BIOSORPTION OF COPPER BY IMMOBILIZED MYRIOPHYLLUM SPICATUM

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Abstract - Biosorption removes pollutants such as heavy metals onto a natural adsorbent, so it can be considered as a promising method of water purification. The objectives of this research were to examine the application of aquatic weed Myriophyllum spicatum immobilized in alginate beads – MsA for the removal of copper from aqueous solutions. Appield biosorbent was characterized by Fourier transform infrared spectroscopy (FT-IR). Experimental results were fitted by six isotherm models, and have showed that MsA holds great potential for copper removal, q = 1.307 mmol/ Results of TOC analyses showed that after Myriophyllum spicatum immobilization process , total organic carbon in MsA was more than four times less than with aquatic weed M. spicatum, 18.8 mg/L compared to 81.2 mg/L of TOC.

Keywords - Biosorption, Removal of Copper, Immobilized Aquatic Weed.

I. INTRODUCTION

Copper is a heavy metal which was one of the first extracted and most commonly used by mankind. Among the other heavy metals, copper is an essential micronutrient, and the lower concentration but large doses can be harmful to humans. It can cause changes in the nervous system, stomach ache, deposition in liver, liver and kidney failure, depression and lung cancer [1,2]. Copper contamination in water streams rises from diverse industrial activities such as: electrical industry, mining, electroplating, smelting operations, alloys, algaecides, chemical catalysis, metal cleaning, metal surface finishing, paper, pulp, wood preservative-employing mills, fertilizer industry etc. [3].

Permissible limits of copper in drinking water according to various standards are: WHO 2.000 mg/L, USEPA 1.300 mg/L, EU Standard 2.000 mg/L and MEP, China 1.000 mg/L [4,5]

Among the common technologies for copper ions removal from aqueous solution (oxidation reduction, iron co-precipitation, ion exchange and adsorption), biosorption has been considered as a cost-effective technology for heavy metal removal at low metal concentrations. Biosorption as an alternative method has advantages such as: low-cost of biosorbents, high removal capacity, environmental-friendly operation [6,7]. Although it has many advantages, its practical application is still limited because of many reasons such as increase of biological/chemical oxygen demand (BOD/COD), increase of total organic content (TOC) in water streams after biosorbent application, low mechanical strength as well as low capacity etc. In order to improve biosorbent performance, different process, such as physical/ chemical/ thermal modification or immobilization, can be used. Biomass immobilization improves biosorbent properties: suitable particle size, mechanical strength and density which makes it more suitable to be used in reactors and columns. Easier separation from solution after the biosorption process and regeneration in various adsorption–desorption cycles without important loss in performance [8,9]. Natural polymers such as: alginate, agarose, chitosan, cellulose derivatives are widely used as immobilization matrices as they are non-toxic, efficient and a cost effective alternative to synthetic polymers [10].

Myriophyllum spicatum L. is an invasive submerged aquatic weed, recorded from at least 57 countries (native to Europe, Asia and North Africa). Once introduced to a new area it spreads rapidly, primarily by vegetative stem fragmentation forming dense beds. It causes a range of problems because it has numerous negative impacts on: water flow, clogs of water supply systems, preventing the sunlight for native aquatic plants [11,12]. In our previous but new studies we have examined performance of aquatic weed - waste Myriophyllum spicatum immobilized in alginate beads for the removal of Pb(II) [13] and properties in lake water samples (multi-element system of nine Serbian lakes) [14].

Present work is designed to evaluate equilibrium, isotherms of the copper biosorption process using Myriophyllum spicatum immobilized in alginate beads (Ms : Alginate 2:1).

II. MATERIALS AND METHODS

A. Preparation of biosorbent

The submerged aquatic weed M. spicatum used for these experiments was taken from artificial Sava Lake where it is regularly harvested with underwater harvester by the public company "Ada Ciganlija" (Belgrade, Serbia). Pretreatment of M. spicatum was same like in our previous studies [13,14]. Low

viscosity alginic acid sodium salt from brown algae was used (A1112, Sigma-Aldrich, St. Louis, MO, USA). M. spicatum beads were prepared according to the method described by [15]. Shortly, biomass powder (dried plant powder particles <0.2 mm) was added in 2% Na-alginate polymer solution Ms : Alginate in ratio 2:1.

B. Biosorbent characterization

Biosorbent M. spicatum beads - MsA was characterized by Fourier Transform Infrared Spectroscopy (FT-IR). FT-IR spectra were gained 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. The influence of immobilization on the release of organic carbon was determined by measuring the TOC in biosorption experiments: Cu(II) initial concentration 3 mM, biosorbents (2g/L): dry aquatic weed M. spicatum (particles <0.2 mm) and beads – MsA with a contact time of 24 hours. TOC concentrations were measured by Analytik Jena, TOC/TN Analyzer (Multi N/C 2100S). Thermo catalytic oxidation, digestion temperature-up to 950 °C, Carbon detection - NDIR (coupled with VITA method).

C. Batch biosorption tests

The biosorption experiments were performed with solutions made from stock solution of 20 mM of Cu(II), made from analytical grade copper(II) nitrate trihydrate. Nitrate was used to avoid forming metal complexes. The effect of the copper ions concentration on adsorption was studied at pH 5.0 in the concentration range from 0.2 to 14 mmol/L. Beads (0.1 g) were placed in contact with the copper solutions (50 mL) in 100 mL glass flasks. The flasks were stirred 24 h at 220 rpm in a Heidolph Unimax 1010 orbital shaker at room temperature (298 K). Initial pH values of the mixtures were adjusted to 5 with diluted HNO_3 and NaOH as needed. During the biosorption process, pH values of the mixtures were carefully monitored with pH Meter Sension MM340.
In order to compare biosorption capacities, biosorption of Cu(II) with M. spicatum (dried plant powder particles < 0.2 mm) and Ca-alginate beads (2 g/L) were investigated on initial concentration of 6 mM at contact time of 24 h. Analytical measurement of Cu(II) concentration was conducted using atomic absorption spectrometry (AAS) (Perking Elmer AAnalyst 300). All sorption experiments were performed in three replications. Metal uptake was calculated from the following expression:

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

where sorption value q is the amount of Cu(II) adsorbed by investigated biosorbent at any time (mg/L), C_i and C_e are the initial and equilibrium metal concentrations (mg/L), V is the volume of Cu(II) solution (L), and m is the mass of the biosorbent (g).
Applied isotherm models in this paper are listed in Table 1.

Isotherm model			Ref.
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	K_L (L/mg): Langmuir constant	[16]
Freundlich	$q_e = K_f C_e^{1/n}$	K_f (mg/g) (L/g)$^{1/n}$: Freundlich constant: heterogeneity factor	[17]
Sips	$q_e = \frac{q_m K_s C_e^{n_s}}{1 + C_e K_s^{n_s}}$	K_s (L/g): Sips constant related to sorption affinity n_s: heterogeneity factor	[18]
Redlich and Peterson	$q_e = \frac{k_{RP} C_e}{1 + a_{RP} C_e^{b_{RP}}}$	a_{RP} (L/mg): Redlich–Peterson isotherm constant b_{RP}: Redlich–Peterson isotherm exponent k_{RP} (L/g): Redlich–Peterson isotherm constant,	[19]
Toth	$q_e = \frac{q_m C_e}{(K_T + C_e^{Th})^{1/Th}}$	K_{Th} ((mg/L)Th):Toth isotherm constant Th: heterogeneity factor	[20]
Temkin	$q = \frac{RT}{b_T} \ln A_T C_e$	A_T (L/mg): Temkin isotherm equilibrium binding constant b_T (J/mol): Temkin isotherm constant	[21]

Table 1. Isotherm Models/equations used for evaluation of Cu(II) biosorption onto MsA

III. RESULTS AND DISCUSSION

A. Biosorbent characterization

FT-IR spectra of: M. spicatum and MsA before and after biosorption of Cu(II) (beads in the range of 4000–400 cm^{-1}) are presented on Fig 1. Characteristic bands of proteins were found between 1800 and 1500 cm^{-1} spectra [22], while the bands between 1700 and 1500 cm^{-1} are specific for primary and secondary amides. The section between 1200 and 900 cm^{-1} shows a sequence of bands due to vibrations from C-O, C-C, C-O-C and C-O-P bonds and indicates polysaccharides presence [23]. FT-IR spectra of Myriophyllum spicatum immobilized in alginate beads before and after the biosorption showed peaks (1603.7 and 1597.6 cm^{-1}) which are moved compared to M. spicatum absorption bands at 1610.9 cm^{-1} (shifts of C=O) [9]Mata et al. (2009).

After biosorption Cu (II) with beads there are clear shifts of carboxyl (-COOH) group moved from 1419.5 cm^{-1} to 1417.2 cm^{-1} and C–OH from 1019.9 cm^{-1} to 1021.6 cm^{-1} indicating that these groups are probably involved in the formation of bonds with copper. Carboxyl, carbonyl and hydroxyl groups probably participate in the process of biosorption of copper by M. spicatum immobilized in alginate beads.

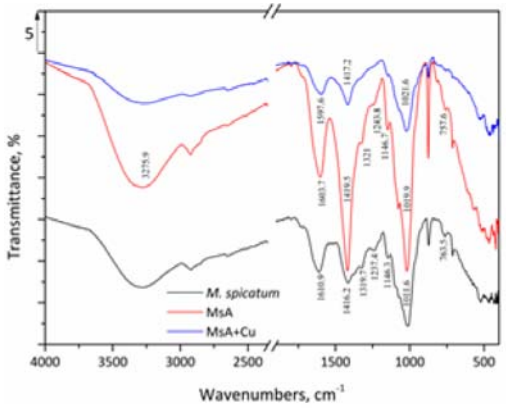


Fig. 1. FTIR spectra: M. spicatum, MsA, and MsA after biosorption of Cu(II) (contact time 24 h, pH = 5, Cu(II) initial conc. 3 mM, agitation rate 220 rpm)

B. Isotherm studies

After biosorption experiments, MsA beads didn't change its shape, size or olour. They have been easily separated from the solution by decanting. Non-linear equilibrium parameters of applied isotherms and the order of the best fitting at room temperature are presented in Table 2. Selection of models was made on the basis of the coefficients of determination R^2 and comparison value of biosorption capacities experimented and calculated by models. Isotherms that best correlated data are showed on Fig. 2.

Isotherm	Parameter		R^2	Reduced Chi-Sqr
Langmuir	q_m	1.287	0.9809	0.00441
	K_L	5.010		
Freundlich	K_f	0.8098	0.8930	0.02473
	1/n	0.2375		
Sips	q_m	1.310	0.9791	0.00483
	K_S	4.040		
	n_S	0.9076		
Redlich–Peterson	k_{RP}	7.036	0.9790	0.00485
	a_{RP}	5.717		
	β	0.9759		
Toth	q_m	1.319	0.9791	0.00482
	K_T	0.2183		
	T_h	0.8529		
Temkin	A_T	125.4	0.9601	0.00922
	b_T	12885		
Experimental value q = 1.307 mmol/g				
Best fit Isotherm				
L>S & Th>RP>T>F				

Table 2. Non-linear equilibrium parameters for copper biosorption onto MsA on 25◦C

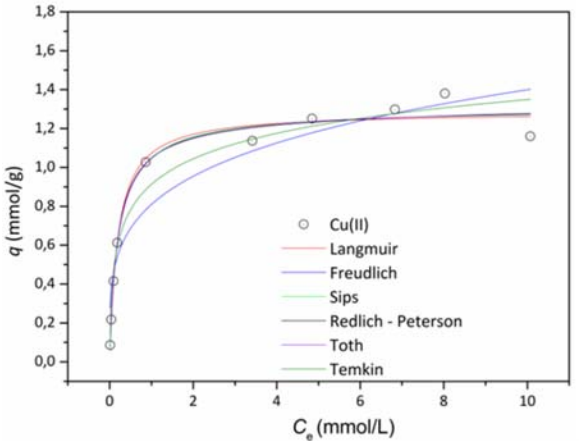


Fig. 2. Experimental data for biosorption of Cu(II) onto MsA on 25◦C fitted to best correlated isotherm models

Biosorption capacities for M. spicatum was 0.96 mmol/g and Ca-alginate beads 1.7 mmol/g. Immobilization has contributed to an increase in capacity by more than 36 %.

Also, benefit from immobilization is also shown in TOC analyses: pure M. spicatum releases 81.2 mg/L of total organic content while immobilized samples, MsA, only 18.8 mg/L, indicating that immobilization reduced more than four times TOC in solution after biosorption. This is very important since used biosorbent has biological origin, so there is a possibility that during the biosorption process, organic matter is released from the biosorbent itself, although biosorbent removes pollutants, which is in this case copper.

According to the Serbian national regulations - Official Gazette of RS 24/2014, surface waters are classified in five classes (I to V). Water within classes I–IV may be used for drinking water supply (after the treatment by appropriate methods for water purification), bathing and recreation, irrigation, industrial use (process and cooling water) whereas water ranked as class V cannot be used for any purpose. Limit values (LV) for TOC for class IV is 50 mg/L [24].

In this paper, the same material MsA was used, as in the previous investigations where MsA was investigated for lead ions removal [13]. In both studies, the MsA material showed significant capacity to remove these heavy metals: Pb(II) q = 1.11 mmol/g (230 mg/g) [13] and 1.307 mmol/g (83.05 mg/g) (this study).

It is probably similar adsorption mechanisms of copper removal onto these granules as the removal of lead. Calcium was replaced by lead from the solution regarding the “egg-box” model. Mechanism of Pb (II) removal by MsA beads includes: chemisorption, complexation and ion exchange mechanism [13]. Myriophyllum spicatum (Sava lake, Serbia) has 5% of calcium [25]. Large amount of calcium is from the water environment in which this submersed aquatic weed lives [14].

“Egg-box” model of cross-linking presents guluronate blocks of one polymer form connections with the guluronate blocks of next polymer chains [26]. Affinity of possibly toxic elements by alginate depends on the amount of guluronic acid and other uronic acids. Carboxyl groups from these acids would be generally involved in metal biosorption [27]. There are two possible ways of binding carboxyl groups and M^{2+} cations where they form bidentate complexes with one carboxyl group and ionic bonds [9]. The order of alginate affinity to divalent ions is given as follows [28]:

Pb > Cu > Cd > Ba > Sr > Ca > Co, Ni, Zn > Mn

IV. CONCLUSION

Aquatic weeds are the invasive plants with fast growth rate, various modes of propagation and global distribution which cause serious economic and ecological damage once they get introduced in an aquatic ecosystem [29].

One of the aquatic weeds, Myriophyllum spicatum was immobilized and applied in copper biosorption process, in order to investigate its ability to bind pollutants from water solutions, Obtained biosorbent (MsA) was characterized by Fourier transform infrared spectroscopy (FT-IR). Carboxyl, carbonyl and hydroxyl groups, exhibited by the infrared spectra results, changed to suggest these groups are involved in the adsorption of copper ions onto MsA. The study showed that MsA can be used for removing Cu(II) from water solution.

Aquatic weed Myriophyllum spicatum is "circular" as it is something that would be discarded as waste, and that would needed to be transported away and incinerated; by its application described in this paper, it is re-valued as a raw material used as biosorbent for copper removal.

Easy application and manipulation, much easier than other biosorbents simplify further investigations and applications of this aquatic weed - waste Myriophyllum spicatum immobilized in alginate beads - MsA in industrial wastewaters and also in the next step of the biosorption processes, flow systems and reactors.

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REFERENCES

[1] Q. Manzoor, R. Nadeem, M. Iqbal, R. Saeed, T.M. Ansari, Organic acids pretreatment effect on Rosa bourbonia phyto-biomass for removal of Pb(II) and Cu(II) from aqueous media., Bioresour. Technol. 132 (2013) 446–452.

[2] B. Kiran, K. Thanasekaran, Copper biosorption on Lyngbya putealis: Application of response surface methodology (RSM), Int. Biodeterior. Biodegradation. 65 (2011) 840–845

[3] M. Ulmanu, I. Anger, D. Dumitriu, Removal of copper and cadmium ions from diluted aqueous solutions by low cost and waste material, 1 (2002) 357–373.

[4] M. Ahmaruzzaman, Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals., Adv. Colloid Interface Sci. 166 (2011) 36–59.

[5] Wikipedia, Drinking water quality standards https://en.wikipedia.org/wiki/Drinking_water_quality_standards

[6] K. Vijayaraghavan, Y.-S. Yun, Bacterial biosorbents and biosorption., Biotechnol. Adv. 26 (2008) 266–291.

[7] I. Anastopoulos, I. Massas, C. Ehaliotis, Use of residues and by-products of the olive-oil production chain for the removal of pollutants from environmental media: A review of batch biosorption approaches, 4529 (2015) 677–718.

[8] M.S. Alhakawati, C.J. Banks, Removal of copper from aqueous solution by Ascophyllum nodosum immobilised in hydrophilic polyurethane foam, J. Environ. Manage. 72 (2004)

[9] Y.N. Mata, M.L. Blázquez, A. Ballester, F. González, J.A. Mu, Biosorption of cadmium , lead and copper with calcium alginate xerogels and immobilized Fucus vesiculosus, 163 (2009) 555–562.

[10] D. Bera, P. Chattopadhyay, L. Ray, Chromium (VI) biosorption by immobilized biomass of Bacillus cereus M 116, (2017) 1–20.

[11] R. Couch, E. Nelson, Myriophyllum spicatum in North America, in: L.W.J. Anderson (Ed.), Proceedings,First Int. Symp. Watermilfoil Relat. Halor-Agaceae Species, Aquatic Plant Management Society, Vicksburg, MS, Vancouver, BC, 1985: pp. 43–45.

[12] Centre for Agriculture and Bioscience International - CABI, The Invasive Species Compendium (ISC) https://www.cabi.org/isc/

[13] J. V Milojković, Z.R. Lopičić, I.P. Anastopoulos, J.T. Petrović, S.Z. Milićević, M.S. Petrović, M.D. Stojanović, Performance of aquatic weed - Waste Myriophyllum spicatum immobilized in alginate beads for the removal of Pb (II), J. Environ. Manage. 232 (2019) 97–109.

[14] J. V Milojković, J.B. Popović-Djordjević, L.L. Pezo, I.D. Brčeski, A.Ž. Kostić, V.D. Milošević, M.D. Stojanović, Applying multi-criteria analysis for preliminary assessment of the properties of alginate immobilized Myriophyllum spicatum in lake water samples, Water Res. 141 (2018) 163–171.

[15] G. Yan, T. Viraraghavan, Heavy metal removal in a biosorption column by immobilized M. rouxii biomass, Bioresour. Technol. 78 (2001) 243–249.

[16] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[17] H.M.F. Freundlich, Over the adsorption in solution, J. Phys. Chem. 57 (1906) 385–470.

[18] R. Sips, Combined form of Langmuir and Freundlich equations, J. Chem. Phys. 16 (1948) 490 – 495.

[19] O. Redlich, D.L. Peterson, A useful adsorption isotherm, J. Phys. Chem. 63 (1959) 1024–1024.

[20] J. Toth, State equations of the solid gas interface layer, Acta. Chem. Acad. Hung. 69 (1971) 311–317.

[21] M.I. Temkin, V. Pyzhev, Kinetic of ammonia synthesis on promoted iron catalyst, Acta Physiochimica. URSS 12 (1940) 327–356.

[22] P. Dumas, L. Miller, The use of synchrotron infrared microspectroscopy in biological and biomedical investigations, Vib. Spectrosc. 32 (2003) 3–21.

[23] W.F. Wolkers, A.E. Oliver, F. Tablin, J.H. Crowe, A Fourier-transform infrared spectroscopy study of sugar glasses, Carbohydr. Res. 339 (2004) 1077–1085.

[24] Official Gazette of Serbia, 2014. Regulation on limit values of pollutants in surface and ground waters and sediments and deadlines for their achievement. No. 24/2014 (In Serbian)

[25] J. V. Milojković, M.L. Mihajlović, M.D. Stojanović, Z.R. Lopičić, M.S. Petrović, T.D. Šoštarić, M.Đ. Ristić, Pb(II) removal from aqueous solution by Myriophyllum spicatum and its compost: equilibrium, kinetic and thermodynamic study, J. Chem. Technol. Biotechnol. 89 (2014) 662–670

[26] G.T. Grant, E.R. Morris, D.A. Rees, P.J.C. Smith, D. Thom, Biological interactions between polysaccharides and divalent cations: The egg-box model, FEBS Lett. 32 (1973) 195–198.

[27] T.A. Davis, M. Ramirez, A. Mucci, B. Larsen, Extraction , isolation and cadmium binding of alginate from Sargassum spp ., J. Appl. Phycol. 196 (2004) 275–284.

[28] S. Datta, M.E. Janes, Q.G. Xue, J. Losso, J.F. La Peyre, Control of Listeria monocytogenes and Salmonella anatum on the Surface of Smoked Salmon Coated with Calcium ... Control of Listeria monocytogenes and Salmonella anatum on the Surface of Smoked Salmon Coated with Calcium Alginate Coating containing Oyster, J. Food Sci. •. 73 (2008) 67–71.

[29] M. Kaur, M. Kumar, S. Sachdeva, S.K. Puri, Aquatic weeds as the next generation feedstock for sustainable bioenergy production, Bioresour. Technol. 251 (2018) 390–402.

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