Removal of Pb(II), Cu(II), and Cd(II) from Aqueous Solution by Alginate-Immobilized Aquatic Weed *M. spicatum*

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Abstract

Biosorption is evolving as a potential alternative to the existing conventional technologies for the removal and/or recovery of pollutants from aqueous solutions. The present work investigates the possible application of waste biomass *Myriophyllum spicatum* (Ms) in removing contaminants, evaluating equilibrium through isotherms of selected heavy metals: lead, copper, and cadmium. As a heavy metal biosorbent, Ms was immobilized in alginate beads (Ms: Alginate 2:1). Applied biosorbent, MsA, was characterized by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM–EDX) and Fourier transform infrared spectroscopy (FT-IR). Experimental results were fitted (nonlinear) by six isotherm models: Langmuir, Freundlich, Sips, Redlich and Peterson, Toth, and Temkin. For lead(II) ion removal, fitting follows the following sequence, F ≈ R-P>S>To>L>Te, while for copper(II) and cadmium(II) ions are as follows: R-P>To ≈ Te ≈ L>S>F and R-P>L>To>S>F>Te, respectively. TOC analyses revealed that *M. spicatum* releases 35.04 mg/L of total organic content while immobilized sample, MsA, only 6.81 mg/L. Finally, this biosorbent was tested on a sample of real wastewater from a coal-fired thermal power plant complex TPP Kostolac (operated by PE "Electric Power Industry of Serbia"). The results indicate that using immobilized aquatic weed *M. spicatum* as a biosorbent has a high potential for heavy metal wastewater treatment applications.

Keywords

Biosorption · Heavy metals · Aquatic weed · Immobilization · Wastewater

1 Introduction

Myriophyllum spicatum L. is a submerged aquatic weed found in at least 57 countries. Therefore, this weed is native to Europe, Asia, and North Africa but is also a major aquatic invader across most of North America (Couch et al., 1985). This weed has been classified as a Category 1 weed due to its widespread negative effects on the environment around the world (Martin & Coetzee, 2014). *M. spicatum* fits the criteria for a prospective biosorbent because of its natural abundance, high availability, and non-toxic nature (Milojković et al., 2019). In our earlier investigations, we also showed good performance of *M. spicatum* immobilized in alginate beads (MsA) for the removal of Pb (Milojković et al., 2019), Cu (Milojkovic et al., 2019), and Cd (Milojković et al., 2016) ions from single-component aqueous solutions.

This study aims to continue previous research and investigate the possible application of alginate-immobilized aquatic weed M. spicatum in removing Pb, Cu, and Cd ions from multimetal aqueous solutions.

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2 Materials and Methods

M. spicatum used to prepare beads MsA originates from Sava Lake (Belgrade, Serbia). *M. spicatum* was immobilized in alginate beads (Ms: Alginate = 2:1), and beads were made according to the method (Yan & Viraraghavan, 2001).

Scanning Electron Microscopy—Energy Dispersive X-Ray Spectroscopy (SEM–EDX) analysis was performed on MsA before and after the biosorption of heavy metals using JEOL JSM 6460 model. The release of organic carbon was determined by measuring the TOC by Analytik Jena, TOC/TN Analyzer (Multi N/C 2100S). In addition, infrared spectroscopy analysis (FT-IR) was performed on a Thermo Scientific Nicolet iS50 FT-IR spectrometer in transmission mode with 256 scans over a range 4000–400 cm^{-1}.

The adsorption of the Pb(II), Cu(II), and Cd(II) was studied at pH 5.0 in the concentration range 0.2–6 mmol/L (for each heavy metal) as batch biosorption tests with two g/L MsA. After 24 h, heavy metal concentrations were determined on an atomic absorption spectrometer Perking Elmer Analyst 300. In addition, Langmuir, Freundich, Sips, Redlich and Peterson, Toth, and Temkin adsorption isotherms were used to fit experimental results. Evaluation of isotherm was made using OriginPro 2021 software.

To determine the effectiveness of the MsA in real wastewater samples, this biosorbent was tested on wastewater samples from the coal-fired thermal power plant complex-TPP Kostolac (PE "Electric Power Industry of Serbia", Branch TE-KO Kostolac).

3 Results and Discussion

3.1 MsA Characterization

The presence of calcium in studied samples could explain the white areas visible on micrographs (Dibdiakova et al., 2015). Granule MsA is ovoid and spherical with rough, uneven edges (Fig. 1a, b). Different porosity is visibly stratified. Macro pores are made up of complex layers, and tiny balls are bonded to the surface of MsA. After biosorption of heavy metals, porosity exists (Fig. 1b) but is not as plain as in granules. EDX confirmed the infiltration of examined heavy metals. After sorption, reduced peaks of Ca, as well as new peaks of Pb(II) Cu(II), and Cd(II), are observed (Fig. 1g) compared to the starting MsA material (Fig. 1f).

TOC analysis showed that MsA releases only 6.81 mg/L of total organic content.

FT-IR showed that carbonyl, carboxyl, and hydroxyl groups are likely involved in the biosorption of detected heavy metals by MsA. Identified chemically active groups are components of polysaccharides, cellulose, hemicellulose, lignin, and proteins, which can be found in aquatic weed *M. spicatum* (Dibdiakova et al., 2015).

3.2 Heavy Metal Adsorption Study

During the biosorption process, the highest removal was obtained for lead ions with a maximum capacity of 0.530 mmol/g, while for copper 0.255 mmol/g, and the

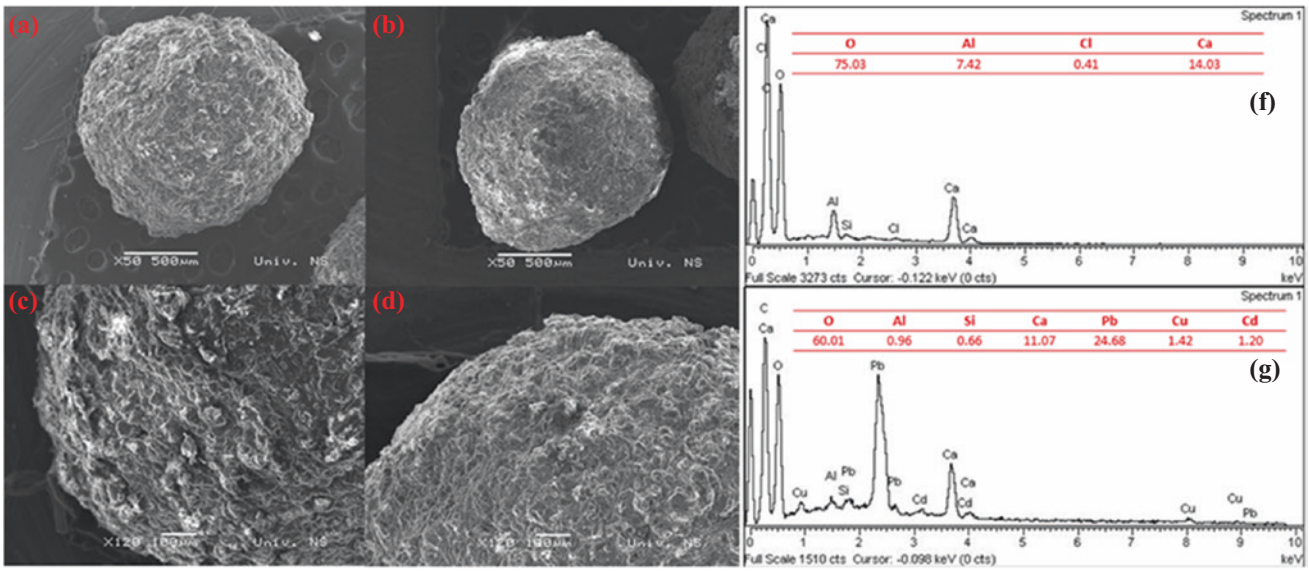

Fig. 1 SEM micrographs of MsA: before biosorption 50× **a** and **c** 120× magnification; after biosorption 50× **b** and **d** 120× magnification; **f** EDX before biosorption and **g** EDX after biosorption

Table 1 Parameters of isotherms obtained for heavy metal ion removal by MsA

Isotherm	Parameters	Pb(II)	Cu(II)	Cd(II)
Langmuir (L)	q_m (mmol/g) K_L/L/mg R^2	0.479 32.166 0.89641	0.251 21.739 **0.97392**	0.130 121.559 **0.86253**
Freundlich (F)	K_f n R^2	0.618 3.337 **0.97939**	0.268 2.354 0.90042	0.134 8.308 0.52145
Sips (S)	q_m K_S (L/g) n_S R^2	5.470 0.144 0.368 0.96457	0.666 0.681 0.426 0.94488	0.078 3.909 0.332 0.79875
Redlich and Peterson (R-P)	k_{RP} (L/g) a_{RP} (L/mg) b_{RP} q_m (mmol/g) R^2	105.235 174.659 0.736 0.602 **0.97790**	7.512 29.165 0.918 0.258 **0.98053**	10.825 87.716 1.081 0.123 **0.88843**
Toth (To)	q_m (mmol/g) K_T (mg/L)Th T_h R^2	1.620 0.234 0.208 0.95469	0.278 0.087 0.697 **0.97661**	0.127 8.125 1.674 0.85988
Temkin (Te)	b_T (J/mol) A_T (L/mg) R^2	89,265.475 921,277.849 0.56652	57,675.715 405.437 **0.97495**	477,630.489 6.386 0.43264

lowest for cadmium, 0.144 mmol/g. For lower initial heavy metal concentrations (2.5 mM), the removal efficiency was 90–100%, while for the highest concentrations (6 mM), MsA adsorbed 72% of lead, 39% of copper, and 14% of cadmium.

To get more information about the removal mechanism, Langmuir, Freundlich, Sips, Redlich and Peterson, and Toth and Temkin models were used to fit experimental results, and characteristic parameters are given in Table 1.

The affinity of MsA for binding heavy metal ions changes in the following order Pb>Cu>Cd. It is common for all three heavy metals that Redlich and Peterson isotherm is one of the best-describing models for their removal from solutions. According to this model, the maximal adsorption capacities of the MsA for lead, copper, and cadmium ions were 0.602, 0.258, and 0.123 mmol/g, respectively, which is in good agreement with ex12%). Lead ions removal was best described by Redlich and Peterson and Freundlich, while copper and cadmium ions removal were best described by Redlich and Peterson and Langmuir model. This suggests that for active centers in internal channels and cavities of MsA materials that are more difficult to access, there was direct competition between these heavy metals. Due to the higher affinity of the biosorbent for lead, copper and cadmium ions were displaced from these hard-to-reach places, so they were mainly bound only to surface-active centers. In contrast, lead ions were bound to the surface and in larger quantities to harder-to-reach centers.

The advantages of immobilization of *M. spicatum* were proven through TOC analysis because it was shown that immobilized biomass releases (6.81 mg/L) 5 times less organic matter compared to the biomass of this water weed (35.04 mg/L) during the treatment of water with the tested heavy metals.

MsA beads showed an excellent percentage of heavy metal removal from an actual sample of wastewater (TPP Kostolac). Chromium was removed in the highest percentage 75%, copper and zinc were released in the same amount 50%, Cd 30.8%, and then other heavy metals: Ni (20%), Pb (7.14%), Fe (5.12%), and Mn (4.45%).

4 Conclusions

Subsequent conversion of plant biomasses into animal feed, biochar, adsorbent, fertilizer, and bioenergy production materials may support a circular economy approach (Kurniawan et al., 2021). It is demonstrated that this water weed can be applied sustainably as alginate granules because it is easy to cut and collect, with no need for additional energy for drying, solving some potential ecological problems and low cost (Milojković et al., 2018).

The application of aquatic weed *M. spicatum* may support a circular economy approach because it is something that would be discarded as waste, and that would have to be

removed, disposed on landfills, and/or burnt; by its application described in this study, it is re-valued as biosorbent for Pb(II), Cu(II), and Cd(II) removal.

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