# Biosorption of Cd (II) by Biomass of Dried Sargassum Baccularia in Aquatic Solution

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1 author:

Khairi Mohamed Alamari
Libyan Academy

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# *Biosorption of Cd (II) by Biomass of Dried Sargassum Baccularia in Aquatic Solution*

Mahmoud, A.Barah[1]. Ibrahim, S. Shaban[2]. Khairy, M. Al-Amari[3]. Aisha M. Al-Majdoub[1]. Ezdehar,A.Al-tllouty[1]
[1]Marine biology research centre,Tajura-Libya.
[2] Environmental chemistry, Libyan Academy,Janzour-Libya.
[3] Environmental science, Libyan Academy,Janzour-Libya



**Abstract – Contamination of wastewater by toxic metals is a global environmental concern. In this study, the possibility of using inactive (dead) *Sargassum baccularia* powder as a natural adsorbent was investigated in the removal of cadmium from aqueous solutions. The biosorption process was found to be highly dependent on a set of variables such as pH, temperature, contact time, shaking speed and initial metal concentration. The results showed an optimum pH value, (6.0) for cadmium, where was the biosorption capacity (842.15±0.252) for cadmium, and the lowest biosorption value for Cd was found at pH 2.0. The optimum temperature in this study was 30 °C. The time required for equilibrium was investigated over a period of 360 min and found to be 180 min. The capacity of biosorption increased with increasing shaking speed, and the highest uptake value was found at 120 rpm. The maximum removal of $Cd^{+2}$ was found at 20 mg/l. The models Freundlich and Langmuir were used to study the equilibrium process of these systems. The Langmuir model was found to be more suitable for the interpretation of these systems by the value of the correlation coefficients higher than 0.99. Brown seaweed powder is an effective, low-cost, and environmentally friendly adsorbent for removing metals from aqueous solutions, according to the results obtained.**

**Keywords – Biosorption; Adsorption; Cadmium; Equilibrium study;seaweed Sargassum baccularia; Coast of Libya.**

## I. Introduction

Heavy metals are one of the most common pollutants found in industrial waste. Paint, pulp and paper, oil refining, electricity, rubber, processing, fertilizers, pharmaceuticals, and battery manufacturing are the major sources of pollution in the aquatic ecosystems [1]. Cadmium is a highly poisonous metal that has impacts for both the environment and humans. Cadmium can accumulate in the tissue of plants growing in industrially polluted areas, and it can be transferred on to humans during food chains [2]. Heavy metals can be removed from wastewater using a variety of techniques, including: precipitation, electrolysis, flocculation, , crystallization, adsorption, chemical precipitation etc[3]. These techniques have been found to be limited because they frequently involve high capital and operational costs, and they may also be associated with the generation of secondary wastes, which pose treatment issues [4]. As a result, the development of a substitute technology must be considered [5]. The use of biological materials for heavy metal recovery from polluted industrial effluent has emerged as a potential alternative method to traditional techniques [6]. Biosorption, which makes use of biological materials' ability to absorb heavy metals, is a relatively new technology for removing heavy metals from industrial wastewater. The main advantages of biosorption technology are its ability to reduce heavy metal ion concentrations to extremely low levels and the use of low-cost biosorbent materials [7]. Biosorbent materials (absorbents) derived from suitable biomass can be used to efficiently remove and recover heavy metal ions from wastewater streams. A few seaweeds, also known as brown algae, have high metal binding capacities. These were greater than those of different types of biomass and sorbents. A few species of seaweeds, known as brown seaweed, have an exceptional ability to bind metals [8]. Brown seaweed cell walls are composed of three components: cellulose, which serves as a structural support; alginic acid, a polymer of mannuronic and guluronic acids and the corresponding salts of sodium, potassium, magnesium, and calcium; and sulphated polysaccharides. As a result, carboxyl and sulphate are the most common active groups in this type of seaweed [9]. The aim of this study was to assess the efficiency of the use of *Sargassum baccularia* as an adsorbent for the removal of cadmium ions from aqueous solutions by studying the effect of some variables (pH, temperature, contact time, shaking speed and initial metal concentration) on the biosorption process.

## II. Materials And Methods

### Biomass

Brown seaweed Sargassum *baccularia*. Will be used in this work is harvested from the sea (Northwestern Coast of Libya).

Initially washing the seaweed biomass with tap water to remove the impurities and sand, and finally with distilled water to remove salt and particulate material from its surface. Drying washed biomass at 60ºC for 24 hours. The biomass was crushed after being dried with mortar and pestle, then the samples were sieved. The samples will be first sieved through a 200 µm mesh, and then through a 63 µm mesh. The milled particles with 63 µm will be used for sorption experiments. Drying milled biomass at 105ºC for 24 hours to calculate the dry weight.

### Metal solutions

The concentration of metal solution was prepared by 1.0 g/l metal (1000 ppm) using atomic absorption spectroscopy standard Fluka.

### Biosorption experiments

The batch experiment was conducted out in 250 ml flasks containing the required quantity of algal biomass (1.0 g) and 50 ml of each metal solution. For each solution, different initial pH (2.0 to 6.0) and temperature range (20°C to 40°C) were used. The flasks were placed in a shaker with constant shaking at 0 to 120 rpm for different time intervals of 30, 60, 120, 180, 240,300 and 360 min. After the requested time interval, the biomass was separated by filtering the content using Whatman No.40 filter paper. The quantity of metal adsorbed on the adsorbent was calculated from the variance between the metal concentration in the solution before and after the biosorption process. Concentration of metal in the solution after the equilibrium was determined using a Perkin Elmer Analyst 400 flame absorption spectrometer.

### Effect of pH

Biosorption experiments were performed at different pH ranges from 2.0 to 6.0. Effect of pH was carried out with *Sargassum baccularia* biomass as biosorbent. The experiment was carried out using the required *Sargassum baccularia* biomass in 50 ml of 5, 10 and 20 ppm metal solution. The optimum pH that gives the maximum removal of metals from this study was determined. NaOH and $H_2SO_4$ solutions are used to adjust pH. The binding sites were not available due to competition between metal and $H^+$ ions when pH was below 2.0, therefore pH values below 2.0 were not followed.

### Effect of temperature

The biosorption experiment was set up with a different temperature range from 20 to 40 °C, using 50 ml of metal stock solution.

### Effect of contact time

In order to study the effect of time on the biosorption process, the contact time ranged from 30 to 360 min using the desired biomass in 50 ml of metal solution adjusted to the appropriate pH. Samples were removed every 1 hour interval and filtered and analyzed for metal concentration on Perkin Elmer Analyst 400 flame absorption spectrometer.

### Effect of shaking speed

The biosorption experiment was performed at different shaking speeds ranging from 0 to 120 rpm for the metal solution.

**Data evaluation**

The metal adsorption (q) and bioremoval efficiency (R) with Sargassum baccularia were calculated using the following formulae..

$$q = \frac{(C_i - C_f)\ V}{M} \qquad (1)$$

$$\text{Removal}(\%) = \frac{(C_i - C_f)}{C_i} \times 100 \qquad (2)$$

Where q =metal adsorption (mg/g); M= dry mass of *Sargassum baccularia* (g); V = volume of initial metal solution used (ml); R = bioremoval efficiency (%); $C_i$ = initial concentration of metal in aquatic solution (mg/L); $C_f$ = final concentration of metal in aquatic solution (mg/L)[10].

**Adsorption isotherm**

During biosorption, the equilibrium between absorbed metal ions on the *Sargassum baccularia* (q) and unabsorbed metal ions in the solution is established ($C_f$ ). This equilibrium, represented by the Langmuir and Freundlich adsorption isotherms, is widely used in data analysis for wastewater treatment applications [11]. Langmuir equation, which is valid for monolayer sorption onto a surface,

with homogeneous sites was given by Eq. 3.

$$q = q_{max} \frac{bC_f}{1+bC_f} \qquad (3)$$

Where $q_{max}$(mg/g) is the maximum amount of the metal ion per unit weights of seaweed to form a complete monolayer on the surface bound at high $C_f$(mg/L), and b is a constant related to the affinity of the binding sites(mg/L),qmax represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and assists in the comparison of adsorption performance[12]. The $q_{max}$ and b can be determined from the liner plot of $C_f$/q versus $C_f$.

The basic features of the Langmuir adsorption model may be expressed in terms of a dimensionless constant called a separation factor ($R_L$) that is defined by the following equation(4).

$$R_L = \frac{1}{1+bC_f} \qquad (4)$$

Value of $R_L$ indicates the nature of the sorption process.

When $R_L$ value lies between 0 and 1 then adsorption is favourable, If $R_L$ is > 1 adsorption is unfavorable, If $R_L$ is =1 adsorption is linear, If $R_L$ is = 0 adsorption is irreversible

The empirical Freundlich equation based on sorption on a heterogeneous surface is given below by Eq. 5.

$$\mathbf{q=K\ C_f^{\ (1/n)}} \qquad \mathbf{(5)}$$

The k and n parameters are the constants of the Freundlich isotherm. The k and n are indicators of adsorption capacity and adsorption intensity, respectively. The Eq.4 can be linearized in logarithmic forms and Freundlich constants can be determined by the plot. Freundlich isotherm is also more widely used as it provides no information on the monolayer adsorption capacity [5].

## III. RESULTS AND DISCUSSION

**Effect of initial pH**

pH is a factor that plays a significant role in the process of biosorption that affects the chemical specifications of metals, activity of functional biomass groups (binding sites) and ion metallic competition for binding sites[13]. As a result, metal sorption studies were conducted at various pH values. Results revealed the maximum biosorption of Cd (II) at pH 6(84.2%) from an aquatic solution containing an initial metal concentration of 20 mg/l (Figure 1). The removal of $Cd^{2+}$ increased clearly as the pH increased from 2.0

to 6.0, with an optimum pH of around 6.0 observed. At pH 2, Cd (II) adsorption was observed to have the lowest uptake. At low pH, biosorption is weak, it may be due to competition between metals and $H^+$ that the binding sites of ions (active sites) on the algae cell be reached, whereas when the pH values increase, the vital absorption of cadmium metal with its positive charge (+2) is reaches equilibrium[14]. More functional groups in the cell wall, such as carboxyl, phosphate, imidazole, and amino groups, would be exposed as the pH increased, and their negative charges would attract metallic ions with positive charges that biosorb onto the cell surface [15]. The initial pH values studied were less than 7 because the insoluble cadmium hydroxide begins to precipitate from solutions with higher pH values [6]. In this study, pH 6 was selected where the highest metal biosorption occurred.

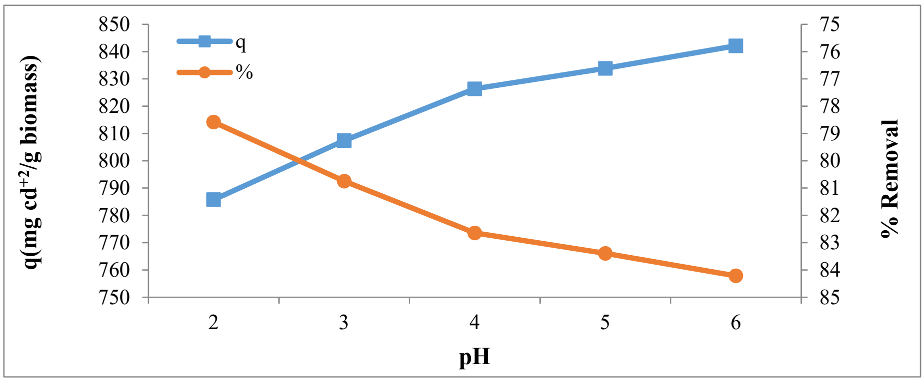


Fig (1): Effect of pH on Cd (II) removal by *S. baccularia* at 20ppm, T=30°C, t=360min, 1g biomass

**Effect of Temperature:**

The dependence of the biosorption rate of cadmium ions on process temperature can be seen in Fig.2 the metal uptake increased with an increase in temperature at 20-30 °C intervals, while metal uptake decreased with an increase in temperature at 30-40 °C intervals. The maximum uptake was occurred at 30°C. The highest biosorption efficiency achieved at 30°C, while the lowest efficiency was found at 47°C, this may be due to damage to binding sites (active sites) on the biomass surface [7]. The decrease in biosorption efficiency with increasing temperature is most likely due to heavy metal desorption from the biosorbent surface [16]. Ions move rapidly at high temperatures, giving them less time to react [17]. Biosorption capacity decreases as temperature increases, as adsorption reactions are usually exothermic [18]. Optimal metal uptake was observed at 30 ° C in this study, where 30 °C was used for subsequent experiments.

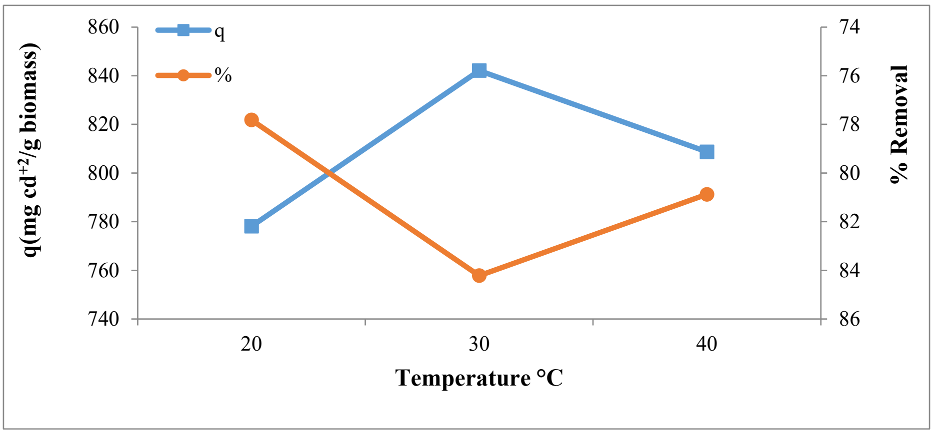


Fig (2): Effect of Temperature on Cd (II) removal by S. baccularia at pH6, 20ppm,1g biomass, t=360 min

**Effect of contact time:**

The effect of contact time on $Cd^{2+}$ biosorption by S. baccularia was studied using a constant initial $Cd^{2+}$ concentration of 20 mg /l at 30 °C. As illustrated in Fig. 3. $Cd^{2+}$ biosorption increases sharply during the first 30 min, gradually increases up to 180 min, and then remains nearly constant after 180 min. the initial fast stages are attributed to the abundance of metal binding sites (active sites) on the biomass cell wall, and biosorption becomes less efficient as a result of the gradual occupation of these active sites in later stages [2]. The latter stage fewer vacant sites are available which are difficult to occupy due to the repulsive forces between the adsorbent surface and the large volume of the liquid phase [19]. Although the equilibrium time for the adsorbent used in this study was 180 min, the contact time was continued to 360 min to ensure that full equilibrium was achieved.

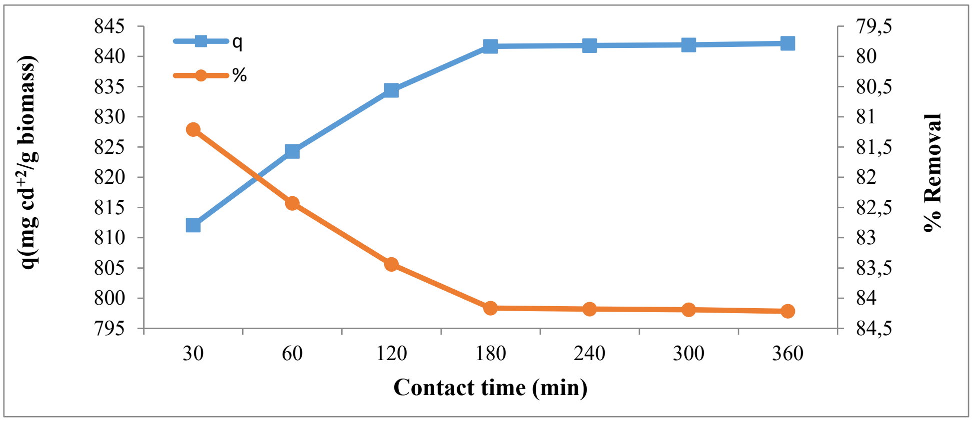


Fig (3): Effect of contact time on Cd (II) removal by S. baccularia at pH=6, 20ppm, T=30°C, 1g biomass.

**Effect of shaking Speed**

Shaking speed is a significant parameter in the transfer of mass between the solid and liquid phases, thus affecting the process of biosorption. The results in Figure (4) showed that the maximum biosorption of Cd was found to be (89.64 %) at 120 rpm. The data indicated that the metal uptake increases with an increase in shaking speed. The minimum metal removal was observed to be (84.17%) without shaking. At low shaking speed, biomass does not diffused in the sample but accumulates, accumulation can cover active sites (binding sites) in the lower biomass layer, and only active sites in the upper layer of biomass adsorb metal ions, in order to ensure that all metal binding sites (active sites) on the biomass surface are available for metal absorption the shaking rate must be adequate [20]. At high shaking speed, sufficient additional energy is available to break the newly formed bond between the metal ions and the biomass surface [21]. Low speed does not allow molecules (biomass) to spread in water to provide metal binding sites for the uptake of metal ions, while high speed does not allow enough time for biomass to bind to ions [22]. In this work, 120 rpm was selected as the best shaking speed at which the highest adsorption of cadmium metal occurred.

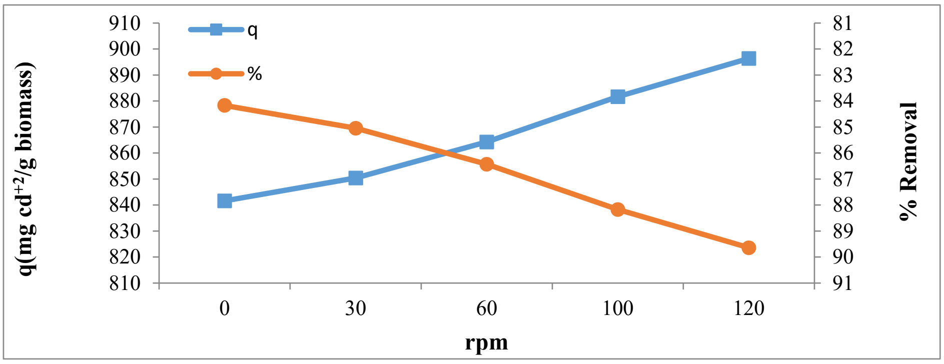


Fig (4): Effect of shaking speed on Cd (II) removal by S.baccularia at pH=6, 20ppm, t=180min, T= 30°C, 1g biomass.

**Effect of Initial metal ion concentration**

As shown in Figure (5), the metal uptake was increased by increasing the initial metal concentration and the maximum removal was occurred at 20 mg / l, whereas the percentage of metal removal decreased with an increase in the initial metal concentration. Biosorption efficiency of biomass increased with increasing in the initial concentration of metal, while the metal removal percentage reduced with an increase in the initial concentration. It was suggested that the increase the initial metal concentration would give a significant driving force to beat mass transfer resistance between solid and aqueous phases [23]. Due to the use of all active sites (binding sites) available at high concentrations, the metal uptake capacity increased. Decreased the metal removal percentage from 98.36% to 84.23, and it has been suggested that this is due to saturation of the active sites, so that other ions remain in the solution not adsorbed at high concentrations[24]. The highest metal uptake was found at an initial concentration of 20 mg/l in this study. Therefore, this concentration was utilized in subsequent experiments.

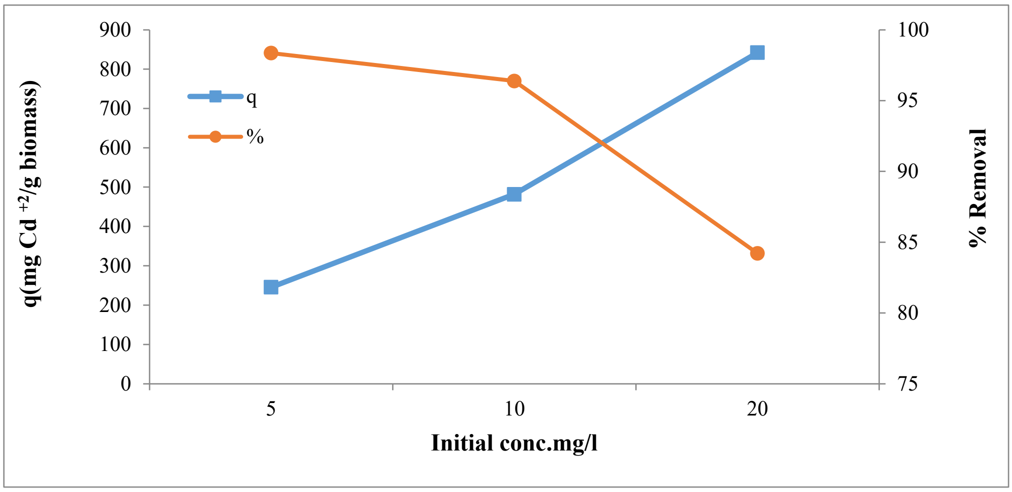


Fig (5): Effect of initial concentration on Cd (II) removal by S.baccularia at pH=6, T=30°C,1g biomass

**Equilibrium study**

The Langmuir isotherm plots and Freundlich isotherm plots for $Cd^{2+}$ biosorption at various concentrations and a fixed a temperature (30°C) are shown in Figs. 6 and 7, respectively, and their values are listed in Table 1, the values of n are all in the 1–10 range, indicating that these biosorption processes are favorable under the previously described conditions [25]. The *n* value showed a significant adsorption by seaweed for heavy metals, since n >1, then adsorption is a physical process. The n value obtained from Freundlich isotherm model for Cd was found to be 3.02 [26]. The k value for $Cd^{+2}$ is 602.6mg/g. Higher k value indicate higher adsorption ability [27] .The correlation coefficient ($R^2$) was used in this study to confirm the best-fit isotherm for this biosorption system. Table 1 shows the results. Because the correlation coefficients for Langmuir's model are higher, it appears to fit the isotherm data better than the Freundlich model. The fit of equilibrium data to the Langmuir model may suggest that $Cd^{2+}$ biosorption onto *S. baccularia* is monolayer biosorption. As also shown in Table 2, the values of the Langmuir constants $q_m$ and b. Maximum metal uptake ($q_m$) values for $Cd^{+2}$ is 909.1 (mg / g). The difference in the maximum capacity of metals may be attributed to a number of factors, such as: types of adsorbents, available binding sites, affinity of binding sites for adsorbed metals, etc. [28]. The *b* value for $Cd^{+2}$ is 3.7. The high value of parameter *b* indicates the desirable steep start of the isotherm, reflects a high affinity of the adsorbent (biomass) to the adsorbate (metal) [29].

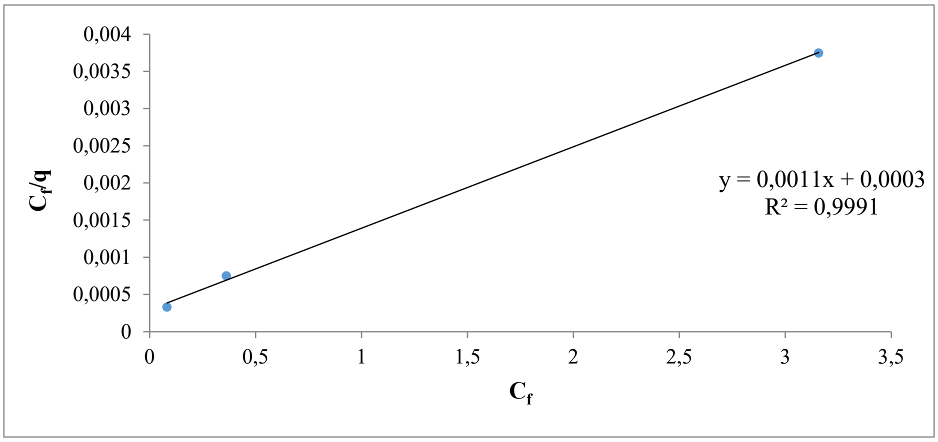


Fig (6): Langmuir isotherm for adsorption of Cd (II) at pH=6,T= 30°C, 1g biomass

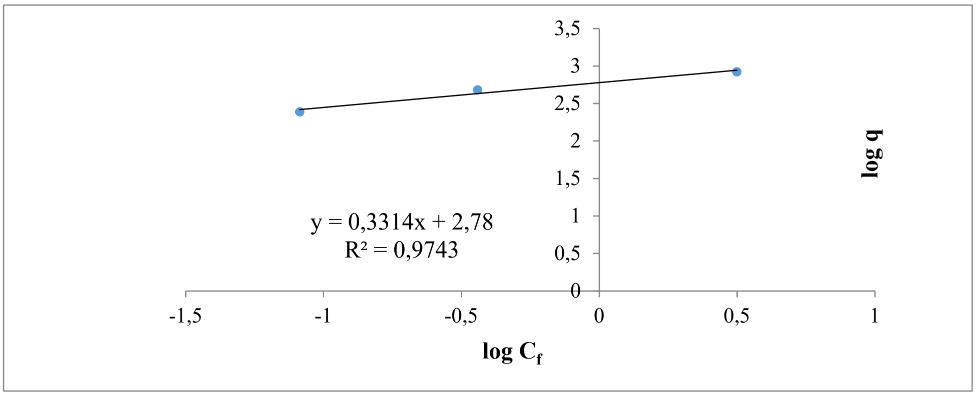


Fig (7): Freundlich isotherm for adsorption of Cd (II) at pH=6,T= 30°C, 1g biomass

Table 1. Isotherm parameters for the biosorption of Cd2+ in solution at different concentrations

| **Bioadsorbent** | **Conc.mg/l** | **Langmuir parameters** | | | | **Freundlich parameters** | | |
|---|---|---|---|---|---|---|---|---|
| Dried *Sargassum baccularia* | | $q_m$(mg/g) | b(l/mg) | $R_L$ | $R^2$ | n | K(mg/g) | $R^2$ |
| | 5.0-20.0 | 909.1 | 3.7 | 0.079-0.769 | 0.9991 | 3.02 | 602.6 | 0.9743 |

### Adsorption Thermodynamics Modeling

Thermodynamic parameters for adsorption of metal onto biomass were calculated using the following equations:

$$\Delta G = \Delta H - T\Delta S \qquad (6)$$

$$\Delta G = -RT \ln k_d \qquad (7)$$

Because $K_d$ is equilibrium constant, its dependence on temperature can be used to estimate both the enthalpy change (ΔH) and the entropy change (ΔS) associated with the biosorption process:

$$\ln k_d = \frac{-\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (8)$$

$$k_d = \frac{q_e}{C_f} \qquad (9)$$

Where R is the universal gas constant (8.314 J/mol K), T the temperature (K), and $K_d$ ($q_e/C_f$) is the distribution coefficient. $q_e$ is the adsorption capacity (mg $g^{-1}$), $C_f$ (mg$L^{-1}$) is the concentration of metal at equilibrium (mg$l^{-1}$).

The plot of ln $K_d$ as a function of 1/T yielded a straight line from which a ΔH value equal to 7.52 (kJ/mol) and a ΔS value equal to 69.4(J/molk) were calculated.

Table 2.Thermodynamic parameters for the adsorption of Cd on brown seaweed (Sargassum baccularia)

| Metal | $\Delta H$(kJ/mol) | ΔS(J/molk) | ΔG (kJ/mol) at different temperatures | | |
|---|---|---|---|---|---|
| | | | 293.15k | 303.15k | 313.15k |
| $Cd^{+2}$ | 7.52 | 69.4 | -12.71 | -13.4 | -14.09 |

Enthalpy change data can be used to distinguish between physisorption and chemisorption. Physisorption is typically associated with adsorption heats ranging from 2.1 to 20.9 kJ/mol (0.5 to 5 kcal/mol), whereas chemisorption is associated with much larger $\Delta H$ values ranging from 20.9 to 418.4 kJ/mol (5 to 100 kcal/mol) [30]. The enthalpy result of brown seaweed is in the first range (2.1 to 20.9 kJ/mol), which suggests that adsorption of metals on brown seaweed is a physisorption process.

These results are consistent with the activation energy ($Ea$) calculated using the Arrhenius equation (5).

$$\ln(\mathrm{k}_{ads}) = \ln(\mathrm{A}) - \frac{E_a}{\mathrm{RT}}$$

The magnitude of activation energy gives an idea about the type of adsorption, which is mainly physical or chemical. Low activation energies (5 to 40 kJ/mol) are characteristics for physisorption, while higher activation energies (40 to 800 kJ/mol) suggest chemisorption [31]. The calculated activation energy ($Ea$) for biomass was 0.661 J/molk for $Cd^{+2}$, this activation energy is characteristic for a physical adsorption.

Table 3.Activation energy for the adsorption of Cd on brown seaweed (Sargassum baccularia)

| Metal | Ea(J/molk) |
|---|---|
| Cd | 0.661 |

## IV. Conclusion

The aim of this paper is to present a study on the biosorption of Cd (II) from aqueous solution using *Sargassum baccularia* as a low-cost adsorbent. Adsorption is moreover affected by various parameters such as initial pH, initial $Cd^{2+}$ concentration, shaking speed, contact time and temperature. The Langmuir and Freundlich models were used to analyze the experimental data. The adsorption was a physisorption process according to the results of the adsorption thermodynamics .Because of its low cost and high sorption capacity, *Sargassum baccularia* can be recommended as an alternative adsorbent for the treatment of wastewater containing Cd (II) ions.

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