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# Industrial Effluent Remediation Using Aquatic Mosses: An Effective Biosorption Approach

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***Abstract:*** *Heavy metals in industrial wastewater pose significant environmental and public health threats. This study explored the use of the aquatic moss Fontinalis antipyretica as a natural biosorbent to eliminate cadmium ($Cd^{2+}$) and lead ($Pb^{2+}$) from simulated wastewater. The study assessed the impact of crucial factors such as initial pH, contact time, and metal ion concentration, utilizing a sorbent dose of 2 g $L^{-1}$. Optimal biosorption occurred at pH levels ranging from 4.0 to 6.0, achieving a maximum uptake capacity of 4.8 mg $g^{-1}$ for both metals at an initial 10 mg $L^{-1}$ concentration. At a concentration of 100 mg $L^{-1}$, the removal efficiency of $Pb^{2+}$ exceeded 78%, demonstrating a stronger affinity for Pb. Among the kinetic models tested, the pseudo-second-order model best fit the experimental data ($R^2 = 0.999$), indicating that chemisorption was a key mechanism in the process. These results highlight the potential of Fontinalis antipyretica as an effective, cost-efficient, and environment-friendly method for treating metal-laden industrial effluents.*

***Keywords***: *Biosorption, Fontinalis antipyretica, freshwater moss, industrial water treatment.*

## 1. INTRODUCTION

Cadmium and lead pollution have been identified as significant threats to air, soil, and water quality [1, 2, 3]. Exposure to elevated levels of these metals in both occupational and residential environments can result in detrimental health outcomes, including cognitive impairment, respiratory disorders, cancer, renal dysfunction, bone damage, and hypertension in both children and adults [4]. The toxicity of lead has been extensively documented, demonstrating its high toxicity in humans at elevated concentrations [5]. Similarly, cadmium exposure has been linked to pulmonary insufficiency, carcinogenesis, and nephrotoxicity [6].

Traditional methods, such as chemical precipitation, coagulation, and complexation, are commonly employed to remove metal ions from aqueous waste streams. However, these conventional techniques often fail to comply with standards set by national and international regulatory authorities [7, 8]. Furthermore, approaches such as ion exchange, activated carbon adsorption, and electrolytic removal incur substantial costs because of the high capital and regeneration expenses associated with activated carbon and ion exchange resins [9, 10]. Consequently, there is increasing interest in investigating low-cost adsorbents as economically feasible alternatives. Various natural, agricultural, and industrial by-products, including biochar [11, 12], zeolites [13], peat [14], clay minerals [15], and lignocellulosic materials [16], have been examined for their potential to remove heavy metals from aqueous solutions. These materials present advantages such as cost-effectiveness, availability, and environmental sustainability, rendering them promising alternatives to conventional adsorbents like activated carbon and ion-exchange resins. Furthermore, physical, chemical, or biological modifications can enhance adsorption efficiency by increasing the surface area, introducing functional groups, or improving the ion exchange capacity [17, 18]. Given these benefits, research continues to optimise low-cost adsorbents for large-scale applications while ensuring high removal efficiency and reusability.

Bryophytes, which include mosses, have garnered attention for their capacity to absorb and tolerate a diverse array of toxic metals [19, 20, 21, 22]. In contrast to vascular plants, bryophytes lack roots, cuticles, and specialized tissues to regulate water and nutrient intake, resulting in direct absorption of dissolved contaminants from the environment [23]. This characteristic renders them highly effective for metal accumulation, particularly in polluted environments. A primary factor contributing to the efficacy of bryophytes in metal uptake is the cell wall, which contains compounds such as polysaccharides and proteins with negatively charged functional groups [24]. These sites naturally attract and bind metal ions, thereby facilitating the trapping and storage of contaminants. Beyond passive adsorption, bryophytes possess internal defence mechanisms to manage metal toxicity, including producing proteins that bind to metals or sequestration in specific compartments to avert damage. According to Gecheva and Yurukova, aquatic bryophytes are particularly beneficial for water purification because of their capacity to thrive under extreme conditions and extensive surface area [25]. Empirical studies have demonstrated their effectiveness in absorbing metals such as cadmium, lead, copper, and zinc from polluted water, positioning them as a natural and cost-effective option for environmental remediation [26, 27, 28]. Because of these characteristics and their prevalence in rivers across the northern region of Portugal, aquatic mosses have emerged as potential biosorbents for removing heavy metals from contaminated waters [29, 30].

In summary, the dangers posed by cadmium and lead pollution demand the creation of effective methods for their extraction and recovery. Traditional approaches often do not meet regulatory requirements, and more sophisticated techniques can be too costly. Bryophytes, with their unique characteristics, such as sensitivity, tolerance, and ability to directly absorb metals, are a promising option for removing heavy metals. The presence of aquatic mosses in the rivers of northern Portugal highlights their potential as affordable bio-sorbents. Exploring and utilizing the capabilities of aquatic mosses for heavy metal extraction could lead to the development of efficient, cost-effective, and environment-friendly wastewater treatment solutions.

## 2. MATERIALS AND METHODS

Fontinalis antipyretica, an aquatic moss, was sourced from the Selho River in Aldão, a tributary of the Ave River located in Northern Portugal (Fig. 1). The collected samples were initially rinsed with river water and subsequently subjected to thorough cleaning with distilled water in the laboratory.

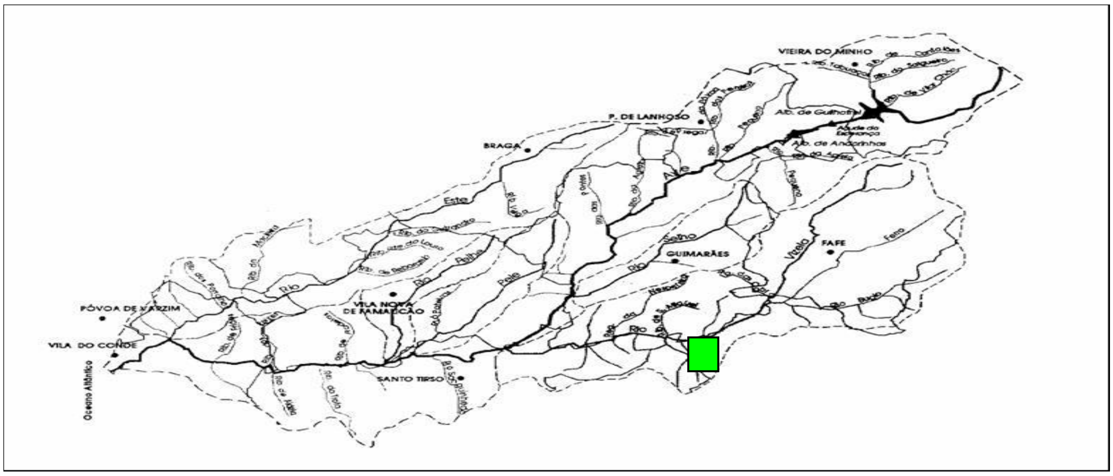

**Figure 1** Moss harvesting point in the Selho River (Portugal).

This process ensured that only green segments of the plants were retained for further analysis (Fig. 2). The plant material was dried in an oven at 70 °C for 24 h. Subsequently, it was ground using a RETSCH ZM 100 ultra-centrifugal mill operating at 1400 rpm for approximately 90 s. For this study, fractions with particle sizes ranging from 150 µm to 300 µm were selected.

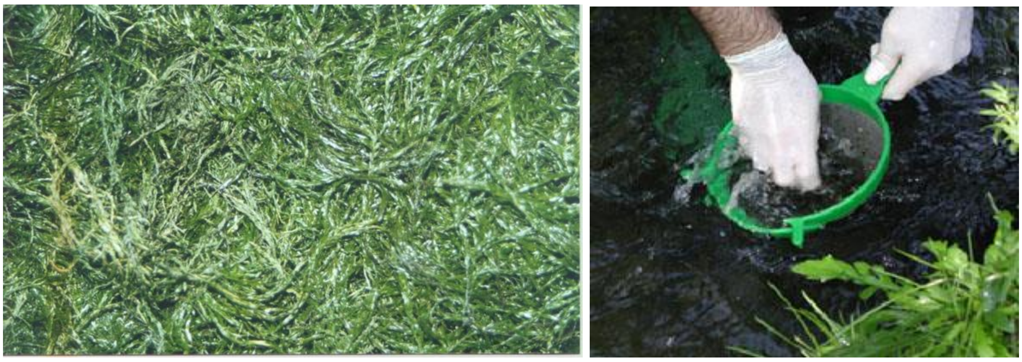

**Figure 2** Depiction of the aquatic moss Fontinalis antipyretica and its rinsing in the river.

Duplicate batch equilibrium sorption experiments (Fig. 3) were performed using 100 mL Erlenmeyer flasks, each containing 50 mL of a metal solution with a precisely determined initial concentration. To ensure uniformity across experiments, a pre-measured quantity of dry biomass was meticulously added to each flask.

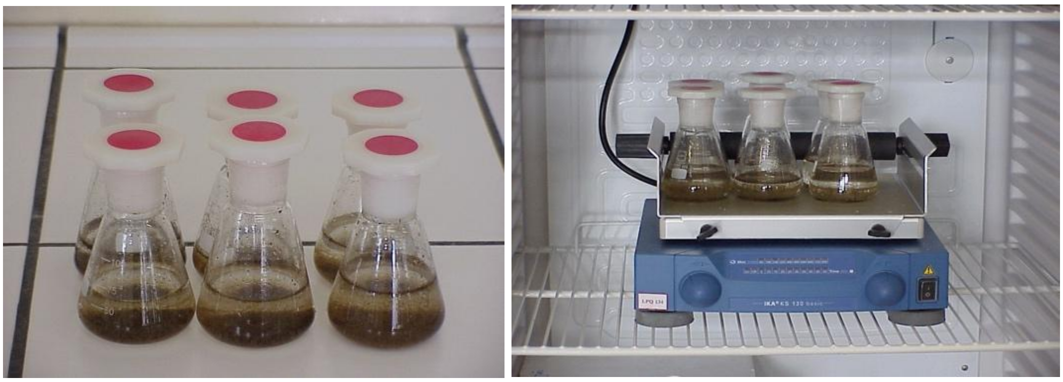

**Figure 3** Series of flasks containing biosorbent and $Cd^{2+}$ and $Pb^{2+}$ ion solutions.

The flasks were then placed on a rotary shaker and agitated at 140 rpm for 300 min to promote uniform interactions between the biosorbent and the metal ions. The experiments were conducted under controlled conditions, with initial metal ion concentrations set at 10 and 100 mg $L^{-1}$, a moss dosage of 2 g $L^{-1}$, a contact time of 24 hours, and a constant temperature of 20 °C.

Kinetic experiments were carried out in duplicate at a constant temperature of 20 °C, with initial metal concentrations of 10 and 100 mg $L^{-1}$. Based on preliminary findings, the working pH was adjusted to 5.0–5.2 using either 0.1 M $H_2SO_4$ or 0.1 M NaOH, as required. The flask was removed from the system at predetermined time intervals (3, 6, 10, 20, 30, 60, 90, 120, 180, and 300 min). The solution was then filtered and the metal concentrations were analyzed using Atomic Absorption Spectrophotometry (AAS, VARIAN SPECTRA, model S220) with an acetylene-air flame. To ensure precise calibration and measurement, standard cadmium and lead solutions (1000 μg $mL^{-1}$) were purchased from Merck.

## 3. RESULTS AND CONCLUSION

The efficiency of metal removal by mosses is influenced by multiple factors, including the specific properties of metal ions, the composition of the aqueous medium, and the physicochemical characteristics of the biosorbent material. This study comprehensively evaluated the biosorption of divalent cadmium and lead by Fontinalis antipyretica, a moss species known for its metal accumulation capability. The key operational parameters investigated included the contact time, biosorbent dosage, initial metal concentration, solution temperature, pH, calcium ion ($Ca^{2+}$) concentration, and type of metal salt used. These factors were selected based on their established influence on adsorption kinetics, equilibrium capacity, and overall system performance. This study presents and discusses the most significant findings related to pH, initial metal concentration, and biosorbent dosage, providing insights into the optimization of metal removal using F. antipyretica.

The pH of the solution is a critical factor in the biosorption process, as it influences both the ionization state of the functional groups present in the moss and the speciation of metal ions in the solution [31]. Experimental results indicate that metal uptake is significantly enhanced at pH values equal to or greater than 4.0 (Fig. 4). At pH 3.0, metal removal was markedly lower, with Cd(II) and Pb (II) uptake reaching only 20% and 40%, respectively. This reduction in biosorption efficiency may be attributed to increased competition from hydrogen ions, which can inhibit the binding of metal ions to the adsorption sites on liver moss. In biological systems, such as aquatic moss, higher pH promotes Cd and Pb uptake due to changes in metal speciation. Phaenark et al. (2024) conducted biosorption studies using moss biomass and identified an optimal pH range for the biosorption of metal ions by aquatic mosses, particularly for removing Pb(II), which is between pH 5.0 and 5.5. Conversely, the removal of Cd(II) ions was unaffected by the pH level [32]. Li et al. (2014) observed a similar pattern, determining that the ideal pH for the biosorption of metal ions using Myriophyllum spicatum biomass was pH 5.0 for Cd(II) ions, achieving a peak biosorption capacity of 29.07 mg $g^{-1}$ [33]. These findings suggest that aquatic mosses could serve as versatile sorption materials with potential applications under various pH conditions.

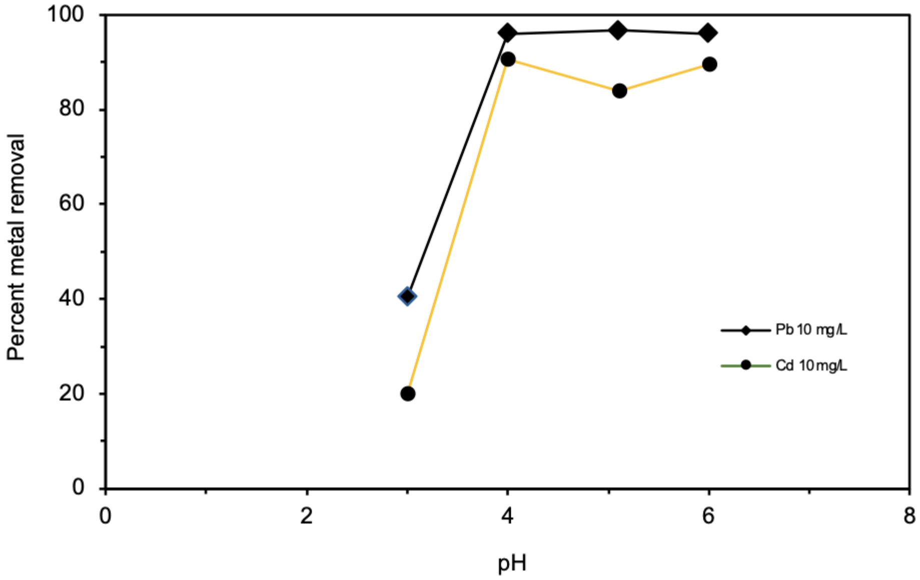

**Figure 4** Effect of pH on biosorption by aquatic mosses.

A notable characteristic of moss-based biosorption is pH-dependent reversibility. At lower pH levels, the metal removal efficiency was significantly reduced, facilitating easy desorption of metal ions through simple pH adjustments. This characteristic is especially beneficial for real-world applications because it enables regeneration and reuse of the biosorbent material. Following these findings, further experiments were conducted at mildly acidic conditions (pH 5.1±0.1).

Preliminary kinetic tests were conducted at pH 5.0 to evaluate the sorption behavior over time while preventing unwanted metal precipitation. The initial metal concentration was set at 100 mg $L^{-1}$, and the moss dosage was maintained at 2 g $L^{-1}$. The results presented in Fig. 5 highlight the typical characteristic of dual adsorption behaviour.

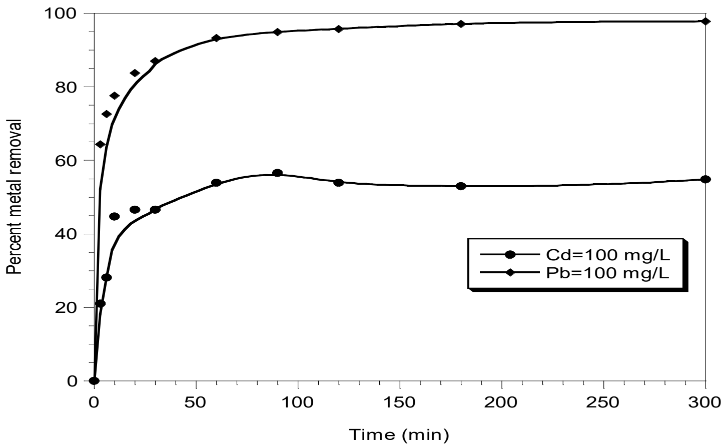

**Figure 5** Biosorption kinetic of Cd(II) and Pb(II) by Fontinalis antipyretica under specified conditions ( $C_0$ = 100 mg $L^{-1}$; X = 2 g $L^{-1}$; pH = 5.0).

During the first 10 minutes, metal removal proceeded rapidly due to the abundance of available binding sites on the moss surface and the strong concentration gradient that facilitated ion diffusion. At this stage, metal ions encounter minimal resistance, allowing efficient adsorption onto the biosorbent. Fick's law describes ions' movement through diffusion, which asserts that the diffusion flux is directly related to the concentration gradient [34]. The concentration gradient is essential to determine the rate at which ions diffuse during the early phases of metal extraction. This facilitates the movement of ions from regions of higher concentration to those of lower concentrations, significantly affecting the effectiveness of ion exchange and electrochemical reactions. As the process continued, the sorption rate gradually declined as fewer high-affinity sites remained, and lower-affinity sites began to be occupied. Despite this slowdown, equilibrium was achieved in less than two hours, demonstrating the effectiveness of moss in capturing metal ions.

A new perspective on diffusion processes has emerged in recent years, centered on a diffusion model driven by the chemical potential gradient. According to this model, the chemical potential gradient, rather than the traditional concentration gradient, is the key driving force for diffusion. This approach suggests that diffusion is more strongly influenced by changes in chemical potential, reflecting both concentration and energy states than by concentration differences alone. This revised understanding provides a more comprehensive framework for explaining the movement of ions or molecules in various systems [35].

The quick equilibrium time is particularly advantageous because it suggests the potential for efficient metal removal using smaller reactor volumes, making the process both practical and scalable.

### Effect of the initial metal concentration

To investigate the impact of initial metal concentration on sorption efficiency, a 300-minute contact time was maintained, with 50 mL of metal-containing solution exposed to 100 mg of biosorbent. The initial metal concentration ranged from 10 to 100 mg L$^{-1}$, while the experiment was conducted at a constant temperature of 20 °C and a pH range of 5.0–5.2. Table 1 presents the results for sorption capacity and rate constants. The first-order reaction rate constant was determined by fitting the equation for the experimental data $t \le 300\,\text{min}$ ($C_e$ = metal concentration at equilibrium, mg L$^{-1}$ and $C_0$ = initial metal concentration, mg L$^{-1}$).

The concentration of metal at the start plays a crucial role in determining the effectiveness of metal removal processes by boosting the driving force needed to overcome mass transfer barriers at the liquid-solid boundary. When higher concentrations, adsorption rates increase, leading to better separation efficiencies. Research conducted by Basić et al. (2020) and Aytac and Altin (2018) indicates that an increase in the initial concentration of metal ions such as Cu, Co, Pb, and Ni leads to a higher quantity of metal being extracted (increased removal rates). However, saturation effects might decrease efficiency [36, 37]. The movement of metal ions from the solution to the surface of the biosorbent is often influenced by fluid film diffusion, which plays a key role in the overall mass transfer process. This effect is particularly important for mesoporous and non-porous materials, where the initial concentration of the metal ions can significantly impact how efficiently they reach and interact with the adsorption sites [38].

Table 1 summarizes the equilibrium uptake values for cadmium and lead at different initial metal concentrations. The results indicate that lead is almost entirely absorbed by the biosorbent, with an impressive removal efficiency of around 98%, regardless of its starting concentration in the solution. In contrast, cadmium exhibits a lower affinity for the biosorbent, with its uptake efficiency decreasing significantly from 83.8% to 47.4% as its initial concentration rises from 10 to 100 mg L$^{-1}$. At lower concentrations, the ratio of initial metal ions to available sorption sites is minimal, making the biosorption percentage independent of the initial concentration. However, at higher concentrations, the number of available biosorption sites diminishes, making the removal of metallic ions reliant on the initial concentration. These findings suggest that diluting highly contaminated effluents could improve the overall effectiveness of the biosorption process.

**Table 1** Equilibrium parameters and removal of Cd(II) and Pb(II) in function of initial metal ion concentration (T = 20°C; pH = 5.0 – 5.2; X = 2 g L$^{-1}$).

| $C_0$ mg L$^{-1}$ | Cadmium | | | Lead | | |
|---|---|---|---|---|---|---|
| | $q_e$ mmol g$^{-1}$ | Uptake % | k x10$^3$ min$^{-1}$ | $q_e$ mmol g$^{-1}$ | Uptake % | k x10$^3$ min$^{-1}$ |
| 10 | 0.037 | 84 | 6.1 | 0.023 | 97 | 11.4 |
| 20 | 0.070 | 79 | 5.2 | 0.047 | 97 | 12.0 |
| 40 | 0.131 | 73 | 4.4 | 0.096 | 99 | 14.9 |
| 60 | 0.159 | 60 | 3.0 | 0.143 | 99 | 15.5 |
| 80 | 0.202 | 57 | 2.8 | 0.191 | 99 | 14.5 |
| 100 | 0.211 | 47 | 2.2 | 0.235 | 97 | 11.9 |

The removal efficiencies for Cd and Pb by aquatic moss vary significantly, with Pb generally showing higher adsorption capacities and removal efficiencies. In adsorption processes, metal ions with higher charge densities typically demonstrate stronger adsorption due to their enhanced electrostatic attraction to negatively charged functional groups on the adsorbent surface. Although $Cd^{2+}$ possesses a higher charge density than $Pb^{2+}$ and is theoretically expected to be more strongly adsorbed, practical adsorption systems are influenced by additional factors [39]. Larger ions such as $Pb^{2+}$ (1.19 Å) can interact more effectively with surface sites owing to their more extensive hydration shell. Affinity to functional groups: $Pb^{2+}$ frequently forms stronger complexes with oxygen-containing groups (e.g., carboxyl, hydroxyl) than $Cd^{2+}$. Consequently, despite the higher charge density of $Cd^{2+}$, $Pb^{2+}$ exhibited often more efficiently removed due to its stronger interactions with the moss F. antipyretica. An additional factor of significance to consider is the adsorption mechanism, which plays a pivotal role in this phenomenon. While $Pb^{2+}$ ions tend to form inner-sphere complexes with carboxyl and hydroxyl groups on adsorbent surfaces, $Cd^{2+}$ ions frequently form outer-sphere complexes. This variation in binding strength contributes to the enhanced adsorption of $Pb^{2+}$ [40]. The findings of this study are consistent with those reported by Li et al. (2023), which demonstrated that the use of calcareous sand resulted in removal efficiencies of 98% for Pb, compared to 66% for Cd, under similar experimental conditions [39].

The lead uptake rate is almost independent of the initial concentration and averages $13.4 \times 10^{-3} \pm 1.64$ $min^{-1}$. On the other hand, the biosorption of cadmium is slower, and the uptake rate decreases by about one-third as the initial concentration increases from 10 to 100 mg $L^{-1}$. The high removal capacities observed for the lower initial metal concentrations in solution (Table 1) are explained by the finite number of adsorption sites at the particle surface. Nevertheless, the uptake of lead remains unaffected by this factor due to its high electronegativity, which enhances its affinity for various functional groups.

In contrast to Cd, the uptake rate for Pb remains relatively constant even when the initial concentration is increased from 10 to 100 mg/L. This observation confirms that lead exhibits a higher affinity for the biosorbent surface than cadmium.

A study conducted by Waqar et al. (2023) utilizing Scenedesmus sp. as a biosorbent reported a maximum lead (Pb) adsorption capacity of 128 mg $g^{-1}$, even at lower initial concentrations [41]. Similarly, Kappaphycus striatum exhibited a high Pb removal efficiency of 97.82% at an initial concentration of 100 mg $L^{-1}$, indicating that the biosorbent surface becomes saturated with Pb at relatively lower concentrations [42]. The consistent uptake rate for Pb can be attributed to its strong affinity for functional groups such as hydroxyl (-OH) and amine ($-NH_2$) on the biosorbent surface. According to Reda et al. (2025) these groups form stable complexes with Pb ions, resulting in the rapid saturation of the surface [43].

## Biosorption kinetic models

Five kinetic models—First-order, Pseudo-first-order, Elovich, Ritchie second-order, and pseudo-second-order—were utilized to analyse the experimental data and determine their effectiveness in characterizing the adsorption kinetics. Each model was applied to the data, and their effectiveness was evaluated using statistical measures such as the correlation coefficient and error minimization criteria. The pseudo-second-order model provided the best fit among these models, indicating that chemisorption mechanisms mainly drive the adsorption process. Consequently, only the findings and graphical representation of the pseudo-second-order model are included in this study.

The pseudo-second-order equation manipulated is represented by Equation 1.

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \qquad \text{Equation (1)}$$

where,

$q_t$, amount of metal adsorbed per unit mass of moss at time t (mg $g^{-1}$)
$q_e$, amount of metal adsorbed per unit mass of moss at equilibrium (mg $g^{-1}$)
k, pseudo-second-order rate constant (g $mg^{-1}$ $min^{-1}$)

Linear plots of $t/q_t$ versus $t$ are shown in Fig. 6 and 7, and the values k and $q_e$ derived from the slopes and intercepts are detailed in Table 2.

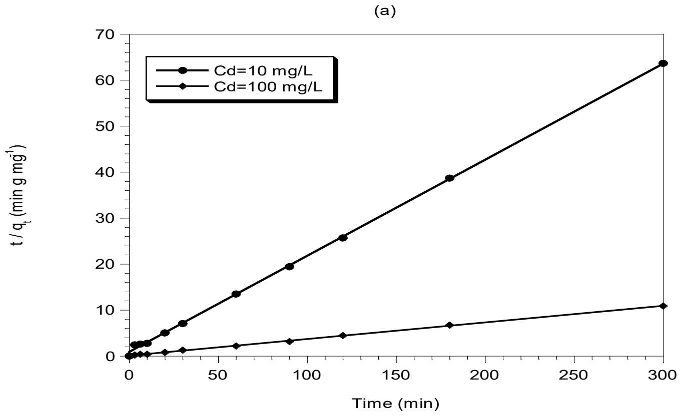

**Figure 6** Pseudo-second-order kinetic model for Cd(II) adsorption.

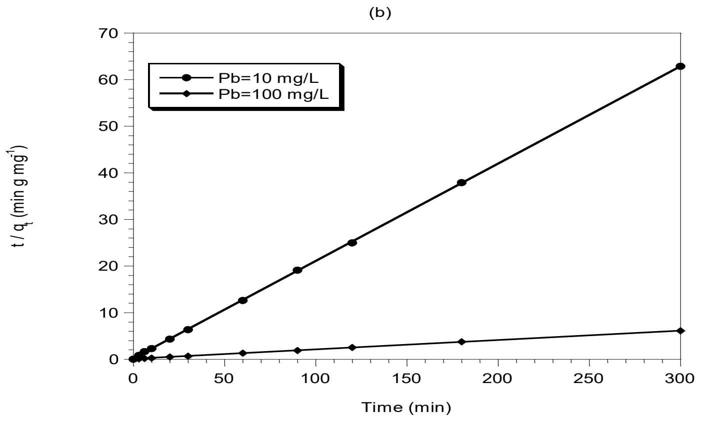

**Figure 7** Pseudo-second-order kinetic model for Pb(II) adsorption.

The correlation coefficients, exceeding 0.999, suggest a strong agreement between the experimental data and the pseudo-second-order kinetic model.

**Table 2** Pseudo-second order rate constants for the removal of cadmium and lead ions by Fontinalis antipyretica.

| Metal | $C_0$ mg $L^{-1}$ | $q_e$ mg $g^{-1}$ (mmol $g^{-1}$) | k g $mg^{-1}$ $min^{-1}$ | h g $mg^{-1}$ $min^{-1}$ | $S^2$ | $R^2$ |
|---|---|---|---|---|---|---|
| Cd | 10 | 4.80 (0.043) | 4.20E-2 | 0.97 | 1.49E-1 | 1.000 |
|  | 100 | 27.7 (0.246) | 1.00E-2 | 7.7 | 1.1E-2 | 1.000 |
| Pb | 10 | 4.79 (0.023) | 0.233 | 5.3 | 1.9E-2 | 1.000 |
|  | 100 | 49.3 (0.238) | 7.00E-3 | 16.5 | 2.6E-4 | 1.000 |

The kinetic constant (k) decreased from $4.20 \times 10^{-2}$ to $1.00 \times 10^{-2}$ g $mg^{-1}$ $min^{-1}$ as the initial cadmium concentration increased from 10 to 100 mg $L^{-1}$. A similar trend was observed for lead, where k declined from 0.233 to $7.00 \times 10^{-3}$ g $mg^{-1}$ $min^{-1}$ over the same concentration range. This downward trend can be linked to various fundamental mechanisms, including alterations in reaction dynamics, the formation of complexes, and diffusion constraints that arise at elevated concentrations. The interplay of these factors reduces the reaction rate constant as the concentration of metal ions increases.

The initial sorption rates (h) were derived from the intercepts of the linear plots presented in Fig. 5. As anticipated, according to values in Table 2, the initial sorption rate exhibited an increase with the higher initial metal concentration, specifically cadmium and lead, underscoring the significant dependence of adsorption kinetics on the availability of metal ions in solution. Reddad et al. (2002) observed similar

behaviour in the adsorption of several metal ions ($Pb^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, and $Ni^{2+}$ cations) onto a low-cost biosorbent (sugar beet pulp) [44].
This behaviour is opposite to the observed by [13] on the sorption of copper, nickel and lead onto Sphagnum moss peat.

Model performance: A simple comparison of the regression coefficients ($R^2$) for the various models of each metal reveals that, although all values are generally high ($>0.90$), the highest values are associated with the pseudo-second-order model.
When the models demonstrate a good fit to the data with reasonable values, it is appropriate to apply an F-test to determine the most suitable model. At a 95% confidence level, with 10 degrees of freedom for both the numerator and denominator, the calculated F-values ($F_{cal}$) for each model pair indicate that, for the biosorption of Cd(II) and Pb(II) by the aquatic moss, the pseudo-second-order model is statistically superior to the other models. However, for cadmium at lower concentrations (10 mg $L^{-1}$), the Lagergren model provides a better fit.
However, the Lagergren model is not statistically more accurate than the Ritchie second-order model ($F_{cal} < 2.98$). The equilibrium sorption capacities predicted by the best model for initial cadmium/lead concentrations of 10 and 100 mg $L^{-1}$ are 0.041/0.023 mmol $g^{-1}$ and 0.246/0.238 mmol $g^{-1}$, respectively.
Therefore, the pseudo-second-order model's better fit indicates that a 1:2 binding stoichiometry applies; that is, one divalent metal ion binds to two monovalent binding active sites. It is perfectly reasonable that a divalent metal would bind to two carboxyl groups, as shown by Schiewer and Wong (1999), in experiments with brown algae. However, it isn't impossible to conclude that the biosorption reaction is the rate-limiting step in all the time range. This conclusion may not be valid because a good model fit does not necessarily indicate the fundamental nature of the rate-limiting step. In many other biosorption cases, diffusion rather than the chemical reaction was the rate-limiting step, at least in the initial instants.

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