

REMOVAL OF ZINC BY BIOMASS OF AQUATIC MOSSES

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Abstract

The utilization of aquatic mosses for the treatment of wastewater containing heavy metals is gaining more attention as a simple, effective and economic means of pollution remediation. The effect of various parameters such as contact time, initial metal ion concentration and temperature on zinc biosorption onto the aquatic moss *Fontinalis antipyretica* was studied. The maximum zinc uptake by *Fontinalis antipyretica* in batch system at pH 5.0, adsorbent dose of 2 g l⁻¹ and 20°C was found to be 15.4 mg g⁻¹. Langmuir and Freundlich isotherm models fit the experimental data. Results showed that nonliving biomass of *Fontinalis antipyretica* is a suitable biosorbent for zinc.

Key words: biosorption, aquatic moss, zinc, adsorbent.

INTRODUCTION

A realistic scenario is that man's use of metals seriously began to affect the environment during the Industrial Revolution. Today, two thousand years later, we can say to be in the Metal Removal Age and we are all too aware of the risks inherent to the uncontrolled dissemination of heavy metals into the environment. From the environmental point of view, the metals that are of greatest concern are those which, either by their presence or their accumulation, can have a toxic or an inhibitory effect on living beings. And, if directly discharged into the sewage system they may seriously damage the operation of biological treatment as well as make the activated sludge unsuitable for application to agricultural land (Madoni *et al.*, 1996). Metals can be dispersed, both naturally and by man's activities, into any of the earth's compartments: water, soil or air. However, water and wastewater constitute the main focus of this work.

The traditional techniques (chemical precipitation, coagulation, complexing) to removing metal ions from aqueous effluents are insufficient to reduce concentration to the levels required by law or prohibitively expensive (ion exchange, activated carbon adsorption, electrolytic removal). High capital and regeneration costs of activated carbon and ion-exchange resins have resulted in increasing search of low cost adsorbents. The use of micro-organisms such as bacteria, fungi and algae in treating wastewaters containing toxic metal ions is today an attractive technique but as yet not suitable for large scale applications (Yin *et al.*, 1999; Cotoras *et al.*, 1992; Yetis *et al.*, 2000). In wastewater treatment, the adsorption process has an edge over other methods due to its sludge-free and clean operation. In related studies, metal removal abilities of various low cost adsorbents have been investigated with great interest: freshwater macrophytes (Schneider and Rubio, 1999), aquatic mosses (Gagnon *et al.*, 1999), alum sludge (Chu, 1999), soybean hulls, cottonseed hulls, rice straw and sugarcane bagasse (Marshall and Champagne, 1995).

The aquatic mosses have proved to be an important support for heavy metals removal from polluted waters. In this way, zinc removal by dead biomass of mosses was studied. In this work, an aquatic moss, *Fontinalis antipyretica*, was tested for treating simulated wastewaters prepared in the laboratory, and containing the selected metal.

MATERIALS AND METHODS

Materials

The aquatic moss *Fontinalis antipyretica*, was picked out in the Selho River, at Aldão, a tributary of the Ave River in northern Portugal. The sampling site is near the river spring, an uncontaminated site, so the metal content in mosses was considered to be of natural origin. The samples were firstly rinsed with river water and after with distilled water in laboratory, selecting only the green parts of the plants. The material was dried in an oven at 70°C for 24 h and then ground in a RETSCH ZM 100 ultra-centrifugal mill at 1400 rpm for approximately 90 seconds. The fraction with particle size between 150 µm - 300 µm was selected for the study.

Metal-bearing solution was prepared by dissolving ZnCl₂ (from Merck) in distilled water. The reference material (the aquatic moss *Platihypnidium riparioides*, CEC Community Bureau of Reference B.C.R. Nr. 61) was used as a control sample for quality control of plant digestion and zinc determination.

Batch experiments

Batch equilibrium sorption experiments were performed in 100 ml Erlenmeyer flasks containing 50 ml of metal-containing solution of a known initial concentration into which a preweighted amount of the dry biomass was added. The suspensions were mildly agitated on a rotary shaking machine at 140 U min⁻¹ operating for 5 h. Kinetic experiments were performed at 20 °C, pH 5.0±0.1, in metal concentration solution 10 and 100 mg l⁻¹, and different amounts of biosorbent. Sorption isotherms were performed in the temperature range 5-30°C, pH 5.0±0.1 and metal concentration range 10-100 mg l⁻¹. The pH was adjusted initially to 5.0±0.1 by adding 0.1 M H₂SO₄ or 0.1 M NaOH, as required. Following the sorption reaction period, the liquid was separated from the biomass by vacuum filtration through 0.45 µm Gelman Sciences sterilized membranes. Metal free and biosorbent-free blanks were used as controls and the metal concentration in solution was determined by atomic absorption spectrophotometry using acetylene-air flame (AAS, VARIAN SPECTRA, model S220). Zinc standard solutions (1000 mg l⁻¹) were obtained from Merck.

The sorption capacity, q_t , at a specified time t , is calculated from the sorption system balance:

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (1)$$

where V is the volume of solution; M , the mass of biosorbent; C_0 , the initial metal concentration in solution; C_t , the metal concentration in solution at time t .

RESULTS AND DISCUSSION

Effect of contact time

The adsorption experiments were carried out for different contact times with a fixed adsorbent mass of 2 g l⁻¹ at pH 5.0 and a fixed temperature of 20°C. The dependence of contact time on sorption of zinc was determined by a batch technique and the results are plotted in Fig 1. The amount of Zn

adsorbed increases steadily with the increase in contact time up to 180 min and then becomes almost constant (87% adsorption).

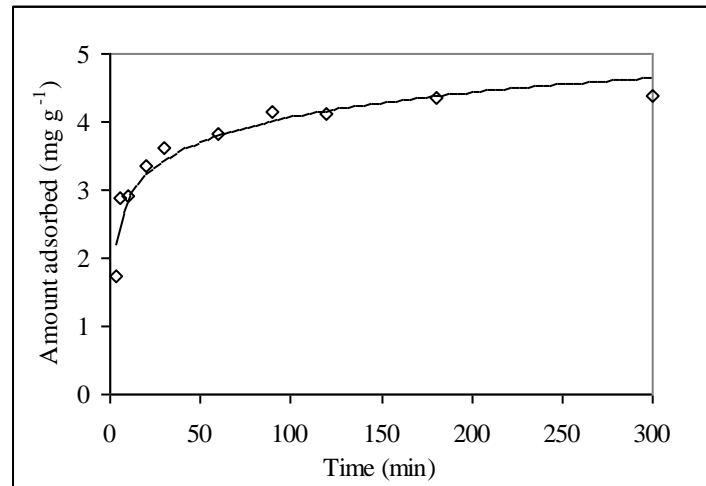


Figure 1. Effect of contact time on the amount zinc adsorbed.

Effect of initial concentration

For 180 min contact time (high enough to reach equilibrium), fixed temperature (20 °C) and pH (5.0±0.1), 50 ml of zinc solution with concentration in the range 10 – 100 mg l⁻¹ was shaken with 100 mg sorbent. In table 1 are presented the results of sorption capacity and rate constant. The first order reaction rate constant, k, was calculated using de equation (2).

$$C_e = C_0 \exp(-kt); \text{ for } t \leq 180 \text{ min} \quad (2)$$

with C_e = concentration of sorbate at equilibrium, mg l⁻¹ and C_0 = initial concentration of sorbate, mg l⁻¹.

The data of table 1 reveal that at low concentration, 10 mg l⁻¹, zinc removal was about 83 percent. When the initial concentration of sorbate increases, the percent of adsorbed Zn decrease although the sorption capacity for Zn increases. Figure 2 shows a plot of percent zinc sorbed versus initial concentration of zinc. The percentage of zinc sorbed onto the moss particles decreases as the initial zinc concentration increases and tends to a constant value (in this case, about 30%). So, in terms of percentage of zinc removal from solution, initial concentration higher than 100 mg l⁻¹ seem not to lead to values above 30%.

Table 1. Effect of concentration on sorption capacity of zinc at 20 °C and pH=5.0

Zn initial (mg l ⁻¹)	Zn at equilibrium (mg l ⁻¹)	Zn sorbed (mg g ⁻¹)	Zn sorbed (%)	Rate constant, kx10 ³ (min ⁻¹)
10	1.7	4.2	83	10.0
20	6.5	6.8	68	6.3
40	20.8	9.6	48	3.7
60	37.5	11.3	38	2.6
80	54.5	12.8	32	2.1
100	69.3	15.4	31	2.0

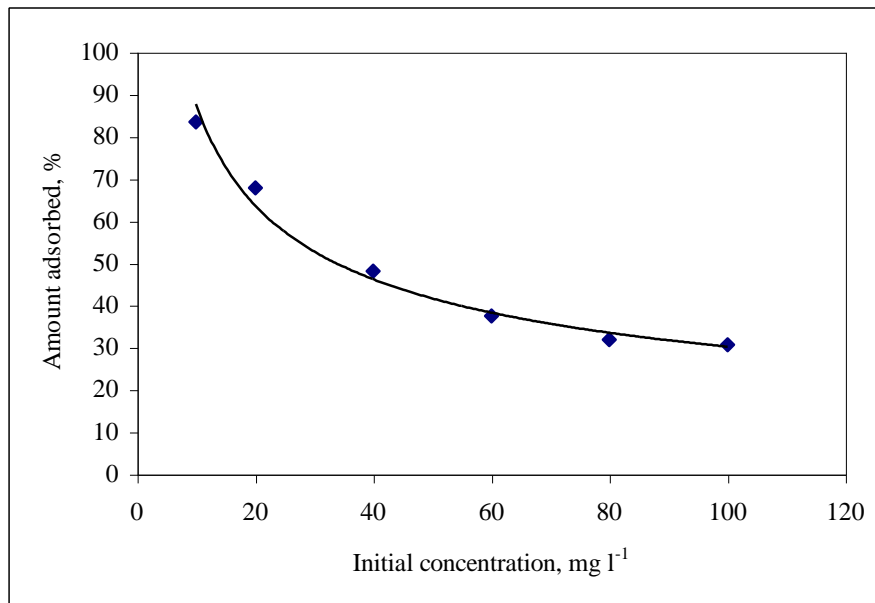


Figure 2 : Effect of the adsorbate initial concentration on the percent zinc adsorbed.

Langmuir and Freundlich isotherms

The results of zinc biosorption were fitted to Langmuir and Freundlich isotherms. Langmuir isotherm has been used in various studies for the sorption of a variety of compounds, and is given by the following equation:

$$q_e = Q_0 \frac{b \cdot C_e}{1 + b \cdot C_e} \quad (3)$$

where

q_e = amount adsorbed, mg g⁻¹

C_e = equilibrium concentration of the adsorbate, mg l⁻¹

b = Langmuir constant related to the energy of adsorption, l mg⁻¹

Q_0 = Langmuir constant related to the maximum adsorption capacity, mg g⁻¹.

The adsorption data of zinc were also fitted into the Freundlich model, which is given by:

$$q_e = K_f C_e^{1/n} \quad (4)$$

where

q_e = amount adsorbed, mg g⁻¹

C_e = equilibrium concentration of the adsorbate, mg l⁻¹

n = Freundlich constant related to adsorption intensity

K_f = Freundlich constant related to adsorption capacity.

Data showed a good positive relationship with both Langmuir and Freundlich sorption models (Fig. 3 and 4). Regression analysis of the experimental results at different temperatures, q_e against C_e , gave the sorption parameters shown in Table 2.

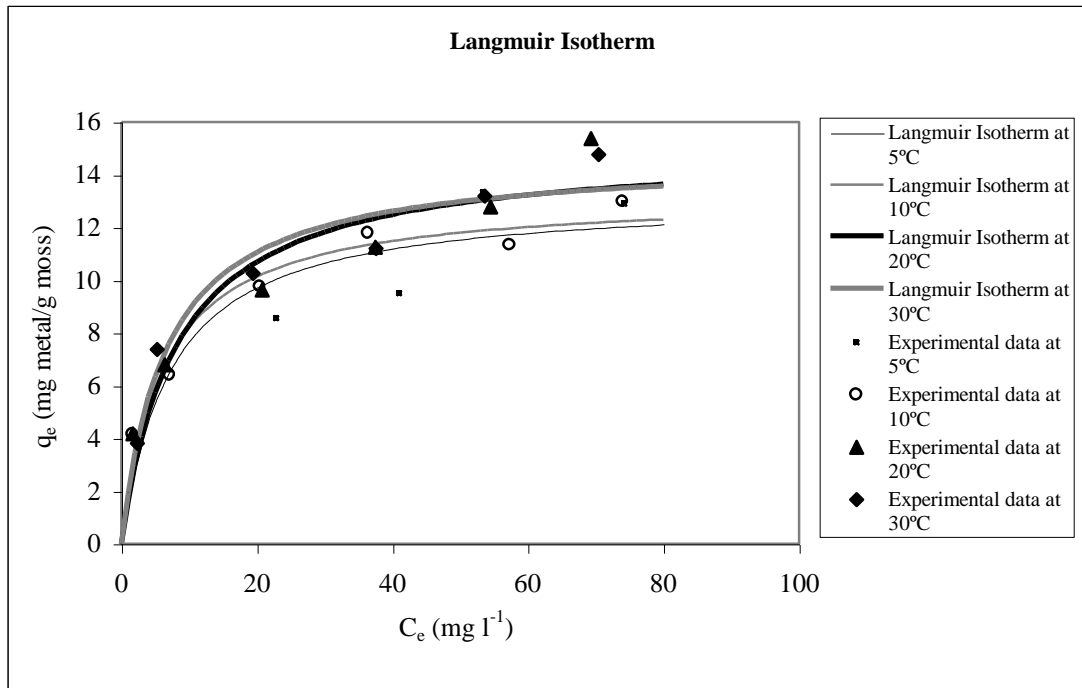


Figure 3. Langmuir adsorption isotherm of zinc onto *Fontinalis antipyretica* for pH 5.0 ± 0.1 and 2 mg ml^{-1} of moss.

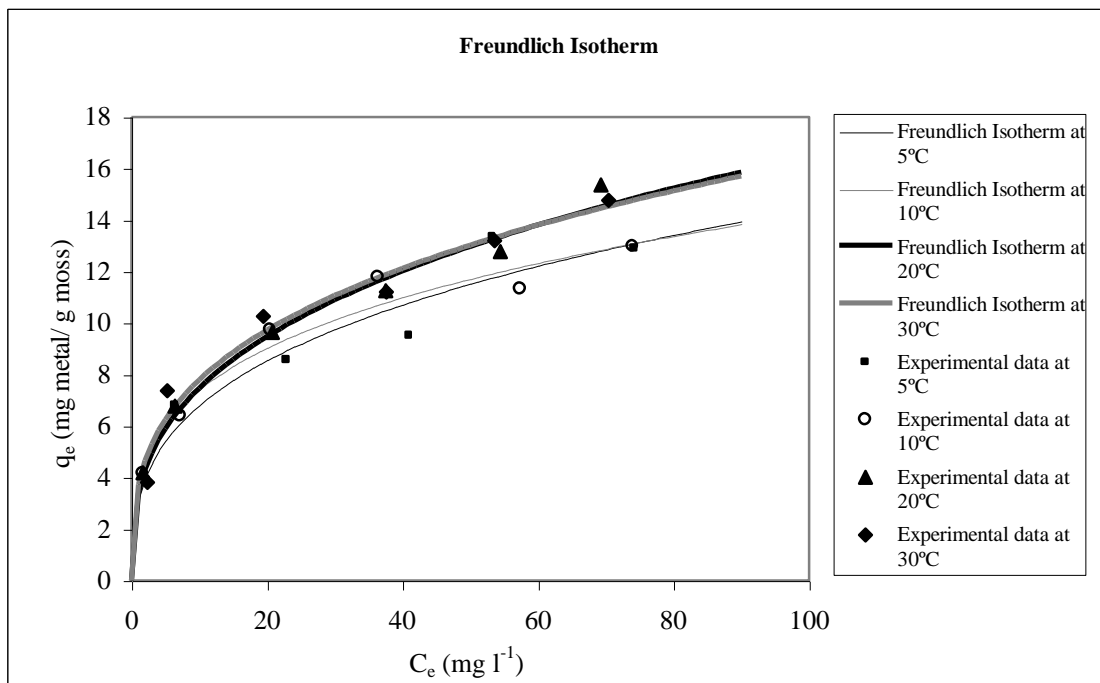


Figure 4. Freundlich adsorption isotherm of zinc onto *Fontinalis antipyretica* for pH 5.0 ± 0.1 and 2 mg ml^{-1} of moss.

Table 2. Langmuir and Freundlich constants for zinc

Adsorbate	Langmuir constants								Freundlich constants							
	Q_0 ($mg\ g^{-1}$)				$bx10^2$ ($l\ mg^{-1}$)				n				K_f			
	5°C	10°C	20°C	30°C	5°C	10°C	20°C	30°C	5°C	10°C	20°C	30°C	5°C	10°C	20°C	30°C
Zn ²⁺	13.21	13.24	15.03	14.69	14.1	16.3	12.4	15.2	3.1	3.6	2.9	3.1	3.25	3.89	3.46	3.74

Figures 3 and 4 shown that the adsorption capacity tends to slightly increase with temperature, whereas the affinity of zinc to the biosorbent is practically independent on the temperature. The sorption mechanism of these biomaterials has been established as ion exchange between metal ions and the weak cation exchanger groups present in the plant surface. Results show that dead biomass of *Fontinalis antipyretica* is a suitable biosorbent for Zn²⁺.

In literature, sorption data from other adsorbents is reported. For sorption of Zn²⁺ ions on nonliving biomass of freshwater macrophytes, Schnider and Rubio (1999) found a Q_0 value of 18.1 $mg\ g^{-1}$ and on hazelnut shell, Cimino *et al* (2000) obtained a maximum value of 1.78 $mg\ g^{-1}$. Gupta and Ali (2000) using bagasse fly ash (a sugar industry waste) as sorbent, determined a maximum uptake capacity of 2.34 $mg\ g^{-1}$.

CONCLUSIONS

Aquatic moss *Fontinalis antipyretica*, a low cost adsorbent, shows a good efficiency in removing toxic ions such as zinc from aqueous solution. The sorption capacity is found very high when compared with other materials. The removal of zinc using aquatic moss takes place by ion exchange mechanism. Zinc uptake by *Fontinalis antipyretica* is only slightly increases with temperature. Probably the adsorption is a swift endothermic process. Adsorption follows both Langmuir and Freundlich models. Zinc is sorbed by moss up to 83% at pH of 5.0 (sorbent dose of 2 $g\ l^{-1}$ and 20°C). The equilibrium conditions are attained after a contact time of 180 min.

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