Kinetic, Equilibrium and Thermodynamic Studies on Removal of Cu(II) and Pb(II) by Activated Carbon Prepared from Macro-Algae (*Kappaphycus alvarezii*)

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Present study was intended to explore the biosorption of Cu(II) and Pb(II) ions in aqueous solution using activated carbon biosynthesized from macro-algae *Kappaphycus alvarezii* under different experimental parameters. Activated carbon was produced *via* zinc chloride chemical activation method. The effect of parameters such as pH, temperature over biosorption, amount of adsorbents, initial Cu(II) and Pb(II) aqueous concentration, and contact time were studies. The pH 4.0 for adsorption of Cu(II) and Pb(II), and metal ions uptake contact time of 60 min were considered as optimum. Equilibrium data of biosorption were analyzed by models of Langmuir and Freundlich isotherm at different initial Cu(II) and Pb(II) aqueous solutions concentration. Fruendlich adsorption isotherm model fitted well into biosorption data with a regression value of 0.9986. Thermodynamic parameters such as change in change of enthalpy (ΔH°), change of entropy (ΔS°) and Gibbs free energy (ΔG°) were also determined.

Keywords: *Kappaphycus alvarezii*, Biosorption, Adsorption isotherms, Thermodynamics.

INTRODUCTION

Copper and lead are the widest spread toxic heavy metals contaminant of environment, that causes instability, disorder, discomfort and harm to the living organisms [1,2]. Lead for instance, may exhibit some long-lasting negative health impacts such colic, constipation and anemia [3]. In addition, bio-accumulation of traces of copper metal in the body may lead to problems such as severe mucosal irritation, hepatic/renal damage capillary damage, and central nervous problems [4].

The current developments of industrial and agricultural activities are being the major source of heavy-metal pollution worldwide [5,6]. Thus, removal of these heavy metal ions from sewage effluents and other water resources is essential to ensure environmental and human safety. The concern of environmentalist as well as the government on this issue, had therefore given rise to vast research on developing an advanced technology for the removal of heavy metals from water and wastewater.

Removal of heavy metal pollutants using activated carbon as an adsorbent is an effective and simple method [7]. Activated carbon is the widely-used adsorbent because of its extremely high internal porosity and consequently high absorptivity [8,9]. Activated carbon adsorption capacity depends upon its surface area and porosity. The textural property of activated carbon depends upon precursor material and method of preparation [10].

Physical activation and chemical activation are the two commonly used methods to prepare the activated carbon. The chemical activation method using $ZnCl_2$ is highly preferred. This is because it results in large surface area, thereby high micropore yield [11,12]. In recent years, high cost of activated carbon has encouraged many researchers for production of activated carbons using renewable and low-cost adsorbent precursors. In this research, activated carbon derived from macro-algae *Kappaphycus alvarezii* was used to evaluate biosorption of copper and lead metal ions in aqueous solution. Macro-algae cultivated in seawater are biological resources that are available in large quantities which could serve as a potential precursor biomaterial to prepare the activated carbon. The effect of factors such as contact time, amount of activated carbon, initial pH, initial concentration of heavy metals and temperature was investigated in terms of biosorption.

EXPERIMENTAL

All reagents and chemicals used were of analytical grade and were procured from the Merck, Darmstadt. The copper(II) and lead (II) ion stock solutions of 100 mg L^{-1} were prepared by dissolving appropriate amounts of Cu(II) and Pb(II) ion solution of 1000 mg L^{-1}, respectively in distilled water. The solution pH was adjusted with 0.1 M HCl and 0.1 M NaOH solution.

Preparation of biomass: The macro-algae *Kappaphycus alvarezii* were obtained from Sempora, Sabah, Malaysia. Prior to experimental procedures, the macro-algae sample was processed by washing several times with the distilled water to remove debris, dirt and sand particles and sieved. The clean macro-algae biomass was then sun dried for 5 days till a constant weight was obtained. Dried macro-algae (200 g) was stirred in a boiling solution of anhydrous ZnCl$_2$ (1 g in 1 L of distilled water) for 1 h and dried at 60 ºC for 12 h [13].

Preparation and characterization of adsorbent: The processed macro-algae sample was put into a ceramic crucible, placed in a furnace (Miditherm 200 MP-BEGO) at 700-800 ºC, and carbonized for 1 h. After cooling, excess zinc chloride was leached out by immersing the carbonized macro-algae into 1 M H$_3$PO$_4$ solution for 24 h in an 80 ºC oven. Then, the activated carbon was repeatedly washed by distilled water (to remove the traces of H$_3$PO$_4$ and ZnCl$_2$), and finally dried [14].

Perkin Elmer System 2000 FTIR spectrometer was used to obtain the spectrum for the macro-algae sample. The sample was grounded and mixed with KBr in 1:100 ratio. The FTIR of the sample was done in the range of 4000 to 400 cm^{-1}. Present study accounts determination of the morphology of bio produced activated carbon by Scanning Electron Microscopy (SEM) bearing Carl Zeiss Leo Supra 50 VP Field Emission equipped with Oxford INCA-X energy dispersive microanalysis system. The total pore volume, pore distribution of the activated carbon and surface area, were measured using surface area and porosity analyzer (NOVA 2200e).

Biosorption studies: The biosorption studies were done by agitating 200 mg of adsorbent at 100 rpm with an orbital shaker in 50 mL of aqueous solution of Cu(II) and Pb(II) ions individually at different level of parameters such as contact time (10-240 min), different pHs (2-8), initial concentrations of aqueous Cu(II) ion solution (1-20 mg L^{-1}) and temperatures (15-60 ºC). Once the system attained equilibrium, the mixture was filtered using Whatman 1 filter paper. Remaining metal concentration in the filtrate was determined by Perkin Elmer A Analyst 700, Atomic Absorption Spectroscopy (AAS). As for the optimization of the biosorption the experiment was also carried out by agitating different amount of adsorbent (100 500 mg) in 50 mL of aqueous solution of Cu(II) ions at pH 4 and room temperature (25 ºC) with 100 rpm using orbital shaker.

RESULTS AND DISCUSSION

Adsorbent characterization: The FT-IR spectrum was obtained for the activated carbon bio-produced from macro-algae (Fig. 1). The data exhibited that activated carbon possesses various functional groups, *e.g.*, carboxyl, hydroxyl, and amide. Major bands appeared around 3500-2900, 1650-1500
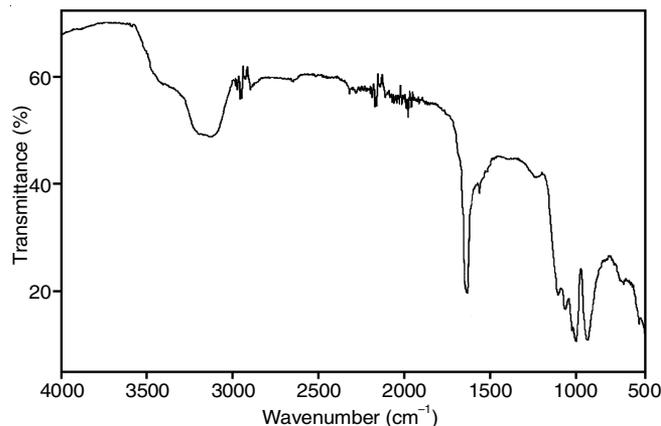

Fig. 1. FTIR spectra of activated carbon produced from *Kappaphycus alvarezii*

and 1100-1000 cm^{-1}. The bands at 3400 and 2930 cm^{-1} are attributed to presence of hydroxyl (O-H *str*.) and carbon aliphatic functional group (C-H *str*.) [14-16]. Band at 1640 cm^{-1} resulted due to presence of C=O group (C=O *str*.) in lactone and carbonyl groups [17-19]. Aromatic rings or C=C bonds displayed a band at 1610-1590 cm^{-1}. The additional small peaks at 1100-1000 cm^{-1} indicates the C=O in carboxylic acid, alcohol and ester as well as S=O and P=O in phosphate ester. The C=O and S=O groups are reported to exhibit high coordination with trace metals [20]. The good adsorption property of bio-produced activated carbon towards Cu(II) and Pb(II) ions may be attributed due to presence of these functional groups. Table-1 shows physical characterization data of bio-produced activated carbon. The SEM micrographs (Fig. 2) of activated carbons show cavities, pores and rough surface on the carbonized sample indicating its potential adsorption capacities [21].

TABLE-1
PHYSICAL CHARACTERIZATION OF ACTIVATED CARBON PRODUCED FROM OF *Kappaphycus alvarezii*

Parameters	Value
Moisture (%)	5.23
Ash (%)	3.95
Density (g/cm^3)	0.26
BET surface area (m^2/g)	649
Total pore volume (cm^3/g)	0.51
Micropore volume (cm^3/g)	0.04
Mesopore volume (cm^3/g)	0.49

Effect of pH: The pH is one of the most crucial parameters which controls the biosorption of heavy metal ions from aqueous solution [22]. The effect of pH on bioadsorption of Cu(II) and Pb(II) using activated carbon produced from *Kappaphycus alvarezii* in aqueous is shown in Fig. 3. Bioadsorption study of this parameter was done at room temperature by varying the pH of solution from 2-8.

The bioadsorption of Cu(II) showed an increase with increasing pH from 2 to 4. The percentage of removal of Cu(II) ions in pH 2, 3 and 4 were 65.89, 84.50 and 95.29 %, respectively. As for Pb(II) ions, the percentage of removal in pH 2, 3 and 4 are 64.52, 82.77 and 95.01 %, respectively. In contrast, the increase of pH of solution beyond pH 4 until pH 8 showed a
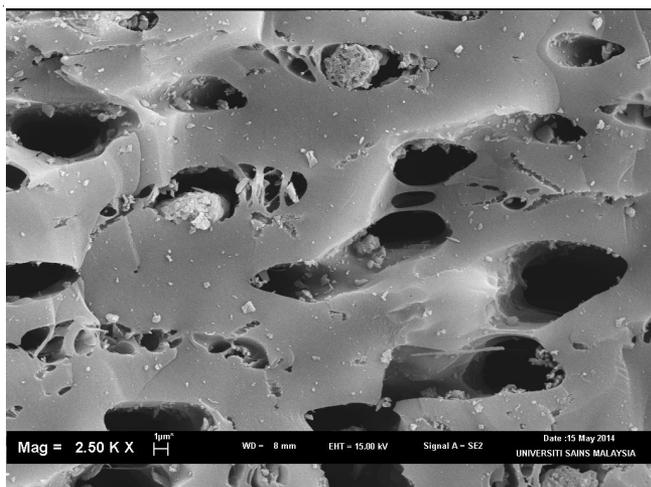
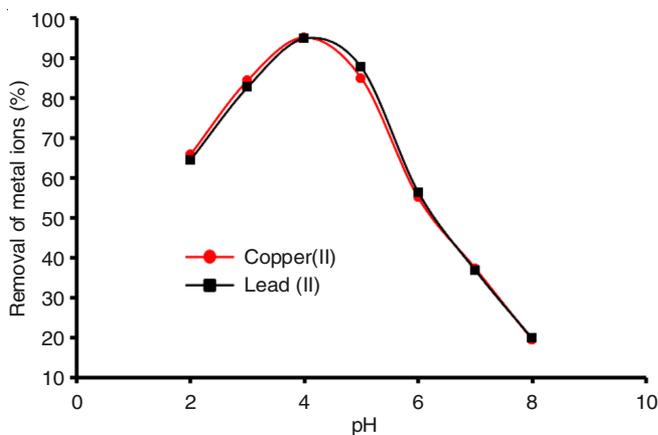Fig. 2. SEM image of activated carbon produced from *K. alvarezii*

Fig. 3. Effect of pH on the percentage removal of Cu(II) and Pb(II) metal ions in aqueous solution using activated carbon of *K. alvarezii*

decrease in the percentage of biosorption. In solution with pH 5, 6, 7 and 8, the percentage of biosorption was 85.06, 55.03, 37.33 and 19.35 %, respectively, for Cu(II) while 87.75, 56.36, 36.81 and 19.68 %, respectively for Pb(II).

The biosorption is optimal at pH 4, as it can be observed that the removal of heavy metal ions was the maximum at pH 4 compared to other pH showing minimal bioadsorption. The low adsorption of heavy metal ions at higher pH is due to the formation of anionic hydroxide complexes [23]. At low pH values there is a lower uptake capacity, since the active sites are protonated. Additionally, the protons may compete with ions for active sites over the surface. An increase in pH lead to predominance of deprotonated sites which favored the ions binding to sites [24].

Effect of contact time: The effect of contact time for the bioadsorption of Cu(II) and Pb(II) ions by activated carbon produced from macro-algae (*Kappaphycus alvarezii*) at pH 4 with 10 mg/L of aqueous heavy metal solution and 0.2 g activated carbon adsorbent is shown in Fig. 4. There was a rapid adsorption of both Cu(II) and Pb(II) in the first 10 min and gradually decreases. The average maximum percentage of Cu(II) and Pb(II) ions removal at the stationary phase was 95.8 and 94.6 %, respectively and was achieved at 60 min.

Effect of adsorbent amount: The results for bioadsorption of Cu(II) and Pb(II) of activated carbon produced from *K. alvarezii*
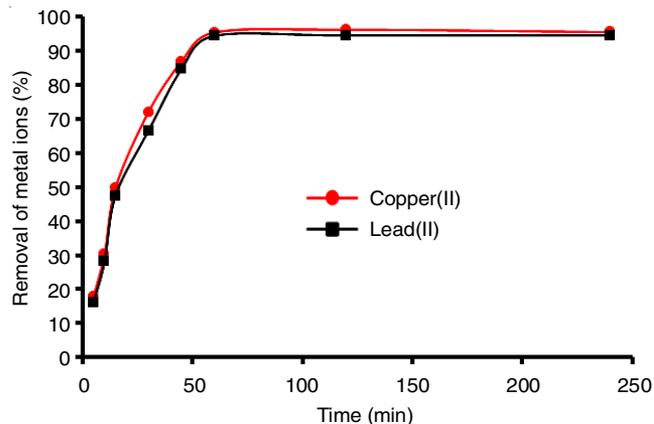

Fig. 4. Effect of contact time on percentage removal of Cu(II) and Pb(II) metal ions in aqueous solution using activated carbon of *K. alvarezii*

with respect to varying adsorbent dose are shown in Fig. 5, over the range of 0.1-0.5 g using 10 mg/L initial metal concentration at pH 4. As per Fig. 5, the percentage removal of metal increased on increase in adsorbent dose. Increase in percentage removal of both Cu(II) and Pb(II) ions with respect to adsorbent dose was observed initially up to a certain limit which are from 88.9 to 95.6 % and 87.9 to 95.4 %, respectively and then remains almost constant. This could be significantly due to the greater availability of the adsorption sites and surface area at initial stage. In addition, the percentage of metal adsorption over adsorbent can be determined by adsorption capacity of adsorbents [25].
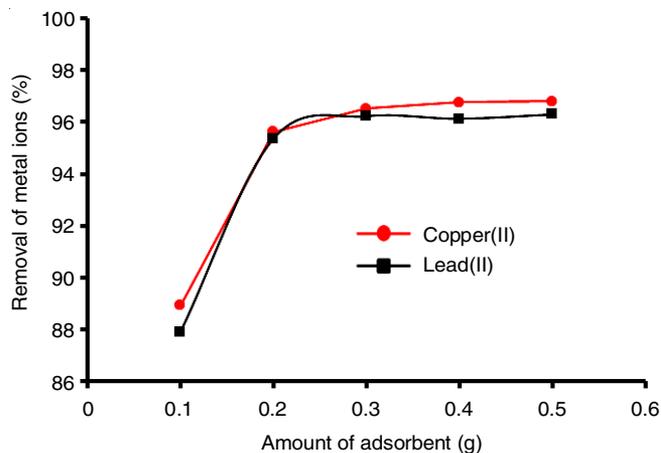

Fig. 5. Effect of amount of adsorbent on the percentage removal of Cu(II) and Pb(II) metal ions in aqueous solution using activated carbon of *K. alvarezii*

Effect of initial concentration: The experimental results of bioadsorptions of metal ions at various concentrations (1, 5, 10, 15 and 20 mg/L) is shown in Fig. 6. The equilibrium data revealed that the percentage removal of heavy metals reduced with increment of initial metal concentration. Although, the actual amount of metal adsorbed per unit mass of adsorbent increased with increment of initial metal concentration. This shows that the adsorption greatly influenced by initial concentration of metal. At low concentration, ratio of initial number of metals for available surface area is low. But subsequently, the fractional adsorption turns out to be independent of initial concentration. Conversely, at high concentration the accessible
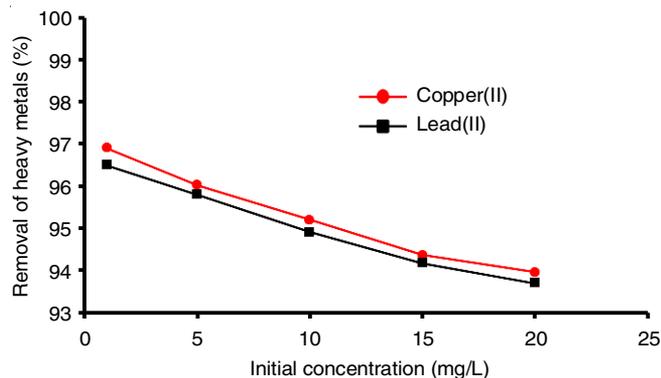
Fig. 6. Effect of initial concentration on the percentage removal of Cu(II) and Pb(II) metal ions in aqueous solution using activated carbon of *K. alvarezii*

sites of adsorption become lesser and thus, the percentage removal of metal depend upon initial concentrations.

Adsorption equilibrium study: The model of Langmuir isotherm is based on the fact that the adsorption occurs with uniform energies onto the surface and there is no transmigration of adsorbent into the plane of surface [26]. The linear form of Langmuir isotherm is given in eqn. 1:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{1}{Q_o} C_e \qquad (1)$$

According to eqn. 1, C_e is equilibrium concentration of aqueous metal solution (mg L^{-1}); q_e is amount of aqueous metal solution adsorbed per unit weight of adsorbent (mg g^{-1}); Q_o and b are Langmuir constants related to adsorption capacity and adsorption rate. When C_e/q_e were plotted against C_e, a straight line with a slope of $1/Q_o$ was obtained. The value of Q_o was determined from the Langmuir plot in the concentration range of 1-20 mg L^{-1}. This assisted in calculation and tabulation of b value (Table-2). Features of Langmuir isotherm can be expressed as dimensionless constant separation factor (R_L) given in eqn. 2:

$$R_L = \frac{1}{1 + bC_o} \qquad (2)$$

The values of R_L were 0.0915 and 0.0911 for adsorption of Cu(II) and Pb(II) ions, respectively suggesting the isotherm to be favourable at the concentrations studied. The Freundlich isotherm model states that the adsorption takes place heterogeneously on the surface of adsorbent that has unequal available sites with different energies of adsorption [27] and this can be represented by eqn. 3

$$\ln q_e = \ln K_f + \frac{1}{n}(\ln C_e) \qquad (3)$$

According to eqn. 3, C_e is defined as the equilibrium concentration of the aqueous metal solution (mg L^{-1}); q_e is amount of aqueous metal solution adsorbed per unit adsorbent weight (mg g^{-1}); and K_f and n are Freundlich constants. Freundlich constants (Table-2) were obtained from slopes and intercepts of log q_e *versus* log C_e. K_f can be defined as the adsorption capacity that represents the quantity of metal ions adsorbed onto the fibers for a unit equilibrium concentration and value of n > 1 indicating the adsorption process favourability. Theoretically, adsorbent possess finite sites. Once adsorbed molecules occupy all sites, the further adsorption is stopped. Considering the effect of indirect adsorbate/adsorbate interactions over adsorption isotherms, Temkin-Pyzhev [28] suggested that heat of adsorption of all molecules in layer decreases linearly with coverage. Temkin isotherm is expressed as eqn. 4:

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \qquad (4)$$

wherein, $B = \dfrac{RT}{b}$.

A plot of q_e *versus* ln C_e determines constants A and B, where constant B is related to heat of adsorption. The constant A and B together with R^2 values are shown in Table-2. As seen from Table-2, a high regression correlation coefficient (R^2) was shown by the Freundlich model for the metal ions. This indicates that the Freundlich model is suitable for describing the adsorption equilibrium of the metal ions by the activated carbon produced from *Kappaphycus alvarezii*. Thus, it is reasonable to conclude that in this study, the adsorptions of metal ions on fibers consisting of heterogeneous adsorption sites.

Adsorption kinetics: To examine the adsorption process mechanism, present study involved two simple kinetic models. First, the kinetics of adsorption was analyzed by Langergren pseudo-first-order equation [29] as depicted in eqn. 5:

$$\log (q_e = q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (5)$$

where, q_e and q_t are the amounts of metals adsorbed (mg/g) at equilibrium at time t (min), respectively; and k_1 (min^{-1}) is the rate constant adsorption. Values of k_1 at ambient temperature were calculated from the plots of log ($q_e - q_t$) *versus* t for an initial concentration of 5, 10 and 20 mg/L for the metals. The set of R^2 values obtained were poor. The experimental q_e values were not in agreement with calculated values determined from linear plots (Table-3). The pseudo-second-order equation based on equilibrium adsorption [30] is expressed as in eqn. 6:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (6)$$

where k_2 (g/mg min) is the rate constant of second-order adsorption. Linear plot of t/q_t *vs.* t at ambient temperature, yielded set of R^2 values that are greater than 0.998 for all the metal at evaluated concentration. It showed a good agreement between

TABLE-2
ISOTHERMS CONSTANTS FOR Cu(II) ION AND Pb(II) ION ADSORPTION USING ACTIVATED CARBON FROM *Kappaphycus alvarezii*

Metal ions	Langmuir				Fruendlich			Temkin-Pyzhev		
	Q_o (mg g^{-1})	b (mg L^{-1})	R_L	R^2	K_f (mg g^{-1})	n	R^2	A	B	R^2
Cu(II)	9.9328	0.9999	0.0915	0.9482	4.1645	1.2369	0.9986	2.2800	0.9913	0.9450
Pb(II)	9.9800	1.0000	0.0911	0.9609	4.0293	1.2093	0.9981	2.9100	0.9861	0.9700

TABLE-3
COMPARISON OF THE PSEUDO-FIRST-ORDER, PSEUDO-SECOND-ORDER ADSORPTION RATE CONSTANTS, CALCULATED AND
EXPERIMENTAL q_e VALUES OBTAINED FOR THE REMOVAL OF Cu(II) AND Pb(II) IONS USING ACTIVATED CARBON FROM *K. alvarezii*

Metal ions	Initial concentrations (mg/L)	$q_{e\,(exp)}$	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
			k_1	$q_{e\,(Cal)}$	R^2	k_2	$q_{e\,(Cal)}$	R^2
Cu(II)	5	1.281	0.054	0.159	0.956	0.717	1.289	0.999
	10	2.381	0.063	0.514	0.929	0.235	2.382	0.999
	20	4.698	0.051	0.612	0.952	1.014	4.688	0.999
Pb(II)	5	1.197	0.069	0.148	0.974	0.798	1.201	0.998
	10	2.372	0.056	0.632	0.963	0.321	2.379	0.999
	20	4.685	0.078	0.435	0.925	1.112	4.683	0.999

experimental and calculated q_e values (Table-3), which indicated applicability of this model to explain the adsorption process of the metals onto the fibers.

Effect of temperature: The effect on temperature on the percentage removal of Cu(II) and Pb(II) ions by activated carbon is shown in Fig. 7. The experiment was carried out at 15, 30, 45 and 60 ºC. Temperature influences the adsorption of metal ions, with increasing temperature as the percentage removal of metals also increases. High temperatures is signifi-cantly favourable for adsorption to take place thus, the adsor-ption of activated carbon is an endothermic process.
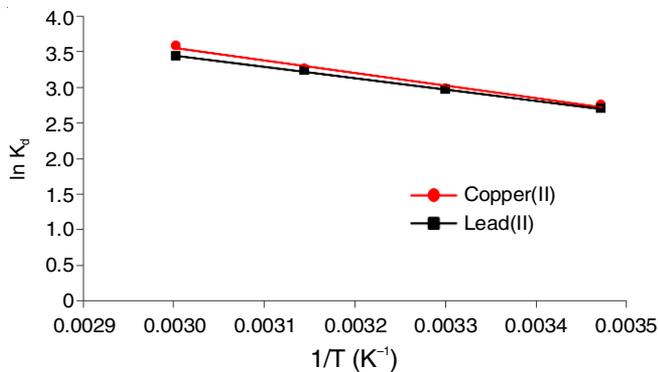

Fig. 7. Thermodynamic parameter values of Cu(II) and Pb(II) metal ions sorbed using activated carbon of *Kappaphycus alvarezii*

Thermodynamic studies: The thermodynamic feasibility and thermal effects of sorption were assessed by determining the Gibbs free energy (ΔGº), entropy (ΔSº) and enthalpy (ΔHº). The ΔGº is the fundamental criterion to determine if a process occurs spontaneously. For a given temperature, a phenomenon is considered to be spontaneous if the ΔGº has a negative value. Moreover, if ΔHº is positive, the process is endothermic and if it is negative, the process is exothermic. The ΔHº value and ΔSº value can be calculated as in eqn. 7:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (7)$$

where, R is the universal gas constant and its value is 8.314 J/mol K; T is the absolute solution temperature in Kelvin; K_d is the

distribution coefficient, ΔSº is the standard entropy and ΔHº is the standard enthalpy. The K_d can be calculated using eqn. 8:

$$K_d = \frac{C_{Ae}}{C_e} \qquad (8)$$

where, C_{Ae} is the amount adsorbed on solid at equilibrium (mg/L); and C_e is the equilibrium concentration (mg/L). The ΔHº and ΔSº values were calculated from the slope and intercept of the slope. While ΔHº can be calculated as follows:

$$\Delta G^\circ = -RT \ln K_d \qquad (9)$$

The graph (Fig. 7) shows the relationship between $\ln K_d$ *versus* 1/T to determine its slope and intercept. The ΔGº values under different temperatures as well as ΔHº and ΔSº values are presented in Table-4. The ΔGº negative values indicated spontaneous nature of sorption, which confirmed the affinity of activated carbon produced from *Kappaphycus alvarezii* for both heavy metals. The positive value of ΔHº indicated sorption of Cu(II) and Pb(II) ions on the activated carbon was endothermic.

Conclusion

In this study, the bioadsorption of copper(II) ion and lead(II) ion on to activated carbon produced from *Kappaphycus alvarezii* macro-algae was investigated. The results and data obtained from this study confirmed the use of activated carbon prepared from macro-algae serves as an effective and cost-efficient way to remove the copper(II) and lead(II) metal ions from aqueous solution. Adsorption was influenced by initial pH, contact time, amount of adsorbent, initial copper(II) and lead(II) ions concentration and temperature. The maximum uptake of copper(II) ion and lead(II) ion occurred at pH of 4.0, while an average of 60 min contact time records the highest metal ions uptake. Increasing amount of adsorbent shows effect in the rate of adsorption but, 0.2 g of adsorbent shows the highest uptake of copper(II) and lead(II) metal ions. Besides that increasing initial copper(II) and lead(II) ions concentration decreases the biosorption rate. The maximum percentage removal of heavy metal was 95.29 and 95.01% for copper(II) and lead(II) ions, respectively. It was attained at pH of 4.0, adsorbent amount of 0.2 g at 10 mg/L initial metal concen-trations. The equilibrium adsorption data are correlated by

TABLE-4
THERMODYNAMIC PARAMETERS FOR BIOSORPTION OF Cu(II) AND Pb(II) USING ACTIVATED CARBON OF *Kappaphycus alvarezii*

Metal ions	-ΔGº (J/mol)				ΔHº (J/mol)	ΔSº (J/mol)
	15 °C	30 °C	45 °C	60 °C		
Cu	6588.36	7525.59	8616.67	9924.04	14661.74	73.5124
Pb	6463.89	7471.00	8543.42	9530.16	13265.82	64.4966

Langmuir and Freundlich isotherm equation, but the experimental data fits the Freundlich isotherm model well. The thermodynamic analysis indicates that the process is of spontaneous and endothermic in nature.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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