

## Biosorption of lead (II) by pre-treated biomass of marine brown algae *Sargassum latifolium* and *Sargassum asperifolium*

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### ABSTRACT

The marine brown algae *Sargassum latifolium* and *Sargassum asperifolium*, harvested from the coast of the red sea, were investigated for their biosorption performance in the removal of lead (II) from aqueous solutions. The pretreatment of the biomass was carried out by using (0.2M) CaCl<sub>2</sub>, NaCl, NH<sub>4</sub>Cl and (1N) HCl, the pretreatment with NH<sub>4</sub>Cl showed the best biosorption capacities for both algal species. The isotherm and kinetic experiments were carried out at the pH 5.0 Isotherms experiments showed that the maximum capacities for lead uptake were 1.44 mmol/g and 1.47 mmol/g for *Sargassum latifolium* and *Sargassum asperifolium* respectively. The metal removal rates were rapid, with 90 % of the total adsorption taking place within 15 min and 45 min for *Sargassum latifolium* and *Sargassum asperifolium* respectively. Comparison with commercial resin indicated that the activated algae *Sargassum latifolium* and *Sargassum asperifolium* could be used as an efficient biosorbents for treatment of wastewater contaminated with lead (II).

**Keywords:** Biosorption; Lead (II); Marine brown algae; Wastewater treatment.

### INTRODUCTION

The removal and recovery of heavy metals from wastewater is important in the protection of environment and human health. A number of technologies such as chemical precipitation, evaporation, electroplating, adsorption and ion exchange processes have been used to remove heavy metals from waste water. However these technologies are most suitable in situation where the concentrations of heavy metal ions are relatively high. They are either ineffective or expensive when heavy metals are present in the waste water at low concentration or when very low concentrations of heavy metals in the treated water are required (Kuyucak and Volesky 1988).

One of the promising techniques for the removal of metals is the use of living or non living

organisms and their derivatives. Indeed, a wide variety of microorganisms (both living and nonviable) have been found to be capable of sequestering trace levels of metal ions from diluted aqueous solutions. The non viable forms have been proposed as potential sorbent, since these are essentially dead materials, which require no nutrition to maintain the biomass. Problems associated with metal toxicity in living biomass and the need to provide suitable growth conditions also don't arise. Indeed, many early studies have shown that non living biomass may be even more effective than living cells in sequestering metallic elements. Over the past two decades, much effort has been directed at identifying readily available biomass which, in its non living state, is capable of effectively removing heavy metals. One of the most promising types of biosorbents is marine algal biomass (Ping *et al.*, 2004).

Marine algae, a renewable natural biomass, have attracted the attention of many investigators as organisms to be tested and used as a new analytical reagents to adsorb metal ions such as Cu, Cd, Pb, Cr, and Au. Such organisms have been shown to perform very well for this type of application because they have a uniform cell size and a number of different metal binding sites on their cell walls. These sites include carboxyl groups from amino acids and polysaccharides and sulfhydryl groups (Hamdy, 2000).

Biosorption of metals is not based on only one mechanism. It consists of several ones that quantitatively and qualitatively differ according to the type of biomass, its origin and its processing. Metal sequestration may involve complex mechanisms, mainly ion exchange (Myklestad, 1968 and Schiewer & Volesky 2000), chelation, (Steginsky *et al.*, 1992), adsorption by physical forces and ion entrapment in inter- and intra fibrillar capillaries and spaces of the structural polysaccharide cell wall network (Davis *et al.*, 2003).

Lead is extremely toxic and can damage the nervous system, kidneys, and reproductive system, particularly in children. Lead has been found in at least 1026 of 1467 National Priorities List sites identified by the US Environmental Protection Agency (EPA). The EPA requires lead in drinking water not to exceed 0.015 mg/L.

In a previous work, (Sahera, 2005) concerned studying the nature of the marine environment in Gizan city, KSA, the study showed that Pb is the common pollutant metal in that area and different species of marine brown algae growing there were able to chelate Pb ions from the sea water with high efficiency. *Sargassum* species, the predominant species, showed high affinity towards Pb. Depending on these results the objective of the present work was to assess the potential of two locally derived marine algae, *Sargassum latifolium* and *Sargassum asperifolium* for the biosorption of lead. Using different methods for pre-treatment of biomass and study the equilibrium isotherm and the uptake kinetics.

## MATERIAL AND METHODS

### The algal biomass

The raw biomass of *Sargassum latifolium* and *Sargassum asperifolium*, (brown algae) were harvested, during the spring season, from Haras El Hedood location on the costs of the red sea at Gizan city, KSA. The biomass was thoroughly washed with running tap water to remove salts and extraneous matters then rewashed with distilled water. The washed algae were then sun dried and ground prior the use.

### Chemicals

Analytical grades, standard solutions of lead nitrate  $Pb(NO_3)_2$  and 0.2M calcium chloride  $CaCl_2$ , sodium chloride NaCl, ammonium chloride  $NH_4Cl$  and 1 N HCl were used. Buffer solutions were prepared from  $CH_3COONa/CH_3COOH$ .

### Pre-treatment of the algal samples

Different methods of pre-treatment were tested in this work before subjecting the algal samples, of both two species, to the heavy metal solution.

#### A) HCl pre-treatment

The method was carried out as described by Hamdy, (2000) 10 g of each alga were suspended in 200 ml distilled water, and the pH values were recorded. The suspension of each alga was then titrated by using HCl (1N) with stirring. Addition of the acid was continued till the evolution of  $CO_2$  ceased and the pH remained constant at pH 2 for 3 min. The algal mass was then separated by centrifugation, suspended in distilled water, stirred for 5 min, and the algal biomass was separated by centrifugation. The process was repeated several times till the pH become almost neutral. The algal masses were then treated with acetone quickly for one minute as recommended by Ofer *et al.*, (2003). By doing so, more metal sites become active because of structural changes in the cell wall. In addition, the acetone treatment also remove most of the water originally present in the biomass, which renders it resistant to microbial spoilage, then the algal samples dried to constant weight.

### Pretreatment with divalent and monovalent cations, (methods B, C and D)

A sample of 20 g of biomass was treated with 0.2M CaCl<sub>2</sub> solution (400ml), divalent cations, for 24 h with slow stirring as described by Kaewsarn and Yu (2001)(method B). Another two sets were prepared for pretreatment with monovalent cations such as 0.2 M NaCl (method C) and 0.2M NH<sub>4</sub>Cl (method D). Sodium chloride was used before as regenerating agent at high concentration 2 M by Feng and Aldrich (2004). Ammonium Chloride was reported to be a good activating agent for treatment of Bentonite where it was used before (Bizreh, 1989). His study showed the ability of ammonium chloride to increase the specific surface of Syrian Bentonite by increasing the adsorptive sites on the surface. The pH of the three experiments was kept constant at (5.0) by using acetate buffer (Hamdy 2000). The treated biomass was washed several times with distilled water to remove excess cations from the biomass, then dried in an oven at 60 °C for 24 h and sieved to get a uniform particle size of 300-600 µm. All experiments were conducted at room temperature (25±1 °C).

### Coupling between HCl and calcium chloride pretreatment (method M)

In this method we made coupling between the above mentioned two methods where we started the pretreatment with HCl as described in the first method but without treatment with acetone. After adjusting the pH of the protonated sample to neutral then centrifuged and the biomass dried in an oven. The dried biomass directly treated with 0.2 M CaCl<sub>2</sub> solution as described in method B.

### Isotherm Determination (Bach equilibrium sorption experiments)

A series of glass vials were prepared containing lead nitrate solution (100 ml containing 5 ml of acetate buffer) of known concentrations in the range 0.5-4.5 mM. Weighed amounts (200 mg, dry) of the five above mentioned pre-treated algal biomass, as well as the native biomass, were added to each vial respectively. The suspensions were mildly agitated at room temperature for 24h. The solutions pH was adjusted to the required value (5). Following the sorption reaction period, the liquid was separated from the biomass by decanting. Metal free blank was used as control and lead concentrations

of the samples supernatant were determined in each vial with an atomic absorption spectrometer (Varian, model spectra A.A 220) to follow lead (II) adsorption by the algal biomass. In all experiments, triplicates were used. Standard deviation did not exceed ± 10%. Biosorption of metal ions (q) in the sorption system was calculated using the mass balance

$$q = \frac{V(C_i - C_e)}{W} \quad \dots 1$$

where V is the solution volume, W is the amount of biomass, and C<sub>i</sub> and C<sub>e</sub> are the initial and final (or equilibrium) metal concentrations, respectively.

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

$$q_e = \frac{q_{\max} \cdot b \cdot C_e}{1 + bC_e} \quad \dots 2$$

where q<sub>max</sub> and b are Langmuir constants which reflects the maximum metal sorption capacity and the affinity between metal ion and biosorbent.

The parameters in equation (2) were then obtained by using a least square linear regression analysis on each set of isotherm data and are presented in Table 1.

### The Kinetic experiment

Kinetic experiments were carried out by using NH<sub>4</sub>Cl pre-treated biomass where it is the method of selection. Kinetic experiments were conducted in continuously stirred beakers (200 rpm) containing 500 ml of lead nitrate solution (1 mM, 2mM and 3.5mM) containing 75 ml of acetate buffer for keeping pH at 5 and 1g of the pre-treated algal biomass. Milliliter samples were drawn from the mixture at pre-determined time intervals for analysis (Kaewsarn and Yu 2001).

### Fourier transform infrared spectroscopy

FT-IR spectroscopy was used to detect vibration frequency changes in the algal sorbents. The spectra were collected by FT/IR300e (Jasco) spectrometer within the range 400-4000cm<sup>-1</sup> using

a KBr window. The background obtained from the scan of pure KBr was automatically subtracted from the sample spectra. All spectra were plotted using the same scale on the transmittance axis.

## RESULTS AND DISCUSSION

### Metal uptake by *Sargassum*

To study the sorption of metals which tend to form insoluble (micro) precipitates is more complicated due to the fact that the collection of the metal species is not due to the straight sequestration mechanism. In the case of lead in particular its solution chemistry is more complex. Addition of NaOH, which may be used to adjust the pH of the solution of lead nitrate results in the formation of insoluble  $Pb(NO_3)_2 \cdot Pb(OH)_2$  and  $Pb(NO_3)_2 \cdot 5Pb(OH)_2$  complexes which in turn result in distortion of the sorption results. This is the reason to use acetate buffer instead of NaOH to adjust the pH. Lead sorption was performed with different algal biomass samples (native and differently pre-treated) using solution of  $Pb(NO_3)_2$  with different initial concentrations (0.5 mM - 4.5 mM).

### Adsorption equilibrium

The isotherm experimental results are shown in figs 1,2. In both cases favorable isotherms are observed, and the data could be well modeled according to the Langmuir adsorption isotherm. Table 1 shows the maximum adsorption capacity ( $q_{max}$ ) and the affinity constant ( $b$ ) under the experimental conditions, i.e., pH 5.0. The comparison of lead sorption by *S. asperifolium* and *S. latifolium* as well as the previously published results, is summarized in Table 1. The results showed that HCl pre-treated biomass showed better results than that with  $CaCl_2$  pre-treated in both algal species that means the removal of  $CaCO_3$  by HCl pre-treatment resulted in increasing the maximum capacity of biomass for lead this observation is agree with that reported by Schiewer and Volesky (1995) where they reported that ion exchange does take place with a metal ion to proton ratio close to 1:2. The maximum uptake capacity ( $Q_{max}$ ) of protonated and  $CaCl_2$  pre-treated *S. latifolium* were 1.37 mmol/g and 1.307 mmol/g respectively. The same observation was detected for *S. asperifolium* where the protonated biomass showed  $Q_{max}$  1.358 mmol/

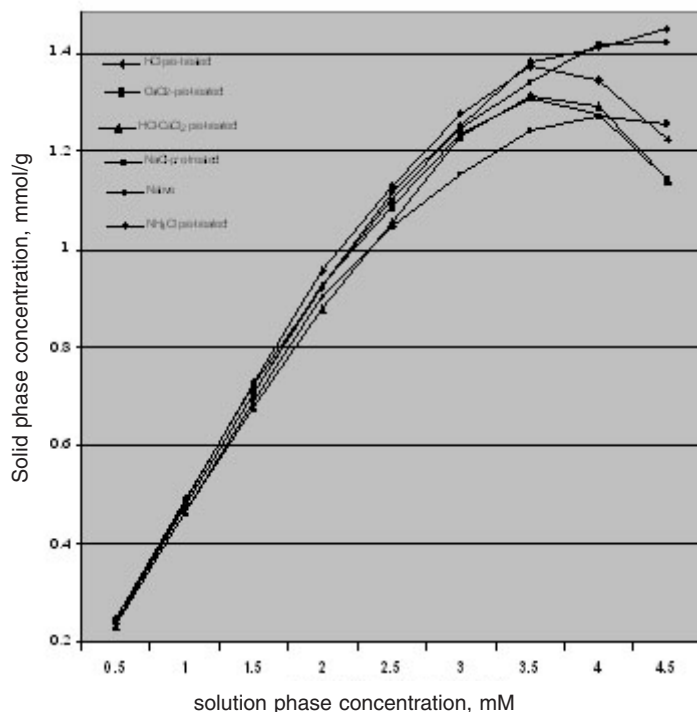
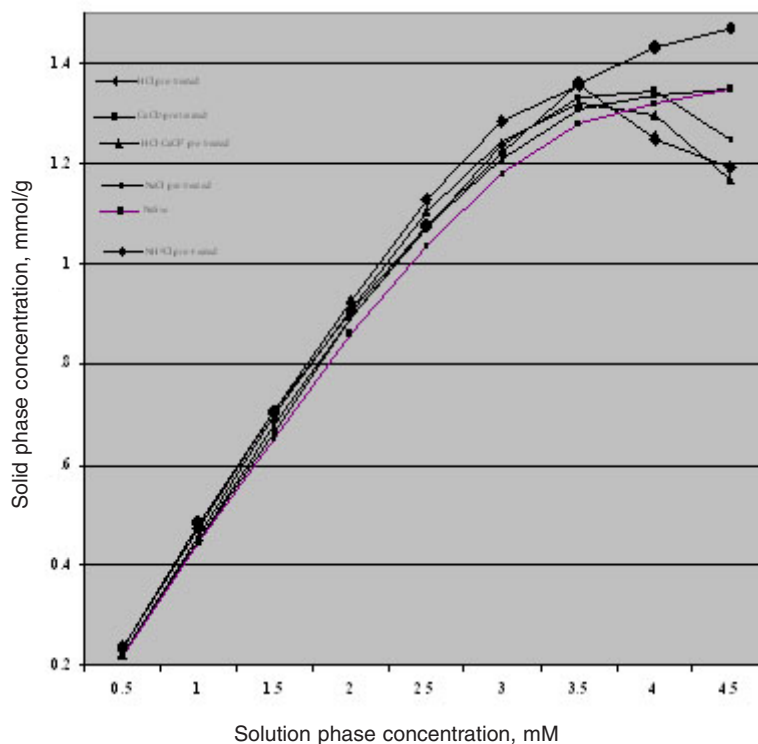


Fig. 1: Adsorption isotherms of lead(II) onto differently pre-treated biomass of *Sargassum latifolium* at pH (5)



**Fig. 2: Adsorption isotherms of lead(II) onto differently pre-treated biomass of *Sargassum asperifolium* at pH (5)**

g while for CaCl<sub>2</sub> pre-treated biomass was 1.332 mmol/g. The coupling between HCl and CaCl<sub>2</sub> for pre-treatment of the biomass resulted in disappearance of the enhancing effect of HCl, the maximum capacity for lead uptake was less than that showed by protonated biomass for both algal species. At the same time, biosorption efficiency of native biomass was higher than that the protonated biomass in *S. latifolium* and was with the same efficiency in *S. asperifolium*. This result with *S. latifolium* also in agrees with that observed by Schiewer and Volesky (1995). They reported that the reason may be due to a loss of binding sites during cross linking and acid washing.

Sodium chloride was used by Feng and Aldrich (2004) as regenerating agent of biosorption at concentration of 2 M. They found that the regenerated algal biomass showed a decreased sorption capacity for fine algal particles while coarse particles loss comparatively less alginate, depending on this observation we used sodium chloride for pre-

treatment of algal biomass as commercial and economic agent with concentration of 0.2 M the results showed that the  $Q_{max}$  for lead biosorption were 1.267 mmol /g and 1.35 mmol/g for both *S. latifolium* and *S. asperifolium* respectively By comparing these results with that of native biomass we well find that the efficiency of NaCl pretreated *S. asperifolium* is as the native biomass. Ammonium chloride pre-treatment showed a promising results where it increased the efficiency of lead uptake in both algal species especially at higher initial concentration of Pb(NO<sub>3</sub>)<sub>2</sub> solution. Fig 1 and 2 shows that the biomass which pre-treated with NH<sub>4</sub>Cl showed increasing in the maximum adsorption capacity  $Q_{max}$  by increasing the residual metal concentration.  $Q_{max}$  for lead uptake was 1.447mmol/g and 1.47mmol/g for *S. latifolium* and *S. asperifolium* respectively at initial metal concentration of 4.5mM.

**Adsorption Kinetics**

Fig (3 and 4) presents a typical set of

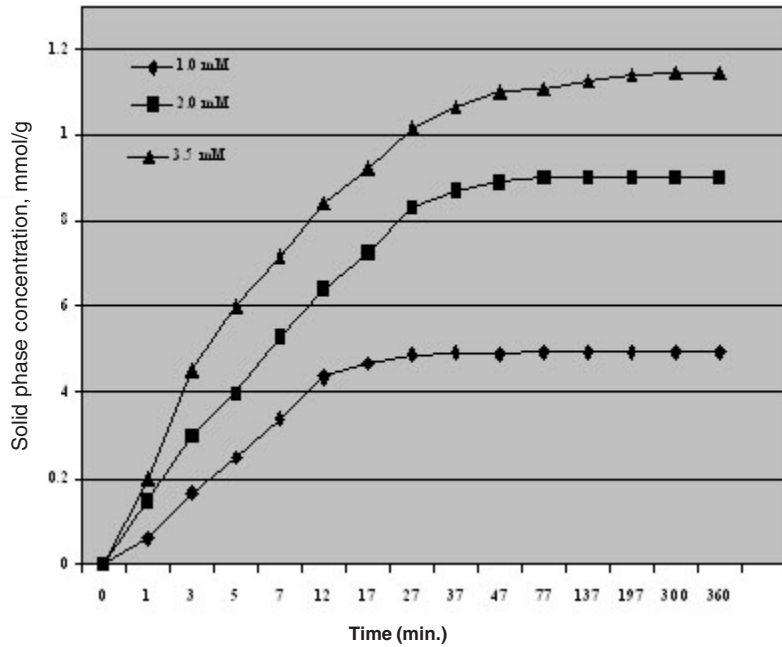


Fig. 3: Adsorption kinetics of lead (II) onto pre-treated biomass of *Sargassum latifolium* at various concentrations (dose: 2g/l, speed: 200 rpm, pH kept at 5)

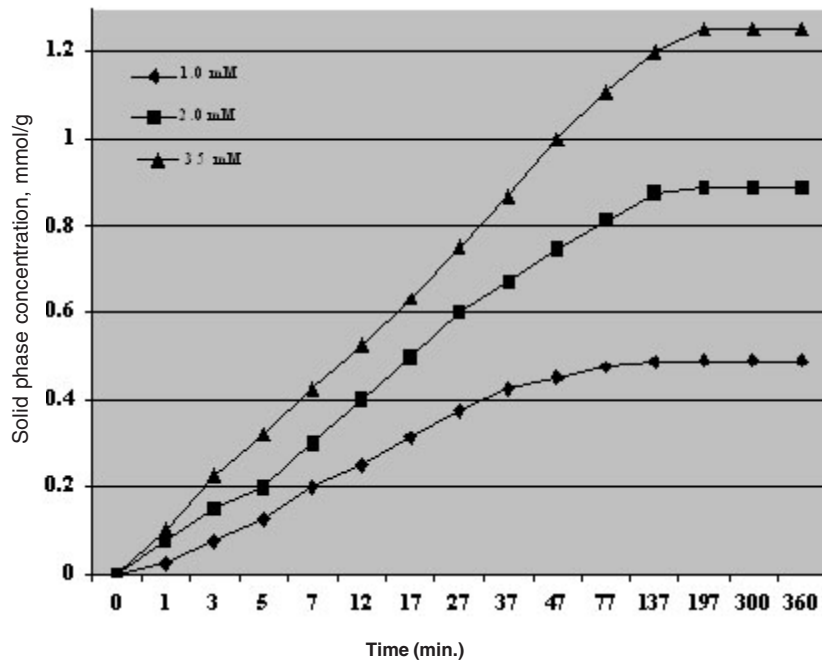


Fig. 4: Adsorption kinetics of lead (II) onto pre-treated biomass of *Sargassum asperifolium* at various initial concentrations (dose: 2g/l, speed: 200 rpm, pH kept at 5)

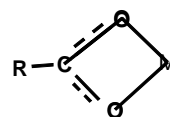


results of experiments of Pb(II) adsorption onto the biomass of *S. latifolium* and *S. asperifolium* respectively at different initial concentration. At initial concentration of 1 mM  $\text{Pb}(\text{NO}_3)_2$ , it was observed that 70% of the total adsorbed Pb from solution were removed within 8 min and 20 min of agitation for *S. latifolium* and *S. asperifolium* respectively. There were slightly slower rates for Pb uptake to about 15 min and 45 min where 90 % adsorption of lead for *S. Latifolium* and *S. asperifolium* were reached respectively. At initial concentration of 2 mM  $\text{Pb}(\text{NO}_3)_2$  the adsorption kinetics was slightly slower where the system reached more than 70% of the total lead uptake capacity within 12 min and 35 min for *S. latifolium* and *S. asperifolium* respectively. Then it goes slightly slower where 90 % of removal of total Pb uptake was occurred after 40 min and 77 min for *S. latifolium* and *S. asperifolium* respectively. At higher lead concentration, 3.5 mM, it was observed that 70% uptake of total adsorbed lead was occurred after 20 min and 70 min for *S. latifolium* and *S. asperifolium* respectively. This result show the good efficiency of *S. latifolium* where the rapid kinetics has significant practical importance because it may facilitate using of smaller reactor volumes, thus ensuring efficiency and economy. Similar rapid metal uptake has been reported for lead uptake by *Ecklonia radiate* biomass (Matheickal and Yu, 1996). It was reported that, in metal biosorption, one of the basic conditions for finding a good and competitive biosorbent (to conventional metal removal process) is metal uptake capacity of approximately 1 mmol metal/g dry weight biomass or 100 mg/g dry biomass ( Schiewer and Volesky, 2000). The lead uptake capacities of *S. latifolium*<sup>(d)</sup> and *S. asperifolium*<sup>(d)</sup> (Table 1) are higher than this value where  $Q_{max}$  were 1.447 and 1.47 mmol/g respectively. Holan and Volesky (1994) reported on lead uptake capacities of different algal species, *S. natans* and *S. vulgare*, the reported values of lead uptake for both algal were lower than of Sargassum species in this study. Ping *et al.*, (2004) reported that *Ulva sp.* (green algae) has higher lead uptake capacity where  $Q_{max}$  is 1.46 mmol/g, comparable with  $\text{NH}_4\text{Cl}$  pre-treated *S. asperifolium* in this study. This result showing that although *S. asperifolium* has slower adsorption kinetics than *S. latifolium* but with higher adsorption capacity recommended for treatment of waste water with high lead pollution with a good efficiency.

#### Fourier transform infrared spectroscopy

The FTIR spectra of the pristine,  $\text{NH}_4\text{Cl}$  (0.2M) pre-treated biomass and lead-loaded brown marine algae *S. latifolium* and *S. asperifolium* are shown in Figs.5 and 6.

For the pristine *S. latifolium* and *S. asperifolium* biosorbents (samples a5 and a6, respectively), it was clear that the carboxylate ions gave rise to two bands: a strong asymmetrical stretching band at  $1627\text{cm}^{-1}$  and  $1631\text{cm}^{-1}$  and a weaker symmetrical stretching band at  $1427\text{cm}^{-1}$  and  $1430\text{cm}^{-1}$  respectively. The double bands of the carboxylate ion were identical with the observations made on Ca-alginate-based resin. After treatment with  $\text{NH}_4\text{Cl}$  the first peak did not shifted in both algal species but the second band did not shifted in *S. latifolium* but a small shift was detected with small extent,  $15\text{cm}^{-1}$  in *S. asperifolium*. After contact with the metal both peaks in (sample c5) were shifted with wave number  $11\text{cm}^{-1}$  but in (sample c6) the peaks shifts were  $27\text{cm}^{-1}$  and  $30\text{cm}^{-1}$ . The peaks values suggested the chelating (bidentate) character of the lead biosorption onto carboxyl groups. The structure of the metal bound to carboxyl ligands on the brown algae is likely to take the form



There is no band was detected at  $1125\text{cm}^{-1}$ - $1127\text{cm}^{-1}$  which corresponding to ether group in both algal sample. The bands at  $1052\text{cm}^{-1}$  (sample a5) and  $1056\text{cm}^{-1}$  (sample a6) wear assigned to the  $-\text{C}-\text{O}$  stretching of alcoholic groups. Both bands of alcoholic groups didn't change after pre-treatment with  $\text{NH}_4\text{Cl}$  but after contact with lead solutions shifted to lower frequencies; the shifts were  $7\text{cm}^{-1}$  and  $3\text{cm}^{-1}$ , respectively. Also the peak area reduced in both algal species.

The FTIR spectroscopic analysis indicated bands at  $2927\text{cm}^{-1}$ (sample a5) and  $2947\text{cm}^{-1}$  (sample a6) were assigned C-H stretch (superimposed on N-H stretch) (Silverstein and Webster 1998). After contact with lead, both band shifted to lower frequency, the shifts were  $30\text{cm}^{-1}$ ,  $23\text{cm}^{-1}$  respectively.

**Table 1: Langmuir isotherm constants for lead(II) adsorption onto pre-treated biomass of *Sargassum latifolium* and *Sargassum asperifolium* compared with Pb Uptake capacities for various adsorbents**

Adsorbents	$Q_{max}$ (mmol/g)	b(mmol/L)	R <sup>2</sup>	References
<i>F. vesiculosus</i> *	1.753			Holan and Volesky 1994
<i>F. vesiculosus</i> ***	1.106			Holan and Volesky 1994
<i>G. marginata</i>	1.53			Holan and Volesky 1994
<i>Ulva.sp</i>	1.46			Holan and Volesky 1994
Amberlite IR-120				
Wet	1.444			Holan and Volesky 1994
Dry	2.144			Holan and Volesky 1994
Duolite GT-73				
Wet	0.657			Holan and Volesky 1994
Dry	1.371			Holan and Volesky 1994
<i>Sargassum sp</i>	1.16			Ping Xin Sheng <i>et al.</i> 2004
<i>Sargassum natans</i>	1.22			Holan and Volesky 1994
<i>Sargassum vulgare</i>	1.10			Holan and Volesky 1994
<i>Sargassum fluitans</i>	1.285			Holan and Volesky 1994
<i>Sargassum asperifolium</i> <sup>a</sup>	1.358	8.64	0.97	Present study
<i>Sargassum asperifolium</i> <sup>b</sup>	1.332	4.3	0.97	Present study
<i>Sargassum asperifolium</i> <sup>m</sup>	1.332	6.12	0.98	Present study
<i>Sargassum asperifolium</i> <sup>c</sup>	1.35	4.12	0.99	Present study
<i>Sargassum asperifolium</i> <sup>d</sup>	1.47	4.98	0.99	Present study
<i>Sargassum asperifolium</i> <sup>n</sup>	1.35	3.71	0.99	Present study
<i>Sargassum latifolium</i> <sup>a</sup>	1.37	16.94	0.97	Present study
<i>Sargassum latifolium</i> <sup>b</sup>	1.307	15.37	0.97	Present study
<i>Sargassum latifolium</i> <sup>m</sup>	1.312	7.26	0.96	Present study
<i>Sargassum latifolium</i> <sup>c</sup>	1.267	7.97	0.99	Present study
<i>Sargassum latifolium</i> <sup>d</sup>	1.447	37.81	0.99	Present study
<i>Sargassum latifolium</i> <sup>n</sup>	1.42	11.47	0.99	Present study

\* cross linked with buffered formaldehyde (pH2)

a) HCl-pretreated biomass

c) NaCl (0.2M) pretreated biomass

m) HCl-CaCl<sub>2</sub> pretreated biomass

R<sup>2</sup> is the correlation coefficients of the isotherms

\*\*\* Native biomass material.

b) CaCl<sub>2</sub> pre-treated biomass

d) NH<sub>4</sub>Cl (0.2M) pretreated biomass

n) Native biomass

The FTIR spectroscopic analysis indicated bands at 640cm<sup>-1</sup> and 636 cm<sup>-1</sup> for (samples a5,a6, respectively) were assigned N-H out-or plane bend. After pretreatment with NH<sub>4</sub>Cl (sample b5) the peak shifted to lower frequency but after contact with lead the peak shifted to the higher frequency again and the peak area did not changed but in (sample b6) the shift was to the higher frequency and after contact with lead (sample c6) the band highly reduced. This result indicating the involvement of the N-H in the biosorption process.

The FTIR spectroscopic analysis indicated bands at 3409cm<sup>-1</sup> and 3397cm<sup>-1</sup> in (sample a5 and a6) representing bonded -OH and -NH groups. After pre-treatment with NH<sub>4</sub>Cl the first peak shifted to lower frequencies the shifts were 11 cm<sup>-1</sup> and 7 cm<sup>-1</sup> and the peak area did not changed, after contact with lead the first peak(sample c5) shift 3cm<sup>-1</sup> where in (sample c6) the interesting phenomenon was the sharp decrease in the band intensity of the bounded -OH and NH groups and shifted to the lower frequency, the shifts were 27cm<sup>-1</sup>. This result suggests the involvement of the amino group in the hydrogen bond formation.



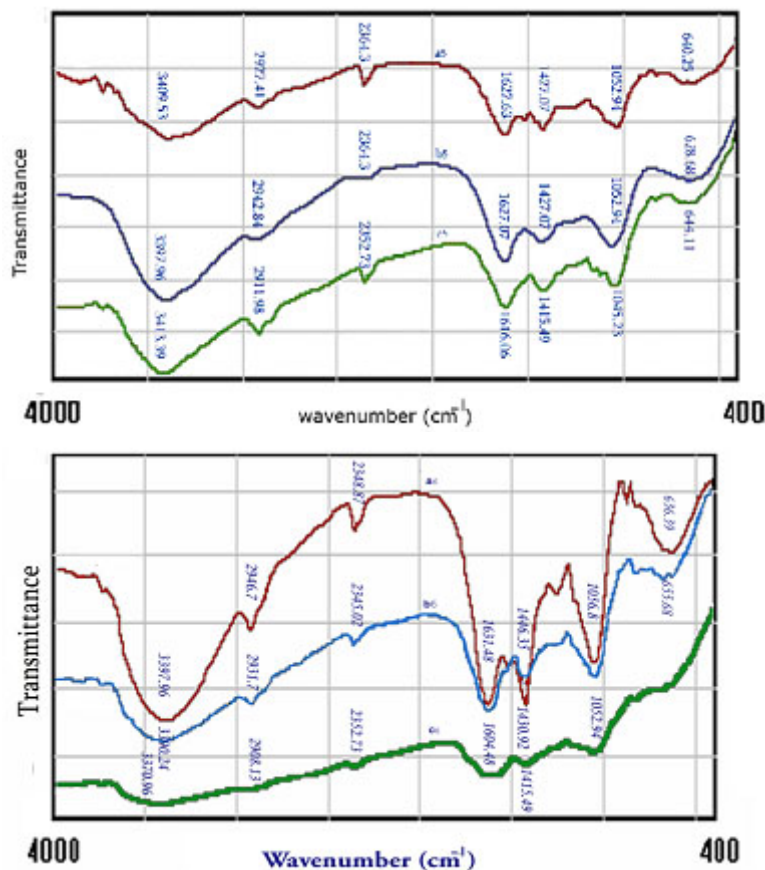


Fig. 5-6: FTIR spectra of *Sargassum .latifolium* and *Sargassum asperifolium*, respectively, (a5,a6) pristine biomass. (b5,b6) NH<sub>4</sub>Cl (0.2M) pre-treated. (c5,c6) lead-loaded.

#### Suggestion of Pb biosorption mechanism

Ping *et al.*, (2004) employed X-Ray – Photoelectron Spectroscopy to study the changes of binding energy (BE) of the coordination carbon atoms (C1s) in the biomass of *Padina sp.* and *Sargassum sp.* before and after metal adsorption. The results showed that in the case of Zn<sup>2+</sup> ion its adsorption was through ionic bonding with the carboxylate group instead of through coordination bonding since it has a completely filled d subshell. Similar spectra of lead and copper were observed in the uptake of lead and copper by calcium alginate based ion-exchange resin. The peak of Pb at 137.0 eV represents the bonding between Pb<sup>2+</sup> ion and carboxylate group where it has completely filled d subshell. At the same time, FTIR analysis showed chelating characteristics of metal coordination to the functional groups in the cell wall of the brown algae.

The functional groups involved in bivalent metal sorption included carboxyl and alcoholic in both algal species where in *S. asperifolium* additional function groups involved in the biosorption process are amino group and NH group. Sulfonate and ether groups were not detected in the spectra of both algal species. Depending on these results we can suggest the mechanism of Pb biosorption by *Sargassum* is based on ionic bond formation. The ion exchange between ammonium ion and the light metals (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>+2</sup> and Mg<sup>+2</sup>) in the pre-treatment stage of the biomass leads to swelling of the cells, facilitate the re-ion exchange stage when the biomass subjected to treatment with Pb(NO<sub>3</sub>)<sub>2</sub> solution. Since the atomic diameter of Pb is 0.65 Å and ammonium 1.43 Å so smaller Pb ions can easily replace ammonium ion so leads to quick Pb uptake kinetic.

The variation in the affinity of some divalent metals to alginates was demonstrated early on by Haug, 1961 and Haug and Smidsrød 1965. The alginate samples varied in affinity for divalent metals as a function of their M: G ratio. Furthermore, the affinity for divalent cations such as  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Zn^{2+}$ , etc. increased with the Guluronic acid content. The higher specificity of polyguluronic acids residues for divalent metals is explained by its zigzag structure. The rod-like shape of the poly-L-guluronic sections results in an alignment of two chain sections yielding an array of coordination sites with cavities suitable for divalent cations. This description is known as the "egg-box" model (Morris *et al.*, 1980 and Rees, 1981).

Alginate from *S. asperifolium* and *S. latifolium* harvested from the Egyptian red sea coast were isolated and their compositions and structures by  $H^1$  NMR were determined by Larsen *et al.*, (2003). They observed that both alginates contain more guluronic acid (G) than Mannuronic acid (M). Depending on this report we can explain why these two algal species involved in this study showed the high affinity towards  $Pb^{2+}$  uptake especially *S. latifolium* that with faster adsorption kinetics.

## Conclusion

Biosorption performance of the two brown macro algae namely *Sargassum latifolium* and *Sargassum asperifolium* were investigated for the removal of lead from aqueous solutions. The study indicated that the pretreated biomass with ammonium chloride could be used as an efficient biosorbent material for the treatment of lead(II) ions bearing wastewater streams. The pre-treated *S. latifolium* showed higher affinity ( $b=37.8$ ) than *S. asperifolium* ( $b=4.98$ ) towards binding with lead consequently the kinetic of adsorption was faster in *S. latifolium* than in *S. asperifolium*. 90 % of the total adsorption occurring within 15 min, at initial concentrations of 1 mM with maximum adsorption capacities ( $Q_{max}$ ) 1.447 mmol/g for *S. latifolium* where for *S. asperifolium* 90 % of the total adsorption occurred within 45 min for initial concentrations of 1 mM and the maximum adsorption capacities ( $Q_{max}$ ) 1.47 mmol/g. Overall, both algal species showed the highest potential as biosorbents for removal of lead from aqueous solutions. FTIR analysis showed that a little changed occurred in the structure of the biomass of *S. latifolium* after contact with lead where many function groups (carboxylic, alcoholic, amino and NH) are involved in the biosorption process in *S. asperifolium*.

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