Original Research Article

Efficiency of pre-treated *Moringa oleifera* for the removal of Cd^{2+} and Zn^{2+} ions from wastewaters

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ARTICLE INFO

ABSTRACT

Increased human activities have led to a rise in environmental pollution. Conventional methods of wastewater treatment are costly and sometimes not efficient. Use of *Moringa oleifera* has been promoted as a cost effective method. Its use as a biosorbent for sequestration of Zn and Cd for both single and mixed systems was investigated. The results show that metal uptake increased with contact time, based on a solid-to-liquid ratio of 1:100 with maximum adsorption occurring at pH 4. However, metal biosorption decreased drastically with increasing pH and Zn^{2+} ions were more efficiently biosorbed than Cd^{2+}. The data fitted into both the Langmuir and Freundlich adsorption isotherms and *Moringa* treated with $KMnO_4$ further enhanced heavy metal biosorption by offering better properties.

1. Introduction

Water bodies are overwhelmed with bacteria and waste matter and among toxic substances reaching hazardous levels are heavy metals (Regine and Volesky, 2000). Those of concern include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, silver, gold, and nickel (Ahalya et al., 2003). Metals are of great concern because they are non-biodegradable and thus persistent; hence they are toxic, bioaccumulative and a threat to human life and the environment. It has been established that dissolved metals, particularly the heavy metals escaping into the environment pose a serious health risk because they tend to accumulate in food chains (Cheresources, 2009; Paknikar et al., 2003).

The traditional methods for the removal of heavy metals from water are generally expensive or inadequate to treat highly diluted solutions. Biosorption is the binding and concentration of heavy metals from aqueous solutions (Macaskie et al., 1992) and is a cost effective alternative that can be appropriate for treating effluents with low metal concentrations (Mata et al., 2008). Heavy metals discharged from many industries (Gupta and Rastogi, 2008; Gupta et al., 2006) can innovatively be removed by utilising inexpensive dead biomass to sequester them during biosorption process. Dead biomass has higher metal uptake rates, being the process nutrient independent (Mehta and Gaur, 2005). Pioneering research on biosorption has led to the identification of a number of microbial types (Benedict et al., 1981) that can sequester metals. Some of these are biomass waste by-products of large scale industrial fermentations such as *Rhizopus* or the bacterium *Bacillus subtilis*.

The present paper reports experimental results on the ability of *Moringa oleifera* to biosorb the two bivalent heavy

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metal ions, Zn^{2+} and Cd^{2+}. This was investigated by measuring the efficiency of the metal removal from artificial aqueous solution by varying contact time and pH in a batch-process series of experiments. The concentration of metal ions adsorbed in each case was determined by inductively coupled plasma – optical emission spectrometer (ICP-OES).

2. Materials and methods

Dry Moringa seeds were de-shelled by hand and crushed by pestle and mortar, washed using distilled de-ionised water, dried and sieved through stainless steel sieves of <1 mm pore size. Forty grams of powder was then shaken with 400 mL of acetone/ethanol mixture for 30 min, centrifuged and dried in the oven at 30 °C overnight.

Batch experiments involving single and mixed heavy metals Zn and Cd were then carried out with stirring. The corresponding analytical grade nitrate metal salts containing 10,000 mg/L Zn^{2+} and Cd^{2+} were used to prepare stock solutions. Serial dilution with distilled de-ionised water gave lower concentrations of 100 mg/L from which 0.5 mL portions were transferred into 50 mL plastic containers and the volume topped up with distilled de-ionised water. Dilute solutions of 0.1 M NaOH and 0.1 M HNO_3 were used to adjust pH to give the required whole number values from 4 to 9.

Absorbance of known standard solutions of each metal ion was determined in order to prepare calibration graphs before taking biosorption values. To the contents in each plastic bottle and at a particular pH, 0.5 g of Moringa was added followed by periodic shaking and allowed to settle before taking absorbance measurements. Three sets of experiments were carried out simultaneously; one set involved metal ions in water without Moringa, another with Moringa alone in water and the other having metal ions in water with Moringa, all in triplicates. Moringa of <1 mm pore size were used for both single and mixed metal ion systems at optimum pH 4. Further experiments were conducted using modified Moringa at pH 4 by treating <1 mm pore size Moringa with 10 mM $KMnO_4$ (aq.) at 30 °C for 30 min followed by washing thoroughly with distilled de-ionised water, centrifuging and then drying in an oven at the same temperature overnight.

Metal concentrations were measured by ICP-OES at time intervals of 5 min over a period exceeding 60 min. Biosorption of mixed metal ions by Moringa was done at the maximum pH 4. The concentration of metal ions biosorbed was found by subtracting the remaining concentrations from the original values and dividing by the corresponding RFM for each metal to determine milliequivalent value, q (mmol/g).

The ICP-OES operating conditions for wavelengths (nm) were Cd = 214.439 and Zn = 213.859 in nm; optimisation nebuliser = 0.68, viewing height = 8 mm, replicate read time = 4 s, replicates = 3, sample uptake delay = 15 s and instrument stabilisation delay = 10 s.

Percentage absorption and kinetics of biosorption were calculated by evaluating changes in concentrations at various times with respect to changes based on maximum biosorption, using expressions $(C_0 - C_t)/C_0 \times 100\%$ and the $w(C_0 - C_t)/(C_0 - C_{max}) \times 100\%$, respectively where

C_0 = original concentration, C_t = concentration at time t and C_{max} = concentration at equilibrium.

In order to predict the adsorption process, the dimensionless equilibrium parameter R_L was determined by using the following equation (Magdy and Daifullah, 1988):

$$R_L = \frac{1}{(1 + bC_0)}$$

where C_0 is the initial concentration and b is the Langmuir isotherm constant (intercept). The parameter R_L indicates the shape of the isotherm. The process is irreversible if $R_L = 0$, favourable if $R_L < 1$, linear if $R_L = 1$ and unfavourable if $R_L > 1$. The calculated R_L was found to be 1 for both Zn and Cd whose initial concentrations were 0.1 and 1.0 mg/L, respectively implying a linear relationship for the two processes.

The Freundlich isotherm is an experimental equation used to describe heterogeneous systems:

$$q_e = K_f C_e^{1/n}$$

The linearised form of Freundlich equation is:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

where q_e is the adsorbent amounts (mg/g) of the Zn^{2+} and Cd^{2+}, C_e is the equilibrium concentration of the ions in solution (mg/L), K_f is the adsorption capacity of Freundlich constant (mg/g) and n is the adsorption intensity of Freundlich adsorption isotherm constant.

The equilibrium adsorption isotherm is of importance in the design of adsorption (Wang et al., 2005). Several isotherm equations are available and the two popular isotherms selected in this study are the Langmuir and Freundlich isotherms. The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has found successful application to many sorption processes of monolayer adsorption (Aikpokpodion et al., 2010). The Langmuir adsorption isotherm can be written as:

$$q_e = \frac{q_m bC_e}{1 + bC_e}$$

3. Results

3.1. Effect of pH and contact time on metal uptake

The adsorption capacity of M. oleifera was dependent on pH of Zn and Cd solutions. The effect of metal biosorption by Moringa seeds was dependent on pH (Figs. 1–3) and the results reported by ICP-OES.

In adsorption system, the contact time plays a vital role irrespective of the other experimental parameters, influencing the adsorption kinetics. Metal biosorption followed the Langmuir adsorption-like isotherm by having steeper slopes at the beginning which slowly reduced with time. In the case of Moringa used as adsorbent, there was an appreciable increase in removal of metals up to about 60 min and thereafter further increase in contact time, the increase in removal was quite minimal.
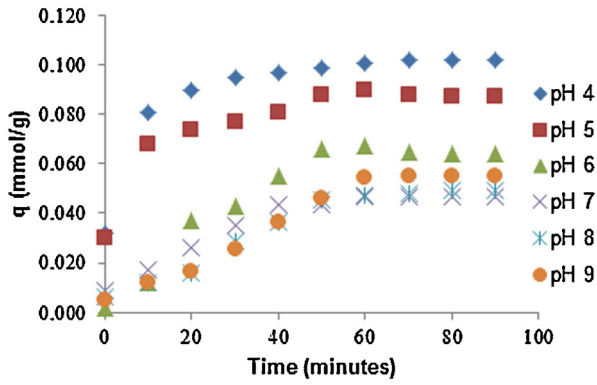
Fig. 1. Biosorption of Zn stirred system using *Moringa* seeds <1 mm pore size at different pH values.
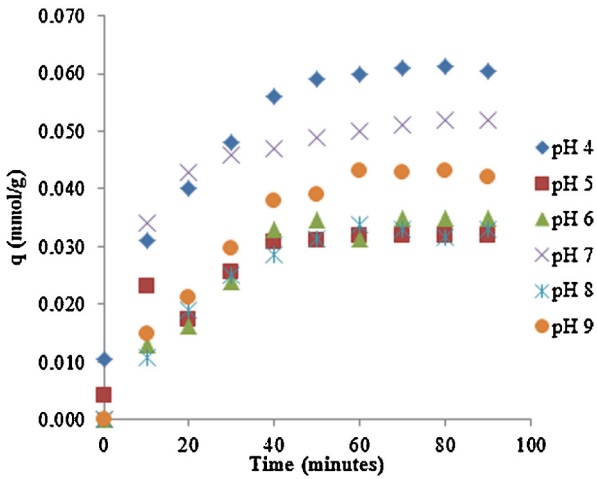

Fig. 2. Biosorption of Cd stirred system using *Moringa* seeds <1 mm pore size at different pH values.

Fig. 3 shows within the experimental pH range of 4–9, pH 4 was the optimum medium for biosorbed metals and they decreased systematically with increased pH.

3.2. Adsorption isotherms

The Langmuir constants were found by fitting the experimental data to the linearised equation derived from
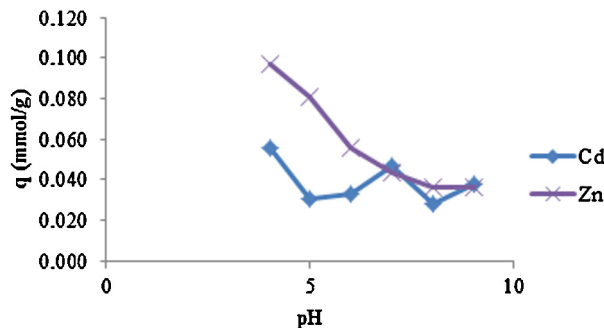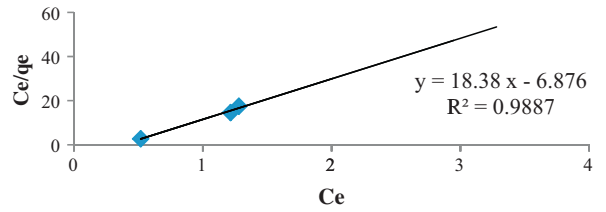

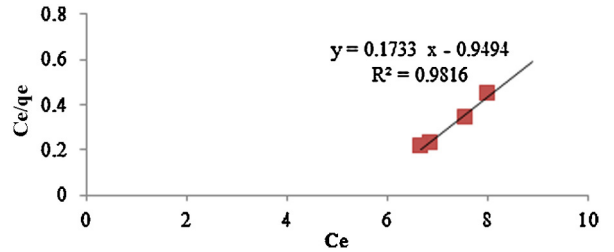**Fig. 4.** Langmuir adsorption isotherm for Zn at pH 4.

Fig. 5. Langmuir adsorption isotherm for Cd at pH 4.

the equation above, which on simplification and rearrangement gave:

$$\frac{C_e}{q_e} = \frac{1}{bq_e} + \frac{C_e}{q_m}$$
$$\frac{1}{q_e} = \frac{1}{bq_e}\frac{1}{C_e} + \frac{1}{q_m}$$

where q_e is the adsorbent amount (mg/g) of the Zn^{2+} and Cd^{2+}, C_e is the equilibrium concentrations of the Zn^{2+} and Cd^{2+} in solution (mg/L), q_m is the monolayer adsorption capacity (mg/g) and b is the constant related to the free energy of adsorption (mg/L).

The constants q_m and b were determined from the linear plots of C_e/q_e versus C_e. The values of the q_m and b were determined from the slope and the intercept, respectively in which q_m is the maximum adsorption while b (mg/L) represents the affinity between the sorbate and the sorbent.

The Langmuir equation used to describe the data derived from the solution by *Moringa* shows that experimental data fitted reasonably with the linearised equation of the Langmuir isotherm in the plot of C_e/q_e versus C_e (Figs. 4 and 5). The respective correlation coefficients of
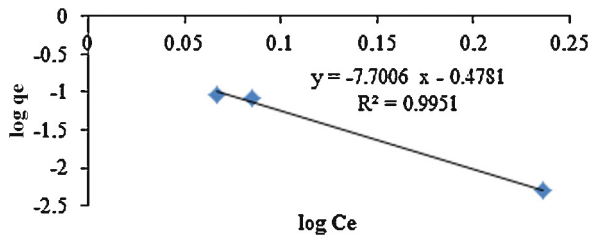

Fig. 3. Biosorption of the Zn and Cd mixed stirred system *Moringa* seeds <1 mm pore size at different pH values.

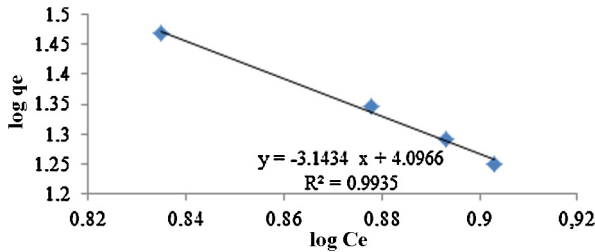**Fig. 6.** Freundlich adsorption isotherm for Zn at pH 4.

Fig. 7. Freundlich adsorption isotherm for Cd.

determination R^2 values of 0.989 and 0.982 further confirmed the fitness of the Langmuir model in describing the adsorption of Zn and Cd by *Moringa*.

The respective q_{max} and b determined from the slope and intercept for Zn and Cd were found to be 18.38 mg/g and −6.876 mg/L and 0.173 mg/g and −0.949 mg/L. From the plots, the R^2 for Zn^{2+} (0.989) >Cd^{2+} (0.982) hence, supporting the finding that Zn was better biosorbed than Cd.

The Freundlich adsorption exponents for the equation above, the K_f and n were determined from the intercept and slopes, respectively of the linear plots of experimental data of log q_e versus log C_e, which are shown in Figs. 6 and 7.

The data obtained from the adsorption isotherms fitted into the Freundlich model show that the adsorption of Zn and Cd on *Moringa* fitted with respective correlation coefficients of determination R^2 values of 0.995 and 0.994, are close to unity. Freundlich equation represents adsorption process very well; the correlation coefficients, R^2 values were, however, higher for the Freundlich isotherms than the Langmuir isotherms and were closer to unity, indicating a very good mathematical fit.
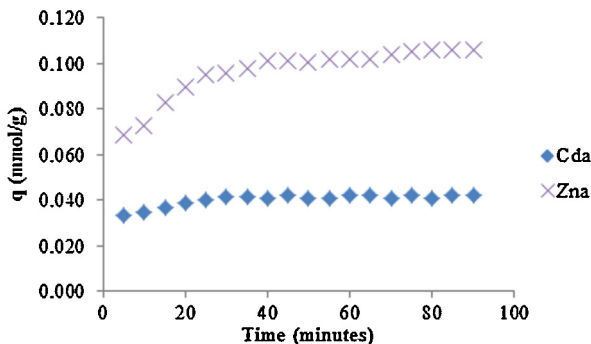

Fig. 8. Biosorption of stirred Zn and Cd mixed system using *Moringa* of pore size <1 mm at optimum pH 4.
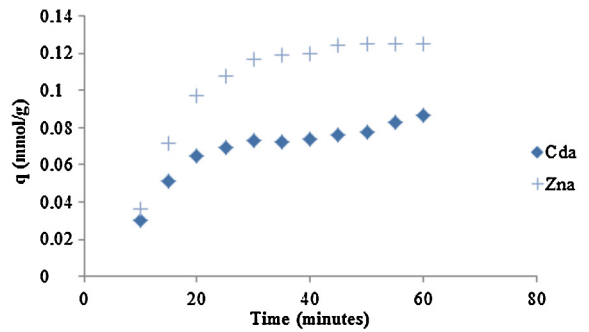

Fig. 9. Biosorption of stirred mixed Zn and Cd system using *Moringa* seeds pore size of <1 mm treated with $KMnO_4$ at optimum of pH 4.

The results also show that metal ions competition in mixed system did not seem to affect the amount of metal biosorbed as depicted in Fig. 8. In this type of system, the amount of metal biosorbed was also not very much different from the single system and Zn was still found to be better biosorbed by the biosorbent than Cd.

3.3. Mixed ions with Moringa treated with KMnO₄

Treatment of the *Moringa* biosorbent with $KMnO_4$ improved biosorption by about 30%. From Fig. 9, $KMnO_4$ gave better biosorption properties without altering the metal biosorption order, i.e., Zn was still better biosorbed than Cd.

4. Discussion

The pH effect could be explained in relation to the competition between H^+/H_3O^+ and metal ions. At low values, the concentration of H_3O^+ far exceeds that of metal ions and hence, occupying the binding sites on the cell walls, leaving metal ions unbound. Further, at lower pH values, the large number of H^+ ions neutralises the negatively charged adsorbent surfaces, thereby reducing hindrance of the Zn^{2+} and Cd^{2+} ions.

It has been established that at low pH values, in non-complexing aqueous medium, Cd, which was the lower biosorbed metal exists predominantly as Cd^{2+} (http://en.wikipedia, 2009). When the pH was increased, the competing effect of H_3O^+ decreased and the positively charged metal ions took up the free binding sites, increasing metal uptake capacity. Thus, the reduction in adsorption of the metals could be due to the abundance of OH^- ions causing increased hindrance to diffusion of Zn^{2+} and Cd^{2+} ions at the high pH values. Both metal ions had maximum biosorption at pH 4 and biosorption drastically decreased with increased pH.

A metal such as Cd was less biosorbed due to insoluble $CdCO_3$ in neutral and alkaline medium while Zn was associated with oxide (Santillan-Medrano and Jurinak, 1975). However, at all pH values the smaller cation, Zn^{2+} was the better biosorbed. This observation is in agreement with the results reported by earlier research work (Reddy et al., 2011). At optimum pH, the surface of the biosorbent is negatively charged and favourable for biosorption of the

ions. Decreased biosorption at higher pH (>4) was due to formation of soluble hydroxylate complexes of metal ions and their competition with active sites, and as a consequence, the retention had been decreased again.

These results are in agreement with those reported by Bhatti et al. (2007) who found that both Langmuir and Freundlich isotherm models fitted well to data of Zn biosorption as represented by high value of their correlation coefficient (i.e., $R^2 \approx 1$). From the values of the Freundlich constant K_f, the uptake of the ions under study from aqueous solution was easy.

It is also generally stated that the values of n in the range of 1–10 represent good adsorption (Magdy and Daifullah, 1988). From the graph of the Freundlich isotherm plot, the n values were calculated reflecting the intensity of sorption. These values also signify that the surface of the *Moringa* biosorbent is heterogeneous in nature because of the fractional value of $1/n$ ($0 < 1/n < 1$) (Khalid et al., 2000).

However, in an earlier study, Shama (2008) highlights the efficacy of shelled *M. oleifera* seeds (SMOS) in the removal of Cd^{2+} and Pb^{2+} ions from aqueous environment both present as single metal and as binary metal solution. The extent of adsorption capacity for Cd^{2+} and Pb^{2+} on *M. oleifera* seeds for binary metal ions was found to be low as compared to single metal ions.

Increased amount after treatment of the biosorbent with $KMnO_4$ could be due to the increased number of binding sites as a result of chemical modification (Aikpokpodion et al., 2010).

This study shows that *M. oleifera* is a suitable biosorbent for the removal of the heavy metal ions Cd^{2+} and Zn^{2+} from wastewater because metal uptake capacity increased with time and could reach equilibrium after some time. The biosorption was pH dependent and the highest uptakes of both metal ions occurred at an optimum of pH 4 and decreased with increasing pH. Biosorption kinetics followed both the Langmuir and Freundlich adsorption isotherms as an indication that this material can offer an alternative option for heavy metal removal. Modified *M. oleifera* using $KMnO_4$ greatly improved metal biosorption. However, biosorption time and pH of the solution affected *M. oleifera*-metal interaction and are crucial factors in biosorption studies.

Acknowledgements

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