Pb(II) removal from aqueous solution by *Myriophyllum spicatum* and its compost: equilibrium, kinetic and thermodynamic study

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**Abstract**

**BACKGROUND:** Lead is one of the frequent contaminants of industrial wastewater. Since it has been shown that aquatic plants can be used for the removal of heavy metals, herein Pb(II) biosorption by *Myriophyllum spicatum* and its compost were investigated. Effects of pH, ionic strength and contact time were analyzed using a batch experiment. Biomasses were characterized chemically and by Fourier transform infrared spectroscopy, scanning electron microscopy and X-ray diffraction techniques.

**RESULTS:** The adsorption process of both biosorbents followed a pseudo-second-order kinetic model. Compost exhibits better Pb(II) removal from solution (71%) compared with the plant (61%). Lead binding capacities for *M. spicatum* and its compost were 0.234 mmol g⁻¹ and 0.287 mmol g⁻¹ at pH 5.0, respectively. Lead binding takes place mainly through an ion exchange mechanism, but chemisorption via identified functional groups cannot be neglected. The Langmuir, Freundlich and Sips adsorption models for compost were applied. The Sips isotherm model gave the best fit with the equilibrium experimental data. The sorption process by compost was endothermic and spontaneous.

**CONCLUSION:** Aquatic weed compost as a low cost biosorbent with high biosorption capacity can potentially be used for the removal of lead from wastewaters.

Supporting information may be found in the online version of this article.

Keywords: compost; aquatic weed; Pb(II) ions; biosorption; isotherm; thermodynamic

**INTRODUCTION**

The presence of heavy metals as non-biodegradable pollutants, originating from various industrial processes, is of great concern today. Lead is one of the frequent contaminants of industrial wastewater. Lead may come from different sources: electroplating, manufacturing of batteries, pigments and ammunition and is toxic to many organs and tissues causing anemia, brain damage, anorexia, malaise, loss of appetite and loss of IQ.¹⁻³ Therefore, it is crucial to remove this element from industrial wastewaters before discharge into natural water systems.⁴

Conventional techniques for heavy metals removal from water effluents, such as coagulation-precipitation, ion exchange, electrolytic extraction, filtration, complexation, reverse osmosis, evaporation, sorption, flotation, etc., have certain limitations that are characterized through high operational cost, high energy requirements, sensitive operation conditions and secondary sludge production. For these reasons, alternative methods which involve removal of contaminants from the solution by biosorption need to be developed, using biomolecules or biomass.⁵,⁶ Biosorption is considered to be a competitive, effective and economically attractive method.⁷

It is well known that aquatic plants are heavy metal accumulators. Therefore, their application for heavy metal removal from wastewaters can be of great significance.⁸,⁹ Processes of metal removal by aquatic plants are twofold, with (1) an initial fast, reversible metal-binding step related to physico-chemical processes such as chelation, ion exchange, precipitation and adsorption, and (2) a slow, irreversible ion-sequestration step involving biological processes such as intracellular uptake, vacuolar deposition and translocation.¹⁰ These uptake processes are identified as biosorption and bioaccumulation.¹¹

*Myriophyllum spicatum* (Eurasian water milfoil) is a submerged aquatic perennial plant which grows on every continent except Antarctica.¹² It reproduces primarily by vegetative fragmentation and grows quickly in a diverse range of aquatic habitats, creating dense infestations which shade out and affects native plants.¹³ The
growth control methods for *M. spicatum* are physical (mechanical harvesters and chopping machines), chemical and biological.

In many countries, as well as in Serbia, *M. spicatum* presents an undesirable aquatic weed which needs to be removed continuously and disposed of several times per year. Compost of *M. spicatum* can be found in large quantities on disposal sites after mowing. It does not have a use value, which makes it a burden on the environment.

Compost is currently successfully used as a soil amendment because of its high water retention capacity with porous character, highly complex mixture of polymeric functional groups and high ion exchange capacity. There is a need to find an alternative application for compost, as its quantity increases during the years. Compost derived from cellulose based materials has shown to be effective in removing heavy metals from wastewater. There are studies related to heavy metals removal by *M. spicatum* but the biosorption of heavy metals by aquatic weed compost has not been widely introduced. In order to utilize the lead binding efficiency, adsorption data for both *M. spicatum* and its compost originating from Serbia were analyzed and compared.

**MATERIALS AND METHODS**

**Preparation of the plant biomass, compost and chemicals**

Samples of freshly harvested *M. spicatum* were taken from the artificial Sava Lake, Belgrade, Serbia. It covers an area of 0.8 km² and is 4.2 km long, and 4 to 6 m deep where the dominant aquatic weed is *Myriophyllum spicatum*. The fresh plant used for analysis was harvested with a mechanical underwater harvester during the summer of 2012. With mowing, the amount of unwanted aquatic weed was significantly reduced (approximately 350–400 m³ per harvesting cycle). The harvested plant material is disposed of in an open landfill used specifically for this purpose and retained in the landfill for 2 years, without turning. During this period, biodegradation takes place in different conditions of oxygen and temperature using a Nicolet 380 spectrophotometer in the spectral range 4000 to 400 cm⁻¹, with a resolution of 4 cm⁻¹. The datasets were averaged over 64 scans. FTIR-ATR spectroscopy was used to identify vibration frequency changes in *M. spicatum* and compost before and after contact with Pb(II) ions.

X-ray diffraction (XRD) patterns were obtained at room temperature using a Philips X-ray diffractometer, model PW-1710. The intensity of the diffracted CuKa X-rays (λ = 1.54178Å) were measured at room temperature at intervals of 0.02° to 5° and time intervals of 0.5 s, in the range 4° to 65° 2θ. The X-ray tube was operated at 40 kV and 30 mA and the slits for routing the primary and diffracted beams were set at 1° and 0.1 mm, respectively.

The pH value of the point zero charge (pHpzc) was determined using the method proposed by Milonjic and Ruvarac (1975).

**Batch experiments**

Batch experiments were performed in order to determine sorption kinetics, isotherms, effect of pH, ionic strength, time and temperature. The experiments were carried out in 100 mL Erlenmeyer flasks with 50 mL of lead solution. The flasks were stirred at 250 rpm in a Heidolph unimax 1010 orbital shaker at the required temperature. Lead solutions with different concentrations were prepared by dilution of the stock solution. Using a precise pH meter (Sension MM340), the pH value was adjusted using 0.1 mol L⁻¹ HNO₃ or 0.1 mol L⁻¹ NaOH (analytical grade). All sorption experiments were done in triplicate.

In order to compare the fresh plant and its compost, 1 g of wet *M. spicatum* fresh tissue (around 0.1 g dry weight) and 0.1 g of compost were used.

In order to determine the effects of ionic strength on biosorption, experiments were conducted by changing the ionic strength using KNO₃ solutions (0.001, 0.01, 0.1 and 1.0 mol L⁻¹). The initial Pb(II) concentration was 1 mmol L⁻¹ and 0.1 g dry weight of each biosorbent was added to 50 mL solution, respectively. The flasks were shaken at 250 rpm for 120 min at pH around 5.

Sorption kinetic studies: experiments for fresh tissue of *M. spicatum* and its compost were carried out at pH values around 5 at an initial Pb(II) concentration of 1 mmol L⁻¹. Samples were taken at defined intervals, up to 160 min.

Sorption isotherms experiments: solutions with concentrations of lead at 0.1, 0.2, 0.5, 1, 1.5 and 2 mmol L⁻¹ with 0.1 g of compost were shaken for 120 min.

The effect of pH on sorption of Pb(II) ions onto compost was examined in the range 2.0–8.0.

Temperature effect: samples were shaken for 2 h at 303 K, 313 K and 333 K.

After the specified contact time, the solid phase was separated from the solution. The Pb(II) concentration in filtrate was determined with an atomic absorption spectrophotometer.

The amount of Pb(II) adsorbed by the biomass was calculated using

\[
q = \frac{V (C_i - C_e)}{M}
\]

where \(q\) (mmol g⁻¹) is the amount of Pb(II) adsorbed by *M. spicatum* or its compost; \(C_i\) and \(C_e\) are the initial and equilibrium metal concentrations (mmol L⁻¹), \(V\) is the volume of Pb(II) solution (L), and \(M\) is the mass of the sorbent (g). Metal removal efficiency (R) is calculated using

\[
R = \frac{C_i - C_e}{C_i} \times 100
\]
Table 1. Chemical composition of M. spicatum and its compost

<table>
<thead>
<tr>
<th>Parameter (%)</th>
<th>M. spicatum</th>
<th>compost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry matter</td>
<td>91.11</td>
<td>97.73</td>
</tr>
<tr>
<td>Moisture</td>
<td>8.89</td>
<td>2.27</td>
</tr>
<tr>
<td>Crude protein</td>
<td>17.95</td>
<td>5.18</td>
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<tr>
<td>Crude fat</td>
<td>1.28</td>
<td>0.06</td>
</tr>
<tr>
<td>Crude cellulose</td>
<td>23.33</td>
<td>2.45</td>
</tr>
<tr>
<td>Ash</td>
<td>17.64</td>
<td>86.49</td>
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<tr>
<td>SEM</td>
<td>30.91</td>
<td>3.55</td>
</tr>
<tr>
<td>Neutral detergent fiber (NDF)</td>
<td>33.38</td>
<td>66.65</td>
</tr>
<tr>
<td>Cellulose + hemicellulose + lignin</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Acid detergent fiber (ADF) Cellulose + lignin</td>
<td>30.96</td>
<td>65.13</td>
</tr>
<tr>
<td>Lignin</td>
<td>6.33</td>
<td>43.20</td>
</tr>
<tr>
<td>Humic acids</td>
<td>/</td>
<td>0.38</td>
</tr>
<tr>
<td>Fulvic acids</td>
<td>/</td>
<td>3.44</td>
</tr>
<tr>
<td>Pb</td>
<td>0.026</td>
<td>0.015</td>
</tr>
<tr>
<td>Mg</td>
<td>0.53</td>
<td>0.46</td>
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<tr>
<td>Zn</td>
<td>0.008</td>
<td>0.0031</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0019</td>
<td>0.0026</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0013</td>
<td>0.004</td>
</tr>
<tr>
<td>Cr</td>
<td>0.00003</td>
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</tr>
<tr>
<td>Fe</td>
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</tr>
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<td>K</td>
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<td>0.16</td>
</tr>
<tr>
<td>Na</td>
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<td>0.038</td>
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<tr>
<td>Ca</td>
<td>5</td>
<td>30.68</td>
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<tr>
<td>S</td>
<td>1.47</td>
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</tr>
<tr>
<td>Mn</td>
<td>0.0017</td>
<td>0.0064</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Characterization

The chemical composition of M. spicatum and its compost is presented in Table 1. Dry matter, moisture and ash content were determined by gravimetric methods. The content of humic and fulvic acids was also determined. Significantly higher contents of cellulose, hemicellulose and lignin were observed in compost than in fresh M. spicatum. Albeit expected that the compost generally contains higher amounts of heavy metals than the plant, only the content of Fe and Ca in the compost exceeded those in the plant, while a small increase in concentration was found for Zn, Cu, Cr and Mn, due to the composting process (Table 1). On the other hand, the fresh plant was found to have higher amounts of Pb, Mg, Ni, Na and K, hence making compost harmless for the possible use in treating wastewaters without the risk of contaminating them. Unlike the plant, the compost of M. spicatum contains lignin, humic and fulvic acids, which are well-known complexing agents. The amount of sulfur is lower in the compost, suggesting that it is probably lost as hydrogen sulfide under anaerobic conditions during biomass degradation.

Scanning electro-micrographs show the surface texture and morphology of M. spicatum and its compost (Figs 1 and 2). The surface of M. spicatum is wavy with a large number of square openings of size 5–10 µm (Fig. 1(a)). At 1000 times magnification, a single rod of biosorbent was focused on, where openings were properly placed in longitudinal rows along the axis of each particle. Examination of this biosorbent indicates that its external layer channels may provide access for the solution into the centre of the particles. Consequently, metal ions could easily penetrate and be further adsorbed at interior sites/acidic centers. Among the particles, diatoms can be observed.

Effect of pH

The pH value of the solution determines the dominant lead species as well as the sorbent surface charge. Pb$^{2+}$ is present as the dominant species at pH < 5.5, Pb(OH)$_2$ at 5.5 < pH < 12 and Pb(OH)$_{2+}$ at pH > 12 (Fig. 4). Various species of lead can be noted as potential sorbates: Pb$^{2+}$, PbOH$^+$, Pb$_2$OH$^{3+}$, Pb(OH)$_{2+}$ and Pb(OH)$_4^{2-}$.
Pb(II) removal by M. spicatum and its compost

Figure 1. SEM micrographs of (a) pure M. spicatum (1000 times magnification); (b) Pb-loaded M. spicatum (1000 times magnification). SEM-EDX analysis of M. spicatum before (c) and after Pb(II) sorption (d).

Pb(OH)₃⁻ (Fig. 4). Although at pH values above pH of the zero point charge (pHpZC = 7 and 6.1 for M. spicatum and its compost, respectively), sorbent surfaces attract cations, the precipitation of Pb(OH)₂ occurs. Yan et al. (2010)⁵ and Keskin et al. (2007)⁹ suggested that heavy metals can be removed by M. spicatum at pH around 5, where, due to the formation of bonds between lead and the functional groups on the surface of the sorbent, the electrostatic repulsion between them is overcome. Therefore, in this study, the removal of Pb²⁺ by M. spicatum and its compost was performed at pH 5.

Effect of ionic strength

The Pb(II) removal by M. spicatum and its compost as a function of ionic strength is shown in Fig. 5. The biosorption yield of the plant and its compost decreased by approximately 30% as ionic strength was increased from 0.001 to 1 mol L⁻¹ KNO₃. This can be attributed to the competition between Pb(II) and K⁺ ions for binding sites of biosorbents. It was also reported that metal uptake is affected by changes in the concentration of the supporting electrolyte if electrostatic attraction is a significant mechanism for metal removal.²⁴ The unfavourable effect of ionic strength on Pb(II) removal may be evidence for an ion-exchange mechanism.²⁵

Effect of contact time

The effect of contact time on both biosorbents was studied with an initial Pb(II) concentration of 1 mmol L⁻¹, initial pH value around 5 and contact time between 5 and 160 min (Fig. 6). The sorption rate was very high and a contact time of 20 min was enough to reach equilibrium. However, to ensure sorption equilibrium the chosen contact time in this experiment was 120 min.

Lead biosorption capacity, qₑ, for M. spicatum and its compost were 0.234 mmol g⁻¹ and 0.287 mmol g⁻¹, respectively, indicating efficient removal of Pb(II) from water solution by both biosorbents, with compost the better of the two.

Kinetic study

In this work, three kinetic models were applied to the experimental data. Reaction based models include a pseudo-first-order or Lagergren model,²⁶ Ho–McKay or pseudo-second-order model²⁷ and diffusion based model, the intraparticle diffusion model.²⁸ The models and their parameters are presented in Table 2.

The Lagergren pseudo-first-order model can be presented in linear form as

\[
\log (q_e - q) = \log q_e - \frac{k_1}{2.303} t
\]

where \(q_e\) and \(q\) (mg g⁻¹) are the amounts of metal ions biosorbed at equilibrium time and \(t\) (min), respectively, and \(k_1\) is the rate constant of pseudo-first-order adsorption (min⁻¹).

A pseudo-second-order kinetic model can be applied assuming that measured concentrations are equal to cell surface concentrations.²⁹ It can be expressed through

\[
\frac{dq_t}{dt} = k_2 (q_e - q_t)^2
\]

where \(k_2\) is the rate constant (g mg⁻¹ min⁻¹), \(q_e\) is the amount of metal ion adsorbed at equilibrium (mg g⁻¹), and \(q_t\) is the amount of
metal ion the surface of sorbent at any time $t$ (mg g$^{-1}$). Linear form of Equation (6), obtained for boundary conditions $t = 0$, $q_t = 0$; $t = t$ and $q = q_t$ results in:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{q_e k_2}$$

(5)

The intraparticle diffusion equation is given as

$$q = K_i d^{0.5} + C$$

(6)

The plot of uptake, $q_t$, versus the square root of time ($t^{1/2}$) did not pass through the origin and this further indicates that the intra-particle diffusion is not the only rate-controlling step, but also other kinetic models may control the rate of adsorption.$^{10}$

The best fitting kinetic model was evaluated using the squared sum of errors (SSE) value. The SSE value was calculated using

$$SSE = \sum (q_{t,\text{exp}} - q_{t,\text{cal}})^2$$

(7)

where $q_{t,\text{exp}}$ and $q_{t,\text{cal}}$ are the experimental biosorption capacities (mg g$^{-1}$) at time $t$ and the corresponding values that are gained from the kinetic models.

The values obtained for calculated sorption coefficients $q_{e,\text{cal}}$ were in very good agreement with the experimental values $q_{e,\text{exp}}$, indicating that biosorption of Pb(II) ions onto M. spicatum and its compost follows the pseudo-second-order model (Table 2).

**Pb (II) removal**

The results obtained show that different types of interaction are involved in the sorption of Pb(II) by the examined biosorbents. Pb(II) concentration in the filtrates after biosorption at different pH values, as well as the amount of exchangeable cations are presented in Table 3. Pb(II) concentration after sorption rapidly decreases in both cases. At pH 5, the concentration of Ca$^{2+}$ in filtrate after biosorption by both sorbents increases, in comparison with its concentration in the deionized water solution. Increase in Ca$^{2+}$ concentration at lower pH is probably a result of the exchange with H$^+$ ions. The lower Ca$^{2+}$ concentration in the solution at higher pH values was noted in both cases. The presence of different exchangeable ion species (Ca$^{2+}$, Na$^+$, Mg$^{2+}$ and K$^+$) in the solutions after biosorption is the result of the chemical composition of biosorbents (Table 1). This is confirmed with EDX spectra which are presented in Figs 1 and 2. The concentrations of Na$^+$ rise with increasing pH value, while Mg$^{2+}$ and K$^+$ concentrations slightly decrease. This could specify that lead binding occurs mainly through the ion exchange mechanism, between Pb(II) and exchangeable cations, Ca$^{2+}$ for compost and Ca$^{2+}$ and Na$^+$ for fresh plant. Matos et al. (2009)$^{31}$ reached a similar conclusion for bioadsorption of Pb(II) and Cr(III) on algae. The lead exchange with calcium in the biosorbent (CaX2) can be characterized by the following reaction:

$$\text{Pb}^{2+} + \text{(CaX)} \leftrightarrow \text{Ca}^{2+} + \text{(PbX)}$$

(8)

In addition to ion exchange, the contribution of other mechanisms such as chemisorption and complexion interactions should not
Table 2. Parameters of pseudo-first-order, pseudo-second-order and intraparticle diffusion models. Experimental conditions: Pb(II) initial conc. 1 mmol L\(^{-1}\), biosorbent dry weight 0.1 g, pH 5.0, agitation rate 250 rpm (bio)sorbent Lagergren pseudo-first-order Pseudo-second-order Weber and Morris

<table>
<thead>
<tr>
<th>biosorbent</th>
<th>(q_e) (experimental (mg g(^{-1}))</th>
<th>(k_1) (L (mg(^{-1})) min(^{-1}))</th>
<th>(R^2)</th>
<th>SSE</th>
<th>(q_e) (mg g(^{-1}))</th>
<th>(k_2) (g mg(^{-1}) min(^{-1}))</th>
<th>(R^2)</th>
<th>SSE</th>
<th>(K_{id}) (mg g(^{-1}) min(^{-0.5}))</th>
<th>(C) (mg g(^{-1}))</th>
<th>(R^2)</th>
<th>SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>M. spicatum</td>
<td>48.50</td>
<td>13.76</td>
<td>0.0315</td>
<td>0.9750</td>
<td>3.266</td>
<td>49.50</td>
<td>0.0057</td>
<td>0.9995</td>
<td>0.2021</td>
<td>0.9547</td>
<td>37.48</td>
<td>0.9610</td>
</tr>
<tr>
<td>compost</td>
<td>59.50</td>
<td>12.12</td>
<td>0.0107</td>
<td>0.8067</td>
<td>4.099</td>
<td>59.52</td>
<td>0.0107</td>
<td>0.9082</td>
<td>0.2476</td>
<td>1.301</td>
<td>42.64</td>
<td>0.9754</td>
</tr>
</tbody>
</table>

Figure 3. FTIR spectra: (a) M. spicatum (washed, particle size less than 0.2 mm) before and after Pb(II) biosorption (contact time 120 min, pH=5, Pb(II) initial conc. 1 mmol L\(^{-1}\), agitation rate 250 rpm); (b) compost before and after Pb(II) biosorption at pH=5 (contact time 120 min, Pb(II) initial conc. 1 mmol L\(^{-1}\), agitation rate 250 rpm; particle size less than 0.2 mm).

Figure 4. Concentration of lead species in the solution (concentration of lead = 1 mmol L\(^{-1}\)).

be excluded. Differences in the structure between M. spicatum and its compost, especially in the content of lignin humic and fulvic acids, as the result of degradation of plant biomass, should be emphasized. Lignin may strongly interact with Pb(II) through formation of stoichiometric bonds involving those easily ionizable functional groups (carbonyl, carboxyl, phenolic, and hydroxyl) of its structure. With respect to the kind of bond, whether it is electrostatic or a chelate remains an open question.\(^{32}\) Humic substances, on the other hand, have a strong affinity to complex metal ions.\(^{15}\)
From the results it can be concluded that after 2 h the fresh plant and its compost can remove about 61% and 71% of lead from the solution at the selected pH, respectively (Table 3). In addition, compost showed better lead binding capacity \( q_e \) (Fig. 6), which classifies it as the preferred lead biosorbent, suitable for further analysis.

### Sorption isotherm models

In this study, three isotherm models, Langmuir, Freundlich and Sips, were applied in order to analyze the experimental data.

The Langmuir equation relates the coverage of molecules on solid surface to the concentration of a medium above the solid surface at constant temperature. This isotherm is based on a monolayer assumption, where all sites possess equal affinity for sorbate.

The Langmuir equation can be described as:

\[
q_e = \frac{q_m K L C_e}{1 + K_L C_e}
\]  

where \( C_e \) is the equilibrium concentration (mmol L\(^{-1}\)), \( q_e \) is the equilibrium adsorption capacity (mmol g\(^{-1}\)), \( q_m \) is Langmuir monolayer saturation capacity (mmol g\(^{-1}\)), and \( K_L \) is the Langmuir sorption constant (L g\(^{-1}\)) related to the free energy of sorption.

The Freundlich isotherm is an empirical equation that assumes a heterogeneous sorption surface. This model has the following form:

\[
q_e = K_f C_e^{1/n}
\]  

where \( K_f \) is a constant of the sorption capacity and \( 1/n \) is an empirical parameter of the sorption intensity. The Sips isotherm presents a combination of Langmuir and Freundlich isotherms. At low sorbate concentrations, the Sips equation reduces to a Freundlich isotherm, while at high sorbate concentrations, it assumes monolayer sorption, characteristic of the Langmuir isotherm.\(^{33}\)

It can be expressed as:

\[
q_e = q_m \left(\frac{a_S C_e}{a_S C_e + 1}\right)^{n_S}
\]  

where \( a_S \) and \( n_S \) are Sips isotherm constants.

Langmuir, Freundlich and Sips isotherm models for sorption of Pb(II) onto compost are given in Fig. 7. According to the value of the correlation coefficient \( R^2 \), the Sips isotherm (\( R^2 = 0.961 \)) gave the best fit to the experimental data (Supplementary material, Table TS1).

### Table 3. Concentration of elements in the biosorbent filtrates

<table>
<thead>
<tr>
<th>pH</th>
<th>Pb(II) (mg L(^{-1}))</th>
<th>Na(^+) (mg L(^{-1}))</th>
<th>Ca(^{2+}) (mg L(^{-1}))</th>
<th>K(^+) (mg L(^{-1}))</th>
<th>Mg(^{2+}) (mg L(^{-1}))</th>
<th>Pb(II) (mg L(^{-1}))</th>
<th>Ca(^{2+}) (mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>169</td>
<td>23.4</td>
<td>81</td>
<td>42.2</td>
<td>6.5</td>
<td>187</td>
<td>580</td>
</tr>
<tr>
<td>3</td>
<td>110</td>
<td>67.4</td>
<td>66</td>
<td>42.4</td>
<td>6</td>
<td>166</td>
<td>370</td>
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<td>4</td>
<td>95</td>
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<td>44</td>
<td>41.9</td>
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<td>82</td>
<td>71.8</td>
<td>29</td>
<td>40.05</td>
<td>5.7</td>
<td>60</td>
<td>96</td>
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<tr>
<td>6.5</td>
<td>3.3</td>
<td>92.6</td>
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<td>41.6</td>
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<td>0.5</td>
<td>73.7</td>
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<tr>
<td>7</td>
<td>2.9</td>
<td>107.8</td>
<td>19</td>
<td>40.6</td>
<td>4.44</td>
<td>0.2</td>
<td>25</td>
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<tr>
<td>8</td>
<td>3.7</td>
<td>292</td>
<td>10</td>
<td>41.2</td>
<td>3.58</td>
<td>0.1</td>
<td>16</td>
</tr>
<tr>
<td>Blind</td>
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<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Deionized H(_2)O(^a)</td>
<td>38.7</td>
<td>3.19</td>
<td>0.4</td>
<td>1.22</td>
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<td></td>
</tr>
</tbody>
</table>

\(^a\) Concentration of the elements in the untreated biosorbent filtrates.
positive value of \( \Delta H^\circ \) and entropy \( \Delta S^\circ \) were calculated using the following equations:

\[
\Delta G^\circ = -RT \ln K_D \tag{12}
\]

\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \tag{13}
\]

\[
-RT \ln K_D = \Delta H^\circ - T \Delta S^\circ \tag{14}
\]

\[
\ln K_D = \frac{- \Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{15}
\]

where \( R \) is the universal gas constant (8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{K}^{-1}), T \) is the temperature (K) and \( K_D (q_e/C_e) \) is the distribution coefficient. The enthalpy change \( \Delta H^\circ \) and entropy change \( \Delta S^\circ \) were determined from the slope and intercept of the plot 1/\( T \) versus \( \ln K_D \) (Equation (11), Supplementary material Fig. S4).

The positive value of \( \Delta S^\circ \) indicates increasing randomness at the solid/liquid interface during the sorption of Pb(II). The positive value of \( \Delta H^\circ \) shows the endothermic nature of Pb(II) adsorption. The decrease of Gibbs free energy \( \Delta G^\circ \) with increasing temperature indicates that spontaneity of the reaction increases with increase of temperature. Removal of lead showed to be most efficient at a temperature of 313 K (Supplementary material Fig. S5 and Table TS2).

**Life cycle of *M. spicatum* compost as biosorbent of Pb(II) removal**

Precipitation of heavy metals as metal hydroxides or sulfides has been carried out as the primary method of treatment for heavy metals in industrial wastewater for many years. Nevertheless, this process creates a special problem of sludge handling and costly disposal. Electrochemical treatment is expensive for high metal concentrations. Ion exchange, membrane technologies and activated carbon adsorption processes are very expensive when treating a large quantity of water and wastewater containing heavy metals in low concentrations; they cannot be used at large scale. Biosorbents possess a metal-sequestering property and can be used to decrease the concentration of heavy metal ions in solution. They can successfully sequester dissolved metal ions out of dilute complex solutions with high efficiency and rapidly; thus, they are an ideal candidate for the treatment of high volume and low concentration complex wastewaters.

The preliminary study of *M. spicatum* compost as potential biosorbent for Pb(II) removal from aqueous solutions has shown that the predominant mechanism present is ion exchange. Although the biosorption capacity is lower than those of synthetic resins, the main advantages are the abundance of this costless material, easy availability and its economic feasibility. Processes included in the stages and sub-stages of the *M. spicatum* compost biosorbent life cycle are presented in Fig. 8. This sorbent is waste material obtained in large quantities in many parts of the world where this invasive aquatic weed is harvested and disposed of in open landfills. Due to its availability, the use of regenerated material for biosorption is not necessary, as also proposed by Yetilmesszy and Demire. They investigated Pb(II) removal using pistachio shells and suggested incineration of metal laden biomass. However, air pollutants emission from the incineration process and the problem of ash disposal in a secure landfill, are the main disadvantages of the proposed procedure. In order to decrease potential emission and environment pollution by treatment of the spent biomass, it is recommended to desorb Pb from exhausted biosorbent, with an appropriate acid, and use it as fertilizer in areas (parks, green spaces) where plants which are not used for human consumption are planted.

### CONCLUSION

In this paper, the most important reaction parameters of Pb(II) biosorption onto *M. spicatum* and its compost were determined. A study of pH influence on the sorption process showed that the best removal of lead was at pH 5 and that 20 min was enough time to reach equilibrium. Further, the biosorbents were characterized chemically and by SEM, FTIR and XRD techniques.

Kinetic studies have shown that the biosorption process with both biomasses best fits the pseudo-second-order kinetic model. Based on results of batch experiments, compost exhibits better Pb(II) removal from solution and higher lead binding capacity than...
plant *M. spicatum*, where lead binding occurs mainly through ion exchange mechanisms. Notwithstanding, the involvement of other mechanisms such as chemisorption and complex formation should not be excluded. The contribution of particular lead sorption mechanisms is mainly affected by the structure of the biomass.

Three isotherm models were applied to experimental data with compost and the Sips model gave the best fit, with a correlation coefficient ($R^2$) of 0.961. According to a temperature dependency study on the compost, the sorption process was endothermic and spontaneous.

Overall, results imply that aquatic weed compost could be used as an efficient sorbent of lead from wastewaters and that its application could be safe, convenient and sustainable.

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**Supporting Information**

Supporting information may be found in the online version of this article.

**REFERENCES**