

Cadmium(II) and zinc(II) adsorption by the aquatic moss *Fontinalis antipyretica*: effect of temperature, pH and water hardness

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Abstract

The biosorption of cadmium(II) and zinc(II) ions onto dried *Fontinalis antipyretica*, a widely spread aquatic moss, was studied under different values of temperature, initial pH and water hardness. The equilibrium was well described by Langmuir adsorption isotherms. Maximum biosorption capacity of cadmium was independent on temperature and averaged 28.0 mg g^{-1} moss, whereas for zinc, capacity increased with temperature, from 11.5 mg g^{-1} moss at 5°C to 14.7 mg g^{-1} moss at 30°C . Optimum adsorption pH value was determined as 5.0 for both metal ions. Cadmium uptake was unaffected by the presence of calcium ions, but zinc sorption was improved when water hardness increased from 101.1 to $116.3 \text{ mg CaCO}_3 \text{ l}^{-1}$. Inversely, as hardness increases, the competition with calcium ions strongly reduces the affinity of the biosorbent for zinc.

Keywords: Aquatic moss; Zinc; Cadmium; Sorption; Heavy metals; *Fontinalis antipyretica*

1. Introduction

The elimination of metal ions from aqueous solutions by biosorption plays an important role in water pollution control. Heavy metals such as zinc and cadmium, often present in industrial wastewaters, are hazardous to the aquatic ecosystem and pose possible human health risk. Besides the toxic and harmful effects to organisms living in water, heavy metals also accumulate throughout the food chain and may affect human beings.

Cadmium and zinc are widely used metals in daily life. In wastewaters from zinc and brass plating, viscose rayon yarn and fibre production and metal processing

industries, zinc ion concentrations are often higher than the discharge limits. Cadmium is also a dangerous pollutant originating from metal plating, metallurgical alloying, mining, ceramics and other industrial operations. The chronic toxicity of cadmium to humans and the environment has been well documented. In Portugal the safety levels of cadmium and zinc in drinking water have been set at $5 \mu\text{g l}^{-1}$.

Different types of biomass (dead and alive) have been investigated for biosorption of Cd, Zn and other heavy metal ions. Those include bacteria [1], yeasts [2], bark [3], fungi [4], agricultural by-products [5], coconut shell [6], marine algae [7], moss peat [8] and aquatic mosses [9,10].

Aquatic mosses and some plants show a high capacity for assimilating nutrients, toxic organics and heavy metals, leading to a concentration inside the plants several times higher than in the surrounding environment

Nomenclature		Q	Langmuir parameter related to the capacity of adsorption (mg g^{-1})
b	Langmuir parameter related to the energy of adsorption (1 mg^{-1})	q_e	amount of adsorbed metal on the moss at equilibrium (mg g^{-1})
C_e	metal concentration in solution at equilibrium (mg l^{-1})		

[11–13]. Due to their characteristics (physiological, ecological, etc.) and the fact that they are widespread in most European rivers, aquatic mosses have been successfully used as biological indicators of surface waters contamination by heavy metals [14–19]. Studies on uptake and release of heavy metals by the aquatic moss *Fontinalis antipyretica* have also been accomplished [13,20,21].

Several authors [22,23] suggested, from batch experiments, that two or three stages could be identifiable during metal uptake by plant cells.

Sorption equilibrium studies provide information about the capacity of aquatic mosses to remove heavy metals under given conditions. Biosorption isotherms depend on certain parameters, whose values express the surface properties and the affinity of the biosorbent. They can also be used to compare the biosorptive capacity for different metal ions. Several models (Langmuir, Freundlich, Brunauer–Emmett–Teller (BET), Dubinin–Radushkevich) have been used to relate metal concentrations in the liquid phase and in the sorbent at equilibrium.

In this work, the Langmuir sorption isotherm model was applied to the sorption of cadmium and zinc ions onto the aquatic moss *F. antipyretica*. The effect of varying water pH and hardness on the model parameters was also evaluated.

1.1. Theoretical approach

Sorption isotherms express the relation between the amount of sorbed metal per unit mass of biosorbent (q_e) and the metal concentration in solution (c_e) at equilibrium.

The Langmuir isotherm model has been shown to be suitable for describing the monocomponent biosorption of heavy metal ions onto aquatic mosses. The model relies on chemical and physical interactions between solute and vacant sites on biosorbent particles and assumes a constant number of free sites, which may be reasonable for a constant pH system. The Langmuir equation is

$$q_e = Q \frac{bC_e}{1 + bC_e}, \quad (1)$$

where q_e is the amount of biosorbed metal on the moss at equilibrium (mg metal g^{-1} moss), C_e the metal

concentration in solution at equilibrium (mg l^{-1}), b the parameter related to the energy of biosorption (1 mg^{-1}) and Q the parameter related to the maximum biosorption capacity (mg metal g^{-1} moss).

The value of Q represents the practical limiting biosorption capacity, i.e. the maximum value of q_e . The initial sorption isotherm curve slope (Qb) indicates the biosorbent affinity for the heavy metal ion.

2. Materials and methods

2.1. Moss sampling and preparation

Aquatic bryophytes—*F. antipyretica*—were collected in the Selho River, at Aldão, not far from the source of this river, a tributary of the Ave River. The sampling site is located at an unpolluted river stretch, so the metal content in the plants is assumed to be of natural origin and represents the background level. Samples were collected at the beginning of autumn. Water level was high enough to keep the plants submerged and these showed a good physiological state, as indicated by the greenish coloration. Besides, when plants are totally submerged and attached to a stable substrate they are representative of water quality at that place.

Samples of *F. antipyretica* were first rinsed in river water and later, in the laboratory, washed in distilled and deionized water, while selecting the green parts and discarding the dark ones. Then, they were dried at 70°C for 24 h. Prior to starting the experiments samples were ground in a RETSCH ZM 100 ultra-centrifugal mill at 1400 rpm for approximately 90 s. The fraction with particle size between 150 and $300 \mu\text{m}$ was selected for the study.

2.2. Sorption equilibrium experiments

For each test, 1, 2, 4, 6, 8 and 10 ml of 500 mg l^{-1} metal stock solution (Zn^{2+} added as ZnCl_2 and Cd^{2+} as $\text{CdCl}_2 \cdot \text{H}_2\text{O}$) were introduced in volumetric flasks and made up to a final volume of 50 ml with distilled water. Solutions were then transferred to 100 ml Erlenmeyer flasks. This way, metal concentrations in the flask were 10, 20, 40, 60, 80 and 100 mg l^{-1} , respectively. The initial solution pH was adjusted to pre-established values.

Finally, 100 mg of ground moss was introduced in each flask.

Moss suspensions were shaken at constant room temperature (20°C) using a rotary shaker (P-Selecta Rotabit) for 24 h. The contact time was previously determined from kinetic studies, carried out at the same environmental conditions, as that allowing to attain equilibrium. The liquid phase was separated from the plants by vacuum filtration through 0.45 µm Gelman Sciences sterilized membranes.

2.3. Analytical methods

The initial pH was adjusted to the pre-selected values with H₂SO₄ 1 M and measured with a METROHM 654 pH-meter.

The metal concentration in solution was determined by acetylene–air flame AAS (Atomic Absorption Spectrophotometer VARIAN SPECTRAA S220). Calibration curves were prepared with a blank and four standards and the metal concentration was calculated as the average of three (sometimes four) replicates. Differences between extreme and average values are in the range 0.3–2.7%. Cadmium and zinc standard solutions (1000 µg ml⁻¹) were obtained from Merck. All the determinations were performed under optimization of the below-indicated parameters:

Metal	Wavelength (nm)	Slit width (nm)	Flame	Detection limit (mg l ⁻¹)
Cd	228.8	0.5	Air/acetylene	0.009
Zn	213.9	1.0	Air/acetylene	0.09

3. Results and discussion

3.1. Sorption equilibrium isotherms

The experimental results obtained for each metal at four different temperatures (5°C, 10°C, 20°C and 30°C) were fitted to the Langmuir isotherm model by non-linear regression using the commercial software Fig P

Table 1

Langmuir parameters (average ± standard error) for Cd and Zn sorption onto *Fontinalis antipyretica* at different temperatures (pH = 5.0; water hardness = 101.0 mg CaCO₃ l⁻¹)

T (°C)	Cd			Zn		
	Q (mg metal g ⁻¹ moss)	b (l mg ⁻¹ metal)	R ²	Q (mg metal g ⁻¹ moss)	b (l mg ⁻¹ metal)	R ²
5	28 ± 2	0.08 ± 0.02	0.977	12 ± 1	0.21 ± 0.07	0.954
10	28 ± 3	0.10 ± 0.03	0.968	13 ± 1	0.17 ± 0.05	0.975
20	28 ± 1	0.09 ± 0.02	0.991	14 ± 1	0.16 ± 0.04	0.975
30	29 ± 2	0.13 ± 0.03	0.981	15 ± 1	0.15 ± 0.04	0.973

from Biosoft. Sorption equilibrium parameters for Cd(II) and Zn(II) are displayed in Table 1 and isotherms are presented in Figs. 1 and 2, respectively. Mosses show a stronger and approximately constant biosorption capacity for cadmium (about 28 mg Cd g⁻¹ moss) whereas the uptake capacity for zinc slightly increases

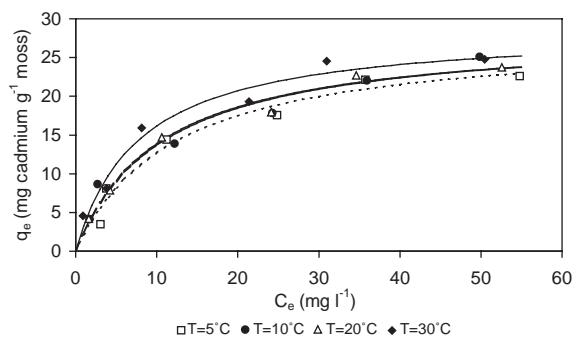


Fig. 1. Cadmium sorption equilibrium isotherms at different temperatures (moss concentration = 2 mg ml⁻¹; pH = 5.0; water hardness = 101.0 mg CaCO₃ l⁻¹): experimental results and model fitting.

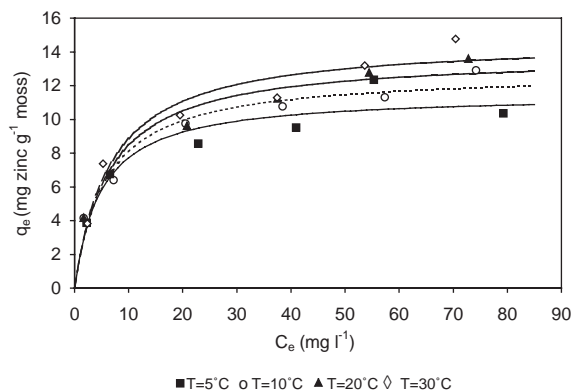


Fig. 2. Zinc sorption equilibrium isotherms at different temperatures (moss concentration = 2 mg ml⁻¹; pH = 5.0; water hardness = 101.0 mg CaCO₃ l⁻¹): experimental results and model fitting.

Table 2
Adsorption capacities for Cd²⁺ and Zn²⁺ using different low-cost adsorbents

Adsorbent	Adsorption capacity (mg g ⁻¹)		Reference
	Cd ²⁺	Zn ²⁺	
Aquatic plant <i>Najas graminea</i>	28.0	—	[25]
Waste tea leaves	31.48	11.77	[26]
Moss (mixture)	10.0	9.87	[9]
Hazelnut shells	5.42	1.78	[27]
Peat	22.5	—	[28]
Peat	—	9.3	[29]
Pine bark	28.0	—	[30]
Aquatic moss <i>Rhytidiadelphus sq.</i>	16.7	—	[31]
Aquatic moss <i>Fontinalis antipyretica</i>	28.0	15.0	This study

with temperature and reaches a maximum value of about 15 mg Zn g⁻¹ moss at 30°C. The order of uptake agrees with that obtained by Lee and Low [24] using the moss *Claymperes delessertii* in sorption studies: Cu²⁺ > Cd²⁺ > Ni²⁺ > Zn²⁺. Table 2 compares maximum adsorption capacities obtained in this study with some other values reported in the literature. The adsorption capacity for cadmium and zinc using the aquatic moss *F. antipyretica* is of the same order of magnitude or greater than that has been found using similar biosorbents.

Zinc uptake by *F. antipyretica* is an endothermic process. The increase with temperature can be caused by enhanced ion exchange and a change in the size of the adsorbent's pores [32]. The affinity of the sorbent, expressed by the product Qb , shows a marked increase for Cd at $T = 30^\circ\text{C}$, but seems not to depend on the temperature for Zn.

3.2. Effect of pH

Cadmium and zinc sorption equilibrium data for different values of the initial pH are also well fitted by the Langmuir isotherm model, as can be observed in Figs. 3 and 4, respectively. The values of the Langmuir parameters are presented in Table 3. A significant increase in cadmium and zinc uptake per weight of moss was obtained as the pH increased from 3 to 5. Maximum biosorption capacities of 28.4 and 13.8 mg metal g⁻¹ moss for Cd and Zn, respectively, were reached for pH = 5. Similar results have been reported by other researchers, e.g. for the uptake of Cu, Pb and Cd by acacia bark [33], for the sorption of Zn, Cd and Cu onto activated carbon [34], for the uptake of Zn,

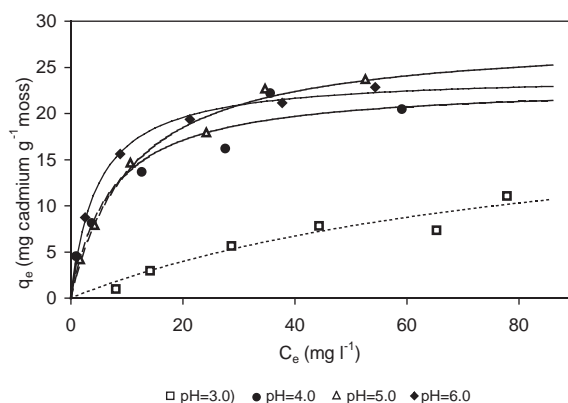


Fig. 3. Cadmium sorption equilibrium isotherms at different pH values (moss concentration = 2 mg ml⁻¹; $T = 20^\circ\text{C}$; water hardness = 101.0 mg CaCO₃ l⁻¹): experimental results and model fitting.

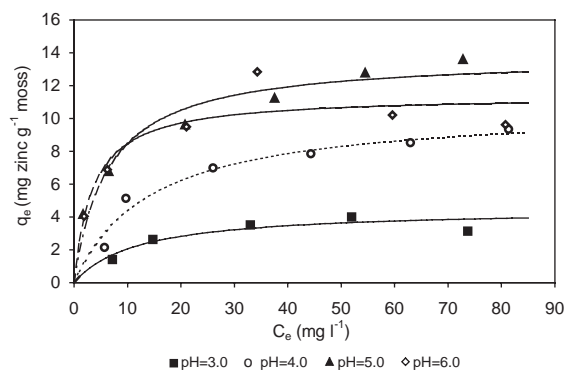


Fig. 4. Zinc sorption equilibrium isotherms at different pH values (moss concentration = 2 mg ml⁻¹; $T = 20^\circ\text{C}$; water hardness = 101.0 mg CaCO₃ l⁻¹): experimental results and model fitting.

Cd and Cu onto a selected mixture of mosses [9], and for the biosorption of Pb, Hg, Cd, Ni and Cu onto chemically treated used tea leaves [35]. The fact can be explained by competition between protons and metal cations for surface sorption sites. In addition, as pH is increased there is a decrease of the positive surface charge, which results in a lower coulombic repulsion of the sorbing metal ions [36]. Inversely, when pH was increased to 6, the maximum uptake capacity diminished (Table 3).

3.3. Effect of water hardness

Experimental results concerning the effect of the water hardness on metal biosorption are presented in Figs. 5 and 6. As water hardness increased from 101.0 to 177.5 mg CaCO₃ l⁻¹, the cadmium sorption behaviour was not altered. Zinc uptake is favoured by the presence

Table 3

Langmuir parameters (average \pm standard error) for Cd and Zn sorption onto *Fontinalis antipyretica* at different pH values (temperature = 20°C; water hardness = 101.0 mg CaCO₃ l⁻¹)

pH	Cd			Zn		
	Q (mg metal g ⁻¹ moss)	b (l mg ⁻¹ metal)	R^2	Q (mg metal g ⁻¹ moss)	b (l mg ⁻¹ metal)	R^2
3.0	11 \pm 1	0.11 \pm 0.05	0.945	4.5 \pm 0.4	0.08 \pm 0.03	0.939
4.0	23 \pm 2	0.14 \pm 0.05	0.959	11 \pm 1	0.07 \pm 0.02	0.977
5.0	28 \pm 1	0.09 \pm 0.02	0.991	14 \pm 1	0.16 \pm 0.04	0.975
6.0	24 \pm 1	0.21 \pm 0.01	0.999	11 \pm 1	0.30 \pm 0.13	0.924

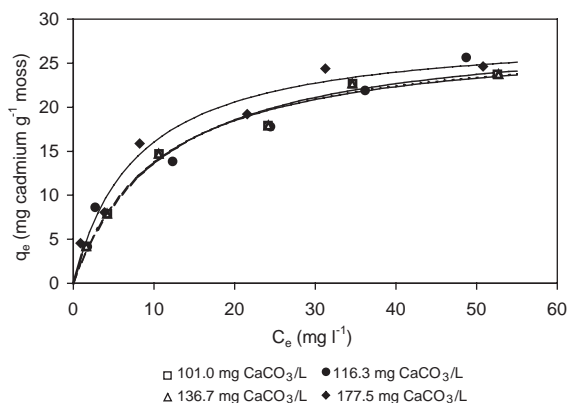


Fig. 5. Cadmium sorption equilibrium isotherms as a function of water hardness (moss concentration = 2 mg ml⁻¹; $T = 20^\circ\text{C}$; pH = 5.0): experimental results and model fitting.

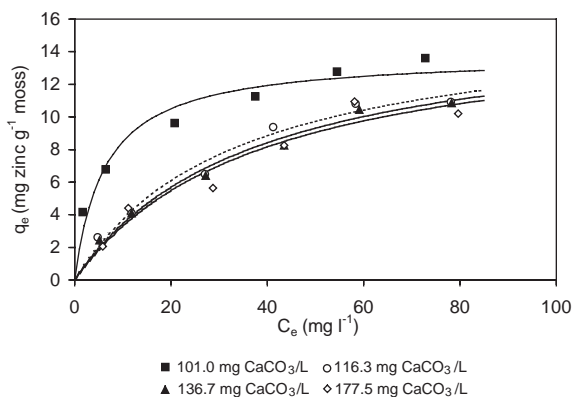


Fig. 6. Zinc sorption equilibrium isotherms as a function of water hardness (moss concentration = 2 mg ml⁻¹; $T = 20^\circ\text{C}$; pH = 5.0): experimental results and model fitting.

of the calcium ions in the range 101.0–116.3 mg CaCO₃ l⁻¹, but remained constant at higher calcium ion levels. Table 4 shows maximum uptake capacities of about 28 and 16 mg metal g⁻¹ moss for Cd and Zn, respectively. Results confirmed that maximum uptake capacity for Cd is about twice that for Zn. The affinity

of Cd for the mosses remained approximately constant in water hardness range 101.0–136.7 mg CaCO₃ l⁻¹, but increased for the higher hardness content. Inversely, as regards Zn, the affinity was greater for the lowest water hardness value, which means that a competitive sorption may exist between zinc and calcium ions.

4. Conclusions

The biomass of the aquatic moss *F. antipyretica* appears to be suitable for the removal of cadmium and zinc from aqueous solutions. So, as this natural material is widely available in most European lakes and rivers, it can be used as sorbent for purification of metal-bearing wastewaters.

The adsorption capacity of this material for cadmium and zinc is of the same order of magnitude or even higher than that has been found using similar biosorbents.

Cadmium and zinc biosorption equilibrium data are well fitted by the Langmuir model. Maximum zinc sorption capacity increased with temperature, from 11.5 mg g⁻¹ moss at 5°C to 14.7 mg g⁻¹ moss at 30°C. Cadmium uptake is about two times higher and practically independent on the temperature.

Cadmium and zinc biosorption by *F. antipyretica* is a pH-dependent process. Maximum uptake capacities for both metals were found to occur at pH = 5.

The simultaneous occurrence of two facts concerning zinc uptake, strongly pH dependency and increase with temperature, suggests an ion-exchange mechanism.

Cadmium biosorption was independent of water hardness. Nevertheless, zinc uptake increased swiftly in the range 101.0 to 116.3 mg CaCO₃ l⁻¹, remaining constant for higher values. However, as hardness increases, the competition with calcium ions strongly reduces the biosorbent affinity for zinc.

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Table 4

Langmuir parameters (average \pm standard error) as a function of water hardness for Cd and Zn sorption onto *Fontinalis antipyretica* (pH = 5; temperature = 20°C)

Water hardness (mg CaCO ₃ l ⁻¹)	Cd			Zn		
	Q (mg metal g ⁻¹ moss)	b (1 mg ⁻¹ metal)	R ²	Q (mg metal g ⁻¹ moss)	b (1 mg ⁻¹ metal)	R ²
101.0	28 \pm 1	0.09 \pm 0.02	0.991	14 \pm 1	0.16 \pm 0.04	0.975
116.3	29 \pm 3	0.09 \pm 0.03	0.966	16 \pm 2	0.03 \pm 0.01	0.986
136.7	28 \pm 1	0.10 \pm 0.02	0.991	16 \pm 1	0.03 \pm 0.01	0.991
177.5	29 \pm 2	0.13 \pm 0.03	0.981	16 \pm 3	0.03 \pm 0.01	0.958

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