Ecological Engineering 93 (2016) 112–119

Contents lists available at ScienceDirect

Ecological Engineering

journal homepage: www.elsevier.com/locate/ecoleng

Selected heavy metal biosorption by compost of *Myriophyllum spicatum*—A chemometric approach

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ARTICLE INFO

Article history:
Received 7 September 2015
Received in revised form 3 March 2016
Accepted 4 May 2016
Available online 20 May 2016

Keywords:
Heavy metal removal
Compost
Myriophyllum spicatum
Chemometric analysis

ABSTRACT

In this study adsorption characteristics of lead, copper, cadmium, nickel and zinc ions onto the compost of *Myriophyllum spicatum* were examined. The effects of sorbent dose, duration of sorption and solution concentration on the sorption of heavy metals have been investigated. Scanning electron microscope (SEM) and thermogravimetric and differential thermal analysis (TG-DTA) were used for the characterization of this biosorbent. Low coefficients of variation have been obtained for each applied assay, which confirmed the high accuracy of measurements. Principal component analysis (PCA) was applied for differentiation of samples. Mathematical models (form of second order polynomials) were developed for prediction of adsorption. Score analysis is being useful for accessing the effect of process parameters and the tool for determination of sorption quality. On the basic of experimental results and model parameters, it can be concluded that compost has a high biosorption capacity can be utilized for the removal of selected metals from wastewater.

1. Introduction

Biosorption was proven to be cost-effective and eco-friendly technology, which engages the use of biological materials for the treatment of wastewater (Kiran and Thanasekaran, 2011). Application of efficient natural materials is more cost effective than artificial materials (Turan and Altundoğan, 2014). Different biosorbents (raw or modified) were tested for the removal of various pollutants. Most studies of biosorption were primarily focused on heavy metal and dye pollutants (Anastopoulos and Kyzas, 2015). Amongst the various technologies for removal of toxic metals from wastewaters, it really represents an inexpensive alternative, because of the application of low-cost materials as sorbents (Veglio et al., 1998).

Majority of the research in the biosorption of heavy metals refers to the removal of divalent cations (Michalak et al., 2013). Divalent heavy metal cations are widespread in ground and surface waters, soils and sediments due to human activity. Furthermore, like divalent cations, heavy metals can easily enter in the food chain, producing different toxic effects on living organisms (Smiciklas et al., 2008). High solubility of heavy metals in the aquatic surroundings allows their adoption by living organisms (Babel and Kurniawan, 2004). The most important factors which affect to heavy metal mobility, toxicity, and reactivity are: pH, sorbent nature, Eh, temperature, presence and concentration of organic and inorganic ligands, etc. (Tessier et al., 1979). Chemical speciation of metal is determined by solution pH. For instance, lead is present as Pb(II) as dominant species at pH < 5.5 (Farooq et al., 2010). Metal species of selected heavy metals (Pb, Cu, Cd, Ni and Zn) are in the +2 oxidation states in aqueous solution where pH is around 5.0 (Vieira et al., 2012). The solubility of heavy metals determines their toxicity. The metals are more toxic at lower pH values, because then their solubility increases (Bečelić and Tamaš, 2004).

Taking into account heavy metal mobility, toxicity, and reactivity for this study Pb(II), Cu(II), Cd(II), Ni(II) and Zn(II) were selected.

Among different biosorbents, the researchers consider on alternative application of composts. It is well known that composts are mainly used as amendments to increase soil fertility (Anastopoulos and Kyzas, 2015). There is a constant increase in the number of papers in which compost is used as biosorbent of pollutants.

Compost of *M. spicatum* can be successfully applied as biosorbent for Pb(II) Milojković et al. (2014a) and selected heavy metals (Pb(II), Cu(II), Cd(II), Ni(II) and Zn(II)) (Milojković et al., 2014b).

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http://dx.doi.org/10.1016/j.ecoleng.2016.05.012
0925-8574/

In this study, effect of sorbent dose, duration of sorption and solution concentration on sorption of selected heavy metals by compost of *Myriophyllum spicatum* were invesigated. Also, objectives of this study were to examine thermal stability with thermal analysis (TG-DTA) and reveal the changes in morphology after biosorption by scanning electron microscope (SEM).

Principal Component Analysis (PCA) was used to discriminate different samples, processed under various process parameters. Simple regression models (second order polynomials – SOP) have been proposed for calculation of heavy metals sorption capabilities as function of proposed process parameters. In order to enable more comprehensive comparison between investigated samples, particularly the contribution of process parameters, standard score (SS), assigning equal weight to all assays applied, has been introduced. Analysis of variance (ANOVA) has been applied to show relations between applied assays.

2. Materials and methods

2.1. Preparation of biosorbent

M. spicatum is harvested from artificial Sava Lake every year. Harvested aquatic weed (around 35 m^3 per day) is disposing to the open landfill used just for that purpose.

Samples of compost were taken from the surface of the landfill (1 year old). The preparation of compost was previously described in detail (Milojković et al., 2014b). The prepared compost was exposed to air and dried for a couple days at room temperature and then dried at 60 °C for 6 h, crushed and sieved to give a particle size less than 0.2 mm.

2.2. Reagents

The heavy metal sorbates used in this study were: $Pb(NO_3)_2$, $Cu(NO_3)_2{\cdot}3H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ and $Zn(NO_3)_2{\cdot}4H_2O$. Stock metal solutions (10 mmol/L each metal) were prepared by dissolving above mentioned metal salts (analytical grade) in deionised water. The working solutions were obtained by diluting the stock solution.

2.3. Batch biosorption experiments

Each experiment was conducted in 100 ml Erlenmeyer flasks containing 50 ml of multimetal solution. The flasks containing multimetal solutions and compost were agitated on orbital shaker Heidolph unimax 1010 at 250 r/min. pH value was regulated to the appropriate value with 0.1 M HNO_3 or 0.1 M NaOH (analytical grade). Measurement of pH value was carried out with a precise pH meter (Sension MM340). Equilibrium studies were performed using different initial concentration of each metal ion (0.2 – 5 mmol/L) at respective optimum solution pH of 5.0. Kinetic of selected heavy metals biosorption by compost of *M. spicatum* was studied by varying the contact time from 10 to 720 min remaining other conditions constant (initial concentration 2.5 mmol/L, pH was around 5.0, biosorbent dose 1.25 g in 50 ml). The concentration of heavy metal ions in solutions was determined by Atomic absorption spectrophotometer (Perkin Elmer AAnalyst 300).

The amount of metal adsorbed by the compost was calculated using Eq. (1):

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

where sorption values q is the amount of metal adsorbed by biosorbent at any time (mmol/g), Ci and Ce the initial and equilibrium metal concentrations (mmol/L), V the volume of multimetal solution (L) and M is the mass of the sorbent (g). Metal removal efficiency (R) is calculated from Eq. (2):

$$R = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

Table 1
ANOVA calculation for biosorption capacities of selected heavy metals.

	q_{Pb}(mmol/g)	q_{Cu}(mmol/g)	q_{Cd}(mmol/g)	q_{Ni}(mmol/g)	q_{Zn} (mmol/g)
m	0.000141*	0.000032	0.000040*	0.000028	0.000042*
m^2	0.000004	0.000000	0.000013	0.000005	0.000009
C_0	0.009427*	0.006054*	0.000170*	0.001165*	0.000905*
$C_0{}^2$	0.000540*	0.000485*	0.000042*	0.000373*	0.000300*
t	0.000135*	0.000087*	0.000092*	0.000018	0.000034*
t^2	0.000269*	0.000112*	0.000036*	0.000045	0.000020*
Error	0.000283	0.000264	0.000059	0.000193	0.000048
r^2	0.976	0.969	0.859	0.883	0.960

* Significant at p < 0.05 level, 95% confidence limit, error terms were found statistically insignificant.

2.4. Biosorbent characterization

2.4.1. Thermal analysis

Thermal analysis of the samples was performed on a Netzsch STA 409 EP. Samples of compost were heated (20–1000 °C) in an air atmosphere with a heating rate of 10 °C/min. The samples were kept in a desiccator at a relative humidity of 23%, prior to analyses.

2.4.2. Scanning electron microscopy (SEM)

In order to directly observe the surface morphology, Scanning electron microscope SEM JEOL JSM-6610LV model, was utilized in this study. Samples of compost were coated under vacuum with a thin layer of gold and then examined.

2.5. Statistical analyses

The experimental data used for the study of experimental results were obtained with three sets of experiment in which only one process parameter was variable (sorbent dose, duration of sorption, solution concentration on sorption of heavy metals), while the other two were constant (Table 1). These experiments were performed to test the sorption quantity of heavy metals (q_{Pb}, q_{Cd}, q_{Cu}, q_{Ni} and q_{Zn}), considering these three factors (Brlek et al., 2013; Madamba, 2002; Montgomery, 1984).

Descriptive statistical analyses of all the obtained results were expressed as the mean ± standard deviation (SD). The evaluation of ANOVA of the obtained results was performed using Statistica software version 12 (STATISTICA, 2012).

2.6. Principal component analysis (PCA)

The algorithm of PCA can be found in standard chemometric material (Otto, 1999; Kaiser and Rice, 1974). In summary, PCA decomposes the original matrix into several products of multiplication into loading (different samples) and score (measured assays) matrices. The different samples were taken as variables (column of the input matrix) and measured data of q_{Pb}, q_{Cu}, q_{Cd}, q_{Ni} and q_{Zn} as mathematical-statistical cases (rows of the matrix). The number of factors retained in the model for proper classification of measuring data, in original matrix into loading and score matrices were determined by application of Kaiser and Rice's rule. This criterion retains only principal components with eigenvalues>1.

2.7. Determination of normalized standard scores (SS)

A standard score is one of the most widely used technique to compare various characteristics of various samples determined