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A fortunate marine algae biomass, *Sargassum cinereum* for removal of Pb(II): Studies on thermodynamics, kinetics and characterization

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ABSTRACT

The present study investigated to examine the biosorption capacity of a new biosorbent *Sargassum cinereum* (macroalgae) biomass for removal of Pb(II) from aqueous solution against pH, initial Pb(II) concentration, biomass weight and temperature. The data was well fitted by Freundlich and Langmuir isotherm models and Freundlich with a R^2 of 0.999. The kinetics study revealed that the following pseudo-second-order with R^2 of 0.995 on Pb(II), sorption capacity (q_e) was 15.384±0.34 mg of Pb(II) per g of biomass and maximum efficiency (q_{max}) was 21.6 mg/g. The biosorption process is exothermic (–ΔH°), feasible and spontaneous nature (–ΔG°). The SEM images revealed that the Pb(II) sorption on biomass *S. cinereum* as asymmetrical spikes. The functional groups, i.e. –OH, CO^-, –NH stretching –CH, C–O, Si–C and $-CH_3$ were specifically implicated in the progression of biosorption. *S. cinereum* (SC) biomass could be regenerated for 3 cycles with 20% loss in its initial biosorption capacity.

Keywords: Biomass; Spontaneity; Lead (II); *Sargassum cinereum;* FTIR; SEM

1. Introduction

Industries, such as textile, paint, battery and metal finishing are causing to release Pb(II) and threat to the ecosystem if untreated, as they could pass through the food chain. The acceptable limit of lead in the potable water was fixed by (WHO) World Health Organization as 10 µg/L [1]. Lead exposure for longer periods causes damage to the brain, kidneys and blood cells ultimately cause to carcinogenicity and genotoxicity [2]. Biosorption technique is explained as potential choice for effluent treatment, as showed high metal binding efficiency and low cost. For previous twenty years, various biomaterials were utilized, i.e. algae biomass [3–5], plant biomass [6–8], bacteria biomass [9], fungus biomass [10–11] as adsorbents for removal process. Marine algae [5,12,13] and freshwater algal species [14] were reported in the literature with varying the removal efficiencies and biosorption capacities (q_{max}) on Pb(II).

Sargassum cinereum is abundant, renewable algae, very rich on a large scale from the coast of oceans. In this investigation, the biosorption capacity of dried algae has been inspected against effect of time, pH, initial metal concentration, temperature and biomass load. Further, kinetic, thermodynamic and equilibrium studies were carried. The biosorption data was applied by Freundlich and Langmuir models and biomass were characterized by FTIR and SEM.

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2. Materials and methods

2.1. Preparation of biosorbent

Sargassum cinereum, macro algae under study was collected in sea coast of portblair, was authentication given by Dr. G.N. Murthy, Dept. of Botany, Andhra University, India. The biomass was cleaned thrice by using demineralized water for removal of surface particles, debris and salts and dried at 70°C for 24 h in hot air oven. Particle size was reduced by a domestic mixture and particles were sieved in #100 sieve and preserved in a humidity control oven for further studies.

2.2. Preparation of adsorbate

Pb(II) solution of 1000 mg/L was prepared in Milli-Q water by dissolving appropriate quantity of $Pb(NO)_3$. The working Pb(II) solutions in the study were prepared by dilution with Milli-Q water of stock and pH was adjusted by 0.1 N NaOH and 0.1 N HNO_3.

2.3. Equilibrium studies

Equilibrium studies were performed in 250 ml flasks (Erlenmeyer), with various lead initial concentrations (24.86±1.23 to 186.71±2.86 mg/L) of 0.1 L solution at a constant shaking speed (160 RPM) and required biomass dosages (2–20 g/l). Initially, the equilibrium time was studied with biomass, *S. cinereum* for biosorption capability. All other experimentations run at attained equilibrium time and repeated thrice for all conditions of study.

2.4. Analytical procedure

The remaining amount of lead (Pb(II)) in sample was determined by AAS (Perkin Elmer AA400) with flame of air acetylene. Initial (C) and residual (C_e) Pb(II) were determined (mg/L), for subsequent analysis the metal uptake (q_e) was calculated using the expression as:

$$q_e = \frac{V(C - C_e)}{M} \tag{1}$$

where q_e is the Pb(II) uptake mg of g *S. cinereum*, '*V*' is 'volume of metal solution' in liters, and '*M*' is quantity of *S. cinereum* in 'g'.

The percent removal of Pb(II) by *S. cinereum* was calculated by expression 2:

$$R(\%) = \frac{C - Ct}{C_t} \times 100 \tag{2}$$

where *R* = percentage of Pb(II) adsorbed on biomass, *S. cinereum*, *C* = initial and C_t = at time 't', concentration of Pb(II) in mg/L.

2.5. Biomass characterization

2.5.1. FTIR and SEM studies

The biomass (native biomass) and Pb(II) loaded biomass (after biosorption) were examined by FTIR (Perkin-Elmer 1600) by KBr disc pellet method in the wavelength of 400–4000 cm^{-1}. The FTIR examination is proposed to provide a deeper understanding of an interaction in between the cell surface and ions of the metal. The dried *S. cinereum* (SC) powder and Pb(II) loaded biomass were first coated with an ultra thin gold film by ion sputter (model: JFC-1100) and then were exposed under (JEOL, JXA-8100) scanning electron microscope.

3. Results and discussion

3.1. Characterization of biomass

3.1.1. Fourier transform infrared spectroscopy (FT-IR)

The broad band at 2917.68 and 2158.84 cm^{-1} is corresponding to stretching vibrations of C–H due to lignins [15] and Thiocynate (–SCN) respectively involved (Fig. 1a) in the biosorption process by shifting the band to 2917.88 and 2133.53 cm^{-1} (Fig. 1b). The peaks at 1973.84 cm^{-1} indicated that the presence of aromatic aryl rings and shifted to 1952.87 cm^{-1}. The peak at 1601.82 cm^{-1} could attributed to the –NH stretching vibration due to the peptide bond of protein and is involved strongly by shifted the peak to 1657.95 cm^{-1}.

The broader peak at 1416.65 cm^{-1} is represented the symmetric bending vibrations of $-CH_3$ bonds, after biosorption of Pb(II) the band and shifted to 1415.77 cm^{-1}. Similarly the sharp peak at 1010.53 cm^{-1} assigned as C–O and is also shifted to 1005.67 cm^{-1}. The peaks at 876.65 and 876.75 cm^{-1} assigned 1, 3 substitutions of –CH at aryl rings [13]. The presence of (Si–C) from diatomaceous earth, could justified for the absorbance peak at 797.71 cm^{-1} which was shifted to 714.78 cm^{-1}. The significant shifts of the specific peaks suggested that amide, thiocynate, bounded –NH, amide N–H bending vibrations, C=H stretching type vibrations, and C=O of carboxylic acid groups of *S. cinereum* could be responsible for biosorption of Pb(II). The similar results were described on various algal species [15–19] for different heavy metals.

3.1.2. Scanning electron microscopy (SEM)

The native biomass has shown the number of pores with different diameter and pore area (Figs. 2a and 2b). Further pores, shiny needles facilitate the [20] excellent option for sorption of Pb(II) on *S. cinereum*. At higher magnification uneven surface texture along with lots of irregular surface was observed, pore area also reduced and were almost closed. Further asymmetrical spikes have also gathered on the surface indicated that the biosorption of metal by biomass.

3.2. Effect of contact time

The optimal contact time was performed on % biosorption of Pb(II) over the time of 5–120 min, using various *S. cinereum* biomass dosages (5–20 g/L), Pb(II) initial concentration of 100±1.26 mg/L, temperature 25°C (Fig. 3a) and 5 'pH'. The percentage of Pb(II) % was increased from 34.25 to 81.74% up to 2 h. The polymeric extra-cellular (ionisable) sites were responsible for quick initial sorption and slower sorption observed may be due to intracellular binding [21].

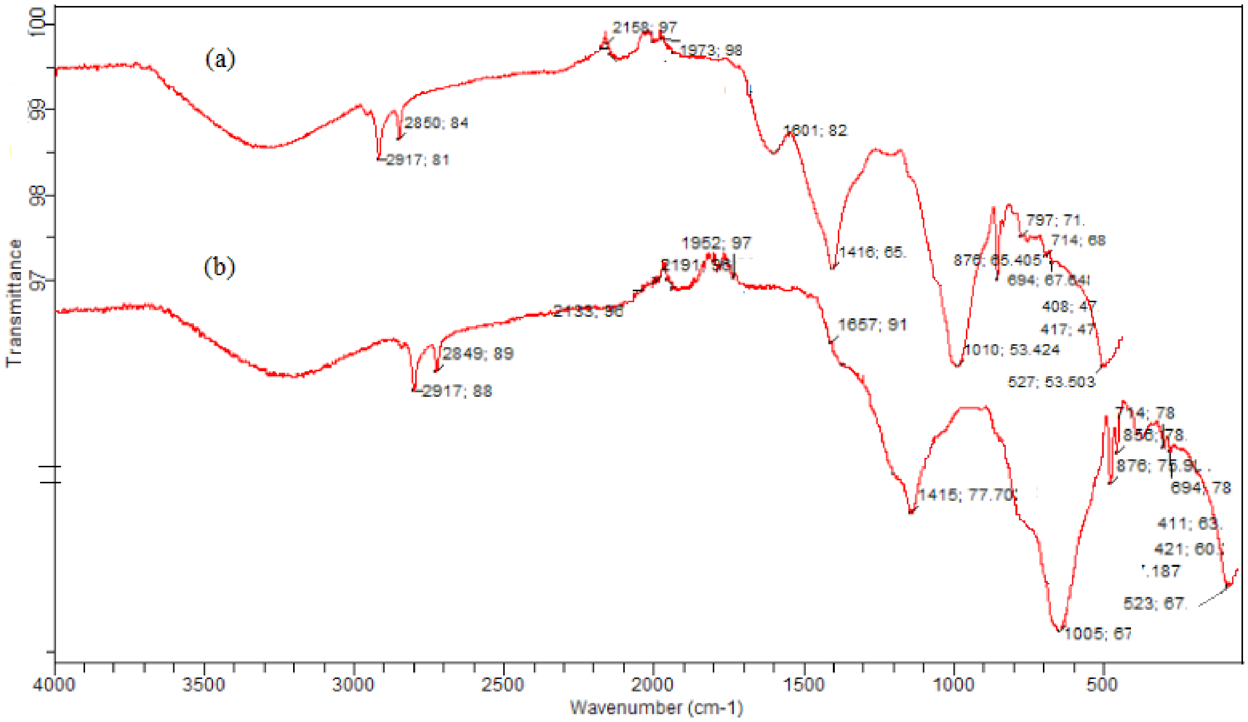

Fig. 1. FT-IR Spectrum (a) unloaded algal biomass and (b) Pb(II) loaded algal biomass.

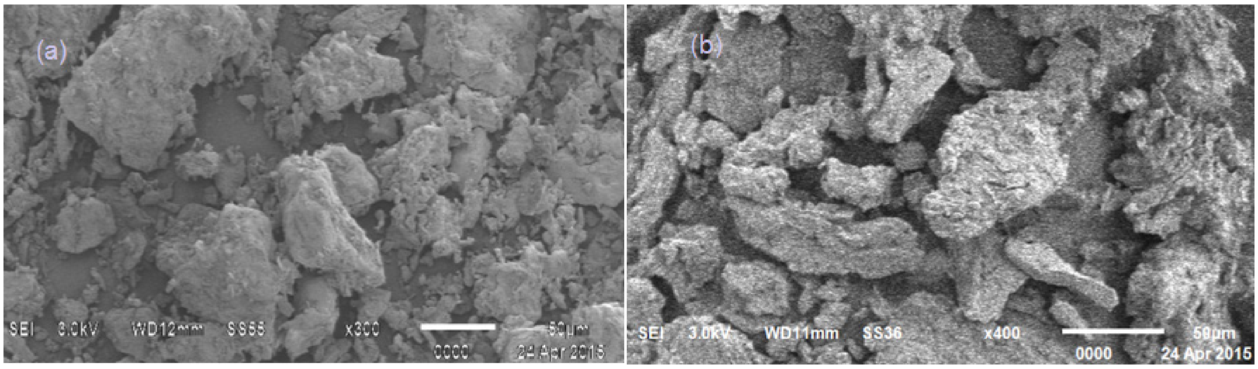

Fig. 2. SEM images of (a) before (b) lead treated *S. cinereum* powder.

In the preliminary stage of contact of biomass with metal ions, the uptake is rapid due to huge numbers of vacant sites were available on the biomass and therefore the uptake is rapid. The decelerate of Pb(II) uptake is owing to the intricacy in engage the residual unoccupied sites. Previous results have been explained similarly for the Pb(II) ions binding on macro algae of *Caulepra fastigiata* [5].

3.3. Effect of pH

pH is straightly associated to the hydrogen ions capability to bind metal ions to on active sites of the biomass surface [12]. Fig. 3b has shown that enhanced Pb(II) uptake from 8.68 to 10.53 mg/g with increase in pH from 2.0 to 5.0 and gradually fall down (9.29 mg/g) at pH 6.0 at initial Pb(II) of 48.31 mg/L. The similar results were drawn on *Ulva lactuca* for Cd(II) removal [22]; The most favorable pH was considered as 5.0, this behavior may be due to the precipitation of lead as $Pb(OH)_2$ and may be the presence of high content of carboxyl groups that make it susceptible to changes in pH [23].

3.4. Effectiveness of initial Pb(II) concentration

The effect of initial Pb(II) concentration on the uptake was showed in Fig. 4(a), biosorption capacity (q_e) of the *S. cinereum* was elevated from 2.879 to 10.536 mg/g with increasing initial Pb(II) concentration from 48.31 to 186.71 mg/L at the dose of 10 g/L at pH 5 and 25°C. While increasing the initial Pb(II) concentration facilitates a superior driving force to conquer mass transfer resistances between an aqueous phase and solid biomass, which out-

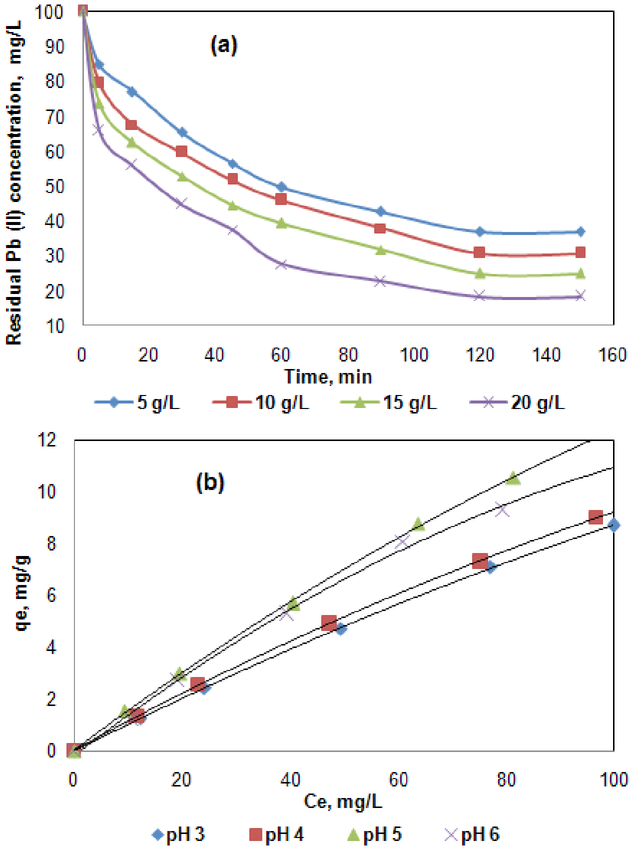

Fig. 3. (a) Effect of time on *S. cinereum* surface at 25°C, 50 mg/L and pH 5, (b) Effect of pH on metal uptake of Pb(II) on *S. cinereum*.

come in better metal ion biosorption. Similar observations were made by earlier investigator [23] on the biosorption of Pb(II).

3.5. The impact of biomass dosage

The behavior of *S. cinereum* biomass dosage was studied on sorption of Pb(II). The percent removal of Pb(II) on *S. cinereum* was from 54.98 to 80.02 (Fig. 4b) at 24.8 mg/L with pH 5, and Pb(II) up taking capacity was warped down as 12.39 to 1.93 mg/g when increasing the biomass dosage from 5 to 20 g/L. The similar trend was observed for various initial Pb(II) concentrations. This could be justified by concentration gradient in between the sorbate and sorbent; rise in biomass dosage caused to decline the quantity of metal uptake onto *S. cinereum* biomass [24]. However, the enhanced percent biosorption by escalating the biomass loading is owed to surface area accessibility and augmented the number of dynamic sites for biosorption [22].

3.6. Effect of temperature

The influence of temperature in the range of 25–50°C was studied, the percentage of removal was decreased from 80.01 to 61% (Fig. 5) initial concentration of 48.31 mg/L.

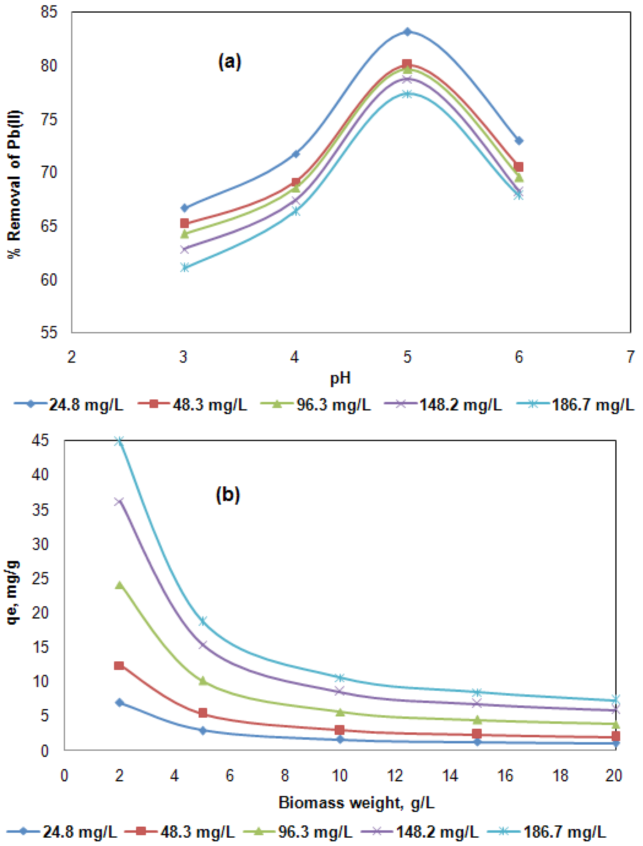

Fig. 4. (a) Effect of pH on % removal of Pb(II), (b) Effect of biomass weight on metal uptake at temperature of 25°C, pH 5.

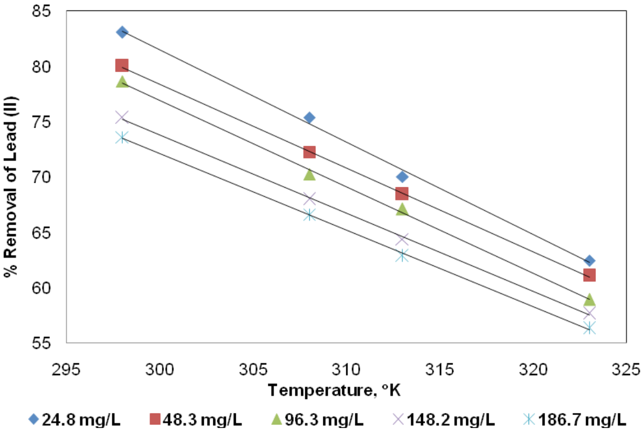

Fig. 5. Variation of % removal of Pb(II) with various temperatures at biomass weight 10 g/L and pH 5.

The similar pattern was observed at various initial Pb(II) concentrations. However, the temperature effect seems to be contradictory, as reported by several authors uptake was increased [25], decreased [26] or remains unaffected the algae ability [27,28]. In this study biosorption capacity of the *S. cinereum* has decreased with augmented temperature, due to a inclination to desorbs the Pb(II) from the surface of biomass into the solution.

3.7. Equilibrium isotherms

3.7.1. Langmuir Isotherm

Langmuir isotherm proposed by Langmuir, (1918) [29], and the linear form equation as:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{4}$$

where 'q_m' (mg g^{-1}) = maximum quantity of the Pb(II) loaded per 'g' of *S. cinereum*, 'q_e' (mg/g) = biosorption capacity at, 'C_e'= concentration of Pb(II) (mg/L) at equilibrium, 'b' = constant for binding sites (L/mg) affinity. From the plots between (C_e/q_e) and C_e the slope ($1/q_m$) and the intercept ($1/q_m b$) can be calculated. The Langmuir constant used to calculate the suitability of the adsorbent to adsorbate by using dimensionless factor R_L by:

$$R_L = \frac{1}{1+bC} \tag{5}$$

$0 < R_L < 1$ assigned favorable, $R_L > 1$ designated un-favorable and $R_L = 1$ be a sign of linear and $R_L = 0$ point out as irreversible biosorption. Biosorption constants and correlation coefficients were shown in Table 1. C_e/q_e vs C_e plot yielded a straight line with R^2 (0.969) indicated the sorption data could be represented by the Langmuir model (Fig. 6a). The elevated biosorption capacity, q_m (»1) designated the strong electrostatic forces of attraction and b is an affinity of the binding sites (L/mg). Moreover, the b values are 0.0159, 0.087 L/mg indicating that biosorption capacity of *S. cinereum* biomass for Pb(II) is higher. From the value of b, a dimensionless factor R_L at different initial metal ion concentrations was calculated (not shown). The biosorption of Pb(II) on algal surface is thus a highly favorable process.

3.7.2. Freundlich Isotherm

Freundlich isotherm (1926) [30] can be expressed as:

$$q_e = K_f C_e^{\frac{1}{n_f}} \tag{6}$$

Taking logarithm on both sides,

$$Inq_e = \ln K_f + \frac{1}{n_f} InC_e \tag{7}$$

where 'q_e' = biosorption capacity (mg/g) at equilibrium, 'C_e' = concentration of Pb(II) at equilibrium in solution, 'K_f' and n_f are constants related capacity of biosorption and intensity respectively. The coefficient of determination in this case is 0.998 (Fig. 6b) and the values of n_f and K_f are found to be 1.283 (g/L) and 2.950 {(mg/g)(mg/L)^n} at 298 K (Fig. 6b). The high R^2 (correlation coefficients) values point out that the Pb(II) biosorption data on biomass, *S. cinereum* was observed that Freundlich model is best isotherm (Table 1). The Freundlich constant n_f was greater than 1, at all temperatures studied as well as initial Pb(II) concentrations representing that biosorption intensity was high and reflecting the favorable sorption. Several researchers applied to explain the data successfully by using Freundlich model. The comparisons of various biosorbents are given in Table 2.

Table 1
Langmuir and Freunlich isotherm model parameters for Pb(II) onto *S. cinereum*

Langmuir constants				Freundlich constants		
Temp. (°K)	q_m (mg g^{-1})	b (L mmol^{-1})	R^2	K_F	n_f	R^2
298	15.408	0.0158	0.969	2.9505	1.2835	0.9981
308	17.361	0.0087	0.948	4.7621	1.2165	0.9997
313	19.531	0.0061	0.993	6.3430	1.1621	0.9987
323	21.598	0.0039	0.969	9.2066	1.1304	0.9998

3.8. Biosorption kinetic models

In the present study pseudo first order and pseudo second order kinetic models have been attempted to fit the present biosorption data (Table 3).

3.8.1. Pseudo-first-order/Lagergren kinetic model

It is widely used kinetic equation [39] and the linearized form of pseudo–first–order can be written as:

$$Log\left(q_e - q_t\right) = \log q_e - \frac{K_1}{2.303} t \tag{8}$$

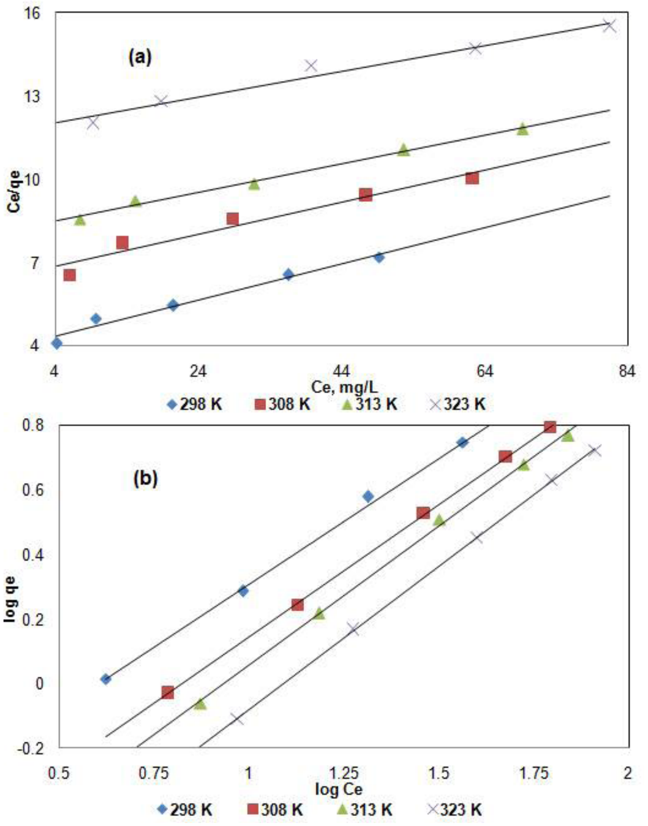

Fig. 6. (a) Langmuir plot (b) Freundlich plot of *S. cinereum* at various temperatures and at pH 5.

Table 2
Comparison of maximum Pb(II) uptake (q_m) by other biosorbents

Biosorbent	q_{max}	Reference
Ulva lactuca	34.7	31
Caulerpa lentillifera	28.7	32
Cephalosporium aphidicola	36.9	33
Cladonia furcata (Lichen)	12.3	34
Fucus vesiculosus (modified)	33.78	35
Sargassum glaucescens (modified)	41.01	36
Pinus sylvestris (modified)	22.22	37
algal waste (modified)	20.5	38
S. cinereum (non modified)	21.6	Present study

Table 3
Kinetic parameters for Pb(II) biosorption on *Sargassum cinereum*

W (g/L)	q_e(cal) (mg/g)	q_e(exp) (mg/g)	K_2 (g/mg-min)	R^2
5	15.3846	12.688	0.000089	0.988
10	8.0645	6.9432	0.005118	0.988
15	5.6497	5.0137	0.000907	0.992
20	4.5045	4.0874	0.014911	0.995

where 'q_e' = the quantity of Pb(II) sorbed on biomass (mg/g) at equilibrium; 'qt' = the extent of Pb(II) adsorbed on biomass (mg/g) at time 't' and 'k_1' = rate constant. From the slope of the plot between $log\ (q_e - q_t)$ and time 't', k_1 was obtained. Fig. 7a shows that it does not follow a straight line, the Lagergren kinetic plot does not fit well for the biosorption of lead onto *S. cinereum*.

3.8.2. Pseudo- second- order kinetic model

The pseudo–second–order reaction model expressed as [40]:

$$\frac{dq_t}{d_t} = k_2(q_e - q_t)^2 \qquad (9)$$

On integration above conditions when $t = 0$ to $t > 0$ and $q_t = 0$ to $q_t > 0$ and further simplifications, Eq. (9),

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (10)$$

The plot of t/q_t versus 't' gave (Fig. 7b) linear relationship (Eq. (10)) from slope and intercepts values of q_e and k_2 were calculated. The constants and the correlation coefficients of *Pseudo–second–order kinetic model* were determined and tabulated in Table 3. The R^2 values are nearly unique, then, it has been confirmed that the pseudo–second–order model is much represented for Pb(II) on *S. cinereum* biomass.

3.9. Thermodynamic parameters

The free energy change ΔG°, Enthalpy ΔH°, Entropy ΔS° for biosorption process can be calculated from the equations:

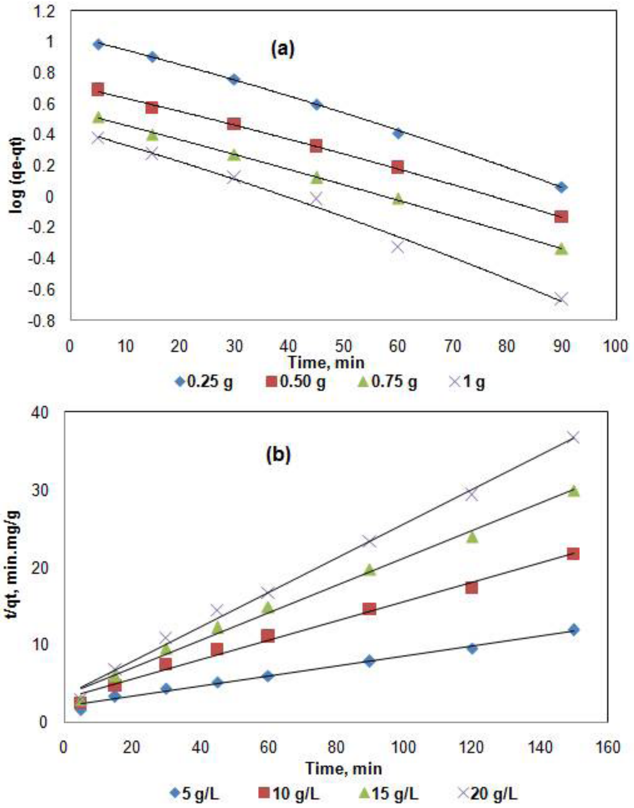

Fig. 7. (a) Pseudo first order kinetic plot (b) Pseudo second order kinetic plot for biosorption of Pb(II) at 25°C, 100 mg/L and pH 5.

$$\Delta G^0 = -RTInK_C \qquad (12)$$

where ΔG° is the free energy change, expressed as J/mol. K_c is the apparent equilibrium constant in the process. K_c could be achieved from Eq. (13):

$$K_C = \frac{C_S}{C_e} \qquad (13)$$

$$\log\left(\frac{C_S}{C_e}\right) = -\frac{\Delta H^0}{2.303RT} + \frac{\Delta S^0}{R} \qquad (14)$$

$\frac{C_S}{C_e}$ can be defined as 'biosorption affinity'. C_s is the concentration of metal ion (mg/g) in solid adsorbent. C_e is equilibrium metal concentration mg/L. The enthalpy changes (ΔH°) and entropy changes (ΔS°) for the biosorption process for all the initial metal concentrations in the aqueous solutions were obtained from the plots of $\log\left(\frac{C_S}{C_e}\right)$ drawn against $1/T$ (Fig. 8a). The calculated thermodynamic data are compiled in Table 4. The free energy ΔG° values decreased negatively (–31.102, –27.544, –28.284 and –25.026) with temperature increases (293, 308, 313 and 323 K) for the biosorption of Pb(II), preferred as the spontaneity of the process. The negative ΔH° values designated [12] as exothermic and –ΔS° values recommended as randomness decreases at solution–biomass boundary throughout the sorption of Pb(II) onto *S. cinereum*.

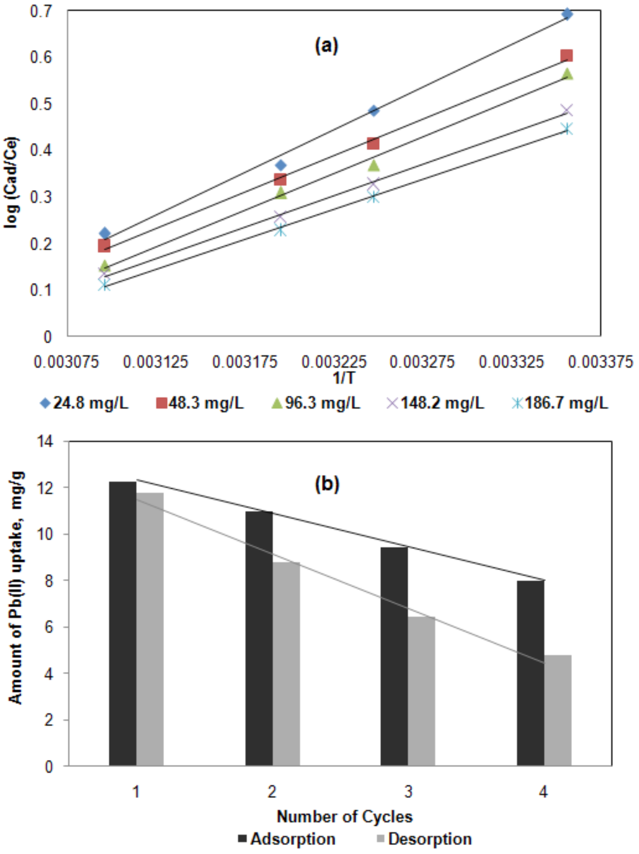

Fig. 8. (a) Vant Hoff plot at various temperatures for biomass 10 g/L and at pH 5 (b) Biomass regeneration capacity for adsorption-desorption cycles.

Table 4
Thermodynamic parameters for Pb(II) biosorption on *S. cinereum*

Temp. (^0K)	C_0 (mg/L)	ΔH° (KJ/mol)	ΔS° (J/mol^{0K})	ΔG° (KJ/mol)
298	24.86	–35.039	–104.488	–31.102
308	48.319	–30.072	–89.528	–27.544
313	96.34	–30.135	–90.462	–28.284
323	148.23	–25.850	–77.561	–25.026

3.10. Regeneration and reuse

In the present investigation, repetitive sorption/desorption experiments were carried out to check the regeneration and reusability of the biomass, *S. cinereum* for Pb(II). The Pb(II) ions adsorbed onto *S. cinereum* was eluted with 0.1 M HNO_3 and desorbed more than 75%. Adsorption–desorption cycles of Pb(II) were performed repeatedly four times (Fig. 8b). The biosorption capability of the *S. cinereum* was altered by about 20% during each adsorption–desorption cycle. This result shows that *S. cinereum* could be repeatedly used for 3 cycles with 20% loss in its initial biosorption capacity at second and third cycles.

4. Conclusions

The present research work concluding that the biosorption capability of a novel biosorbent *Sargassum cinereum* (SC) biomass for recovery of Pb(II) from the solution is excellent against pH, initial Pb(II) concentration, sorbent dosage and temperature. The biosorption data was well described by Freundlich model with R^2 of 0.999 and pseudo-second-order model was best represented the data with R^2 of 0.995. The sorption capacity (q_e) was noted as 15.384±0.34 mg of Pb(II) per g of *S. cinereum* and maximum efficiency (q_{max}) was 21.6 mg/g. The biosorption process is (–ΔH°) exothermic, feasible and (–ΔG°) spontaneous nature. The functional groups, i.e. –OH, CO^-, –NH stretching –CH, C–O, Si–C and $-CH_3$ were intensively involved in the process. *S. cinereum* biomass could be repeatedly used for 3 cycles with little loss in its initial biosorption capacity. Hence algae *Sargassum cinereum* is promising biosorbent to remove Pb(II) metal ions from waste waters.

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