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Preparation, Characterization and Lead Biosorption Performance of Immobilized *Cystoseira merica* Collected from Jazan Coasts

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Abstract : Immobilized *Cystoseira merica* showed increasing intraparticular diffusion of lead, stability of the metal binding and affinity for lead. Equilibrium lead concentration was attained after 10 h. The maximum lead uptake was 1.43 mmol/g. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) microanalysis showed a uniform distribution of lead on the immobilized biomass. Immobilized *Cystoseira merica* could be repeatedly used with high efficiency.
Keywords : *Cystoseira merica*, Immobilization, Lead, Biosorption.

Introduction

Contamination of water supplies with metal is an area of concern both nationally or internationally where the challenge to remediate the hazardous metal containing waste streams from present or former mining operations, industrial sites, and ground waters is immense. With increasing environmental awareness and the toughening of government policies, it has necessary to develop new environmental friendly ways to clean up contaminants using low-cost methods and materials (1). It is well known that heavy metals ions such as Pb^{+2} may cause severe health problems in animal and human because it can specially bind to proteins, nucleic acid and small metabolites in living organisms inhibiting their function.

Different methods have been proposed for the treatment of water and industrial waste water containing heavy metals (2). Such as biological treatment, procedures using a filtration membrane, advanced oxidation processes, electrochemical methods and adsorption processes have proven to be more viable alternative due to low cost of processing and instrumentation, ease of operation and no need for large facilities (3).Biomass immobilization is an essential step for an industrial scale-up of biosorption. Unlike biomass is its native state, immobilized provides biosorpent particles with the adequate size, density, and mechanical strength required by continuous systems, Besides, immobilization can save the cost of separating the biomass from the treated solution which can represent up to 60% of the total cost. This process also enables biomass regeneration in various adsorptions-desorption cycles. Alginate, a component of the outer cell wall polysaccharide of brown algae, preferred to be used for immobilization. The immobilized biomass showed higher affinity towards lead. Its affinity was about 25 times that alginate alone and about 30 times that of free alga, indicating a synergic effect between both components (4). This work describes the process of lead recovery from the solution by using immobilized *Cystoseira merica*. Kinetic and isotherm models were used for the quantitative description and prediction of the metal uptake behavior of thisimmobilized biomass. The beads were characterizedwith and without metal using field emission-scanning electron microscopy (FE-SEM) to determine the possible metal

binding mechanism and mapping of lead inside the biomass beads by using electron dispersive X-ray (EDX) analysis.

Materials and methods

1- Chemicals

Sodium alginate (by Sigma, molecular weight in the range 70-100 kDa), extracted was used for immobilization. Calcium chloride dehydrate (by Fluka) was used to prepare calcium alginate (Ca-AA) gel beads. Stock and test solution of lead were prepared from anhydrous $Pb(NO_3)_2$. Aqueous solutions were prepared with distilled water. Acetate buffer with pH5 was prepared.

2- Immobilization of algal biomass

The brown alga, *Cystoseira merica* was collected from the coast of the Red Sea at Jazan, Kingdom of Saudi Arabia.

Figure 1: The brown alga *Cystoseir america*

The alga was thoroughly washed with running tap water to remove salts and extraneous matters then washed with distilled water, dried in an oven at 40 ^oC to constant weight, ground, and sieved into fractions. The preparation of alginate xerogel beads and immobilized biomass beads is described elsewhere (5)

3-Isotherm studies

The biosorption experiments were carried out with monometallic solutions prepared from stock solutions of 0.5M of Pb^{+2} from chemical reagent of analytical grade. $Pb(NO_3)_2$. Initial pH value of the solutions was adjusted to be 5 with acetate buffer as recommended before (4). One gram of immobilized biomass was placed in contact with the metal ion solution-100 ml containing 5% buffer v/v- of different concentrations in the range 0.5- 4 mM in glass 250 cm^3Erlenmeyer's flasks. The flasks were left on shaker at 150 rpm at 32^oC overnight to allow complete equilibration. Initial and final metal concentrations were measured by Flam atomic absorption spectrometer (Varian model spectra AA220). In all experiments, triplicates were used. Biosorption of metal ions (q) in the sorption system was calculated using the mass balance.

$$q_e = \frac{V(C_i - C_e)}{W} \qquad (1)$$

Where V is the solution column (cm^3),W is the weight of hydrogel pieces (g), and C_i and C_e are the initial and final (or equilibrium) metal ion concentration (mmol of metaldm^{-3}) respectively.

The Langmuir sorption isotherm was used to fit the experimental biosorption data

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (2)$$

Where q_e is the metal uptake at equilibrium (mmol of metal g^{-1} of biomass) q_{max} is the maximum Langmuir uptake (mmol of metal g^{-1} of biomass), C_e is the final metal concentration at equilibrium (mmol of metal dm^{-3}), and b is the Langmuir affinity constant (dm^3 $mmol^{-1}$ of metal). The Langmuir affinity constant indicates the affinity between the biomass and a certain metal. The greater its value the greater is the affinity.

These sorption parameters can be calculated from the isotherm using a linear representation of the Langmuir model (C_e/q_e vs. C_e):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b q_{max}} \quad (3)$$

4-Sorption kinetic experiments

Samples of 1 g dm^{-3} immobilized biomass were exposed to a certain lead concentration (2.5 mM) under the same conditions as described for the batch experiments. At definite time intervals of contact, the lead concentration and the calcium released into the supernatant solution were measured by FAAS.

5-**Biosorption characterization, SEM and EDX analysis**

Examination of the immobilized biomass surface, before and after lead uptake, coated with a thin layer of gold, was made by using a scanning electron microscope (JEOL-JX-840). To analyze the cross section of metal loaded immobilized biomass coated with a thin layer of graphite, an electron probe X-ray microanalyzer in EDX mode (JEOLJX- 840) was used.

6-Biosorption-desorption cycles

The biosorption of lead by immobilized biomass is followed by desorption by washing the immobilized biomass after metal uptake with deionized water to remove any residual unbounded lead. The biomass (0.1 g dry weight) was thoroughly mixed with 100 cm^3 of 0.5 M $CaCl_2$. By stirring at room temperature, lead released then measured. Following each desorption process the biomass was washed with distilled water and reloaded with lead. The processes were repeated 4 times to assess the ability of the immobilized biomass to re-adsorb lead.

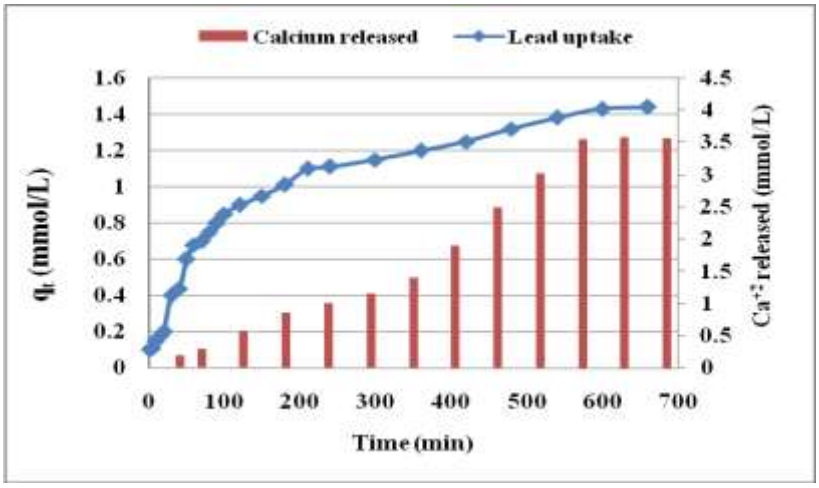
Results and Discussion

Biosorption equilibria

The evaluation of the sorption process as a unit operation was done by studying the equilibrium and the kinetics of biosorption. Sorption equilibrium is established when the concentration of metal in a bulk solution is in dynamic balance with that of the interface.

The kinetic studies

The results of kinetic experiment are presented in Figure (2). The amount of Pb^{+2} (mmol) adsorbed per gram of immobilized algal biomass versus contact time at initial metal ion concentration 2.5 mM and temperature 37^oC is shown. The increase of contact time leads to an increase in the amount of metal ion adsorbed. To follow lead uptake mechanism, the concentration of released Ca^{+2} was estimated parallel with lead uptake. The data showed that by increasing the contact time lead uptake as well Ca^{+2} release increase and the equilibrium reached within 10 h. This suggests that calcium could be involved in the metal uptake through an ion-exchange mechanism (5-7).



Figuer 2: Effect of contact time on adsorption of Pb^{+2} by immobilized biomass and Ca^{+2} ions released in the solution

Biosorption isotherm

Figuer.**3** shows the sorption isotherms of lead with both immobilized biomass and alginate xerogels as control. The initial solute concentration ranged from 0.5-4 mmol/L and the sorbent mass was 1g. The concentration of Pb^{+2} in the sorbent phase was calculated according to the equation 1. The sorption isotherm was obtained by plotting metal adsorbed (mmol) per unit mass (g) of sorbent against concentration of metal remaining in solution at equilibrium. The sorption isotherm was fitted to the Langmuir model Figuer. **3a&b**, and the corresponding parameters that quantify this process are shown in Table **1**. The equilibrium metal uptake of alginate xerogels was 1.11 mmol/g lower than that of immobilized algae (1.43 mmol/g). These values were compared with those of other sorbents found in the literature (8), indicating that immobilized alga is among the best biosorbents for the treatment and recovery of lead from aqueous streams.

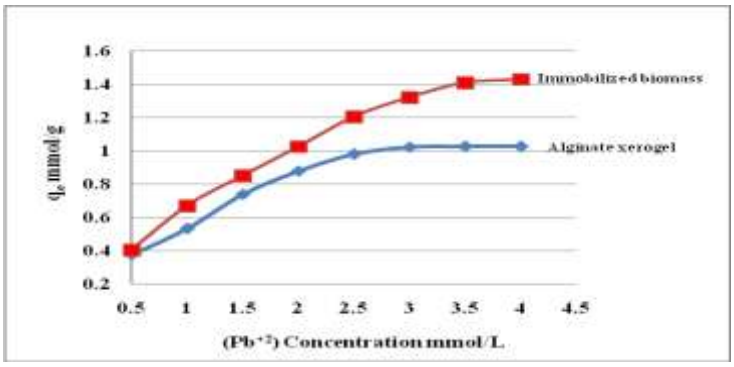


Figure 3a: The Langmuir adsorption isotherm of Pb^{+2} onto immobilized *Cystoseira merica*

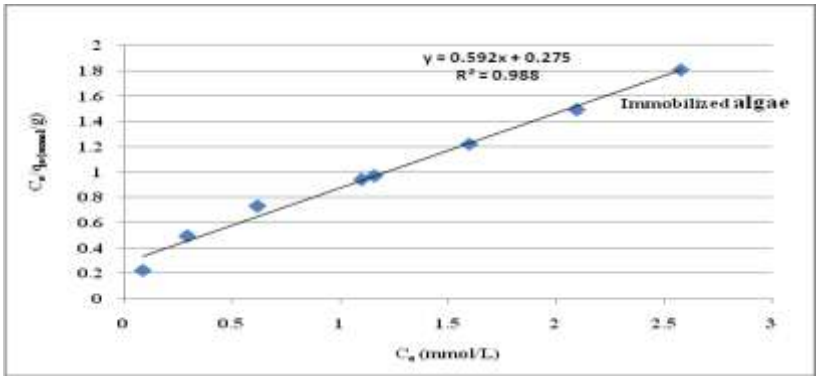


Figure 3b: Langmuir isotherm plot for adsorption of Pb^{2+} ions onto immobilized *Cystoseira merica*

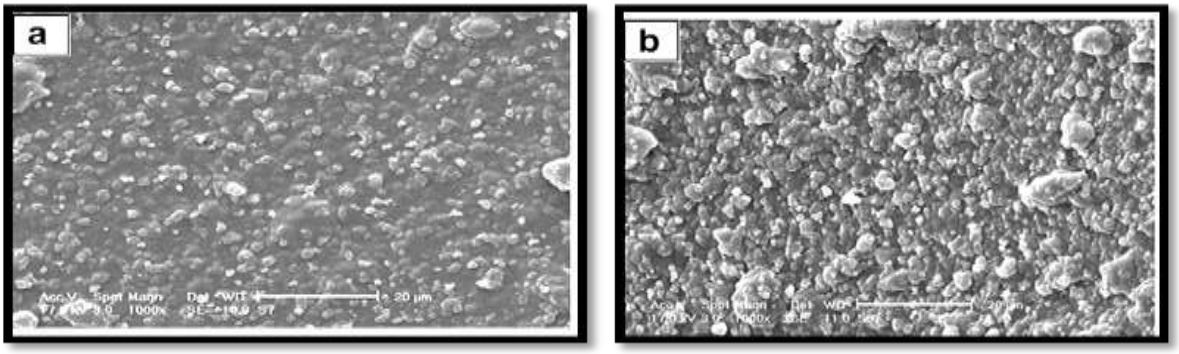
The presence of *Cystoseira merica* also increased the stability of the metal binding and the affinity for lead with respect to alginate xerogels. Therefore, immobilized biomass has different biosorbent properties than its isolated components. It was suggested that the alginate's affinity for heavy metals is related to the amount of guluronic and other uronic acids (8). These acids contain most of the carboxyl groups in alginate and would be mainly responsible for metal biosorption.

Table 1: Coefficients of Langmuir isotherm model for Pb^{+2} ions adsorbed onto immobilized algae

Model	Pattern	Value
Langmuir isotherm	q_{max} (mmol/L) b(L/mmol) R^2	1.68 2.15 0.988

Biosorbent characterization

The immobilized biomass beads are characterized by surface with high porosity with channels and open pores throughout the structure. Lead ions interacted with the functional groups on the external surface of the immobilized biomass beads. Figure 4a&b show SEM micrograph of immobilized biomass before and after lead uptake respectively.



Figuer4: SEM micrograph of immobilized C*yctoseira merica* surface before (a) and after (b) lead uptake

Mapping of lead distribution inside the immobilized biomass beads was determined using EPMA-EDX (electron probe X-ray microanalysis in EDX mode) micrographs. Figure 5 show the EDX micrograph of the cross section of immobilized biomass beads after lead uptake at pH 5. The distribution pattern of lead was measured on a unit surface area of 20 lm of beads.

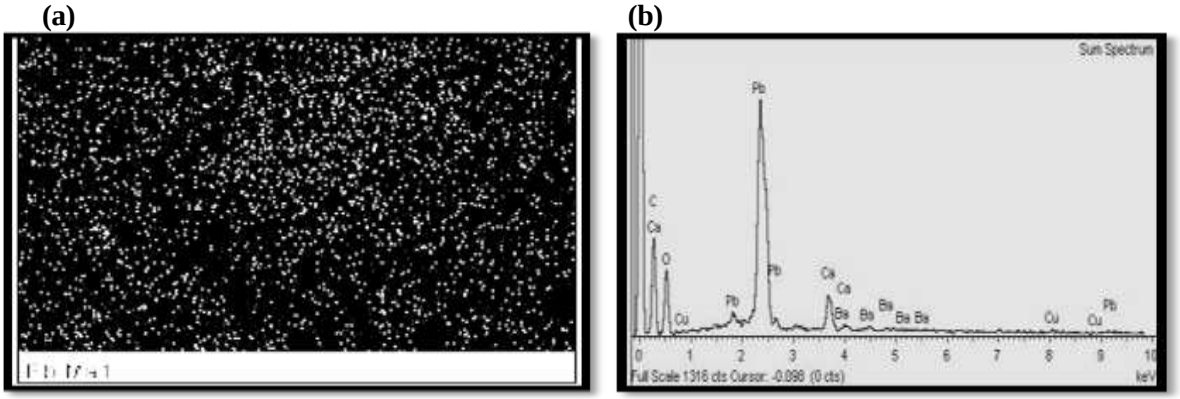


Figure 5: EDX monograph of immobilized C*yctoseira merica* beads after lead uptake (a) andthe sum spectrum for quantities of lead ions inside the beads (b).

As shown in Figure 5a the lead distribution on the algal tissue is homogeneous, that indicate Pb^{+2} ions are capable of penetrating into the beads and reacting with functional groups. Therefore, the immobilized

biomass beads can be considered as porous ion exchanger having high permeability.Carboxyl groups are the most abundant groups in polysaccharides and are the main groups involved in the biosorption of heavy metals with algae and other biomass (9-11).

Cadmium biosorption with fungi and sargassum diminished after blocking these groups with methanol (12, 13). The majority of these groups are located in the alginate of the algal cell wall and their negative charge can attract metal cations (14). Raize et al reported less nickel biosorption when alginate was extracted from the brown alga Sargassum (15).

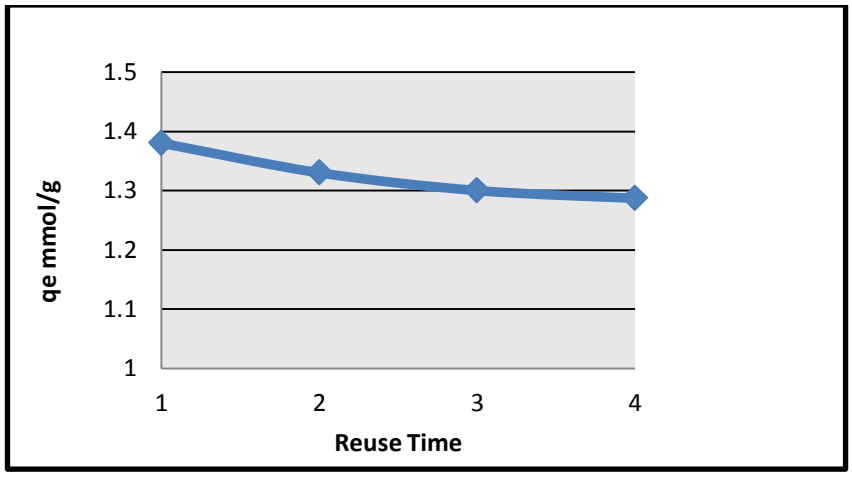


Figure 6: The reusability of immobilized C*yctoseira merica*

In order to show the reusability of the immobilized algal biomass, an adsorption-desorption cycle of lead ions was repeated four times using the same preparation. The adsorption capacity did not noticeablychange onlya maximum 10% reduced capacity was observed after the fourth time. This result showed that the produced immobilized biomass could be repeatedly used in heavy metal adsorption studies without significant losses in their initial adsorption capacities.

Conclusion

The immobilized algal biomass, C*yctoseira merica* showed high affinity towards lead. The kinetic studies showed that the mechanism of biosorption depended on ion exchange between lead and calcium and the equilibrium metal uptake of alginate xerogels was 1.11 mmol/g lower than that of immobilized algae (1.43 mmol/g). The mapping of Pb distribution showed a homogenous distribution, indicating that Pb ions are capable of penetrating into the beads which are highly permeable. Also the immobilized C*yctoseira merica* could be repeatedly used in heavy metal adsorption processes and available for dilute industrial and wastewater treatment.

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