# Thermodynamic Function

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Yusra Mahmoud Alobaidi
University of Anbar

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# Thermodynamic Function of Adsorption Methylene blue on Nanocellulose Synthesized from Corn cobs

# Función termodinámica de adsorción de azul de metileno sobre nanocelulosa sintetizada a partir de mazorcas de maíz

**Ismail Ibrahim (Al-Khateeb),**
Department of Chemistry, College of Science, Al-Anbar University Ramadi, Iraq.
iskhibkh@yahoo.com

**Sabri M. Hussin,**
Department of Chemistry, College of Science, Al-Anbar University Ramadi, Iraq,
sabri1959@yahoo.com

**Yusra M. Al-Obaidi,**
Yusra_alobaidy@uoanbar.edu.iq

**ABSTRACT/** In this work, the use of nanocellulose (NC) prepared from one of the useless agricultural waste, corncobs, was used to remove pollution in one of the organic dyes, namely, methylene blue dye. NC known to have interesting characteristics such as nano scale dimensions, high surface area, optical properties, rigidness, strength, rheology and crystalline structure Adsorption isotherms are carried out by three isothermal mathematical models; Langmuir, Freundlich and Temkin. It is clear that the adsorption process on NC corn cobs is fitted very well with isotherm models. The efficiency of NC to remove Methylene Blue dye (MB) was also studied at different temperatures to measure the efficiency of the NC to remove pollutants from environment. It was found that excellent removal process occurred by using NC as adsorbent for MB dye. The measured adsorption quantity of MB dye by NC was noticed to be decreased with the increasing of temperature, besides that, the adsorption quantity of MB on NC nanofibers has been found to be higher than of adsorption quantity of nanoparticles NC. The thermodynamic study of adsorption isotherm was accomplished and investigated. The Gibbs free energy change (ΔGo), entropy change (ΔSo) and enthalpy change (ΔHo) were revealed. The negative sign of ΔGo indicated that adsorption of MB dye on the surface of prepared NC was spontaneous process, in other hand, the negative values of ΔH o signified that the adsorption is exothermic process and the negative values of ΔSo reflect that decrease in randomness in the solid- liquid surface during the adsorption was undertaken Keywords: Nanocellulose, adsorption Isotherm, methylene blue, thermodynamic **RESUMEN /** En este trabajo, el uso de nanocelulosa (NC) preparada a partir de uno de los residuos agrícolas inútiles, las mazorcas de maíz, se utilizó para eliminar la contaminación en uno de los colorantes orgánicos, a saber, el colorante azul de metileno. Se sabe que NC tiene característica s interesantes tales como dimensiones a escala nanométrica, área de superficie alta, propiedades ópticas, rigidez, resistencia, reología y estructura cristalina Las isotermas de adsorción se llevan a cabo mediante tres modelos matemáticos isotérmicos; Langmuir, Freundlich y Temkin. Está claro que el proceso de adsorción en las mazorcas de maíz de Carolina del Norte se ajusta muy bien con los modelos isotérmicos. La eficiencia de NC para eliminar el colorante azul de Methelyne (MB) también se estudió a diferentes temperaturas para medir la eficiencia de NC para eliminar los contaminantes del medio ambiente. Se descubrió que se produjo un excelente proceso de eliminación al usar NC como adsorbente para el tinte MB. Se observó que la cantidad de adsorción medida de colorante MB por NC disminuía con el aumento de la temperatura, además de eso, se descubrió que la cantidad de adsorción de MB en las nanofibras de NC era mayor que la cantidad de adsorción de nanopartículas de NC. El estudio termodinámico de la isoterma de adsorción se realizó e investigó. Se revelaron el cambio de energía libre de Gibbs (ΔGo), el cambio de entropía (ΔSo) y el cambio de entalpía (ΔHo). El signo negativo de ΔGo indicaba que la adsorción de tinte MB en la superficie del NC preparado era un proceso espontáneo, por otro lado, los valores negativos de ΔH o significaban que la adsorción es un proceso exotérmico y los valores negativos de reflectSo reflejan esa disminución en aleatoriedad en la superficie sólido-líquido durante la adsorción se llevó a cabo
Palabras clave: Nanocelulosa, isoterma de adsorción, azul de metileno, termodinámica.

## 1. Introduction

Nanocellulose (NC) represents the crystalline regions extracted from cellulose. NC has extensive applications in wide range of materials related domains. Physical characteristics such as strength, weight, rheology, and optical properties that affected in a very positive manner [1]. NC is one of the strongest and rigidness organic molecules with high crystallinity that has power over impressive mechanical properties [2] with a modulus of 145 GPa and a strength expected up to 7500 MPa. NC has high surface areas (~250 $m^2/g$), and can be regarded as hydrophilic material that quite amenable to surface derivatization [3].There are several methods to obtain NC from natural materials [4]:Such as mechanical treatments by ultrasonication, high-pressure homogenizer and grinding have been applied to assist chemical processes [5]

Dyes are widely used in industries such as textiles, rubbers, papers, plastics, cosmetics. Some of them have been reported to be carcinogenic and mutagenic for aquatic organisms. Release of these dyes to the water stream is very undesirable and has serious environmental hazards [6] Adsorption is used to remove these dyes from aqueous solutions. Adsorption functions in most ordinary physical, biological, and chemical systems, also fields like activated charcoal, synthetic resins and water purification can be regarded as industrial applications of adsorption [7] Cellulose is considered to be one of the most economical materials for the elaboration of several types of adsorbent. Cellulose is not only renewable, biodegradable and inexpensive, but it also possesses numerous essential active hydroxyls, which led to various reactions, such as the free radical reaction, esterification, halogenation, oxidation and Etherification [8]. Thermodynamics is the division of physical chemistry concerned with the transformations of energy and heat into work and vice versa. It main concern is with the method of how reactions reach equilibrium [9]. The main thermodynamic characteristics of any adsorption system in equilibrium are standard free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°). The ΔG° can be regarded a flag of spontaneity of the chemical reaction. Both enthalpy and entropy factors must be considered the Gibbs free energy determination of adsorption process [10].

## 2. Experimental Part

### 2.1 Materials

#### 2.1.1 Adsorbent

Nanocellulose (NC) as adsorbent for adsorption process was synthesized by sonicated raw materials of corn cobs as described in prior work [11]. Corn cobs samples were grinding into fine powder which treated with (1%) sodium hydroxide, bleached and hydrolyzed with a sulphuric acid at diverse concentration (30,40,50,60%) with strong stirring. The samples were filtered, collected and treated with Ultra Sonic device with 80 amplitude for different periods of time (30,60,120) hr. The product powder is kept in plastic containers for later process.

#### 2.1.2 Adsorbate

Methylene blue dye which supplied from HIMEDIA India was used to adsorb on the surface of prepared nanocellulose.

### 2.2 Methods

#### 2.2.1 Equilibrium Time

Equilibrium time was determined by doing series of measurements by adding 10 ml of MB (500 mg/L) in eight conical flasks containing 0.1g of NC for each. Flasks were shaken at different times ;10, 20, 30, 40, 50, 60, 90, 120 min at 200 rpm/min. Then they were centrifuged at 4000 (rpm/min) for 20 min to complete the separation of the samples.

#### 2.2.2 Adsorption Isotherm

Adsorption isotherm of methylene blue dye on corncobs- NC was supported by mixing 10 mL of MB dye at different concentrations (250, 500, 750, 1000) ppm to 0.1 g of prepared NC at different temperatures (283, 298, 323) K for 60 min at 200 (rpm/min). Samples were centrifuged at 4000 (rpm/min) for 15 min and the adsorbed amount of MB was determined by following equation [12].

$$Q_e = V_{sol}(C_o - C_e/m) \quad \ldots\ldots \quad (1)$$

Where: $Q_e$ is the quantity of adsorbate (mg/g), $V_{sol}$ denote total volume of adsorbate solution (L), $C_o$ represent Initial concentration of adsorbate solutions ($mgL^{-1}$) and $C_e$ equal concentration of adsorbate solution at equilibrium ($mgL^{-1}$).

The percentage of adsorption Q% was calculated using equation 2 [13].

$$\mathbf{Q_{\%} = 100 * (C_o - C_e/C_o)} \quad \ldots\ldots \quad (2)$$

Adsorption isotherms are carried out by three isotherms mathematical models ;Langmuir isotherm, Freundlich isotherm, Temkin isotherm. The form of linear Langmuir isotherm for solid-liquid interaction was expressed in following equation (3) [14]:

$$\frac{C_e}{Q_e} = \frac{1}{K^L.a} + \frac{1}{a}.C_e \quad \ldots\ldots \quad (3)$$

Where $C_e$ is the concentration of MB dye at equilibrium, $Q_e$ is the amount of MB dye adsorbed (mg/L) at equilibrium. Functions of a and $k_L$ are represented the Langmuir constants related to the adsorption capacity and the energy of the adsorption respectively. The Freundlich linear isotherm is given by the equation [15] (4) :

$$\log Q_e = \log K_f + \frac{1}{n}.\log C_{e.} \quad \dots \dots (4)$$

Where $k_f$ is Freundlich constant refer to adsorption capacity (mg/g). 1/n is the heterogeneity factor scale for measuring adsorption intensity or heterogeneity.

Temkin linear isotherm could be formulated by equation [16] (5):

$$Q_e = \mathrm{B}.\, lnk_t + B.\, ln\, C_e \quad \dots \dots (5)$$

Where $k_t$ and B represent Temkin constants which can be determined from the slope and intercept of the linear relationship plot between ln Ce and Qe respectively.

**2.2.3 Thermodynamic Functions**

The Gibbs free energy change calculated by equation (6) [17]:

$$\Delta G^o = \Delta H^o - T.\Delta S^o \quad \dots \dots \dots \quad (6)$$

Where $\Delta G^o$ represents Gibbs free energy, $\Delta H^o$ represents the enthalpy change, $\Delta S^o$ is the change in entropy. Both fundamental thermodynamic functions ($\Delta H^o$, $\Delta S^o$) were determined from the slope and intercept respectively of the linear plotting of log $k_f$ against (1/T) according to Vant's Hoff equation [18]:

$$\log k = \frac{\Delta S^o}{2.303\, R} - \frac{\Delta H^o}{2.303\, R\, T} \quad \dots \dots \dots \dots \dots .(7)$$

**3. Results and Discussion**

**3.1 Preparations of Nanocellulose from Corn Cobs**

The TEM micrographs showed a rod-like shape and very interesting nanoparticles with diameter of 2-17 nm as indicated in (Fig.1) for a sample sonicated for 120 minutes and 30% $H_2SO_4$ (30H). The aggregation of nanoparticles composed with an average diameter of 42.3 nm for 120 minutes of sonication and 50% acid (50H) is clarified in figure 2. While the non-uniform nanoparticles with average diameter of 72.3-250 nm along with spherical nanoparticles at average diameter of 25-40 nm are obtained at 120 minutes as sonication time and 60% acid (60H) (Fig. 3).

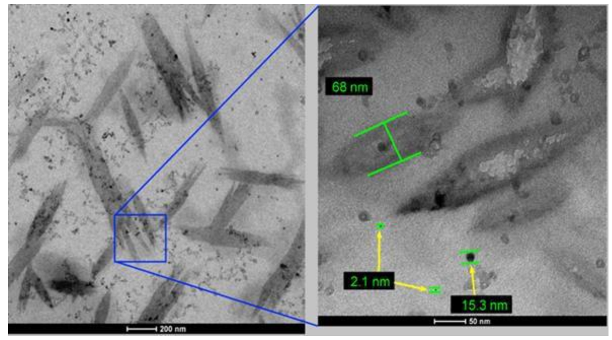


Figure (1). TEM image of nanocellulose prepared from corn cobs sonicated for 120 min at 30% acid (30H).

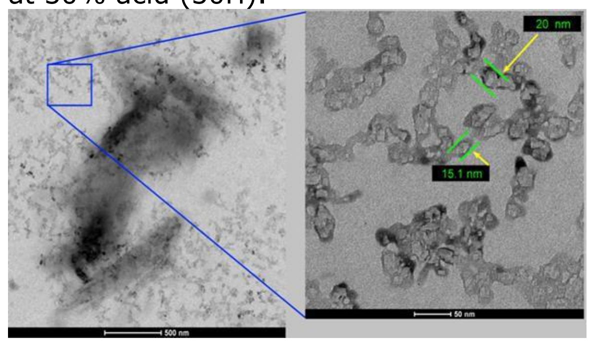


Figure (2). TEM image of nanocellulose prepared from corn cobs sonicated for 120 min at 50% acid (50H).

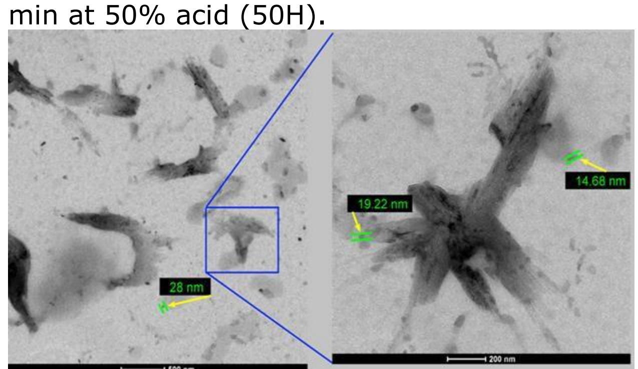


Figure (3). TEM image of nanocellulose prepared from corn cobs sonicated for 120 min at 60% acid (60H).

**3.2 Equilibrium Adsorption**

Adsorption isotherms carried out by three isotherms mathematical models (Langmuir isotherm, Freundlich isotherm, Temkin isotherm). It is clear that the adsorption of MB on the NC- corn cobs is the fitted very well with these models. Adsorption experiment data of Langmuir isotherm for MB dye on surface NC at different temperature (283, 298, and 323K) examined by plotting Ce/Qe versus Ce according to equation (3). All NC samples exhibit linear relationship with a decrease in adsorption capacity by increasing temperature and reassert exothermic sorption process. The values of Freundlich constant ( n and $k_f$ ) can be determined from slope and intercept of equation (4) by plotting the relationship between Log(Qe) and log(Ce). It is well known that if n is greater than 1 indicated a favorable adsorption of MB dye on the surface [19]. The adsorption capacity of adsorbent increased by increasing the $k_f$ values.[22][23][24]

Temkin constants can be determined from the slope and intercept of the linear relationship in equation (5). Very high correlation coefficient ($R^2$) values for all models were noticed (Table 4) which indicated that the adsorption processes are favorite and suitable for isotherm [20] Meanwhile, it can be seen that $R^2$ values of Freundlich model are higher than that of Langmuir and Temkin models (Table 4). The MB adsorption percentage on the prepared NC increases with temperature increases. Thus, the adsorption percentage reached to maximum values at 298 K, while, the adsorption percentage decreased by increasing the temperature. (Tables 1-3).[25][26][27]

Table (1): The values of $C_o$ ,Ce ,Log Ce, Qe Ce/Qe, Log Qe, ln Ce and Q % for the adsorption methylene blue dye on nanocellulose prepared from corn cobs at 283 K

| sample | $C_o$ (mg/L) | $C_{e(mg/L)}$ | Log $C_e$ | $Q_{e(mg/g)}$ | Log $Q_e$ | $C_e/Q_{e(g/l)}$ | ln $C_e$ | Q% |
|---|---|---|---|---|---|---|---|---|
| 30H | 250 | 11.051 | 1.043 | 23.895 | 1.378 | 0.462 | 2.403 | 95.580 |
| | 500 | 27.399 | 1.438 | 47.260 | 1.674 | 0.580 | 3.310 | 94.520 |
| | 750 | 48.095 | 1.682 | 70.191 | 1.846 | 0.685 | 3.873 | 93.587 |
| | 1000 | 73.576 | 1.867 | 92.642 | 1.967 | 0.794 | 4.298 | 92.642 |
| 60H | 250 | 10.229 | 1.010 | 23.977 | 1.380 | 0.427 | 2.325 | 95.909 |
| | 500 | 36.445 | 1.562 | 46.356 | 1.666 | 0.786 | 3.596 | 92.711 |
| | 750 | 91.680 | 1.962 | 65.832 | 1.818 | 1.393 | 4.518 | 87.776 |
| | 1000 | 145.945 | 2.164 | 85.406 | 1.931 | 1.709 | 4.983 | 85.406 |

Table (2): The values of $C_o$ ,Ce ,Log Ce, Qe Ce/Qe, Log Qe, ln Ce and Q % for the adsorption methylene blue dye on nano cellulose prepared from corn cobs at 298 K

| sample | $C_o$ (mgL) | $C_{e(mg/L)}$ | Log $C_e$ | $Q_{e(mg/g)}$ | Log $Q_e$ | $C_e/Q_{e(g/l)}$ | ln $C_e$ | Q% |
|---|---|---|---|---|---|---|---|---|
| 30H | 250 | 11.061 | 1.044 | 23.894 | 1.378 | 0.463 | 2.403 | 95.576 |
| | 500 | 22.126 | 1.345 | 47.787 | 1.679 | 0.463 | 3.097 | 95.575 |
| | 750 | 39.381 | 1.595 | 71.062 | 1.852 | 0.554 | 3.673 | 94.749 |
| | 1000 | 65.690 | 1.818 | 93.431 | 1.971 | 0.703 | 4.185 | 93.431 |
| 60H | 250 | 9.474 | 0.977 | 24.053 | 1.381 | 0.394 | 2.249 | 96.210 |
| | 500 | 25.735 | 1.411 | 47.427 | 1.676 | 0.543 | 3.248 | 94.853 |
| | 750 | 47.683 | 1.678 | 70.232 | 1.847 | 0.679 | 3.865 | 93.642 |
| | 1000 | 80.539 | 1.906 | 91.946 | 1.964 | 0.876 | 4.389 | 91.946 |

Table (3): The values of $C_o$ ,Ce ,Log Ce, Ce/Qe, Log Qe, ln Ce and Q % for the adsorption methylene blue dye on nano cellulose prepared from corn cobs at 323 K

| sample | $C_o$ (mg/L) | $C_{e(mg/L)}$ | Log $C_e$ | $Q_{e(mg/g)}$ | Log $Q_e$ | $C_e/Q_{e(g/l)}$ | ln $C_e$ | Q% |
|---|---|---|---|---|---|---|---|---|
| 30H | 250 | 15.739 | 1.197 | 23.426 | 1.370 | 0.672 | 2.756 | 93.705 |
| | 500 | 38.912 | 1.590 | 46.109 | 1.664 | 0.844 | 3.661 | 92.218 |
| | 750 | 62.897 | 1.799 | 68.710 | 1.837 | 0.915 | 4.142 | 91.614 |
| | 1000 | 98.247 | 1.992 | 90.175 | 1.955 | 1.090 | 4.587 | 90.175 |
| 60H | 250 | 18.255 | 1.261 | 23.174 | 1.365 | 0.788 | 2.904 | 92.698 |
| | 500 | 40.556 | 1.608 | 45.944 | 1.662 | 0.883 | 3.703 | 91.889 |
| | 750 | 80.990 | 1.908 | 66.901 | 1.825 | 1.211 | 4.394 | 89.201 |
| | 1000 | 134.431 | 2.129 | 86.557 | 1.937 | 1.553 | 4.901 | 86.557 |

Table (4): The values of Langmuir, Freundlich and Temkin constants at different temperatures (283,298,323)K

| Samples | T (K) | Langmuir constants | | | Freundlich constants | | | Temkin constants | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $R^2$ | a | $k_L$ | $R^2$ | n | $k_f$ | $R^2$ | B | $k_t$ |
| 30D | 283 | 0.9666 | 112.8668 | 0.0188 | 0.987 | 1.934 | 6.606 | 0.959 | 24.510 | 0.192 |
| | 298 | 0.9279 | 143.6782 | 0.0161 | 0.992 | 1.618 | 5.386 | 0.940 | 30.103 | 0.175 |
| | 323 | 0.9671 | 142.2475 | 0.0131 | 0.992 | 1.655 | 4.981 | 0.913 | 28.725 | 0.154 |
| 60D | 283 | 0.9940 | 129.0323 | 0.0140 | 0.989 | 1.695 | 4.894 | 0.984 | 28.111 | 0.141 |
| | 298 | 0.9815 | 155.5210 | 0.0131 | 0.997 | 1.538 | 4.829 | 0.965 | 31.863 | 0.160 |
| | 323 | 0.9169 | 139.4700 | 0.0111 | 0.967 | 1.586 | 3.972 | 0.952 | 29.927 | 0.116 |
| 30H | 283 | 0.9802 | 191.2046 | 0.0124 | 0.998 | 1.394 | 4.315 | 0.959 | 35.621 | 0.161 |
| | 298 | 0.935 | 214.592 | 0.012 | 0.971 | 1.307 | 4.073 | 0.996 | 39.014 | 0.161 |
| | 323 | 0.9671 | 206.1856 | 0.0078 | 0.997 | 1.340 | 3.016 | 0.955 | 36.146 | 0.110 |
| 60H | 283 | 0.9592 | 105.7082 | 0.0233 | 0.993 | 2.134 | 8.212 | 0.956 | 22.131 | 0.259 |
| | 298 | 0.9875 | 150.6024 | 0.0189 | 0.995 | 1.581 | 5.922 | 0.970 | 31.490 | 0.205 |
| | 323 | 0.9916 | 147.2754 | 0.0106 | 0.974 | 1.526 | 3.683 | 0.993 | 31.393 | 0.110 |

## 3.3 Thermodynamic Study

The thermodynamic functions (ΔG°, ΔH° and ΔS°) relationship of the adsorption of MB dye on the prepared NC surface from corn cobs were illustrated in figures (4) and (3).

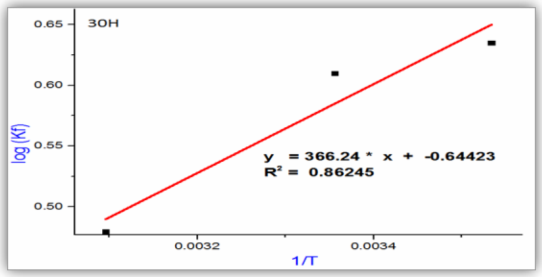


Figure (4 ). Relation of log k and 1/T for MB dye with nanocellulose prepared form corn cobs sonicated for 120

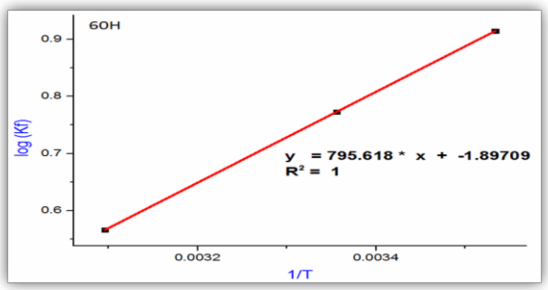


Figure (5). Relation of log k and 1/T for MB dye with nanocellulose prepared form corn cobs sonicated for 120 min at 60 % acid

Negative values of ΔH° indicated that the adsorption of MB dye on NC was exothermic process and all the observed values are less than 20 ($kJ.mol^{-1}$) (Table 5). These small changes in enthalpy were indicated that a physisorption was occurred with adsorption

Table (5). Thermodynamic functions of the adsorption of MB dye on the NC at different temperatures

| No. | Sample | $\Delta^o H$ kJ.mol$^{-1}$ | $\Delta^o S$ J.mol$^{-1}$.K$^{-1}$ | $\Delta^o G$ kJ.mol$^{-1}$ | | |
|---|---|---|---|---|---|---|
| | | | | 283 k | 298k | 323k |
| 1 | 30D | -5.2 | -2.810 | -4.4 | -4.3 | -4.2 |
| 2 | 60D | -4.1 | -1.178 | -3.8 | -3.8 | -3.8 |
| 3 | 30H | -7.0 | -12.335 | -3.5 | -3.3 | -3.0 |
| 4 | 60H | -1.5 | -36.324 | -5.0 | -4.4 | -3.5 |

## 4. Conclusions

The present investigation showed excellent removal obtained using NC prepared from agriculture waste such as corncobs as adsorbent for methylene blue dye with high efficiency .The process of adsorption on nanocellulose fits all the isotherm equilibrium adsorption models with a very high correlation coefficient. The thermodynamic study of adsorption Methylene blue on nanocellulse indicated that the adsorption was exothermic process and and the adsorption was spontaneous process.

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