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Thermodynamics Modelling of Lead (II) Biosorption using *Cystoseira stricta* Biomass

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ABSTRACT

Lead (II) biosorption using *Cystoseira stricta* data from a previous study was used for thermodynamics investigation. Thermodynamics study of sorption is very important as it can reveal precious information regarding the spontaneity and reaction types. This study computed thermodynamics parameters for the biosorption reaction of Pb (II) by *Cystoseira stricta* biomass, energy change (ΔG= −18.74, −20.80, and −21.82 kJ/mol at 30, 35 and 40°C respectively), enthalpy change (ΔH= 75.01 kJ/mol) and entropy change (ΔS= 309.78 J/mol). The parameters were found to be spontaneous (−ΔG), endothermic (+ΔH) and the (+ΔS) value indicates increased randomness of the reaction. Likewise, the reaction process was found to be physical, deriving energy in the form of heat from the surrounding. Confidence interval (95%) for each of the parameter was also calculated.

INTRODUCTION

Industrial operations are generally considered to be responsible for heavy metals contamination [[1–3]]. Heavy metals, which are non-biodegradable, can be distributed between air, water and soil or may be absorbed into the living organisms or nonliving biomass [4,5]. Lead is a heavy metal ion harmful to the human biosystem and is one of the most commonly known heavy metal of high economic importance [4,6]. Accumulation of relatively small quantities of lead over a long period of time in the human body can lead to organ failure and chronic toxicity. According to the WHO the maximum allowable limit (MPL) of lead in drinking water is 0.05 mg/L [4].

Biosorption is normally used to model the treatment of different contaminants with the advantages of low cost, easy and safe operation, and environmental friendliness [7–10]. In the previous study Iddou *et al.,* [4], *Cystoseira stricta* biomass was used as a novel biosorbent to extract Pb (II) from aqueous solution. The goal of the study was to establish a comparison between the adsorption ability of the chemically treated algae and the non-treated algae. Some parameters affecting biosorption, such as the size of biosorbent particles, chemical treatments and temperature, were investigated and data on adsorption isotherms were obtained and adapted for isothermal models, such as the Langmuir and Freundlich [7,11].

In this study, data from fig 8 from Iddou *et al*., [4], was used for thermodynamics analysis. Several studies have reported the effect of temperature on biosorption mechanism [7,12,13]. The effect of temperature on the rate of chemical reaction is calculated in the simplest way by the empiric law of Van't Hoff's. According to this law, an increase in temperature by 10 K induces a 2-4-fold increase in the response rate [7,14]. As a result, an improvement in temperature from 20 to 100^{0}C could shorten the length of the reaction, i.e., from 1 h to 1 min. Overall, the reaction rate can be experimentally calculated at several temperatures [13,15]. In this review, the thermodynamics adsorption parameters were used to show the type of reaction of the solution. The parameters include Gibbs

energy change (ΔG), enthalpy change (ΔH) and the entropy change (ΔS) [14,16].

MATERIALS AND METHODS

Using Webpotdigirizer 2.5 software, data from Fig 8. from Iddou *et al.,* [4] was processed. This program digitizes data and has been used and appreciated by many researchers for its reliability [17–19]. The data were regressed using Langmuir non-linear regression and converted were to dimensionless [7,13].

Thermodynamic analysis

Using van't Hoff's linear equations below, thermodynamics parameters (ΔH, ΔS and ΔG) were calculated [7,12–14]. Equally, 95% CI for each temperature was calculated [20].

Equation 1:

$$lnK_C = \frac{-\Delta H^\circ}{R} \times \frac{1}{T} + \frac{\Delta S^\circ}{R}$$

Equation 2:

$$\Delta G^\circ = -RTlnK_C$$

Equation 3:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Note: R is the universal gas constant (0.00831 kJ/mol×K)

RESULTS AND DISCUSSION

Thermodynamics parameters have been known to describe the key difference between physical and chemical adsorption process [7]. Physical biosorption demonstrate weak physical reaction while chemical adsorption chemical reaction which is far stronger than the physical [7,13]. The parameters are Gibbs energy (ΔG), enthalpy (ΔH) and the entropy change (ΔS) [12]. As shown in Table 1, the reaction was found to be endothermic. An endothermic reaction process shows (+ΔH) that energy in the form of heat was gained from the surrounding [7]. In contrast, many literatures reported that increase in temperature coincide with decrease in adsorption process [7,14]. Thus, the process is said to be exothermic (-ΔH) reaction, were by heat in form of energy is being released to the surrounding. The reaction process either involves physical (physisorption) or chemical (chemisorption) adsorption or the combination of both processes (comprehensive adsorption) [7,13].

In the endothermic process, the total energy released in bond breaking is lower than the total energy adsorbed in bond making between the Pb (II) and the fungi biomass of the *Cystoseira stricta.* That is to say, that the process adsorbed energy in the form of heat from the surrounding [7,14,21]. The enthalpy (ΔH) was calculated by substituting equation 1 and 2 into equation 3 above.

The spontaneity of the adsorption process was determined by calculating the Gibbs energy change (ΔG). Higher negative value of the Gibbs energy change demonstrates a spontaneous and a favorable adsorption process at a given temperature [7,22,23]. In **Table 1**, all the temperatures (30ºC, 35ºC and 40ºC) were revealed to be spontaneous and feasible adsorption process because of the negative values of the Gibbs energy (-ΔG). In contrast, it would have been non-spontaneous and non-feasible were (+ΔG) is positive. This equally displays the type of the reaction process (physisorption or chemisorption) [7].

Furthermore, the entropy change (ΔS) was computed and discovered to be positive, which indicates the degree of randomness of the adsorbate in the reaction mixture interface during the reaction process. Negative value of the entropy change (-ΔS) implies associative reaction process while positive value of the entropy (+Δ) represents dissociative reaction process [12,16]. More so, the positive value of ΔS implied an increase in degree of freedom of the Pb (II) in the reaction mixture. The entropy change (ΔS) in Table 1 below, shows an increase in randomness of the reaction process. All the thermodynamic parameters (ΔG, ΔH and ΔS) were computed using the above Van Hoff's equations [5,21]. Confidence interval (95%) for each of the parameter was calcuted as shown in **Table 1**.

Table 1. Thermodynamics parameters for biosorption of Pb (II) at the different temperatures.

		95% C.I. upper	95% C.I. lower	Conclusion
ΔH kJ/mol	75.01	19.59	130.42	Endothermic reaction
ΔS J/mol	309.78	132.81	486.75	Increase in the randomness
ΔG at 30 ºC kJ/mol	-18.74	-19.62	-17.85	Spontaneous and feasible reaction
ΔG at 35 ºC kJ/mol	-20.80	-21.29	-20.32	Spontaneous and feasible reaction
ΔG at 40 ºC kJ/mol	-21.82	-21.82	-21.82	Spontaneous and feasible reaction

Fig. 1 presents the enthalpy and entropy change which is a plot of lnK against 1/T.

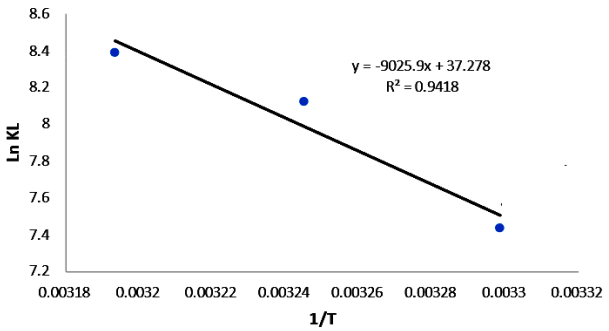

Fig. 1. Van't Hoff plot for the effect of temperature on the sorption of pb (II) on *Cystoseira stricta*.

CONCLUSION

The computed thermodynamics parameters for the bioadsorption reaction of Pb (II) by *Cystoseira stricta* biomass were revealed to be spontaneous (-ΔG), endothermic (+ΔH) and the (+ΔS) value indicates increased randomness of the reaction. Equally, the reaction process can be said to be physical, deriving energy in form of heat from the surrounding. Confidence interval (95%) for each of the parameter was calcuted as shown in Table 1.

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