Aluminium removal from wastewater by refused beach cast seaweed. Equilibrium and dynamic studies.

Pablo Lodeiro^a, Ángel Gudiña^a, Luz Herrero^b, Roberto Herrero^a and Manuel E. Sastre de Vicente^{a*}

^aDepartamento de Química Física e Ingeniería Química I, Facultad de Ciencias. Universidad de A Coruña, Alejandro de la Sota 1, 15008, A Coruña (Spain)

^bCentro Tecnológico AIMEN. Relva, 27 A, 36410, Torneiros, Porriño, Pontevedra (Spain)

*Corresponding author e-mail: eman@udc.es; phone: (+34) 981 167000 (ext. 2198);
Fax: (+34) 981 167065

Abstract

Aluminium removal has been investigated in synthetic and real wastewaters provided by an aluminium surface treatment plant. Marine algae, obtained as beach cast seaweed (a refuse substance) were used as adsorption material. The influence of pH, metal concentration and time for aluminium elimination was studied by use of synthetic solutions. The optimum pH value was 4.0, which provided a maximum adsorption capacity of $22.5 \text{ mg}\cdot\text{g}^{-1}$. The adsorption percentage surpassed 80% in less than 30 minutes of contact time. Real solutions from the industrial unit were fully characterized and tested in two different fixed bed columns. One column was filled with 27.5 g of dried beach cast seaweed. Three cycles of adsorption and two of desorption were carried out. The first cycle ($12 \text{ mg}\cdot\text{g}^{-1}$ maximum sorption capacity) was enough to reach the maximum adsorption capacity at $15 \text{ mL}\cdot\text{min}^{-1}$ flow rate. The second column was packed with 1100 g of seaweed and its behaviour was compared to another column filled with activated charcoal, following both the same experimental procedure. Maximum sorption capacity was $14 \text{ mg}\cdot\text{g}^{-1}$ for seaweed, whereas the activated charcoal only reached $1.6 \text{ mg}\cdot\text{g}^{-1}$ (flow rate of $250 \text{ mL}\cdot\text{min}^{-1}$).

Keywords: Aluminium, seaweed, column, wastewater, biosorption.

1. Introduction

Aluminium is the most abundant metallic element in Earth, as it is included in many silicates (aluminosilicates); besides the ion Al^{3+} is involved in a great number of natural processes. Nevertheless, very few information related to its recovery from the environment is reported in literature. This is because it is not considered a major pollutant, as a consequence of its low solubility at pH observed for natural waters (between 5.5 and 7.5). At this pH values the aluminium is mainly found in particulate form.

Aluminium is thought to be responsible for neurological disruptions such as Alzheimer's disease since some aluminosilicates were found in Alzheimer's neurons interrupting axonal transport [1].

Aluminium is also involved in acidification processes in natural waters; therefore its presence might indicate some anthropogenic activities.

Aluminium is commonly used in industrial processes due to its lightness, resistance to corrosion, good electrical conductivity properties and ductility. A large number of practical daily devices are made from aluminium, consequently extrusion (giving shape to metallic aluminium) and anodising (disposing an aluminium oxide layer to avoid corrosion) are aluminium manufacturing processes widely spread.

Most of the plants working on aluminium surface treatment processes use traditional methods for aluminium elimination, mainly chemical precipitation, due to its simple application. However, such practice and similar ones generate toxic sludge that constitutes a serious environmental and economical problem. Alternative techniques, that reduce waste generation and water consumption, should be used [2].

During the last ten years there has been a great development of low cost techniques for removing metals from wastewater, such as biosorption. However, very

few papers are related to aluminium uptake [3-7]. It is well known the great ability of certain types of biomass to retain relatively large quantities of metal ions by “passive” adsorption [8,9], so the purpose of this work is testing biosorption as an appropriate technique for aluminium removal.

Beach cast seaweed frequently occurs in Galician Coast (NW of Spain), which has become a serious problem for fishing, seashell and tourism industries.

In this paper, marine algae, obtained as beach cast seaweed, have been used as adsorption material. The adsorption process has been analysed through batch experiments with regard to the influence of both the initial aluminium concentration and the equilibrium solution pH. Based on these preliminary results, the studies have been focused on a precise description of the equilibrium behaviour at different pH values, but also on the kinetic evolution of the process at two different concentrations. In addition, these results have been applied to the treatment in a column of real effluents from an aluminium surface treatment plant, which constitutes a novelty in aluminium biosorption studies. Moreover, these results were compared to the ones obtained with an activated charcoal.

2. Experimental methods and materials

2.1 Biomaterials

Beach cast seaweed was characterized and it was found that the brown alga *Cystoseira baccata* was its principal constituent (the alga was visually identified by experts of Coast Biology research group from University of A Coruña). Seaweed was conditioned following a simple procedure. First of all, the biomass was washed using tap water to eliminate major impurities, afterwards it was dried in an oven at 60 °C for at least 12 hours, ground with an analytical mill (IKA A 10) and, finally, it was sieved

to particles of 0.5-1 mm diameter. The samples for the potentiometric titrations were acid-treated, in order to transform the biomass into its fully protonated form. Samples were soaked and shaken in a $0.2 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 solution in a rotary shaker (175 rpm) for 4 h, at a biomass concentration of $10 \text{ g}\cdot\text{L}^{-1}$. Afterwards, the material was rinsed thoroughly with deionised water until pH 4.5 was attained in the supernatant solution. Following filtration, treated biomass was also dried, ground and sieved.

2.2 Chemicals

The chemicals used in this work were $\text{AlK}(\text{SO}_4)_2\cdot 12\text{H}_2\text{O}$ (Merck pro analysis), NaOH (Merck p.a.), HCl (Merck p.a.), H_2SO_4 (Panreac p.a.), $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$ (Panreac PRS), CH_3COOH (Panreac PRS) and Erichrome cyanine R.G. (Sigma-Aldrich), Activated Charcoal granulated n° 3 (Panreac, QP).

2.3 Kinetic studies

Kinetic experiments were carried out using 0.25 g of beach cast seaweed added to 100 mL of aluminium solution (10 and $100 \text{ mg}\cdot\text{L}^{-1}$). Experiments were done at 25.0 ± 0.1 °C in a double-wall thermostated beaker (200 mL), under magnetic agitation (175 r.p.m). pH was measured during the studies but it was not adjusted. Aliquots were taken periodically in order to determinate aluminium concentration following the Eriochrome cyanine R method [10].

2.4 Adsorption Isotherm studies

Seven aluminium solutions were prepared with a concentration range between 5 and $500 \text{ mg}\cdot\text{L}^{-1}$, by diluting a $500 \text{ mg}\cdot\text{L}^{-1}$ stock solution of Al, prepared by dissolving $\text{AlK}(\text{SO}_4)_2\cdot 12\text{H}_2\text{O}$ salt in deionised water. A biomass dose of $2.5 \text{ g}\cdot\text{L}^{-1}$ was employed. Solution pH was controlled and adjusted during the experiments to three different equilibrium values: 1.0, 2.5 and 4.0.

All the experiments were developed at constant room temperature during five hours and agitated at 175 rpm using a rotary shaker. Afterwards, all samples were centrifuged (Nahita centrifuge) for 5 minutes at 10000 r.p.m., and aluminium concentration was determined using the Eriochrome cyanine R method.

2.5 Potentiometric titrations

For each titration, ca. 0.5 g of protonated algal biomass was placed in a thermostated titration cell at 25.0 ± 0.1 °C, with 100 mL of deionised water. Inert gas (nitrogen 99.9995%) was bubbled into the solution. A certain amount of HCl was also added to yield an initial pH value ca. 2. The titrating solution ($0.05 \text{ mol}\cdot\text{L}^{-1}$ NaOH, prepared with boiled deionised water and standardised with potassium hydrogen phthalate, Carlo Erba PRE) was added from a Crison microBu 2031 automatic burette. Emf measurements were done by a Crison micropH 2000 meter equipped with a GK2401C Radiometer combination glass electrode (saturated Ag/AgCl as reference). The procedure followed for the titrations and glass electrode calibrations is described in greater detail elsewhere [11].

2.6 Column studies

Column studies were carried out in two types of fixed bed columns. Real solutions, coming from an aluminium surface treatment plant, were studied in order to test the practical applicability of the process. The first column employed (40 cm length and 3 cm of internal diameter) was filled with 27.5 g of dried beach cast seaweed. Three cycles of sorption and two cycles of desorption, at a flow rate of $15 \text{ mL}\cdot\text{min}^{-1}$, were carried out using this column. HCl acid ($0.01 \text{ mol}\cdot\text{L}^{-1}$) was employed as desorbing agent. The second column (80 cm length and 12 cm of internal diameter) was filled with 1100 g of the alga in order to achieved more advantageous conditions (ensure enough contact time between contaminant and adsorbent). Besides, the same experimental

procedure was applied using activated charcoal instead of biomass, in order to compare both materials. In this case, just one cycle of sorption was performed (flow rate of 250 mL·min⁻¹).

A porous membrane was attached at the bottom of the columns in order to support the algal bed and to ensure uniform inlet flow, and a good liquid distribution into the column. The inlet solution was fed through the bed in up-flow mode with a peristaltic pump (from Watson Marlow) connected at the bottom of the columns. Two glass beads (6 mm in diameter) layers of 3 cm depth each were also displayed in the columns at their top and bottom, to avoid the loss of adsorbent due to the solution flow and to facilitate its homogeneous distribution. Aluminium concentration in the effluent was periodically analysed as described above. The data obtained correspond to average values from at least two replicates.

Moreover, a complete analysis of real waters samples from the anodising process has been done. Following this analysis, possible interferences (e.g. ion competition for adsorption sites) could be identified.

3. Results and discussion

3.1 Kinetic Studies

The main purpose of these experiments was to identify the necessary contact time required to reach equilibrium, in order to be aware of the time needed to develop it. Two different initial concentrations (10 and 100 mg·L⁻¹) were tested. The process was reasonably fast, because the equilibrium value was almost attained in 40 and 60 minutes for 10 mg·L⁻¹ and 100 mg·L⁻¹, respectively (see Figure 1). For contact time above the ones mentioned, slow adsorption variations were observed. Likewise, it is noticeable

that more than 80% of the maximum adsorption capacity was reached in less than 30 minutes for both initial concentrations.

These results are quite positive in order to apply beach cast seaweed to water purification in continuous columns, as a large amount of aluminium is adsorbed in a short period of time.

3.2 Adsorption Isotherms

Equilibrium studies allow us to determine maximum adsorption capacity value, related to the distribution of aluminium between beach cast seaweed and solution. Data obtained at three different pH values were adjusted to three different adsorption isotherm equations: Langmuir, Langmuir-Freundlich and Freundlich (Table 1).

The amount of metal adsorbed at equilibrium, Q , was calculated from the difference between metal concentration in the aqueous phase before and after sorption, following the equation:

$$Q = \frac{V(C_i - C_e)}{m} \quad (1)$$

where V is the volume of metal solution, C_i is the initial metal concentration, C_e is the equilibrium concentration of metal in solution and m is the mass of sorbent (considering dry weight).

The parameters obtained after data fitting with these functions are contained in Table 2. No results are showed at pH 1, because none of the three functions provide a good fitting. Langmuir and Langmuir-Freundlich models provide, statistically, the same values, and as it can be observed in Figure 2, very close to experimental data. The coincidence of these two functions is because “ n ” parameter is statistically 1, so both fittings correspond to the same equation.

The best sorption results for beach cast seaweed were obtained at pH 4, at which maximum sorption capacity ($Q_{\max}$) was $22.5 \text{ mg}\cdot\text{g}^{-1}$ ($0.833 \text{ mmol}\cdot\text{g}^{-1}$). This value is

considerably higher than that obtained with commercial activated carbon (BDH) at the same pH value, with a $Q_{\max}$ value of $6.562 \text{ mg}\cdot\text{g}^{-1}$ [12], rice husk carbon ($Q_{\max} 9.78 \text{ mg}\cdot\text{g}^{-1}$) [13] or results obtained using *P. aeruginosa* loaded in Chromosorb 106, with a $Q_{\max}$ value of $10.5 \text{ mg}\cdot\text{g}^{-1}$ (Tuzen and Soylak, 2008). These results remark the better behaviour shown by macroalgae when it is used as sorbent at pH values in which aluminium precipitation is negligible (although experimental design were not the same in all the literature works mentioned, the best sorption conditions for each material were selected in all cases). In addition biomass treatment is further more simple than others reported in literature [12,14].

Uptake capacity at lower pH values (2.5) is reduced to $11.5 \text{ mg}\cdot\text{g}^{-1}$, approximately half of the $Q_{\max}$ obtained for pH 4. Despite this reduction, data at this pH was also fitted well to both Langmuir and Langmuir-Freundlich functions, as it occurs at pH 4.

Sorption capacity of beach cast seaweed at the most acidic pH (1) is much lower: $3.5 \text{ mg}\cdot\text{g}^{-1}$ is the highest value achieved in the isotherm, so working cannot be considered at this pH value in aluminium wastewaters treatment.

Maximum sorption values for other metal ions, such as inorganic mercury, lead(II) and cadmium(II) using *Cystoseira baccata* as sorbent material (the main constituent of the biosorbent used in the present study), were $0.9 \text{ mmol}\cdot\text{g}^{-1}$ for Cd, Hg and Pb at pH values between 4 and 4.5 [15,16]. In a similar way, the obtained result in this work for aluminium adsorption is $0.83 \text{ mmol}\cdot\text{g}^{-1}$. This similarity could be ascribed to the fact that the same acid groups (carboxylic functionalities) are responsible for the adsorption of these metals. The small difference between both values might be due to the fact that beach cast seaweed was used instead of pure *C. baccata* macroalgae.

3.3 Acid-base properties

In order to estimate the total amount of active sites in protonated beach cast seaweed biomass, a simple potentiometric titration was carried out with a NaOH solution. The number of acid groups per gram of alga, $[A]_{\text{total}}$ (mmol g^{-1}), was calculated by estimation of the position of equivalent point (V_{eq}) in the resulting titration curves (Figure 3), using the following equation:

$$[A]_{\text{total}} = \frac{V_{eq} [NaOH]}{m} \quad (2)$$

Sulphate groups are known to be present in *C. baccata*, the main constituent of this beach cast seaweed [17], however, no evidence of their presence was found in the titration curves. The total number of weak acid groups found was $2.61 \pm 0.1 \text{ mmol} \cdot \text{g}^{-1}$, determined in deionised water. A very close number of groups were found in the potentiometric titration of *C. baccata* in $0.05 \text{ mol} \cdot \text{L}^{-1} \text{ NaNO}_3$ [15]. As expected, ionic strength does not influence in the number of acidic groups titrated. This amount is around 3 times greater than the maximum aluminium uptake capacities obtained with the raw biomass at pH 4 ($0.83 \text{ mmol} \cdot \text{g}^{-1}$). It is reasonable to think that not all these groups available for protons will be available for other cations, such as aluminium. There is a combination of factors that could justify this fact. First, since the raw biomass is stabilised with Na, K, Ca and Mg ions present in seawater, metal ions must compete with these major ions for the active binding sites, and therefore the metal does not occupy all the binding sites. Second, it can be expected a certain degree of multidentism in the binding mechanism, i.e., more than one acid group can be involved in the binding to a single metal ion. Third, at pH 4, not all weak acid groups in alga are ionised.

3.4 Column studies

Fixed bed column data are commonly described using breakthrough curves, which represent the shape of the concentration-time profile. The breakthrough point was defined as the time when effluent concentration is $3 \text{ mg} \cdot \text{L}^{-1}$. This value is the

maximum allowed concentration for the wastewaters effluents analysed, and it is based on regional legislation coming from European Directives. Using these data, fixed bed columns could be designed attending to sorption process and economical criteria.

In order to calculate the maximum aluminium sorbed it is necessary to solve a numerical integration, to determine the area above the breakthrough curve. The following equation was used:

$$Q_{Al,max} = \frac{F}{m} \times \int_{t=0}^{t=t_c} (C_i - C_{Al}) \cdot dt \quad (3)$$

Where F is the flow rate ($\text{mL} \cdot \text{min}^{-1}$), t is the time (min), C_{Al} is the aluminium effluent concentration and C_i its feed concentration, both in $\text{mg} \cdot \text{L}^{-1}$.

Real wastewater samples from the aluminium surface treatment plant were fully characterized. The analysed parameters and its values are shown in Table 3. However, it should be noticed that these data depend strongly on the date that samples have been picked, as well as the number of pieces treated in each process cycle, type of treatment, etc. They all have a great influence in the composition of the bath tanks. Aluminium concentration is very high, around $500 \text{ mg} \cdot \text{L}^{-1}$, and there are many substances that could interfere in metal adsorption.

Pilot tests should also be used to generate scale up factors for the full-scale design of the real effluents treatment. Moreover, it is important to analyse the necessary number of columns required, their dimensions for continuous treatment, the optimal flow rate and the adequate bed depth [18]. These parameters can only be optimized by dynamic test in column.

Typical flow rates suggested in bibliography for column studies development should be, ideally, between $40\text{-}240 \text{ L/min} \cdot \text{m}^2$ [19]. Nevertheless, a flow rate about $20 \text{ L/min} \cdot \text{m}^2$ should be adequate for the firsts experiments. We started testing the aluminium sorption behaviour of a fixed bed column (40 cm length and 3 cm of internal

diameter) filled with 27.5 g of beach cast seaweed (21 cm of bed depth and 7.07 cm² bed area). Taking into consideration the recommended superficial flow rate described above, we chose a flow rate of 15 mL·min⁻¹ for this first experience. The effectiveness of the column for aluminium elimination from solution was tested by three sorption and two desorption cycles.

The breakthrough adsorption curve obtained is shown in Figure 4. Maximum sorption capacity was reached in the first cycle (12 mg·g⁻¹). This $Q_{\max}$ value is considerably lower than the one obtained from the isotherm, but it must be taken into account that there may be competition for adsorption sites among different compounds in the wastewater (see Table 3). In the following cycles the column effectiveness was reduced to values near to 5 mg·g⁻¹, and it seemed to stay stable at this value (see Table 4). This additional diminution in adsorption capacity could be ascribed to the reduction of the pH of the influent, due to the previous acid desorption cycle (see Figure 5 for pH evolution along breakthrough curves). As it can be observed in Figure 4, the breakthrough time (at which aluminium effluent concentration reaches a value of 3 mg·L⁻¹) is shorter for the second and third cycles of sorption, and the saturation point is also reached earlier.

Variations in the chemistry of the influent (pH, buffer capacity, etc.) may affect the performance and capacity of the adsorbent. It should be mentioned that sorption effectiveness in continuous columns usually decreases in comparison to the effectiveness in batch studies. Moreover, it must be considered that column studies were done using real wastewaters, instead of the synthetic solution used for batch experiments.

The breakthrough curves obtained for the desorption process are shown in Figure 6. After the first use, desorption with acid solution showed excellent percentages of

recovery, and could be considered a complete desorption cycle. In the second desorption cycle a recovery percentage over 100 % is reached, mainly because a great difference is generated while calculating the area below the curve, caused by a small change in the desorption maximum value. Desorption cycles show the opposite behaviour to adsorption ones: less aluminium has to be desorbed in the second cycle, so maximum metal desorption is reached in a shorter time (Figure 6). The efficiency of acid solutions in metal desorption from biomass has also been verified in other batch and column studies [20].

Another important operating parameter that must be considered in column study is the empty bed contact time (EBCT). It is obtained dividing bed volume by volumetric flow rate, and it gives an idea of the contact time between biomass and solution. It is known that EBCT should be between 10 and 50 minutes, in order to ensure enough contact time for contaminant and material to achieved equilibrium [19]. Nevertheless, this value could change in systems with very fast or low kinetics. In our case, the EBCT for the column described above is around 10 minutes, and it seems that is not high enough for this kind of system.

We tried to improve the conditions for column studies, increasing EBCT up to 26 minutes. In this case, we used a new column of 0.12 m diameter, filled with 1100 g of material, seaweed or activated charcoal (0.57 and 0.18 m bed depth, respectively) and working at a flow rate of $250 \text{ mL} \cdot \text{min}^{-1}$ (comparable to the suggested working conditions found in the literature).

Breakthrough curve shape for the alga (Figure 7) is very similar to the obtained with the smallest column (Figure 4). In both cases the curves posses a high steep character, reflecting the efficiency in the overall use of the alga. Q_{max} value for beach cast seaweed reaches $14 \text{ mg} \cdot \text{g}^{-1}$, while for activated charcoal is only $1.6 \text{ mg} \cdot \text{g}^{-1}$.

Moreover, when breakthrough point ($3 \text{ mg}\cdot\text{L}^{-1}$) was achieved using the alga, an aluminium effluent concentration, around $225 \text{ mg}\cdot\text{L}^{-1}$, was already measured at the same time for activated carbon.

This illustrates that macroalgae works much better than activated charcoal even under real conditions. The Q_{max} values are consistent with the ones achieved in the previous experiments, despite of the great scale change carried out. Maximum sorption capacity showed in the isotherms was not reached due to the utilisation of real solutions; moreover, many factors might influence this diminution, such as pH value or the presence of interfering ions, as it was mentioned above.

4. Conclusions

Beach cast seaweed is able to eliminate aluminium from synthetic solution up to $0.833 \text{ mmol}\cdot\text{g}^{-1}$ at pH 4. At pH values lower than 4 the adsorption efficiency is diminished. The adsorption percentage surpassed 80% in less than 30 minutes of contact. Wastewaters from an aluminium surface treatment plant were successfully treated for aluminium elimination in fixed bed columns. Maximum adsorption capacity obtained in column was around 0.520 mmol of Al per gram of beach cast seaweed. Aluminium recovery from the alga is simple. An acidic stripping solution allows the metal recuperation; although the recuperation of the waste material implies a great attenuation in its adsorption capacity. Commercial activated charcoal was not as effective as the alga in Al elimination from real solution (around ten times less efficient).

FIGURE CAPTIONS

Figure 1. Kinetics of aluminium elimination in deionised water at 25°C by 2.5 g·L⁻¹ of beach cast seaweed. Initial metal concentration of 100 mg·L⁻¹ (left axis, open triangles) and 10 mg·L⁻¹ (right axis, open circles). pH value was not adjusted (100 mg/L pH= 3.6-3.9; 10 mg/L pH= 4.3-4.9).

Figure 2. Aluminium adsorption isotherms for suspensions of 2.5 g·L⁻¹ (beach cast seaweed) at pH= 4 ± 0.1 (open circles), 2.5 ± 0.1 (open triangles) and 1 ± 0.1 (open squares). The lines represent the fits to Langmuir (solid lines), Freundlich (dashed-dotted lines) and Langmuir-Freundlich equations (dotted lines).

Figure 3. Titration curve (pH vs. NaOH volume) for 0.5 g of beach cast seaweed in deionised water. Open circles represent experimental data points and solid line is the derivative of the experimental curve

Figure 4. Successive breakthrough curves for aluminium adsorption with real solution ($C_i = 481 \text{ mg} \cdot \text{L}^{-1}$) by beach cast seaweed biomass (27.5 g) at constant flow rate (15 mL·min⁻¹).

Figure 5. pH evolution during aluminium adsorption cycles in column.

Figure 6. Successive elution curves for aluminium desorption at constant flow rate (15 mL·min⁻¹), employing HCl 0.01 mol·L⁻¹ as eluant.

Figure 7. Breakthrough curve for aluminium adsorption with real solution ($C_i = 481 \text{ mg} \cdot \text{L}^{-1}$) using beach cast seaweed (squares) and activated carbon (diamonds) (1100 g) at constant flow rate (250 mL·min⁻¹).

FIGURES

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

TABLES

Table 1

Adsorption isotherm equations.

Isotherm	Equation
Langmuir	$Q = \frac{Q_{\max} \cdot b \cdot C_e}{1 + b \cdot C_e}$
Langmuir-Freundlich	$Q = \frac{Q_{\max} \cdot (b \cdot C_e)^{1/n}}{1 + (b \cdot C_e)^{1/n}}$
Freundlich	$Q = k_f \cdot C_e^{1/n}$

Table 2

Obtained values for the parameters used in Langmuir, Langmuir-Freundlich and Freundlich functions, for isotherms at pH values 2.5 and 4.

Isotherm		Langmuir		
	$Q_{\max}$	$b \text{ (mg}\cdot\text{L}^{-1})$	r^2	
pH = 4	22.5 ± 0.6	0.28 ± 0.04	0.992	
pH = 2.5	11.1 ± 0.4	0.14 ± 0.03	0.98	
Isotherm		Langmuir Freundlich		
	$Q_{\max}$	$b \text{ (mg}\cdot\text{L}^{-1})$	n	r^2
pH = 4	22.4 ± 0.8	0.29 ± 0.05	0.9 ± 0.1	0.992
pH = 2.5	11.5 ± 0.8	0.13 ± 0.04	1.2 ± 0.2	0.98
Isotherm		Freundlich		
	K_f	n	r^2	
pH = 4	8 ± 2	5 ± 2	0.78	
pH = 2.5	3.6 ± 0.9	5 ± 1	0.81	

Table 3

Main constituent concentrations for the real wastewater used in columns.

Constituent	C (mg·L ⁻¹)	Constituent	C (mg·L ⁻¹)
Total C	11.9	Sulphide	1493
Al	481	Chloride	6.26
Na	15.1	Fluoride	921
Total Cr	0.15	Ammonia	285
Ca	2.4	COD*	91
Total P**	2.58	pH	4.58

*Measured with a COD5000A Shimadzu (sample combustion, oxidation to CO₂ and analyse with a non dispersed infrared detector)

**Measured with a ICP-MS

Table 4

Maximum aluminium sorption capacity (from the area above breakthrough curves, Eq. 3) and percentage of metal recovery, obtained during the removal of aluminium (C_i= 481 mg·L⁻¹) by beach cast seaweed in a fixed bed column (27.5 g of biomass: 21 cm of bed depth and 7.07 cm² bed area).

	Al adsorbed in biomass (mg)	Q _{max,Al} (mg·g ⁻¹)
1 st sorption	298	12
2 nd sorption	122	5
3 rd sorption	144	5
	Al desorbed (mg)	Metal recovery (%)
1 st desorption	296	99
2 nd desorption	142	116

Acknowledgments

This work was funded by the projects CTM2006-03142 (from the Ministerio de Educación y Ciencia of Spain) and PGDIT06TAM00401CT (from Xunta de Galicia). The authors would like to thank Dr. I. Bárbara and Dr. J. Cremades (University of A Coruña) for the collection and classification of the algae species. P. Lodeiro gratefully acknowledges financial support through Ángeles Alvariño project AA 10.02.56B.444.0 (from Xunta de Galicia) co-funded by 80 % with European Social Funds.

REFERENCES

- [1] E. Merian, T.W. Clarkson, Metals and their compounds in the environment : occurrence, analysis, and biological relevance, VCH, Weinheim ; New York, 1991.
- [2] E. Álvarez-Ayuso, Approaches for the treatment of waste streams of the aluminium anodising industry, J. Hazard. Mater. 164 (2009) 409-414.
- [3] E.N.V.M. Carrilho, A. Ferreira, T.R. Gilbert, Characterization of sorption sites on *Pilayella littoralis* and metal binding assessment using ^{113}Cd and ^{27}Al nuclear magnetic resonance, Environ. Sci. Technol. 36 (2002) 2003-2007.
- [4] S.E.-S. Ghazy, S.E.-S. Samra, M.A. E-F.M., S.M. El-Morsy, Removal of aluminium from some water samples by sorptive-flotation using powdered modified activated carbon as a sorbent and oleic acid as a surfactant, Anal. Sci. 22 (2006) 377-382.
- [5] B.C. Hard, C. Walther, W. Babel, Sorption of aluminum by sulfate-reducing bacteria isolated from uranium mine tailings, Geomicrobiology Journal 16 (1999) 267-275.
- [6] H.S. Lee, B. Volesky, Characteristics of aluminium biosorption by *Sargassum fluitans* biomass, Marine Biotechnology 1 (1999) 380-383.
- [7] H. Xia, G.D. Rayson, Investigation of aluminum binding to a *Datura innoxia* material using ^{27}Al NMR, Environ. Sci. Technol. 32 (1998) 2688-2692.

- [8] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, *Water Res.* 33 (1999) 2469-2479.
- [9] P. Lodeiro, R. Herrero, M.E. Sastre de Vicente, Thermodynamic and kinetic aspects on the biosorption of cadmium by low cost materials: A review, *Environ. Chem.* 3 (2006) 400-418.
- [10] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, Standard Methods for the Examination of Water and Wastewater, in: A.P.H. Association (Ed.), Washington, DC, 1998, pp. 366-368.
- [11] C. Rey-Castro, P. Lodeiro, R. Herrero, M.E. Sastre de Vicente, Acid-base properties of brown seaweed biomass considered as a Donnan Gel. A model reflecting electrostatic effects and chemical heterogeneity, *Environ. Sci. Technol.* 37 (2003) 5159-5167.
- [12] S.A. Al-Muhtaseb, M.H. El-Naas, S. Abdallah, Removal of aluminum from aqueous solutions by adsorption on date-pit and BDH activated carbon, *J. Hazard. Mater.* 158 (2008) 300-307.
- [13] T.S. Singh, B. Parikh, K.K. Pant, Investigation on the sorption of aluminium in drinking water by low-cost adsorbents, *Water SA* 32 (2006) 49-54.
- [14] M. Tuzen, M. Soylak, Biosorption of aluminum on *Pseudomonas aeruginosa* loaded on Chromosorb 106 prior to its graphite furnace atomic adsorption spectrometric determination, *J. Hazard. Mater.* 154 (2008) 519-525.
- [15] P. Lodeiro, J.L. Barriada, R. Herrero, M.E. Sastre de Vicente, The marine macroalga *Cystoseira baccata* as biosorbent for cadmium (II) and lead (II) removal: kinetic and equilibrium studies, *Environ. Pollut.* 142 (2006) 264-273.

- [16] R. Herrero, P. Lodeiro, C. Rey-Castro, T. Vilariño, M.E. Sastre de Vicente, Removal of inorganic mercury from aqueous solutions by biomass of the marine macroalga *Cystoseira baccata*, Water Res. 39 (2005) 3199-3210.
- [17] E. Percival, R.H. McDowell, Chemistry and enzymology of marine algal polysaccharides, Academic Press, London New York, 1967.
- [18] B. Volesky, Sorption and biosorption, BV Sorbex, St. Lambert, Quebec, 2003.
- [19] U.S. Army Corps of Engineers, Adsorption design guide, University Press of the Pacific, Honolulu, 2005.
- [20] P. Lodeiro, R. Herrero, M.E. Sastre de Vicente, Batch desorption studies and multiple sorption-regeneration cycles in a fixed-bed column for Cd(II) elimination by protonated *Sargassum muticum*, J. Hazard. Mater. B127 (2006) 1649-1655.