

APPLICATION OF MARINE SEAWEEDS AS LEAD (II) BIOSORBENTS: ANALYSIS OF THE EQUILIBRIUM STATE

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ABSTRACT

Through the use of non-living biomass, the brown seaweeds *Lessonia nigrescens* Bory and *Macrocystis integrifolia* Bory were evaluated as adsorbents for the removal of lead (II) ions from aqueous solutions at room temperature. The effects of initial pH, mass of adsorbent, initial concentration of the metal, ionic strength and particle size were examined in batch experiments; pH exhibited a strong response to the levels of the lead (II) in the aqueous chemistry. Yet at the same time, and due to due to competition for the adsorption sites, and undesirable increase in ionic strength during the adsorption process was revealed. Moreover, in the equilibrium state, the mathematical adsorption model of Langmuir efficiently describes the competitive adsorption mechanism by both algae. The calculated parameters show a high adsorbent/adsorbate affinity, highlighting their potential utilization in the elimination of lead (II) from residual waters.

Key words: Alga, lead (II), adsorption isotherm, pH, alginate, biosorption.

INTRODUCTION

Lead's attributes have been well established for more than 5000 years, with its toxicity determined by greek, roman and arabian cultures. For example, the Roman Empire reported many chronic health problems due to the intensive use of lead-based households items and other common devices made of the metal. Also, many painters, among them Goya, suffered lead-poisoned as a consequence of their daily contact with lead-based paints. The air of major cities has been contaminated through the use of combustible fuels which have in the past contained high levels tetraethyllead, commonly used to prevent another form of pollution: motor noise. As measures have been taken to reduce additives in many countries around the world, positive results have followed.

In addition to environmental lead pollution, another source of lead poisoning in humans comes from diet. Fortunately, ingestion permits minimal absorption due to the easy formation of insoluble compounds such as phosphates $Pb_3(PO_4)_2$, or basic carbonate $Pb_3(CO_3)_2(OH)_2$.

A portion of absorbed lead eventually accumulates in the bones, where it acts as a detoxifying agent.

Acute and chronic poisoning in humans can produce nausea and lack of appetite in addition to kidney malfunction and nerve damage. Incidents of these ailments increase when patients lack sufficient amounts of calcium and iron in their diets¹.

Numerous conventional methods have been utilized in the removal of heavy metals from wastewaters. They include chemical precipitation, electrochemical deposition and ionic exchange. However, these techniques require costly investments for industries employing

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them and involve complicated post-treatment of by-products^{2,3}. Biosorption is an area of research that offers benefits to both industries and government alike, because it is considered a so-called “clean” technology utilized in the elimination of toxic metals from liquid effluents resulting from industrial production⁴⁻⁶. Since 1987, Peru has increased the extractive production of almost all of its metals of economic importance: Cu, Pb, Zn, Ag, Au, Sn and Mo. As a result, Peru is one of the world's leading producers of tin, copper and gold^{7,8}. Consequently, waste volumes of the mining industry also pose an increase in pollution risk of water sources.

Biosorption follows principles rooted in organic, inorganic, analytical and physical chemistry. The process of interaction between biological and naturally-occurring materials with metals can be described by adequate mathematical models in equilibrium and thermodynamic studies^{9,10}.

This present work proposes the use of brown marine seaweed in the removal of lead (II) ions. Marine seaweed has previously demonstrated a high affinity towards heavy metals by other research groups¹¹⁻¹³. Some of which have utilized fungi, bacteria, yeast and other adsorbents to accomplish the same purpose¹⁴⁻¹⁷. However, very few have to date laid out the obtained equilibrium parameters required for their future use in scaled-up processes. In building on these studies, we continue investigating the marine algae *Lessonia nigrescens* Bory and *Macrocystis integrifolia* Bory, whose acid-base properties were elaborated upon in previous studies¹⁸ as a pollutant-filter in lead-contaminated runoff.

MATERIALS AND METHODS

Reagents and solutions

Stock solutions of 1000 ppm were prepared by dissolving $Pb(NO_3)_2$ (analytical grade, MERCK) in 1 L of deionized water. Solutions of varying concentrations were produced through dilution of the stock solution until the desired concentration was reached. All the dilutions were prepared with type I water, purified by reverse osmosis using a Barnstead/Thermolyne purifier (Dubuque IA) D2714 that provides water with a maximum conductivity of 18 m Ω .

The initial pH of each solution was adjusted to the required values by adding aliquots of 0.1N HCl and 0.1N NaOH upon contact with the adsorbent.

Adsorbents

The brown marine seaweeds *Lessonia nigrescens* Bory (L13) and *Macrocystis integrifolia* Bory (S12) were obtained from the beaches of Tacna and Marcona in Peru, respectively. After collection, both marine algae were washed twice with tap water in order to remove adhering soil, other microscopic algae, insect larvae, etc. In the laboratory, they were washed, taxonomically identified and kept under refrigeration. Then, the seaweed samples were washed with type I water, dried at room temperature, ground, separated according to their particle size by means of sieves (150 μ m-diameter-106 μ m) and stored in a desiccator until use.

Adsorbent characterization

To complete preliminary studies of the characterization of both algae by infrared spectroscopy¹⁹ and potentiometric titrations¹⁸, the surface texture and morphology of the two algae were differentiated by scanning electron microscopy (PHILLIPS ESEM XL-30 TMP). Prior to the observation, the surfaces of both samples were coated with a thin and electrically conductive layer of gold.

Adsorption experiments

Batch experiments were carried out in duplicate at room temperature combining variable masses of L13 and S12 with 100 mL of a solution of Pb (II) with orbital agitation at 200 rpm for 24 h. Initial solution pH was adjusted depending on the type of experiment. Changes in the pH were observed upon reaching the equilibrium within the range 0 and -0.8 of the initial pH value. Experiments at high initial pH and at high adsorbent dose reported the higher changes in the final solution pH. Thereafter, the suspensions were filtered and the remaining concentration of lead (II) was determined through flame atomic absorption spectrometry (Perkin Elmer 3110).

Effect of initial solution pH

The initial pH of a lead (II) solution of concentration of 100 ppm was adjusted between the integer values of 2 and 6. Precipitation of lead as lead hydroxide $\text{Pb}(\text{OH})_2$ was observed at $\text{pH} > 6$, not allowing for their study at higher pH values. Finally, 20 mg of algae L13 and S12 were added to each solution.

Adsorption isotherms and effect of adsorbent dosage

Solutions of lead (II) were prepared at different concentrations with the pH adjusted to the optimum value as determined in the previous section. Then, a variable mass of algae L13 and S12 were added.

Effect of the ionic strength

Considering the optimum values of initial pH, adsorbent mass and initial concentration of the metal, assays were carried out with different concentrations of sodium nitrate (analytical grade, MERCK) in the range 0.01 – 1 M to study the interference of ions Na^+ y NO_3^- as competitive adsorbates of lead (II) ions for the adsorption sites of the algae.

Data analysis

The amount of divalent lead adsorbed on the marine seaweeds was expressed as Adsorption Capacity (q , $\text{mg}\cdot\text{g}^{-1}$) and calculated as shown in equation (1):

$$q = \frac{(C_i - C_{eq}) V}{m} \quad (1)$$

where m is the mass of the adsorbent expressed in g, V is the volume of the solution in L and C_i and C_{eq} are the initial and at the equilibrium concentrations of lead (II) expressed in $\text{mg}\cdot\text{L}^{-1}$.

RESULTS AND DISCUSSION

Characterization of the adsorbent

The scanning electron micrographs clearly reveal the surface texture and morphology of both seaweed types (figure 1). It is evident that the two adsorbents show a very well defined organization of the polysaccharic chains of the “egg-box” type²⁰ on their surfaces where there is a homogeneous surface texture. This structure is an intrinsic characteristic of pectines and alginates, where the alginates belong to a family of linear polysaccharides composed by units of 1,4 β -D-mannuronic (M) and α -L-guluronic (G) acid, irregularly arrange in their primary sequence, co-existing amongst the sequences MM, GG, MG y GM²¹. This particular geometry attributes to alginate the property of gelification in the presence of divalent ions²⁰. The stabilization of these polysaccharic chains is the product of the dimerization in solution of two

chains, forming the so called “egg-box” where the divalent cations are “trapped” inside the dimer^{9,20}.

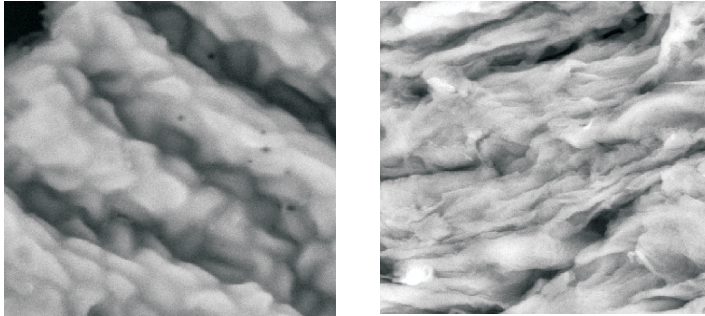


Figure 1: SEM images showing the morphologies of the surfaces of the algae L13 (left) and S12 (right).

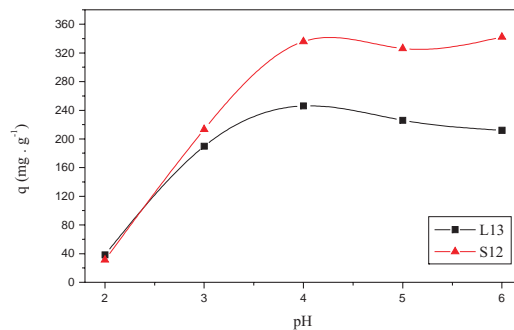


Figure 2: Effect of initial pH on the adsorption of Pb^{+2} . Conditions: 20 mg of adsorbent, 100 mL of a solution with initial concentration of 100 ppm, agitation of 200 rpm for 24 h.

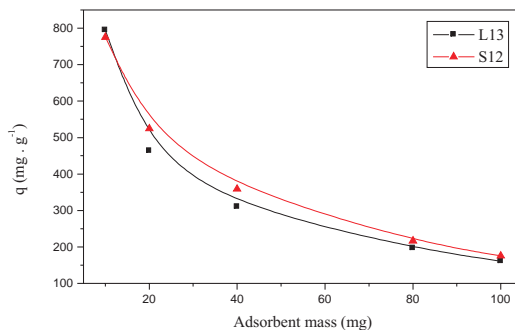


Figure 3: Effect of the adsorbent dosage on the adsorption of Pb^{+2} . Conditions: 100 mL of a solution with initial concentration of 100 ppm, pH 4 and 5 for L13 y S12, respectively, agitation of 200 rpm for 24 h.

Effect of initial pH

It is well known that the adsorption of heavy metals strongly depends on the pH solution^{6,10,19}. The pH does not only affect the availability of metallic ions in solution, but also the availability of adsorption sites on the surface of the adsorbent. Figure 2 shows the behavior of the adsorption capacity in function of the pH, exhibiting optimum pH values of 4 and 5 for the marine seaweeds L13 and S12, respectively. From the point of view of the aqueous chemistry of lead (II) ions solution, these ions stay under they soluble form at pH lower than 6, maximizing their adsorption. In that way, the adsorption of divalent lead would only depend on the nature and accessibility of the adsorption site on the surface of the adsorbents.

Navarro et al. carried out FTIR analysis and determined the presence of carboxyl, sulphonic, hydroxyl and amino groups in the composition of the seaweeds L13 and S12¹⁹. Likewise, the apparent ionization constants (pK_a) of the same marine algae have been demonstrated to be close to 3.0¹⁹. These results completely agree with the optimum pH values observed in the adsorption of lead (II). At pH values higher than 3, the active sites of the seaweed are under their deprotonated form (polianions alginate) and thus are able to bind to heavy metals, whereas at pH value lower than 3 in the alginate are mostly protonated and in theory their adsorption capacity should noticeably decrease.

Contradictorily, figure 1 shows that at pH values lower than 3, the adsorption capacity certainly decreases, but still maintains an acceptable level of adsorption ($\approx 40 \text{ mg.g}^{-1}$). The explanation of this phenomenon has been cited elsewhere^{6,9} postulating that the existence of fucoidans ($pK_a \approx 2$) in the structure of marine algae play an important role at low pH but with a lower affinity than alginates.

Effect of the adsorbent dosage

A study was done of the maximum adsorbent mass that saturates the adsorption sites on the surface of the seaweed at an initial concentration of 100 ppm of Pb (II). This assay constitutes an important parameter for future studies on the subject of scaling-up processes and continuous flow experiments. Figure 3 exhibits the differences in adsorption capacity at different masses of both algae. As seen, at 60 mg of the algae L13 and S12 the adsorption capacity value levels off. Therefore, the addition of more adsorbent will not affect the equilibrium nor improve the process. From the results of figure 3, we can also conclude that at higher adsorbent dosages, the adsorption capacity decreases upon reaching a minimum plateau ($q \approx 150 \text{ mg.g}^{-1}$). This phenomenon has also been cited in the adsorption of phenolic compounds with marine seaweed, attributable to partial aggregation of algae in solution, reducing the number of available adsorption sites²².

Sari et al.²³ required up to 2 g of the green alga *Ulva lactuca* biomass to reach the saturation of the adsorbent with lead (II), whereas the microalga *Spirulina maxima* required approximately 120 mg to level off the adsorption capacity of divalent lead²⁴.

Adsorption isotherms

The adsorption of lead (II) was analyzed using the models given by Langmuir and Freundlich. The Langmuir theory assumes uniform adsorption energy on the surface of the adsorbent, where the migration of the adsorbed pollutant among neighboring active sites is restricted. The linear form of the Langmuir isotherm is calculated as follows:

$$1/q = 1/q_{\max} + 1/(b q_{\max} C_{\text{eq}}) \quad (2)$$

where q_{\max} (mg g^{-1}) and b (L mg^{-1}) are the Langmuir constants related to the maximum adsorption capacity and to the adsorption energy, respectively. The constant q_{\max} represents the total number of available adsorption sites for one adsorbent at monolayer coverage whereas, the constant b is important for the comparison of adsorption efficiency between two different adsorbents under identical experimental conditions. A higher b constant represents a higher adsorbent/pollutant affinity.

The adsorption model of Freundlich assumes that different sites with several adsorption energies are involved in the adsorption process. This mathematical model has a logarithmic expression given by equation (3):

$$\ln q = \ln k_f + (1/n) \ln C_{\text{eq}} \quad (3)$$

k_f and $1/n$ are the Freundlich constants related to the adsorption capacity and the adsorption intensity, respectively.

Figure 4 shows the isotherms obtained in the experiments. As seen, all the isotherms are non-linear which indicates the predominance of a competitive adsorption mechanism. It has been suggested that small, charged adsorbates are far apart from each other on the surface of the adsorbent in such a way that there are no interactions amongst them. Otherwise the repulsion of their charges (in the case of lead with a +2 charge) or size would avoid the adsorption²⁵. Moreover, each adsorption site (mostly alginates) would act independently and try to reach stability by attracting the opposite charge or by establishing hydrophobic interactions²⁶.

The equilibrium studies were adjusted to the conventional adsorption theories of Langmuir and Freundlich as demonstrated in previous studies^{4,9,27,28}. The results of the experiments revealed that both processes follow the Langmuir isotherm at all the different adsorbent masses of L13 and S12 utilized. Since, the sorption isotherm represents the distribution of the solute (metal ion) between solid and liquid phases at equilibrium at a given temperature; we expected a superimposition of the curves in figure 4. This is not observed in the experimental results, corroborating the variations of the final solution pH, mentioned above. The change in pH at equilibrium with increasing adsorbent doses leads to changes in the adsorption capacity.

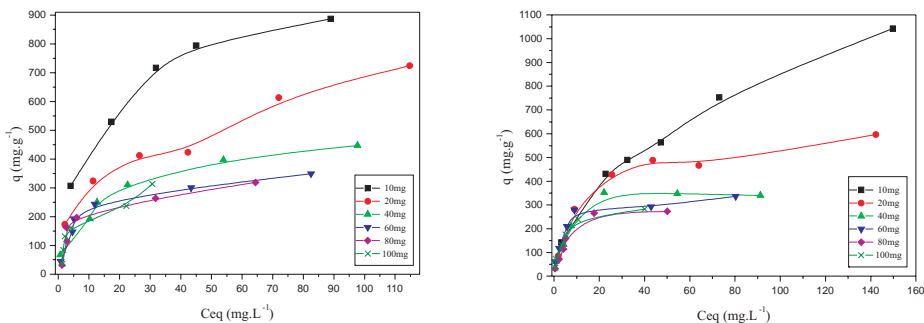


Figure 4: Adsorption isotherm of Pb^{+2} by L13 (left) and S12 (right). Conditions: 100 mL of solution of Pb (II) at pH 4 (L13) and 5 (S12), agitation of 200 rpm for 24 h.

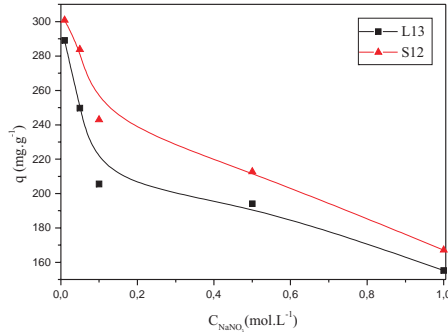


Figure 5: Effect of the ionic strength on the adsorption of Pb²⁺. Conditions: 100 mL of solution with initial concentration of 100 ppm, pH 4 and 5 for L13 and S12, respectively, agitation of 200 rpm during 24 h.

Tables 1 and 2 show the calculated parameters in the linear regression of both adsorption isotherms. According to the regression and the correlation coefficients, the process mostly follows the Langmuir theory with a high value of q_{max} of 893 and 730 mg.g⁻¹ observed with 10 mg of the algae L13 and S12, respectively. On the other hand, the Langmuir constant b , related to the affinity between adsorbate and adsorbent shows a maximum value around 40 mg for L13 (0.455 L.mg⁻¹) and 60 mg for S12 (0.499 L.mg⁻¹). This corroborates the results shown by the effect of adsorbent dosage, whereas the use of more than 60 mg of adsorbent does not report significant effect on the adsorption of lead ions (II).

The Freundlich model was also fitted to the process, but the data does not adjust to the regression as well as the Langmuir model. The q_{max} and b values reported in the present study are higher than others' biological and non-biological adsorbent literature featuring the study of fungi²⁹, yeast³⁰ and others^{27,31}.

Table 1: Langmuir and Freundlich calculated parameters for the biosorption of Pb²⁺ by L13 (*Lessonia nigrescens* Bory) at different adsorbent dosages.

Adsorbent Mass (mg)	Langmuir model		Freundlich model	
	Parameter	Value	Parameter	Value
10 mg	q_{max}	892,9	K_f	222,8
	b	0,13	n	3,37
	R^2	0,98	R^2	0,90
20 mg	q_{max}	505,1	K_f	158,5
	b	0,25	n	3,43
	R^2	0,98	R^2	0,95
40 mg	q_{max}	337,8	K_f	87,3
	b	0,46	n	2,75
	R^2	0,99	R^2	0,95
60 mg	q_{max}	340,1	K_f	66,7
	b	0,19	n	2,29
	R^2	0,99	R^2	0,86

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80 mg	q_{\max}	483,1	K_f	45,7
	b	0,06	n	1,75
	R^2	0,99	R^2	0,81
100 mg	q_{\max}	278,6	K_f	96,3
	b	0,32	n	3,68
	R^2	0,94	R^2	0,87

Table 2: Langmuir and Freundlich calculated parameters for the biosorption of Pb^{+2} by S12 (*Macrocystis integrifolia* Bory) at different adsorbent dosages.

Adsorbent Mass	Langmuir model		Freundlich model	
10 mg	q_{\max}	730	k_f	89,6
	b	0,08	n	2,15
	R^2	0,99	R^2	0,94
20 mg	q_{\max}	531,9	k_f	84,1
	b	0,11	n	2,24
	R^2	0,98	R^2	0,91
40 mg	q_{\max}	347,2	k_f	78,5
	b	0,33	n	2,37
	R^2	0,99	R^2	0,95
60 mg	q_{\max}	315,5	k_f	89,2
	b	0,50	n	3,06
	R^2	0,99	R^2	0,94
80 mg	q_{\max}	250,6	k_f	53,8
	b	0,32	N	2,05
	R^2	0,99	R^2	0,93
100 mg	q_{\max}	289,9	k_f	69,9
	b	0,29	n	2,23
	R^2	0,99	R^2	0,90

Effect of the ionic strength

Although heavy metal-containing wastewaters from mines and industry are composed of organic and inorganic substances, there is a limited number of studies dedicated to the evaluation of ionic strength as an important role in the adsorption of heavy metals³²⁻³⁴. This study however has indicated far better results using a variety of metals and ions as opposed to use single metals.

The adsorption capacity is related to several types of electrostatic interactions (complexation, ionic exchange, electrostatic forces, etc.) between the adsorbent and the adsorbate. These coulombic interactions strongly depend on the electrostatic environment of the system that can decide the existence or non-existence of that interaction. The presence of other ions in the solution represents a strong competition for the heavy metals for the adsorption sites³⁴.

Figure 5 shows the effect of the ionic strength, expressed in the experiment as sodium nitrate. The results show that the interaction between the divalent lead ion and the adsorbent is negatively affected to a great degree by the presence of Na^+ y NO_3^- ions, competing for the

adsorption site in the same intensity for both types of marine seaweed. The sodium ion would directly compete for the alginic adsorption sites, whereas the nitrate anion would be shielding the lead ion, thus increasing the volume of its ionic atmosphere and avoiding easy access to the active sites³⁴. Figure 5 indicates that only 0,01M of sodium nitrate is enough to decrease the adsorption capacity by approximately 40% and the addition of 1,0M of the salt decreases the adsorption by 70%.

In this experiment sodium and nitrate were chosen as representative ions due to their presence in all types of water (potable and industrial runoff). However, future studies with binary or ternary solutions will demonstrate the effect of common divalent ions such as calcium and magnesium on the adsorption of heavy metals. Since these ions are related to the hardness of water, they constitute an extra competition for the same electrically charged ions for the adsorption sites.

CONCLUSIONS

This present work demonstrates that marine seaweed types *Lessonia nigrescens* Bory (L13) and *Macrocystis integrifolia* Bory (S12) can potentially be utilized as adsorbents of divalent lead ions from aqueous solutions at room temperature. Batch experiments exhibit a strong solution initial pH effect, reporting a maximum adsorption capacity at pH values of 4 and 5 for the seaweed L13 and S12, respectively. These results completely align with the acid-base properties previously described¹⁹, correlating the apparent ionization constants of the ionizable functional groups present on the surface of both adsorbents with the pH where the maximum adsorption capacity is observed. The effect of adsorbent dosage was studied as well, showing a decreasing adsorption capacity at increasing masses of adsorbent. This phenomenon is explained by the formation of adsorbent aggregates that diminish the number of adsorption sites and effective surface. An increment in the ionic strength of the solution, represented by sodium nitrate, produced adverse effects on the elimination of lead (II) ions due to competition with the sodium ions for the adsorption sites. Finally, the mathematical models of Freundlich and Langmuir were applied to the experimental data. The result was a better description of the lead adsorption mechanism by the theory of Langmuir for both marine algae. The calculated parameters from the adsorption isotherms demonstrate an interesting affinity between adsorbate and adsorbent and a high maximum adsorption capacity when compared to those reported in the literature. This indicates their applicability to real lead (II) containing solutions from mine and lead consuming industries.

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