Biosorption of zinc (II) ions from aqueous solution using msasa tree (*Brachystegia spiciformis*) leaf powder

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Abstract

The purpose of this study was to explore the effectiveness of the Brachystegia spiciformis leaf powder for the removal of zinc (II) ions from aqueous solution. Batch experiments for the effect of pH, contact time, biomass dose and initial metal ion concentration were carried out in the laboratory. The adsorbent was characterized before and after biosorption of zinc ions by Fourier Transform-Infrared Spectroscopy (FT-IR). The investigation showed that the highest metal uptake was at solution pH 6, contact time of 120 mins and biomass dose of 2.0 g. The experimental data for the biosorption zinc (II) ions by Brachystegia spiciformis leaf powder was modelled to the Langmuir and Freundlich isotherms. The biosorption of zinc (II) ions fits better to the Langmuir than to the Freundlich model having correlation coefficients of 0.9902 and 0.9569 respectively. The maximum adsorption capacity Q_{max} was found to be 1.85 mg/g indicating the ability of the biosorbent to remove zinc from aqueous solution.

Keywords: *Brachystegia spiciformis*, biosorption, Zn (II) ions, adsorption isotherms.

Introduction

Heavy metal ions are nowadays among the most important pollutants in surface and ground water. The rapid and tremendous industrial development during the last decade has increased heavy metal pollution in the environment. Heavy metals are non-biodegradable and have a tendency of accumulating inside the human body when they are incorporated through the food chain (Wang and Chen, 2009). Major industrial operations units like metallurgy, steel production, paint and pigment industry, copper smelting, mining, electroplating, galvanizing units and metal finishing significantly contribute to zinc pollution in natural water streams (Ahluwalia and Goyal, 2007). Soluble zinc acid salts in large doses (about 10 g), have caused internal organ damage and death (Gupta and Sharma, 2003).

Various conventional remedial technologies like reverse osmosis, electro-coagulation and flocculation,

23

solvent extraction, hydroxide precipitation and membrane separation have been adopted to remove heavy metals across liquid phases (Abu Al-Rub *et al.*, 2006b). These aforementioned techniques are all generally expensive and might possibly generate by-products dangerous to human health (Sabriye *et al.*, 2005).

For these reasons, alternative technologies that are cheap, efficient and practical at low metal concentrations are being explored. Biosorption has been emerging as the most prominent alternative technology for this purpose (Matheickal and Yu, 1999). Recent studies have shown that heavy metals can be removed using plant materials such an palm pressed fibers, coconut husk, water fern, peat moss, duck weed, lignocellulosic substrate extracted from wheat bran and fungi (Fagundes-Klen *et al.*, 2007). In particular, recent studies have also revealed the removal of zinc (II) ions from aqueous solution using *Reynoutria japonica* leaves (Melèáková and Rùžoviè, 2010), pulm tree leaves (Abu Al-Rub, 2006a) and *erythrina variegate* leaves (Venkateswarlu *et al.*, 2008).

So far, literature does not indicate specific studies on the removal of Zn (II) ions using *Brachystegia spiciformis* leaves. *Brachystegia spiciformis* remain in abundance as an indigenous plant in Southern Africa. This study was aimed at utilizing *Brachystegia spiciformis* leaves as a cheap method for Zn (II) ions removal from aqueous solution.

Materials and methods

Chemicals and instruments
All the chemicals used in this study were of analytical grade. $ZnSO_4.7H_2O$, HNO_3 and NaOH were supplied by Skylabs. Instruments used were an analytical balance (GA-110 OHAUS), pH meter (Az-8601), Flame Atomic Absorption Spectrometer (FAAS) (Shimadzu, 50B, Japan), Fourier Transform Infra-red Spectrophotometer (FT-IR) (Digilab Merlin 2000 model Samitar), heating oven (Cycilo DHG-9070A) and a mechanical shaker (Vasal-401 208 Rajendra Electrical).

Preparation of biosorbent
Mature *Brachystegia spiciformis* leaves were collected from Midlands State University grounds (18° 55' 0" South, 29° 49' 0" East), Gweru, Zimbabwe. The samples were collected in clean polythene bags, washed with distilled water repeatedly to remove dust and soluble impurities, stored in a shade at room temperature and then sun dried until crisp. It was then ground and passed through a 300 ìm particle size sieve. The resulting powder was washed with distilled water several times to remove colour and turbidity, oven dried at 70æ%C to constant mass and then put in air tight bottles and stored in a desiccator for further use in batch experiments.

24

Characterization of biosorbent

FT-IR spectroscopy was used to identify the functional groups in the *Brachystegia spiciformis* biosorbent. FT-IR spectra of the biosorbent before and after biosorption of Zn (II) were recorded in the range 4000-400 cm^{-1} using a Digilab Merlin 2000 model FT-IR spectrometer with KBr discs (Sigma).

Preparation of Zn (II) stock solution

Stock solution (1000 mg/L) of Zn (II) was prepared by dissolving 4.439 g of $ZnSO_4.7H_2O$ in deionized water. Synthetic solutions of different Zn (II) concentrations for batch experiments and calibration curve were prepared by appropriate dilutions of this stock solution. The pH of the solution was adjusted using either 0.1 M HNO_3 or 0.1 M NaOH solutions.

Batch experiments

Batch experiments were carried out using 100 mL of Zn (II) solution of known concentrations in 250 mL conical flasks at a specified pH, contact time and adsorbent dosage. In each case the mixture was agitated on a shaker at a speed of 120 rpm at room temperature for a specified amount of time which was sufficient for the zinc uptake process to reach equilibrium. Optimization studies were performed at room temperature at different pH (2, 4, 6, 8, 10 and 12), sorbent amount (0.5 g, 1.0 g, 1.5 g, 2.0 g, 2.5 g and 3.0 g) initial Zn (II) concentration (20, 40, 60, 80, 100, 120 and 140 mg/L) and contact time (30, 60, 90, 120, 150 and 180 mins) to obtain the equilibrium data. All experiments were performed in replicates with reprocidubility within at most 5% error and the results average was reported.

After attainment of equilibrium, the samples were filtered through Whatman No. 1 filter paper and the residual Zn (II) concentration in the filtrate was estimated using the FAAS at wave length of 213.9 nm. The amount of metal ion adsorbed per gram of biomass was calculated according to the expression below ;

$$Q_e = \frac{(C_0 - C_e)V}{M} \quad \dots\dots\dots\dots\dots\dots(1)$$

Where where, Q_e is the amount of Zn (II) biosorbed per gram of biomass (mg/g), C_0 and C_e are the initial and equilibrium concentrations of Zn (II) (mg/L), V the volume of solution (L), and M is the mass of biosorbent (g). The equilibrium data obtained form the batch experiments was used to test the applicability of Langmuir and Freundlich isotherm models from their linearized equations.

Results and Discussion

FT-IR analysis of Brachystegia spiciformis leaf powder

The FT-IR spectra of *Brachystegia spiciformis* indicated the presence of hydroxyl, carboxyl, carbonyl and amine groups which are important sorption sites (Fig. 1). A peak at 3400 cm^{-1} indicates the presence of OH and NH groups. The band at 2920 cm^{-1} indicates C-H stretching vibration of methyl, methylene and methoxy groups. Peaks at 1640

cm⁻¹, 1400 cm⁻¹ and 1040 cm⁻¹ indicate the presence of carbonyl, ionic carboxylic groups and stretching vibrations of C-OH alcohols respectively. After biosorpton the peak at 3400 cm⁻¹ lost intensity due to the participation of OH and NH groups in sorption. The shift of the carbonyl group from 1640 cm⁻¹ to about 1600 cm⁻¹ indicated its involvement in sorption (Suleman *et al.*, 2009). The change in intensity of the peaks at 1400 cm⁻¹ and 1040 cm⁻¹ after sorption also reveal the involvement of ionic carboxyl groups and C-OH alcohols respectively. Similar FT-IR results were also reported for the biosorption of metals on eucalyptus biomass (Leon *et al.*, 2011).
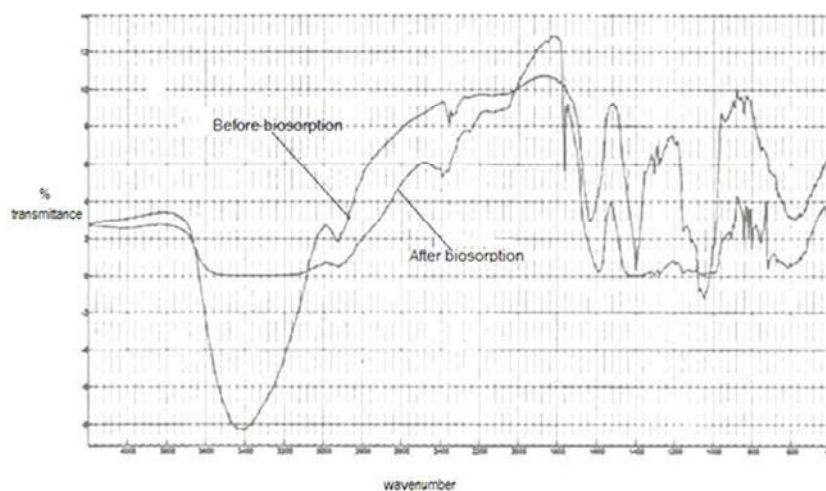
Fig. 1: FT-IR spectrum of *Brachystegia spiciformis* before and after biosorption

Effect of pH

Biosorption processes are strongly pH dependent and different species may have different pH optima, possibly due to the different solution chemistry of the species (Pagnanelli *et al.*, 2003). The influence of pH on the adsorption of Zn (II) ions was studied within the range of 2.0-12 as shown in Fig. 2. The results showed that the uptake of the metal increases with an increase in solution pH up to pH 6. Q_e was initially low at pH 2 due to protonation of the biomass active sites by H⁺ ions and this led to the overall surface charge on the cells to be positive, and thus the approach of positively charged zinc metal ions was limited. At pH values around 6, there is a net negative charge on the cell wall components, which promoted reaction with metal ions. After pH 6, biosorption capacity decreased because of the presence of hydroxyl ions which resulted in precipitation of the metal ions to form $Zn(OH)_2$ (Bailey *et al.*, 1999).
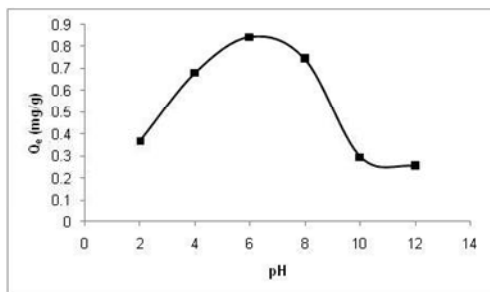
26

Fig. 2: Effect of pH on biosorption of zinc (II) ions

Effect of contact time

There is a general increase in the adsorption of the zinc metal ions with an increase in contact time up to 120 minutes (Fig.3). However, the adsorption reached equilibrium in 120 minutes. The higher sorption rate in the first 60 minutes may be a result of an increased number of vacant sites available on the adsorbent surface. With the progressive occupation of these sites, the process became slower resulting in a decrease in the sorption capacity after 120 minutes since there were no more vacant sites for the metal ions to occupy (Bishnoi *et al.*, 2007).
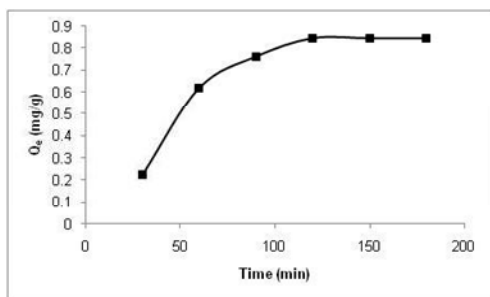

Fig. 3: Effect of contact time on biosorption of zinc (II) ions

Effect of adsorbent dosage

The effect of adsorbent dosage was investigated by varying the biomass from 0.5 to 3.0 g (Fig. 4). The fraction of the zinc metal ions removed from the aqueous phase increased with an increase in the dosage from 0.5 to about 2.0 g because the numbers of active sites available for metal biosorption were more as the dosage increased. There was no significant change beyond the dose of 2.0 g possibly because of the overlap of biosorbent sites, electrostatic interactions and poor mixing at high biomass concentrations (Aksu, 2001).
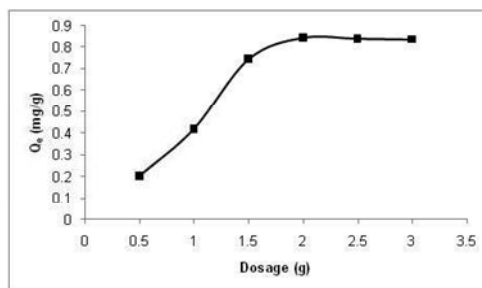

Fig. 4: Effect of adsorbent dosage on bisorption of zinc (II) ions

Effect of initial zinc concentration

It was observed that the biosorption capacity of the zinc metal ions to the surface of biomass increased as initial metal concentration was increased from 20 to 100 mg/g (Fig. 5). The reason for this could be the increased migration of zinc (II) ions into the vacant sites of the sorbent at high initial zinc (II) ions (Michalak *et al.*, 2007). Beyond 100 mg/g the absorption uptake remained constant. This might have been due to the agglomeration of adsorbent particles at

higher concentration leading to a decrease in the total surface area of the adsorbent particles available for adsorption. The results correlate with the observations by Melèáková and Rùžoviè (2010) in the biosorption of zinc (II) ions by *Reynoutria japonica* leaves.
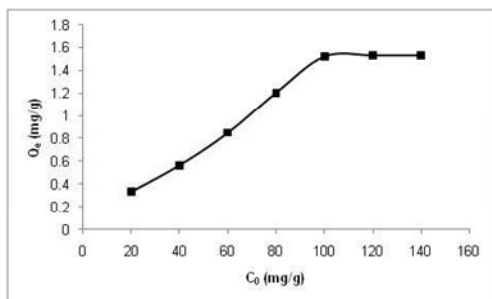

Fig. 5: *Effect of initial zinc (II) ions concentration on biosorption capacity*

Adsorption isotherms
An isotherm is the equilibrium relationship between the concentration in the fluid phase and the concentration in the adsorbent at a given temperature. The isotherms are important in the design of adsorption systems. The Langmuir and Freundlich isotherms are the most widely applied. The Langmuir isotherm assumes that biosorption takes place with a finite number of identical sites and uniform adsorption energies where there are interactions between the adsorbed molecules. It can be linearized as:

$$\frac{C_e}{Q_e} = \frac{1}{bQ_{max}} + \frac{C_e}{Q_{max}} \quad \text{..........................(2)}$$

Where Q_e is the zinc ions adsorbed in mg/g, b is the Langmuir constant related to energy of sorption in L/mg, Q_{max} is the maximum sorption capacity corresponding to complete monolayer coverage in mg/g and C_e is the equilibrium solute concentration in mg/L. A plot of C_e/Q_e against C_e from the linearized equation gave a straight line as shown in Fig. 6. The Langmuir parameters for the biosorption of zinc on *Brachystegia spiciformis* leaves were found from the slopes and intercepts of the straight line shown in Fig. 6 and are listed in Table 1. The correlation coefficient of the linear regression (R^2 = 0.9902) indicate that the Langmuir model could describe the biosorption of zinc leaves. The maximum adsoption capacity Q_{max} was found to be 1.85 mg/g and was comparable to other biosorbents in literature. The Q_{max} values for the removal of zinc for other biosorbents used previously by other researchers were lower than that obtained in this study [(cork biomass, 0.34 mg/g (Natalia *et al.*, 2004); hazelnut shells, 1.78 mg/g (Cimino *et al.*, 2000)].
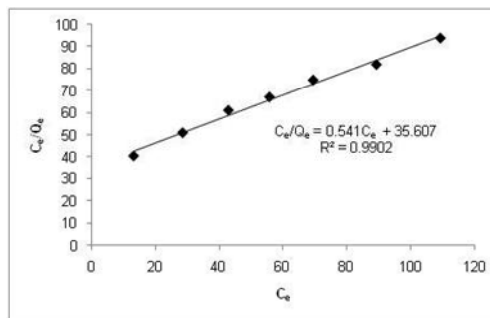

Fig. 6: *Langmuir isotherm for biosorption of zinc (II) ions*

28

The empirical Freundlich isotherm model is based on a heterogenous surface. This can be linearized as;

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad \ldots\ldots\ldots\ldots(3)$$

Where Q_e is the amount of zinc uptake by *Brachystegia spiciformis* biomass (mg/g), C_e is equilibrium adsorbate concentration in mg/L, K_f is the adsorbent capacity measure and n is the adsorption intensity.

Fig. 7 shows Freundlich isotherm model with the correlation coefficient (R^2 = 0.9569) being lower than that obtained for the Langmuir isotherm. The values of K_f (0.041) and n (1.235) were calculated from the intercept and slope respectively of the plot of $\log Q_e$ against $\log C_e$. The obtained n, K_f and R^2 values indicate that the sorption process in less heterogeneous and thus the Langmuir model is more applicable in this case. The Langmuir and Freundlich isotherm parameters are shown in Table 1.
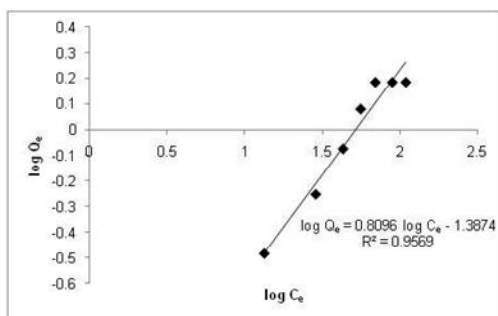

Fig. 7: *Freundlich isotherm for biosorption of zinc (II) ions*

Table 1: Langmuir and Freundlich parameters for biosorption of zinc ions by *Brachystegia spiciformis*

Adsorption Isotherm	Parameter	Value
Langmuir	Q_{max} (mg/g)	1.85
	b (L/g)	0.0152
	R^2	0.9902
Freundlich	K_f (mg/g)(L/mg)ⁿ	0.041
	n (g/L)	1.235
	R^2	0.9569

Conclusion

This work has demonstrated the possibility of utilization of biomass of *Brachystegia spiciformis* for biosorption of zinc ions from aqueous solution. The binding capacity of Zn^{2+} ions to biosorbent has been shown to depend upon optimum pH of 6, contact time of 120 minutes and optimum adsorbent dosage of 2 g. The FT-IR analysis showed the involvement of hydroxyl, carbonyl, amine and carboxyl groups in the uptake of zinc. The uptake of zinc showed an increase with an increase in initial metal concentration. The Langmuir isotherm model best described the sorption of zinc onto *Brachystegia spiciformis* R^2 value being 0.9902 and the maximum adsorption capacity of 1.85 mg/g.

Acknowledgements

29

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30

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