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Full Length Research Paper

Kinetic and equilibrium studies on the adsorption of Cu^{2+} and Zn^{2+} ions from aqueous solutions by bamboo root biomass

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The adsorption of Cu^{2+} and Zn^{2+} ions on bamboo root biomass from an aqueous solution was studied. Some parameters that determine metal uptake including contact time, adsorbent dose and initial concentration of the metal ions were evaluated. The optimum contact time to attain equilibrium is of the order of 15 to 20 min for both metal ions. The kinetic studies showed that the sorption rates could be described by a pseudo-second order process. Rate constants were determined as 9.13 x 10^{-2} and 6.30 x 10^{-2} g mg^{-1} min^{-1} for Cu^{2+} and Zn^{2+} ions, respectively. The equilibrium sorption capacity of Cu^{2+} and Zn^{2+} ions were determined from the Langmuir equation as 28.57 and 50.00 mg g^{-1}, respectively. The results from this study showed that acid treated bamboo root could be a good adsorbent for the removal of Cu^{2+} and Zn^{2+} ions from industrial effluents. The sorption process is adjudged endothermic as the apparent free energy change (ΔG^o_{ad}) values were found to be 4.14 and 5.22 kJ mol^{-1} for Cu^{2+} and Zn^{2+} ions, respectively.

Key words: Industrial effluents, adsorption, adsorbent, biomass, endothermic.

INTRODUCTION

The presence of heavy metals with its intrinsically undesirable effects in the environment cannot be overemphasized. The genuine concern of researchers has over the years led to the development of techniques for the removal of these pollutants from wastewater. Notable among these methods are hydroxide precipitation, sulphide or carbonate precipitation, complexation – ultra filtration, solvent extraction, chemical metal reduction, granular activated carbon, reverse osmosis and the novel magnetic separation techniques. These methods are relatively expensive involving either elaborate and costly equipment or high cost of operation with ultimate disposal problems (Donbebe and Horsefall, 2007). The removal of heavy pollutants from the environment using natural products without additional pollution inherent in the use of chemicals is imperative and efforts have been actively geared towards the use of the abundant biological system. Quite a number of biomaterials have been investigated for the removal of heavy metal ions from waste streams and these include, cassava waste (Horsefall et al., 2003), fluted pumpkin waste (Horsefall and Spiff, 2005), *Caladium biocolor* (wild cocoyam) (Horsefall and Spiff, 2005), cotton seed hull (Marshall and Champagne, 1995), green alga (*Chollera vulgaris*) (Fraie et al., 2005), dyed coconut polles (Agiri et al., 2007), maize cob (Igwe and Abia, 2007) and wheat bran (Nameni et al., 2008). It is imperative that more biomaterials be studied for their potential effectiveness as adsorbents for heavy metals. The objective of this study is to investigate the potential of bamboo root biomass as an adsorbent for Cu^{2+} and Zn^{2+} ions from aqueous solutions. Both metal ions are toxic and relatively widespread in the environment.

MATERIALS AND METHODS

Collection and preparation of adsorbent

Bamboo roots were obtained from the University of Lagos Akoka, Lagos, Nigeria. They were washed, sun dried and cut into small pieces before grinding into powder using a mill. The powdered bio-

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mass was sieved to a particle size of 150 µm and about 500 g of the mass was soaked in excess 0.3 M HNO_3 for 12 hr to remove any metal and soluble biomolecules, followed by washing with deionized H_2O until a pH of 7.0 was attained The sample was air dried for two days and in the oven at 50℃ to constant weight.

Sorption experiments

Kinetic studies on the adsorption of the metal ions were carried out by agitating 10 ml of 100 mg l^{-1} standard metal ion solutions of Cu^{2+} and Zn^{2+} with 0.025 g each of biomass in five centrifuge cups to represent contact times of 5,10,15,20 and 30 min. The suspensions at a fixed pH value of 5.8 were agitated using a Gallenkamp flask shaker. At the end of each agitation period, each suspension was centrifuged for 5 min at 2800 x g and the supernatant separated.

The equilibrium adsorption of Cu^{2+} and Zn^{2+}, on the biomass were determined using 10 ml of various concentrations (10, 20, 30, 40 and 50 mg l^{-1}) of metal ions on fixed biomass weight of 0.025 g and constant metal ion – substrate contact time (90 min) at a temperature of 30℃ and pH of 5.8. The biomass weights were also varied (0.025, 0.050, 0.075, 0.100 and 0.150 g) to sorption metal ions from 10 ml of fixed metal ion concentration (100 mg l^{-1}) each for 90 min to give another set of data.

Analysis of metal content

The metal ions, Cu^{2+} and Zn^{2+} contents in each experiment were determined with a Perkin elmer precisely atomic absorption spectrometer (AAS) model 200A. Spectroscopic grade standards were used to calibrate the instrument which was checked periodically throughout the analysis for instrument response. The batch experiments were performed in duplicates and the means were computed for each set of values.

Data analysis

The mean metal ion adsorbed by the biomass was determined using a mass balance equation by Chu and Hashin (2001);

$$q_t = \frac{V}{m}\left(C_o - C_t\right) \qquad (1)$$

where q_t is the metal ion adsorbed per unit weight of biomass (mg/g biomass) at time t, C_t the metal ion concentration in solution (mg l^{-1}) at time t, C_o the initial metal ion concentration in solution used in (mg l^{-1}) and m is the mass of biomass used.

Kinetic treatment of experimental data

In order to investigate the mechanism of adsorption, the pseudo - second order equation developed by Ho et al. (1995) was used.

The linear form of Ho's pseudo- second order model is expressed as equation (2);

$$\frac{t}{q_t} = \frac{1}{h_o} + \frac{1}{q_e}t \qquad (2)$$

where q_t is the amount of divalent metal ion on the biomass surface (mg g^{-1}) at time t, h_o is the initial sorption rate, h_o is defined as $h_o = k_2 q_e^2$ where k_2 is the pseudo-second order rate constant (g mg^{-1} min^{-1}). A linear plot of t/q_t against t confirms the model.

Sorption equilibrium

Equilibrium studies that give the sorption capacity of the adsorbent are described by adsorption isotherms which are usually the ratio between the quantity adsorbed and the quantity remaining in solution at equilibrium at a fixed temperature. The earliest and simpliest relationship describing the adsorption equation by Langmuir and Freundlich isotherm is given in equation (3) (Horsefall et al., 2006);

$$\frac{\theta}{1-\theta} = KC \qquad (3)$$

where θ is the fraction of biomass surface covered by a metal ion at any time t, K is equal to k_a/k_d. The amount of metal ion adsorbed, q, will be proportional to θ for a specified adsorbent; hence $q = q_{max}\,\theta$ where q_{max} is the maximum adsorptivity of the biomass. Substitution for θ in equation (3) gives equation (4);

$$q = \frac{q_{max}\,KC}{1 + KC} \qquad (4)$$

Equation (4) can be rearranged to give (5)

$$\frac{1}{q} = \frac{1}{q_{max}} + \frac{1}{q_{max}\,KC} \qquad (5)$$

RESULTS AND DISCUSSION

Kinetics of adsorption

The rate at which adsorption takes place is an essential factor in designing batch sorption system. Consequently, it is important to establish the time dependence of such systems under various process conditions. The experimental results for the rate of adsorption of Cu^{2+} and Zn^{2+} ions on acid treated bamboo root biomass at 30℃ are presented in Table 1.

The plots of C_t/C_o against time are presented in Figure 1. These plots show that the rate of metal uptake decreases with increasing contact time down to a minimum of about 20 min after an equilibrium metal is attained. There is no significant difference in the behaviour of the rate of biomass surface coverage by Cu^{2+} and Zn^{2+}. This similarity of behaviour between Zn^{2+} and Cu^{2+} could be attributed to the closeness in their ionic sizes. The adsorption rates of these metal ions on acid treatedbamboo root biomass were quite rapid and within 5 to 20 min more than 70% of the metal ions were removed. After 20 min of adsorption, the removal rates of the ions slowed significantly, probably due to saturation on the biomass surface.

The kinetic parameters in Table 1 were regressed against Ho's pseudo- second order model equation (2). The plots of t/q_t against t for the metal ions are linear with correlation coefficients greater than 0.998 signifying compliance with the pseudo-second order rate law of equation (2). The sorption capacities at equilibrium, q_e,

Table 1. Mean values of initial (C_o) and final concentration (C_t) (mg/l) of Cu^{2+} and Zn^{2+} ions in solutions after agitation with fixed mass of biomass (5.0 g/l) at regular time interval and pH of 5.8.

	Cu^{2+}		Zn^{2+}	
Time (min)	**C_t (mg l^{-1})**	**$C_o - C_t$ (mg l^{-1})**	**C_t (mg l^{-1})**	**$C_o - C_t$ (mg l^{-1})**
5	24.57	25.43	26.48	23.48
10	20.20	29.80	22.62	27.38
20	12.95	37.50	18.34	31.66
40	12.92	37.08	18.18	31.82
60	12.90	37.10	18.19	31.81

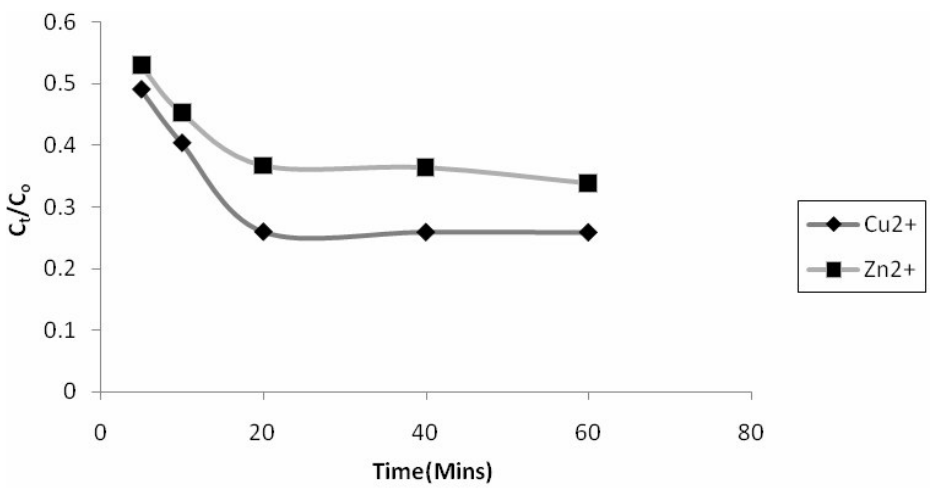

Figure 1. Adsorption rate of copper and zinc ions on acid treated bamboo biomass.

Table 2. Kinetic parameters (q_e = mg g^{-1}; k = g mg^{-1} min^{-1}; h_o = g mg^{-1} min^{-1}) for the sorption of Cu^{2+} and Zn^{2+} on bamboo root biomass.

Metal ions	q_e	k × 10^{-2}	h_o
Cu^{2+}	7.40	9.13	5.00
Zn^{2+}	6.25	6.30	3.44

the initial sorption rate, h_o and the pseudo-order rate constant, k_2 were determined from the slope and intercept of the plots and presented in Table 2.

The data in Table 2 showed that the sorption process was rapid and this can be attributed to the presence of high affinity ligands on the surface of the biomass providing fast metal ion binding. The initial sorption values suggest physical adsorptions in the process.

Equilibrium sorption

The experimental data for the equilibrium sorption of the metal ions are presented in Table 3. The distribution of metal ions between the solution and the biomass can be described by fitting the equilibrium data into a form of Langmuir isotherm in equation (3). The plots of the surface coverage values, θ, against initial metal ion concentrations ranging from 10 to 50 mg l^{-1} with a fixed dose of 0.025 g of biomass at a pH value of 5.8 are presented in Figure 2. The plots show that increase in initial metal ion concentration produced increase in surface coverage on the biomass until the surface was nearly fully covered with a mono-molecular layer.

At high concentration of metal ion, it was observed that further increase in metal ion concentration produced little changes in the amount of metal ion adsorbed. This signifies that significant adsorption took place at low concentrations of the metal ion. Surface coverage behaviour was similar for Cu^{2+} and Zn^{2+}. This similarity indicates that the two metals may be quantitatively removed by the biomass.

In order to account for the surface phenomenon, the Langmuir adsorption isotherm plots, of q_e^{-1} against C^{-1}, computed from the experimental data in Table 3 are linear with correlation coefficients greater than 0.986. The Langmuir constant, q_{max}, the maximum adsorption capacity of the biomass for metal ions obtained from the plots are 50.00 for Zn^{2+} and 28.57 for Cu^{2+}. The values show that the biomass is a good adsorbent for the metal ions. The order of metal ion uptake was $Zn^{2+} > Cu^{2+}$ ions.

Table 3. Mean equilibrium concentration of Cu^{2+} and Zn^{2+} ions in solution after agitation at different initial concentrations of metal ions (10 - 50 mg l^{-1}) with fixed amount of biomass (0.025 g) at pH 5.8 and 30°C.

		Cu^{2+}			Zn^{2+}		
C(mg l^{-1})	C^{-1}	q_e^{-1}	q_{max}	θ	q_e^{-1}	q_{max}	θ
50	0.02	0.13	28.57	0.16	0.12	50.00	0.167
40	0.025	0.17		0.123	0.14		0.154
30	0.03	0.21		0.10	0.19		0.118
20	0.05	0.33		0.069	0.30		0.067
10	0.10	0.58		0.036	0.58		0.034

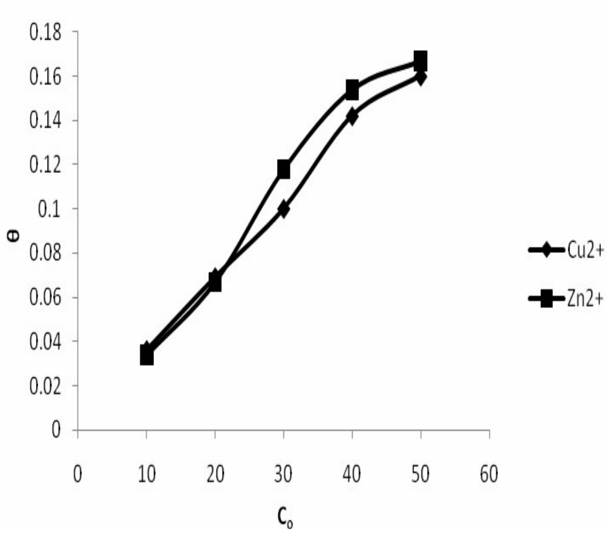

Figure 2. A plot of surface coverage θ against metal ion concentration (mg/L) for Cu^{2+} and Zn^{2+} ions.

Differential sorption capacity of metal ions from aqueous solution by the adsorbent has been generally ascribed to three principal processes; (1) differences in ionic sizes of metal ion, (2) difference in the affinity of metal ions for active groups on the adsorbent and (3) nature of the salt of the metal ion. Generally, the element with smaller ionic radius will compete faster for exchange sites than those of larger ionic radius (Ho et al., 1995). However, the carboxylate ligands present in wood based biomasses (adsorbents) have good affinity for metals with larger ionic radii. Since binding to the carboxylate ligands was preferentially based on size, the uptake from aqueous solution of Zn^{2+} ions may be more favourable than those of Cu^{2+}.

Effect of adsorbent dose

The effects of adsorbent dose on the adsorption properties of bamboo root was studied at a pH of 5.8 with different adsorbent doses varying from 2.5 g l^{-1} to 10 g l^{-1} and a fixed initial metal ion concentration of 50 mg l^{-1} and are presented in Table 4. The plots of the percentage of metal ions removal against adsorbent dose for Cu^{2+} and Zn^{2+} ions are presented in Figure 3. The Figures show that the initial increase in adsorbent dose produced increased percentage removal of metal ions up to an adsorbent dose of 10 g l^{-1}. Further increase in adsorbent dose produced little change in the percentage removal of metal ion for both Cu^{2+} and Zn^{2+}.

Thermodynamics

Thermodynamic model can be used to describe the absorption of adsorbate on adsorbent (Abiola, 2003). The Gibb's free energy change (ΔG^o_{ad}) of the adsorption processes of the two ions on the biomasswas determined using the relationships (Abiola et al., 2007) in equation (6).

$$\log \frac{\theta}{1-\theta} = \log K + \log C \tag{6}$$

$$K = \frac{1}{55.5} \exp \frac{-\Delta G_{ad}}{RT} \tag{7}$$

where K is the equilibrium constant of the adsorption process, C the ion concentration in the solution, R, the universal gas constant and T, the absolute temperature. The plots of log (θ /1- θ) versus log C gave linear plots (R^2 > 0.990) from where the values of ΔG^o_{ad} were evaluated. The sorption process is adjudged as endothermic as the apparent free energy change (ΔG^o_{ad}) values were found to be 4.14 and 5.22 kJ mol^{-1} for Cu^{2+} and Zn^{2+} respectively.

Conclusion

Bamboo, the perennial plant with unique rhizome is abundant in southern Nigeria and the full potential of this natural resource is yet to be tapped in terms of commercial use. In this study, the root of the plant has been found to be a good adsorbent for the removal of Cu^{2+} and

Table 4. Mean equilibrium concentration of Cu^{2+} and Zn^{2+} ions in solution after agitation at different initial concentrations of metal ion (50 mg ml^{-1}) with fixed amount of biomass (0.025 g) at pH 5.8 and 30℃.

Mass of biomas ($g\ l^{-1}$)	Cu^{2+}			Zn^{2+}		
	C_e ($mg\ l^{-1}$)	C_o - C_e ($mg\ l^{-1}$)	% adsorbed	C_e ($mg\ l^{-1}$)	C_o - C_e ($mg\ l^{-1}$)	% adsorbed
2.5	20.425	29.58	59.00	21.50	28.5	56.60
5.0	18.525	31.48	62.95	19.33	30.67	61.13
10.0	15.750	34.25	68.50	16.13	33.86	67.75
15.0	15.350	34.65	69.30	10.875	39.13	78.25
20.0	15.050	34.95	69.99	10.500	39.50	79.00

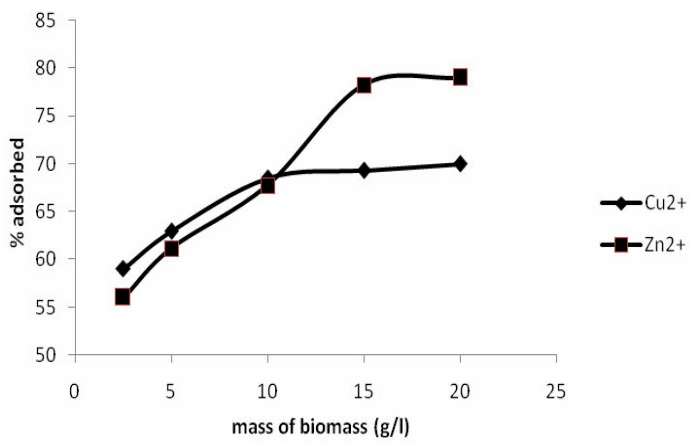

Figure 3. The effect of adsorbent dose on the percentage removal of Cu^{2+} and Zn^{2+} ions from solution.

Zn^{2+} ions from aqueous solutions. The kinetics of the sorption rates could be described by a pseudo-second order process while the equilibrium data fitted the Langmuir isotherm satisfactorily.

REFERENCES

Abiola OK, Oforka NC (2004). Adsorption of (4 – amino – methyl – pyramidinyl methylthio) acetic acid on mild steel from hydrochloric acid solution (HCl – Part 1, Mater. Chem. Phys. 83: 315-322.

Abiola OK, Oforka NC, Ebenso EE, Nwinuka NM (2007). The inhibitive action of Delonix Regia extract for thr corrosion of aluminium in acidic media, Anti-Corrosion Methods Mater. 54(4): pp. 219-224.

Agiri GO, Akaranta O, Ajayi IO (2007). Equilibrium and kinetics studies of metal adsorption on dyed coconut pollen. Afr. J. Biotechnol. 6(7): 933- 938.

Chu KH, Hashim MA, (2001). Desorption of copper from polyvinyl alcohol immobilized seaweed biomass. Acta Biotechnol. 21(4): 295-306.

Wankasi D, Horsefall M. (2006). Sorption kinectic of Pb^{2+} and Cu^{2+} ions from aqueous solution by Nipah palm (*Nypa fruticans Wurmb*) shoot biomass. Elect. J. Biotech. ISSN: 0717-3458, Retrieved 9th July, 2007 http://www.ejibiotechnology.info/content/vo19/issue5/full5/index.html

Ho YS, Wase DAJ, Forster CF (1995). Batch nickel removal from aqueous solution by sphagnum moss peat. Water Res. 29(5): 1327-1332.

Horsefall M, Abia AA, Spiff A (2003). Removal of Cu (II) and Zn (II) ins form waste water by cassava (Manihot esculenta Cranz) waste biomass. Afr. J. Biotechnol. 2(10): 360-364.

Horsefall M, Spiff Ayebaemi I (2005). Sorption of lead, cadmium and zinc on sulphur-containing chemically modified wastes of fluted pumpkin (Telairia occidentalis Hook f.). Chem. Biodiver. 2(3): 373-385.

Horsefall M, Abia AA, Spiff A (2006). Kinetic studies on the adsorption of Cd^{2+} Cu^{2+} and Zn^{2+} ions from aqueous solutions by cassava (*Manihot esculenta* Cranz) tuber bark waste. Bioresour. Technol. 97: 283-291.

Frailes A, Penche S, Gonzales F, Blazques ML, Munoz JA, Ballester A (2005) Bisorption of copper, zinc, cadmium and nickel by Chollera vulgaris. Chem. Ecol. 21(1): 61-75.

Igwe JC, Abia AA (2007). Adsorption isotherm studies of Cd (II), Pb (II), and Zn (II) ions bioremediation from aqueous solution using unmodified and EDTA – modified maize cob. Ecl. Quim., Sao Paulo, 32(1): 33-42.

Marshall WE, Champagne ET (1995). Agricultural by products as adsorbents in laboratory prepared solutions and in manufacturing waste water. J. Environ. Sci. Health, Part A; Eviron. Sci. Eng. 3(2): 241-261.

Nameni M, Alavi M, Arami MR (2008). Adsorption of hexavalent chromium from aqueous solutions by wheat bran. Int. J. Environ. Sci. Technol. 5(2): 161-168.