POSSIBILITY OF USING ALGAE BIOMASS FOR REMOVING Pb (II) IONS FROM AQUEOUS SOLUTIONS

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Abstract

In this study, the possibility of using algae biomass for removal of Pb(II) ions from aqueous solutions was studied. This material was chosen as adsorbent in this study due to being of its natural, renewable and low-cost. Batch adsorption experiments were carried out as a function of initial solution pH, adsorbent dose, initial Pb(II) concentration and contact time at 22 °C. About 0.2 g of algae biomass was found to be enough to remove 93 % of 175.6 mg/L Pb(II) from 25 mL of aqueous solution in 30 min. The optimum initial pH value was found to be 5.0. The Langmuir and Freundlich isotherm models were used to describe the equilibrium data and the isotherm constants were determined. The experimental adsorption data were fitted to the Langmuir isotherm model. The maximum adsorption capacity was 105.26 mg/g, at studied temperature. The biomass of the marine algae *Ulva lactuca* sp. demonstrated a good capacity for Pb (II) ions adsorption, and can be considered a potential adsorbent for effluents treatment process.

Key words: algae biomass, adsorption, Pb(II), equilibrium studies.

The release of heavy metal ions into environment by industrial activities is a serious problem because they ar e non-biodegradable and tend to circulating and accumulating throughout the food chain (Periasamy, K., Namasivayani, C., 1995).

Different conventional methods (chemical precipitation, ion exchange, electrochemical processes, membrane processes, etc) (Dabrowski, A., et al., 2004; Rusten, B., et al, 1997; Lianos, J., et al, 2010) are commonly used for the treatment of industrial effluents. But, the utilization of such methods is often limited due to economical or technical reasons.

Adsorption of heavy metal ions is one alternative technology, widely applied for the removal of toxic heavy metals from industrial and municipal waste streams, which can use low-cost adsorbents (Bailey, S.E., et al, 1999). It is a rapid, reversible, economical and environmental friendly technology, in contrast with enumerated conventional methods, of removing metal ions from aqueous effluents.

In the recent years, the adsorption of metal ions from aqueous solutions using different kinds of biomass, including algae, fungi or bacteria, has gained importance (Cetinkaya, Donmez G., et al, 1999). Many types of biomass have been reported to have significant uptake capacities for various heavy metals. It is the case of different species of green algae, which represent a renewable ubiquitous natural marine source, available in large quantities in littoral zone and therefore, an inexpensive sorbent material (Senthilkumar, S. et al, 2000).

Green algae are mainly cellulose, and a high percent of cell walls are proteins bonded to polysaccharides to form glycoprotein's (Senthilkumar, S. et al, 2000; Donmez, G. et al, 1999).These components contains several types of functional groups (amino, carboxyl, sulphate, hydroxyl, etc.) (Donmez, G. et al, 1999), which could play an important role in the adsorption process.

Lead has special industrial significance since it is employed in batteries, paints, pigments and ammunition, petrol, cables, alloys and steels, plastics, the glass industry and the metal industry. As a consequence, lead contamination is due to effluents of these industries, and also vehicular traffic and affect human life-quality, including by agricultural soils pollution (Goyer, R.A., 1993).

In this study we have investigated the possibility of using algae biomass for removal of Pb(II) ions from aqueous solution. The algae biomass (*Ulva lactuca* sp.) used as adsorbent were sampled from Black Sea coast of Romania. Experimental parameters affecting the adsorption process such as pH, biomass dosage, initial metal ion concentration and contact time, were studied, in batch experiments. The equilibrium adsorption data were evaluated by Langmuir, Freundlich isotherm models, and the equilibriums parameters were evaluated.

MATERIAL AND METHOD

The algae biomass (*Ulva lactuca* sp.) was sampled from Romanian Black Sea cost, in summer (July – August 2009). The collected samples were washed with distilled water several times for to remove the salts. The washed samples were then dried in air (at 110 °C, 6 h), grounded and sieves, until the granulation of particles was lower than 1.0 mm. The resulting material was directly used as adsorbent.

Stock solution of Pb (II) concentration 2200 mg/L was prepared by dissolving lead nitrate (from Aldrich) in distilled water. The working solutions were obtained by diluting the stock solution with distilled water.

The adsorption experiments were performed by batch technique mixing samples of 0.2 g algae biomass with volume of 25 mL solutions of known initial concentration of Pb (II) (44.0 – 702.5 mg/L) in 150 mL conical flasks. The initial solution pH was adjusted to required value (2.0 – 6.0) by addition of dilute solutions of HNO_3 or NaOH, before mixing the adsorbent. After a determined time (generally 24 h), the phases were separated by filtration and the filtrate was analyzed for the residual Pb (II) concentration by spectrophotometric method with 4-(2-pyridyl-azo)-resorcinol (λ = 530 nm, 1-cm glass cell, against blank solution) (Dean J.A., 1995).

In experiments concerning the effect of adsorbent dose, a range of algae biomass samples from 4.0 to 20.0 g/L were used. For contact time experiments, the procedure was similar with those presented above, with the difference that the phases were separated after a determined period of contact time. All adsorption experiments were performed at room temperature 22 ± 0.5 °C.

The performance of algae biomass for removal of Pb (II) from aqueous solutions was quantitatively evaluated using amount of Pb (II) adsorbed on mass unit of algae biomass (q, mg/g):

$$q = \frac{(c_0 - c)\cdot V}{m} \quad (1)$$

and percent of Pb (II) adsorbed (R, %):

$$R = \frac{(c_0 - c)}{c_0}\cdot 100 \quad (2)$$

where: c_0, c – initial and residual concentration of Pb (II) in solution (mg/L), V – volume of aqueous solution (L), m – mass of dry adsorbent (g).

RESULTS AND DISCUSSIONS

1. Effect of initial solution pH: The initial solution pH is one of the most important environmental factors in the adsorptive removal of heavy metals from aqueous solutions, because this parameter affects not only the site dissociation, but also the speciation and solubility of metal ions (Esposito, A., et al, 2002).

The effect of initial solution pH on the adsorption of Pb (II) on the algae biomass at 22 °C, 131.72 mg/L initial metal ion concentration and 0.2 g of adsorbent is presented in *fig. 1*.

The percent of Pb(II) adsorbed increase from 18.04 to 93.14 %, for an initial Pb (II) concentration of 131.72 mg/L, with an increase of initial solution pH from 2 to 5. The maximum value of Pb(II) removal has been obtained at pH 5.

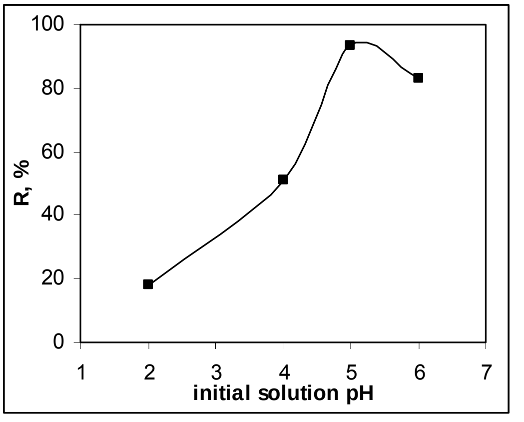


Figure 1 **Effect of initial solution pH on Pb (II) adsorption onto algae biomass**

At initial solution pH higher than 5, lower adsorption capacity for Pb (II) was observed, and this can be due to the precipitation and lower polarity of Pb (II) ions in this pH range. At lower pH values, the surface of adsorbent would be surrender by H^+ ions, which decrease the probability of Pb (II) interaction with functional groups from adsorbent surface due to repulsive forces. As initial solution pH increase, the functional groups from algae biomass surface became negative and the adsorption increase.

On the basis of these observations, the optimum initial solution pH for Pb (II) adsorption was found as 5.0, and all other adsorption experiments were performed at this pH value.

2. Effect of algae biomass dose: *Figure 2* present the effect of algae biomass dose on the adsorption efficiency of Pb (II) from aqueous solutions, at pH 5.0, initial metal ion concentration of 131.72 mg/L and after 24 h contact time.

It can be observed that varying the adsorbent dose from 4 to 20 g/L a decrease of amount of Pb(II) adsorbed (from 25.02 to 6.20 mg/g) was obtained. In the same adsorbent dose range, a relatively slow decrease of percent of Pb (II) adsorbed (from 76 to 92 %) was also observed. Further increase in the algae biomass dose does not change significantly the values of adsorption parameters. This can be obvious attributed to the increase of algae biomass surface area.

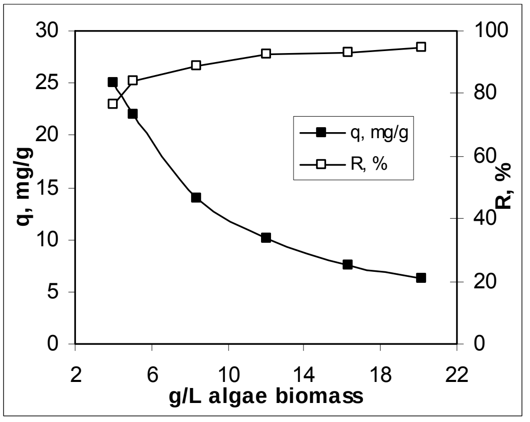


Figure 2 **Effect of algae biomass dose on the adsorption efficiency of Pb(II)**

Therefore 4 g/L of algae biomass dose was selected as the optimum value for the adsorption experiments.

3. Effect of equilibrium contact time**:** The effect of contact time between adsorbent (algae biomass) and a Pb(II) solution with an initial concentration of 175.63 mg/L and pH 5.0 at 22 °C, on lead removal is presented in *fig. 3*.

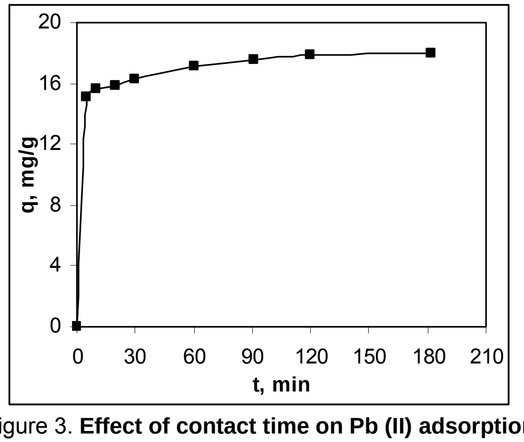


Figure 3. **Effect of contact time on Pb (II) adsorption by algae biomass**

It can be seen that the amount of Pb (II) adsorbed increase with increasing of contact time. The rate of adsorption is faster during of initial stage (above 78.75 % of Pb (II) removal occurred in the first 30 min), and this is probably due to the large number of free available adsorption sites. Thereafter, the adsorption became slower near to equilibrium, which is practically obtained after 60 min (the value of q after 24 h of contact time was found to be higher by a 12.35 % than those at 60 min contact). In consequence, for the quantitative removal of Pb (II) ions from aqueous solutions by using algae biomass, in mentioned experimental conditions, a contact time of minimum 60 min is required.

4. Effect of initial Pb (II) concentration: *Fig. 4* illustrates the effect of initial Pb(II) concentration (c_0, mg/L) on the adsorption onto algae biomass. The increasing of initial Pb(II) concentration from 44.0 mg/L to 702.52 mg/L decrease the percent of Pb (II) adsorbed from 94.12 % to 84.01 %, at an adsorbent dose of 4 g/L and an initial solution pH 5.0.

This behaviour is explained by increasing ratios between initial number of Pb (II) moles and limited number of adsorption sites from algae biomass surface (Krishnan, KA., Anirudhan, T.S., 2003).

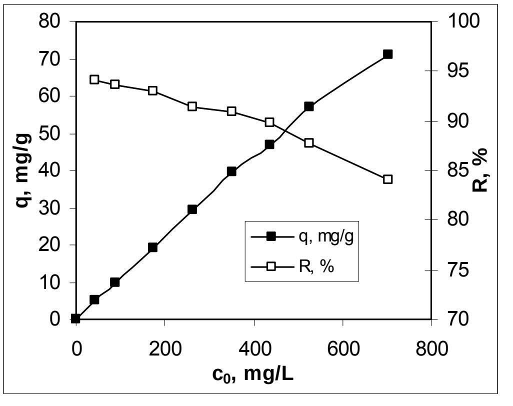


Figure 4 **Influence of initial Pb (II) concentration on the removal of lead on algae biomass**

At the same time, the amount of Pb (II) adsorbed on mass unit of algae biomass increased with increasing of Pb (II) concentration. The opposite variation of these two parameters (q (mg/g) and R (%)) is determined by the fact that at high concentrations of Pb (II) the available superficial functional groups are occupied, and in consequence the diffusion of Pb (II) ions to the un-reacted functional groups are inhibited (Uncun H., et al, 2003).

5. Equilibrium modelling: The equilibrium adsorption isotherm models are very important in the design of adsorption systems. The parameters calculated from these equilibrium models often provide some insight into both the adsorption mechanism and the surface properties and affinity of the adsorbent (Bulgariu, L. et al, 2007).

The adsorption isotherm, which represents the equilibrium distribution of Pb (II) ions between the solid phase of adsorbent and aqueous solution is shown in *fig. 5*.

Two linear isotherm models equations, Langmuir and Freundlich, are used for the mathematical description of adsorption mechanism between Pb (II) and algae biomass.

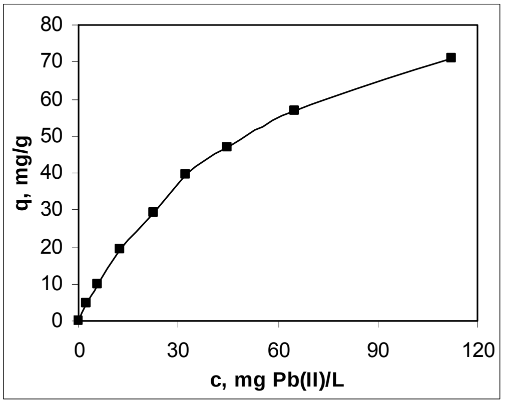


Figure 5 **Adsorption isotherm of Pb (II) on algae biomass (pH = 5, 4 g algae biomass/L, time = 24 h)**

The Langmuir isotherm model (Chong, K.H., Volesky, B., 1995; Ho, Y.S. et al, 2002) is based on the monolayer adsorption onto homogeneous surface containing a finite number of accessible sites, and can be used to estimate the maximum adsorption capacity, corresponding to adsorbent surface saturation (q_{max}, mg/g).

The constants of Langmuir model can be determined from linear form, expressed by the relation:

$$\frac{c}{q} = \frac{c}{q_{\max}} + \frac{1}{q_{\max} \cdot K_L} \qquad (3)$$

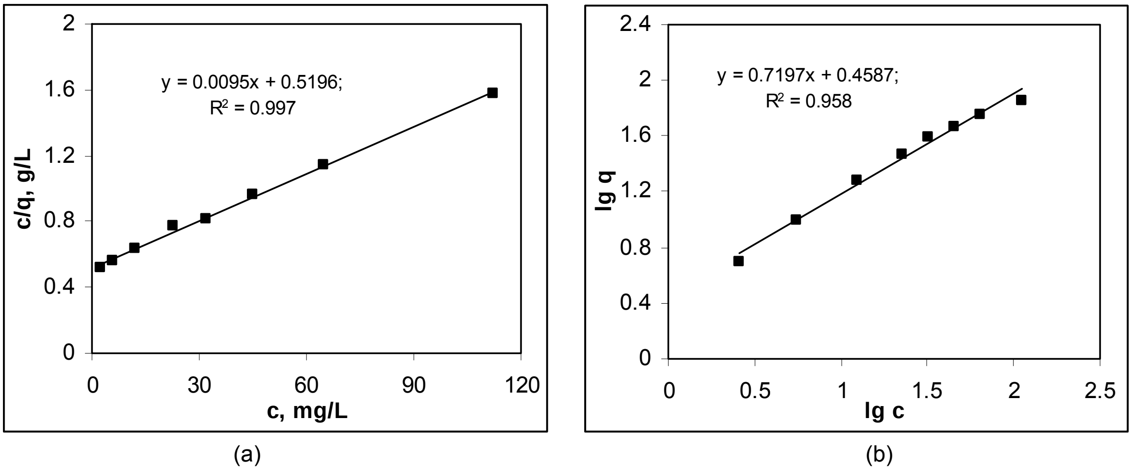
where: q_{max} – maximum adsorption capacity upon complete saturation of adsorbent surface, K_L – Langmuir constant.

The Freundlich adsorption model (Chong, K.H., Volesky, B., 1995; Ho, Y.S., et al, 2002) is refers to the adsorption on highly heterogeneous surface and describe the adsorption process from diluted solutions. The Freundlich constants can be determined from linearized equation:

$$\lg q = \lg K_F + 1/n \cdot \lg c \qquad (4)$$

where: K_F is an indicator of adsorption capacity, and n is a constant that characterized the affinity between adsorbent and Pb (II) ions.

The graphical representations of Langmuir and Freundlich isotherm models for Pb(II) adsorption onto algae biomass are presented in *fig. 6*, and the values of isotherm models constants are summarized in *tab. 1*. The best –fit equilibrium model was determined based on the linear regression correlation coefficient (R^2).



(a) (b)

Figure 6 **Linear representation of Langmuir (a) and Freundlich (b) isotherm models for Pb (II) adsorption on algae biomass**

Table 1

Isotherm constants for Pb (II) adsorption by algae biomass

Langmuir model			Freundlich model		
R^2	q_{max}, mg/g	K_L, L/mg	R^2	n	K_F, mg $L^{1/n}$/g $mg^{1/n}$
0.997	105.263	0.018	0.958	1.389	2.875

The values of correlation coefficients (R^2) show that the adsorption data are very well represented by Langmuir isotherm model, indicating the formation of monolayer coverage of the adsorbate on the outer surface of adsorbent. The maximum adsorption capacity (q_{max}, mg/g) is 105.263 and the Langmuir constant (K_L) if 0.018 L/g. The value of Langmuir constant, which characterize the binding energy of adsorption, confirm the chemical nature of the Pb (II) adsorption by algae biomass.

On the other hand, the Freundlich constant (n), which estimate the adsorption intensity of the Pb (II) ions on the algae biomass surface, is higher than 1, indicating the favourable adsorption process, even at high metal ion concentrations.

The variation of free Gibbs energy (ΔG) was calculated from Langmuir constant, using the following equation:

$$\Delta G = - RT \ln K_L \qquad (5)$$

where: R is the universal gas constant (8.314 J/mol K), and T is the absolute temperature.

The negative value of ΔG (-20.17 kJ/mol) indicates that the adsorption process of Pb (II) ions from aqueous solutions onto algae biomass is feasible and spontaneous.

CONCLUSIONS

The biomass of the marine algae *Ulva lactuca* sp. demonstrated a good capacity for Pb (II) ions adsorption, and can be considered a potential adsorbent for effluents treatment process.

The efficiency of adsorption process depends by the initial solution pH, algae biomass dose, metal ion concentration and contact time. The optimum experimental conditions were found to be an initial solution pH of 5.0, 4 g/L algae biomass dose and a contact time of minimum 60 min. The algae biomass possesses a relative high adsorption capacity of 71.10 mg/g (for an initial Pb (II) concentration of 702.52 mg/L), confirming that under these experimental conditions this material can be effectively used as adsorbent.

The equilibrium data concerning the adsorption of Pb (II) ions onto algae biomass are very well fitted by Langmuir isotherm model. The calculated isotherm constants indicate chemical nature of adsorption process and a monolayer capacity of 105.26 mg/g.

In addition, the negative ΔG value confirms that the adsorption process of Pb (II) ions from aqueous solutions onto algae biomass is feasible and spontaneous.

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