ISSN: 0128-7680
Pertanika J. Sci. & Technol. **2(2)**: 197-206 (1994)

Removal of Zinc by the Moss *Calymperes delessertii* Besch

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Received 23 September 1993

ABSTRAK

Kebolehan satu lumut, *Calymperes delessertii* Besch, untuk menyinkir zink daripada larutan telah dikaji. Dalam eksperimen kelompok, parameter-parameter yang telah dikaji termasuk kesan pH dan kepekatan awal larutan zink pada pengerapan. Satu siri eksperimen turus telah dilakukan untuk mengkaji system ini di bawah keadaan dinamik. Model 'bed depth service time' (BDST) yang dicadangkan oleh Hutchins telah digunakan dengan kejayaan kepada sistem ini. Eksperimen 'fixed bed' pun dijalankan dengan menggunakan air-buangan dari satu kilang penyaduran zink. Keputusan menunjukkan turus lumut boleh digunakan sebagai satu sistem pembersih untuk menyinkir zink daripada air-buangan pengelektrosaduran.

ABSTRACT

Studies were conducted to assess the capability of a moss, *Calymperes delessertii* Besch, to remove zinc from solutions. In the batch experiments, parameters studied included effect of pH and initial zinc concentration on sorption. A series of fixed bed experiments were performed to study the system under dynamic conditions. The bed depth service time (BDST) model proposed by Hutchins was successfully applied to the system. The fixed bed experiments were also carried out using wastewater from a zinc plating factory and results indicated that moss columns could be used in a clean-up system to remove zinc from electroplating wastewater.

Keywords: moss, zinc, sorption, uptake, simulated wastewater, electroplating wastewater, BDST model.

INTRODUCTION

Heavy metals represent a major risk to the environment because of their toxicity. Their removal from water supply and wastewater is thus of utmost importance.

Zinc, one of the heavy metals, is used in the production of non-corrosive alloy, brass, in galvanizing steel and iron products and in electroplating industries. The problems associated with ingestion of zinc are well documented (Elinder 1986).

Various methods have been proposed for the removal of zinc from the wastewater of the metal finishing industries. They include the use of evaporation, reverse osmosis and precipitation as hydroxides. These methods are, however, either costly and complicated or incomplete in metal removal. Hence the search for more efficient and economical means of zinc removal continues.

The use of bryophytes as a sorbent of metal ions in wastewater has not been fully investigated. Mosses appear to be suitable sorbents for heavy metals because they possess several interesting properties (Johnson 1980). The cell wall has a high polyuronic acid content which makes moss a very good natural ion exchanger. In addition, the highly reduced presence or absence of cuticle in the moss means the ions have direct access to the cell wall.

Ruhling and Tyler (1970) reported that woodland moss, *Hylocomium splendens,* had a high capacity to sorb heavy metals from solution mainly via an ion exchange process. The sorption of some heavy metals by the moss *Calymperes delessertii* Besch has been reported; the moss could sorb lead, copper and cadmium efficiently (Low and Lee 1987, 1991; Lee and Low 1989).

This study investigates the sorption characteristics of zinc by the moss, *Calymperes delessertii* Besch, and the possibility of using it to treat electroplating wastes.

MATERIALS AND METHODS

Sample Preparation

The collection and preparation of the moss, *Calymperes delessertii* Besch, have been described earlier (Lee *et al.* 1983). Air-dried samples of the moss in its natural condition were used in all the experiments.

A simulated wastewater prepared from A. R. grade anhydrous zinc chloride in 0.001 M sodium chloride solution was used in all the experiments studying the characteristics of zinc sorption by the moss. Sodium chloride solution was used to maintain constant ionic strength. Wastewater collected from an electroplating factory situated in an industrial park was used in the later experiments. The factory specializes in zinc plating and does not have any facility for wastewater treatment. The wastewater collected was alkaline and contained traces of nickel and iron in addition to zinc.

Contact Time Experiments

In all the contact time experiments, except where the effect of pH was investigated, 0.50 g of moss sample was shaken in 400 cm^3 of zinc solution. Various concentrations of zinc solution (250, 100 and 50 mg dm^{-3}) in 0.001 M sodium chloride were studied.

All batch experiments were performed in duplicates at room temperature (27°C). The zinc solution containing the preweighed moss was shaken in polyethylene bottles at 200 revolutions per minute (rpm) on a gyratory shaker. Aliquots of 1 cm^3 solutions were withdrawn at predetermined intervals.

In the study of the effect of pH, 0.20 g of moss was equilibrated with 100 cm^3 of 100 mg dm^{-3} zinc solution with pH ranging from 2 to 13 for four hours. The pH of the solution was adjusted by addition of 0.1 M hydrochloric acid or 0.1 M sodium hydroxide.

Sorption Isotherm

In the study of the sorption capacity of the moss for zinc, 0.20 g samples of moss were shaken in 100 cm^3 of zinc solution for four hours. The concentrations of the solution were varied from 0.5 to 500 mg dm^{-3}.

Fixed Bed Study

In the flow studies, a vertical glass column of internal diameter 14 mm was used. The moss was packed to a height of 10, 15 and 20 cm, corresponding to 1.25 g, 1.88 g and 2.50 g of moss. The flow rates were controlled by means of a peristaltic pump attached to one end of the column. Zinc solutions of 50 mg dm^{-3} were passed through the column at flow rates of 20 to 50 cm^3 min^{-1}. Eluants were collected in 100 cm^3 and analysed for zinc. The experiments were repeated using wastewater containing 200 mg dm^{-3} of zinc and flow rates of 10 to 100 cm^3 min^{-1}.

Adsorption-Desorption Study

In the adsorption-desorption study, a glass column was packed with 2.50 g of moss to a height of 20 cm. One litre of 2.5 mg dm^{-3} zinc solution was passed through the column at a rate of 10 cm^3 min^{-1}.

The eluant was collected and checked for its zinc concentration. The column was then eluted with 1 M nitric acid. Twenty fractions of eluant with a volume of 10 cm^3 each were collected and analysed for zinc.

After the first adsorption-desorption process, the moss was washed free of acid by rinsing it with deionized water. The process was then repeated twice on the same column of moss.

Analysis of Zinc

The concentration of zinc in all the experiments was determined using a sequential scanning inductively coupled plasma atomic emission spectrometer (Labtest 710 - 2000).

RESULTS AND DISCUSSION

Zinc Content in Moss

The average concentration of zinc in the moss used in this study was 80 μg g^{-1} moss. The zinc content was low compared to that of mosses from contaminated areas, which was about 1914 μg g^{-1} moss (Lee *et al.*

1983). Zinc, together with other heavy metals in the atmosphere, was brought in contact with moss tissues in the form of precipitation and dust (Ruhling *et al.* 1968; Lazarus *et al.* 1970).

Contact Time Experiments

The reproducibility of the sorption capacity of the moss was demonstrated by equilibrating six replicates of 0.50 g moss in 100 cm^3 of 250 mg dm^{-3} zinc solution. A mean of 2.69×10^{-4} mol g^{-1} moss and relative standard deviation of 5.32% were obtained. Although no attempt was made to group the moss according to maturity, results from this reproducibility study suggest that sorption of zinc by moss was fairly uniform.

The rates of zinc sorption by the moss at various initial concentrations are shown in *Fig. 1.* A very rapid initial uptake followed by a more gradual process after the first 5 minutes was observed. This could be due to a rapid ion-exchange process followed by chemisorption. This is a typical sorption pattern for most biological materials (Okieimen *et al.* 1985). The fractional uptake was inversely proportional to the initial concentration. Equilibrium was achieved at 30 minutes' contact time regardless of the initial concentration. This indicates the potential for rapid removal of zinc from solution.

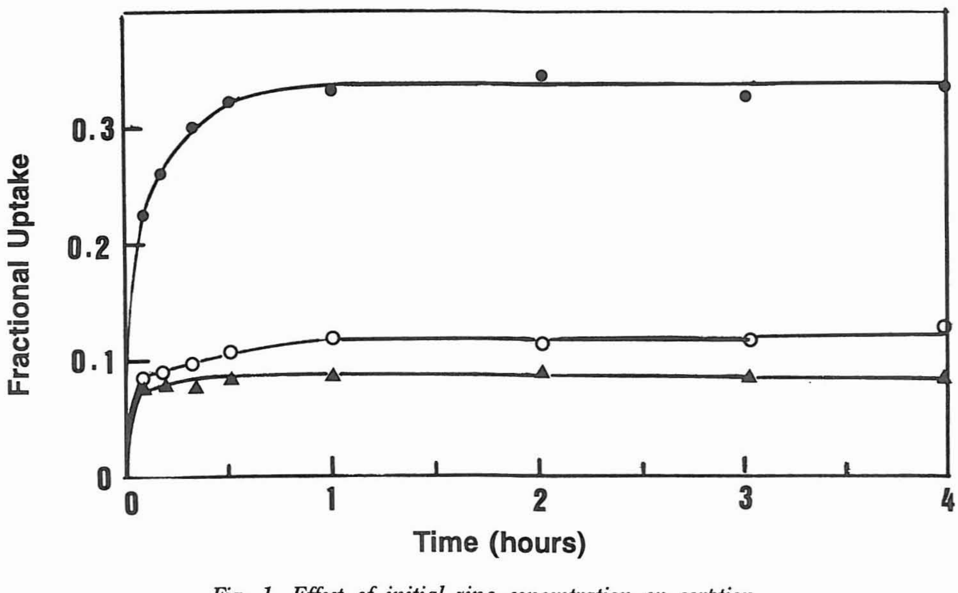

Fig. 1. Effect of initial zinc concentration on sorption.
● *50 mg* dm^{-3} ○ *100 mg* dm^{-3} ▲ *250 mg* dm^{-3}

The effect of pH on sorption of zinc is shown in *Fig. 2.* In the pH range of 2.45 to 4.70 there was an increase in sorption. As pH increases, the availability of sorption sites increases and hence the increase observed. At pH higher than 7, precipitation of zinc hydroxide started to occur.

A similar pattern was observed in the study of copper, lead and cadmium ion (Lee and Low 1989; Low and Lee 1991). Gjengedal and Steinnes (1990) found that at pH lower than 4 the amount of cadmium accumulated by the moss, *Hylocomium splendens,* decreased rapidly. This could be due to the hydrogen ions competing for the sorption sites. At pH 12 zinc hydroxide redissolved to form $[Zn(OH_4)]^{2-}$. There was, however, no uptake of zinc by the moss. As the pH of the electroplating wastewater collected was 12, it would be necessary to adjust the pH before experimentation using the wastewater.

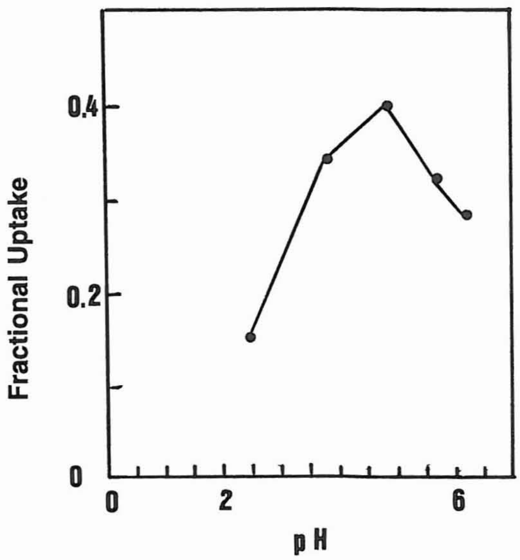

Fig. 2. Effect of pH on sorption

Sorption Isotherm

The results from sorption studies were fitted into a modified Langmuir adsorption isotherm as shown below :

$$C_i/N_i = 1/N^*b + C_iN_i/N^*$$

N_i is the number of moles sorbed per gram of moss at equilibrium concentration C_i. With this equation, the maximum number of moles of metal ion sorbed per gram of the moss (N^*) can be calculated. A plot of C_i/N_i against C_i is shown in *Fig. 3.* The linearity of the plot indicates the Langmuir isotherm can be applied successfully. The maximum sorption capacity is 21.50 mg or 329 μmol zinc g^{-1} moss.

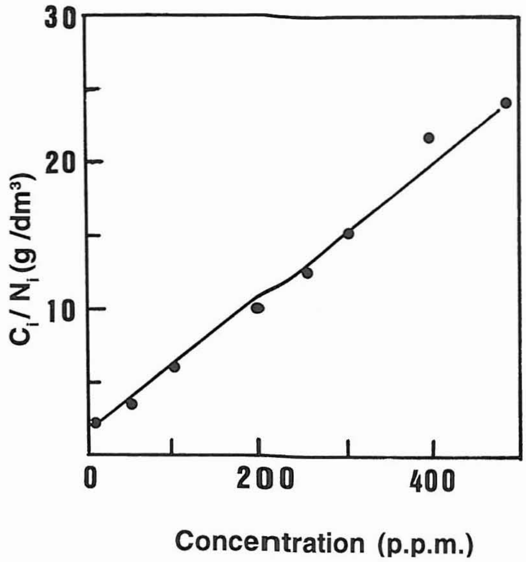

Fig. 3. Sorption isotherm of zinc on moss

Fixed Bed Experiments

There is a need to perform flow tests because the data obtained under equilibrium conditions were not applicable in most treatment systems where the contact time is not sufficiently long for the attainment of equilibrium. The usefulness of the column is related to how long the bed will last before regeneration is necessary. For this purpose, determination of breakthrough curves at various feed concentrations and bed depths is necessary.

Fig. 4 shows three breakthrough curves at bed-depths of 10, 15 and 20 cm and flow rates (μ) of 20 cm^3 min^{-1} with initial zinc concentration of 50 mg dm^{-3}. An arbitrary point of 50% breakthrough is chosen in this study as the level where effluent concentration is unacceptable. The time at which this occurred is labelled as $t_{1/2}$. Breakthrough curves with flow rates of 50 and 100 cm^3 min^{-1} were similar although breakthrough occurred faster.

The performance of a column can be evaluated using the bed depth service time (BDST) model (Hutchins 1973). The model states that bed depth and service time bear a linear relationship. The equation can be expressed as

$$t = ax + b$$

Plots of BDST ($t_{1/2}$) at breakthrough volume ($C/C_0 = 0.5$) against bed depth at different flow rates are shown in *Fig. 5*.

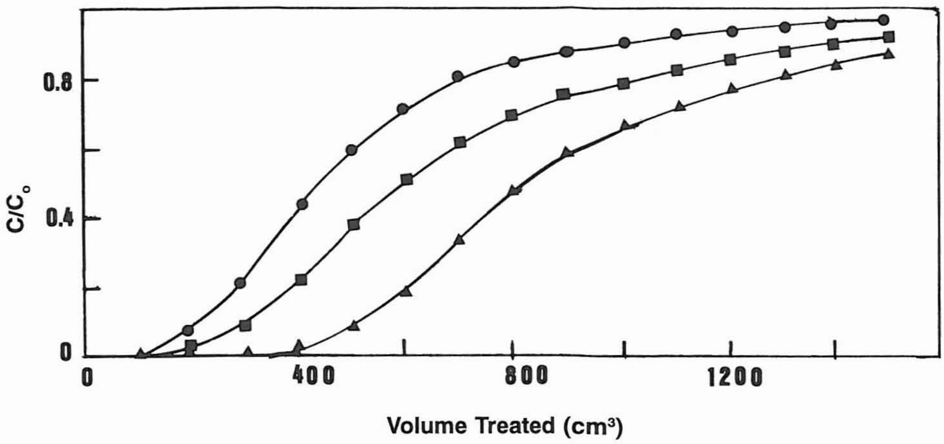

Fig. 4. Breakthrough curves for simulated wastewater at a flow rate of 20 cm^3 /min and different bed depths
● 10 cm, ■ 15 cm, ▲ 20 cm

The linearity of the plots in *Fig. 5* indicates that the BDST model can be successfully applied to the zinc-moss system. After developing a BDST equation for one flow rate, equations for other flow rates can be calculated. Using the BDST equation for the flow rate of 50 cm^3/min, equations for other flow rates were calculated and plotted as shown in *Fig. 5*. There is good agreement between experimental and calculated values. Using this procedure, laboratory tests can be reliably scaled up without further test runs.

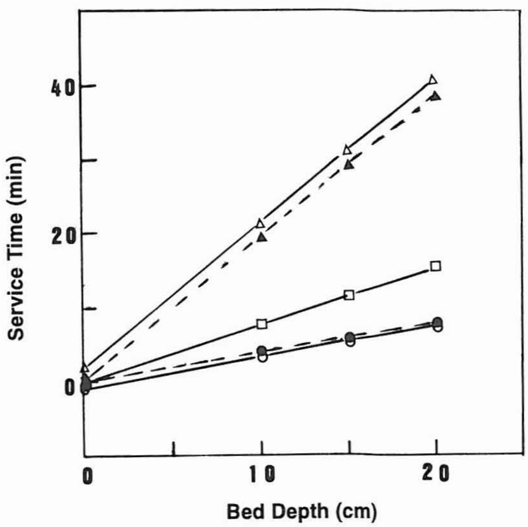

Fig. 5. BDST plots at 50% breakthrough for different flow rates
○, ● 100 cm^3/min, □ 50 cm^{-3}/min, Δ, ▲ 20 cm^3/min
——— Experimental values; — — calculated values

When the fixed bed experiments were carried out using electroplating wastewater after adjusting the pH to 4.2, similar breakthrough curves were obtained. The agreement between experimental and calculated BDST equations is shown in Table 1. The breakthrough times of both the simulated and real systems are listed in Table 2. The concentration of zinc in electroplating wastewater was four times that of the simulated system; however $t_{1/2}$ for the latter varied from 1.2 to 3 times that of the former depending on flow rates. At a low flow rate of 10 $cm^3\ min^{-1}$ where equilibrium could be achieved, comparable $t_{1/2}$ can be obtained for the two systems with markedly different zinc concentrations. This supports the earlier results that equilibrium time is independent of initial concentration. It thus appears that the moss column can be used to remove zinc from electroplating waste albeit a much larger column is required in order to achieve a concentration of < 1 $\mu g\ cm^{-3}$ zinc in the effluent.

TABLE 1
Experimental and calculated BDST equations for flow rates based on $\mu = 100\ cm^3\ min^{-1}$

$\mu (cm^3\ min^{-1})$	Experimental	Calculated
100	$t_{1/2} = 0.094x + 0.466$	-
50	$t_{1/2} = 0.194x + 1.026$	$t_{1/2} = 0.188x + 0.466$
10	$t_{1/2} = 1.224x + 5.303$	$t_{1/2} = 0.940x + 0.466$

TABLE 2
BDST($t_{1/2}$) of simulated and actual electroplating wastewater

		Simulated $C_0 = 50\ mg\ dm^{-3}$	Actual $C_0 = 200\ mg\ dm^{-3}$
Bed depth (cm)	Flow rate ($cm^3\ min^{-1}$)	$t_{1/2}$ (min)	$t_{1/2}$ (min)
10	100	3.4	1.4
15	100	5.3	1.8
20	100	7.7	2.4
10	50	7.7	3.1
15	50	11.4	3.8
20	50	15.4	5.0
10	10	22.0	17.5
15	10	29.8	23.8
20	10	41.2	29.7

Adsorption-Desorption Study

Fig. 6 shows the result of three consecutive adsorption-desorption processes using the same column of moss. In all cases no breakthrough was detected prior to elution with 1 M HNO_3. Zinc was almost completely eluted in the 100 cm^3 of acid. About 98% of zinc was eluted in the first desorption, 87% in the second and 103% in the third. The results indicate that elution with acid does not affect the performance of the moss as a sorbent, and the moss column can be repeatedly used to remove zinc from treated wastewater where the concentration is low.

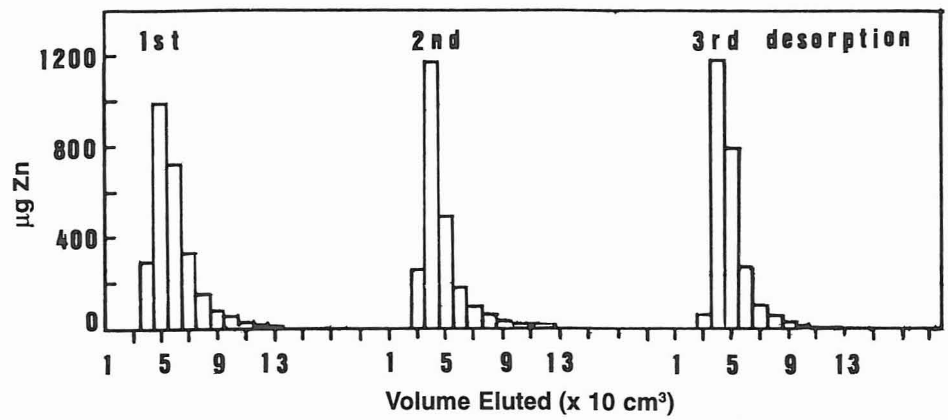

Fig. 6. Adsorption-desorption process of zinc in moss column

CONCLUSION

The moss, *Calymperes delessertii* Besch is an efficient sorbent for zinc from solution. The rate of sorption is rapid and the mechanism appears to involve ion exchange. The flow studies indicate that the behaviour of the zinc-moss system can be predicted using Hutchin's BDST model. Moss columns are potentially useful in the removal of zinc from electroplating wastewater.

ACKNOWLEDGEMENT

The authors are grateful to Majlis Penyelidikan Kemajuan Sains Negara, Malaysia for their financial support (grant no. 04-07-05-017).

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