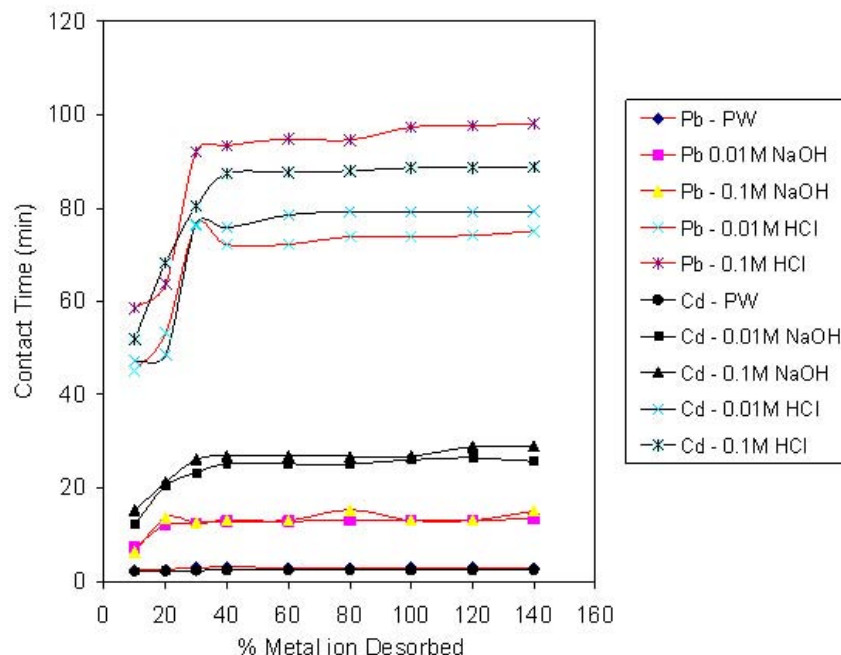


Figure 2. Effect of acidic, basic and neutral media on the recovery of Pb^{2+} and Cd^{2+} from *Caladium bicolor* biomass.

(Pb^{2+}); 26.13% (Cd^{2+}) were recovered from the metal-laden biomass in the basic media with concentrations of 0.01 M NaOH and 0.1 M NaOH respectively. A poor recovery was also observed for distilled water in which less than 3% of sorbet Pb^{2+} and Cd^{2+} were recovered from the metal-laden biomass. The highest metal recovery from the metal-laden *C. bicolor* biomass was observed in acidic media. This is because in acidic medium the carboxyl, carbonyl or hydroxyl groups in the biomass become protonated and does not attract the positively charged metal ions and therefore releases the metal ions into recovery solution. Again, in acidic medium, the protons in solution replaces the metal ions on the biomass surface, while the apparent poor recovery of less than 20% observed in basic media such as NaOH, may be due to the coordinating ligands being deprotonated, hence bound-metal ions finds it difficult to be detached from the biomass. A control experiment using distilled water at pH 7.0 demonstrated negligible metal recoveries within the entire contact time tested in this study. The data in this investigation revealed that, on a comparative basis, recovery of bound metal ion from the biomass is greater for Pb^{2+} than Cd^{2+} in all the recovery media investigated. This observation may be as a result of the stronger Cd^{2+} - biomass bond as a result of smaller ionic radius. It has been severally observed (Okimen et al. 1987; Ho et al. 1995; Horsfall and Spiff, 2004a; Horsfall and Spiff, 2004b; Horsfall and Spiff, 2005a; Horsfall and Spiff, 2005b) that, the smaller the ionic radius the greater the tendency of such metal ions to stick to binding sites. The ionic radii of Pb^{2+} and Cd^{2+} are 1.20 Å and 0.97 Å, respectively. The larger ionic radius of Pb^{2+} may have resulted in steric hindrance on the binding

surfaces and subsequently releases greater amount into recovery media upon slight agitation. Again several functional groups on the surface of a biomass are capable of interacting with heavy metal ions (Ho et al. 1995). These groups also found in *C. bicolor* exhibits different binding affinities for metal ions. The binding of Cd^{2+} to high affinity sites due to its small ionic size may be the principal factor responsible for the observed fractions of Cd^{2+} that it's recovery was less than that of Pb^{2+} .

Although complete desorptions were not achieved, it is clear from the results that the HCl acidic media is a better eluent than the NaOH basic media. This is because acidic media contain high concentrations of protons present in the recovery reagent which may displace bound metal ion from the active sites on the biomass than hydroxonium ions. Macroscopic observations indicate that the initial biomass weight and colour changed in the acid and basic media with these changes increasing with increase in eluent concentration. Although distilled water is ineffective in recovering the metal ions on the biomass, it leaves the biomass for several recyclability. Generally, the influence of the recovery media tested for the recovery of Pb^{2+} and Cd^{2+} from the biomass is of the order 0.01 M HCl > 0.1 M HCl >> 0.01 M NaOH > 0.1 M NaOH >> distilled water.

CONCLUDING REMARKS

The recovery with dilute hydrochloric acid solution was found to be better option in all the reagents tested because it leaves the biomass for further reuse. Since a single cycle of adsorption-desorption equilibrium studies is not enough to sufficiently access the recovery capacity of an effluent,

hence, five cycles was tested. The results of the investigation are quite useful for metal ion recovery eluent selection using batch or stirred flow reactors. Additional research is on-going to elucidate the recovery efficiency of this and other adsorbent with respect to volume of eluent, biomass reloading efficiency and biomass regeneration/recycling.

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