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Biosorption of Pb(Ii) from Aqueous Solution by Brown Seaweeds

KEYWORDS: kinetics isotherms, Pb(II) biosorption, Padina tetrastromatica, Sargassum ilicifolium

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ABSTRACT *Removal of Pb(II) ions from aqueous solution was attempted using dried biomass of brown seaweeds Sargassum ilicifolium (Turner) C. Agardh and Padina tetrastromatica Hauck. The equilibrium absorption capacity varied with the concentration of heavy metal and maximum removal efficiency was observed at pH 2.5 in both the materials. Analysis of data using adsorption isotherms revealed that Langmuir equation is a better fit to the experimental data than the Freundlich equation. The pseudo-first-order and pseudo-second-order models were applied to the adsorption kinetics of Pb(II) ions. Results demonstrated that dried biomass of the seaweeds under investigation can be effectively used for the removal of Pb(II) ions from aqueous solutions. Characterization of the biomass was done using Fourier transform spectroscopy (FTIR) and Scanning electron microscopy (SEM) along with EDX.*

INTRODUCTION

Heavy metal pollution caused by industrial wastewater is increasing day by day and has become a most significant problem of this century (Park et al. 2006). Common techniques used for the removal of toxic heavy metals are too expensive and difficult to apply at low levels of heavy metals in wastewater (Banerjee 2002). Use of algal biomass as an adsorbent has lately been introduced by Volesky (1990). Amongst the various adsorbents marine algae are gaining attention due to their high capacity for metal uptake and availability in nature. The algal cell wall is made of a multilayer microfibrillar framework generally consisting of cellulose and amorphous material. A high proportion of alginate (14-40%) is present in marine algae. The major component of the alginate is alginic acid, a polymer composed of unbranched chains of 1, 4-linked β-D-mannuronic and α-L-guluronic acids (Percival and McDowell, 1967). Other negatively charged functional groups, such as the sulphonate groups of fucoidan, may contribute to heavy metal complexation. Fucoidan is a branched polysaccharide sulfate ester with L-fucose building blocks which are predominantly α (1→2) linked (Davis *et al.,* 2003).

Brown algae are known to have a high capacity for heavy metal removal as compared to red and green species (Davis et al., 2003; Hashim and Chu, 2004). In the present study the ability of brown seaweeds to remove heavy metals from aqueous solution was tested. The two seaweeds selected for the work are *Sargassum ilicifolium* (Turner) C. Agardh and *Padina tetrastromatica* Hauck. Both belong to the class Phaeophyceae. A search for a low-cost and easily available adsorbent material of biological origin has led to the investigation of potential metal biosorbents. The potential of metal uptake by these seaweeds was investigated using dried, powdered biomass. The process of biosorption was monitored with respect to different kinetic parameters.

In the present study dried biomass of brown algae was tested for removal of lead from aqueous solution. The adsorption capacity of two brown algal sps. Viz *Sargassum ilicifolium* and *Padina tetrastromatica* was determined. Kinetic studies involving the effect of pH, contact time, concentration of metal and biomass on the process of biosorption, FTIR and SEM-EDX was carried out to study the biosorption mechanism.

EXPERIMENTAL

Materials

Preparation of biosorbent

Sargassum ilicifolium (Turner) C. Agardh and *Padina tetrastromatica* (Hauck) thalli were collected from Malvan and Kunakeshwar (District -Sindhudurg) along the west coast of Maharashtra. Algal material was cleaned, washed with distilled water to remove dust and soluble impurities, then sundried, milled and stored at room temperature in airtight containers.

Chemicals

A stock solution of Pb(II) ions (1000mg/l in distilled water) was prepared using an analytical grade (S. D. Fine Chem. Ltd. India.) lead nitrate. This solution was diluted as required to obtain the desired concentrations of metal ranging from 100-1000 mg/l of Pb(II) ions.

Biosorption experiments

The experiment was set up in 250ml Erlenmeyer (Perkin Elmer, AAnalyzer 300) flask containing 50 ml metal solution and 100 mg of algal biomass. The flasks were kept on a rotary shaker at constant speed of ~170 rpm. After a desired time interval the biomass was separated using a filter paper. Initial and final concentration of metal was measured on AAS.

Effect of pH

The effect of pH variation from 2.0 - 5.0 was studied by adjusting the pH of metal solution using 0.1N HCl or NaOH. The experiment was set up using 100 mg biomass in 50 ml of lead nitrate (100 mg/l).The samples were analyzed after 80 min. The range for pH was set at 2-5 because most of the industrial effluents containing heavy metals are acidic (Macchi et al.1993). At more than 5 pH precipitation may occur.

Effect of contact time

In order to understand the effect of time on the processes of biosorption the agitation period was varied from 0 to 80 min. The experiment was set up at pH 2.5 using 100 mg biomass in 50 ml of lead nitrate solution (100 mg/l).The Samples were removed after every 10 min interval and analyzed on AAS.

Effect of biomass

The experiment was carried out using 50 ml of 100 mg/l lead nitrate at pH 2.5. The biomass dosage was varied from 20 mg to 100 mg and the samples were analyzed after 80 min on AAS.

Effect of metal concentration

The effect of metal ion concentration on the biosorption by *S.ilicifolium* and *P.tetrastromatica* was studied by varying it from 100 mg to 1000 mg/l. The experiment was set up at pH 2.5, using 100 mg biomass and was run for 80 min.

The amount of metal uptake, q was determined using the following equation (Eq.1):

$$q_e = \frac{(C_o - C_e)}{M} \times V \qquad (1)$$

Where 'q_e' represents the amount of adsorption at equilibrium (mg/g),

M is mass of the alga (mg),

C_o and C_e are the initial and final concentrations of metal ion (mg/l).

V is the volume (ml)

The removal efficiency was determined by the formula (Eq.2):

$$\text{Biosorption}(\%) = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (2)$$

The mechanism of biosorption was explained using Langmuir and Freundlich isotherms.

Langmuir isotherm

Langmuir isotherm is best known and most widely applied metal adsorption isotherm (Langmuir 1918). This isotherm model assumes that chemisorption occurs between the adsorbent and adsorbate through the formation of an ionic or covalent bond. The Langmuir model is expressed by the equation (Eq.3):

$$C_e/q_e = C_e/q_m + 1/q_m b \quad (3)$$

Where, q_e is metal sorbed at equilibrium (mg/g), C_e is equilibrium metal ion concentration (mg/l), q_m is the maximum amount of metal sorbed (mg/g), b and c are constants.

Freundlich isotherm

Freundlich isotherm does not provide information on the monolayer adsorption capacity of biosorbent. Following equation is used to explain the metal adsorption (Eq.4):

$$q_e = k_f C^{1/n} \quad (4)$$

This equation can be converted in the linear form by taking the logarithm of both sides (Arivoli et al. 2008) as expressed in (Eq.5):

$$\log q_e = \log k_f + 1/n \log C_e \qquad (5)$$

Where, q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/l) and K_f and n are the Freundlich constants. The values of K_f and n can be calculated from the intercept and slope.

Kinetic models

Kinetic models are often used to explain the process of metal biosorption.

The pseudo-frist-order kinetic equation may be written as (Eq. 6):

$$dq_t/dt = k_1(q_e - q_t) \qquad (6)$$

The integrated form of above equation becomes (Eq.7):

$$\log\,(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (7)$$

q_e and q_t are the amount of adsorption at equilibrium (mg/g) and time t (min), k_1 is the rate constant of the pseudo-first-order adsorption (Babu and Gupta 2008).

The corresponding pseudo-second-order rate equation is written as (Eq.8):

$$dq_t/dt = k_1(q_e - q_t)^2 \qquad (8)$$

Whereas k_2 is the rate constant of pseudo-second-order adsorption (g mg $^{-1}$ min^{-1}) (Ho and McKay 1998).

RESULTS AND DISCUSSION

Effect of pH

Maximum sorption of lead took place at pH 2.5 in both *S.ilicifolium* and *P.tetrastromatica*. The value obtained for *S.ilicifolium* was 42.64 ± 0.10 and for *P.tetrastomatica* it was 45.01 ± 0.06 (mg/l) within 80 min. The decreased rate of biosorption at higher pH may be due to decrease in the solubility of metal, forming complexes and causing precipitation (Vijayaraghavan and Yun , 2008).

Effect of contact time

The maximum adsorption of lead occurred after 30 min in *S.ilicifolium* (42 ± 0.10mg/l, or 85.28 %) whereas it was after 60 min in *P.tetrastromatica* i.e. 45 ± 0.06, or 90.02 %.

Effect of initial metal concentration

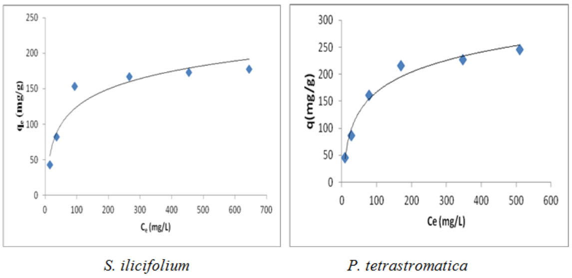
As the initial concentration of metal increased, the amount adsorbed also increased in both the biosorbents. The uptake of metal ions raised from 42.64 ± 0.10 mg/g to177.365 ± 0.06 mg/g in *S.ilicifolium* and 45.01±0.06 mg/l to 245.135 ± 0.00 in *P.tetrastromatica*. This may be due to large number of metal ions available for adsorption.

Effect of Biomass

Lead adsorption increased with increase in the biomass. Maximum adsorption was observed with 100 mg biomass in both the materials. Removal efficiency increased with increase in the biomass dose, as contact surface area increased.

Adsorption Isotherms

The adsorption isotherm indicates how the adsorbed molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. Fig 1 presents the plot of amount of Pb(II) adsorbed against its concentration in aqueous phase at equilibrium. Isotherm data obtained with a range of initial lead concentration showed an increase in the amount of lead adsorbed when the initial lead concentration was raised from 100-1000 mg/l. The adsorption data has been analyzed using two adsorption models applying Langmuir and Freundlich isotherm equations.



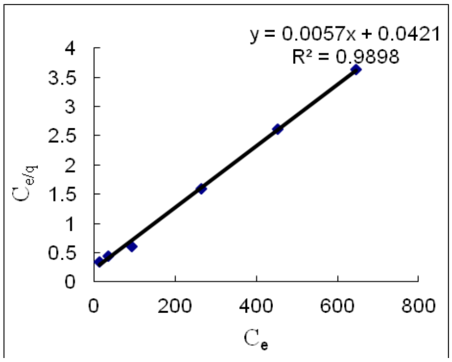
S. ilicifolium ***P. tetrastromatica***

Fig.1. Adsorption isotherms for Pb (II) ions on *S .ilicifolium* and *P .tetrastromatica.*

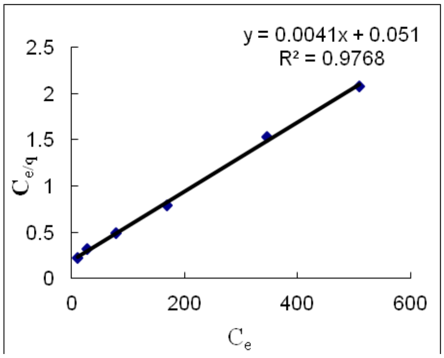
Langmuir model

The experimental data of adsorption of Pb(II) ions onto *S.ilicifolium* and *P.tetrastromatica* is better explained by the Langmuir isotherm model.

The magnitude of R_L was 0.011- 0.334 for *Sargassum* and 0.023 - 0.554 for *Padina* which is consistent with the requirement for the favorable adsorption. The high value of the correlation coefficient, R^2, suggested better co-ordination between the parameters and indicated monolayer adsorption of Pb(II) ions onto the biosorbent surface (Fig. 2).



S. ilicifolium

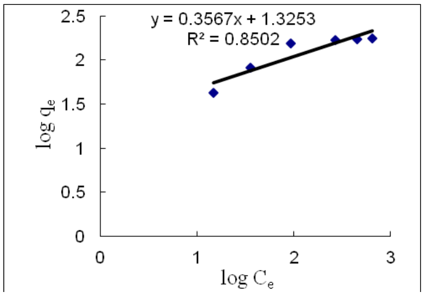


P. tetrastromatica

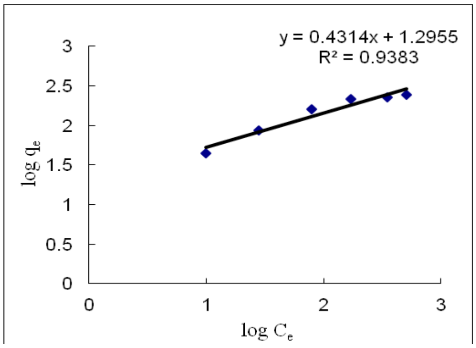
Fig.2. Langmuir constants for the adsorption of Pb(II) ions by *S.ilicifolium* and *P.tetrastromatica.*

The Freundlich model

The values of K_f and n obtained in the present work are given in the Table 1. The values of the correlation coefficient, R^2, in this case indicated that Freundlich model is less fitted to the experimental data than the Langmuir equation (Fig. 3).



S. ilicifolium



P. tetrastromatica

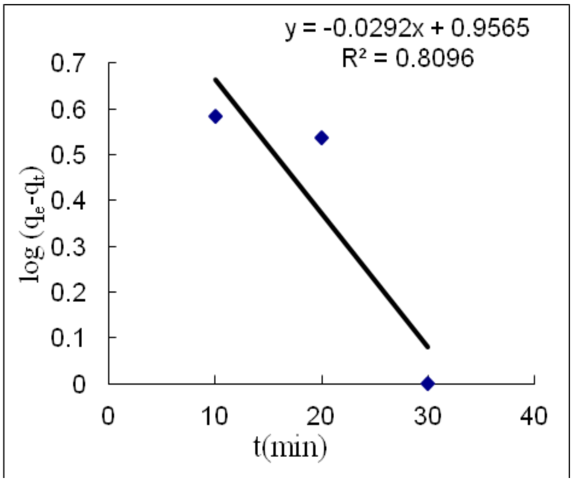
Fig.3. Freundlich constants for the Adsorption of Pb(II) ions by *S. ilicifolium* and *P.tetrastromatica.*

Table 1. Langmuir and Freundlich constants for the adsorption of Pb(II) ions by brown seaweeds.

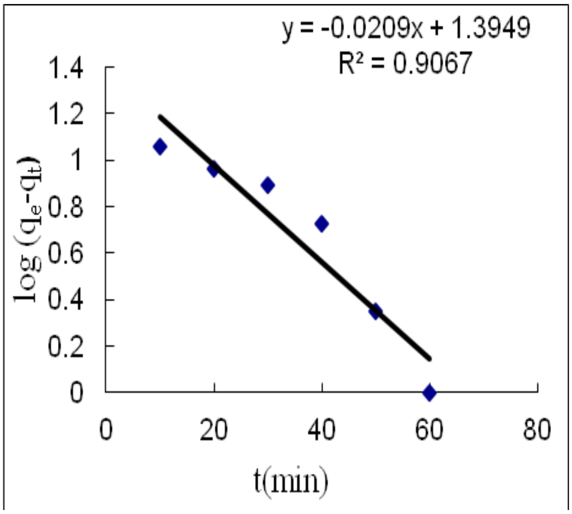
Seaweeds	Langmuir constant			Freundlich constant		
	q (mg/g)	b(1/ mg)	R^2	K_f (mg/g)	n	R^2
S.ilicifolium	175.83	0.1354	0.9898	21.14	2.8034	0.8502
P.tetrastromatica	243.90	0.0804	0.9768	19.74	2.3180	0.9383

Rate Kinetics

The pseudo-first- order and the pseudo – second - order models explain the mechanism of the adsorption process. According to Arivoli et al., (2008) a plot of log (q_e- q_t) versus time should be linear, if the pseudo-first-order kinetics are obeyed. Fig 4 explains pseudo-first-order kinetic model for biosorbents under investigation.



S. ilicifolium



P. tetrastromatica

Fig. 4. Pseudo-first-order biosorption of Pb(II) ions by *S.ilicifolium* and *P.tetrastromatica.*

Pseudo-second-order is based on the assumption that the adsorption follows second order chemisorptions (Fig. 4). The pseudo-second-order model provided better approximation to the experimental kinetic data than the pseudo-first-order model.

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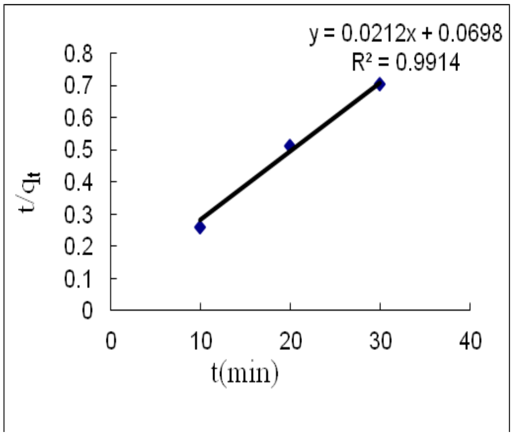
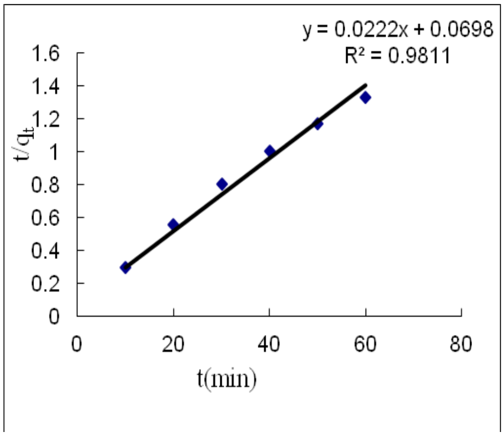


S. ilicifolium



P. tetrastromatica

Fig.5. Pseudo-second-order biosorption of Pb(II) ions by *S.ilicifolium* and *P .tetrastromatica.*

The linear regression correlation coefficient values (R2) were higher which confirmed that the adsorption data are well represented by pseudo-second -order kinetics and supported the chemisorption process occurring during the adsorption in the present biosorbents (Table 2).

Table 2. Kinetic Parameters for the adsorption of Pb(II) ions by seaweeds.

Constant	S.ilicifolium	P.tetrastromatica
Pseudo-first-order		
$q_{e\ (}$exp.)(mglg)	42.64	45.01±
q_e (calc.)(mglg)	9.04	24.82
K_1 x 10^{-3}(min^{-1})	2.92	2.09
R^2	0.8096	0.9067
Pseudo-second-order		
$q_{e\ (}$calc.) (mglg)	47.16	45.04
K_2 [mg/(g min)]	2.22	2.02
R^2	0.9914	0.9811

CHARACTERERIZATION OF THE BIOSORBENT

Charactererization of biosorbent was done by FTIR Spectroscopy (Perkin Elmer Spectrum 100). The data obtained from FTIR spectra (Fig. 6 & 7) is presented in Table 3. Surface morphology of the biosorbent was studied after the biosorption process under the scanning electron microscope (Jeol- Jsm 6360). In the micrographs irregular structures with large surface area were observed. (Fig.8 & 9). EDX was carried out to study metal distribution and ion exchange mechanism. Ions such as Cu, Zn, Mo, Cd and Sn were present in both *S. ilicifolium* and *P.tetrastromatica*.

Table 3. FTIR analysis of *S. ilicifolium* and *P. tetrastromatica* biomass.

Biosorbents	Wave number (cm^{-1}) Before biosorption*	Wave number (cm^{-1}) After biosorption	Functional group
S.ilicifolium	3395.53, 2922.76,2849.78 1617.94, 1424.43, 1241.01, 1133.31, 614.85.	3394.70, 2918.83, 1637.98, 1426.91, 1033.12, - - 618.96.	N-H, OH CH_2, C=O, C-N, N-H, $(CH_3)_3N^+$, CH_2,CO_2^{-1}, - - PO^-_2,C-O,C=O
P. tetrastromatica	3353.35, 2922.71, 1640.04, 1472.02, 1101.79,1105.27 602	3409.48, 2914.96, 2852.96 1630.29 1423.03 - -	N-H,OH CH_2, C=O, C-N, N-H, C=O $(CH_3)_3N^+$, - -

***Sabale and Waghmode (2010), *Waghmode and Sabale (2012).**

Fig. 6. FTIR analysis of *S. ilicifolium* biomass after biosorption.

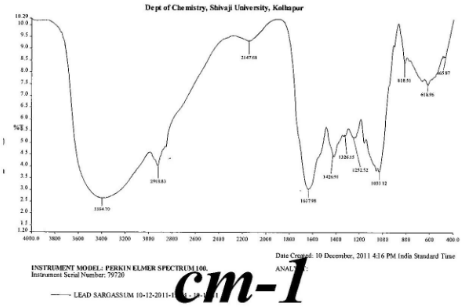


Fig. 7. FTIR analysis of *P. tetrastromatica* biomass after biosorption.

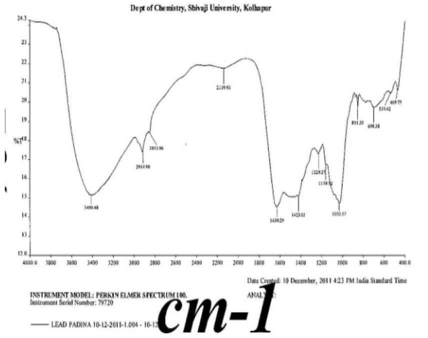


Fig. 8. SEM micrograph and EDX data of *S.ilicifolium* biomass.

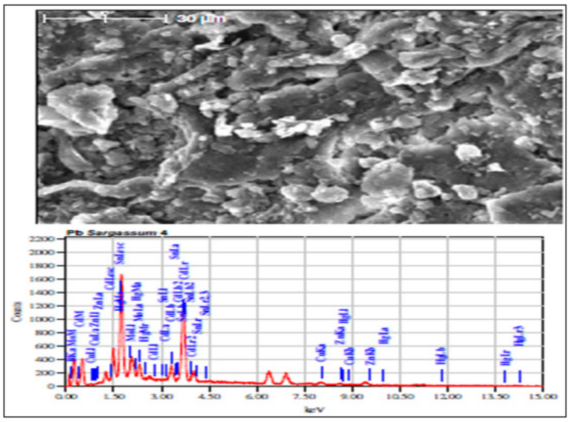
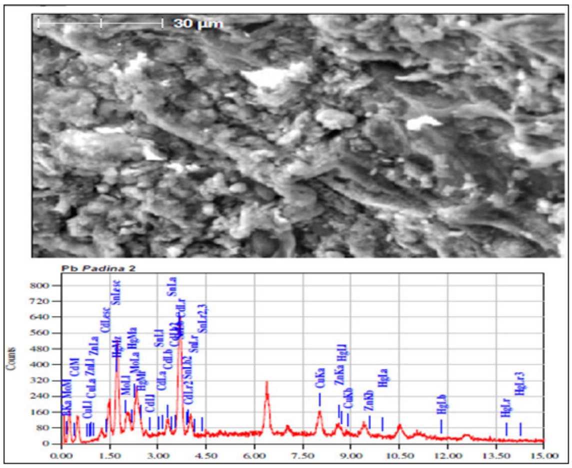


Fig.9. SEM micrograph and EDX data of ***P. tetrastromatica* biomass.**



CONCLUSIONS

Under optimum conditions (pH 2. 5 and metal concentration 100mg/l) the removal of Pb(II) ions was 42.64 mg/g (85.28%) in *S.ilicifolium* while for *P.tetrastromatica* it was 45.01 mg/g (90.02%). The process required 30 min for *S. ilicifolium* and 60 min for *P.tetrastromatica*. As the metal ion concentration increased there was an increase in the metal uptake due to increase in driving force i.e. concentration gradient but the percent biosorption declined. At lower concentration, most of the Pb(II) ions in the solution could interact with the binding sites and thus the percentage of biosorption is higher. As the initial metal ion concentration increases, percent biosorption decreases due to the saturation of biosorption sites. Similar observations are recorded by Lahari et al., (2010).

According to Kratochvil and Volesky (1998) a good metal sorbent should have a high q_m as well as a low b particularly for the sorption of metals. In the present study a similar trend has been observed and suggested the effective use of seaweeds in removal of Pb(II) from waste water.

The experimental data for the adsorption process well fitted the Langmuir adsorption isotherm than the Freundlich adsorption model. The adsorption process followed pseudo-second -order kinetics. FTIR spectrum analysis suggested that amine, alcoholic, hydroxyl, carboxyl and carbonyl groups could participate in the adsorption of Pb(II) ions.

EDX spectrum suggested that ion exchange mechanism might be involved in the biosorption process. The brown algal cell wall mainly consist of alginic acid or alginate (salt of alginic acid) and a small amount of fucoidan (sulfated polysaccharide) (Brinza et al. 2007). Due to this characteristic, Pheophycean matrix possesses a high capacity of heavy metal removal (Davis et al. 2003; Hashim and Chu 2004). Present study demonstrated a promising use of dried biomass of *Sargassum* and *Padina* species in the removal of lead from wastewater.

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