European Journal of Sustainable Development (2016), **5**, 4, 457-463 ISSN: 2239-5938
Doi: 10.14207/ejsd.2016.v5n4p457

Removal of Pb(II) using alginate – immobilized *Myriophyllum spicatum* beads

J. Milojković*[1], M. Stojanović[1], M. Mihajlović[1], Z. Lopičić[1]

Abstract
Directive 1999/31/EC requires that biowaste with more than 3% organic content isn't accepted for landfilling directing toward more efficient use of biological material from the landfill. Myriophyllum spicatum is an aquatic weed which grows on every continent except Antarctica and it is noted for its capability to cause different problems, so its growth must be controlled. Utilization of bio-waste in the bioeconomy can be achieved with biosorption. In this study was investigated M. spicatum/alginate (5:1) biosorbent (MsA) for the removal of Pb(II) ions from aqueous solutions. MsA was characterized by Fourier transform infrared spectroscopy. The batch equilibrium was expressed by 5 isotherms and Redlich-Peterson isotherm model provided the best fit with the experimental data. Since, alginate-immobilized M. spicatum beads have superb Pb(II) uptake 200 mg/g they are appropriate cost-effective, environmental friendly biosorbent with potential application for continuous flow reactors. Managing and processing bio-waste must be deployed and integrated to meet the requirements of the sustainability.

Keywords: bioeconomy, biosorption, aquatic weed, Myriophyllum spicatum, alginate, lead, Environmental sustainability

1. Introduction

Human exploitation of biomass or biogenic materials as feedstock isn't new; but currently there is a renewed interest in effective exploitation of unavoidable organic wastes, in order to reduce eco-footprint and achieve a further secure supply of renewable resources (Mohan et al., 2016). The biomass as locally applicable strategic tool, can contribute to sustainable development, which in each case should be evaluated (Silvina and Judith, 2015).

A new conversation is emerging on the function of biogenic waste materials in modern bioeconomies. 'Bioeconomy' has some conceptual alignment with the plans of 'sustainability' and utilization of biomass and renewables. Bioeconomy may possibly create new directions and opportunities for some sustainability requirements (O'Callaghan, 2016).

Introducing stringent technical requirements for waste and landfills Directive 1999/31/EC aims to avoid or reduce negative effects from the landfilling of waste on the environment: surface water, groundwater, soil, air, and on human health (Landfill waste). There is estimation that by 2020 the EU Member States possibly will be

[1]Institute for Technology of Nuclear and Other Mineral Raw Materials, 86 Franchet d'Esperey St. Belgrade, Serbia.

generating 45% more waste than in 1995. Directive 1999/31/EC discourages the landfilling of biodegradable waste and set downs the basis for developing new technologies for biowaste reuse (EUBIA).

Today, very important environmental problems are: water and soil pollution by heavy metals. There are successful methods of wastewater treatment but significant amounts of low concentration of heavy metals in effluents still find their way to the soil and groundwater and at last into the food chain (Christoforidis et al., 2015). Human industrial activities: mining, power industry, electroplating, fertiliser, petrochemical and waste depositing can caused lead contamination. Continuously exposure to lead even in low concentration, can cause problems with kidney and liver, brain and the nervous system deterioration, Alzheimer's disease (Naseem and Tahir, 2001)

Development of cost-effective technologies for removal and recovery of heavy metals from wastewaters is becoming a significant. Biosorption is showed to be promising for heavy metal removal because of its low cost, environmental friendly, high efficiency for low concentration of metal ions (Mehta and Gaur, 2005).

Origin of *M. spicatum* L. (Eurasian watermilfoil) is Eurasia (Europe, Asia) and North Africa but it could be also found in North America where it is invasive species (Couch and Nelson 1985). This aquatic weed is tolerant to a wide range of water pH. Due to vegetative reproduction and forceful growth dense stand considerably impacts water flow and clog industrial and potable water supply systems, blocks sunlight for native aquatic plants and creates habitats favorable for mosquitoes (Aiken et al., 1979). Methods for growth control are physical (harvesting), chemical and biological (Milojković et al., 2014)

Myriophyllum spicatum has been investigated for their potential in heavy metal removal. Mechanisms of metal removal by biosorption can be classified as: extracellular accumulation/precipitation, intracellular accumulation and cell surface sorption/precipitation (Rai et al., 2002).

Applications of biosorbents in powdered form have difficulties associated with separation of biomass after biosorption process. Biosorbents should be immobilized, which make them more suitable to be used in reactors and columns. Improved mechanical strength provides an easier separation from the solution and also immobilized biosorbents have potential for successive regeneration and recovery without important loss in performance (Alhakawati and Banks, 2004). Most usually used immobilization matrices are: alginate, silica gel, agar, polysulfone (Chatterjee et al., 2008)
In this work, beads made by immobilizing dried *Myriophyllum spicatum* with alginate – MsA were investigated for their ability to remove Pb(II) ions from water solution using a batch technique.

2. Materials and Methods

2.1 *Myriophyllum spicatum* propagation and fabrication of *M. spicatum* - alginate beads

Samples of freshly harvested M. spicatum were collected from the artificial Sava Lake, Belgrade, Serbia. Dominant aquatic plant in Sava Lake is aquatic weed Myriophyllum spicatum. This lake covers the area of 0.8 km2 and is 4.2 km long, 4 to 6 m deep (Milojković et al., 2014). The fresh plant employed for analysis has been harvested with a mechanical underwater harvester for the period of summer 2015 as it presented on Figure 1.

a)

b)

c)

Figure 1 Harvesting (cutting) of M. spicatum with a mechanical underwater harvester at Sava Lake (a) loading mown plant material (b) Fresh harvested plant M. spicatum from Sava Lake

Harvested fresh plant material was first washed with tap wather and then 3 times with distilled water. Afer washing *M. spicatum* was dried in air at ambient conditions of 35 ° C during several days. Dried plant was milled and sieved to particles <0,2 mm.

Production of *M. spicatum* beads was based on a method used by Viraraghavan and Yuan (2001). Polymer solution 2% was prepared dissolving sodium alginate (Sigma Aldrich Germany) and after homogenization biomass powder 10 g was added. Gained beads MsA had high amount of aquatic weed, so ratio *M. spicatum* - alginate was 5:1.

2.2 Fourier Transform Infrared Spectroscopy

MsA was characterized by Fourier Transform Infrared Spectroscopy (FT-IR) in order to determine the vibration frequency changes of the functional groups. The Fourier transform infrared (FT-IR) spectra were collected with a Thermo Scientific Nicolet iS50 spectrometer with a diamond attenuated total reflectance (ATR) smart accessory at a spectrum resolution of 2 cm^{-1} with 256 scans over a range of 4000–400 cm^{-1}. A background scan was acquired before scanning the samples.

2.3 Batch sorption experiments

As a source of lead analytical grade $Pb(NO_3)_2$ was used. In order to determine isotherms, batch experiments were performed in 100 ml Erlenmeyer flasks with 50 ml of lead solution and 0,1 g *M. spicatum* beads – MsA (5:1). That amount was chosen because it corresponds to the amount of wet *M. spicatum* biomass (1 g) which was used in previous studies of Milojković et al., (2014). Lead solutions, with different concentrations (0.2, 0.5, 1, 1.5, 2, 2.5, 3, 3.5 and 4 mmol/l), were prepared by dilution of the stock solution (10 mmol/l). In order to compare the fresh plant and its compost, 1 g of wet *M. spicatum* fresh tissue (around 0.1 g dry weight

The flasks were shaken for 24 h at 200 rpm in a Heidolph unimax 1010 orbital shaker. Using a precise pH meter (Sension MM340), the pH value was adjusted to 5. During the biosorption experiments pH was controlled and had a value of about 5. After a contact time of 24 hours, MsA (5:1) was easy separated from the solution by decantation. All sorption experiments were done in duplicate.

The analytical measurements of lead ions concentration were made using atomic absorption spectrometry (Perking Elmer AAnalyst 300)

The amount of Pb(II) adsorbed by the MsA (5:1) was calculated using Equation 1:

$$q = \frac{V(C_i - C_e)}{m} \quad (1)$$

where q (mmol/g) is the amount of Pb(II) adsorbed by MsA (5:1); C_i and C_e are the initial and equilibrium metal concentrations (mmol/l), V is the volume of Pb(II) solution (l), and m is the mass of the biosorbent (g).

Experimental data were fitted to two-parameter: Langmuir, Freundlich, Temkin, and Dubinin-Radushkevic and three-parameter Redlich−Peterson isotherm models.

3. Results and discusion

The absorption spectrum of Pb-loaded MsA (5:1) was compared with MsA (5:1) and Ms biomass. The FT-IR spectrum for Pb-loaded MsA (5:1) showed lower intensity of some peaks and their wave number (in most cases) were shifted to lower than those before biosorption MsA (5:1) and natural Ms - *Myriophyllum spicatum*. Fig. 2 confirmed that the Pb-loaded MsA showed spectra with clear shifts of the stretching carbonyl C=O (bands at 1577cm^{-1} moved from 1598 and 1607) carboxyl –COOH (bands at 1409cm^{-1} moved from 1421 and 1413). Characteristic peak for polysaccharides is identified as strong band C–OH around 1100–1000 cm^{-1} (Aravindhan et al., 2004). Peaks identified in region < 900 cm^{-1} can be transferred to bending modes of aromatic compounds (Nagy et al., 2013).

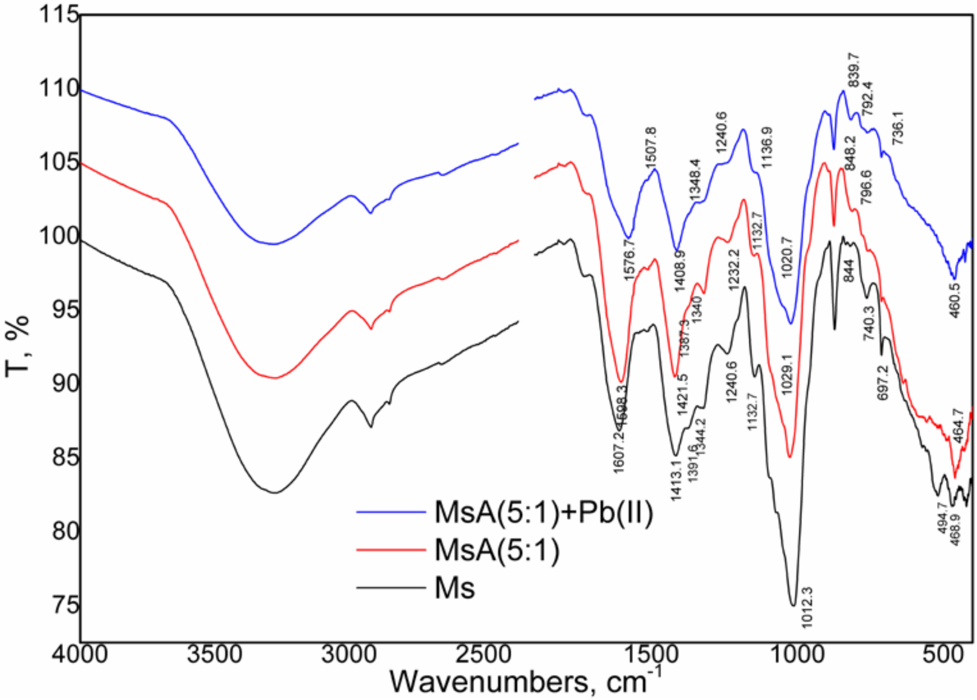

Figure 2. *FT-IR spectra: M. spicatum (washed, particle size less then 0.2 mm), MsA (5:1) before and after Pb(II) biosorption (contact time 24 h, pH=5, Pb(II) initial conc. 3 mmol/l, agitation rate 200 rpm)*

The results of FT-IR exposed that carbonyl, carboxyl and hydroxyl are main binding sites for Pb(II) on beads MsA(5:1).

Sorption isotherms of Pb(II) on MsA (5:1) are presented in Fig. 3. Based on coefficients of determination R^2 its values experimental data excellent fits within the following isotherms order:

Redlich−Peterson > Temkin > Langmuir > Freundlich > Dubinin-Radushkevic

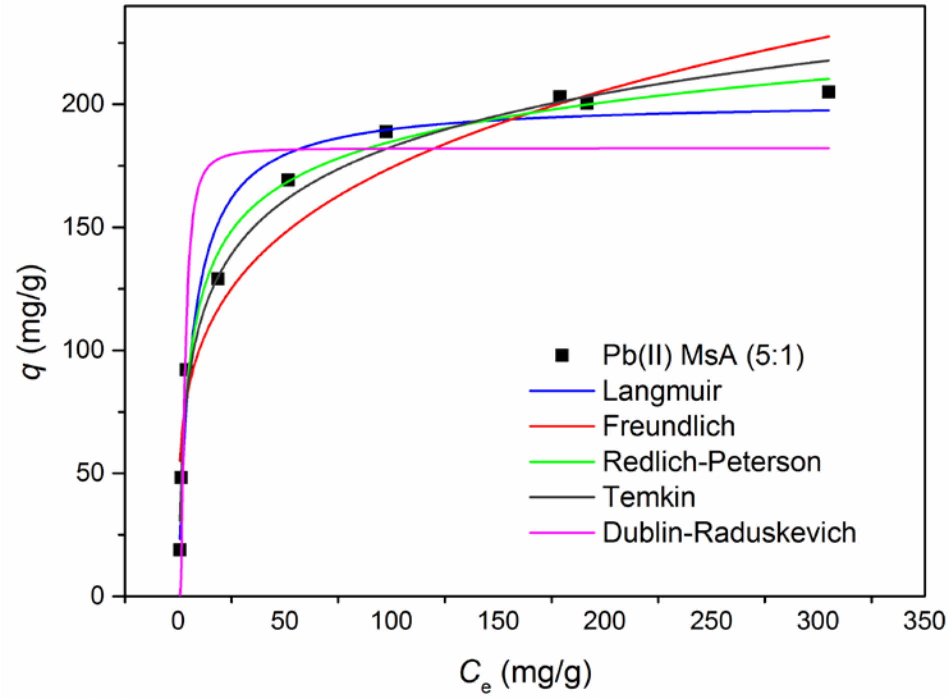

Figure 3 Lead sorption isotherms of MsA(5:1) bead at pH 5 (initial concentrations: 0.2 - 4 mmol/l; m = 0.1 g; pH 5; agitation rate 200 rpm).

Redlich and Peterson (1959) joined elements from Langmuir and Freundlich equations into an empirical three parameters isotherm. Mechanism of adsorption doesn't follow ideal monolayer adsorption (Redlich and Peterson, 1959). It can be expressed as:

$$q = \frac{k_{RP} C_e}{1 + a_{RP} C_e^{\beta}}$$

q_e: amount of Pb(II) ions adsorbed per unit mass of the biosorbent MsA (mg g^{-1}), C_e: concentration of Pb(II) in the solution at equilibrium (mg/L) k_{RP} and a_{RP}: Redlich–Peterson affinity constant for adsorption (L mg^{-1}), β: Redlich–Peterson model exponent index of heterogeneity, should be $0 < \beta \leq 1$. When $\beta = 1$ the Redlich–Peterson equation becomes the Langmuir equation.

The maximum lead sorption capacity on MsA (5:1) was 0.968 mmol/g or 200 mg/g

Conclusions

It is reported that *Myriophyllum spicatum* is one of the most problematic aquatic weeds worldwide due to its intense growth in water bodies. Results presented in this work show the successful application of the using alginate – immobilized *Myriophyllum spicatum* beads MsA (5:1) for biosorption of lead ions in water. The FT-IR analysis approved the presence of the functional groups: carbonyl, carboxyl and hydroxyl that acted as the binding sites for adsorption of lead. Isotherm studies confirmed that the biosorption of Pb(II) follows the Redlich-Peterson isotherm. Maximum experimental adsorbed amount of Pb(II) with MsA was 0.968 mmol/g or 200 mg/g which is high value. This result of lead removal capacity is important considering that aquatic weed biomass has quite simple processing before use and also easy application in alginate – immobilized beads form. Utilization of invasive plants as biosorbents certainly contribute for their sustainable management in treatment of wastewater.

Acknowledgements

These results are part of the project supported by the Ministry of Education and Science of the Republic of Serbia, TR 31003: "Development of technologies and products based on mineral raw materials and waste biomass for protection of natural resources for safe food production"

References

Aiken, S.G., Newroth, P.R. and Wile, I. (1979). The biology of Canadian weeds 34 *Myriophyllum spicatum* L. Canadian Journal of Plant Science 59, 201-215.

Alhakawati, M.S. and Banks, C.J. (2004). Removal of copper from aqueous solution by *Ascophyllum nodosum* immobilised in hydrophilic polyurethane foam. Journal of Environmental Management 72, 195–204.

Aravindhan, R., Madhan, B. and Rao, J.R. (2004). Bioaccumulation of chromium from tannery wastewater: an approach for chrome recovery and reuse. Environmental Science & Technology 38, 300–306.

Chatterjee, A. and Ray, L. (2008). Biosorption of Cu(II) by immobilized biomass of *Bacillus cereus* M116 from aqueous solution. Journal of Scientific and Industrial Research, 67, 629–634.

Christoforidis, A.K., Orfanidis, S., Papageorgiou, S.K., Lazaridou, A.N., Favvas, E.P. and Mitropoulos A.Ch. (2015). Study of Cu(II) removal by *Cystoseira crinitophylla* biomass in batch and continuous flow biosorption. Chemical Engineering Journal 277, 334–340.

European Biomass Industry Association (EUBIA), On line at: http://www.eubia.org/
http://www.eubia.org/index.php/about-eubia/projects/ongoing-projects/161-newapp

Landfill waste, On line at: http://ec.europa.eu/environment/waste/landfill_index.htm

Manrique, S. and Franco, J. (2015). Experiences and Participatory Tools for Evaluation of Sustainability of Local Development Projects. European Journal of Sustainable Development 4, 3, 1-12.

Mehta, S.K. and Gaur, J.P. (2005). Use of algae for removing heavy metal ions from wastewater: progress and prospects. Critical Reviews in Biotechnology 25, 113–152.

Milojković, J.V., Mihajlović, M.L., Stojanović, M.D., Lopičić, Z.R., Petrović, M.S., Šoštarić, T.D. and Ristić M.Đ. (2014). Pb(II) removal from aqueous solution by *Myriophyllum spicatum* and its compost: equilibrium, kinetic and thermodynamic study. Journal of Chemical Technology & Biotechnology 89(5), 662–670.

Nagy, B., Măicăneanu, A., Indolean C., Mânzatu, C., Silaghi-Dumitrescu, L. and Majdik, C. (2014). Comparative study of Cd(II) biosorption on cultivated *Agaricus bisporus* and wild *Lactarius piperatus* based biocomposites. Linear and nonlinear equilibrium modelling and kinetics. Journal of the Taiwan Institute of Chemical Engineers 45(3), 921–929.

Naseem, R. and Tahir S.S. (2001). Removal of Pb(II) from aqueous/acidic solutions by using bentonite as an adsorbent. Water Research 35, 3982-3986.

O'Callaghan K. (2016). Technologies for the utilisation of biogenic waste in the bioeconomy. Food Chemistry 198, 2–11.

Rai, U.N., Tripathi, R.D., Vajpayee, P., Jha, V. and Ali, M.B. (2002). Bioaccumulation of toxic metals (Cr,Cd, Pb and Cu) by seeds of *Euryale ferox Salisb* (Makhana). Chemosphere 46, 267–272.

Redlich O. and Peterson, D.L. (1959). A Useful Adsorption Isotherm. The Journal of Physical Chemistry, 63(6), 1024-1026.