BANANA TRUNK FIBERS AS AN EFFICIENT BIOSORBENT FOR THE REMOVAL OF Cd(II), Cu(II), Fe(II) AND Zn(II) FROM AQUEOUS SOLUTIONS

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ABSTRACT

The biosorption of Cd(II), Cu(II), Fe(II) and Zn(II) from aqueous solutions by an agrowaste, namely banana trunk fibers (BTF), was investigated. The effect of pH, contact time, metal ions concentration, adsorbent dose and change in $[M^{2+}]$ /biomass were studied at ambient temperature (25 °C). The equilibrium process was described well by the Freundlich isotherm model with adsorption capacity, K_f of 8.49, 2.68, 6.58 and 1.74 mg/g for Cd(II), Cu(II), Fe(II) and Zn(II), respectively. Kinetic studies showed good correlation coefficients for a pseudo-second-order kinetic model. The BTF were subjected to different chemical modification methods (mercerization, acetylation, formaldehyde treatment, peroxide treatment, stearic acid treatment and sulphuric acid treatment) and the adsorption capacity (q_e) of each modified BTF for the metal ions was obtained. Our findings hitherto reveal that the q_e values are practically similar to that of the unmodified BTF confirming that the latter by its nature, that is its chemical composition, is already an efficient biosorbent for the removal of the heavy metal ions.

Keywords: Banana Trunk Fibers; Agrowaste; Biosorption; Heavy Metal Ions; Isotherm

INTRODUCTION

Industrialization has enhanced the degradation of our environment through the discharge of wastewaters. This has resulted in significant amounts of heavy metal ions such as Cd(II), Cu(II), Fe(II) and Zn(II) being deposited into our ecosystems¹. These metals are not biodegradable and known to cause severe dysfunction of the kidney, reproductive system, liver, brain and central nervous system². Several methods for removing heavy metal ions such as chemical precipitation, electrodeposition, ion exchange, reverse osmosis and adsorption have been used to treat wastewater. Of these methods, chemical precipitation is the most economic but is inefficient for dilute solution. Electrodeposition, ion exchange and reverse osmosis are generally effective, but have rather high maintenance and operation costs and subject to fouling. Biosorption, a process that utilizes biomass³ for the decontamination of metal-containing effluents is a promising alternative. Low-cost natural sorbents such as cork and yohimbe bark⁴, spent grain⁵, peanut hull pellets⁶, rice milling by-products⁷, grape stalk waste⁸, pectin rich fruit wastes⁹ and biowaste from fruit juice industry¹⁰.

Banana plants are of the family Musaceae and cultivated primarily for their fruit. As such, after harvesting the fruit, the matured pseudostems are generally disposed at a landfill or left to decompose slowly in a plantation field. The composition of a typical BTF obtained by elemental analysis, as determined by Bilba et al.¹¹ is as follows: Cellulose (31.27 ± 3.61 %), Hemicellulose (14.98 ± 2.03 %), Lignin (15.07 ± 0.66 %), Extractives (4.46 ± 0.11 %), (Moisture 9.74 ± 1.42 %) and Ashes (8.65 ± 0.10 %).

The aim of the study is to evaluate the efficiency of the removal of Cd(II), Cu(II), Fe(II) and Zn(II) from aqueous solutions by unmodified BTF. The effect of various operating parameters such as pH, contact time, metal ions concentration, adsorbent dose and change in $[M^{2+}]$ /biomass was studied. The adsorption isotherm study was also carried out on two isotherm models, namely Langmuir and Freundlich. The adsorption capacity were determined and compared by first and second order kinetic models.

MATERIALS AND METHODS

Biosorbent material

BTF from the family of *Musa acuminata x balbisiana* Colla (ABB Group) cv 'Pisang Awak' were obtained locally, Penang, Malaysia. The pseudostems were chopped into cubes of average size of 2 cm x 2 cm. The cubes were submerged in boiling water for 1 hr and then dried in an oven at 70 °C until a constant weight was obtained. The resulting material was ground using a Waring Commercial high speed blender and sieved to isolate fibers of the size 212 - 350 micron. The native metal content the BTF were observed by using a scanning electron microscopy (SEM-EDX) machine Model Leica Cambridge AS-360 at an accelerating voltage 15kV. Prior to examination, a surface of specimen was coated with a thin layer of gold approximately 30 nm using Sputter Coater Polaron SC 515.

Metal Solution

Cd(II), Cu(II), Fe(II) and Zn(II) standard solutions (1000 ± 2 mg/L) from Merck were diluted to desired concentrations for Atomic Absorption Spectroscopy (AAS) analysis. The experiment was conducted at pH value range 2 to 6. The pH was adjusted by adding appropriate amount of either 0.1 M NaOH or 0.1 M HCl solution before each experiment

Equilibrium studies

Adsorption experiments were carried out by adding 0.2 g of sorbent into 250-mL Erlenmeyer flasks containing 50 mL solutions of different concentrations (1, 10 and 100 mg/L) of metal ions. The temperature was controlled at 25 °C. Agitation was provided at 150 rpm for 180 min. The initial and equilibrium metal concentrations were determined by absorbance measurement using the Atomic absorption Spectroscopy (AAAnalyst 700, Perkin-Elmer, Waltham, MA, USA). When the equilibrium was established, the supernatant was carefully filtered through Whatman filter paper (No. 1) which was pre-saturated with distilled water. It is worthwhile to note that no adsorption of the metals occurred on the filter paper: a comparative study was done by measuring the concentration of the metal solution before and after filtering, and the result showed insignificant variation of concentration of the metal solution meaning that the amount of the metals adsorbed on the filter paper, if any, was negligible. It was then computed to metal concentration using standard calibration curve. The adsorption at equilibrium, q_e (mg/g), was calculated using equation (1).

$$q_e = (C_o - C_e) \frac{V}{W} \quad (1)$$

where C_o and C_e (mg/L) are the liquid-phase concentrations of metals at initial and equilibrium, respectively. V is the volume (L) of the solution and W is the weight (g) of dry sorbent. For the determination of rate of sorption and the sorption equilibrium time, the residual metal in the supernatant was determined by allowing metal-BTF contact for different periods between 5 and 180 min. The metal-BTF sorption suspension was equilibrated at different pH values of 2 – 6. For the adsorption isotherms studies, metal concentrations used for sorption ranged between 1 and 500 mg/L. The quantity of biomass was varied between 0.1 and 1.0 g to determine the BTF required for optimum level of sorption.

Treatments of Banana Trunk Fibers

The BTF were modified according to the methods reported in literature: (i) mercerization, the fibers were immersed in 5% NaOH solution for 48 hr at 25 °C¹², (ii) acetylation, the mercerized fibers were soaked in glacial acetic acid for 1 hr, separated by decantation and then soaked in acetic anhydride containing 2 drops of concentrated H_2SO_4 for 2 min¹³, (iii) formaldehyde treatment, using 1% formaldehyde in the weight to volume ratio of 1:5 at 50 °C for 4 hr¹⁴,

(iv) peroxide treatment, the mercerized fibers (30 g) were immersed in 1 L of a 6% solution of benzoyl peroxide in acetone for 30 min¹³, (v) stearic acid treatment, a mixture containing 1.0 g of the fibers, 0.2 g of stearic acid, 2 drops of concentrated H_2SO_4 in 100 mL of n-hexane was refluxed in a Dean–Stark apparatus at 65 °C for 6 hr¹⁵, and (vi) sulphuric acid treatment, 1 : 1 weight ratio of the fibers : concentrated H_2SO_4 was heated in a muffle furnace for 24 h at 150 °C¹⁴. All resulting fibers were washed ample amount of water till a pH close to neutral was obtained.

RESULTS AND DISCUSSION

Elemental and Surface Area Analysis

The results obtained by energy dispersive X-ray (EDX) analysis of BTF are presented in Figure 1. It shows that BTF contained several elements such as carbon (40.25 %), oxygen (55.85%), potassium (2.41%), calcium (1.49%) and the presence of the metals under study were not observed. Surface area of BTF was characterized according to method described by Horsfall and Spiff¹⁶ and was found to be $28.75 \pm 1.57 \text{ m}^2/\text{g}$.

Figure 1: Energy dispersive X-ray (EDX) scan of BTF

Effect of pH on metal ion sorption

pH of solution has been identified as the most important variable governing metal ions uptake because it influences the ionization of functional groups at the surface of a sorbent and hydrogen ions themselves may compete strongly with the adsorbates^{17,18}. Hence, comparative studies on metal ions uptake must be carried out in solutions of similar pH value as any variation in the pH can drastically change the adsorption capacity of a sorbent¹⁹. With this in view, the uptake of Cd(II), Cu(II), Fe(II) and Zn(II) by BTF was investigated at various pH values (Figure 2). At the pH 2, it was observed that the sorptions were poor. This was attributed to the active sites being widely protonated which limits the adsorbing sites for the metal ions²⁰. In the pH range of 3 – 5, a prominent increase in the sorptions was observed. The increase in metal removal as the pH increases can be explained on the basis of decrease in competition between protons and metal cations for the same binding sites²¹. Furthermore, the decrease in the positive surface charges resulting in a lower electrostatic repulsion between the surface and metal ions²². Further increase in sorptions was insignificant as the optimum biosorption for all the four metals was reached at about pH 5.

Figure 2: Dependence of q_e of Cd(II), Cu(II), Fe(II) and Zn(II) with pH at 25 °C (concentration = 10 mg/L, volume = 50 mL, BTF dosage = 0.2 g, agitation speed = 150 rpm and contact time = 120 min)

Effect of contact time and metal concentration on metal adsorption

Figure 3 illustrates the time-course studies on sorption of Cd(II), Cu(II), Fe(II) and Zn(II) that were performed by contacting 10 mg/L of the solutions containing metal ions at pH 5 with 0.2 g of BTF in 50 mL of the solutions. All the four metal ions showed a fast rate sorption during the initial 15 min (first stage) and the equilibrium (second stage) was reached at about 60 mins. The two-stage sorption, the first stage which is quantitatively predominant and the second slower stage which is quantitatively insignificant, has been extensively reported in literature²³. The rapid stage is attributed to the abundant availability of active sites on the biomass and with the gradual occupancy of these sites, the sorption becomes less efficient in the slower stage²⁴. The adsorption capacity (q_e) for Cd(II), Cu(II), Fe(II) and Zn(II) of 2.43, 2.39, 2.42 and 2.18 mg/g, respectively. These results are in keeping with conclusion by Romera et al.,²⁵ Pejic et al.²⁶ and Nasernejad et al.²⁷. The uptake level of the metal ions can be explained, similar to that provided by Okieimen et al.²⁸ and Ricordel et al.²⁹ in terms of (i) the difference in the ionic size of metals, (ii) the nature and distribution of active groups on the biosorbent, (iii) the mode of interaction between the metal ions and the biosorbent (iv) hydration energy, (v) ionic mobility and (vi) diffusion coefficient.

Figure 3: Dependence of q_e of Cd(II), Cu(II), Fe(II) and Zn(II) with time at 25 °C (concentration = 10 mg/L, volume = 50 mL, BTF dosage = 0.2 g, agitation speed = 150 rpm and pH = 5)

Optimization of amount of adsorbent

This adsorption study was carried out with 10 mg/L metal solution at pH 5 in an orbital shaker agitated at 150 rpm with 50 mL of the metal ions solution in a 250 mL Erlenmeyer flask. Results shown in Figure 4 indicate that the adsorbent dosage apparently increases proportionately to the availability of the adsorbent sites. The increase of adsorbent sites and surface area of contact with the metals increases the amount of metal uptakes and consequently leads to a better adsorption. This observed trend is mainly due to the increase in sorptive surface area and availability of more adsorption sites.

Figure 4: Dependence of q_e of Cd(II), Cu(II), Fe(II) and Zn(II) with weight of fibers (g) at 25 °C (concentration = 10 mg/L, volume = 50 mL, agitation speed = 150 rpm, time = 60 min and pH = 5)

Concentration dependent study

The experimental results of the sorption of the metals on BTF at various concentrations are shown in Figure 5. The uptake rate of the metal ions will increase along with increasing concentration if the amount of biomass is kept unchanged. At low concentrations metals adsorb by available sites and with increasing metal concentrations the sites become saturated. The adsorption experiments related to the concentration of metals were carried out over a range of 1 – 500 mg/L at pH 5 using 0.2 g of the fibers in 50 mL of metal ion solutions with an agitation speed of 150 rpm. The adsorption capacity of Cd(II), Cu(II), Fe(II) and Zn(II) increased from 0.24 to 20.82, 0.22 to 23.18, 0.22 to 22.67 and 0.19 to 22.23 mg/g, respectively. The metal concentration provides the necessary driving force to overcome the resistances to the mass transfer of metal between the aqueous and the solid phases. The increase in concentration also enhances the interaction between metal and the sorbent. Therefore, an increase in concentration of the metals enhances the adsorption uptake of metal ions. This indicates that the metal ions concentration plays an important role in the adsorption capacity of metal onto the sorbent. It was also observed that the q_e value increases as the C_e value increased¹⁶. It is also worthwhile to note that the q_e of all the four metal ions were steep at lower equilibrium concentration which is desirable for a sorbent to possess a high affinity for the sorbate species³⁰.

Figure 5: Dependence of q_e of Cd(II), Cu(II), Fe(II) and Zn(II) with concentration (mg/L) at 25 °C (BTF dosage = 0.2 g, volume = 50 mL, agitation speed = 150 rpm, time = 60 min and pH = 5)

Effect of change in $[M^{2+}]$ /biomass

Various $[M^{2+}]$ /biomass ratio were obtained by increasing the mass of BTF while the concentration and volume of the metal ions solution are kept constant. The quantity of BTF was varied between 0.5 and 20 g L⁻¹ to determine the optimum quantity of biomass needed for maximum sorption. From 10 mg/L metal ion solution at pH 5, the q_e of Cd(II), Cu(II), Fe(II) and Zn(II) of 1.21, 1.19, 1.26 and 1.05 mg/g, respectively achieved using 10 g L⁻¹ BTF. Further increase in the BTF weight to 20 g L⁻¹ increased the adsorption capacity. Table 1 indicates the change in $[M^{2+}]$ /biomass based on the concentration of the metal solution. The results obtained indicate a decrease in $[M^{2+}]$ /biomass. This is attributed to an increase in the adsorption of these metal ions due to the increase of BTF biomass. The increase in BTF biomass increases the adsorption surface area of the biomass³¹. The obtained results are in keeping with the conclusion by Saeed et al³².

Table 1: Effect of change in $[M^{2+}]$ /biomass ratio on biosorption of Cd(II), Cu(II), Fe(II) and Zn(II) (metal concentration = 10 mg/L, pH 5, volume = 0.2 L, agitation speed = 150 rpm, time = 60 min).

Biomass Concentration (g/L)	$[M^{2+}]$ /biomass (mg/g)	Metal adsorbed, q_e (mg/g)			
		Cd(II)	Cu(II)	Fe(II)	Zn(II)
1	10	8.97	8.62	8.90	8.16
2	5	4.46	4.38	4.41	4.08
4	2.5	2.43	2.39	2.42	2.18
10	1	1.21	1.19	1.26	1.05
20	0.5	0.46	0.48	0.65	0.41

Adsorption Isotherms

Langmuir isotherm model assumes the uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface³³. The linear form of Langmuir isotherm equation is given in equation (2).

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{1}{Q_o} C_e \quad (2)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Q_o and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. When C_e/q_e was plotted against C_e , a straight line with slope of $1/Q_o$ was obtained. The value of Q_o was determined from the Langmuir plot at the concentration range 1 to 500 mg/L and then the b value was calculated and tabulated in Table 2. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given in equation (3).

$$R_L = \frac{1}{1 + bC_o} \quad (3)$$

The values of R_L were found to be 0.385, 0.769, 0.417 and 0.935 for Cd(II), Cu(II), Zn(II) and Fe(II), respectively suggesting the isotherm to be favorable at the concentrations studied. The Freundlich isotherm model³⁴ considers a heterogeneous adsorption surface that has unequal available sites with different energies of adsorption and can be represented by equation (4).

$$\ln q_e = \ln K_f + \frac{1}{n} (\ln C_e) \quad (4)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), K_f and n are Freundlich constants. The Freundlich constants were derived from the slopes and intercepts of $\log q_e$ versus $\log C_e$ and are presented in Table 2. K_f can be defined as the adsorption capacity that represents the quantity of metal ions adsorbed onto the fibers for a unit equilibrium concentration and value of $n > 1$ giving an indication of favorability of the adsorption process³⁵. In this work, it is found that K_f increased in the order of Zn(II) (1.74 mg/g) < Cu(II) (2.68 mg/g) < Fe(II) (6.58 mg/g) < Cd(II) (8.49 mg/g) and the value of n to be 1.016, 1.036, 1.138 and 1.149 for Zn(II), Cu(II), Fe(II) and Cd(II), respectively. As seen from the Table 2, a high regression correlation coefficient, R^2 , was shown by the Freundlich model for all the metal ions. This indicates that the Freundlich model is very suitable for describing the sorption equilibrium of the metal ions by the BTF. When the linearity of the plots of the Freundlich and Langmuir models was compared, it is found that the former has a better fit. Thus it is reasonable to conclude that the adsorption of the metal ions on the fibers that consist of heterogeneous adsorption sites that are very similar to each other in respect of adsorption phenomenon.

Table 2: Langmuir and Freundlich isotherm constants and correlation coefficients for biosorption of Cd(II), Cu(II), Fe(II) and Zn(II) at ambient temperature (25 °C).

Isotherms	Metal ions			
	Cd(II)	Cu(II)	Fe(II)	Zn(II)
Langmuir				
Q_o (mg/g)	71.43	63.69	54.35	263.15
b (mg/L)	0.16	0.03	0.14	0.007
R^2	0.891	0.747	0.991	0.978
Freundlich				
K_f (mg/g)	8.49	2.68	6.58	1.74
n	1.149	1.036	1.138	1.016
R^2	0.997	0.999	0.997	0.998

Adsorption Kinetics

Two simplified kinetic models were adopted to examine the mechanism of the adsorption process. First, the kinetics of adsorption was analyzed by the Lagergren pseudo-first-order equation³⁶ as depicted in equation (5).

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (5)$$

where q_e and q_t are the amounts of the metals adsorbed (mg/g) at

equilibrium and at time t (min), respectively, and k_1 (min^{-1}) is the rate constant adsorption. Values of k_1 at ambient temperature were calculated from the plots of $\log(q_e - q_t)$ versus t for an concentration of 10 mg/L for the metals. The set of R^2 values obtained were poor and the experimental q_e values did not agree with the calculated values obtained from the linear plots (Table 3). On the other hand, the pseudo-second-order equation based on equilibrium adsorption³⁷ is expressed as equation (6):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

where k_2 (g/mg min) is the rate constant of second-order adsorption. The linear plot of t/q_t versus t at ambient temperature yielded set of R^2 values that are greater than 0.999 for all the metal at 10 mg/L. It also showed a good agreement between the experimental and the calculated q_e values (Table 3), indicating the applicability of this model to describe the adsorption process of the metals onto the fibers.

Table 3: Comparison of the pseudo-first-order, pseudo-second-order adsorption rate constants and calculated and experimental q_e values obtained for a concentration of 10 mg/L of Cd(II), Cu(II), Fe(II) and Zn(II).

Metal Ions	Concentrations (mg/L)	q_e (Exp)	Pseudo First Order Kinetic Model			Pseudo Second Order Kinetic Model		
			k_1	q_e (Cal)	R^2	k_2	q_e (Cal)	R^2
Cd(II)	10	2.433	0.035	0.088	0.962	1.04	2.176	1.000
Cu(II)	10	2.390	0.033	0.142	0.978	0.63	2.284	0.999
Fe(II)	10	2.415	0.015	0.030	0.941	3.54	2.409	0.999
Zn(II)	10	2.181	0.038	0.084	0.918	1.16	2.186	1.000

Adsorption capacity of the modified biomass

The adsorption experiment related to the treated banana fibers were carried out at 10 mg/L at pH 5 using 1.0 g/L of the fibers with an agitation speed of 150 rpm. Mercerization and acetylation leads to the leaching out of the amorphous waxy cuticle layer. Peroxide treatment is found to fibrillate the fibers due to the leaching out of the waxes, gums and pectic substances¹². Carvalho et al.,³⁸ reported that formaldehyde treatment had reduced the fiber elasticity but increased the tensile strength. The stearic acid treatment reduced the moisture content of the fiber and improved the mechanical properties of the fibers³⁹. Acid treatment is generally used for cleaning the cell wall and replacing the natural mix of ionic species bound on the cell wall with protons and other functional groups exposing new active sites for metal removal causing increase in sorption capacity⁴⁰⁻⁴². It is observed in this study (Tab.4) that all modified BTF except peroxide treated BTF showed a further slight increase in sorption capacity. The order of the sorption capacity is sulphuric acid treated BTF > mercerized BTF, formaldehyde treated BTF > acetylated BTF, stearic acid treated BTF > untreated BTF > peroxide treated BTF. The slight drop in sorption capacity of the peroxide treated BTF is attributed to delignification of the fibers¹² since lignin plays an important role in heavy metal adsorption⁴³. The slight variation in the adsorption capacity of the modified BTF as compared to that of the unmodified BTF suggests the latter is by its nature already an efficient biosorbent for the removal of Cd(II), Cu(II), Fe(II) and Zn(II).

Table 4: q_e values for untreated and treated BTF

	Metal adsorbed, q_e (mg/g)			
	Cd(II)	Cu(II)	Fe(II)	Zn(II)
Untreated	2.43	2.39	2.42	2.18
Types of Treatment				
Mercerization	2.45	2.43	2.44	2.23
Acetylation	2.44	2.41	2.43	2.19
Formaldehyde treatment	2.45	2.41	2.44	2.21
Peroxide treatment	2.41	2.38	2.40	2.16
Stearic acid treatment	2.44	2.41	2.43	2.19
Sulphuric acid treatment	2.48	2.44	2.45	2.25

CONCLUSION

The present work establishes that banana pseudostem fibers, an agro-waste

is an efficient biosorbent in the removal of Cd(II), Cu(II), Fe(II) and Zn(II) ions from aqueous solutions at pH 5. The kinetics of sorption of the four metal ions on BTF follows a pseudo-second-order pattern. Moreover, sorption capacity is strongly dependent on the metal concentration and pH of solution. Banana trunk fibers are very cheap, easily available and renewable. This study revealed that this biosorbent could be used as a tool for the development of low-cost biomaterial-for the treatment of heavy metal waste. It is also worthwhile to note that by introducing new chemical sites on the biomass may not necessary aid in the adsorption capacity of BTF.

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