

Evaluation of thermodynamic parameters of cadmium adsorption on sand from Temkin adsorption isotherm

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Thermodynamic parameters provide clues for finding the spontaneity of a given process at a given temperature. In the present work, the Temkin adsorption model was applied for evaluation of the thermodynamic parameters of cadmium adsorption studied on sand. The lateral interaction energy parameter was found to be unity, which showed that the heat of adsorption is directly proportional to the fraction of free adsorption sites. The values of ΔH° and ΔS° were -4.8 kJ mol^{-1} and $42 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The value of ΔG° was negative, indicating the spontaneity of cadmium adsorption on sand.

Key Words: Thermodynamic parameters, spontaneity, Temkin adsorption model, cadmium, sand, modified isotherm

Introduction

Adsorption is a natural process and may be characterized on the basis of different adsorption models.^{1–5} Adsorption is considered an effective process for the removal of impurities from the environment.^{6–9} The adsorption study of metal ions on natural adsorbents is of vital importance for finding cheap adsorbents.^{10–13} Sand is one of the most abundantly available cheap adsorbents that can be considered as a natural filter for water purification.

The knowledge of thermodynamic parameters is of fundamental importance for learning about the spontaneous occurrence of a given process at a given temperature. Adsorption is a spontaneous process that occurs with the evolution of heat, called the heat of adsorption.³ The spontaneity of the adsorption process may be found on the basis of the sign of standard Gibbs free energy, ΔG° , related to the equilibrium constant by the following relationship:⁸

$$\Delta G^\circ = -RT \ln K, \quad (1)$$

where R is the universal gas constant ($8.3143 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature in kelvins, and K is the equilibrium constant for the adsorption and desorption processes. The magnitude and sign of ΔG° depends on the value of K . When the rates of the adsorption and desorption processes are equal in magnitude, then K becomes unity and $\Delta G^\circ = 0$. The value of ΔG° is negative for $K > 1$ and positive for $K < 1$. If adsorption occurs spontaneously, with the rate of adsorption being higher than desorption, ΔG° will always be a negative quantity. In fact, the adsorption process is useful only if it occurs spontaneously. The spontaneity of the adsorption process is also affected by the thermodynamic parameters ΔH° (heat of adsorption) and ΔS° (entropy change). The relation of ΔG° with ΔH° and ΔS° is generally expressed as:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \quad (2)$$

According to Eq. (2), ΔG° will always be negative at any given temperature for a system with negative values of ΔH° and positive values of ΔS° . Thus, knowledge of the signs of various thermodynamic parameters is highly important in determining the spontaneity of a given process.

The Temkin adsorption model³ is based on the spontaneity of the adsorption process and may be applied to find various thermodynamic parameters. Thus, the aim of the present work was to elaborate on the Temkin adsorption model for the evaluation of the thermodynamic parameters of cadmium adsorption studied on sand.

Experimental

All chemicals were of analytical grade purity. A model 174A potentiostat/galvanostat and model RE 0089 X-Y recorder from Princeton Applied Research (New Jersey, USA) were used for differential pulse voltammetric measurements at a hanging mercury drop electrode. A Stuart[®] SFI flask shaker (Bibby Sterilin Ltd., Stone, Staffordshire, OSA, UK) was used for shaking the samples and a Gallenkamp Thermostirrer-100 (Cat. No. BKL-235, EEC) was used to maintain temperature. Washed and dried sand (250-300 μm) was used to obtain adsorption data of cadmium at pH 2 under optimized conditions of 4 g of sand per 10 mL of solution with a shaking time of 1 h.

Results and discussion

The number of moles of cadmium adsorbed per gram of sand increased with increasing equilibrium concentration, as shown in Figure 1, at 25 °C. The equilibrium constant and monolayer capacity of sand for cadmium adsorption were evaluated by using the following linear Langmuir adsorption isotherm expression:^{1,6,8}

$$\frac{1}{(X/m)} = \frac{1}{X^\circ} + \frac{1}{X^\circ K C_{eq}}, \quad (3)$$

where X is the number of moles of adsorbate adsorbed on m grams of sand, X° is the monolayer capacity of sand in terms of the number of moles of cadmium adsorbed per gram of sand, C_{eq} is the equilibrium concentration (in mol L^{-1}), and K is the equilibrium constant (in $\text{mol}^{-1} \text{ L}$). The values of K and X° were evaluated from the slope and intercept of the plot (Figure 2), respectively, and are presented in Table 1. The average value of K obtained from the slope of the plot (Figure 2) was used to evaluate ΔG° from Eq. (1). The value of ΔG°

was negative, indicating the spontaneity of cadmium adsorption on sand. In order to find the effect of coverage on the equilibrium constant, Eq. (3) may be rearranged to obtain the following relationship:

$$K = \frac{\theta}{(1 - \theta)C_{eq}}, \quad (4)$$

where

$$\theta = \frac{X}{mX^\circ}. \quad (5)$$

Table 1. Langmuir adsorption isotherm parameters at 25 °C for cadmium adsorption on sand.

Kinetic parameters	Observed values
X° (mol g ⁻¹)	6.3×10^{-6}
K (mol ⁻¹ L)	1097
ΔG° (kJ mol ⁻¹)	-17.3

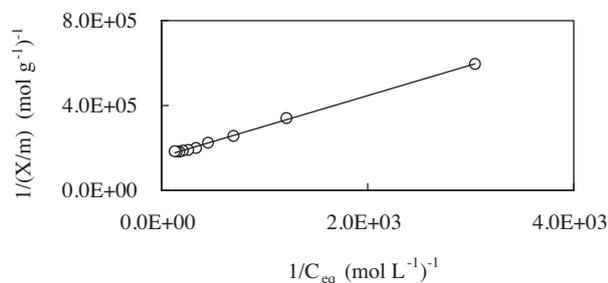
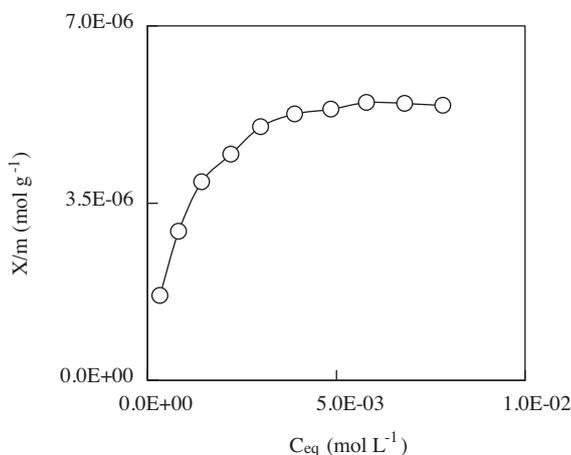


Figure 1. Plot of X/m (mol g⁻¹) versus C_{eq} (mol L⁻¹) at 25 °C for cadmium adsorption on sand.

Figure 2. Langmuir adsorption isotherm at 25 °C for cadmium adsorption on sand.

The magnitude of X° was used to evaluate θ (fraction of covered sites) for finding the value of K at different equilibrium concentrations. It is obvious from Figure 3 that K is a function of coverage, and it decreases significantly as θ approaches unity. The variation of K with coverage may be interpreted on the basis of the Temkin adsorption model^{3,8} and attributed to the variation of ΔG° with coverage. Thus, Eq. (2) may be rewritten as:

$$\Delta G_\theta^\circ = \Delta H_\theta^\circ - T\Delta S_\theta^\circ, \quad (6)$$

where the subscript θ indicates the dependence of the thermodynamic parameters on coverage. If ΔS° is assumed to be independent of coverage, then, based on Eq. (6), Eq. (1) may be rearranged to give:

$$K = K^\circ \exp\left(\frac{-\Delta H_\theta^\circ}{RT}\right), \quad (7)$$

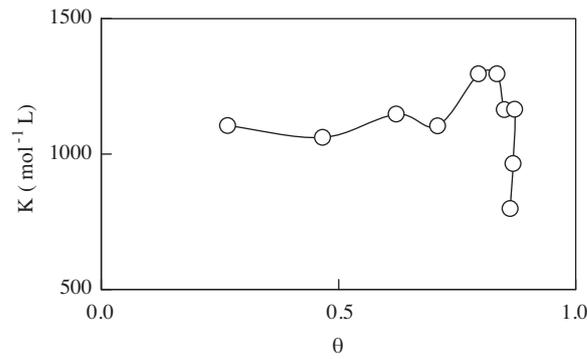


Figure 3. Plot of equilibrium constant K versus fraction of covered adsorption sites θ at 25 °C, with θ calculated from Eq. (5) using $X^\circ = 6.3 \times 10^{-6} \text{ mol g}^{-1}$ as obtained from the Langmuir adsorption isotherm.

where

$$K^\circ = \exp\left(\frac{\Delta S^\circ}{R}\right). \quad (8)$$

According to the Temkin adsorption model, adsorption is a spontaneous process and occurs with the evolution of heat, ΔH_θ° . Let q be a positive quantity of evolved heat; ΔH_θ° may then be related to q by the following relationship:

$$q = -\Delta H_\theta^\circ. \quad (9)$$

The evolved heat is initially high when all adsorption sites are free from adsorbate, but it decreases with increasing coverage according to the following relationship:³

$$q = q^\circ(1 - \alpha\theta), \quad (10)$$

where q is the heat evolved at any given coverage, q° is the heat evolved at zero coverage, and α is the lateral interaction energy parameter. In light of Eqs. (9) and (10), Eq. (7) becomes:

$$K = K^\circ \exp\left(\frac{q^\circ(1 - \alpha\theta)}{RT}\right). \quad (11)$$

Upon solving Eqs. (4) and (11), taking the logarithm, rearranging it, and substituting θ from Eq (5), the following relationship is obtained in the intermediate range of coverage with $q^\circ \alpha \gg RT$:

$$\frac{X}{m} = X^\circ \left(\frac{RT}{q^\circ \alpha} \ln(K^\circ) + \frac{1}{\alpha} \right) + \frac{X^\circ RT}{q^\circ \alpha} \ln(C_{eq}). \quad (12)$$

This is the Temkin adsorption isotherm expression, which gives the relationship between the amount adsorbed per gram of adsorbent and the logarithm of the equilibrium concentration at any given temperature. The X° , K° , α , and q° values are considered independently of temperature. In Eq. (12), both the intercept and slope are temperature dependent and have a common parameter, X° , that is equal to X/m for complete monolayer coverage. Thus, Temkin adsorption isotherms plotted at 2 different temperatures would intersect each other at $X/m = X^\circ$. Figure 4 shows that Temkin adsorption isotherms plotted at 25 and 60 °C are linear in the

intermediate range of coverage. If the linear portion of the plot at 25 °C is extrapolated upward, it intersects the plot at 60 °C at $X/m = 6.20 \times 10^{-6} \text{ mol g}^{-1}$ with a corresponding equilibrium concentration of $6.52 \times 10^{-3} \text{ mol L}^{-1}$. At the intersection point, the x and y coordinates of the plots at 25 and 60 °C are equivalent, and therefore the subtraction of Eq. (12) at 2 different temperatures gives the following relationship between K° and C_{eq} :

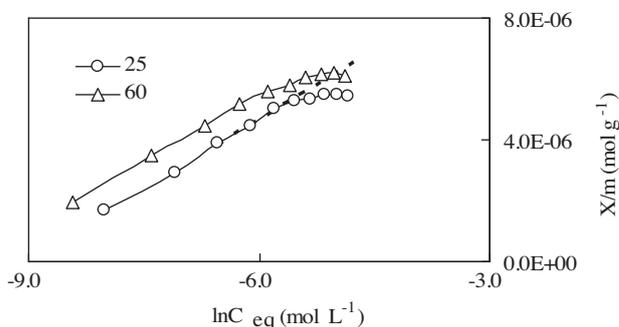


Figure 4. Plot of X/m versus $\ln C_{eq}$ at 25 and 60 °C for evaluation of Temkin and modified adsorption isotherm parameters.

$$K^\circ = \frac{1}{(C_{eq})_{int}}, \quad (13)$$

where $(C_{eq})_{int}$ is the equilibrium concentration at the intersection point. The K° value is used to calculate ΔS° from Eq. (8). The calculated values of kinetic and thermodynamic parameters are presented in Table 2. The value of α is close to unity, while q° is equal to 11 kJ mol^{-1} . The positive value of q° indicates that, according to Eq. (9), the value of ΔH_0° at zero coverage must be a negative quantity. In other words, the adsorption of cadmium on sand is an exothermic process. For the unit value of α , Eqs. (10), (11), and (12) may become as follow.

Table 2. Temkin adsorption isotherm parameters for cadmium adsorption on sand.

Kinetic parameters	Observed values
X° (mol g^{-1})	6.2×10^{-6}
K° ($\text{mol}^{-1} \text{L}$)	153
ΔS° ($\text{J mol}^{-1} \text{K}^{-1}$)	42
α (J mol^{-1})	0.95
q° (kJ mol^{-1})	11

$$q = q^\circ(1 - \theta) \quad (14)$$

$$K = K^\circ \exp\left(\frac{q^\circ(1 - \theta)}{RT}\right) \quad (15)$$

$$\frac{X}{m} = X^{\circ} \left(\frac{RT}{q^{\circ}} \ln(K^{\circ}) + 1 \right) + \frac{X^{\circ} RT}{q^{\circ}} \ln(C_{eq}) \quad (16)$$

Eq. (14) indicates that the heat of adsorption is directly proportional to the fraction of free adsorption sites. The values of X° , K° , and q° in Eq. (16) were evaluated from the plots shown in Figure 4, in the same manner as adopted in the treatment of Eq. (12). The calculated values of different parameters in Eq. (16) for the unit value of α are presented in Table 3. The values of K° and q° were used to calculate the average value of K from Eq. (15) in the intermediate range of coverage. It is obvious from the data in Table 4 that the average value of K is close to that obtained from the Langmuir adsorption isotherm (Table 1) at 25 °C. The slight difference is attributed to the assumption made in the derivation of Eq. (16). Since the values of ΔS° and ΔG° are 42 J mol⁻¹ K⁻¹ and -17.3 kJ mol⁻¹, respectively, according to Eq. (2), the value of ΔH° is -4.8 kJ mol⁻¹. The negative sign of ΔH° indicates that cadmium adsorption on sand is an exothermic process. Since ΔS° is positive while ΔH° is negative, the value of ΔG° from Eq. (2) will be a negative quantity for cadmium adsorption on sand at any given temperature. The negative sign of ΔG° indicates the spontaneity of the adsorption process, which is highly desirable for maintaining the concentration of metal ions at permissible levels in natural systems.

Table 3. Modified adsorption isotherm parameters for cadmium adsorption on sand.

Kinetic parameters	Observed values
X° (mol g ⁻¹)	6.2×10^{-6}
K° (mol ⁻¹ L)	153
ΔS° (J mol ⁻¹ K ⁻¹)	42
q° (kJ mol ⁻¹)	10.4

Table 4. Equilibrium constant data at 25 °C as a function of coverage; θ was evaluated from Eq. (5), while K was calculated from Eq. (15) using the modified isotherm parameters given in Table 3.

θ	(1 - θ)	K (mol ⁻¹ L)
0.271	0.729	3267
0.474	0.526	1391
0.632	0.368	718
0.721	0.279	494
0.808	0.192	343
0.848	0.152	289

Average $K = 1084$ mol⁻¹ L

Conclusions

The thermodynamic parameters of cadmium adsorption on sand were evaluated on the basis of the Temkin adsorption model. The unit value of the lateral interaction energy parameter indicated that heat of adsorption

is directly proportional to the fraction of free adsorption sites. The values of ΔH° and ΔS° were -4.8 kJ mol^{-1} and $42 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The negative value of ΔH° and positive value of ΔS° result in a negative value of ΔG° at any temperature, indicating the spontaneity of cadmium adsorption on sand.

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