



"Gheorghe Asachi" Technical University of Iasi, Romania



BIOSORPTION OF ANTIMONY BY BROWN ALGAE

S. muticum AND *A. nodosum*

Gabriela Ungureanu, Sílvia Santos*, Rui Boaventura, Cidália Botelho

LSRE – Laboratory of Separation and Reaction Engineering, Associate Laboratory LSRE/LCM, Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

Abstract

Environmental contamination by antimony has been described as a critical issue in many articles. In this study, the Sb(III) removal by two brown algae, *Sargassum muticum* and *Aschophylum nodosum*, has been tested. Algae were collected in Viana do Castelo beach (Portugal). Preliminary tests were carried out and, based on the results, *Sargassum muticum* was chosen for subsequent experiments. Kinetic data were described by pseudo second order model. After about four hours contact time the equilibrium was achieved. A slight effect of pH was observed in the removal efficiency of Sb by *S. muticum*. Adsorption equilibrium isotherm was determined for pH 5. Langmuir model predicted a maximum adsorption capacity of 5.4 ± 0.8 mg/g. The present study revealed that the alga *S. muticum* can be used as a low-cost adsorbent for antimony removal from aqueous solution.

Key words: algae, antimony, biosorption, low cost adsorbents, oxyanions

Received: November, 2014; Revised final: February, 2015; Accepted: February, 2015

1. Introduction

Antimony is a natural occurring metalloid, but can also be introduced in environment by anthropogenic sources since it is used in brake linings, in semiconductor components, flame retardants, as catalyst in plastics, additive in glassware and ceramics and in ammunition.

In aqueous solution, antimony is present as oxyanion and speciation is defined by pH and pE conditions. Antimony can exist in four oxidation states, Sb(V), Sb(III), Sb(0) and Sb(-III), but in the environment it is usually present in the oxidation state (+5), antimonate, in aerobic environments, and (+3), antimonite, in anaerobic environments (Wilson et al., 2010). Sb(III) is considered ten times more toxic than Sb(V) (Bencze, 1994; Stemmer, 1976). The guideline of the World Health Organization is a maximum concentration of 5 µg/L antimony in water for human consumption (WHO, 2011). The most common form of a body being exposed to contamination by antimony is through the ingestion

of food and water. Antimony is classified as a toxic pollutant, potentially carcinogenic to humans and therefore considered a pollutant of priority interest by entities such as the Environmental Protection Agency of the United States (USEPA, 1979) and the European Union (UE, 1976).

References for purification of water containing antimony, especially for drinking water, are quite limited. The most common studied methods for antimony removal are coagulation/flocculation (Guo et al., 2009; Wu et al., 2010), membrane processes (Kang et al., 2000; Saito et al., 2004), electroprocesses (Koparal et al., 2004; Zhu et al., 2011) and adsorption (Sarı et al., 2010; Shan et al., 2014; Xi et al., 2013). Adsorption has been viewed as a simple and relative low-cost process, suitable for removing low levels of contaminants and applicable for point-of-use treatment. A broad range of adsorbents comprising metal oxides, hydroxides and minerals (Li et al., 2012; Xu et al., 2011), sorbents based on residues and waste materials (Biswas et al., 2009) and biomaterials (Sun et al., 2011;

* Author to whom all correspondence should be addressed: e-mail: scrs@fe.up.pt; Phone: (351) 22 508 1885; Fax: (351) 22 508 1674

Vijayaraghavan and Balasubramanian, 2011) have been studied for antimony removal from water. A good adsorbent should have a low cost while providing high removal efficiency. Biosorption has been increasingly studied in recent years because this technique has the great advantage to have a lower cost compared to conventional methods. The biosorbents capacity improvement has been evaluated by surface modification treatments such as protonation or iron pre-treatment (Davis et al., 2003).

Algae are divided into three broad categories: brown algae (Phaeophyta), red algae (Rhodophyta) and green algae (Chlorophyta) (Dunn, 1998). Brown algae are classified into about 265 genera of more than 1500 species are all multicellular, present chloroplasts (golden brown) containing chlorophyll a and c, and β -carotenoid fucoxanthin (pigment), which masks the green color of chlorophyll. Polysaccharides represent more than 65% of the cellular constituents of the algae and alginic acid is the major polysaccharide from brown algae (Davis et al., 2003).

Algal biomass is an available natural material with a very low cost. Algae, especially the brown type, have been extensively used as biosorbents for heavy metals, and several studies have demonstrated the good adsorption ability for metal cations (Cazón et al., 2012; Dittert et al., 2013; Freitas et al., 2008; Kleinubing et al., 2011; Lupea et al., 2012; Sheng et al., 2004). However, its use as biosorbent for metal or metalloid anions is scarcely studied (Vijayaraghavan and Balasubramanian, 2011). In this research, the antimony removal by marine brown macroalgae *Sargassum muticum* and *Aschophyllum nodosum*, has been tested. *Sargassum muticum* belongs to domain Eukaryota, kingdom Chromalveolata, phylum Heterokontophyta, class Phaeophyceae, order Fucales, family Sargassaceae, and genus *Sargassum*. *Aschophyllum nodosum* belong to kingdom Chromalveolata, phylum Heterokontophyta, class Phaeophyceae, order Fucales, family Fucaceae and genus *Aschophyllum*. Araujo et al. (2006) characterized the existing macroalgae communities in the pools in the intertidal zone and rocks, over 60 km from the northwest coast of Portugal. The authors found that the *Sargassum muticum* is located preferably in the pools in the intertidal zone (98.8%) and *Aschophyllum nodosum* is almost entirely on the rocks (99.1%). Chemical characterization of biosorbents under study was performed. The algae were previously tested in virgin form and pre-treated with nitric acid. Equilibrium and kinetic studies were performed in batch, testing the effect of pH and concentration.

2. Experimental methods

2.1. Chemicals

Antimony standard solutions were prepared from a standard solution 1000 mg/L Sb(III) solution (*CarloErba*). The pH was adjusted to the required

values using HNO₃ and NaOH aqueous solutions, prepared from HNO₃ 65% PA (*Sigma Aldrich*) and NaOH pellets 99% purity (*Merck*). All the solutions were prepared in ultrapure water produced by *Millipore system (Direct-Q model)*.

2.2. Glassware preparation

All the glassware and plastic material used in experimental tests were washed by soaking for 24 hours in HNO₃ 20% solution, rinsed with distilled water and dried in the oven.

2.3. Biomass preparation

The two brown seaweeds, *Sargassum muticum* and *Aschophyllum nodosum*, were collected in Viana do Castelo beach (Portugal) in February of 2013. The seaweeds were firstly washed with tap water and following with distilled water until achieving a low conductivity. The seaweeds were air-dried during 2 days, and then dried overnight in the oven at 60°C, milled in 5 mm granulometry and stored in a desiccator. In this paper these seaweeds, without further treatment, will be named as virgin algae: virgin *S. muticum* (VM) and virgin *A. nodosum* (VN).

It was also decided to perform a protonation of the seaweeds. The main purpose of this chemical treatment is to facilitate the contact of the functional groups responsible for metal binding, creating new groups and reinforce biomass capacity. Untreated biomass generally contains light metal ions (potassium, sodium, calcium, magnesium). The protons in the strong acid treatment displace these light metals from the binding sites (Davis et al., 2003). However, the use of pretreatments is economically unadvisable in cases where the increase in process efficiency is not significant.

The virgin seaweed (8 g/L) was contacted for 6h with 1M solution of HNO₃, under agitation (150-200 rpm). After contact, the alga was washed with distilled water in several cycles until the wash water achieved a pH about 4 – 4.5. This protonated alga was also dried in the oven at 60°C and stored in desiccator. In this paper, the acid treated algae were designated as protonated *S. muticum* (PM) and protonated *A. nodosum* (PN).

2.4. Analytical procedures

Atomic adsorption spectrometry (AAS; spectrophotometer *GBC 932 Plus*) was the technique used to determinate the concentration of antimony in aqueous solution. Analyses were done using the following technical parameters: air/acetylene flame, 10mA lamp current, 217.6 nm wavelength, 2 nm slit, deuterium background correction, with triplicate readings and a detection limit of 0.4 mg/L. Before AAS analysis the samples were filtered using cellulose acetate membrane filters (45 μ m porosity).

Total antimony concentrations in algae were also measured. Samples were analyzed by graphite

furnace (*GBC SenAA Dual*) due to the very low levels of antimony detected. The analysis was performed with 217.6 nm wavelength, slit 0.2 nm, 10 mA lamp current and background correction. The detection limit was 3 µg/L.

2.5. Chemical characterization

Volatile matter was analyzed by calcination at 550°C for 2 hours (Method no. 2540E; APHA, 1999). Metals contents (Fe, Mn, Al, K, Mg, Na, Ca, Sb) present in virgin and protonated algae were determined by digesting 1.5 g of biomass in glass tubes at 150°C for 2h with 5.0 ml of distilled water, 12 ml of HCl (*Merck*) and 4ml of HNO₃ (*Merck*). After digestion, solutions were filtered through cellulose acetate membrane filters (*SantoriusStedim*). Samples were digested in duplicate and a blank digestion was also performed.

Metal concentrations were determined by flame AAS and antimony concentration by graphite furnace.

2.6. FTIR - Fourier transform infrared analysis

Infrared spectroscopy (*Shimadzu FTIR IRAffinity*) was performed in order to identify the predominant functional groups on the biosorbent surface. The algae were ground and used in solid form using diffuse reflectance accessory. Spectra were registered between 4000 and 400 cm⁻¹.

2.7. Screening adsorption tests

These simple adsorption tests were conducted to evaluate the adsorption ability of the different seaweeds (in virgin and treated forms). Adsorption tests were performed in Erlenmeyer flasks containing 50 mL of 10 mg Sb/L solution, at different pH (2,3, 4 and 5), and 100 mg of VM, VN, PM and PN, accurately weighed. The suspensions were stirred (*PlacaMulti 15 Stirrer, Velp*), at 200 rpm, under room temperature (23°C±1).

pH was monitored regularly and readjusted if necessary, in order to maintain a constant value (±0.5). After a 6h contact time, samples were filtered and concentrations of antimony in liquid phase analyzed by AAS. The amount of antimony adsorbed in the equilibrium (q , mg/g) was calculated by a mass balance equation (Eq. 1):

$$q = \frac{C_0 - C}{C_s} \quad (1)$$

where C_0 is the initial Sb concentration in the liquid phase (mg/L), C is the concentration after adsorption (mg/L) and C_s is the sorbent dosage (g/L).

2.8. Adsorption kinetic studies

Based on the results of screening tests, the algae VM was selected for further equilibrium and kinetics studies. Adsorption kinetic studies were done

in Erlenmeyer flasks containing 50 mL of 10 mg Sb/L solution in contact with 2 g/L of VM, under magnetic agitation (*PlacaMulti 15 Stirrer, Velp*, at 200 rpm) and room temperature (23°C±1). The stirring rate values considered sufficient to ensure that all active centers of biomass are available for metal removal, ranges between 150 rpm (Martins et al, 2006) and 300 rpm (Yang and Volesky, 1996). It is considered therefore that the effect of external diffusion in the film can be assumed as negligible.

The dynamic kinetic study was conducted for various constant pH values (2; 3; 4 and 5), adjusted on the beginning of the test and corrected when necessary. The content of each Erlenmeyer flask was let in agitation for previously established time intervals in order to obtain the Sb concentration decay at different contact times. The quantity of antimony removed from the solutions by algae material was determined by the difference between the initial concentration of antimony on that sample and the final concentration in the same sample, measured by AAS and calculated with Eq. (1).

2.9. Adsorption equilibrium studies

Sorption isotherms were performed at pH 5 and room temperature (23°C±1). The initial antimony concentration ranged between 2-20 mg/L. Equilibrium studies were performed in Erlenmeyer flasks. The volume of antimony solution in each flask was 50 mL and the biomass concentration 2 g/L (accurately weighed for each sample). The contact between the sorbent and antimony solution was under constant magnetic stirring (200 rpm). After the equilibrium point reached (about 4 hours), the residual antimony concentration (C) was determined by AAS and the amount of Sb adsorbed per algebra mass unity (q) calculated by Eq. (1).

3. Results and discussion

3.1. Chemical characterization

The values obtained for the volatile matter concentrations were calculated based on the dry weight of samples. Table 1 presents the results of volatile matter contents for algae *Sargassum muticum* and *Aschophylum nodosum*, in virgin and protonated forms, expressed in percentage of loss of weight.

Table 2 presents metallic elements content in virgin and protonated algae. Predominant elements are sodium, potassium, calcium and magnesium, which are in fact the predominant elements in the constitution of seawater. After the acid treatment, the concentration of all components decreased by dissolution in the aqueous phase. The values obtained for antimony concentration in seaweeds are negligible.

3.2. FTIR – Fourier transform infrared analysis

The Infrared Spectroscopy by Fourier Transform allows identifying functional groups

present in the biosorbents surface that can help to evaluate the adsorption mechanism. The functional groups are identified by the presence of bands at certain characteristic frequencies. Fig. 1 shows the FTIR spectra of both the virgin biosorbents.

Table 3 summarizes the dominants stretching frequencies observed in seaweeds. The broad band between 3000-3750 cm^{-1} confirms the presence of the O-H group of glucose, constituent of the cell wall of a vegetal cell, and the N-H groups of proteins (Deng et al., 2007). The absorption band at 3000-2800 cm^{-1} may be due to C-H distention of aliphatic chains, asymmetric and symmetric respectively (Murphy et al, 2007; Sheng et al., 2004). The small band detected at about 1700-1680 cm^{-1} and those at 1550 and 1460 cm^{-1} correspond to the distention C=O of chelate and to the distention C=O of carboxyl groups (Fourest and Volesky, 1996). The band at 1180 cm^{-1} may be due to C-N distention in proteins (Park et al., 2005). The 830 cm^{-1} band suggests the presence of S=O bonds (Fourest and Volesky, 1996).

The IR spectrum indicates that several types of functional groups are present in the structure of VM and VN and these groups can interact with metal ions from aqueous solutions during the sorption process. Therefore, metal ions can be bound by specific chemical interactions.

3.3. Screening Tests results

Preliminary tests were performed with VM, PM, VN and PN for pH 2, 3, 4 and 5. Fig. 2 shows the results of these preliminary tests.

Antimony concentration in the solid phase, q (mg/g), evaluates the capacity of the algae to adsorb antimony from aqueous solutions. The results of screening tests suggest that the best biosorbents for antimony are VM and PM at pH 4 and 5. A slight increase in the adsorbed amount was observed with the increase in pH from 2 to 4-5, especially for VM and PN algae.

Table 1. Percentage of volatile matter in studied algae

<i>Sargassum muticum</i>	VM	74 %
	PM	98 %
<i>Aschophylum nodosum</i>	VN	79 %
	PN	99 %

Table 2. Metals content in virgin and protonated algae

	Fe (mg/g)	Mn (mg/g)	Al (mg/g)	K (mg/g)	Mg (mg/g)	Na (mg/g)	Ca (mg/g)	Sb ($\mu\text{g/g}$)
VM	0.24	<0.05	<0.05	83	11	14	12	< 0.7
PM	0.15	<0.05	<0.05	0.27	0.28	0.55	1.10	< 0.7
VN	0.09	<0.05	0.06	25	10	25	16	< 0.7
PN	0.21	<0.05	0.09	0.76	0.48	0.47	0.21	< 0.7

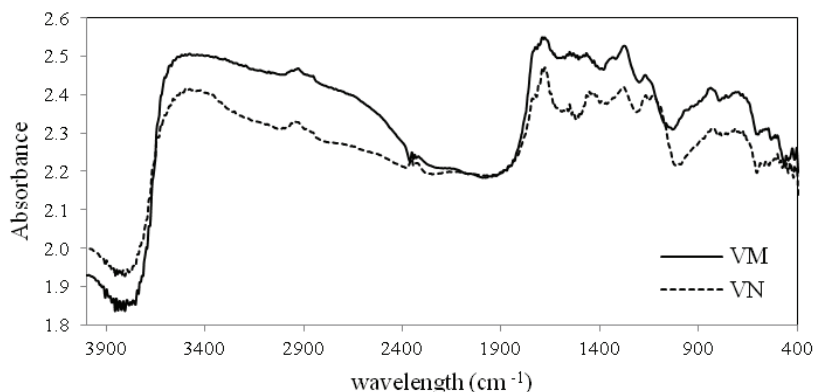


Fig. 1. FTIR spectra of VM and VN

Table 3. Dominants stretching frequencies in seaweeds FTIR spectra

Band	Symbol of functional groups	Name of functional groups
3750 - 3000	O-H	Hydroxyl
3000 - 2800	C-H	Methyl
1680 - 1700	C=O	Carboxyl
1550	C=O	Carboxyl
1460	C=O	Carboxyl
1290	S=O	Sulfate
1180	C-N / C-O	Ether
830	S=O	Sulfate

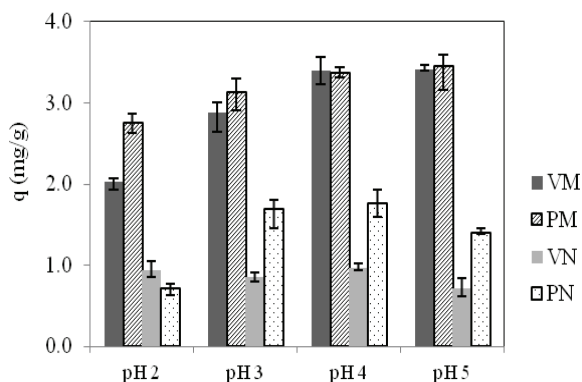


Fig. 2. Adsorbed amount of Antimony by *VM*, *PM*, *VN* and *PN* using 10mg/L Sb solution, 2g/L algae concentration and different pHs

This behavior can be explained considering the charge of both adsorbent and adsorbate in different pH conditions. According to speciation diagrams available in literature (Filella et al., 2002), Sb(III) occurs in water under the form of $\text{Sb}(\text{OH})_2^+$ (extreme acidic pH), H_3SbO_3 or $\text{Sb}(\text{OH})_3$ (pH 2-10) and H_2SbO_3^- or $\text{Sb}(\text{OH})_4^-$ (strong alkaline pH). On the other side, the charge of the adsorbent tends to be more positive for lower pH values. At extreme acidic pH values, alga and Sb appeared as positively charged and adsorption was then limited by repulsion. In the present study, pH values higher than 5 were not studied, since it was expected that the majority of the wastewaters contaminated with antimony (from mining, for example) are acidic.

VM and *PN* algae showed the most interesting results with similar adsorbed amounts at pH 4-5. However, *PN* performance at pH 2 was significantly worse than *VM*. *PN* also requires a pre-treatment step (with strong acid) which implies higher costs. *VM* was then selected, instead of *PM*, for kinetic and equilibrium studies.

3.4. Adsorption kinetic 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 behavior. Experimental results obtained in the kinetic study of Sb(III) biosorption by *VM* seaweed are presented in Fig. 3.

The kinetic curves can be divided into two phases, a first phase fast enough (0 - 30 minutes) and a second slower phase (30-480 minutes). More than 35% of the biosorption equilibrium capacity occurs in the first 15 min. In 30 minutes of biosorption, more than 50% of the equilibrium capacity was achieved. The equilibrium time, for the different systems is about 4h, since there were no further significant changes on the biosorbed amount of Sb. Several authors have reported fast kinetics for antimonite removal, with contact times lower than

few hours (Uluozlu et al., 2010; Vijayaraghavan and Balasubramanian, 2011; Wu et al., 2012).

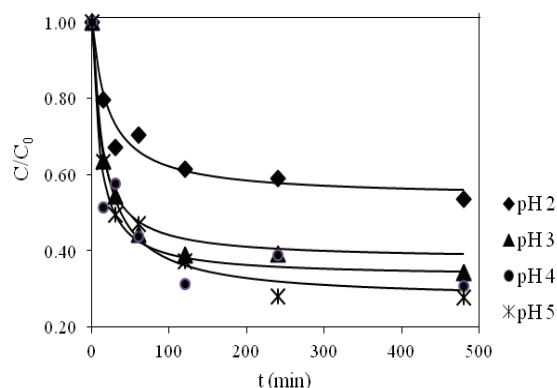


Fig. 3. Kinetics for Sb(III) biosorption on *VM* at different pH (initial concentration 10mg/L Sb solution, alga dosage 2g/L and 23°C): experimental data and pseudo-second order model

In fact, the fast biosorption kinetics of metals present a very significant practical importance, allowing the use of smaller columns with continuous operation, in an efficient and economical way (Aksu, 2001).

The most commonly used models to describe adsorption kinetics are the pseudo 1st order and pseudo 2nd order models. The pseudo 1st order model or Lagergren (1898) considers that the occupancy rate of the active centers by the metal in aqueous solution is proportional to the number of available centers. It also assumes that the surface is homogeneous and active centers have the same affinity for the metal ion. Pseudo-1st order model is expressed by Eq. (2), where q (mg g^{-1}) is the biosorption capacity for a determined contact time t (min), q_e (mg g^{-1}) the biosorption capacity in equilibrium and k_1 (min^{-1}) is the kinetic constant.

$$q = q_e(1 - e^{-k_1 t}) \quad (2)$$

In accordance, the initial uptake rate, h_1 ($\text{mg g}^{-1} \text{min}^{-1}$) is given by Eq. (3).

$$h_1 = k_1 q_e \quad (3)$$

The pseudo 2nd order model (Ho et al., 1996) is based on the sorption capacity of the solid phase and assumes a homogeneous surface and metal binds to two active centers. Pseudo 2nd model is represented by the Eq. (4), where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the kinetic constant of second order.

$$q = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (4)$$

The initial biosorption rate, h_2 ($\text{mg g}^{-1} \text{min}^{-1}$) is determined by Eq. (5):

$$h_2 = k_2 q_e^2 \tag{5}$$

Pseudo 1st and pseudo 2nd order models were fitted to experimental kinetic data by non-linear regression using *CurveExpert* software. The obtained parameters for the models are presented in Table 4. Fig. 4 presents the modeled curves for the experimental data obtained for pH 5.

It was found that the models of pseudo 1st order and pseudo 2nd order adequately represent the experimental results, with coefficients of determination values (R^2) exceeding 0.9. Pseudo-second order model presented however the best determination coefficients. It also predicted q_e values closer to the experimental ones. Fig. 3 presents modeled curves (pseudo-second order model) for the different pH conditions data.

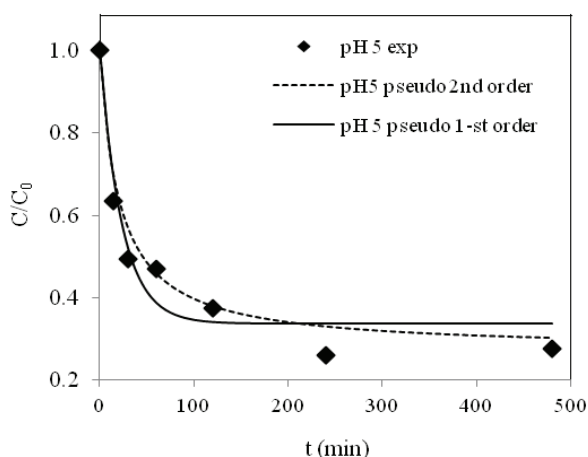


Fig. 4. Kinetics for Sb biosorption on VM at pH 5 (initial concentration: 10mg/L Sb solution; alga dosage: 2g/L alga and 23°C): experimental data and modeling

It is observed that as the pH increased from 2 to 4, maximum biosorbed amount also increased. Similar values (3.3 ± 0.5 mg/g and 3.5 ± 0.1 mg/g) were obtained at pH 4 and 5. This is in agreement with the results obtained in the screening tests. In the present study, pH above 5 was not tested, since most important effluents containing antimony (mine effluents) present pH typically in acidic range. Although different maximum adsorbed amounts were achieved in different pH conditions, kinetic constants are relatively close.

Considering the pseudo-second order model, initial biosorption rates (evaluated by Eq. 5) are 0.095, 0.25, 0.33 and 0.25 $\text{mg g}^{-1} \text{min}^{-1}$, at pH 2, 3, 4 and 5, respectively. However, considering the

corresponding 95% confidence interval, the initial biosorption rates do not vary significantly with pH, lying in the range 0.06-0.8 $\text{mg g}^{-1} \text{min}^{-1}$.

3.5. Adsorption equilibrium studies

Equilibrium isotherms represent the relation between the concentration of a solute in the liquid phase and the equilibrium concentration on the biosorbent particles, at a given temperature. The isotherms give information about the affinity of adsorbent to the adsorbate and the maximum biosorption capacity.

The biosorption isotherm for Sb(III) adsorption by VM seaweed is presented in Fig. 5. Results were obtained at 23°C, using an adsorbent dosage of 2 g/L and varying the initial concentration of antimony from 2 to 20 mg/L. Langmuir and Freundlich models were adjusted to experimental data. The Langmuir model (1918) assumes: the active centers are uniformly distributed over the surface of the adsorbate, with constant adsorption energy and the same affinity; a monolayer coverage of adsorbed species; no interactions between the adsorbed species in adjacent sites. The expression of Langmuir model is given by the Eq. (6).

$$q_e = \frac{K_L Q_{max} C_e}{1 + K_L C_e} \tag{6}$$

where q_e (mg g^{-1}) the equilibrium concentration of solute in the solid phase, C_e (mg L^{-1}) the equilibrium concentration of solute in the liquid phase, Q_{max} (mg g^{-1}) the maximum biosorption capacity and K_L (mg L^{-1}) Langmuir constant.

According to Hall et al. (1966), Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor (R_L), defined by the following Eq. (7).

$$R_L = \frac{1}{1 + K_L C_0} \tag{7}$$

Therefore, it is possible to predict, from the profile of the isotherm, if the biosorption system is favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$).

The Freundlich isotherm (1906) is an empirical expression given by Eq. (8). This model assumes a heterogeneous sorption surface with different energy active centers.

Table 4. Parameters for kinetic models (value \pm interval for 95% confidence)

	Pseudo first order			Pseudo second order		
	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2
pH 2	1.79 \pm 0.01	0.04 \pm 0.01	0.92	2.08 \pm 0.09	0.022 \pm 0.006	0.96
pH 3	2.65 \pm 0.08	0.056 \pm 0.008	0.98	2.85 \pm 0.03	0.031 \pm 0.002	0.99
pH 4	3.1 \pm 0.6	0.06 \pm 0.05	0.89	3.3 \pm 0.6	0.03 \pm 0.02	0.93
pH 5	3.2 \pm 0.4	0.04 \pm 0.02	0.94	3.5 \pm 0.1	0.021 \pm 0.003	0.98

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

where K_F ($(\text{mg g}^{-1})(\text{L m}^{-1})^{1/n_F}$) 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).

Model fitting to Eqs. (6) and (8) was performed by non-linear regression using *CurveExpert* software and the model parameters are presented in Table 5.

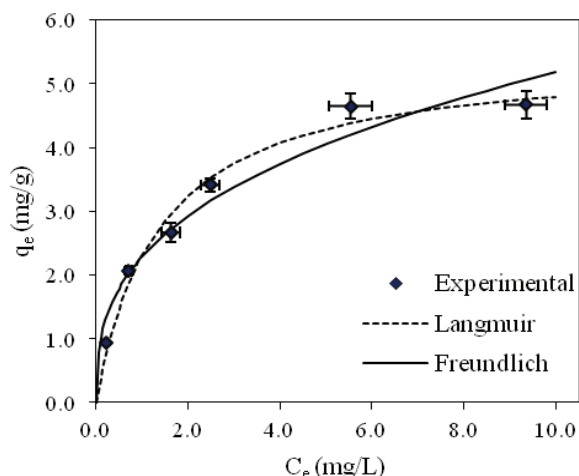


Fig. 5. Equilibrium isotherm for Sb biosorption on VM at pH 5, 2g/L alga and 23°C: experimental data and modeling

Table 5. Parameters for equilibrium models (value ± interval for 95% confidence)

Langmuir	Freundlich
$Q_{max} = 5.5 \pm 0.8 \text{ mg/g}$	$1/n_F = 0.36 \pm 0.04$
$K_L = 0.7 \pm 0.3 \text{ L/mg}$	$K_F = 2.3 \pm 0.1 \text{ mg g}^{-1} (\text{mg L}^{-1})^{-1/n}$
$R^2 = 0.99$	$R^2 = 0.97$

Both models represent quite well the experimental data, with values for the determination coefficients higher than 0.97. Even so, the Langmuir model best describes equilibrium data, with a correlation coefficient of 0.99, and predicted a maximum biosorption capacity close to that obtained experimentally. Also, the separation factor R_L calculated by Eq. (7), and using the highest initial Sb concentration is 0.07, a value between 0 and 1, which indicates a favorable process.

The Langmuir model revealed a maximum biosorption capacity of 5.5 mg/g for the VM seaweed. Wu et al. (2012) used *Microcystis* biomass and obtained an adsorption capacity of 4.88 mg/g for Sb(III), at pH 4. This value is quite similar to the one reported in present study, but it was obtained using much higher initial concentration ranges (0 to 400 mg/L). Cyanobacteria *Synechocystis sp.* was tested by Mu (2011) and a maximum biosorption capacity of 4.68 mg/g, using a initial concentration range from 5 to 100 mg/L Sb(III) was reported. Other authors presented higher adsorption capacities, such as 81.1 mg/g, for lichen, *PhysciaTribacia* (Uluozlu et al.,

2010), 14.9 mg/g (at pH 6) for *Sargassum sp.* (brown alga) (Vijayaraghavan and Balasubramanian, 2011). Much higher adsorption capacities have been obtained by binary metal oxides, for example 214 mg/g, at pH 3, for a Fe-Mn oxide (Xu et al., 2011); this kind of material requires however synthesis and then costs of preparation.

4. Conclusions

Algae are effective biosorbents for the removal of antimony(III) from aqueous solutions. The maximum adsorption capacity of the *Sargassum muticum* is 5.5 mg/g, at pH 5 and 23 °C. Equilibrium data was adequately described by both Langmuir and Freundlich models. The biosorption equilibrium was reached in approximately 4 hours.

The pseudo-second order kinetic model reasonably described the biosorption kinetics. It is important to note that this study was conducted using a biosorbent found in abundance in nature that requires no preparation. The study was conducted in a range of Sb concentration found in typical conditions in liquid effluents contaminated with antimony.

Acknowledgements

This work was partially supported by project Pest-C/EQB/LA0020/2013 financed by FCT and FEDER through COMPETE, and by QREN, ON2 and FEDER. G. Ungureanu acknowledges her PhD scholarship (SFRH/BD/77471/2011) by FCT. S. Santos acknowledges her postdoctoral scholarship by ON2 (NORTE-07-0124-FEDER-000008 RL1-P3).

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, APHA/AWWA/WEF, American Public Health Association (APHA), 20th Ed., Washington, DC.
- Araujo R., Sousa-Pinto I., Barbara I., Quintino V., (2006), Macroalgal communities of intertidal rock pools in the northwest coast of Portugal, *Acta Oecologica*, **30**, 192-202.
- Benze K., (1994), *Antimony. Handbook on Metals*, In: *Clinical and Analytical Chemistry*, Seiler H.G., Sigel A., Sigel H. (Eds.), New York, Marcel Dekker, 227-236.
- Biswas B.K., Inoue J., Kawakita H., Ohto K., Inoue K., (2009), Effective removal and recovery of antimony using metal-loaded saponified orange waste, *Journal of Hazardous Materials*, **172**, 721-728.
- Cazón J.P.H., Benítez L., Donati E., Viera M., (2012), Biosorption of chromium(III) by two brown algae *Macrocyctispyrifera* and *Undariapinnatifida*: equilibrium and kinetic study, *Engineering in Life Sciences*, **12**, 95-103.
- CEC, (1976), Council Directive 76/substances discharged into aquatic environment of the community, Council

- of the European Communities, *Official Journal, L*, **129**, 23–29.
- Davis A.T., Voleskya B., Mucci A., (2003), A review of the biochemistry of heavy metal biosorption by brown algae, *Water Research*, **37**, 4311–4330.
- Deng L., Su Y., Su H., Wang X., Zhu X., (2007), Sorption and desorption of lead (II) from wastewater by green algae *Cladophora fascicularis*, *Journal of Hazardous Materials*, **143**, 220-225.
- Dittert I., Vilar V., Silva E., Souza S., Souza A., Botelho C., Boaventura R., (2013), Turning *Laminaria digitata* Seaweed into a Resource for Sustainable and Ecological Removal of Trivalent Chromium Ions from Aqueous Solutions, *Clean Technologies and Environmental Policy*, **15**, 955-965.
- Dunn C.E., (1998), *Seaweeds as Hyperaccumulators*. In: *Plants that Hyperaccumulate Heavy Metals. Their Role in Phytoremediation*, Microbiology, Archaeology, Mineral Exploration and Phytomining, Brooks R.R. (Ed.), CAB International, New York, 119-125.
- Filella M., Belzile N., Chen Y.W., (2002), Antimony in the environment: a review focused on natural waters I. Occurrence, *Earth-Science Reviews*, **57**, 125-176.
- Fourest E., Volesky B., (1996), Contribution of sulfonate groups and alginate to heavy metal biosorption by the dry biomass of *Sargassum fluitans*, *Environmental Science Technology*, **30**, 277-282.
- Freitas O.M.M., Martins R.J.E., Delerue-Matos C.M., Boaventura R.A.R., (2008), Removal of Cd(II), Zn(II) and Pb(II) from aqueous solutions by brown marine macro algae: kinetic modeling, *Journal of Hazardous Materials*, **153**, 493–501.
- Guo X.J., Wu Z.J., He M.C., (2009), Removal of antimony(V) and antimony(III) from drinking water by coagulation-flocculation-sedimentation (CFS), *Water Research*, **43**, 4327-4335
- Hall K.R., Eagleton L.C., Acrivos A.E., Vemeulen T., (1966), Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions, *Industrial and Engineering Chemistry Fundamentals*, **5**, 212-223.
- 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.
- Kang M., Kawasaki M., Tamada S., Kamei T., Magara Y., (2000), Effect of pH on the removal of arsenic and antimony using reverse osmosis membranes, *Desalination*, **131**, 293-298.
- Kleinubing S.J., Silva E.A., Silva M.G., Guibal E., (2011), Equilibrium of Cu(II) and Ni(II) biosorption by marine alga *Sargassum filipendula* in a dynamic system: competitiveness and selectivity, *Bioresource Technology*, **102**, 4610–4617.
- Koparal A.S., Ozgur R., Ogutveren U.B., Bergmann H., (2004), Antimony removal from model acid solutions by electrodeposition, *Separation and Purification Technology*, **37**, 107-116.
- Lagergren S., (1898), About the theory of so-called adsorption of soluble substances, *Kungliga Svenska Vetenskapsakademiens Handlingar*, **24**, 1-39.
- Langmuir I., (1918), The adsorption of gases on plane surfaces of glass, mica and platinum, *Journal American Chemical Society*, **40**, 1361-1403.
- Li X., Dou X., Li J., (2012), Antimony(V) removal from water by iron-zirconium bimetal oxide: performance and mechanism, *Journal of Environmental Sciences (China)*, **24**, 1197-203.
- Lupea M., Bulgariu L., Macoveanu M., (2012), Biosorption of Cd(II) from aqueous solution on marine green algae biomass, *Environmental Engineering and Management Journal*, **11**, 607-615.
- Martins B.L., Cruz C.C.V., Luna A.S., Henriques C.A., (2006), Sorption and desorption of Pb²⁺ ions by dead *Sargassum* sp. Biomass, *Biochemical Engineering Journal*, **27**, 310-314.
- Murphy V., Hughes H., McLoughlin P., (2007), Cu(II) binding by dried biomass of red, green and brown macroalgae, *Water Research*, **41**, 731-740.
- Park D., Yun Y.S., Park J.M., (2005), Studies on hexavalent chromium biosorption by chemically-treated biomass of *Ecklonia* sp., *Chemosphere*, **60**, 1356-1364.
- Saito T., Tsuneda S., Hirata A., Nishiyama S., Saito K., Saito K., Sugita K., Uezu K., Tamada M., Sugo T., (2004), Removal of antimony(III) using polyol-ligand-containing porous hollow-fiber membranes, *Separation Science and Technology*, **39**, 3011-3022.
- Sari A., Citak D., Tuzen M., (2010), Equilibrium, thermodynamic and kinetic studies on adsorption of Sb(III) from aqueous solution using low-cost natural diatomite, *Chemical Engineering Journal*, **162** 521–527.
- Shan C., Ma Z.Y., Tong M.P., (2014), Efficient removal of trace antimony(III) through adsorption by hematite modified magnetic nanoparticles, *Journal of Hazardous Materials*, **268**, 229-236.
- Sheng P.X., Ting Y.P., Chen J.P., Hong L., (2004), Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms, *Journal of Colloid and Interface Science*, **275**, 131–141.
- Stemmer K.L., (1976), Pharmacology and Toxicology of Heavy-Metals – Antimony, *Pharmacology and Therapeutics. Part A*, **1**, 157-160.
- Sun F.H., Wu F.C., Liao H.Q., Xing B.S., (2011), Biosorption of antimony(V) by freshwater cyanobacteria *Microcystis* biomass: Chemical modification and biosorption mechanisms, *Chemical Engineering Journal*, **171**, 1082-1090.
- Uluozlu O.D., Sari A., Tuzen M., (2010), Biosorption of antimony from aqueous solution by lichen (*Physciatribacia*) biomass, *Chemical Engineering Journal*, **163**, 382–388.
- USEPA, (1979), *Water Related Fate of the 129 Priority Pollutants*, vol. 1, USEPA, Washington, DC Doc. 745-R-00-007.
- Vijayaraghavan K., Balasubramanian R., (2011), Antimonite Removal Using Marine Algal Species, *Industrial and Engineering Chemistry Research*, **50**, 9864-9869.
- WHO, (2011), *Guidelines for drinking-water quality*, 4th Edition, World Health Organization, Geneva, On line at: http://www.who.int/water_sanitation_health/en/.
- Wilson S.C., Lockwood P.V., Ashley P.M., Tighe M., (2010), The chemistry and behaviour of antimony in the soil environment with comparisons to arsenic: A critical review, *Environmental Pollution*, **158**, 1169–1181.
- 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.
- Wu Z.J., He M.C., Guo X.J., Zhou R.J., (2010), Removal of antimony (III) and antimony (V) from drinking water by ferric chloride coagulation: Competing ion

- effect and the mechanism analysis, *Separation and Purification Technology*, **76**, 184-190
- Xi J.H., He M.C., Wang K.P., Zhang G.Z., (2013), Adsorption of antimony(III) on goethite in the presence of competitive anions, *Journal of Geochemical Exploration*, **132**, 201-208.
- 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.
- Yang J., Volesky B., (1996), Intraparticle diffusivity of Cd ions in a new biosorbent material, *Journal of Chemical Technology and Biotechnology*, **66**, 355-364.
- Zhu J., Wu F.C., Pan X.L., Guo J.Y., Wen, D.S., (2011), Removal of antimony from antimony mine flotation wastewater by electrocoagulation with aluminum electrodes, *Journal of Environmental Sciences China*, **23**, 1066-1071.