



“Gheorghe Asachi” Technical University of Iasi, Romania



APPLICATION OF *Sphagnum moss* PEAT IN ECOLOGICAL REMEDIATION OF OXYANIONS CONTAMINATED AQUEOUS SOLUTIONS

Gabriela Ungureanu¹, Catalin D. Balan², Irina Volf^{2*}

¹University of Porto, Faculty of Engineering, Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Department of Chemical Engineering, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

²“Gheorghe Asachi” Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof. Dr. docent Dimitrie Mangeron Street, 700050 Iasi, Romania

Abstract

The potential of *Sphagnum* moss peat to adsorb oxyanions (As(III), As(V), Sb(III), Sb(V) and Se(VI)) from aqueous solution was studied in batch mode. For arsenic (both species) and selenium, the results were negative: moss peat is not able to retain these oxyanion. For antimony, the hydroxyl and carboxyl groups from the *Sphagnum* moss peat surface seems to be responsible for Sb uptake. Kinetic studies were conducted for both Sb(III) and Sb(V) and a fast uptake process was observed, equilibrium being achieved in about 2 hours. Equilibrium studies reveals considerable adsorbed amounts of Sb(III) and Sb(V). The experimental sorption capacity resulted for Sb(III) was around 3 mg/g and nearly 3.3 mg/g for Sb(V), at pH 2 and $23 \pm 1^\circ\text{C}$. The influence of pH (in the 2-8 range) is modest in case of Sb(III) and insignificant for Sb(V) sorption. Following the results, it is possible to conclude that *Sphagnum* moss peat could be used in ecological remediation of antimony contaminated aqueous solutions.

Key words: oxyanions, remediation, sorption, *Sphagnum* moss peat

Received: May, 2017; Revised final: February, 2018; Accepted: March, 2018; Published in final edited form: April 2018

1. Introduction

The toxic metals and metalloids, frequently found in wastewaters, represent an important class of environmental contaminants. Arsenic, antimony and selenium occur naturally, arsenic being the most abundant of them, but environmental contamination may occur also due to anthropogenic sources including coal combustion, mining, agriculture, industry (Ungureanu et al., 2015b). Arsenic and antimony have chemical and toxicological similarities, and they usually co-occur as pollutants (Fu et al., 2010). Toxicity of As(III) is referred to be nearly 70 times higher than organic forms of As and 10 times higher than As(V) (Ben Issa et al., 2011; Jain and Ali, 2000; Larios et al., 2012). Antimony trioxide

(Sb₂O₃) and antimony trisulfide (Sb₂S₃) are respectively assigned by IARC, as “possibly carcinogenic to humans” (group 2B), and “not classifiable as to its carcinogenicity to humans” (group 3). Selenium is quite different from arsenic and antimony; it is an essential micronutrient and a trace element with biological importance for humans and animals. A particularity of selenium is that the boundary between toxicity and deficiency is narrow (Thiry et al., 2012) and still not clarified. The toxicity of selenium is not only related to its chemical similarity to sulphur and to its ability to be substituted during the assembly of proteins, but also to the oxidative stress (Lavado et al., 2012).

In order to remove arsenic, antimony and selenium from contaminated waters, several methods

* Author to whom all correspondence should be addressed: e-mail: iwolf@tuiasi.ro

are available namely coagulation/flocculation, ion-exchange and adsorption, oxidation, electrochemical methods and membrane processes (Santos et al., 2015; Ungureanu et al., 2015b), but also phytoremediation or bioremediation. Adsorption has been noticed as a simple and relative low-cost process appropriate for removing low levels of contaminants. A good adsorbent must guarantee good removal efficiency with a low cost of use. The removal capacity of natural sorbents can be improved by surface modification treatments, but any intervention to alleviate this capacity involves an increase in costs. The use of pre-treatments is economically unadvisable in cases where the increase in process efficiency is not significant.

The sorption of various toxic metals, anions, but especially the cationic ones (Moța et al., 2017; Rashed et al., 2017), has been widely investigated using various adsorbents (Ahmed et al., 2017; Bulgariu et al., 2015; Carolin et al., 2017). Nonetheless, studies regarding the sorption of toxic metallic/metalloid oxyanions using natural sorbents are quite limited, especially using sorbents without any previous treatment (Tuzen and Sari, 2010; Ungureanu et al., 2015a). Ungureanu et al. (2015b) and Santos et al. (2015) published comprehensive reviews about adsorption capacity for arsenic, antimony and selenium, detailing the maximum adsorption capacities reported for different sorbents.

The high availability around the world makes the moss peat an interesting resource for adsorption studies. The removal of oxyanions on *Sphagnum* moss peat has never been tested and published until now. The aim of this study is to investigate the efficiency of Romanian moss peat in removal of oxyanions from polluted aqueous solutions in order to provide useful information about the mechanism of the process.

2. Material and methods

2.1. Chemicals and glassware preparation

The sorption process of arsenic was tested for the main oxidation states, As(III) and As(V); similarly, the two antimony predominant oxidation states Sb(III) and Sb(V) were studied. In case of selenium, only Se(VI) was tested because of its high solubility in aqueous solutions and also due to its low adsorption capacity that made this oxyanion more problematic to be removed. Adsorbate solution was prepared by diluting an appropriate volume of AAS commercial standards: As(III) from 1000 ± 1 mg As(III)/L in 2-5 % HCl (*ChemLab*), As(V) from As₂O₃ solution, 1001 ± 3 μg As(V)/L in HNO₃ 4 % (*SCP Science*), Sb(III) from K₂SbO₄·H₂O solution 1000 ± 2 mg Sb(III)/L, in 2-5 % HCl (*Carlo Erba*); Sb(V) from 1000 ± 2 mg Sb(V)/L, in 4 % HNO₃ (*Chem Lab*) and Se(VI) from 1000 ± 2 mg Se(VI)/L, in 2-5 % HNO₃ (*SCP Science*). The pH was adjusted to the required values using diluted solutions of NaOH and HCl or HNO₃ prepared from analytical grade chemicals: NaOH pellets (purity $\geq 99.0\%$, *Merck*), concentrated HNO₃ 65% analytical grade (*Sigma*

Aldrich) and concentrated HCl 37% p.a. (*Merck*). All solutions were prepared in distilled water. Glassware and plastic material were acid-washed (soaked for 24 hours in HNO₃ 20% solution) and rinsed with distilled water.

2.2. Sorbent preparation

The *Sphagnum* moss peat, collected from Poiana Stampei – Romania, was initially air-dried and ground (3-6 mm), using an electric grinder (*GM-100 Retsch Knife Mill Grindomix*). The moss peat was dried again, at 40 °C and stored in a desiccator until use.

2.3. Moss peat characterization

2.3.1. Humidity content

For the determination of physically bound water from moss peat and moisture content (MC) calculation the method described by Balan et al. (2012) was followed. Approximately 2 g of peat was weighed into a pre-weighed weighing bottle. The weighing bottle with the sample was maintained at 105°C in an oven for 4 hours, then cooled in a desiccator and weighed again. The moisture content of the analysed sample is calculated by:

$$MC \text{ (wt \%)} = \frac{A-B}{A} * 100 \quad (1)$$

where *A* is the mass of the moss peat sample before drying (g) and *B* represents the sample mass after drying at 105°C (g).

2.3.2. Ash content

The identification of mineral (inorganic) composition of moss peat was performed as previously (Balan et al., 2012) using an electric furnace *Nabertherm L3/11/B180*. In a porcelain crucible (previously calcined at 600°C and weighed) a sample of about 2 g of moss peat was weighed and firstly dried at 105°C and weighed again, then calcined in an electric furnace at 600°C for 2 hours. After calcination, the ash crucible was cooled in a desiccator and weighed. The ash content was calculated with the relation:

$$Ash, \% = \frac{B-C}{A} * 100 \quad (2)$$

where *A* is the mass of initial sample of moss peat (g), *B* represents the sample mass after drying at 105°C (g), and *C* is the sample mass after calcination at 600°C (g).

By the difference from 100%, the organic material content of the moss peat is calculated (Eq. 3):

$$Organic \text{ substances, \%} = 100 - moisture\% - ash\% \quad (3)$$

2.3.3. pH

The pH of the aqueous solution of moss peat was measured by immersing a sample of 1 g of moss peat in a beaker with 50 mL double distilled water.

After 24 hours with intermittent stirring, the pH of the suspension was measured with a pH meter equipped with a combined glass electrode.

2.3.4. Infrared spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the functional groups presented on the moss peat surface. Infrared spectra were obtained by a Shimadzu FTIR, model IR Affinity equipment, in triplicate readings, on a sample of moss peat ground to finer and homogeneous particles, in a wave number range from 400 to 4000 cm^{-1} , 50 scans, with a resolution of 8.0 cm^{-1} .

2.4. Adsorption studies

2.4.1. Analytical procedures

Adsorption tests were conducted using solutions with 2-50 mg/L contaminant concentration since these levels are typically found in wastewaters. Equilibrium and kinetic studies were performed in batch, testing the effect of pH and initial contaminant concentration. The concentration of arsenic, antimony and selenium in aqueous solution was measured by flame AAS (GBC 932 plus), deuterium background correction, in triplicate readings. As, Sb and Se were measured at wavelengths of 193.7 nm, 217.6 nm and 196.0 nm, respectively, with a lamp current of 5.0 mA and slit widths of 0.5 nm for arsenic, 0.2 nm for antimony and 1.0 nm for selenium. Acetylene and dinitrogen monoxide were used as combustible/oxidant gases for As and Se determinations, and acetylene/air for Sb analysis. Calibration curves were obtained and accepted for a determination coefficient $R^2 > 0.995$. All experiments were performed under orbital agitation at 120 rpm (orbital rotator GFL 3031), at constant temperature (23 ± 1 °C). Before AAS analysis, the samples were filtered using cellulose acetate membrane filters (45 μm porosity).

2.4.2. Screening tests

Preliminary assays were performed in order to test the sorption ability of moss peat for As(III), As(V), Sb(III), Sb(V) and Se(VI) removal. The experiments were conducted in duplicate, at constant pH 5.0 ± 0.5 . Contaminant solutions of 25 mg/L concentration were stirred with rigorously recorded moss peat mass of 10 g/L, in 100 mL capped Erlenmeyer flasks. After 6h-contact time, samples were filtered and final concentrations of the contaminant were analysed. The adsorbed amount per unit mass of adsorbent (q , mg/g) was calculated by mass balance (Eq. 4):

$$q = \frac{c_{in} - c_f}{m} * v \quad (4)$$

where C_{in} is the initial concentration (mg/L), C_f is the final concentration (mg/L), m is the mass of moss peat used (g) and v is the volume of solution (L).

2.4.3. Effect of pH

The pH conditions are known to have a significant influence in the adsorption process. In order to study the influence of this variable on the

sorption of Sb(III) and Sb(V) by moss peat, adsorption tests were conducted at different pH values. The experiments were carried out in duplicate, following the procedure described previously (section 2.4.2). The pH was adjusted in the initial solution, to values between 2 and 8, and was regularly controlled throughout the experiment, in order to be approx. constant (± 0.5).

2.4.4. Kinetic studies

The effect of contact time on the biosorption of Sb(III) and Sb(V) on moss peat was studied in batch mode, at pH 2 for both Sb(III) and Sb(V). The experimental conditions were 25 mg Sb(III) and Sb(V)/L, using 10 g/L moss peat dosage. Sb solution with the pH selected after preliminary tests (regularly controlled) and the sorbent were stirred for different pre-established contact times. Suspensions were filtered and antimony in the liquid phase analysed.

2.4.5. Equilibrium adsorption isotherm

Biosorption isotherms were performed for Sb(III) and Sb(V), at pH 2, adjusted regularly, in duplicate. Experimental data was obtained by stirring Erlenmeyer flasks containing Sb solutions, with different initial concentrations (2-50 mg/L), with 10 g/L of sorbent, for 6 hours (enough to reach the equilibrium state). The suspensions were filtered and Sb was analysed in the liquid phase. The amount of Sb(III) and Sb(V) adsorbed in equilibrium was calculated by (Eq. 4). In this case, q and C_f are the values observed at equilibrium (q_e and C_e , respectively).

2.4.6. Desorption studies

Experiments regarding the desorption of Sb(V) from loaded-moss peat were performed. Initially, simple tests were conducted using four different eluents (NaOH 0.1 mol/L, HCl 0.1 mol/L, NaCl 0.5 mol/L and Na_2HPO_4 0.5 mol/L) and a dosage of 10 g of loaded-peat per L of eluent, for 6 h-contact time. For further experiments, NaOH 0.1 mol/L was selected as eluent. Three adsorption/desorption cycles were then carried out. The contact time for each adsorption/desorption process was 4 hours. In the adsorption step, initial Sb(V) concentration and moss peat dosage were 25 mg/L and 10 g/L, respectively. For desorption assays, loaded-moss peat dosage was 15 g/L.

3. Results and discussion

3.1. Biomass characterization

3.1.1. Physical-Chemical analysis

The moss peat from Poiana Stampei is exploited since 1950. The peat deposits from Dorna watershed, falls into the category of oligotrophic peat deposits, characterized by the existence in the region of rich precipitations, cold climate, bulging appearance of peat lands and by characteristic vegetation which consists mainly of *Sphagnum* and

spruce. The main peat characteristics (Table 1) suggest a peat with a low degree of decomposition.

Table 1. Characteristics of *Sphagnum* moss peat

Properties	Value
Moisture content (wt %)	10.5
Ash content (wt %)	4.85
Organic matter (wt %)	84.65
pH (1:50, w:v deionized water)	4.00 ± 0.05

3.1.2. FTIR analysis

Fourier Transform Infrared Analysis (FTIR) (Fig. 1) permits the registration of infrared spectra for *Sphagnum* peat moss.

The main constituents of moss peat - cellulose, lignin, humic and fulvic acids - contain a large number of carbon, hydrogen, oxygen atoms bound together, and their valence and deformation vibrational movements are connected together in a complex way. As a result, the infrared spectrum has a very complex structure and is quite difficult to assign all the absorption bands to specific vibration from molecule or groups of atoms.

IR spectra of *Sphagnum* moss peat can be divided into several areas highlighting bands with different intensities of valence vibration and deformation of the groups OH, CH, CH₂, CO, COOH, etc. (Balaban et al., 1983; Romao et al., 2007).

Absorption band from 3410-3420 cm⁻¹ is assigned to the valence vibrations of hydroxyl groups involved in the inter- and intra-molecular hydrogen bonds. Valence vibrations of the CH₂ and CH groups determine the absorbance at 2920 cm⁻¹. The area between 2000 - 1500 cm⁻¹ is characterized by the valence vibrations of the double bonds C = O (carboxyl, aldehyde, ketone groups 1732 cm⁻¹) or aromatic structures (lignin or other compounds with low molecular weight, 1514 cm⁻¹).

The area between 1500 - 1200 cm⁻¹ includes absorption bands attributed to deformation vibrations of different atomic groups such as CH₂, CH, OH. The adsorption band of 1200-950 cm⁻¹ is characterized by a very broad absorption band assignable to the valence vibrations of the bonds C-O, C-C in the cyclic structure. Strong absorption in this spectral range is characteristic for all polysaccharides. Between 900-400 cm⁻¹, among a broad absorption, more peaks caused by vibrations of OH group are observed.

3.2. Adsorption studies

3.2.1. Screening Tests

Preliminary adsorption tests were carried out in order to compare the performance of *Sphagnum* moss peat as regards the adsorption of As, Sb and Se. Different species, with different charges and oxidation states, can be present in aqueous solution, depending on the pH and redox potential, which determines their chemistry to be complex. Fig. 2 presents a simplified diagram for As(III), As(V), Sb(III), Se(IV) and Se(VI) in water, as a function of pH (Filote et al., 2017); these diagrams can help to a better understanding of the results from these preliminary experiments.

Preliminary tests performed with *Sphagnum* moss peat and arsenic, antimony and selenium revealed that the moss peat is unable to remove both As(III) and As(V) and also Se(VI). According to the speciation diagram, at pH 5, As(III) mainly exists as a neutral compound (H₃AsO₃) and As(V) as an oxyanion (H₂AsO₄⁻). In case of antimony, the adsorption capacity of moss peat was 1.5 mg/g for Sb(III) and 2 mg/g for Sb(V). At pH 5, Sb(III) is present in aqueous solution as a neutral specie (Fig. 3) but, contrarily to As(III), it was removed considerably. Possibly, the electrostatic attraction is not the adsorption mechanism in this case, but most probably the complexation reactions between Sb(III) and carboxylic and hydroxyl groups is the explanation.

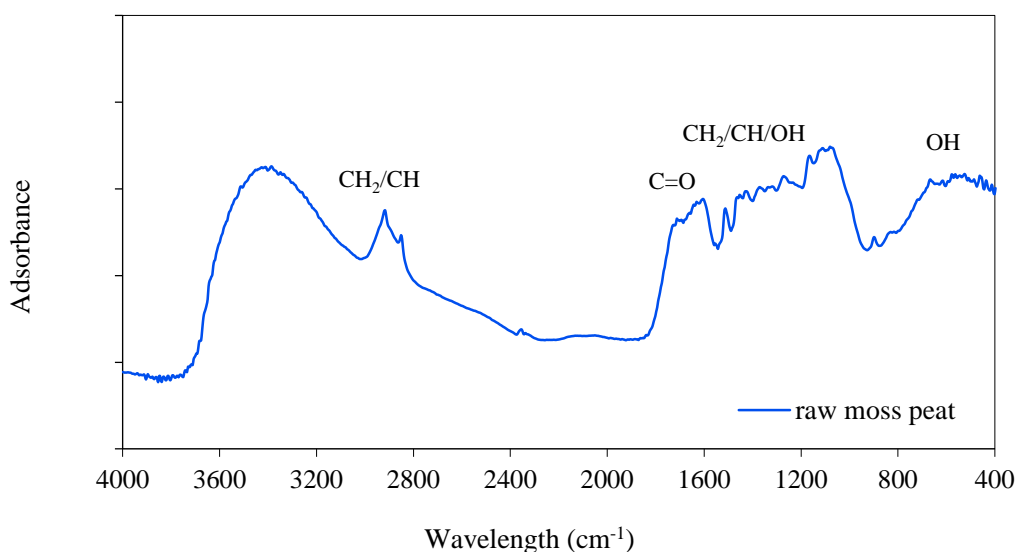


Fig. 1. FTIR spectra of raw peat moss

pH	2	7	9	11	13
As(III)	H_3AsO_3			$H_2AsO_3^-$	$HAsO_3^{2-}$
As(V)	H_3AsO_4	$H_2AsO_4^-$	$HAsO_4^{2-}$		AsO_4^{3-}
Sb(III)	$Sb(OH)_2^+$	H_3SbO_3 $Sb(OH)_3$		$H_2SbO_3^-$ $Sb(OH)_4^-$	
Sb(V)	$Sb(OH)_5$	$Sb(OH)_6^-$			
Se(IV)	H_2SeO_3	$HSeO_3^-$		SeO_3^{2-}	
Se(VI)	$HSeO_4^-$	SeO_4^{2-}			

Fig. 2. Schematic diagrams for speciation of As(III), As(V), Sb(III), Sb(V), Se(IV) and Se(VI) in aqueous solution (adapted upon Filote et al., 2017)

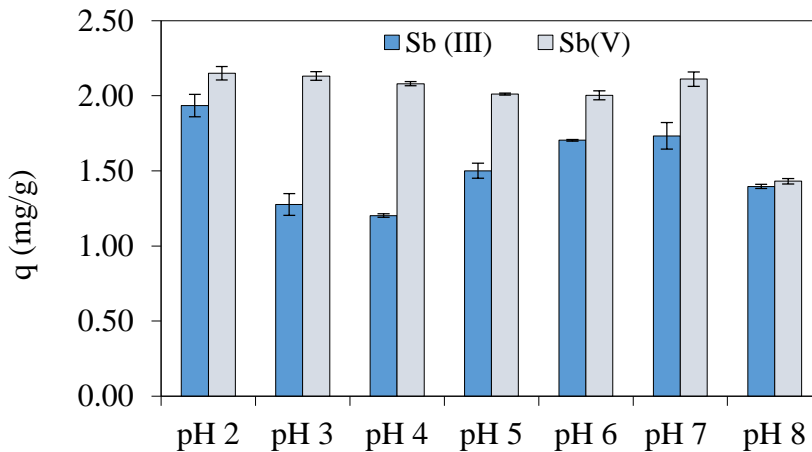


Fig. 3. Biosorption of Sb(III) and Sb(V) on *Sphagnum* moss peat as a function of pH (initial solution concentration 25 mg/L, moss peat dosage 10 g/L, 4 h contact time)

Tella and Pokrovski (2009) also observed the formation of complexes in solution, between antimonite and poly-functional carboxylic and hydroxy-carboxylic acids. Similarly, Wu et al. (2012) proposed for the adsorption of Sb(III) on *Microcystis* biomass the complexation reactions as the dominant mechanism, but additionally, considering that $Sb(OH)_3$ possesses three OH ligands, hydrogen bonding may also be involved in the adsorption process.

3.2.2. Effect of pH

The pH influences the chemical form of the adsorbate and the charge of the functional groups on the sorbent surface and for this reason it is an important parameter that usually affects the adsorption of metal ions in solution. The results found for sorption tests in different pH conditions are described in Fig. 3, as amount of antimony adsorbed, q (mg/g), calculated by mass balance equation (Eq. 3).

The error bars presented in Fig. 4 were calculated considering the maximum error in the measurements involved in the calculation of the adsorbed amount (i.e., error in volumes measurement, mass of moss peat and in the Sb concentration readings) and explains the global uncertainty of each result.

$$q = \frac{C_0 - C}{C_s} \quad (5)$$

In Eq. (5), C_0 and C are the initial and the final Sb concentrations (mg/L) in the liquid phase, respectively, and C_s the moss peat dosage (g/L). The sorption of antimonite by moss peat is modestly affected by pH (Fig. 3). The amounts of Sb(III) adsorbed ranged between 1.2 and 1.94 mg/g. Regarding Sb(V), the sorption was less influenced by pH, with sorbed amounts around 2 mg/g (from pH 2 to pH 7), but at pH 8, the amount of Sb(V) adsorbed reduced evidently. These results demonstrate that Sb(III) and especially Sb(V) uptake by moss peat is significant over the entire pH range studied (pH 2-8), which is an important advantage. Many sorbents require an optimum pH to achieve a maximum (or a considerable) uptake. In a practical situation, considering the huge volume of wastewater generated, it is impractical to alter the pH of solutions (Vijayaraghavan and Balasubramanian, 2015).

According to the speciation diagram from Fig. 2, neutral $Sb(OH)_3$ is the predominant form of antimonite in solutions in the whole pH range studied. Concerning antimonate, for pH 2-3 it is predominantly in neutral form ($Sb(OH)_5$), but for higher pH it acquires the form of the oxyanion $Sb(OH)_6^-$.

This confirms that electrostatic attraction is not involved in the uptake of Sb(III) or Sb(V), since there are not opposite charges (adsorbate/adsorbent) at any pH value. Previous works (Tella and Pokrovski, 2008; 2009; 2012) have provided an important support to the proposed adsorption mechanisms and to the results obtained in this study. The authors demonstrated the construction of stable complexes of Sb(III) and Sb(V) with poly-functional carboxylic, hydroxyl carboxylic acids and phenolic hydroxyl in aqueous solution. Considering the functional groups of the moss peat, the mechanism for sorption is probably the surface complexation, involving carboxylic and hydroxyl groups.

Other studies have reported comparable results concerning the pH effect on Sb(III) uptake. Iqbal et al. (2013) described a constant uptake by green bean husk between pH 3 and 10, and a diminution for pH below 3 or above 10. Wu et al. (2012) have also found an irrelevant dependence on the pH in the range from 2.0 to 7.0, but they obtained an optimum at pH 4. The studies regarding Sb(V) uptake by natural sorbents are very scarce, but Sun et al. (2014) reported a decrease of the sorption as pH increased in pH 3-10.

3.2.3. Kinetics studies

The kinetic study represents the first step in determining the inter-dependencies between equilibrium phenomenon and mass transfer, establishing a predictive model of the sorption behaviour.

Experimental results obtained in the kinetic study of Sb(III) and Sb(V) sorption by *Sphagnum* moss peat are presented in Fig. 4 as the amount of Sb adsorbed (q) as a function of contact time (t). The biosorption of antimony is a fast process (Fig. 4). The contact time required to reach equilibrium is about 120 min. In the first 30 min, the process is very quick; more than 60 % of the maximum adsorbed amount was already attained. The kinetic curves can be divided into two phases, a first phase very fast (0 – 30 minutes) when more than 60 % of the maximum adsorbed amount was already attained and a second slower phase (30 – 120 minutes).

The equilibrium time, for both systems is about 2-3 hours, since there were no further significant changes on the adsorbed amount of Sb. Various authors described fast kinetics for antimony removal, with contact times lower than few hours (Uluozlu et al., 2010; Ungureanu et al., 2015a; Ungureanu et al., 2016; Vijayaraghavan and Balasubramanian, 2011; Wu et al., 2012). Speedy sorption kinetics of metals/metalloids is very important in practical terms, allowing the use of smaller columns with continuous operation, in an efficient and economical way (Aksu, 2001). The most known models used to describe adsorption kinetics are the Lagergren's pseudo-first-order (Lagergren, 1898) and the pseudo-second order (Ho et al., 1996). Both models were fitted to the experimental data by non-linear regression using *CurveExpert* software (Ungureanu et al., 2016;

Ungureanu et al., 2017). Pseudo-2nd order showed much better results, higher correlation coefficients, lower standard error (SE) and a predicted value for the equilibrium adsorbed amount (q_e) closer to the experimental ones. Pseudo-2nd order model, expressed by (Eq. 5), was then selected to describe the experimental data for Sb(III) and Sb(V) biosorption.

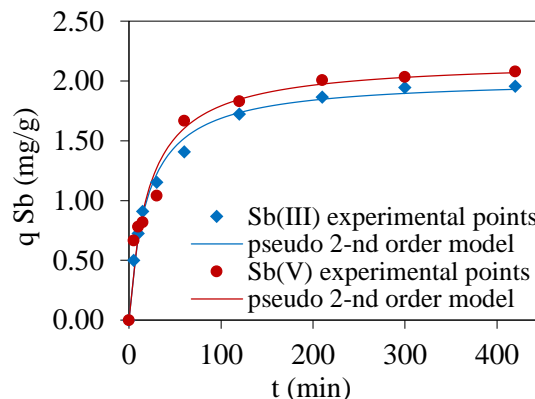


Fig. 4. Biosorption kinetics for Sb(III) and Sb(V) (pH 2) at 23 ± 1 °C and initial Sb concentrations of $C_{in}=25$ mg/L and $C_s=10$ g/L moss peat. Experimental data and pseudo-second-order model

This model assumes a homogeneous surface and metal binding to two active centres. In Eq. (6), q_e (mg g⁻¹) denotes the biosorbed amount in equilibrium and k_2 (g mg⁻¹ min⁻¹) the pseudo-second order kinetic constant. The initial rate of biosorption (r , mg g⁻¹ min⁻¹) was also calculated, using the parameters of pseudo-second order model (Eq. 7).

$$q = \frac{q_e^2 \cdot k_2 \cdot t}{1 + k_2 \cdot q_e \cdot t} \quad (6)$$

$$r = k_2 \cdot q_e^2 \quad (7)$$

The pseudo-2nd order model parameters were presented in Table 2.

3.2.4. Equilibrium studies

Isotherm provides information about the attraction of the adsorbent to the adsorbate and about the maximum sorption capacity, at a specified temperature. Equilibrium isotherms for Sb(III) and Sb(V) sorption on the moss peat were determined at constant pH 2 with synthetic antimony solutions, varying the initial concentration of antimony from 2 to 50 mg/L and using an adsorbent dosage of 10 g/L. The equilibrium results are described in Fig. 5, as Sb sorbed amount in equilibrium (q_e), calculated by (Eq. 3), where C was replaced by the equilibrium Sb concentration in the liquid phase (C_e).

Considerable adsorbed amounts were reached in the concentration range studied (Fig. 5). The experimental adsorbed amount obtained for Sb(III) was approx. 3 mg/g, whereas for Sb(V) nearly 3.3 mg/g was observed, at pH 2.

Table 2. Parameters for pseudo-second order kinetic model (value± 95 % confidence)

C_{in} (mg/L)	C_s (g/L)	k_2 (g mg ⁻¹ min ⁻¹)	q_e (mg/g)	r (mg g ⁻¹ min ⁻¹)	SE (mg/g)
Sb(III)					
25	10	0.025 ± 0.006	2.02 ± 0.09	0.102	0.06
Sb(V)					
25	10	0.02 ± 0.01	2.1 ± 0.2	0.1016	0.13

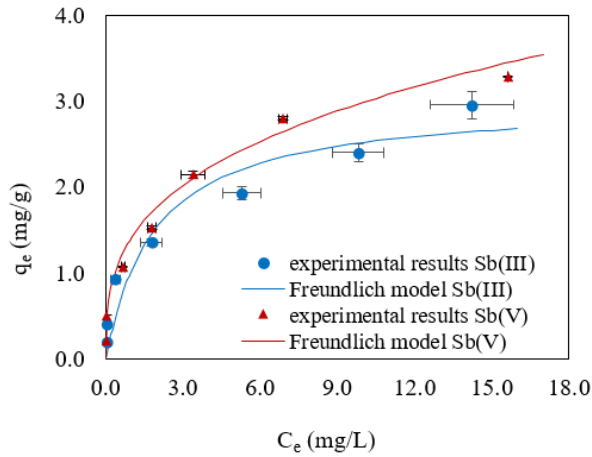


Fig. 5. Equilibrium isotherms for Sb(III) and Sb(V) biosorption on *Sphagnum* moss peat, experimental data and Freundlich model

For both Sb(III) and Sb(V), Langmuir and Freundlich models were adjusted to experimental data by non-linear fitting CurveExpert software and Freundlich model shows a better fitting. The Freundlich isotherm (1906) is an empirical expression (Eq. 8) that assumes a heterogeneous sorption surface with different energy active centres.

$$q_e = K_F C_e^{1/n_F} \quad (8)$$

where K_F ((mg g⁻¹)(L m⁻¹)^{1/n_F}) is a constant for the adsorbate-adsorbent system and n_F is a constant that indicates the intensity of adsorption ($n_F > 1$ favorable isotherm; $n_F \leq 1$ unfavorable isotherm). The values calculated are presented in Table 3.

The standard errors of the regressions have a reasonably low value, indicating a good agreement between observations and Freundlich predictions. The adsorbed amounts obtained in this study are comparable with adsorption capacities reported in literature. The maximum adsorption capacity of raw *Sargassum muticum* for Sb(III) (Ungureanu et al., 2015a) was 5.5 mg/g at pH 5, 2 g/L alga and initial concentration of 10 mg/L Sb(III) solution. Wu et al. (2012) testing the affinity of *Microcystis* biomass found a removal capacity of 4.88 mg/g for Sb(III), at pH 4. This value is slightly higher than the one reported in the present study, but it was achieved using much higher initial concentration in ranges 0 to 400 mg/L. *Cyanobacteria Synechocystis* sp. was tested by Mu (2011) and a maximum adsorption capacity of 4.68 mg/g was reported, using an initial Sb(III) concentration range from 5 to 100 mg/L. Other authors

presented higher adsorption capacities, such as 81.1 mg/g, for lichen, *Physcia Tribacia* (Uluozlu et al., 2010) and 14.9 mg/g (at pH 6) for the brown alga *Sargassum* sp. (Vijayaraghavan and Balasubramanian, 2011). Considerable higher adsorption capacities have been reported in case of binary metal oxides, for example 214 mg/g, at pH 3, for a Fe-Mn oxide (Xu et al., 2011); this category of material requires however, synthesis and consequently implies high costs of preparation.

Table 3. Parameters for Freundlich equilibrium model (values ± confidence intervals for 95 % confidence)

	n_F	$K_F = \text{mg g}^{-1} (\text{mg.L}^{-1})^{-1/n}$	SE (mg/g)
Sb(III)	2.9 ± 0.1	1.1 ± 0.5	0.23
Sb(V)	3.1 ± 0.4	1.4 ± 0.1	0.24

3.2.6. Desorption and reuse

Sphagnum moss peat is a material with several possible utilisations and for this reason the reuse potential of a loaded-*Sphagnum* moss peat might be an essential condition to evaluate the process design for a practical application. Considering that the *Sphagnum* moss peat is a natural and available adsorbent and its cost is low, the relevance of biomass regeneration might be questionable depending in the efficiency of the process. Preliminarily, desorption experiments were conducted with *Sphagnum* moss peat loaded with Sb(V) and different eluents. The results are revealed in Fig. 6. The eluents provided desorption levels ranging between 2 and 31 % for Sb(V) loaded in the moss peat and sodium hydroxide solution 0.1 M was the best desorbent.

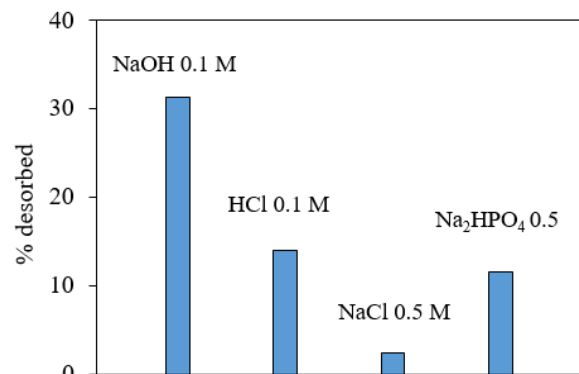


Fig. 6. Desorption percentages from Sb(V)-loaded *Sphagnum* moss peat (dosage 25 g/L), using different eluents

The process was repeated in three adsorption/desorption cycles and results are depicted

in Fig. 7. The adsorbed amount of Sb(V) was practically the same for the first two cycles but in the third cycle, the adsorption capacity of the moss peat decreased to 36 % of the initial capacity. The batch desorption studies also evaluate the strength of the interaction between Sb and moss peat. The amount of desorbed Sb, moderately increased from the first cycle to the second one, from 19 % to 34 %, respectively. In the third step, the desorption of loaded Sb(V) grew drastically, to 71 %.

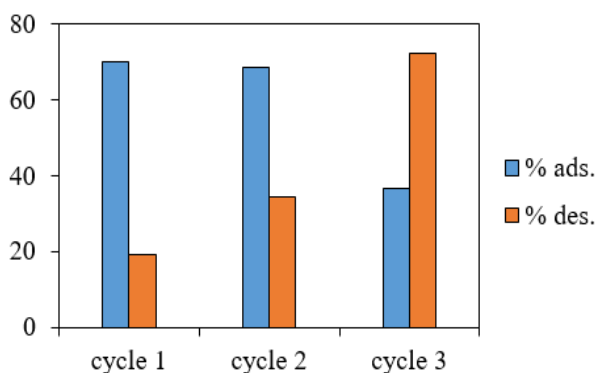


Fig. 7. Adsorbed and desorbed amounts, in repeated Sb(V) adsorption-desorption cycles, using *Sphagnum* moss peat

Iqbal et al. (2013) described a marginal reduction (less than 10 %) over seven repeated reuse cycles of the adsorption capacity of green bean husk, using HCl 0.1 M as eluent. Wu et al. (2012) used HCl 4.0 M as eluent and found a constant Sb(III) removal in the first four cycles on *Microcystis* biomass and reports approx. 20 % decrease only in the fifth cycle.

4. Conclusions

Sb(III) and Sb(V) biosorption from aqueous solutions was studied using *Sphagnum* moss peat. Infrared spectra showed the presence of carboxylic and hydroxyl groups, which were proposed to be involved in antimony uptake by surface complexation. Regarding the effect of pH, a moderate effect was visible for Sb(III) and no significant effect was recorded for Sb(V) biosorption.

Biosorption kinetics of both Sb(III) and Sb(V) were fast and well described by pseudo-second-order model. For both Sb(III) and Sb(V), Freundlich model shows a good fitting. The experimental adsorbed amount found for Sb(III) was around 3 mg/g and nearly 3.3 mg/g for Sb(V), at pH 2. Regeneration and reutilization of the moss peat with NaOH solution is possible, but limited to very few adsorption/desorption cycles, and is not encouraged.

Considering that the *Sphagnum* moss peat is a natural widespread material and requires a reduced number of operations for preparation, it can be considered a good sorbent; the good capture capacity revealed in this study and the weak influence of pH are positive arguments for a real utilisation of the *Sphagnum* moss peat for remediation of antimony-contaminated waters.

With consecutive regeneration, the sites on *Sphagnum* moss peat that become available to uptake Sb(V) will provide weaker interactions. It is probable that from cycle to cycle, the adsorption was established by weaker interactions and then the efficiency of desorption increased. The results of the desorption study are much more limited than others reported in literature.

References

- Aksu Z., (2001), Equilibrium and kinetic modelling of cadmium(II) biosorption by *C. vulgaris* in a batch system: effect of temperature, *Separation and Purification Technology*, **21**, 285-294.
- APHA, (1999), *Standard Methods for the Examination of Water and Wastewater*, 20th APHA/AWWA/WEF, American Public Health Association (APHA), Washington, DC.
- Balaban A.T., Banciu M., Pogany I., (1983), *Applications of Physical Methods in Organic Chemistry* (in Romanian), Scientific and Encyclopaedic Publishing House, Bucharest, Romania.
- Ben Issa N., Rajakovic-Ognjanovic V.N., Marinkovic A.D., Rajakovic L.V., (2011), Separation and determination of arsenic species in water by selective exchange and hybrid resins, *Analytica Chimica Acta*, **706**, 191-198.
- Ahmed M.B., Zhou L.J., Ngo H.H., Guo W., Thomaidis N.S., Xu J., (2017), Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: A critical review, *Journal of Hazardous Materials*, **323**, 274-298.
- Bulgariu L., Gavrilescu M., (2015), *Bioremediation of Heavy Metals by Microalgae*: In: *Handbook of Marine Microalgae. Biotechnology Advances*, Kim S.-K. (Ed.), Elsevier, 457-469.
- Carolin C.F., Kumar P.S., Saravanan A., Joshiba G.J., Naushad Mu., (2017), Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review, *Journal of Environmental Chemical Engineering*, **5**, 2782-2799.
- Filote C., Ungureanu G., Boaventura R., Santos S., Volf I., Botelho C., (2017), Green macroalgae from the Romanian coast of Black Sea: Physico-chemical characterization and future perspectives on their use as metal anions biosorbents, *Process Safety and Environmental Protection*, **108**, 34-43.
- Fu Z.Y., Wu F.C., Amarasiriwardena D., Mo C.L., Liu B.J., Zhu J., Deng Q.J., Liao H.D., (2010), Antimony, arsenic and mercury in the aquatic environment and fish in a large antimony mining area in Hunan, China, *Science of the Total Environment*, **408**, 3403-3410.
- Ho Y.S., Wase D.A.J., Forster C.F., (1996), Kinetic studies of competitive heavy metal adsorption by *Sphagnum* moss peat, *Environmental Technology*, **17**, 71-77.
- Iqbal M., Saeed A., Edyvean R.G.J., (2013), Bioremoval of antimony(III) from contaminated water using several plant wastes: Optimization of batch and dynamic flow conditions for sorption by green bean husk (*Vigna radiata*), *Chemical Engineering Journal*, **225**, 192-201.
- Jain C.K., Ali I., (2000), Arsenic: occurrence, toxicity and speciation techniques, *Water Research*, **34**, 4304-4312.
- Lagergren S., (1898), About the theory of so-called adsorption of soluble substances, *Kungliga Svenska Vetenskapsakademiens Handlingar*, **24**, 1-39.
- Larios R., Fernandez-Martinez R., Lehecho I., Rucandio I., (2012), A methodological approach to evaluate arsenic speciation and bioaccumulation in different plant

- species from two highly polluted mining areas, *Science of the Total Environment*, **414**, 600-607.
- Lavado R., Shi D., Schlenk D., (2012), Effects of salinity on the toxicity and biotransformation of l-selenomethionine in Japanese medaka (*Oryzias latipes*) embryos: Mechanisms of oxidative stress, *Aquatic Toxicology*, **108**, 18-22.
- Moța A.S., Prodan M., Ghicioi E., Nălboc I., Moldovan C., (2017), Heavy metals removal from mining drainage acid water by use of natural zeolites, *Environmental Engineering and Management Journal*, **16**, 1383-1388.
- Rashed M.N., Soltan M., Ahmed M.M., Abdou A.N.E., (2017), Removal of heavy metals from wastewater by chemically activated sewage sludge, *Environmental Engineering and Management Journal*, **16**, 1531-1542.
- Romao L., Lead J.P., Rocha J.C., Oliveira L.C., Rosa A.H., Mendonca A.G.R., Ribeiro A.S., (2007), Structure and properties of Brazilian Peat: analysis by spectroscopy and microscopy, *Journal of the Brazilian Chemical Society*, **18**, 711-720.
- Santos S., Ungureanu G., Boaventura R., Botelho C., (2015), Selenium contaminated waters: an overview of analytical methods, treatment options and recent advances in sorption methods, *Science of the Total Environment*, **521-522**, 246-260.
- Sun H.J., Rathinasabapathi B., Wu B., Luo J., Pu L.P., Ma L.Q., (2014), Arsenic and selenium toxicity and their interactive effects in humans, *Environment International*, **69**, 148-158.
- Tella M., Pokrovski G.S., (2008), Antimony(V) complexing with O-bearing organic ligands in aqueous solution: an X-ray absorption fine structure spectroscopy and potentiometric study, *Mineralogical Magazine*, **72**, 205-209.
- Tella M., Pokrovski G.S., (2009), Antimony(III) complexing with O-bearing organic ligands in aqueous solution: An X-ray absorption fine structure spectroscopy and solubility study, *Geochimica Et Cosmochimica Acta*, **73**, 268-290.
- Tella M., Pokrovski G.S., (2012), Stability and structure of pentavalent antimony complexes with aqueous organic ligands, *Chemical Geology*, **292-293**, 57-68.
- Thiry C., Ruttens A., De Temmerman L., Schneider Y.J., Pussemier L., (2012), Current knowledge in species-related bioavailability of selenium in food, *Food Chemistry*, **130**, 767-784.
- Tuzen M., Sari A., (2010), Biosorption of selenium from aqueous solution by green algae (*Cladophora hutchinsiae*) biomass: equilibrium, thermodynamic and kinetic studies, *Chemical Engineering Journal*, **158**, 200-206.
- Uluozlu O.D., Sari A., Tuzen M., (2010), Biosorption of antimony from aqueous solution by lichen (*Physcia tribacia*) biomass, *Chemical Engineering Journal*, **163**, 382-388.
- Ungureanu G., Santos S.C.R., Volf I., Boaventura R.A.R., Botelho C.M.S., (2017), Biosorption of antimony oxyanions by brown seaweeds: Batch and column studies, *Journal of Environmental Chemical Engineering*, **5**, 3463-3471
- Ungureanu G., Filote C., Santos S.C.R., Boaventura R.A.R., Volf I., Botelho C.M.S., (2016), Antimony oxyanions uptake by green marine macroalgae, *Journal of Environmental Chemical Engineering*, **4**, 3441-3450.
- Ungureanu G., Santos S., Boaventura R., Botelho C., (2015a), Biosorption of antimony by brown algae *S. Muticum* and *A. Nodosum*, *Environmental Engineering and Management Journal*, **14**, 455-463.
- Ungureanu G., Santos S., Boaventura R., Botelho C., (2015b), Arsenic and antimony in water and wastewater: overview of removal techniques with special reference to latest advances in adsorption, *Journal of Environmental Management*, **151**, 326-342.
- Vijayaraghavan K., Balasubramanian R., (2011), Antimonite removal using marine algal species, *Industrial and Engineering Chemistry Research*, **50**, 9864-9869.
- Vijayaraghavan K., Balasubramanian R., (2015), Is biosorption suitable for decontamination of metal-bearing wastewaters? A critical review on the state-of-the-art of biosorption processes and future directions, *Journal of Environmental Management*, **160**, 283-296.
- Wu F.C., Sun F.H., Wu S., Yan Y.B., Xing B.S., (2012), Removal of antimony(III) from aqueous solution by freshwater cyanobacteria *Microcystis* biomass, *Chemical Engineering Journal*, **183**, 172-179.
- Xu W., Wang H.J., Liu R.P., Zhao X., Qu J.H., (2011), The mechanism of antimony(III) removal and its reactions on the surfaces of Fe-Mn Binary Oxide, *Journal of Colloid and Interface Science*, **363**, 320-326.