

Full Length Research Paper

Dynamics of zinc sorption from aqueous matrices using plantain (*Musa sp.*) peel biomass

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The influence of climate change on freshwater resources has undoubtedly affected the availability and quality of freshwater resources. However, the demand for water for agricultural, domestic, industrial and recreational purposes increases by the day globally. The need for remediation and reuse of large volumes of industrial wastewaters being generated globally therefore cannot be over-emphasized. The potential ability of plantain peel (*Musa sp.*) biomass to remove metal ions (Zn^{2+}) from aqueous matrices was studied. Influence of contact time, adsorbent weight, pH, metal concentration, temperature and shaking speed were investigated. Physico-chemical characterization (proximate and infra-red spectroscopic analyses) of the biomass was carried out to elucidate information on adsorption mechanisms. Desorption studies were also performed to determine possible recovery potential of Zn^{2+} and the re-usability of the biomass. Zn^{2+} adsorption increased with increasing metal concentration in solution, adsorbent weight and contact period. Optimal pH value for adsorption was 3 after which Zn^{2+} uptake decreased. Corresponding values for contact time, biomass weight and Zn^{2+} concentration were 150 min, 24 g/L and 600 mg/L, respectively. Experimental data fitted into Freundlich's isotherm. Carboxylic and hydroxyl groups were among the prominent functional groups on the surface of the biomass. Desorption of Zn^{2+} from the biomass was less than 10%. Alternative compounds may be further investigated to improve on metal desorption from plantain peel biomass. This cannot be over-emphasized if the several advantages of this biomass (lesser cost than for synthetic resins, abundance and biodegradability) will be utilized for industrial applicability especially in emerging economies like Africa.

Key words: Adsorption, zinc, isotherms, waste utilization, wastewaters.

INTRODUCTION

Heavy metals commonly have industrial applications in the manufacture of pesticides, batteries, alloys, electroplated metal parts, textile dyes, steel and so forth (Prasad and Freitas, 2000). A major source of these compounds into aquatic systems therefore, is via wastewaters from industrial processes. Industrial effluents in developing

economies are often released into water bodies without taking care of the inorganic components or pollutants embedded in most wastewaters (Horsfall et al., 2006). The absence or ineffectiveness of most treatment facilities of these industries has been attributed to be the cause pollution of water bodies.

Conventional techniques currently being used for metal removal include chemical precipitation, electrochemical deposition, evaporation, cementation, membrane process, ion exchange and activated carbon adsorption (Janson et al., 1982). These methods have limitations due to their inefficiency, high capital investment or operational costs. There is therefore an increasing need for a

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Abbreviations: DMRT, Duncan's multiple range test; FTIR, Fourier transform infrared spectroscopy.

novel, efficient and cost-effective technique for the remediation of metal bearing waste before discharge into the environment. Over the last two decades, an approach which showed considerable potential for metal removal from aqueous media is biosorption. The term 'biosorption' means the use of natural raw materials and wastes from industrial and agricultural activities to adsorb metal ions from aqueous solutions (Bailey et al., 1999; Volesky, 2003).

A number of metal binding mechanisms has been postulated in biosorption; they include chemisorption, ion – exchange, complexation, chelation, physical adsorption and micro precipitation (Volesky, 2003). Several biomaterials have been used for heavy metals' removal. They include moss (Martins et al., 2004), activated carbon (Mohan and Singh, 2002), tree leaves (Kumar et al., 2006), agricultural wastes (Bailey et al., 1999), biosolids (Norton et al., 2004), corn cobs (Khan and Wahab, 2007), fungal biomass (Zhou and Kiff, 1991), peanut hull pellets (Brown et al., 2000), sea nodule residue (Agrawal et al., 2004), crop milling waste (Saheed et al., 2005), peanut husks carbon (Taha et al., 2001) humified sphagnum and carex peat (Ringqvist and Oborn, 2002), chemically modified wastes of fluted pumpkin (Horsfall et al., 2000), agricultural by-products (Orhan and Buyukgungor, 1993) and crab carapace (Shuguang et al., 2007).

Knowledge about the applicability of biosorption to solving water pollution prompted research into locally available biosorbents in Africa. There is no known study on biosorptive properties of plantain peel biomass. This work therefore focused on the potential capacity of plantain peel as an adsorbent for Zn^{2+} removal from aqueous solutions.

MATERIALS AND METHODS

Reagents, biomass preparation, effluent collection and instrumentation

All chemicals used were of analytical grade. A 1000 mg/L stock solution of Zn^{2+} was prepared from $ZnCl_2$ (Merck, Germany). Standard Zn^{2+} solutions in the range 50 to 600 mg/L were then prepared from stock solution; the synthetic resin used was dowex (BDH-Dow Chemical Co., Midland, USA.). Batch samples of plantain peel were collected as waste materials from domestic waste bins. The peels were cut into smaller sizes, thoroughly washed, first with tap water and then, with distilled deionized water and then oven-dried at 90°C for 24 h. The dried samples were then ground using a wooden mortar, sieved using a 100 mesh screen. The sieved fraction of the biomass was washed twice with 0.01 M HCl to remove any metals or debris that might be in the biomass prior to experimental metal ion exposure. The acid washed biomass samples were again washed twice with distilled- deionized water to remove acid and then, oven-dried at 70°C for 48 h. This pretreated biomass was then stored in plastic containers at room temperature for further experimentation (Khan and Wahab, 2007).

Influence of pH on metal removal was measured using a Jenway pH meter (Dunmow Essex, England, model 3015). Zn^{2+} concentration was measured using the Alpha 4 atomic absorption

spectrophotometer (Chemtech Analytical, UK) which employs a hollow cathode lamp.

Adsorption experiments

Equilibrium conditions of adsorbents' weight (capacity studies), contact time (kinetics), pH and adsorbate (Zn^{2+}) concentrations (equilibrium isotherm), temperature, particle size and agitation speed were studied using Zn^{2+} standard solutions (Opeolu et al., 2009).

Kinetic studies

Kinetic parameters for the adsorption process were studied on batch adsorption of 100 mg/L Zn^{2+} at 32°C. Six sets of a mixture of plantain peel biomass (0.6 g) in 25 ml of 100 mg/L Zn^{2+} in 100 ml conical flasks were allowed to stand at different time intervals of 30, 60, 90, 120, 150 and 180 min respectively for adsorption to take place. Each mixture was then filtered to separate the adsorbent and the filtrate to allow for analysis of residual Zn^{2+} ; thereafter, the percent removal of Zn^{2+} was measured (Kadirvelu and Namasivayam, 2003).

Capacity studies

Different weights of each of the adsorbents (plantain peel biomass and dowex) in the range of 0.025 and 0.6 g in 25 ml solution were used to remove Zn^{2+} from 100 mg/L Zn^{2+} standard solution. A 25 ml aliquot of the Zn^{2+} solution was accurately measured into 100 ml conical flask and the adsorbent added to the flask; a contact time of 150 min was maintained for all the experiments. After 150 min contact time, the mixture was filtered through Whatman No 1 Filter paper (medium flow rate and porosity with particle retention of 11 μ m) and the filtrate analysed for residual Zn^{2+} by atomic absorption spectrophotometer (AAS) (Dakiky et al., 2002).

Effect of pH on adsorption capacity

The pH of 100 mg/L Zn^{2+} solution prepared from 1000 mg/L stock solution was adjusted to desired value and kept constant with the addition of either 0.1 M NaOH or 0.1 M HCl. The pH values investigated were 2, 3, 4, 5, 6 and 8. Plantain peel biomass (0.6 g) aliquot was weighed and added to 25 ml of 100 mg/L Zn^{2+} solution at the desired pH and left for 150 min. The mixture was then filtered and the filtrate analyzed for Zn^{2+} . The procedure was repeated for each of the adsorbents (Horsfall and Spiff, 2004).

Effect of concentration on adsorption

Zn^{2+} standard solutions with concentration range of 50 and 600 mg/L was prepared from the stock solution. Adsorbents' weight of 0.6 g in 25 ml solution was also used for adsorption isotherm studies with a contact period of 150 min (earlier established as equilibrium time or adsorption). Each mixture was then filtered for analysis of Zn^{2+} (Goksungur et al., 2003).

Effect of shaking speeds

Each of the adsorbents was weighed to determine the effects of shaking speeds. A 0.6 g aliquot of each of plantain peel biomass and dowex were weighed into 25 ml solution of 100 mg/L Zn^{2+} in a 100 ml conical flask. The mixtures were shaken in an orbital shaker

Table 1. Effect of plantain peel biomass weight on Zn²⁺ removal from aqueous solutions.

Weight (g)	Residual Zn ²⁺ (Mean ± SE)	% Adsorption
0.025	0.40 ± 0.01 ^e	99.60
0.05	0.29 ± 0.01 ^d	99.71
0.10	0.28 ± 0.06 ^{cd}	99.72
0.2	0.25 ± 0.02 ^c	99.75
0.40	0.21 ± 0.05 ^b	99.79
0.60	0.16 ± 0.02 ^a	99.84

Values followed by the same letter within a column do not differ significantly according to Duncan's multiple range test (DMRT) at 5% level of probability.

(Edmund Buhler, GmbH & Co., Germany) at speeds in the range of 50 and 300 rpm. After 30 min, the mixtures were filtered using Whatman No 1 filter paper and filtrates analyzed for Zn²⁺ content (Kok et al., 2001).

Effect of temperature

To each adsorbent (0.6 g), 25 ml of 100 mg/L Zn²⁺ solution was equilibrated by shaking for 30 min at 250 rpm at different temperatures (30, 40, 50, 60, 70 and 80°C in a water bath (Techne Cambridge Limited, Duxford Cambridge, England). These were centrifuged immediately at 2500 rpm for 5 min and the supernatant decanted. The supernatants were then analyzed for residual Zn²⁺ (Horsfall and Spiff, 2005).

Characterisations of plantain peel biomass

Some physico-chemical properties of the biomass were carried out. They included infrared spectroscopy using KBr discs and proximate analysis. The methods of Horsfall and Spiff (2004) and those listed in AOAC (1990) were used.

Desorption studies

Desorption studies were carried out to assess recovery and reuse potentials of Zn²⁺ and the biomass respectively. The methods of Marshall and Johns (1996) and Periasamy and Namasivayam (1994) were modified and adopted. Zinc-loaded biomass was separated and gently washed with distilled deionized water to remove any unadsorbed Zn²⁺. The biomass was then agitated in 100 ml of 0.1 M HCl for 1 h and the amount of desorbed Zn²⁺ estimated.

Quality assurance/ quality control

(i) To examine whether the filter paper used during the test adsorbed or released Zn²⁺, filtered and unfiltered samples were compared. Filtered and unfiltered distilled-deionized water were analyzed by AAS to determine if Zn²⁺ was leached from the filters. Samples of filtered and unfiltered 100 mgL⁻¹ Zn²⁺ solutions were also examined to determine whether the metal was retained by the filters.

(ii) Each sample was analysed in triplicate by AAS and a mean concentration was calculated. The relative standard deviation (RSD) for each sample was calculated as the standard deviation of the samples divided by the average of the samples. The value was

multiplied by 100 to put it on a percent basis (Brown et al., 2000).

(iii) Standard solutions of Zn²⁺ were prepared from 1000 mgL⁻¹ stock solution. These were analyzed for Zn²⁺ concentrations; the results were used to plot the calibration curve to determine the linearity of concentration with absorbance.

(iv) The detection limit of the instrument was also determined. Seven distilled-deionized water blanks were analyzed for metals for the determination. Detection limit was evaluated as thrice the standard deviation of seven blanks (Opeolu et al., 2009).

RESULTS AND DISCUSSION

Effect of adsorbent weight

The adsorption increased with increasing adsorbent dosage; increasing adsorbent dosage provided greater surface area available for adsorption due to increased active sites on the biomass (Table 1). Similar results have been reported by several authors (Kok et al., 2001; Addour et al., 1999; Normanbhay and Palanisamy, 2005; Mahvi et al., 2005; Opeolu et al., 2009). They explained that increasing adsorption with adsorbent weight can be attributed to increased number of unsaturated active sites as well as high accessibility of metals to the binding sites.

Effect of Zn²⁺ concentration

Metal concentration is an important parameter considered. The principle is based on the fact that the amount of metal available to be sorbed could determine the amount actually sorbed. The influence of concentration on metal removal is presented in Figure 1. Increase in concentration resulted in increased percentage adsorption. The adsorption efficiency of plantain peel biomass was greater 99% of Zn²⁺ solution. Corresponding values for dower was lower. However, at 100 mg/L and beyond that concentration, there was no significant difference in adsorption. The results were consistent with those of Horsfall and Spiff (2004) who worked on sorption of Pb²⁺ and Cd²⁺ ions from aqueous solution by wild cocoyam biomass and Goksungur et al. (2003), who worked on biosorption of copper ions by caustic treated waste bakers

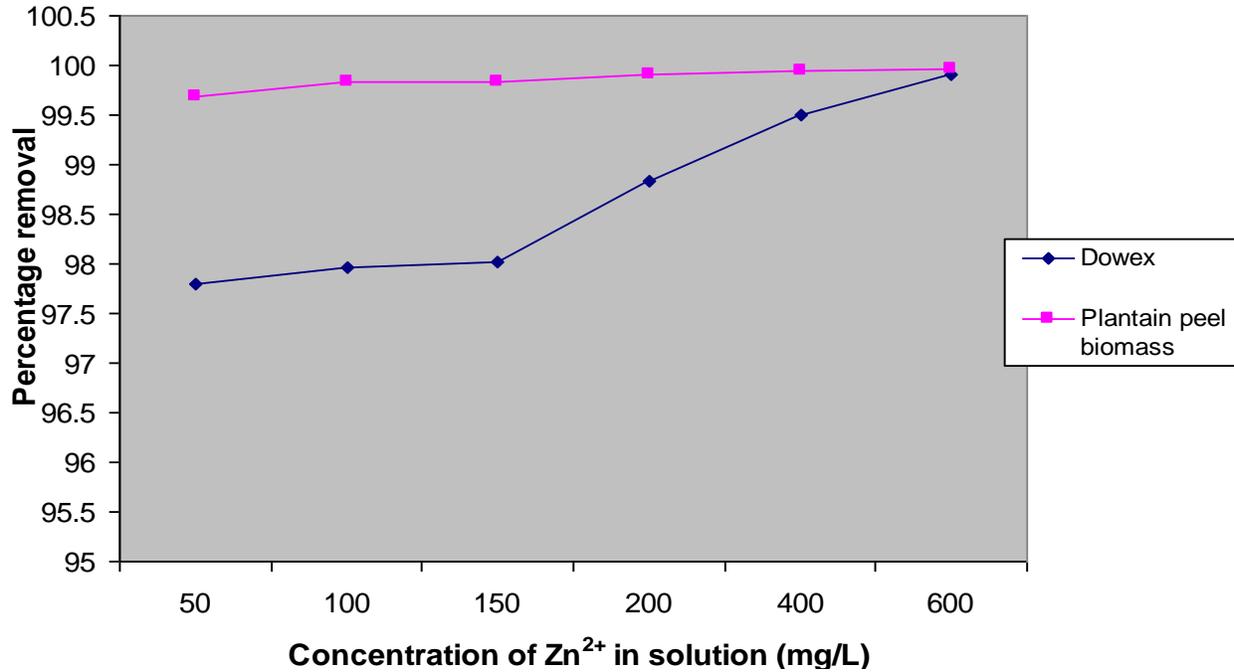


Figure 1. Influence of Zn²⁺ concentration on removal efficiency of adsorbents.

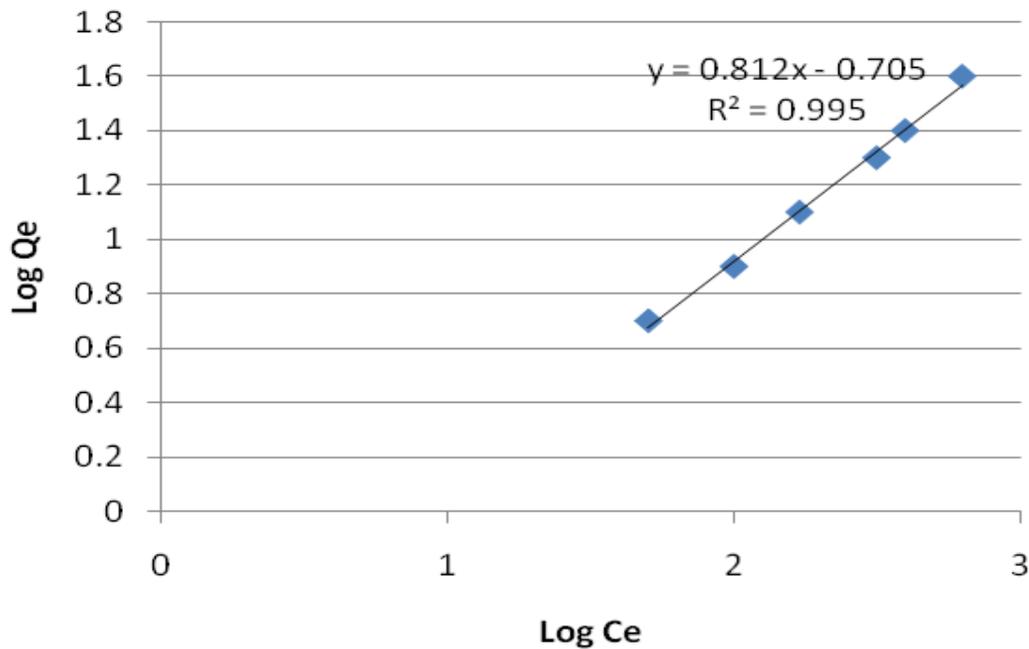


Figure 2. Freundlich's isotherm for plantain peel biomass.

yeast biomass. They both reported that saturation and the surface of adsorbent will lead to negligible adsorption with increasing concentration. Horsfall and Abia (2003) also demonstrated that the active biomass surface has the capacity to continue to adsorb metal ions as much as

the active sites not saturated. Experimental data fitted well into Freundlich Isotherm with an R^2 value greater >0.99 (Figure 2). Consequently, significant adsorption may therefore take place at high metal concentrations, suggesting multi-layer sorption. Therefore adsorption

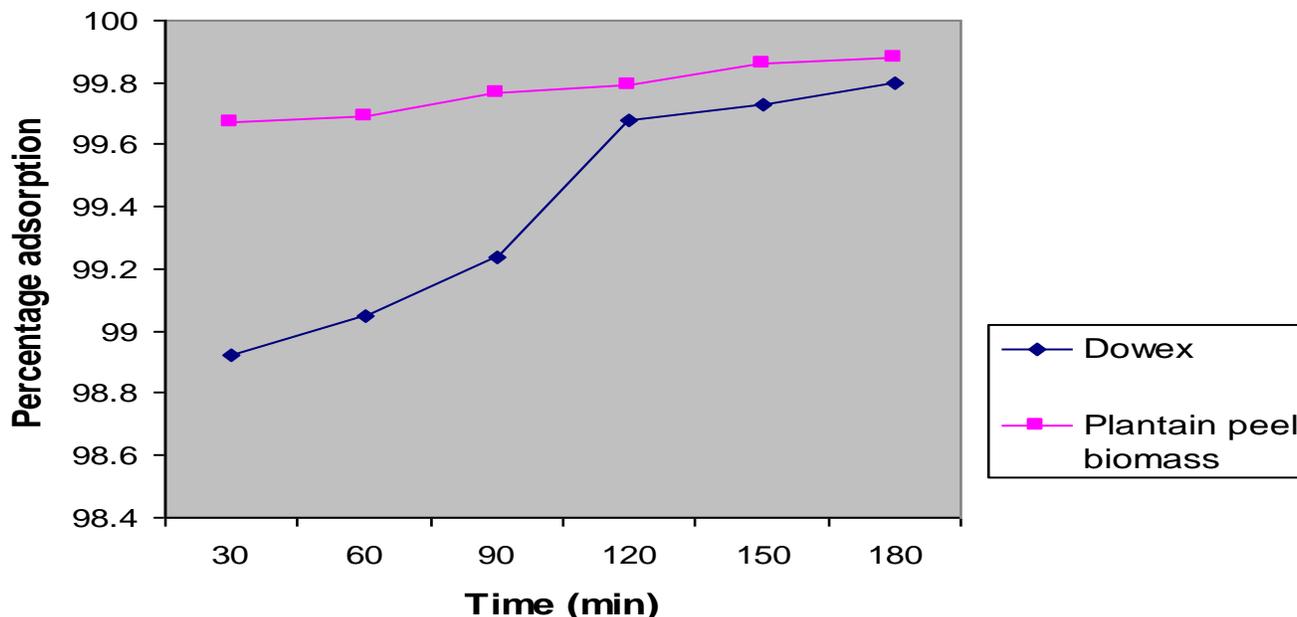


Figure 3. Influence of contact time on Zn²⁺ adsorption by adsorbents.

Table 2. Effect of pH on percentage adsorption by plantain peel biomass.

pH value	Residual Zn ²⁺ (Mean ± SE)	% Adsorption
2	0.1800 ± 0.0116 ^c	99.82
3	0.1000 ± 0.0116 ^a	99.90
4	0.1200 ± 0.0058 ^{ab}	99.88
5	0.1400 ± 0.0116 ^b	99.86
6	0.2467 ± 0.0067 ^d	99.85
8	0.4000 ± 0.0058 ^e	99.60

Values followed by the same letter within a column do not differ significantly according to DMRT at 5% level of probability.

would be random due to existence of energetically different active sites (Dakiky et al., 2002).

Effect of contact time and shaking speed

The effects of contact time on adsorption of Zn²⁺ on plantain peel biomass are presented (Figure 3). Increase in contact time and agitation speed led to increases in adsorption and the optimum was achieved at 150 min. Equilibrium was established earlier for higher adsorbent doses. The results follow similar trend reported by Anwar et al. (2010) who reported that low speed accumulates the adsorbent at bottom, instead of spreading in the solution that result in burial of various active sites under the layers of adsorbent. Since adsorption is a surface phenomenon, layers buried under do not play their role in metal uptake. Shaking rate should be adequate to

guarantee all the binding sites available for metal uptake. However, extremely higher speed lowered the metal removal, not allowing enough time for metal ions to adsorb.

Effect of pH

The pH of the aqueous metal solutions had significant impact on metal uptake because it influenced the surface charge of biosorbent, degree of ionization and the speciation of biosorbent (Cho et al., 2005). There were significant differences in percentage adsorption at different pH values (Table 2). Adsorption increased between pH 2 and 4 and a slight decrease was exhibited between 4 and 5 which indicate that Zn²⁺ uptake is highest at acidic conditions. Optimal adsorption was observed at pH 3 and decreased with increasing pH.

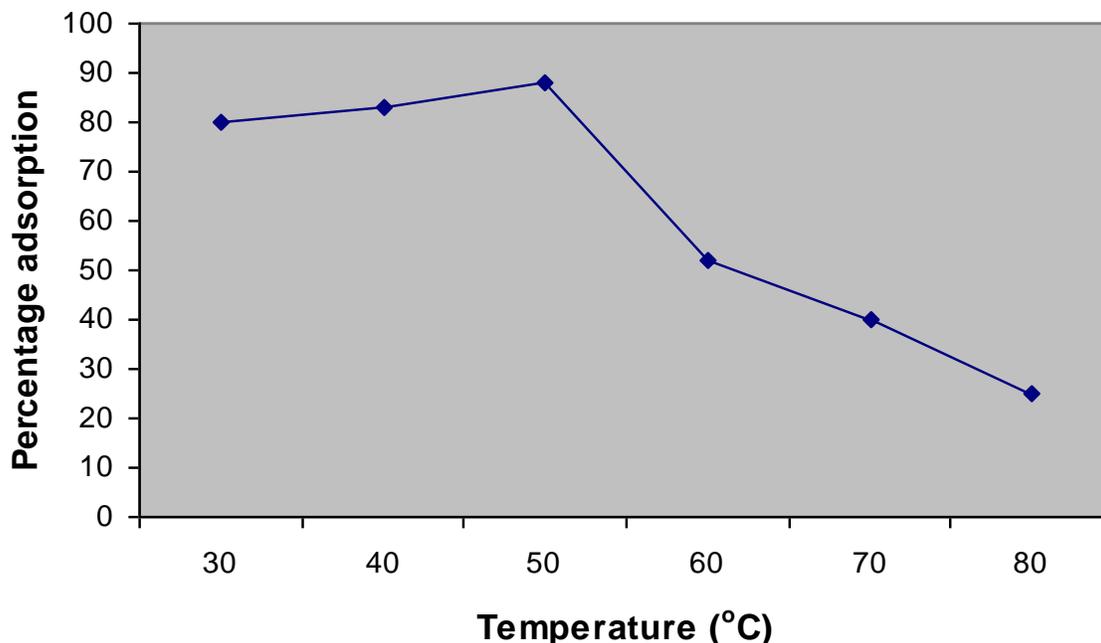


Figure 4. Effect of temperature on Zn^{2+} uptake by plantain peel biomass.

Complexation of Zn^{2+} at the surface of biomass due to zinc amphoteric property of the metal seems to be responsible. This is consistent with the work of Aklil et al. (2004) who worked on heavy metal removal by calcined phosphate. They showed that adsorption was initially high at pH 2 and later dropped, this was attributed to increase in H_3O^+ ions in solution at pH below 3

Effect of temperature

Effect of temperature on percentage adsorption is presented (Figure 4). Optimal temperature for adsorption by plantain peel biomass was 50°C. Increased temperature above 50°C resulted in sharp decrease in metal removal from solution. High temperatures tend to decrease the boundary layer thickness; the metal ions therefore had increased tendency to escape from the biomass surface to the solution phase. The decreased adsorption with increasing temperature also suggests weak adsorption interaction between biomass surface and the metal ion, which supports physisorption (Horsfall and Spiff, 2005).

Physico-chemical characteristics of plantain peel biomass

Plantain peel biomass was characterized by Fourier transform infrared spectroscopy (FTIR) spectroscopic analysis at room temperature. Results are presented in Table 3. Carbonyl and hydroxyl groups were very

prominent functional groups on the surface of the biomass. These were potential binding sites for Zn^{2+} since hydroxyl group is easily displaced by Zn^{2+} . Main mechanisms influencing the adsorption characteristics seems to include chelation, ion – exchange adsorption and complexation mechanisms. Proximate analysis of the biomass is presented in Table 4.

Desorption studies

Results of desorption study is presented in Table 5. Desorption studies on the biosorbent indicated that Zn^{2+} was poorly desorbed from the biomass. Percentage desorption was less than 20 for the concentration range studied. There was no clear trend in desorption with respect to concentration. However, lesser amounts of Zn^{2+} were desorbed from biomass with higher Zn^{2+} concentration. This suggests that strong bonds exists between the biomass and Zn^{2+} implying possible presence of strong complexes and ligands between biosorbent and Zn^{2+} .

Conclusion

Plantain peel biomass was used to bind Zn^{2+} from standard aqueous solutions. Effects of initial concentration, biomass weight, contact time, agitation speed, pH and temperature of solution were investigated. Physico-chemical characterization of biomass and desorptive potential of Zn^{2+} was also studied. In most of the

Table 3. Structural elucidation of plantain peel biomass using FT-IR spectroscopy.

S/N	cm ⁻¹	Suspected group	Remark
1.	535.72 – 535.60	C – H	CH of aromatic / benzene ring present
2.	887.43	C-H (bend) C=C	C-H (bend) out of plane, C=C(out of plane)
3.	1034.48 - 1077.56	C=N (bend) C-O and C=H	C-H (bend), C=C, C-H (in plane) R-N, C-O (alcohol) present
4.	1101.66	C-O, C-H	C-O (alcohol), C-H (bend)
5.	1152.67	C=N (bend), C-O, C-H	R-N, C-O (alcohol), C-H (in plane) aromatic.
6.	1245.79 – 1417.00	C-H (bend) C-O, C-N, OH	C- H, C – O (alcohol), OH (Carboxylicacid present.)
7.	1636.51 – 1830.25	C – H, C=C, C=O (Stretch)	C – H (alkene), C=C (aromatic) C=O (either), RCOOR anhydride
8.	2852.33 – 2921.36	C–H, CH ₂ and CH ₃ (alkane) RCO – OH	C – H, CH ₂ CH ₃ alkanes present alongside RCO – OH (Carboxylic acid)
9.	3438.31 – 3854.53	OH (Stretch) OH (Non–Bonding) N-H (Stretch) C-H (Stretch)	OH of alcohol and Carboxylic acid confirmed present N – H amine present.

Table 4. Proximate analysis of plantain peel biomass.

Parameter	Percentage (%)
Proteins	3.65
Crude fibre	56.20
Crude fat	1.08
Moisture content	3.35
Ash content	11.41

Table 5. Percentage desorption of Zn²⁺ from plantain peel biomass.

Initial concentration (mg/L)	Concentration adsorbed	% Desorbed
50	49.86	14.00
100	99.88	11.00
150	149.75	11.40
200	199.92	12.00
400	399.90	5.00
600	599.86	3.10

experiments, percentage adsorption was over 90 in contrast to percentage desorption capacity that

was quite low. Prominent surface groups on the biosorbent included hydroxyl and carboxylic groups.

Further studies should however be carried out to explore other solvents that may be more effective

for Zn²⁺ desorption from plantain peel biomass.

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