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Full Length Research Paper

Removal of Cu (II) and Zn (II) ions from wastewater by cassava (*Manihot esculenta* Cranz) waste biomass

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The ability of cassava waste biomass (untreated and acid treated) to remove heavy metals (Cu(II) and Zn(II)) from single-ion solution and wastewater was investigated. All experiments were conducted using 10mM solutions of mixed metal ions of $CuSO_4.5H_2O$ and $ZnCl_2$. The uptake capacities of the two metal ions tested on the untreated and acid treated cassava waste biomass were 71.3 and 85.2 mg/g for Cu(II), and 43.4 and 58.1 mg/g for Zn(II) in single-ion solution. For wastewater, the uptake capacities of untreated and acid treated biomass was found to be 40.1 and 59.7 mg/g for Cu(II), and 38.6 and 38.7 mg/g for Zn(II), respectively. Metal ion uptake capacities in wastewater were lower than in single-ion solution probably due to competition of metal ions of different sizes on available binding sites. Uptake capacities of these metal ions on the biomass surface increased with acid treatment. Equilibrium sorption studies showed that the extent of metal uptake was enhanced by chemically modifying the cassava waste biomass by thiolation. Cassava waste biomass saturated with metal ions shows remarkable ability for metal recovery by dilute acid treatment, and can be used repeatedly for removal of heavy metals in single-ion solution and in wastewater effluents.

Key words: Wastewater, bioremediation, heavy metals, biosorption, cassava waste.

INTRODUCTION

Removal of heavy metals from industrial wastewater is of primary importance. This is because contamination of wastewater by heavy metals is a very serious environmental problem. Disposal of agricultural byproducts such as cassava wastes from processing activities is becoming a concern in Nigeria due to its foul dour. Contamination of water by heavy metals is another serious ongoing problem because of indiscriminate discharges of wastewater containing heavy metals by small and medium-scale industries. These industries do not have the financial ability to invest on conventional wastewater treatment method, since such techniques are quite expensive; hence they tend to discharge their effluents in a non-environment friendly manner.

Some of the conventional techniques for removal of metals from industrial wastewater include precipitation, ion exchange, and electrolytic techniques, to mention a few (Blanco et al., 1999). Of recent, the use of non-living biomaterials as metal-binding compounds has been gaining advantage because high levels of contamination do not affect them. 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; Gardea-Torresdey et al., 1996). The unique ability of

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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 such as cassava have also been used as cheap materials capable of removing metals from their solutions (Abia et al., 2002). More recently, low-value cassava waste biomass has been used effectively for removal of Cd(II), Cu(II) and Zn(II) ions from single-metal ion aqueous solutions (Abia et al., 2003). Conversion of these low-value cassava wastes into biosorbent that can remove toxic and valuable metals from industrial wastewater would increase their market value and ultimately benefit the millions of cassava starch, garri and foofoo producers. Cassava peeling wastes were selected for this study for their relative abundance and availability all season. Cassava is a major staple food in Nigeria and therefore produces large volumes of wastes, which has been creating environmental nuisance in the region. In the present investigation, untreated and acid treated cassava peelings wastes were examined in an attempt to remove Cu(II) and Zn(II) in synthetic wastewater system.

MATERIALS AND METHOD

Cassava

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^{o}C to constant weight. The dried samples were ground using a Wiley Mill and sieved to obtain a particle size of 100 µm and stored in a desiccator.

Activation of the cassava waste biomass

Soaking 500 g cassava waste biomass in excess 0.3 M HNO_3 for 24 h, followed by washing with distilled deionized water until a pH of 7.1 is obtained, activated the cellulose biomass. The paste obtained was filtered and air-dried.

Acid treatment of activated cassava waste biomass

The air-dried activated biomass was divided into two equal portions. The first portion was left untreated. The other portion was acid treated as follows: 25 g activated biomass was mixed with 250 ml of 1.00 M concentration of thioglycollic acid solution and mechanically stirred for 6 h at 30^{o}C while maintaining a pH of 7.1. The mixture was allowed to settle overnight and then centrifuged at 2500 X g for 10 min. The supernatant discarded and the paste air-dried.

Determination of the Degree of Acid Treatment

The thiol content of the acid treated biomass was further determined by reacting 0.5 g with 20 mL of iodine solution at pH 7.2 ± 0.2, followed by back titration of the unreacted iodine with standard thiosulphate solution. The degree of acid treatment was calculated and the thiol content obtained as 3.74%.

Preparation of Synthetic Wastewater

Individual metal ion solutions of 10mM metal ion concentration of Cu^{2+} (from $CuSO_4$) and Zn^{2+} (from $ZnCl_2$) from HPLC – analytical grade standards of these metal ions were prepared. The synthetic wastewater solution was then prepared by taking 250 mL of the separate metal ion solutions and mixed in a 1 L volumetric flask and diluted to the mark. The pH of the wastewater was adjusted to 5 to prevent hydrolysis. The final concentration of metal ion in the wastewater was analyzed by atomic absorption spectrometer (AAS). For the quality control purpose, distilled deionized water used in preparing the solutions was digested and analyzed with every sample group to track any possible contamination source.

Metal ion uptake study in wastewater

The biomass was wet with 100 mL 0.01 M HCl to obtain a biomass concentration of 5mg/mL. The metal ion uptake was studied by adding 100 mL of mixed metal ion solution at pH 4.5 containing equal concentrations of Cu(II) and Zn(II) into 5 g wet untreated and acid treated cassava waste biomass. The suspension was mechanically shaken at room temperature for 1 h. The content of the flask was centrifuged at 28000 X g for 5 min and the supernatants collected. The spent biomass was then air dried in readiness for desorption study. The metal content in all the experiment was determined by a Buck Scientific Flame Atomic Absorption Spectrometer (FAAS) model 200A

Calculation of Cu(II) and Zn(II) uptake by biomass

The amount of metal ion uptake by the untreated and acid treated cassava waste biomass during the series of batch investigations were determined using a mass balance equation (Chu and Hashim, 2001) expressed as:

$$q_e = \frac{V}{m}\left(C_o - C_e\right)$$

where

q_e = metal ion uptake capacity(mg/g biomass) at equilibrium C_e
= metal ion concentration in solution (mg/L) at equilibrium C_o =
initial metal ion concentration in solution (mg/L)
v = volume of initial metal ion solution used (L)
m = dry weight of biomass used (g)

Desorption study of Cu(II) and Zn(II) at pH 5.0

2.50 g of dry untreated and acid treated cassava waste biomass used for metal ion uptake study was subsequently placed in 20 mL distilled deionized waster and then poured as a slurry into a chromatographic column. The flow rate was 1 mL/min, the column height 15 cm, the column volume 30 mL and the temperature 30^{o}C. The metal concentration was 2.5 mM of each [Cu(II) and Zn(II)] ions, pH 4.5. The column was washed with distilled deionized water and desorbed with 0.1 M solution of H_2SO_4. The desorption was repeated five times.

Analysis of metal content

The metal content in the entire single-metal-ion and the synthetic wastewater solutions were determined by a Buck Scientific Flame Atomic Absorption Spectrometer (FAAS) model 200A. The following analytical wavelengths were used for the metals studied: copper 327.4 nm and zinc 213.9 nm. 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.

RESULTS AND DISCUSSION

Previous screening experiments has been performed in order to determine how long the cassava waste biomass would bind to metal ions at optimal pH and a contact time of 1 h was observed to be sufficient for optimal and reproducible biosorption (Abia et al., 2003). The time dependency experiments conducted for the binding of Cu (II) and Zn (II) ions to cassava waste biomass at optimum pH is shown in Figure 1. As can be seen in the figure, the individual metal ions bound to the cassava waste biomass in less than twenty-five minutes and remained stable. The rapid uptake of metal ions in solution by biomaterials has been explained that binding occurs on the cell walls of the biomass.

The series of batch experiments showed that cassava waste biomass has the ability to bind Cu (II) and Zn (II) ions and remove them from solution. The metal ion uptake capacities for the untreated and acid treated cassava waste biomass in single-metal-ion solutions are shown in Figure 2. The uptake capacities showed that Cu (II) had a higher uptake capacity than Zn (II). This differential soption of the two ions may be ascribed to the difference in their ionic sizes. The ionic size of Cu (II) is 0.72 Å, while that of Zn (II) is 0.74 Å. The smaller the ionic size, the greater its affinity to reactive sites, of the hydroxyl and sulfhydryl ligands in the untreated and acid treated biomass. This trend in smaller ionic size was also observed for Cu (II) and Zn (II) with other biological adsorbents (Brauckmann, 1990). According to Huheey (1983), metals with smaller hydrolysis constant, pK_h, has the increasing tendency to hydrolyze because of larger charge-size function (z^2/r). The pK_h for Cu (II) and Zn (II) as shown in Table 1 indicates that Zn (II) will hydrolyse to a greater extent than Cu (II) indicating a higher binding for Cu (II).

The metal affinity to the biomass whether untreated or acid treated in the wastewater is similar to that of single-metal-ion solution. It was found that in wastewater experiments, the metal ion uptake capacities order for Cu was higher than Zn. Again; the data indicates that there was no significant difference in the uptake capacities of

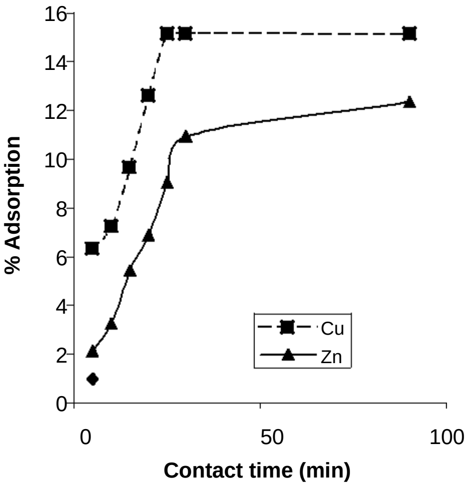

Figure 1. Effect of agitation on metal ion adsorption in a mixed metal ion solution by cassava waste biomass.

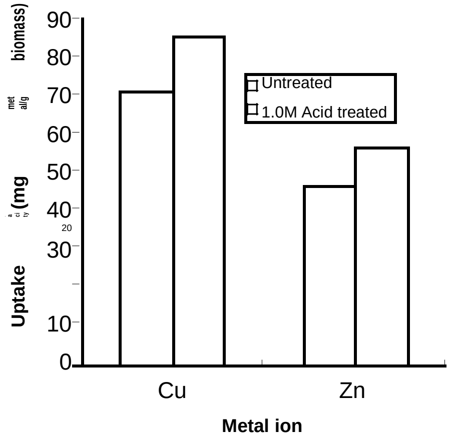

Figure 2. Metal ion uptake capacities of untreated and acid treated cassava waste biomass in a single-metal-ion adsorption tests.

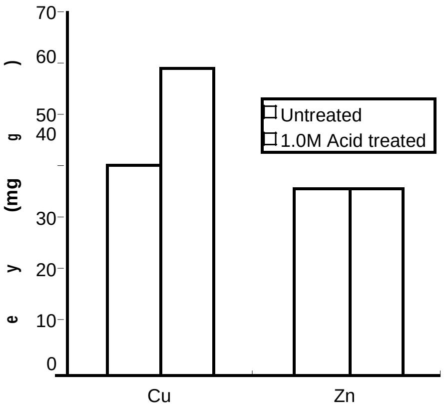

Figure 3. Metal ion uptake capacities of untreated and acid treated cassava waste biomass in synthetic wastewater adsorption tests.

Table 1. Metal desorption capacities from cassava biomass after acid treatment.

Metal ions	Metal desorption Capacities, %	pK_h	Z^2/r	Ionic radii Å	Hydration energy, KJ/mol
Cu (II)	87%	14.1	7.53	0.73	2100
Zn (II)	94%	9.6	13.7	0.74	2046

Table 2. Rate coefficients of Cu (II) and Z(II) ions in single-ion solution and wastewater.

Tests	K_{MA} (min^{-1})	
	Cu (II)	Zn (II)
Single-ion	0.014	0.012
Wastewater	0.003	0.001

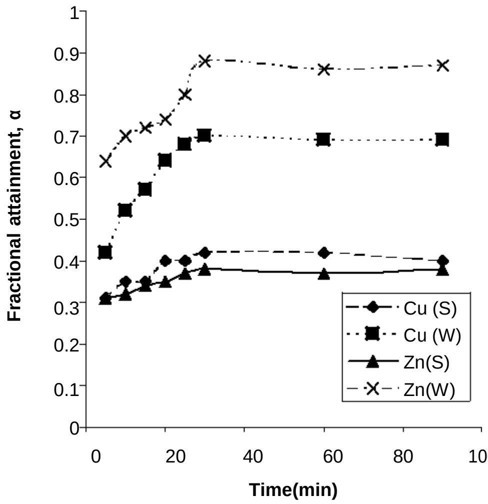

Figure 4. A plot of rate of fractional attainment of equilibrium (α) against time (t) for Cu(II) and Zn(II) in single-ion solution (S) and wastewater (W).

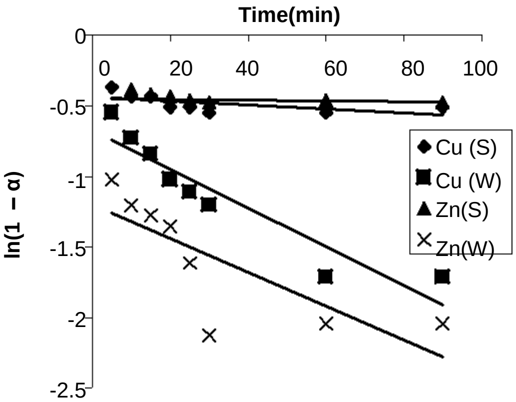

Figure 5. A plot of particle diffusivity [In(1-α)] against time (t) for Cu(II) and Zn(II) in single-ion solution (S) and wastewater (W).

the untreated and acid treated biomass toward Zn (Figure 3). It was further observed that, in the case of wastewater tests uptake capacities are significantly lower than those of the single-metal-ion, because there are a certain number of binding sites where the ions can be adsorbed. In this case, the number is competitively divided between the different metal ions present in the waste effluent. In terms of affinity for the biomass, Cu appeared to be most easily removable in wastewater.

The metal ion recovery using a single system chromatographic column packed with either untreated or acid treated cassava waste biomass from waste water experiment was further used in assessing the reuse of the biomass. The results of the desorption test as indicated in Table 1 revealed that for untreated and acid treated biomass, over 85% of each of the metals were recovered. Five bed volumes were used and combined to measure the total metal removed. After the first three cycles, metal content from the eluent were found to be < 0.01 mg. The data showed that the cassava waste biomass are stable after acid treatment and can be used repeatedly.

Equilibrium isotherms

Kinetic model was applied in the present investigation to describe the reaction rate and was based on the assumption that sorption of metal ions onto the cassava waste biomass is a reversible process. The hypothetical reaction may be expressed as:

$$X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Y$$

where K_1 and K_2 are the adsorption and desorption constants respectively. A linear driving force concept earlier developed by Vinod and Anirudhan (2001) for rate equation was used to obtain the fractional attainment. The equation is expressed as:

$$\ln(1-\alpha) = -K_{MA}t$$

where α is the fractional attainment of equilibrium, and K_{MA} is the overall rate constant or diffusion time constant. The fractional attainment of equilibrium (*α*) is the ratio of the amounts of metal ion removed from solution after a certain time to that removed when sorption equilibrium is attained. A plot of *α* against time (*t*) is shown in Figure 5. The plot shows that the values of α increase with time of agitation, indicative that increased time of agitation afforded the metal ions more opportunity to be taken up by the biomass, however, in less than thirty minutes, majority of the metal ions in either single metal ion solution or wastewater has been removed. From the figure (Figure 4), it was observed that fractional attainment of equilibrium, α, was higher in wastewater effluent than single-ion metal solution probably due to the extra time spent by metal ions to compete for available sites on the biomass. A plot of *ln(1 – α)* against *t* for untreated and acid treated biomass for wastewater gave the kinetics sorption (Figure 5). From the slope of the plots, the values of K_{MA} were determined and are presented in Table 2. The data indicates that Cu(II) is removed from solution at a faster rate (K_{MA} = 0.14 min^{-1} for single metal ion and 0.003 min^{-1} for wastewater) than that of Zn (II) (K_{MA} = 0.12 min^{-1} for single metal ion and 0.001 min^{-1} for wastewater). The lower rate constant observed for waste could be explained by the fact that in wastewater metal ions compete for vacant sites and within the shortest possible time, uptake by binding sites has been completed.

The rate of attainment of equilibrium may also be explained in terms of adsorption being controlled by film-diffusion or particle-diffusion. If the plot of *ln(1 – α)* against *t* give a linear relationship, then adsorption is controlled by particle-diffusion and the diffusivity of the metal ions onto the biomass surface is independent of the extent of sorption and a non-linear plot indicates biomass film-diffusion controlled. From the plot (Figure 5) it was observed that the relationship between metal ion diffusivity, *ln(1 – α)* and time is non-linear, indicting that the diffusivity of the ions onto the biomass surface is film-diffussion controlled. Hence, the time of uptake is dependent on the initial metal ion concentration both in single-ion metal solution and in wastewater effluent system.

Conclusion

Cassava waste biomass can be used for the removal of metals from wastewater. Batch metal ion uptake capacity tests have shown that the adsorption process can be described by the first-order reversible reaction. The degree of removal by the biomass may be enhanced by chemical modification. Maximum recovery of > 90% metal ion adsorbed from the biomass can be achieved by acid treatment indicative of possible recycling of the biomass. The results of the investigation will be useful for the removal of metals from wastewater effluents. The recovered metals may be recycled and the recovered biomass is biodegradable and therefore environment friendly. Additional research is going on to characterize the physicochemical parameters of the biomass and also the elucidation of the efficiency of this biomass with respect to organic pollutants and real industrial wastewater.

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