Thermodynamic Study on the Adsorption of Cd^{+2} Ions from Aqueous Solution by Seagrasses

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Abstract

This work was to study batch biosorption of Cd (II) ions from aqueous solution by Powdered Seagrasses (PSG). The optimum conditions for the adsorption of Cd (II) ions from aqueous solution by seagrasses were investigated by considering the extent of adsorption with respect to contact time, initial metal ion concentration and temperature. The results obtained indicates that the extent of metal ions removed decreases with increasing contact adsorption equilibrium data best fitted Freundlich adsorption isotherm. Thermodynamic study indicated that the adsorption of Cd (II) ions onto seagrasses was spontaneous and endothermic in nature.

Keywords: Thermodynamic; kinetics; adsorption; Cd (II); seagrasses.

1. Introduction

Industrial waste water may contain some toxic metals such as Cd^{+2}, Cr^{+2}, Ni^{+2}, Co^{+2}, Pb^{+2} ... etc. The release of toxic metals by electroplating, leather tanning, cement, dyeing, metal processing, textile and paint industries into the environment in quantities that pose risk to human health [1]. Cadmium is among the toxic heavy metals that have been deeply studied [2],the release of toxic metals by electroplating, leather tanning, cement, dyeing, metal processing, textile and paint industries into the environment in quantities that pose risk to human health [3]. Therefore, the removal of these metal ions is necessary in order to forestall the manifestation of their toxic impact through bioaccumulation and bio magnification along the food chain [4]. The higher concentration causes harmful effects like headache dizziness, nausea, dry cough, tightness of the chest, vomiting, shortness of breath, cyanosis, chest pain and rapid respiration [5]. The aim of this study was to remove the metal ions from aqueous solution.

2. Results and Discussion

2.1. Characteristics of the Adsorbent

The chemical nature and pore structure generally determines the sorption activity. The physico chemical properties of the adsorbent are listed in Table (2.1).

Table 2.1: Characteristics of the Adsorbent

SI. NO.	Properties	PSG
1	Particle size (μ)	500
2	Density (g/cc)	0.036
3	Moisture content (%)	0.2986
4	pH of aqueous solution	6.0

2.2. Effect of pH

The pH level of the aqueous solution is an important variable for the adsorption of metals on the adsorbent. For above reason, in many studies, it has been pointed out that the solution pH was one of the most important parameters affecting adsorption yield. In order to know the influence of this parameter on the adsorption of Cd (II) ions by PSG, so 100 (mg.L^{-1}) of PSG was contacted with 100 (mg.L^{-1}) of Cd (II) ions with different pH values which varies from (1 to 10). The results of these experiments are given in Figure (2.1). As seen, removal percentage is low at strong acidic medium. Removal percentage increases s up to pH6 and thereafter they stay almost constant for grater pHs up to pH8.
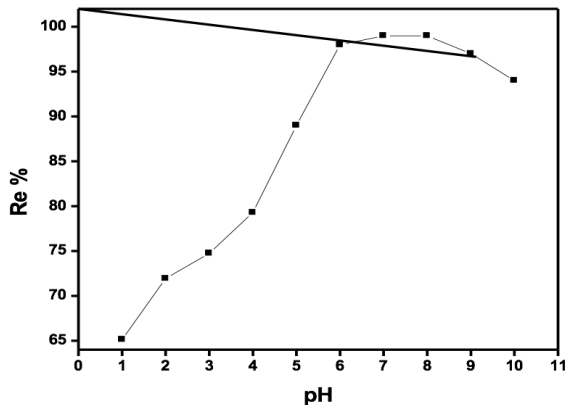
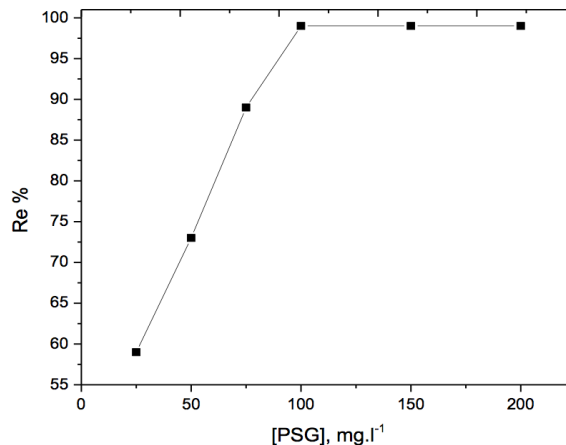**Figure 2.1:** The effect of pH on the removal of Cd (II)

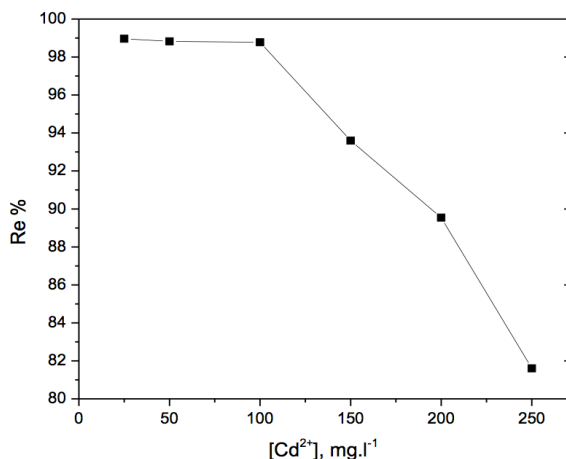**Figure 2.3:** The effect of adsorbent dosage

Figure 2.2: The effect of initial metal ion concentration

2.3. Effect of Initial Metal Ion Concentration

The data depicted in Figure (2.2) demonstrate the effect of initial metal ion concentration on the adsorption of Cd (II) ions by PSG. As seen, when the initial concentration of Cd (II) ions was increased from 25 - 250 (mg.L^{-1}), so the extent of removal decreased after 100 (mg.L^{-1}). From the Figure (2.2), it can be observed that the ion removal percentage increases when the initial ion concentration decreases. At low ion concentrations the ratio of surface active sites to the total metal ions in the solution is high and hence all metal ions may interact with the adsorbent and be removed from the solution. Therefore, the optimum Cd (II) ions concentration is 100 (mg.L^{-1}).

2.4. Effect of Adsorbent Dosage

The effect of adsorbent dose in the ranged of 25 - 200 (mg.L^{-1}) at fixed amount of pH, temperature on the removal percentage of Cd (II) of initial concentration of 100 (mg.L^{-1}) is shown in Figure (2.3). From the figure it can be observed that increasing of adsorbent dose from 25 - 100 (mg.L^{-1}) increased the removal percentage of Cd (II) from (58.1 - 99.38%) then the removal percentage remains almost constant till 100 (mg.L^{-1}) of PSG sorbent so the optimum dosage of PSG was 100 (mg.L^{-1}). As expected, the removal efficiency increased with increasing the adsorbent dose for a given initial metal concentration, because for a fixed initial adsorbate concentration increasing adsorbent dose provides greater surface area or more adsorption sites.

2.5. The Effect of Contact Time

The removal percentage (Re %) of Cd (II) ions by PSG as a function of contact time is presented in Figure (2.4). The adsorption of Cd (II) ions increased with time up to 60 min and then remains almost constant corresponding to (99.38 %) removal, so a time of 60 min was selected as a suitable contact time for all experiments.

2.6. Effect of Temperature

The temperature has two major effects on the sorption process. Increasing the temperature is known to increase the rate of diffusion of the sorbate while changing the temperature will change the equilibrium capacity of the sorbent for a particular sorbate. In this study, a series of experiments were conducted on the adsorption of 200 (mg.L^{-1}) of Cd (II) ions onto 100 (mg.L^{-1}) of PSG at 298, 308 and 318 K to investigate the effect of temperature on the sorption dynamics at different shaking times. The results

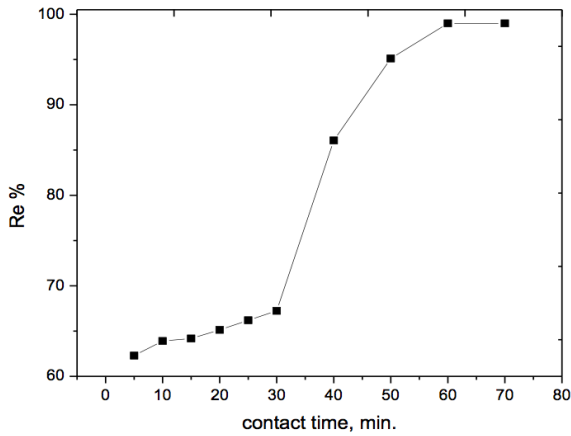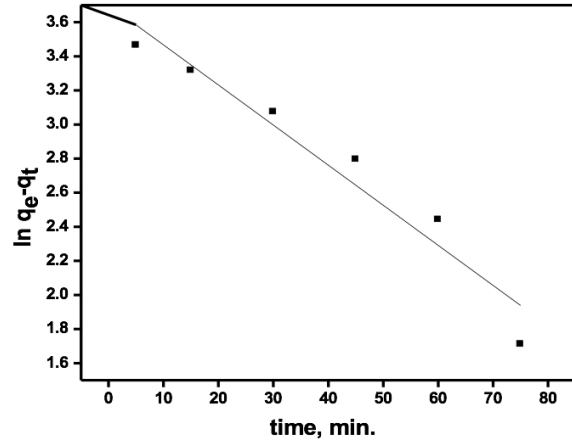**Figure 2.4:** The effect of contact time on the removal of Cd (II)

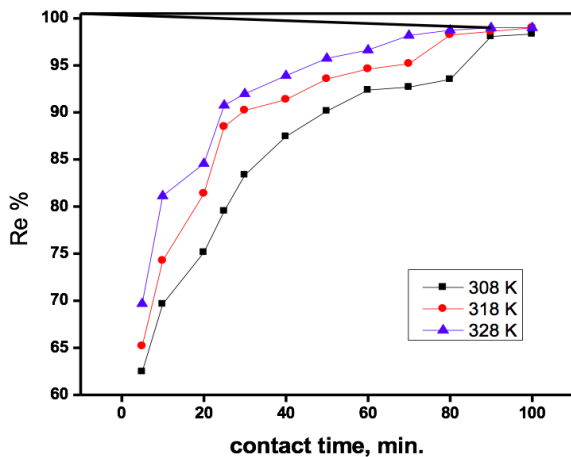**Figure 3.1:** Pseudo-first-order kinetic model

Figure 2.5: The effect of temperature on the removal of Cd (II)

depicted in Figure (2.5) showed that the sorption capacity increases as the temperature increases confirming that the process is endothermic in nature.

3. Adsorption Kinetic Studies

3.1. Pseudo-first-order Model

Lagergren proposed a pseudo-first-order kinetic model. The integral form of the model is:

$$ln\,(q_e - q_t) = ln\,q_e - k_1\,t \qquad (3.1)$$

Where: q_t is the amount of Cd $^{+2}$ ions sorbed (mg.L^{-1}) at time t (min), q_e is the amount of metal ions

sorbed at equilibrium (mg.L^{-1}), and k_1 is the equilibrium rate constant of pseudo-first-order adsorption (mg.L^{-1}). This model was successfully applied to describe the kinetics of many adsorption systems [4, 5].

3.2. Pseudo-second-order Model

The adsorption kinetics may also be described by a pseudo second-order reaction. The linearized integral form of the model is:

$$\frac{t}{q_t} = \frac{1}{k_2\,q_e^2} + \frac{t}{q} \qquad (3.2)$$

Where: K_2 is the pseudo-second-order rate constant of adsorption [6, 7].
The applicability of the above two models can be examined by each linear plot of $ln\,(q_e - q_t)$ versus t, and (t/q) versus t, respectively and are presented in Figures (3.1) and (3.2). To quantify the applicability of each model, the correlation coefficient, (r^2) was calculated from these plots and given in Table (3.1).The linearity of these plots indicates the applicability of the two models.

3.3. Intra-particle Diffusion Model

This possibility was tested in terms of a graphical relationship between the amount of Cd $^{2+}$ ions adsorbed and square root of time Figure (3.3). The plot has an initial curved portion, followed by an intermediate linear portion. The initial portion of the plot is related to mass transfer i.e. transport of adsorbate from the bulk solution to the external surface of adsorbent across the liquid boundry layer

Table 3.1: Estimated kinetic models

Cd (II) Ions	1st Order Kinetic Model $(ln\,(q_e - q_t) = ln\,q_e - k_1 t)$	2nd Order Kinetic Model $(t/q_t = 1/k_2\,q_e^2 + t/q_e)$	Intra-particle Diffusion Model $\left(q_t = k_d\,t^{1/2}\right)$
q_e $(mg.g^{-1})$	40.52	74.626	
Rate Const.	$k_1 = 7.005\,(min^{-1})$	$k_2 = 0.0128\,(l.mol.min^{-1})$	$k_d = 4.378\,(mg.g^{-1}.min^{-1})$
r^2	0.929	0.968	0.971
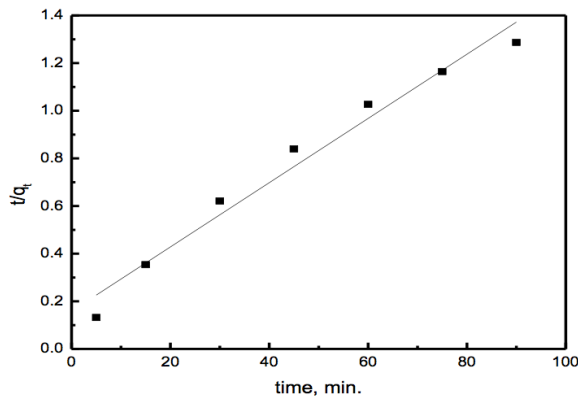
Figure 3.2: Pseudo-second-order kinetic model
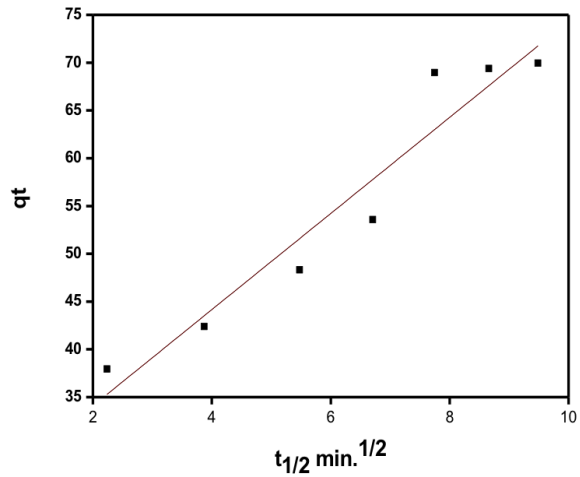
Figure 3.3: Intra-particle diffusion kinetic model

(film diffusion) and the linear part is due to intra-particle diffusion i.e. diffusion of adsorbate within the pores of adsorbent. Previous studies showed the same features of the plots of $\left(q_t$ vs. $t^{1/2}\right)$ which characterize the different steps of adsorption process (84,85). The values of rate constant for intra-particle diffusion, K_d was determined from the slope of the plot and is given in Table (3.1).

4. Adsorption Isotherm Studies

4.1. Langmuir Isotherm Model

Langmuir theory was based on the assumption that adsorption was a type of chemical combination or process and the adsorbed layer was unimolecular. The theory can be represented by the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{k_a \cdot q_{max}} + \frac{C_e}{q_{max}} \qquad (4.1)$$

Where: C_e is the equilibrium concentration (mg.L^{-1}), q_e is the amount adsorbed at equilibrium (mg.L^{-1}) and q_{max} (mg.L^{-1}) and k_a $(L.mg^{-1})$ are Langmuir constants related to adsorption capacity and energy

of adsorption respectively. The linear plot of (C_e/q_e) vs. C_e shows in Figure (4.1) that the adsorption obeys Langmuir isotherm model. The values of q_{max} and k_a were determined from intercept and slope of the linear plot of (C_e/q_e) vs. C_e in Table (4.1). The good fit of the experimental data and the correlation coefficients (r^2) higher than 0.94 indicated the applicability of the Langmuir isotherm model [7, 8]. In the present study, the value of R_L is observed to be 0.34 i.e. in the range of $(0 - 1)$, indicating that the adsorption process is favorable for the prepared powdered sea grasses (PSG).

4.2. Freundlich Isotherm Model

The Freundlich adsorption model stipulates that the ratio of solute adsorbed to the solute concentration is a function of the solution. The empirical model was shown to be consistent with an exponential distribution of active centers, characteristic of heterogeneous surfaces. The amount of solute adsorbed, q_e, is related to the equilibrium concentration of solute in solution, C_e, as following:
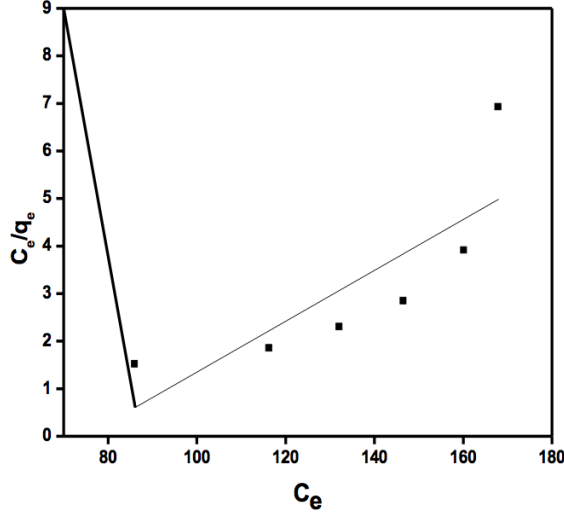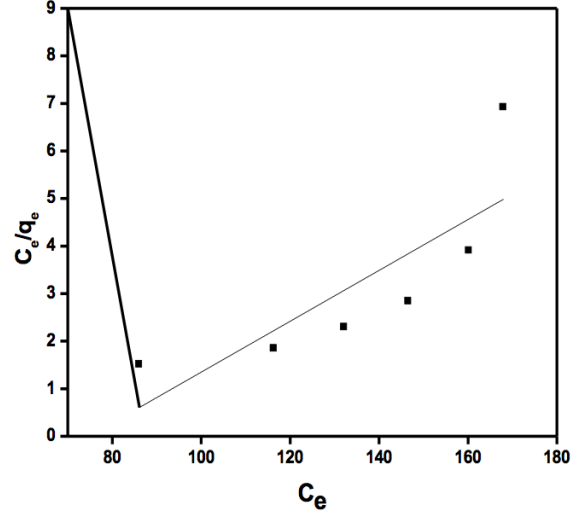
Figure 4.1: Langmuir isotherm model

Figure 4.2: Freundlich isotherm model

$$q_e = k_f \, C_e^{1/n} \qquad (4.2)$$

This expression can be linearized to give the following equation:

$$ln \, q_e = ln \, k_f + (1/n) \, ln \, C_e \qquad (4.3)$$

Where: k_f is a constant for the system, related to the bonding energy. k_f can be defined as the adsorption or distribution coefficient and respects the quantity of metal ion adsorbed onto adsorbent for a unit equilibrium concentration (a measure of adsorption capacity, mg.g^{-1}). The slope, $(1/n)$, ranging between (0 - 1), is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [8]. A value for $(1/n)$ below one indicates a normal Frendlich isotherm while $(1/n)$ above one is an indicative of cooperative adsorption [8, 9]. A plot of $(ln(qe)$ vs. $ln(C_e))$ is shown in Figure (4.2), where the values of k_f and $(1/n)$ are determined from the intercept and slope of the linear regression as summarized in Table (4.1).

4.3. The Tempkin Isotherm Model

Tempkin isotherm plot was chosen to evaluate adsorption potentials of sorbent for sorbate. The heat of sorption of the molecules in layer decreases linearly with coverage due to sorbate and sorbent interactions. Tempkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic. Tempkin isotherm model is shown:

$$q_e = a + b \, ln \, C_e \qquad (4.4)$$

Where: q_e is the amount adsorbed (mg.g^{-1}), C_e is the equilibrium concentration of the adsorbate (mg.L^{-1}), a and b are constants related to energy and capacity of adsorption.

When q_e was plotted against $(ln \, C_e)$, straight line was obtained in Figure (4.3), which shows that the adsorption of Cd (II) ions follow the Tempkin isotherm. The constants $(a$ and $b)$ and (r^2) values are calculated from Figure (4.3) and tabulated in Table (4.1).

4.4. Dubinin-Radushkevich Isotherm Model (D–R Isotherm)

The sorption data was modeled by D–R isotherm Figure (4.4), to determine the adsorption type (physical or chemical). The linear form of this model [10, 11] is expressed by:

$$ln \, q_e = ln \, q_m - \beta \, \varepsilon^2 \qquad (4.5)$$

Where: $q_e \, (mol.L^{-1})$ is the amount of the Cd (II) ions adsorbed per unit dosage of the PSG, $q_m \, (mol.g^{-1})$ is the monolayer capacity, $\beta \, (mol^2.J^{-2})$ is the activity coefficient related to mean sorption energy and ε is the Polanyi potential described as:

$$\varepsilon = R \, T \, ln \, (1 + 1/C_e) \qquad (4.6)$$

Where: T is the absolute temperature (K) and R is the universal gas constant 8.3143 (J.mol^{-1}.K^{-1}). The mean sorption energy, $E \, (kJ.mol^{-1})$, can be calculated by the following equation [12, 13]:
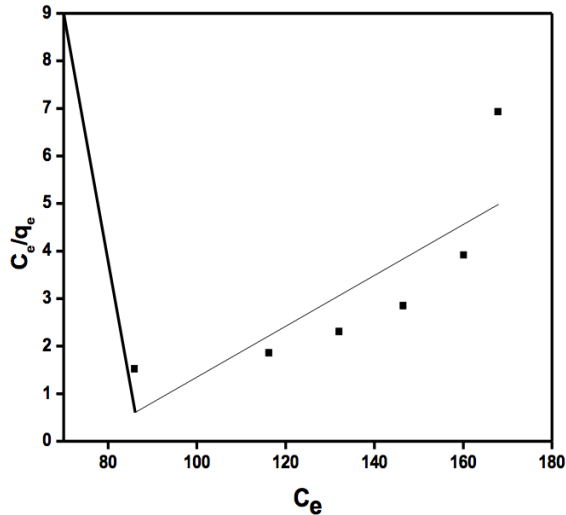
$$E = (-2 \, \beta)^{-1/2} \qquad (4.7)$$
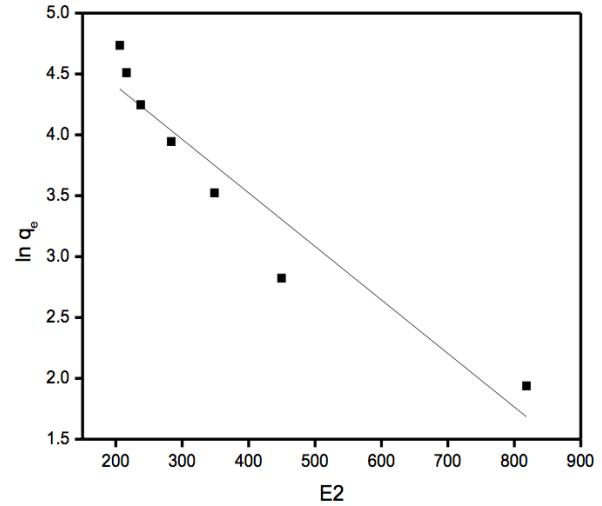
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Figure 4.3: Tempkin isotherm model

Figure 4.4: Dubinin-Radushkevich isotherm model

As seen in Figure (4.4), the slope of the D–R plot gives β activity coefficient and was evaluated as -0.004 $\left(mol^2.J^{-2}\right)$. The mean sorption energy (E) was found to be 11.23 $\left(kJ.mol^{-1}\right)$. The E value ranges from 1.0 to 8.0 $\left(k.J.mol^{-1}\right)$ is for physical adsorption and from 9.0 to 16.0 $\left(kJ.mol^{-1}\right)$ and more for chemical adsorption [14]. Therefore, the E value calculated for the adsorption of Cd (II) ions onto PSG showed that the sorption may be chemical in nature. The values of (q_m) and (r^2) values are calculated from Figure (4.4) and tabulated in Table (4.1). The obtained parameters illustrate that the trend of fitting the equilibrium adsorption data to various isotherms were as: Freundlich $\sim$ Langumir Tempkin > Dubinin- Redushkevich.

4.5. Determination of Thermodynamic Parameter

In order to investigate the thermodynamic parameters for the adsorption of Cd (II) ions by PSG, the distribution coefficient k_d $(l.g^{-1})$ was calculated at the temperatures 298, 308, 318, 328 and 338 K according to the following equation [15, 16]:

$$k_d = q_e/C_e \qquad (4.8)$$

The K_d values calculated for the sorption of Cd (II) ions by PSG are given in Table (4.2). These results show that the K_d increased as the temperature increased from 298 to 338 K and revealing that the sorption of Cd (II) ions by PSG may be endothermic in nature. The enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from the slope

and intercept of the plot of $(ln\,K_d)$ against $(1/T)$, respectively as depicted in Figure (4.5) and according to the following equation [17]:

$$ln\,k_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R\,T} \qquad (4.9)$$

The Gibbs free energy change (ΔG°) was calculated by:

$$\Delta G^\circ = -R\,T\,ln\,k_d \qquad (4.10)$$

Where: R is the universal gas constant $(8.314 J.mol^{-1}.K^{-1})$ and T is the absolute temperature (K).
The calculated enthalpy change ΔH° was +59.04 $\left(kJ.mol^{-1}\right)$ for the sorption of Cd (II) ions by PSG. The positive value of ΔH° clarified that the sorption process was endothermic. The entropy change (ΔS°) was found to be +138.07 $\left(J.mol^{-1}.K^{-1}\right)$. Accordingly, this result showed that Cd (II) ions in bulk phase (aqueous solution) is in a much chaotic distribution compared with the relatively ordered state of solid phase (sorbent surface) [15]. Also, the positive value of (ΔS°) suggest the increased randomness at the solid-solution interface during the adsorption of Cd (II) ions on PSG surface, since adsorbed Cd (II) ions led to decreasing number of water molecules surrounding Cd (II) ions and thus the degree of freedom of the water molecules increases. The endothermic nature is also shown by the increase in the amount of adsorption with rising temperature. Moreover, the Gibbs free energy change (ΔG°) was between -5.302 and -5.629 $\left(kJ.mol^{-1}\right)$ for the adsorption of Cd (II) ions by PSG at the
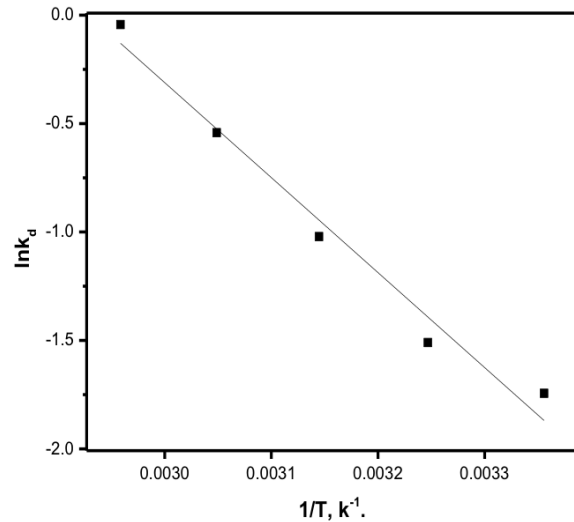
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Table 4.1: Estimated isotherm models

	Cd (II) Ions		r^2
Langmuir Isotherm	$q_{max}\ (mg.g^{-1})$	$k_a\ (L.mg^{-1})$	
$C_e/q_e = 1/k_a.q_{max} + C_e/q_{max}$	188.6	0.013	0.576
Freundlish isotherm	$(1/n)$	$k_f\ (mg.g^{-1})$	
$ln\,q_e = ln\,k_f + (1/n)\,ln\,C_e$	0.248	10.30	0.984
Tempkin Isotherm			
$q_e = a + b\,ln\,C_e$	$b = 14.247$	$a = 64.598$	0.768
D-R isotherm	$\beta\ (mol^2.J^{-2})$	$q_m\ (mg.g^{-1})$	
$ln\,q_e = ln\,q_m - \beta\,\varepsilon^2$	-0.004	196.76	0.896

temperatures 298, 308, 318, 328, and 338 K. The Gibbs energy change $(\Delta G°)$ for the adsorption process is not very large, but its negative values indicated that the equilibrium:

Cd (II) ions + PSG = Cd (II) ions - - - - - - PSG shifts to the right hand direction in a spontaneous manner leading to binding of the Cd (II) ions to the PSG particles. So, the adsorption of Cd (II) ions on PSG was feasible and spontaneous thermodynamically.

Table 4.2: Estimated thermodynamic parameters

Temp (K)	k_d $l.g^{-1}$	$\Delta G°$ kJ.mol^{-1}	$\Delta H°$ kJ.mol^{-1}	$\Delta S°$ kJ.mol$^{-1}K^{-1}$
298	8.5	-5.302		
308	8.7	-5.340		
318	9.0	-5.443	+59.04	+183.0
328	9.4	-5.551		
338	9.7	-5.629		

Figure 4.5: Plot of $(ln\,k_d)$ vs. $(1/T)$

5. Conclusion

Sea grasses can be used as an adsorbent for the removal of Cd^{+2} from aqueous solutions. The adsorption behavior of Sea grasses can be optimized by controlling the period of contact, initial metal ion concentration and temperature. The thermodynamic parameters such as $\Delta H°$, $\Delta S°$ and $\Delta G°$ indicates the spontaneous and endothermic nature of the adsorption process. In this work, PSG has been found to be a good adsorbent for the removal of cadmium ion from aqueous solutions. Thermodynamic principles can adequately be used to predict the direction of the adsorption process.

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