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Biosorption of Zn(II) by Sphagnum Peat

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In this study, continuous up-flow fixed-bed column experiments were performed to investigate the biosorption potential of sphagnum peat to remove Zn(II) ions from aqueous solutions. The effect of influent metal ion Zn(II) concentration (10 and 100 mg/L) on Zn(II) removal was investigated and the experimental breakthrough curves were obtained. The breakthrough time decreased from 264 hours to 8 hours by increasing the influent Zn(II) concentration. The highest biosorption capacity of 2731 mg/g was obtained at 10 mg/L Zn(II) concentration. Desorption studies revealed that the sphagnum peat could be regenerated using 0.1 M HCl solution with higher than 99 % recovery during 80 minutes or 6 desorption cycles. The results indicated that the sphagnum peat can be used as an effective and low-cost biosorbent for the removal of Zn(II) in polluted aqueous solutions.

1. Introduction

Environmental contamination with heavy metals is a serious problem due to their toxicity to human, plants and animals. Wastewaters from a variety of industry are an important source of environmental pollution. Zinc(Zn(II)) is a very common heavy metal which contaminates water from a variety of industrial activities like mining, manufacturing and products such as batteries, wood, ceramics, textiles, fertilizers, paints and etc. [Katsou et al., 2010]. If the untreated industrial wastewater were discharged into the aquatic ecosystem or directly into the sewerage system, it may pose risks and hazards to humans through contact with contaminated soil or drinking of contaminated water [Balintova et al., 2012]. According to the World Health Organization (WHO) drinking water standards, the maximum acceptable concentration of Zn(II) ions is 3 mg/L [WHO, 1996]. Higher concentrations of Zn(II) may cause difficulties to respiratory activity such as breathing rate, coughing and problems like abdominal pain, vomiting and nausea [Plum et al., 2010]. Therefore, the removal of Zn(II) ions from aqueous solutions is necessary and very important.

Nowadays, various methods have been applied to remove dissolved metal ions from aqueous solutions and include chemical precipitation, ion exchange, filtration, electrochemical treatment and reverse osmosis [Kargi and Cikla, 2007; Shanmugaprakash and Sivakumar, 2015]. These methods are basically effective, but expensive and often have problems with the removal of residual metal sludge. Biosorption is an alternative technology employing low-cost filtration materials and high removal efficiency of different metal concentrations [Witek-Krowiak et al., 2011; Oguz and Ersoy, 2014]. A number of studies on removal of Zn(II) ions from aqueous solutions with different low-cost materials such as chicken feathers [Aguayo-Villarreal et al., 2011], orange peels [Liang et al., 2011], rice wine processing waste sludge [Liu et al., 2011], cocoa pod husk [Njoku, 2014], pine bark [Cutillas-Barreiro et al., 2016] have been reported.

In the present study, sphagnum peat was investigated as an alternative, inexpensive filter material, as well as widely available natural biosorbent [Wase and Forster, 1997]. Some previous studies have reported the removal of Zn(II) ions from aqueous solutions using sphagnum peat [Ringqist and Oborn, 2002; Kalmykova et al., 2008], however they have been mainly focused on the sorption capacity of Zn(II) in batch systems. But from a practical point of view, continuous fixed-bed column studies are necessary to demonstrate the practical applicability of the biosorbent in treatment of real industrial wastewaters. However, biosorbent performance at continuous mode which is substantial for high loading rates is still a challenge.

Therefore, the aim of this research was to evaluate Zn(II) removal efficiency by sphagnum peat and subsequent Zn(II) recovery from the sorbent material in a fixed-bed column. The regeneration experiments were conducted in order to investigate the possibility of potential recovery of the biosorbent material. And, the effectiveness of the sphagnum peat in fixed-bed column was described through the concept of the breakthrough curve.

2. Materials and Methods

2.1 Biosorbent

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

2.2 Preparation of Zn(II) ion solutions

The synthetic Zn(II) solutions were prepared by dissolving the appropriate amount of $ZnSO_4 \cdot 7H_20$ (Reachem Slovakia, Slovakia)in tap water.

2.3 Biosorption experiments

Biosorption experiments were conducted in a glass column of 30 cm length and 3.2 cm of inner diameter. The column was packed with 45 g of dry sphagnum peat to yield a total effective bed depth of 25 cm. Two stainless sieves with a mesh size of 220 µm were placed at the top and the bottom of the glass column in order to avoid the washing out of biosorbent material. Figure 1 shows the experimental setup of fixed-bed biosorption column used for the present study.

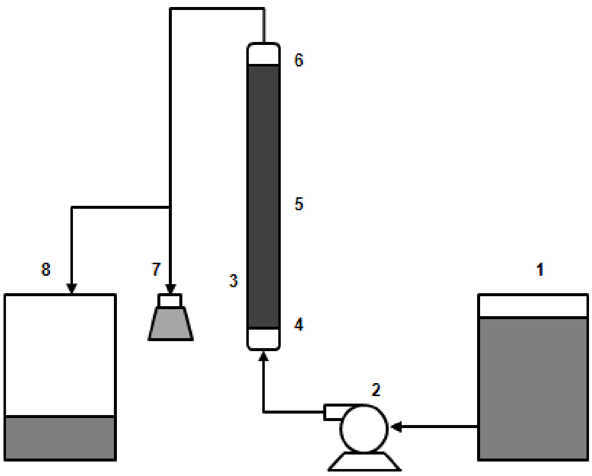

Figure 1: Experimental setup of the continuous up-flow fixed-bed biosorption column: 1 – influent zinc solution; 2 – peristaltic pump; 3 - column; 4 –bottom sieve; 5 –Sphagnum peat moss; 6 –top sieve; 7 –sample collection; 8 –effluent storage.

Before each experiment, the biosorbent material was washed with tap water using continuous flow to remove brown-colored water. After this procedure, Zn(II) solution with an initial concentration of 10 and 100 mg/L at pH 7.6 ± 0.1and 7.2 ± 0.1respectively, was fed through the up-flow fixed-bed column at a flow rate of 15 mL/min by peristaltic pump (MasterFlex L/, model 77202-50, Cole-Parmer Instrument Co.). All experiments were carried out at room temperature (20 ± 2 ºC). Samples of Zn(II) solution were taken periodically from the top of the column and have been acidified with concentrated nitric acid (HNO_3 65%, Lach-Ner Ltd., Czech Republic) to reach a concentration of 2% v/v; then the samples was filtered with 0,45 µm membrane filter (Filtropur S, Sarstedt, Germany). Afterwards, the samples were analyzed for the remaining Zn(II) concentrations by using flame Atomic Absorption Spectrometer (PerkinElmer, AAS, Aanalyst 200). All the results were expressed in milligrams of Zn(II) per litre (mg/L). Operation of the column was stopped when equilibrium between influent and effluent Zn(II) ion concentration was achieved (99% of an initial Zn(II) concentration). 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.

2.4 Biosorbent regeneration

For the regeneration experiments, Zn(II) containing biosorbent was exposed to 0.1M HCl which was fed into the top of the fixed-bed column at a flow rate of 15 mL/min. The elution effluent samples were collected from the bottom of the column after every bed volume or 200 mL. All the samples were analyzed by the same procedure used in biosorption experiments.

2.5 Biosorption and desorption curves

The efficiency of the fixed-bed column can be described through the breakthrough curve concept. The breakthrough curves show the loading behaviour of metal to be removed from solution and are usually expressed by the ratio of effluent metal concentration to influent metal concentration (C_{eff} / C_{inf}) versus the operating time or volume of the effluent (V_{eff}). The volume of the effluent V_{eff} (mL) at breakthrough is calculated by the following equation [Martin-Lara et al., 2012]:

$$V_{eff} = Q \cdot t_{total} \tag{1}$$

where t_{total} is the total operating time in the biosorption experiment in minutes (min), Q is the flow rate of Zn(II) ion solution which passed through the column in mL/min.
The column capacity q_{total} (mg), the total mass of metal ions biosorbed into the biosorbent in fixed-bed column experiments is calculated by the following integration:

$$q_{total} = \frac{Q}{1000}\int_{t=0}^{t=t_{total}} C_R dt \tag{2}$$

where C_R is the concentration of metal removal in mg/L.
The total amount of heavy metal ions sent to the column m_{total} (mg) until breakthrough is calculated from the following expression:

$$m_{total} = \frac{C_{inf} \cdot Q \cdot t_{total}}{1000} \tag{3}$$

where C_{inf} is the influent metal concentration in mg/L.
The total metal removal percentage (%) at breakthrough can be calculated from the ratio of total mass of metal biosorbed (q_{total}) to the total amount of metal ions sent to the column (m_{total}) as follows:

$$\% = \frac{q_{total}}{m_{total}} \cdot 100 \tag{4}$$

The biosorption capacity q_e (mg/g), the weight of Zn(II) sorbated per unit dry weight of biosorbent can be determined as following:

$$q_e = \frac{q_{total}}{m} \tag{5}$$

where m is the total mass of biosorbent in the column in g.
The efficiency of Zn(II) removal or desorption yield was calculated from the ratio of the amount of Zn(II) ions desorbed and the total Zn(II) ions biosorbed into the biosorbent in a fixed-bed column using the following equation:

$$\text{Desorption yield} = \frac{\text{Amount of Zn(II) ions desorbed}}{\text{Amount of Zn(II) ions biosorbed}} \cdot 100 \tag{6}$$

3. Results and discussions

3.1 Biosorption experiments

The influent metal concentration is one of the most important parameter in affecting the performance of a biosorption process in a continuous fixed-bed column.The results showed (Figure 1) that at low influent zinc concentration (10 mg/L), the removal efficiency of Zn(II) was 99 % for the 170 hours. The removal efficiency of Zn(II) decreased to 92 % through the next 48 hours, 70 % after 264 hours. Filter sorption capacity was exhausted after 338 hours. At the highest zinc concentration (100 mg/L), the removal efficiency of 91 % was retained for only 7 hours, afterward it decreased to 72 % (25 hours of biosorption). Filter sorption capacity was exhausted after 50 hours.

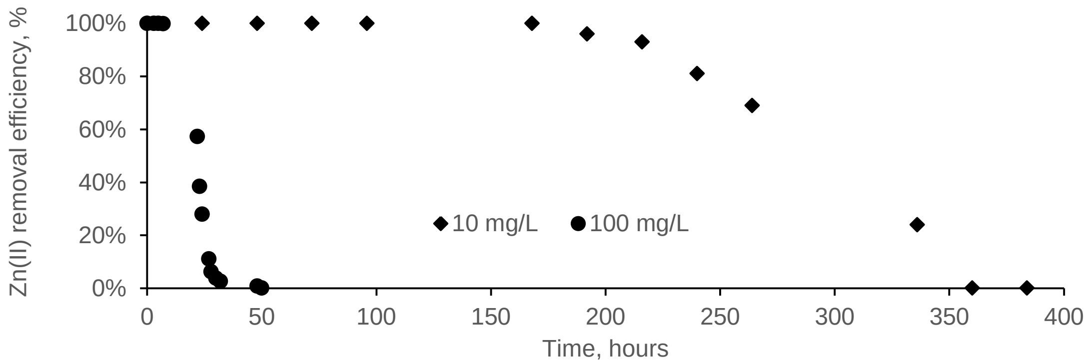

Figure 1: The effect of Zn(II) influent concentrations (10 and 100 mg/L) on Zn(II) removal efficiency by sphagnum peat. The data represent the average values of three experiments for each influent Zn(II) concentration.

The effect of two different influent Zn(II) concentrations (10 and 100 mg/L) on the breakthrough curves are shown in Figure 2, using a constant biosorbent bed depth of 25 cm at a flow rate of 15 mL/min. Zn(II) biosorption parameters of breakthrough curves are shown in Table 1, and were calculated according to abovementioned equations (see paragraph 2.5). The breakthrough time (t_b) was fixed as the time when the effluent Zn(II) concentration achieved a value of 3 mg/L, which is the maximal acceptable concentration of Zn(II) ions in drinking water according WHO.

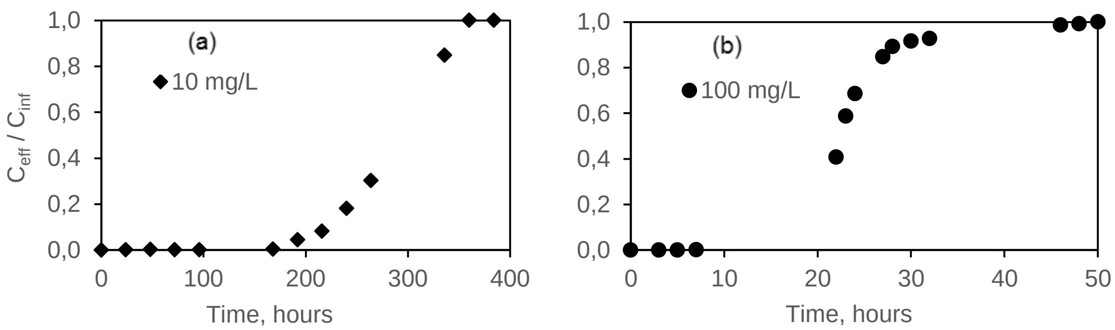

Figure 2: Breakthrough curves for Zn(II) biosorption onto sphagnum peat at two different influent concentrations: (a) 10 mg/L and (b) 100 mg/L at a flow rate of 15 mL/min.

The curves show that the breakthrough time decreased from 264 to 8 hours with increasing influent Zn(II) concentration from 10 to 100 mg/L respectively. Similarly, the total operating time and the treated volume of effluent decreased with the increase in Zn(II) influent concentration, as shown in Table 1. According to the obtained results, the Zn(II) biosorption capacity was higher at lower Zn(II) influent concentration.

Table 1: Biosorption parameters of breakthrough curves at continuous up-flow fixed-bed column experiments

Parameter	$C_{influent}$ = 10 mg/L	$C_{influent}$ = 100 mg/L
Biosorbent mass (m, g)	45	45
Breakthrough time (t_b, h)	264	8
Total operating time (t_{total}, h)	384	50
Volume of effluent (V_{eff}, L)	345.6	45
Column capacity (q_{total}, mg)	122904	44502
Total amount of Zn(II) ion sent to the column (m_{total}, mg)	3850	4624
Total Zn(II) removal percentage (%)	97%	90%
Biosorption capacity (q_e, mg/g)	2731	989

The biosorption capacity of sphagnum peat decreased from 2731 to 989 mg/g with increased Zn(II) concentration from 10 to 100 mg/L. This can be explained by the fact that at higher metal concentration, the biosorbent binding sites become more quickly saturated in the fixed-bed column. The same behaviour of metal initial concentration dependency was reported for Cu(II) biosorption onto coconut shell [Acheampong et al., 2013]. The total Zn(II) removal percentage was 97 % at 10 mg/L while 90 % at 100 mg/L.

3.2 Desorption experiments

The regeneration of the biosorbent is the key factor in order to investigate the possibility of potential recovery of the biosorbent material. In the present study, sphagnum peat saturated with Zn(II) were regenerated by passing 0.1 M HCl solution at a flow rate of 15 mL/min through the exhausted column and desorption yield was investigated 160 minutes or twelve desorption cycles. Figure 3 shows the percentage of Zn(II) desorbed in function of time.

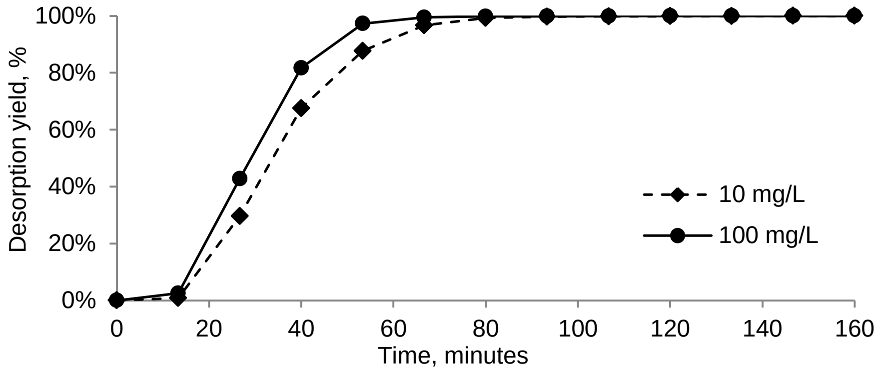

Figure 3: Percentage of Zn(II) desorbed from sphagnum peat in time by using 0.1 M HCl.

The desorption efficiency was achieved higher than 99 % during 80 minutes or 6 desorption cycles. Figure 4 shows the desorbed concentrations of Zn(II) in function of desorption cycles. The results showed that the maximum values of desorbed Zn(II) concentrations were achieved in the first 3 desorption cycles using only 0.6 mL of 0.1 M HCl. The desorbed concentrations of Zn(II) from sphagnum peat were 2845 ± 394 and 2753 ± 786 mg/L for influent Zn(II) concentration of 10 and 100 mg/L, respectively. And during the next 3 desorption cycles, the Zn(II) desorbed concentration decreased with cycle number.

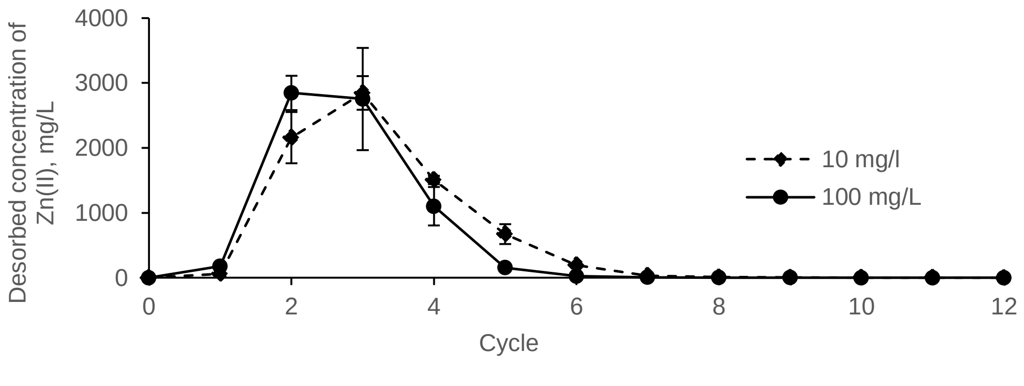

Figure 4: The desorbed concentration of Zn(II) from sphagnum peat during twelve desorption cycles by using 0.1 M HCl.

Biosorption efficiency decreased with the increase of desorption cycles. Results showed that 0.1 M 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.

4. Conclusions

The biosorption of Zn(II) by sphagnum peat from aqueous solutions in a fixed-bed column has been studied. The biosorption capacity for Zn(II) concentration of 10 mg/L and 100 mg/L was obtained as 2731 mg/g and 989 mg/g, respectively. The breakthrough time is found decreasing as the influent Zn(II) concentration increases. The results of this study show that the sphagnum peat can be successfully used for the biosorption of Zn(II) ions from aqueous solutions.

Acknowledgments

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