Bruguiera gymnorhiza (Mangrove leaf powder) for removal of Pb (II): Characterization, Kinetics, Isotherms and Thermodynamic Studies

M. Krishna Prasad[a], K. Jyothi [b]

[a] Department of Chemical Engineering, GMR Institute of Technology, Rajam, Andhra Pradesh.
[b]Department of Microbiology, Andhra University, Visakhapatnam, Andhra Pradesh.
Corresponding Author: jyothikaparapu@gmail.com

Article History: Received: 11 January 2021; Revised: 12 February 2021; Accepted: 27 March 2021; Published online: 4 June 2021

Abstract: In this study green plant material Bruguiera gymnorhiza (Mangrove leaf powder) was used for the biosorption of lead (II) ions by Atomic absorption spectrometry. In a batch process, Bruguiera gymnorhiza was exposed to several aspects, pH (2-6) and temperature (25-55°C) in the presence of different lead concentrations (25-125 mg/L) for 2h. This paper studies the Equilibrium isotherms, kinetic and thermodynamic parameters calculations. The highest occupied lead concentration was found at pH 5 which was 97.6% at an initial concentration is 25 mg/L. The maximum lead accumulation was obtained at 25◦C as 10.044 mg/g in 125 mg/L at pH 5.0, and the minimum was at 55◦C as 1.821 mg/g at a dosage of 10 g/L and initial concentration of 25 mg/L. Lead adsorption increased up to 75 mg/L but did not change significantly in the 75–100mg/L range. Equilibrium data fit well to the Freundlich isotherm. The kinetic data follows the pseudo-first-order model. Finally, the adsorbent was characterized by FT-IR and XRD. The biomass of Bruguiera gymnorhiza is an optimistic and cost-effective, biosorbent for lead (II) removal from aqueous environment and adsorption capacity it's good, easy of sampling analysis, as well as availability

Keywords: Biosorption; Bruguiera gymnorhiza; kinetics; Isotherms; Thermodynamics.

1. Introduction

In recent years Lead has been introduced into natural water from a variety of sources such as storage batteries, lead smelting, electro plating and finishing, printing, photographic materials, pigment and dye industries, explosive manufacturing, tetraethyl lead manufacturing, ceramic and glass industries, etc. (Majumdar et al., 2010; Yurtsever and Sengil, 2008; Gercel and Gercel, 2007). The permissible limit of lead in drinking water is 0.05 mg/l as per United States environmental protection agency. Excess Lead in drinking water can also cause a variety of adverse health effects. In individuals of all ages, lead can cause anaemia, kidney malfunction, impaired function of peripheral nervous system, high blood pressure, reproduction abnormality, developmental defects, abnormal vitamin D metabolism, coliclike abnormal pains, dementia, madness and, in some situations, death (Ferreira et al., 2011; Hurd et al., 2008, Kazi et al., 2008; Okoro and Ejike, 2007, Afridi et al., 2006). Due to toxic effects of lead and other toxic metal ions, the removal of them from water and wastewater is important in terms of protection of public health and environment (Unlu and Ersoz, 2006). There are several techniques for removal of lead such as precipitation, evaporation, reverse osmosis, electroplating, ion-exchange, membrane separation, etc. from the aqueous solution. When heavy metals are present in low concentrations almost all of these methods were found to be either prohibitively costly or unacceptably inefficient (Sulaymon et al., 2013).The most common technique is adsorption and it is a wellestablished and powerful technique for treating both domestic and industrial effluents (Ozcan et al., 2009 and Sulaymon et al., 2012).

Bioadsorbents have emerged as one of the potential alternatives for removal of heavy metals and metalloids. Plants, algae, fungi are some of the biomass derived adsorbents which are capable of removing heavy metals and metalloids from aqueous solution by adsorption (Mohan et al, 2007). Cinnamomum camphora leave's powder was investigated as a biosorbent for the removal of Cu (II) and Pb (II) ions from aqueous solutions (Chen et al., 2010). Furthermore, it was reported that Moringa oleifera leaves extract is a good sorbent for Pb (II) from aqueous solution (Reddy et al., 2010). A batch adsorption study of Cd (II) ions from aqueous solution by Hevea brasiliensis (HB) leaf powder has also been reported (Hanafiah et al., 2006). Sharma and Bhattacharyya, (2005) have studied the adsorption of Cd (II) using neem leaf powder. In addition, the leaves of the olive tree (Olea europaea) were proposed as a novel adsorbent for the removal of Cd (II) from solutions (Hamdaoui, 2009). Recently, extensive studies on Cd (II) adsorption taking powdered leaves of a variety of trees have been carried out (Pandey et al., 2008).

Several biomaterials had been exploited for the removal of Pb (II) from aqueous solution, such as using fungal biomass of *Aspergillus niger* (Jianlong et al., 2001), biomass of marine algae (Jalali et al., 2002), bacterial dead *Streptomyces rimosus* biomass (Selatnia et al., 2004), activated carbon prepared from biomass plant material of *Euphorbia rigida* (Gercel and Gercel et al., 2007), *Chrysophyllum albidum* Seed Shell (Amuda et al., 2007), wheat Stems biomass (Tan and xiao 2008), biomass of hazelnut and almond shell (Pehlivan et al., 2009), biomass of *Phaseolus vulgaris* (Ozcan et al., 2009), *Mucor rouxii* biomass (Majumdar et al., 2010), biomass of *Brevundimonas vesicularis* (Resmi et al., 2010), *filamentous* fungal biomass-loaded TiO2 nanoparticles (Bakircioglu et al., 2010), pine cone activated carbon (Milan et al., 2011), a nonliving moss biomass (Bamidele et al., 2012), Ficus Hispida leaves powder (Namdeti and Pulipati 2013) and biomass of *Maize stover* (Guyo et al., 2015).

Andaman and Nicobar archipelago is one of the mega-biodiversity hotspots of India. The archipelago located in the Bay of Bengal, lying between 6450 –13450 N and 92120 –93570 E in the Indo Burmese microplate junction. The islands are spread over a distance of 1,120 km with a coast line of 1,962 km. The close proximity of these groups of islands to the equator and the irregular and deeply indented coast line, creeks, bays and estuaries facilitate the rich and diverse mangrove forests. Rozaini et al. (2010) identified that mangrove bark has a potent adsorbent for Ni(II) and Cu(II) ions from aqueous solutions. The current study was aimed to determine the capability of mangrove leaves from Andaman and Nicobar islands as a potent adsorbent to remove the Lead (II) from aqueous solutions.

The aim of this work is removal of Pb (II) on *Bruguiera gymnorhiza*, there has been no reported work on lead ions from aqueous solution. In this study, the biosorption behavior of Pb (II) from aqueous solution using *Bruguiera gymnorhiza* was studied under various conditions, such as contact time, solution pH, temperature and different concentrations, with the aim of determining the mechanism for the removal of Pb (II) from aqueous solution by biomass of *Bruguiera gymnorhiza*. In addition, equilibrium and kinetic studies were carried out. Langmuir and Freundlich isotherm models were applied to fit the experimental data. FTIR, SEM, and XRD were also used to illuminate the biosorption process.

2.Materials iand imethods 2.1Preparation iof ibiosorbent iBruguiera igymnorhiza

The Mangrove leaves (Bruguiera gymnorhiza) under study were collected from from mangrove plants located in the Minnie Bay area, Port Blair, Andaman and Nicobar islands, India. The collected Mangrove leaves were washed with deionized water several times to remove dirt on the surface of the leaves. The washed leaves were dried in sunlight for 15 days and were powdered using domestic mixer. The powdered biomass was sieved through 200 mesh sieves and biomass powder was preserved in a humidity control oven to maintain a standard humidity throughout for equilibrium studies during the entire period of study.

2.2.Preparation iof istock isolution

All the chemicals used were of analytical reagent grade. Stock Pb (II) solution (1000 mg/L) was prepared by dissolving required amount of $Pb(NO_3)_2$ in double distilled water. All the experimental solutions were prepared by diluting the stock solution. The test solutions of the pH were adjusted by reagent grade 0.05N of Hcl and 0.05N of H_2SO_4.

2.3.Equilibrium iStudies

The experiments were carried out in 250 ml Erlenmeyer conical flasks, at a constant agitation speed (200 rpm) with 50ml solution with various metal concentrations (19.21, 36.12, 68.056, 73.85 and 109.44mg/L) and required amount of adsorbent (5, and 10, g/L) using orbital shaker. Initially the effect of contact time (0-120 min) on the sorption capacity of *Bruguiera gymnorhiza* was evaluated.

2.4.Analytical iprocedure

An atomic absorption spectrophotometer (Perkin Elmer AA400) with an air acetylene flame was determining the concentrations of un-adsorbed Pb (II) ions in the sample supernatant liquid. C_o and C^* were determined and tabulated for subsequent analysis of the experimental data. The metal uptake (C_s) was calculated using the general definition:

$$C_s = \frac{V(C_o - C_*)}{M}$$

(1)

WhereC_s is the metal uptake mg/g biomass, V is the volume of metal containing solution in contact with the biosorbent in L, C_o and C^* are the initial and equilibrium (residual) concentration of metal in the solution mg/L, respectively, and M is the amount of added biosorbent in g. Metal % of removal by Bruguiera gymnorhiza was determined by equation 2 as follows:

$$R(\%) = \frac{C^o - C^*}{C_o} \square 100 \quad (2)$$

Where R is the percentage of Pb (II) adsorbed by biomass, C_o is the initial concentration of metal ions in mg/L and C^* is the concentration of metal ions at time t in mg/L.

2.5.Biomass icharacterization

2.5.1.FTIR istudies i

The powdered biomass, prior and after adsorption was air dried, and demoisturized at 60 _C in humidity control oven. The powder was analysed by Fourier transform infra red spectrophotometer. FTIR studies were conducted by Potassium Bromide (KBr) pellet method (Jasco 5300) in the wave number range of 400.00–4000.00 cm_1.

2.5.2.Scanning ielectron imicroscopy i

The dried bio mass powders and the corresponding metal ion loaded powders were coated with ultra-thin film of gold by an ion sputter (JFC-1100), exposed under electron microscope (JEOL, JX8100) at working height of 15 mm with voltage ranging between 10 and 25 kV.

3.Results iand idiscussion

The experimental data on biosorption were obtained batch wise to study the effect of various parameters on the removal of lead ions from the aqueous solutions prepared in the laboratory by using *Bruguiera gymnorhiza* (mangrove leaf powder). Effect of contact time

Experiments were conducted to estimate the time required to reach the sorption equilibrium by taking an initial charge of 50 ml of aqueous solution containing Pb (II) ions and the required quantities of biomass. The mixture was shaken in an orbital shaker, the samples were drawn at regular time intervals and the metal concentration was estimated using AAS. The data of concentration of metal ion C_t, in solution with time are shown for different quantities of biomass in Fig .1.

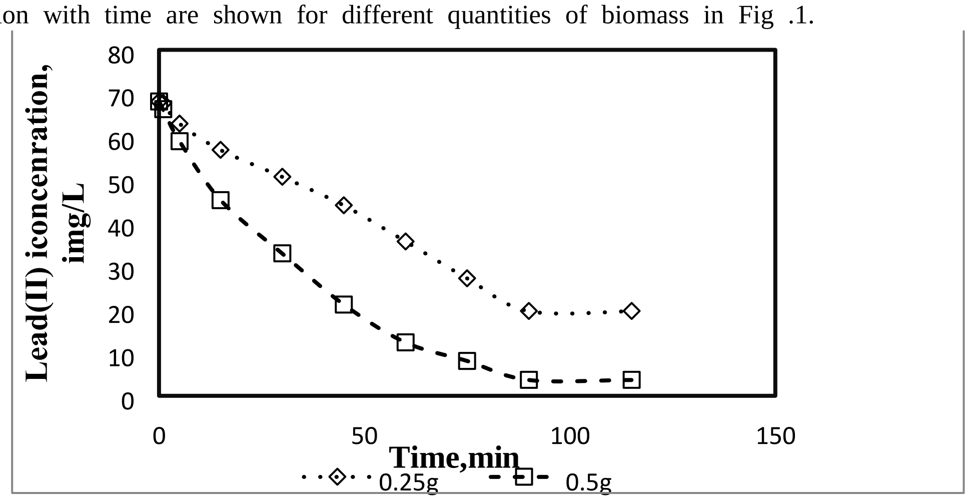

Figure 1: Variation of Pb (II) concentration in solution with time at various quantities of biomass at 25°C, 50 mg/L and pH 5.

The effect of contact time was studied on % adsorption of Pb (II) over a time period of 1-120 min, using 0.25 g of *Bruguiera gymnorhiza* biomass powder (diameter of particle; dp = 0.074mm), initial Pb (II) concentration is 50□0.324 mg L^{-1} at pH 5 and temperature 25□C. Percentage adsorption increased from 35.3 to 71.24% during a contact time period from 1 min to 120 min. The rapid initial sorption was likely due to extra-cellular polymeric sites (ionizable) binding and the slower sorption resulted from intracellular binding (Areco and Afonso, 2010, Maria and Maria dos, 2010, sarada et al., 2013) on adsorbent. Similar studies was performed with 10 g/L of biomass concentrations in aqueous solutions and the results indicated that the 2h is the optimum time of contact for the range of concentrations used. Effect of pH The pH effect of solution on the adsorption of Pb (II) ions onto *Bruguiera gymnorhiza* was studied

by changing the solution pH values with in the pH range of 2.0–6.0 and the results are shown in Fig.

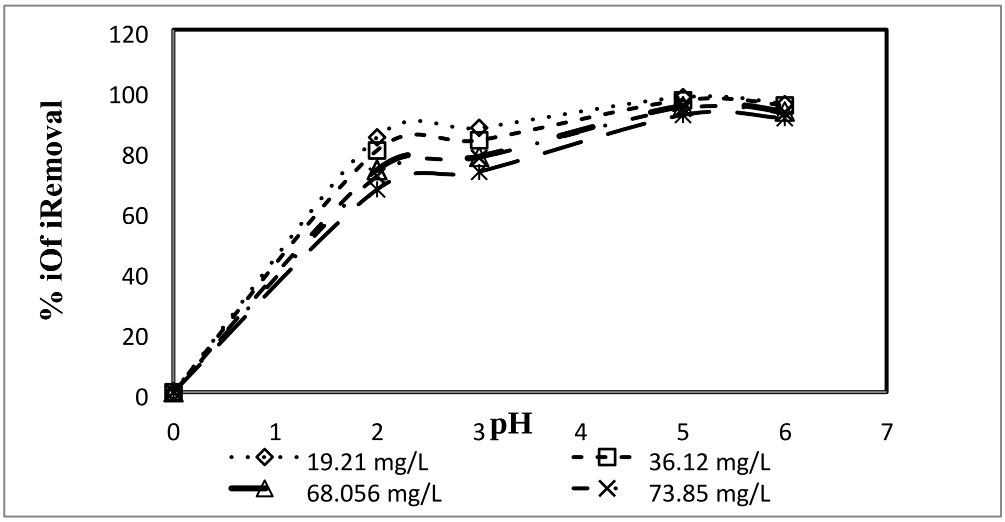

Figure 2: Effect of pH on the lead removal percentage at various initial Pb (II) concentrations

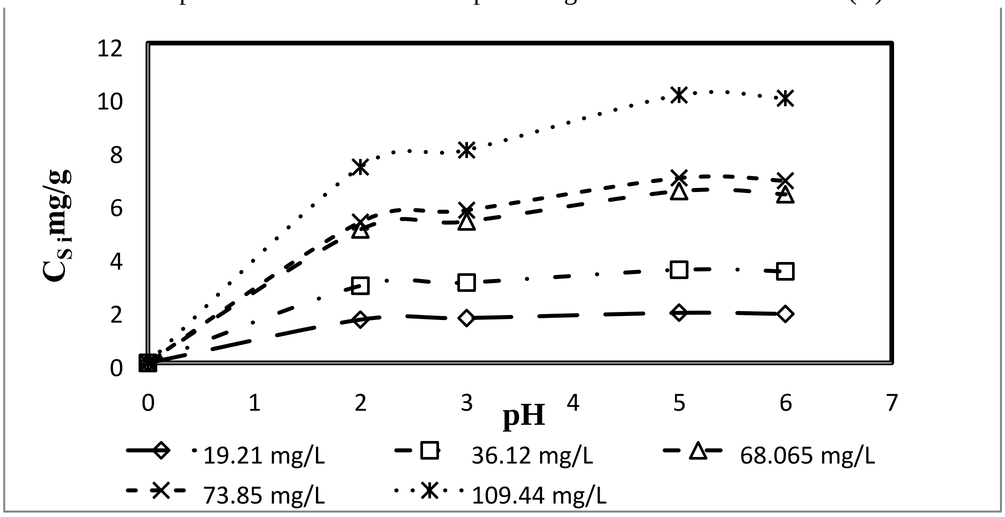

Figure 3: Metal uptake at various pH solutions.

The uptake of biomass was found to increase with the increase in pH as shown in fig.3. It was found to have a high content of carboxyl groups that render it susceptible to pH changes. Similar observations were reported earlier by several investigators (Wang and Chen, 2009; Yi-Chao and ShuiPing 2011). Fig.2 shows that an increase in initial pH from 2.0 to 5.0 resulted increased % biosorption of Pb (II) from 84.3% to 97.6% at an initial metal concentration of 19.21 mg/L. A drastic fall in % biosorption as low as 95.44% was observed at pH value of 6.0, It may be because of the tendency of precipitation of lead as $Pb(OH)_2$ (Yi-Chao and Shui-Ping 2011). Consequently, a pH value of 5.0 was used as the optimum of pH throughout the experimental conditions to avoid the formation of metal hydroxides. Similarly, for all other concentrated solutions, similar trend was observed. As the pH increased the ligands such as carboxylate groups in *Bruguiera gymnorhiza*. would be exposed, increasing the negative charge density on the biomass surface, increasing the attraction of metallic ions with positive charge and allowing the biosorption onto the cell surface (Namdeti and Pulipati, 2014). Effect of temperature

All the experiments with Pb (II) were conducted in the temperature range of 25-55C, the % removal of lead by *Bruguiera gymnorhiza* biomass decreases from 97.6 to 94.1% with increase in temperature in the range 25-55C at initial concentration of 19.21 mg/L (Fig.4). The similar trend was observed at all initial Pb (II) concentrations. In most of the chemical reactions the temperature is expected to activate the process increasing the heat or mass transport processes. Sorption capacity of the biomass has decreased with increase in temperature, rise in temperature has a tendency to desorb the adsorbed metal ions from the surface to the solution. The same trend was observed for other initial metal concentrations and was supported by the earlier report (Aksu, 2001).

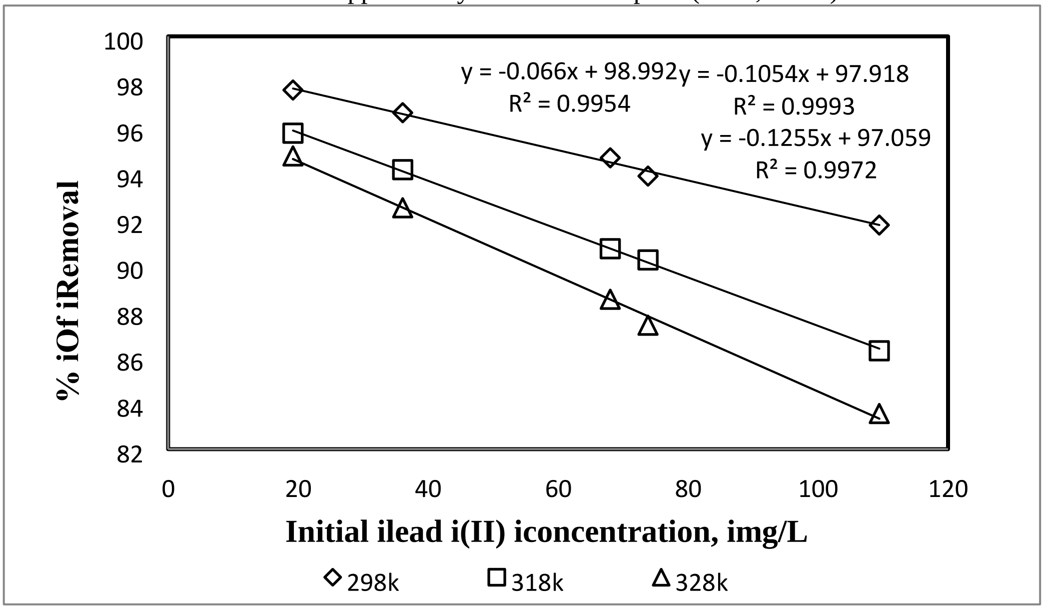

Figure 4: Variation of % removal of Pb (II) with various temperatures at different initial concentration of Pb (II) at biomass 10 g/L and pH 5.

4.Effect iof imetal iion iconcentration

The effect of initial Pb (II) concentration on the metal uptake was shown in Fig.5. The adsorption capacity (qe) of the biomass increased from 2.879 to 10.536 mg g-1 with increasing Pb (II) concentration from 48.31 mg L-1 to 186.71 mg L-1 at sorbent dose of 10g L-1 with the temperature of 25C and pH 5. An increase in the initial ion concentration provides a larger driving force to overcome all mass transfer resistances between the solid and the aqueous phase, which results in higher metal ion adsorption. Similar observations also were made by earlier investigators (Mohammad et al, 2011) in their studies on the adsorption of Lead.

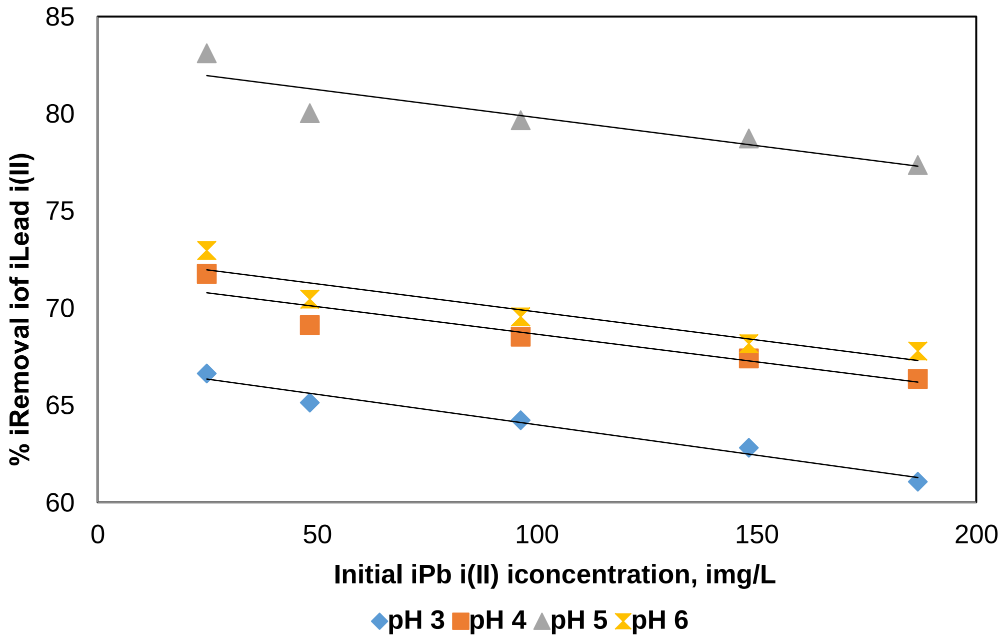

Fig. 5. Variation of % removal of Pb (II) with various Initial concentrations at temperature of 25C, pH 5 and biomass 10 g L-1.

5. Effect iof iadsorbent idosage

Biosorbent dosage determines the potential of biosorbent through the number of binding sites available to remove metal ions at a specified initial metal ion concentration. The effect of amount of biomass was studied on the biosorption of Pb (II) using *Bruguiera gymnorhiza*. The % removal of Pb (II) on *Bruguiera gymnorhiza* ranged from 54.98 to 80.02 (Fig.4) at a pH value of 5 at 24.8 mg/L and the uptaking capacity declined from 12.39 to 1.93 mg g-1 when increasing the biomass dosage from 5 g L-1 to 20 g L-1. The similar trend was observed for all initial metal ion concentrations. This decrease could be due to the concentration gradient between the sorbent and the sorbate; an increase in biomass caused a decrease in the amount of metal sorbed onto a unit weight of the algae. Moreover, the increase in percentage biosorption of metals by increasing the biomass dosage is due to an increase in the number of active sites and surface area available for biosorption. Similar trends have been reported in the literature (Taqvi et al, 2006; Gupta and Rastogi, 2008; Yi-Chao and Shui-Ping 2011). From Fig.6 we can conclude that percentage adsorption increased with decrease in biomass dosage.

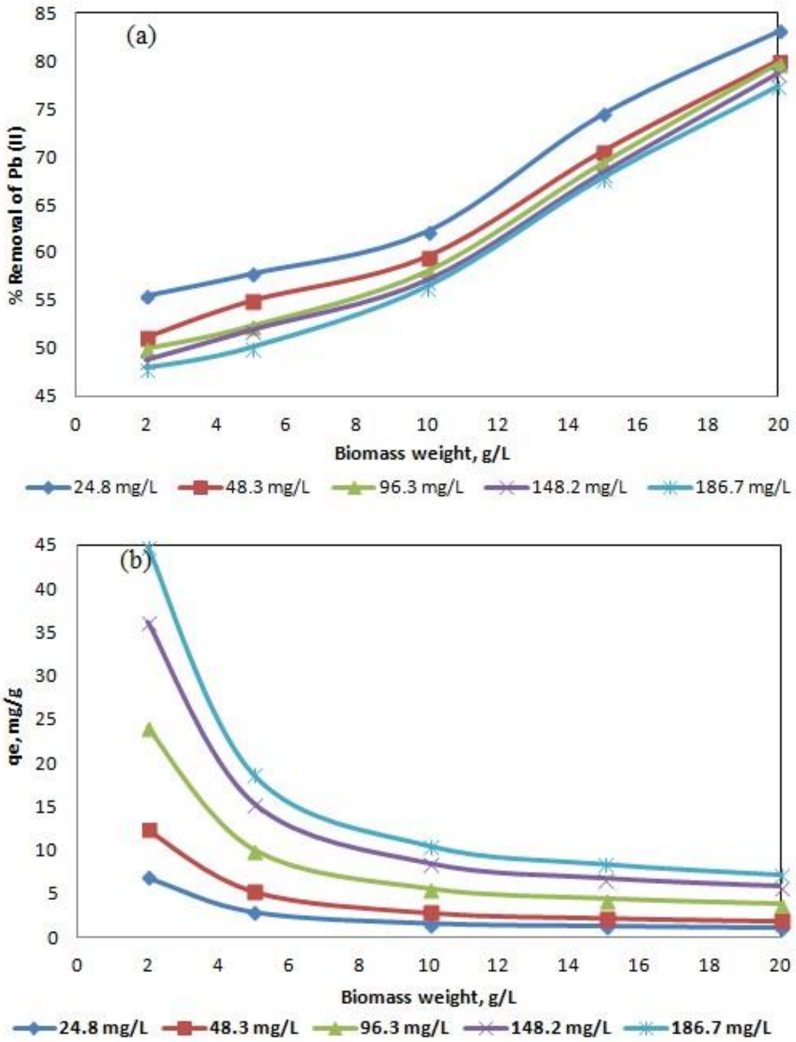

Fig. 6. Effect of Biomass wieght (a) Variation of % Pb (II) sorption (b) metal uptake with biomass weight at temp 25□C, pH 5 and at various initial metal concentrations.

6.Equilibrium iisotherms

Langmuir Isotherm

The equation proposed by Langmuir is universally applicable to chemisorption with some limitations involving physical adsorption (Dąbrowski, 2001). This equation is applicable to the physical or chemical adsorption on solid surface with one type of adsorption active center. Linear form of the Langmuir equation is given by

$$\frac{C^*}{C_s} = \frac{1}{C_m b} + \frac{C^*}{C_m} \qquad (3)$$

Where 'C_m'(mg/g) is the maximum amount of the metal ion per unit weight of adsorbent to form a complete monolayer on the surface. 'C_s' is equilibrium adsorption capacity (mg/g), 'C*' is the equilibrium concentration of the adsorbate in solution (mg/L), and b is a constant which accounts for the affinity of the binding sites (L/mg). C_m represents the limiting adsorption capacity when the surface is fully covered with metal ions and helps in the evaluation of adsorption performance, particularly in cases where the sorbent did not reach its full saturation during contact. It is the most widely used simple two parameter equation (Langmuir, 1918). From the plots between (C^*/C_s) and $C^*$the slope ($1/C_m$) and the intercept ($1/ C_m b$) can be calculated.

The Langmuir constant used to determine the suitability of the adsorbent to adsorbate by using dimensionless factor R_L (Hall separation factor) calculated by:

$$R_L = \frac{1}{1+bC} \quad (4)$$

0 <R_L <1 indicates favorable for adsorption, RL> 1indicates un-favorable for adsorption R_L = 1 indicates linear adsorption, RL = 0 indicates irreversible adsorption.

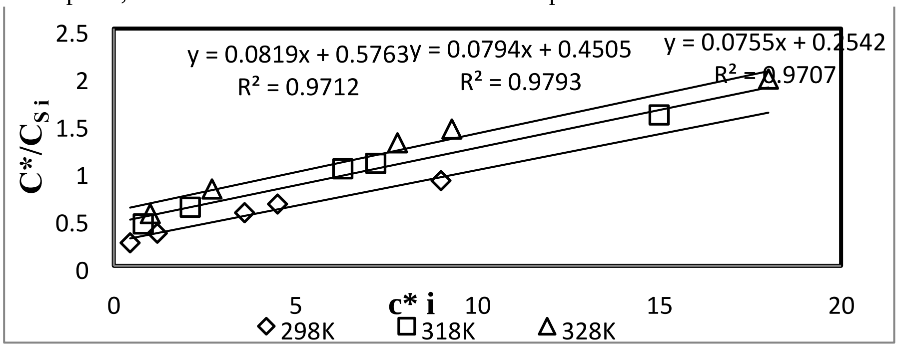

Figure 7: Langmuir plot of *Bruguiera gymnorhiza* at various temperatures at pH 5

The linearized Langmuir adsorption isotherms of Pb (II) onto *Bruguiera gymnorhiza* were obtained at different temperatures. Adsorption constants and correlation coefficients are shown in Table.1 C^*/C_svsC^*plot yielded a straight line with R^2 (0.970) indicating the sorption data could be represented by the Langmuir model (Fig. 7). The higher adsorption capacity, q_m(»1) indicated the strong electrostatic force of attraction and b is a constant which accounts for the affinity of the binding sites (L/mg) Moreover, the b values are 1.030928, 1.02145, 1.029866L/mg indicating that biosorption capacity of *Bruguiera gymnorhiza* biomass for Pb (II) is higher. The adsorption of Pb (II) on powder surface is thus a highly favourable process. Further, it is observed that the sorption of lead is more favourable at higher Pb (II) initial concentration (109.44 mg/L) than for the lower ones (19.21 mg/L).

Table .1. Langmuir and Freundlich isotherm model parameters for Pb (II) onto *Bruguiera gymnorhiza*

Langmuir constants				Freundlich constants		
Temp.(K)	C_m(mg g^{-1})	b (L $mmol^{-1}$)	R^2	K_F	n_f	R^2
298	13.333	0.295276	0.9701	0.32961	1.792115	0.997
318	12.658	0.311024	0.979	0.464515	1.782531	0.996
328	12.3456	0.318898	0.971	0.535797	1.792115	0.998

7.Freundlich iIsotherm

An adsorption isotherm was proposed by Boedecker (Dąbrowski, 2001) which was later modified by Freundlich (Freundlich, 1926). The Freundlich adsorption equation can be written as:

$$\frac{1}{}$$

s f

(5)

Taking logarithm on both sides,

$$In_{C_s} = \ln K_f + \frac{1}{n_f} InC^*$$

$$C = K C^{*n}{}_f$$

(6)

Where 'Cs' is equilibrium adsorption capacity (mg/g), 'C^*' is the equilibrium concentration of the adsorbate in solution, 'K_f' and n_f are constants related to the adsorption process such as adsorption capacity and intensity respectively. This empirical model has shown best fit for non-ideal sorption on heterogeneous surfaces as well as multilayer sorption. The Freundlich isotherm is also more widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model. Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. The coefficient of determination for this case is 0.997 and the values of n_f and K_f (table 1) are found to be 1.79 (g/L) and 0.329 {(mg/g)(mg/L)^n}at 25C. Freundlich constant n_f between 1 and 10 indicates a trend more favorable (Fig.8) for biosorption by macro algae *Bruguiera gymnorhiza*. This is also suggestive that the metal ion under study could well be separated from its aqueous solution with high adsorption capacity.

The values of high correlation coefficients indicated that the Pb(II) sorption data was very well represented by Freundlich model. The Freundlich constant n_f was greater than 1, at all temperatures as well as initial metal concentrations representing that adsorption intensity of the sorbate on the sorbent surface was high, reflecting the favorable sorption even at high metal concentration.

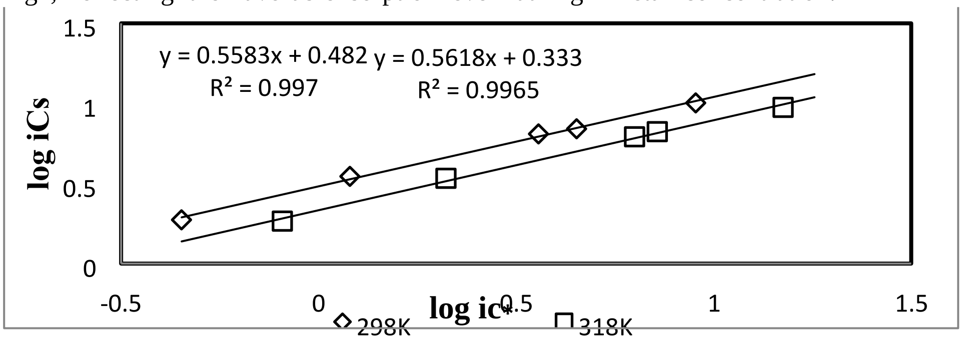

Figure 8: Freundlich plot of *Bruguiera gymnorhiza* at various temperatures at pH 5.

8.Adsorption iKinetic iModels

The kinetic data helps in tracing the rate determining step of transport mechanism and is required for selecting optimum operating conditions for full-scale batch or continuous process. In the present study Pseudo first order and Pseudo second order kinetic models have been attempting to fit the present biosorption data (Table. 2).

9 Pseudo-first-order/Lagergren ikinetic imodel

The Pseudo-first-order or Lagergren kinetic rate equation for the adsorption of liquid-solid system was derived based on solid adsorption capacity. It is one of the most widely used adsorption rate equations for the adsorption of a solute from a liquid solution (Taqvi et al, 2006; Suddhodan and Mishra, 2006).

The pseudo first order kinetic equation can be expressed as:

$$\underline{dc}dt = k_1\left(C_S - C_t\right) \tag{7}$$

Where 'C_s' is the amount of solute adsorbed at equilibrium per unit mass of adsorbent (mg/g), 'C_t' is the amount of solute adsorbed at any given time 't' and 'k_1' is the rate constant. By using the boundary conditions and simplifying, the equation 7 yields.

$$\ln(Cs - Ct) = \ln Cs - k_1 t \tag{8}$$

'k_1' can be computed from the slope of the linear plot between $\ln(C_s\text{-}C_t)$ vs. 't' for different adsorption parameters such as pH, temperature. The pseudo first order rate constant $k_1$could be obtained from the slope of the plot between log (C_s –C_t) and time t'. Fig. 9 shows that the Lagergren pseudofirst order kinetic plot does not fit well for the adsorption of Pb (II) onto *Bruguiera gymnorhiza*, as it does not follow a straight line.

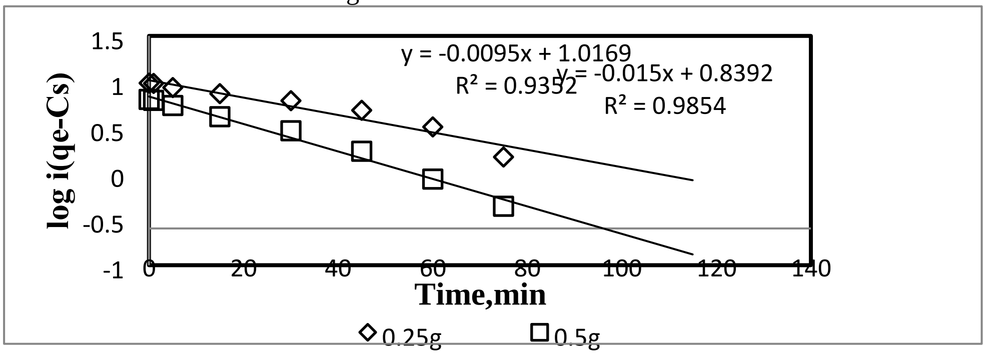

Figure .9: Pseudo first order kinetic plot for biosorption of Pb (II) at 25°C, 50 mg/L and pH 5.

10.Pseudo- isecond- iorder ikinetic imodel

In view of the above the fitness of the sorption data was tested using pseudo- second- order reaction model .The pseudo-second-order reaction model could be expressed by the rate expression as (Ho and Mckay, 1999; 2000).

$$\underline{dc}dt = k^2(C^s - C^t)2$$

(9)

On integration for boundary conditions when t=0 to t>0 and q_t=0 to q_t>0 and further simplifications, equation 9 becomes,

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

The plot (Fig.8) of t/q_t versus t of Eq. (10) gave a linear relationship from which the q_e and k_2 values were determined.

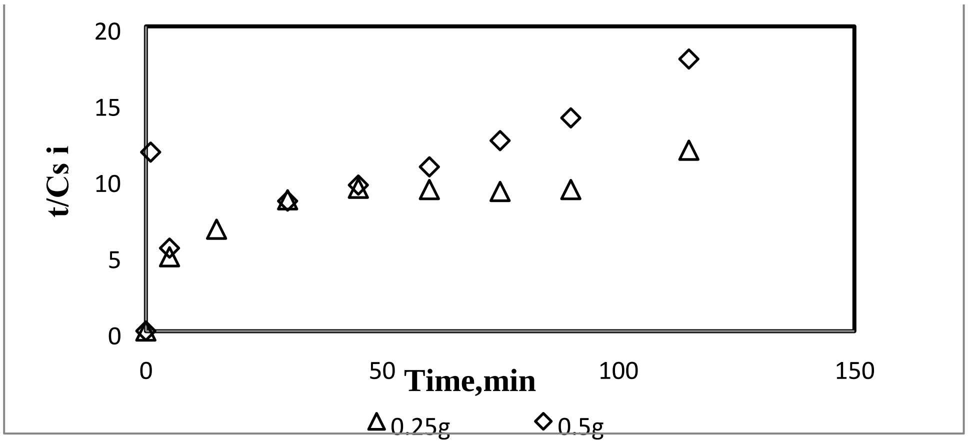

Figure. 10: Pseudo second order kinetic for biosorption of Pb (II) at 25°C, 50 mg/L and pH 5.

W (g/L)	C_e(exp) (mg/g)	K_1(g/mg-min)	R^2
5	3.66	-0.009	0.939
10	4.57	-0.015	0.986

Table .2: Kinetic parameters for Pb (II) biosorption on *Bruguiera gymnorhiza*

The rate constants and the correlation coefficients for Pseudo-First-order kinetic model were calculated and summarized in Table. 2. These values showed that the pseudo-first order kinetic plot fits well the adsorption data. The value of correlation coefficient R^2 for the pseudo-first-order adsorption model is relatively high (>0.9909), and the adsorption capacities calculated by the model are also close to those determined by experiments. However, the values of R^2 for the pseudo-second-order are not satisfactory. Therefore, it has been concluded that the pseudo-first-order adsorption model is more suitable to describe the adsorption kinetics of lead over this *Bruguiera gymnorhiza* biomass.

11.Thermodynamic iparameters

Gibbs Free Energy ΔG is the Thermodynamic criterion at constant P and T for deciding whether the chemical process does proceed or not. The spontaneity of the reaction can also be judged by the sign and magnitude of ΔG^0. A negative sign for ΔG^0 is an indicative of the spontaneity of any chemical process. To design any chemical process system one should have the knowledge of the changes that are expected to occur during a chemical reaction.

In view of the above, analysis has been carried out on the values of thermodynamic parameters on the biosorption of Pb (II) by *Bruguiera gymnorhiza*. The thermodynamic parameters such as changes in standard free energy change ΔG^0, Enthalpy ΔH^0, Entropy ΔS^0 for any given adsorption process could be determined from the Equations:

$$\Delta G^0 = -RT\ln K_c \qquad (11)$$

Where ΔG^0 is the free energy change, expressed as J/mol. Kc is the apparent equilibrium constant for the process. Kc can be derived from:

$$K_C = \frac{C_S}{C_*} \qquad (12)$$

$$\log\left(\frac{C_S}{C^*}\right) = \frac{-\Delta H^0}{2.303RT} + \frac{\Delta S^0}{R} \qquad (13)$$

$\frac{C_S}{C_*}$ Can be defined as adsorption affinity. C_s is the concentration of metal ion (mg) in solid adsorbent. C^* is equilibrium metal Concentration mg/L. The enthalpy changes (ΔH^0) and entropy changes (ΔS^0) for the adsorption process for all the initial metal concentrations in the aqueous solutions were obtained from the plots of $\log\left(\frac{C_S}{C^*}\right)$ drawn against 1/T (Fig.11). The calculated thermodynamic data are compiled in Table .4.

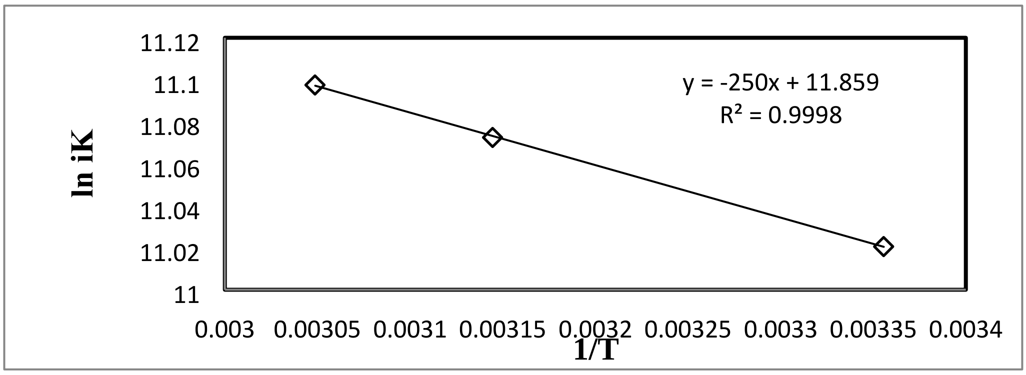

Fig.11. Vant Hoff plot for adsorption of Pb (II) onto *Bruguiera gymnorhiza* at various temperatures for biomass 10 g/Land at pH 5.

A Large negative value for ΔG□ indicates the spontaneity of biosorption process at a given temperature. The free energy values increased positively with increase in temperature for the adsorption of Pb (II), shows that the spontaneity of the biosorption process reduces with increase in temperature. The negative ΔH□ values indicated the exothermic nature of the adsorption. The negative values of ΔS□suggested a decrease (Ahmet et al., 2008) in the randomness at solid/solution interface during the adsorption of Pb (II) ions onto *Bruguiera gymnorhiza* **Table. 4:** Thermodynamic parameters for Pb (II) biosorption on *Bruguiera gymnorhiza*

Temp. (^{0}K)	□H□(KJ/mol)	□S□(J/mol^{0}K)	□G□(KJ/mol)
298	2078.5	98.5209	-27.2807
318	2078.5	98.5209	-29.2511
328	2078.5	98.5207	-30.2364

12.Characterization iof iBiomass 12.1.Fourier iTransform iInfrared iSpectroscopy i(FTIR)

The FTIR differences of spectra in pure *Bruguiera gymnorhiza* biomass adsorbent were compared to the spectra obtained in Pb(II) loaded *Bruguiera gymnorhiza* to determine whether the observed differences are due to interaction of the metal ions with functional groups (Fig. 12 and 13). The absorption peaks were tabulated in table 4 for pure biomass and Pb^{2+} loaded algal biomass.

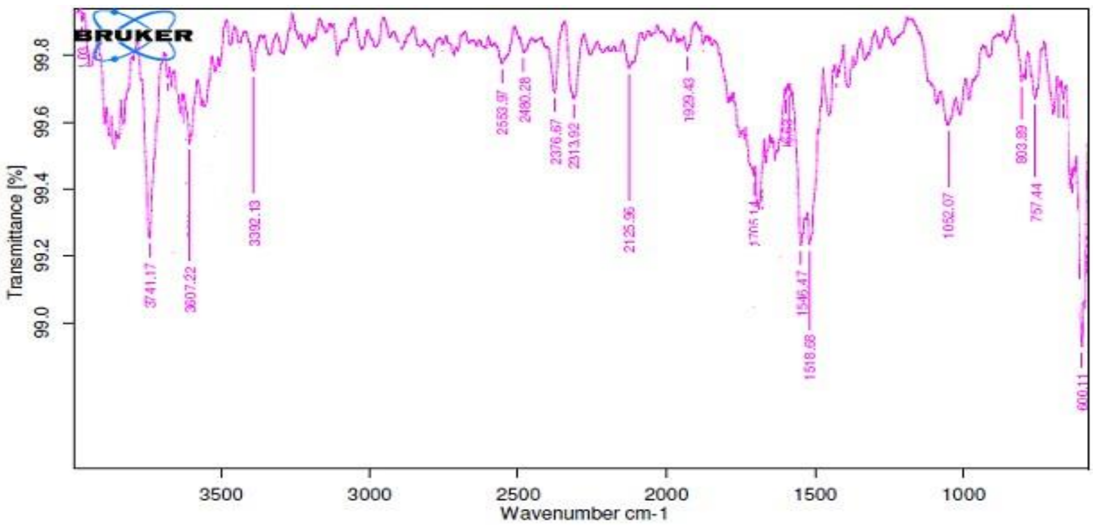

Figure 12: FTIR Spectrum of *Bruguiera gymnorhiza* before treatment

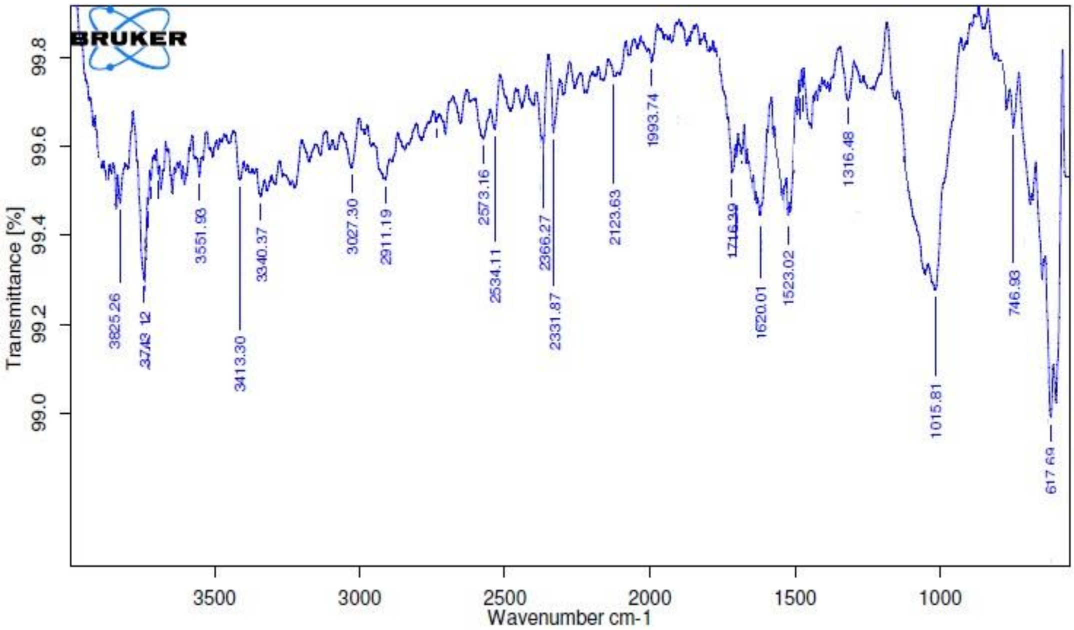

Figure 13: FTIR Spectrum of *Bruguiera gymnorhiza* after treatment with Pb (II)

The broad bands at 3607.22 and 3392.13 cm^{-1} were due to –OH and $–NH_2$ stretching vibrations due to lignins (Lalhruaitluanga et al., 2010) and –OH stretching vibrations respectively involved in the biosorption by shifting the band to 3351.93 and 3340.37 cm^{-1}. The bands at 3051.31 cm^{-1} indicate the presence of CH_2 stretching vibrations of aromatic aryl rings and shifted to 3021.30 cm^{-1}. The band at 2376.67 cm^{-1} can be attributed to –C≡N in the polyacrylonitrile (Sarada et al., 2014) and is involved intensely by shifting to 2366.27 cm^{-1}. The band peak at 1705.14 cm^{-1} is assigned to Carbonyl functional group of, after adsorption of Pb^{2+} the band slightly shifted to 1716.30 cm^{-1}. Further the sharp peak at 1376.07 cm^{-1} representing the presence of $–CH_2$ bending vibrations in the biomass and is also shifted to 1316.48 cm^{-1} indicating the involvement in biosorption process.

The presence of siliceous from diatomaceous earth, in mangrove plant waste and composite material, can justify for the absorbance peak at 757.44 cm^{-1} (Si–C) and N containing bioligands is shifted to the 746.93 cm^{-1}. The bands present below 800cm^{-1} are finger print zone of phosphate and sulphur functional groups and N containing bioligands. The significant changes in the wave numbers of the specific peaks suggested that –OH and $–NH_2$, bounded $–CH_2$, amide N-H bending vibrations and C=O of carboxylic acid groups could be predominantly involved in the biosorption of Pb^{+2} onto *Bruguiera gymnorhiza*. Similar results were reported for the biosorption of different heavy metals on various plant species (Sibel et al, 2009; Suleman et al, 2009; Lalhruaitluanga et al, 2010; Munagapati et al, 2010; Sarada et al, 2014)

13 conclusion

Experimental data were obtained for removal of Pb (II) ions using *Bruguiera gymnorhiza* as biosorbent. Based on the analysis the following conclusions were made.

The biosorption performances are strongly affected by parameters such as initial concentration, pH, and temperature.The percentage biosorption Pb (II) ions of increases with increasing contact time.The equilibrium uptake was increased and percentage biosorption was decreased with increasing the initial concentration. The plot of pH versus percentage biosorption shows the significant biosorption takes place at 5.The percentage biosorption Pb (II) of increases with increase in the biosorbent dosage.The percentage biosorption Pb (II) of decreases with increase in the temperature.The removal data of lead ions follows the Freundlich model with the best fit.The kinetics of the biosorption of lead ions on *Bruguiera gymnorhiza* can be better described with First-order kinetics. Intra-particle diffusion might also have a significant role in the biosorption process slowing down the approach towards equilibrium.The thermodynamic parameters such as free energy change, enthalpy change and entropy changes were calculated and the biosorption process was exothermic. **References**

1. Ademoroti, iC. iM. iA., i(1996). iEnvironmental ichemistry iand itoxicology. iPollution iby iheavy imetals. iFoludex ipress, i171- i172 i

2. Afridi iH. iI., iKazi iT. iG., iKazi iG. iH., iJamali iM. iK., iShar iG. iQ., i2006. iEssential itrace iand itoxic ielement idistribution iin ithe iscalp ihair iof iPakistani imyocardial iinfarction ipatients iand icontrols. iBiol. iTrace iElem. iRes. i113, i19-34.
3. Ahmet, iS., iDurali, iM., iMustafa, iT., iMustafa, iS., i"Biosorption iof iCd i(II) iand iCr i(III) ifrom iaqueous isolution iby imoss i(Hylocomiumsplendens) ibiomass: iEquilibrium, ikinetic iand ithermodynamic istudies," iChem. iEngg. iJ, ivol. i144, ipp. i1–9, i2008
4. Ahmet, iS., iMustafa, iT., i"Biosorption iof iPb(II) iand iCd(II) ifrom iaqueous isolution iusing igreen ialga i(Ulva ilactuca) ibiomass," iJ. iHazard. iMater, ivol. i i152, ipp. i302–308, i2008.
5. Aksu, iZ.," iEquilibrium iand ikinetic imodeling iof icadmium i(II) ibiosorption iby iC. iVulgaris iin ia ibatch isystem: ieffect iof itemperature," iSepn.Purifi. iTechno, ivol. i21, ipp. i285–294, i2001.
6. Amuda iOS, iOjo iOI, iEdewor iTI i(2007). iBiosorption iof iLead ifrom iIndustrial iWastewater iUsing iChrysophyllum ialbidum iSeed iShell. iBioremed. iJ. i11 i(4): i183- i194
7. Areco, iM.M., iAfonso, iM.D.S., i"Copper, izinc, icadmium iand ilead ibiosorption iby iGymnogongrustorulosus: ithermodynamics iand ikinetics istudies," iColloid.Surf. iB: iBioint, iVol. i81, ipp. i620–628, i2010.
8. Bakircioglu iY, iBakircioglu iD, iAkman iS i(2010) iBiosorption iof ilead iby ifilamentous ifunal ibiomass-loaded iTiO2 inanoparticles. iJ iHazard iMater i178(1–3):1015–1020
9. Bamidele iI. iOlu-Owolabi i i, iPaul iN. iDiagboya i, iWilliam iC. iEbaddan. i iMechanism iof iPb2+ iremoval ifrom iaqueous isolution iusing ia inonliving imoss ibiomass. iChemical iEngineering iJournal i195-196 i(2012) i270–275
10. Chen iH, iDai iGL, iZhao iJ, iZhong iAG, iWu iJY, iYan iH i(2010). iRemoval iof icopper i(II) iions iby ia ibiosorbent-Cinnamomum icamphora ileaves ipowder. iJ. iHazard. iMater. i177: i228-236.
11. Dąbrowski, iA., iAdsorption-from itheory ito ipractice, iAdv. iin icolloid. iInter. iSci.vol. i93, i i i i i ipp135-224, i2001.
12. Freundlich, iH., i"Colloid iand icapillary ichemistry," iMethuen, iLondon, i1926. i
13. Gercel iO., iGercel iF., i2007, iAdsorption iof ilead i(II) iions ifrom iaqueous isolution iby iactivated icarbon iprepared ifrom ibiomass iplant imaterial iof iEuphorbia irigida, iJ. iChem. iEng. i132, i289-297
14. Gupta, iV.K., iRastogi, iA., i"Biosorption iof ilead i(II) ifrom iaqueous isolutions iby inon-living ialgal ibiomass iOedogoniumsp. iand iNostoc isp. iA icomparative istudy," iColloids iand iSurfaces iB: iBiointerfaces, ivol. i64, ipp. i170–178, i2008.
15. Guyo, iU., iMhonyera, iJ., iMoyo, iM. iPb(II) iadsorption ifrom iaqueous isolutions iby iraw iand itreated ibiomass iof imaize istover i– ia icomparative istudy. iProcess iSaf. iEnviron. iProt. i2015;93:192–200.
16. Hanafiah iMAKM, iShafiei iS, iHarun iMK, iYahya iM. i2006 iKinetic iand ithermodynamic istudy iof iCd2+ iadsorption ionto irubber itree i(hevea ibrasiliensis) ileaf ipowder. iMater. iSci. iForum i517, i217-221.
17. Jalali iR1, iGhafourian iH, iAsef iY, iDavarpanah iSJ, iSepehr iS. iRemoval iand irecovery iof ilead iusing inonliving ibiomass iof imarine ialgae. iJ iHazard iMater. i2002 iJun i10;92(3):253-62
18. Jianlong, iW., iXinmin, iZ., iDecai, iD., iand iDing, iZ., i2001. iBiosorption iof ilead(II) ifrom iaqueous isolution iby ifungal ibiomass iof iAspergillus iniger. iJ. iBiotechnol. i87, i273-277.
19. Kazi iT. iG., iJalbani iN., iKazi iN., iJamali iM. iK., iArain iM. iB., iAfridi iH. iI., iKandhro iA., iPirzado iZ., i2008. iEvaluation iof itoxic imetals iin iblood iand iurine isamples iof ichronic irenal ifailure ipatients, ibefore iand iafter idialysis. iRenal iFailure. i30, i737-745.
20. Langmuir, iI., i"The iadsorption iof igases ion iplane isurfaces iof iglass, imica iand iplatinum," iJ. iAm. iChem. iSoc, ivol. i40, ipp. i1361-1403, i1918.
21. Majumdar, iS.S., iS.K. iDas, iR. iChakravarty, iT. iSaha, iT.S. iBandyopadhyay iand iA.K. iGuha: iA istudy ion iPb iadsorption iby iMucor irouxii ibiomass. iDesalination, i251, i96-102 i(2010).
22. iMaria iMar iAreco., iand iMaria idos iSantos iAfonso., iColloids iand iSurfaces iB: iBiointerfaces. iVol i81, ipp i620–628, i2010
23. Milan iMomcilovic i, iMilovan iPurenovic, iAleksandar iBojic, iAleksandra iZarubica, iMarjan iRandelovic. iRemoval iof ilead(II) iions ifrom iaqueous isolutions iby iadsorption ionto ipine icone iactivated icarbon. iDesalination i276 i(2011) i53–59

24. Mohan, iM., iPittman iJr., iC., iU., i(2007), iArsenic iremoval ifrom iwater/wastewater iusing iadsorbents-A icritical ireview, iJournal iof iHazardous iMaterials i142, i1–53. i i
25. Mohammad iM.M.R.,Parisa iR., iAtefeh iA., iAli iR.K., iKinetics iand iequilibrium istudies ion ibiosorption iof icadmium, ilead, iand inickel iions ifrom iaqueous isolutions iby iintact iand ichemically imodified ibrown ialgae, iJ. iHazard. iMater, ivol. i i185, ipp. i401–407, i2011. i
26. Munagapati iV.S., iYarramuthi iV., iNadavala iS.K., iAlla iS.R., iAbburi iK., i"Biosorption iof iCu(II), iCd(II) iand iPb(II) iby iAcacia ileucocephala ibark ipowder: iKinetics, iequilibrium iand ithermodynamics," iChem. iEngg. iJ,vol. i157, ipp. i357–36, i2010.
27. Namdeti, iR., iPulipati, iK., i"Lead iremoval ifrom iaqueous isolution iusing iFicusHispida ileaves ipowder," iDesalination iand iWater iTreatment, ivol. i52, ipp.339–349, i2014.
28. Okoro, iI. iA, iEjike, iE. iN.(2007). iSorption imodels iof iPb i(II) iremoval ifrom iaqueous isolution iusing icommon iedible ifruit iwastes. iEur. iJ. iSci. iRes., i17 i(2), i270-276.
29. Ozcan iA.S., iTunali iS., iAkar iT., iOzcan iA. i2009. iBiosorption iof ilead(II) iions ionto iwaste ibiomass iof iPhaseolus ivulgaris iL.: iestimation iof ithe iequilibrium, ikinetic iand ithermodynamic iparameters. iDesalination, i244: i188-198
30. Pandey iPK, iVerma iY, iChoubey iS, iPandey iM, iChandrasekhar iK. i2008 iBiosorptive iremoval iof icadmium ifrom icontaminated igroundwater iand iindustrial ieffluents. iBioresour. iTechnol i99, i4420-i4427.
31. Pehlivan iE, iCetin iS, iYanık iBH i(2009) iEquilibrium istudies ifor ithe isorption iof izinc iand icopper ifrom iaqueous isolutions iusing isugar ibeet ipulp iand ifly iash. iJ iHazard iMater i135(1–3):193–199
32. Resmi, iG i, iThampi, iS. iG. iand iChandrakaran, iS. i(2010). iBrevundimonas ivesicularis:A iNovel iBio-sorbent ifor iRemoval iof iLead ifrom iWastewater. iInt. iJ. iEnviron. iRes., i4(2):281-288.
33. Sarada, iB., iPrasad, iM., iKumar, iK.K., iMurthy, iC.,"Potential iUse iOf iLeaf iBiomass, iAraucaria iheterophylla iFor iRemoval iOf iPb+2," iInternational iJournal iof iPhytoremediation, ivol. i15, ipp. i756–773, i2013. i
34. Selatnia, iA., iBoukazoula, iA., iKechid, iN., iBakhti, iM.Z., iChergui, iA., iand iKerchich, iY., i2004. iBiosorption iof ilead(II) ifrom iaqueous isolution iby ia ibacterial idead iStreptomyces irimosus ibiomass. iBiochem. iEng. iJ. i19, i127-135.
35. Sibel iT.A., iAsli iG., iBurcu iA., i"Zerrin iK., iTamer iA., iInvestigation iof ithe ibiosorption icharecterestics iof ilead i(II) iions ionto iSymphoricarpusalbus: iBatch iand idynamic iflow istudies,"J. iHazard. iMater. i165, i126-133. i(2009).
36. Suddhodan iP., iMishra iV., i"Inorganic iparticulates iin iremoval iof iheavy imetal itoxic iions-Part iX: iRapid iand iefficient iremoval iof iHg(II) iions ifrom iaqueous isolutions iby ihydrous iferric iand ihydrous itungsten ioxides," iJ. iColloid. iInterfSci, ivol. i296, ipp. i383-388, i2006.
37. Suleman, iQ., iAnwar, iR.S., iMuhammad, iU., i"Biosorption iof ilead ifrom iaqueous isolution iby iFicus ireligiosa ileaves: iBatch iand icolumn istudy," iJ. iHazard. iMater, ivol. i166, ipp. i998–1005, i2009.
38. iSulaymon iAH, i iMohammed iAA, iand i iAl-Musawi iTJ. iCompetitive ibiosorption iof ilead, icadmium, icopper, iand iarsenic iions iusing ialgae. iEnviron iSci iPollut iRes iInt. i2013 iMay; i20(5): i3011–3023.
39. Sulaymon iAH, iEbrahim iSH, iRidha iMJ i(2012) iEquilibrium, ikinetic, iand ithermodynamic ibiosorption iof iPb(II), iCr(III), iand iCd(II) iions iby idead ianaerobic ibiomass ifrom isynthetic iwastewater. iEnviron iSci iPollut iRes. idoi:10.1007/s11356-012-0854-8
40. Tan, iG.Q., iXiao, iD., i2009. iAdsorption iof icadmium iion ifrom iaqueous isolution iby iground iwheat istems. iJ. iHazard. iMater. i164: i1359–1363.
41. Taqvi, iS.I.H., iBhanger, iM.I., iShah, iS.W., i"Exploitation iof ibeach isand ias ia ilow icost iadsorbent i i ifor ithe iremoval iof iPb(II) iions ifrom iaqueous isolutions. iSepn," iSci. iTechnol.Vol. i41, ipp i531-547, i2006.
42. Wang, iJ., iChen, iC., i"Biosorbents ifor iheavy imetals iremoval iand itheir ifuture." iBiotechnology iAdvances, ivol. i27, ipp. i195–226, i(2009).
43. Yi-Chao, iL., iShui-Ping, iC., i"The ibiosorption iof iheavy imetals ifrom iaqueous isolution iby iSpirogyra iand iCladophora ifilamentous imacroalgae," iBioresour. iTechnol.vol. i102, ipp. i5297–5304, i2011.