Agronomy Research **16**(4), 1622–1629, 2018
https://doi.org/10.15159/AR.18.163

Extended use of Sphagnum peat as a biosorbent for Zn(II): repetitious sorption-desorption process

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Abstract. In this study, continuous biosorption-desorption cycles in a fixed-bed column were performed to evaluate the extended use of sphagnum peat as biosorbent material to remove Zn(II) ions from aqueous solutions. Biosorption-desorption studies revealed that the sphagnum peat as biosorbent could be regenerated using 0.1M HCl as eluting agent with more than 70% recovery in four successive biosorption-desorption cycles. The results showed that the sphagnum peat should be used as an alternative, effective and low-cost biosorbent for Zn(II) ions removal from polluted aqueous solution.

Key words: biosorption-desorption process, fixed-bed column, zinc, sphagnum peat.

INTRODUCTION

Heavy metal pollution is a serious environmental problem and represents a threat to human and ecosystem due to its toxic effect and accumulation tendency throughout the food chain. Wastewaters from a variety of industry are an important source of environmental pollution due to their high content of heavy metal such as cadmium, copper, chromium, lead and zinc. They may induce human health hazards through contact with contaminated surface or drinking water in result of emission of the untreated industrial wastewater discharged into the aquatic ecosystem (Kobielska et al., 2018). Therefore, the removal of heavy metal ions from aqueous solutions is necessary and very important.

Zn(II) is an essential micronutrient for human health and is involved in numerous biological routes within the human body, however, it is also toxic at levels of 100–500 mg per day (Volesky & Holan, 1995; Chapman, 2006). At high concentration it may cause damages to human health such as respiratory diseases, coughing and problems like abdominal pain, vomiting and nausea (Plum et al., 2010). In recent years, the removal of Zn(II) ions from wastewater has gained a significant attention due to the need to protect the environment (Parmar & Thakur, 2013). Zinc (Zn(II)) is widely used in industrial activities like mining, manufacturing and production of products such as batteries, wood, ceramics, textiles, paints and fertilizers (Katsou et al., 2010).

Various techniques have been applied to remove heavy metal ions from wastewaters, e.g., coagulation, chemical precipitation, ion exchange, membrane filtration, electrochemical treatment, reverse osmosis and adsorption (Carolin et al.,

2017). Biosorption is an alternative technology employing low cost filtration materials like orange peel (Liang et al., 2011), cocoa pod husk (Njoku, 2014), pine bark (Cutillas-Barreiro et al., 2016), hay (Tihomirova et al., 2017) and palm kernel shell (Karri & Sahu, 2018) for removal of toxic metals from industrial wastewaters. Another inexpensive and widely available natural biosorbent is sphagnum peat. Despite being defined as a slowly renewable fuel material (Crill et al., 2000), the main advantages of sphagnum peat as biosorbent are free availability in large quantities in temperate climate zones and high biosorption capacity which has demonstrated a high uptake capacity of dissolved Zn(II) (Denisova et al., 2017). Nevertheless, currently biosorption is mainly carried out in batch systems, but from a practical point of view, dynamic fixed-bed column studies are necessary to demonstrate the practical applicability for industrial wastewater treatment (Jin et al., 2018). The desorption performance or the biosorbent regeneration is important for cost-effective implementation of the biosorption process in fixed-bed column operation. The regeneration process is related to the repeated reuse of the biosorbent with minimum loss of efficiency. Thus, the regeneration process can minimise the need of new adsorbent and reduce the utilization problem of used biomass; therefore, desorption studies are important to evaluate biosorbent recycling and metal recovery (Akar et al., 2009; Rizzuti et al., 2015).

The aim of this research was to investigate the regeneration potential of sphagnum peat for enhanced Zn(II) removal and subsequent recovery by successive biosorption-desorption process in a continuous fixed-bed column.

MATERIALS AND METHODS

Preparation of the biosorbent

Commercialsphagnum peat moss (AS EESTI TURBATOOTED, Estonian peat products Ltd, Estonia) was used in the biosorption-desorption experiments as a biosorbent. It had an organic matter content of 98%, ash content of 2% and pH values ranged from 3.6–4.4 after rinsing with tap water. Humification degree wasH2-H4 according to the von Post scale (von Post, 1924).

Preparation of Zn(II) solution

The synthetic Zn(II) ion solution was prepared by dissolving the appropriate quantity of $ZnSO_4 \cdot 7H_2O$ (Reachem Slovakia, Slovakia) in tap water to achieve Zn(II) concentrations of 100 mg L^{-1}. The concentration was determined by Atomic Absorption Spectrometer (AAS) (Aanalyst 200, Perkin Elmer, USA) with air-acetylene flame.

Biosorption experiments

Continuous biosorption experiments were performed in up-flow fixed-bed column. The glass column with 3.2 cm inner diameter and 30 cm length was filled with 40 g of dry sphagnum peat to obtain a bed depth of 25 cm. Stainless steel sieves with a mesh size of 220 μm were installed at both top and bottom of the packed glass column in order to avoid the washing out of biosorbent material. Before the first experiments, the biosorbent material was intensively washed with tap water for 24 h using continuous up-flow at a flow rate of 15 mL min^{-1} by peristaltic pump (MasterFlex L/, model 77202-50, Cole-Parmer Instrument Co.) to remove brown-coloured water and small particles of dirt.

After this washing procedure, synthetic Zn(II) ion solution with an initial concentration of 100 mg L^{-1} at pH 6.6 ± 0.1 was fed through the up-flow fixed-bed column with the same flow rate as used in washing procedure. All the experiments were carried out at room temperature (22 ± 2 °C).

Samples of Zn(II) solution were collected periodically from the top of the column (Fig. 1, a) and acidified with a concentrated nitric acid (HNO_3 65%, Lach-Ner Ltd., Czech Republic) to obtain a concentration of 2% v v^{-1} HNO_3; then the samples were filtered with 0.45 µm membrane filter (Filtropur S, Sarstedt, Germany). Afterwards, the samples were analysed for the remaining Zn(II) concentrations by using flame AAS. The pH, conductivity and temperature of the influent and effluent of collected samples were measured by using digital benchtop meter (inoLab® Multi 9420 IDS, WTW, Germany). Each experiment was performed in triplicate, and the average results are reported in this study.

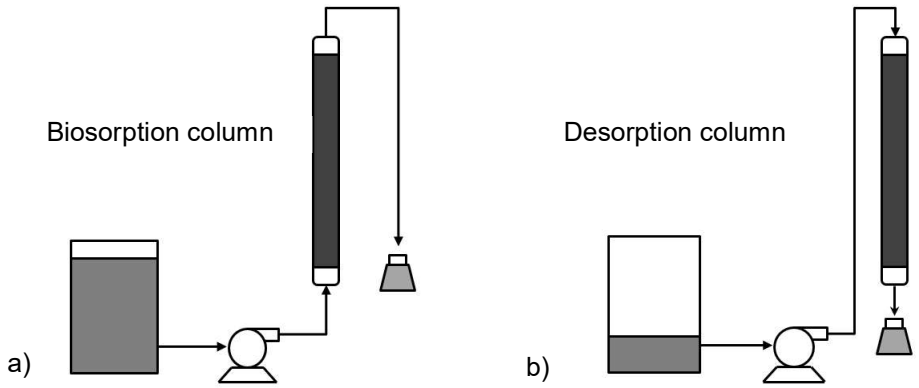

Figure 1. Schematic diagram of the experimental set-up for a continuous process in a fixed-bed: a) biosorption; b) desorption column.

The biosorption efficiency of the fixed-bed column can be described through the breakthrough curve concept when equilibrium between influent and effluent Zn(II) ion concentration is achieved (99% of an initial Zn(II) concentration).

The maximum column capacity q_{total} (mg), the total mass of metal ions acquired by the biosorbent in fixed-bed column experiments can be calculated by the following equation (Martin-Lara et al., 2012):

$$q_{total} = \frac{Q}{1{,}000} \int_{t=0}^{t=t_{total}} (C_0 - C_t)dt \quad (1)$$

where C_0 – the influent metal concentration (mg L^{-1}); C_t – is the effluent metal concentration (mg L^{-1}); Q – the flow rate of Zn(II) ion solution which passed through the column (mL min^{-1}).

The total metal removal efficiency (%) at the breakthrough can be calculated as:

$$\text{Removalefficiency } (\%) = \frac{q_{total}}{m_{total}} \cdot 100 \quad (2)$$

where q_{total} – total mass of metal adsorbed into biosorbent (mg); m_{total} – the total amount of metal ions sent to the column (mg).

The biosorption capacity q_e (mg g^{-1}), the amount of Zn(II) adsorbed (mg) per unit dry weight of biosorbent can be determined using the following equation:

$$q_e = \frac{q_{total}}{m} \quad (3)$$

where m – the total mass of biosorbent in the column (g).

Regeneration of biosorbent

Zn(II) containing biosorbent was regenerated using 1.2 L of 0.1M hydrochloric acid (HCl) as eluting agent. The acid was fed into the top of the fixed-bed column (Fig. 1, b) at the same flow rate used in the biosorption cycle. The effluent samples were collected from the bottom of the column after every bed volume or 200 mL. All samples were analysed with the same procedure as used in biosorption experiments.

After metal elution, the biosorbent was washed thoroughly byup-flow tap water until pH 6.5 and reused for next cycle of biosorption. The biosorption-desorption process was continued for six cycles.

The efficiency of Zn(II) removal or desorption yieldwas calculated from the ratio of the amount of Zn(II) ions desorbed and the total Zn(II) ions adsorbed into the biosorbent in a fixed-bed column using the following equation:

$$\text{Desorption yield (\%)} = \frac{\text{Amount of Zn(II) ions desorbed}}{\text{Amount of Zn(II) ions biosorbed}} \cdot 100 \quad (4)$$

The surface structure of the biosorbent material, before and after Zn(II) successive biosorption-desorption experiments, were characterized by a stereo microscope (Zeiss Stemi 508, Germany).

Statistical analysis

In order to ensure the accuracy and reproducibility of the collected data, all biosorption-desorption experiments were performed in triplicate. Microsoft Excel 2013 *t-test* (two tailed distribution) and ANOVA single parameter tool (significance level, $p \leq 0.05$) were used in data analysis.

RESULTS AND DISCUSSION

The regeneration of the biosorbent is one of the key factors in demonstrating the practical applicability of biosorbent use in industrial wastewater treatment. Different types of eluent agents have been used for recovery of the adsorbed heavy metal ions from biosorbent materials. Akar et al. (2009) regenerated *Symphoricarpusalbus* biomass from Pb(II) in five biosorption-desorption cycles using 0.01M HNO_3 solution; Martin-Lara et al. (2012) showed good efficiency for Pb(II) removal using 0.3M HCl from acid-treated olive stone; Jin et al. (2018) and Freitas et al. (2018) used 0.1M HNO_3 as eluting agent and showed a good reusability of Cd(II), Cu(II) and Ag(II) for *Pleurotusostreatus* spent substrate and Verde-lodo bentonite. Here removal of Zn(II) ions from the sphagnum peat with the smallest possible volume of an eluting solution was evaluated to reduce the aggressive effect of the acidic eluent on binding sites of biosorbent (Hammaini et al., 2007). Moreover, lower amounts of chemicals required for the process will facilitate its cost-efficiency.

In the present study, successive biosorption-desorption cycles of Zn(II) by sphagnum peat were repeated six times. The effect of repetitious sorption-desorption process on Zn(II) removal was shown in Fig. 2. The results showed that the highest removal efficiency of Zn(II) was 99% in the first four successive biosorption-desorption cycles within 48 hours. These results indicate that the sphagnum peat sorption capacity was exhausted after 48 hours. Based on this observation, an equilibrium time of 48 hours was considered as a maximum contact time for biosorption process. The average biosorption capacity of sphagnum peat was 47 ± 11 mg Zn(II) g^{-1}. No significant difference ($p > 0.05$) was observed between four successive biosorption-desorption cycles.

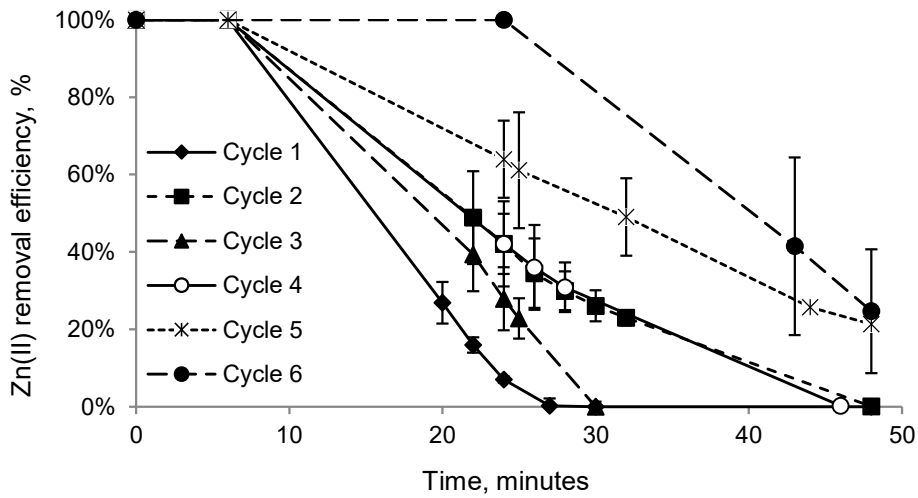

Figure 2. The effect of biosorption cycle number on Zn(II) removal efficiency by sphagnum peat. The initial Zn(II) concentration – 100 mg L^{-1}. The data represent the average values of three experiments for each biosorption experiment cycle and the correlation coefficients (R^2) were from 0.962 to 0.989. The error bars represent the standard deviation (SD).

The sorption capacity of sphagnum peat increased in the following two biosorption-desorption cycles. At the same time, the increase in biosorption time to more than 50 hours did not allowed to recover of the adsorbed metal.

The overall recovery was $1{,}608 \pm 42$ mg of Zn(II) per L of 0.1M HCl used for desorption (around 71% from the total amount of adsorbed Zn(II) during four biosorption-desorption cycle). The maximum desorbed concentration of Zn(II) was achieved in the first 40 minutes by using 0.6 L or 3 fixed-bed column volume of 0.1M HCl (Fig. 3).

The results showed that the maximum desorption efficiency was achieved 93% after first biosorption-desorption cycle (Fig. 4). The desorbed concentrations of Zn(II) from sphagnum peat were $1{,}573 \pm 39$ mg L^{-1}. No significant difference ($p > 0.05$) was observed of desorbed concentration of Zn(II) during 80 minutes of desorption process. And during the next 3 desorption cycles, the amount of desorbed Zn(II) decreased to 60%, but during next two cycles decreased with cycle number (Fig. 4).

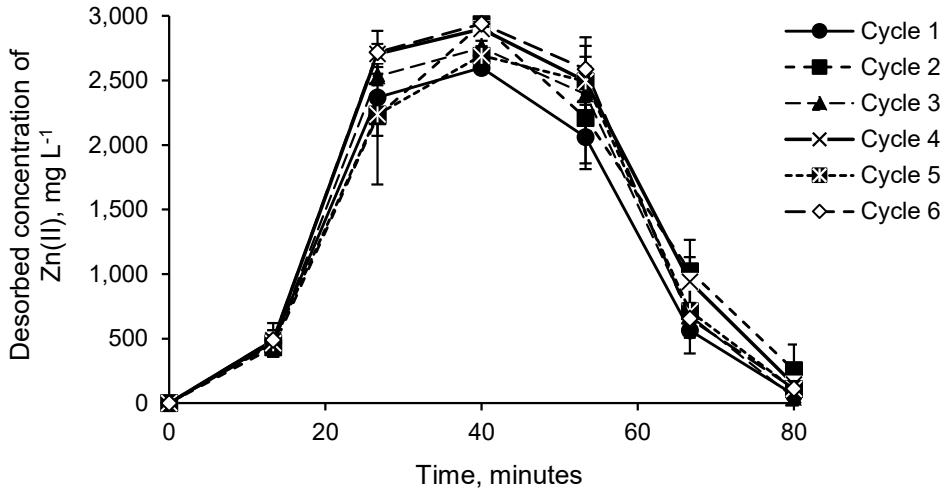

Figure 3. The desorbed concentration of Zn(II) from sphagnum peat during 80 minutes by using 0.1M HCl. The initial Zn(II) concentration – 100 mg L^{-1}. The data represent the average values of three experiments for each biosorption experiment cycle. The error bars represent the standard deviation (SD).

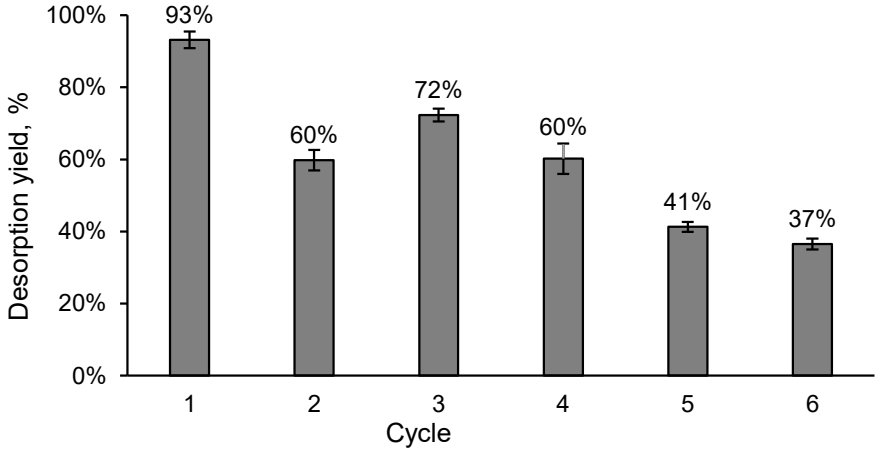

Figure 4. Percentage of Zn(II) desorbed from sphagnum peat in successive biosorption-desorption cycles by using 0.1M HCl as eluting agent. The data represent the average values of three experiments for each biosorption-desorption cycle. The error bars represent the standard deviation (SD).

The results showed that 0.1M HCl as eluting agent allows to remove the loaded Zn(II) ions from the column in a short period of time and had suitable efficiency in the sphagnum peat recovery. Other eluting agents are possible, however, wide availability, price and good test results set HCl as a superior eluting agent.

In order to characterize the biosorbent surface structure, micrographs with stereo microscope were taken before (Fig. 5, a) and after (Fig. 5, b) the Zn(II) regeneration with 0.1M HCl to verify any changes.

Micrographs with a 2.0 x magnification (Fig. 5) indicated some deformation and tendency of sphagnum peat particles to granulate. The biomass before Zn(II) biosorption-desorption cycles had smaller particle size (Fig. 5, a).

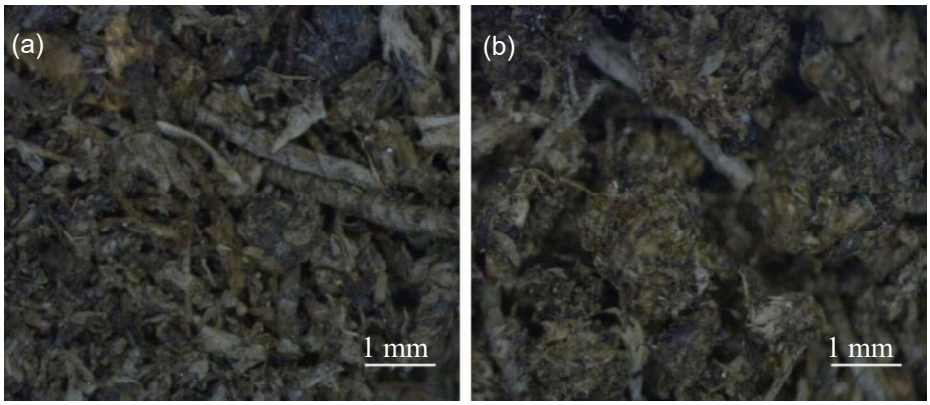

Figure 5. Micrograph (2.0 x magnification) of sphagnum peat surface before (a) and after (b) Zn(II) biosorption-desorption cycles.

To further demonstrate the applicability of sphagnum peat and its re-use upgrades in the technological process are advisable. This could include immobilization onto granular adsorbent to limit a blockage in the column and to increase Zn(II) removal efficiency. Moreover, the possible over-extensive use of the resource should be evaluated due to its specific classification (Crill et al., 2000).

CONCLUSIONS

The results of this study indicated that the sphagnum peat can be successfully used for biosorption in continuous fixed-bed column. Biosorption and desorption cycles were carried out and revealed that the maximum successive number of cycles with 0.1M HCl as efficient eluent were four.

The regenerated sphagnum peat characterization demonstrated tendency to granulate, although no further changes were observed in adsorbent material surface.

ACKNOWLEDGEMENTS. This work has been funded by IPP3: INNO INDIGO Programme Project B-LIQ 'Development of an Integrated Process for Conversion of Biomass to Affordable Liquid Biofuel', No. ES/RTD/2017/18 (PVS ID 2802).

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