Equilibrium, Thermodynamic and Mechanism Studies of Malachite Green adsorption on Used Black Tea Leaves from Acidic Solution

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Abstract. This study reports the equilibrium adsorption mechanism and thermodynamics for the removal of Malachite Green (MG) from acidic solution using Used Black Tea Leaves (UBTL) as a low cost adsorbent. The effect of initial dye concentration, processing temperature and the presence of electrolytes on the adsorption from acidic solutions were investigated in batch process. Adsorption process was attained to the equilibrium at about 24 hours. Adsorption isotherms of MG on UBTL for different temperatures were constructed at pH 2.0 and the equilibrium adsorption data were analyzed using different model equations such as Langmuir, Freundlich, Temkin, Dubinin-Radushkevich (D-R), Harkin-Jura, Halsey, Elovich-Larionov and Flory-Huggens isotherms. The experimental results were reasonably correlated by Langmuir, Flory-Huggins and D-R models than other isotherm models. The maximum adsorption capacity (q_m), intensity of adsorption (b) and separation factor (R_b) were calculated from Langmuir plot and activation energy of adsorption (E_{ad}) was determined from D-R isotherm. At pH 2.0, the equilibrium adsorption capacity of UBTL to MG is $110 \text{ mg}\cdot\text{g}^{-1}$ at 30°C , which was increased with increasing temperature suggested endothermic nature of adsorption. Thermodynamics parameters: ΔG_{ads} , ΔH_{ads} and ΔS_{ads} were calculated from Langmuir constant (b). The positive values of enthalpy and free energy, and negative value of entropy suggested that the adsorption is less spontaneous and surface migration or fragmentation of MG molecules on UBTL surface might be occur. Again, the low value of activation energy of adsorption ($E_{ad} = 0.3 \text{ kJ}\cdot\text{mol}^{-1} < 8 \text{ kJ}\cdot\text{mol}^{-1}$) suggested that the adsorption is controlled by physical in nature. A possible mechanism involvement of protonation is proposed from the effect of electrolytes during the adsorption of MG on UBTL at pH 2.0.

1. Introduction

Most of the dyes are toxic and carcinogenic compounds. These are widely used in different industries like food, acrylic, paint, paper, leather, drugs, petroleum and plastic. MG is one of these that is difficult to biodegrade and remove from waste water due to its complex aromatic structures [1]. There are several techniques to apply for removal of dyes from waste water such as chemical, biological and physical process [2]. Due to economic reasons, adsorption is the best process for removal of different pollutants from waste water [3]. Several kinds of low cost adsorbents such as buffing dust of leather industry [4], coconut husk [5], wheat bran [6], vetiver roots [7], date stones [8-9], pistachio nut shell [10], apple pomace and wheat straw [11] were studied to evaluate their applicability for the removal of dyes from aqueous solutions by adsorption process. In recent year, high adsorption capacity of used black tea leaves (UBTL) as a low cost adsorbent to Cr(VI) [12-14] and dyes [15-20] were reported.

Therefore, the aim of the present research work was to evaluate the applicability of UBTL as an adsorbent for the removal of Malachite Green (MG) from aqueous solution by investigating the equilibrium capacity and adsorption mechanism. The effects of different variables such as contact time, initial concentration of dye, processing temperature and the presence of electrolytes were studied. Then, the equilibrium adsorption data were analyzed by using different model isotherm equations. Thermodynamic parameters and effect of electrolytes on the adsorption were investigated to elucidate the mechanism of the adsorption of MG on UBTL.

2. Materials and Methods

2.1 Adsorbent

The fresh tea leaves were collected from Dhaka city in Bangladesh. The UBTL were prepared as described elsewhere [15]. The UBTL were sieved through the metallic sieve of particle size 0.425 mm and 0.500 mm and stored in air tight bottles which were kept into a desiccator for desired adsorption experiments.

2.2 Adsorbate

Malachite Green is an aromatic basic dye and commonly used in dyeing of cotton, silk, paper, bamboo, weed, straw and leather as well as in manufacturing of paints and printing inks. Malachite Green is a green crystalline powder with chemical formula of $[C_6H_5C(C_6H_4N(CH_3)_2)_2]Cl$. Its IUPAC name is 4-[(4-dimethylaminophenyl)phenyl-methyl]-*N,N*-dimethyl aniline. Aniline Green, Basic Green 4, Diamond Green B and Victoria Green B are synonyms of Malachite Green. Molecular mass of MG is $382.93 \text{ g}\cdot\text{mol}^{-1}$. The structural formula of Malachite Green is shown in Fig. 1. A stock solution of dye was prepared by dissolving 1.0 g of MG (Analytical grade) in distilled water into a 1000 mL volumetric flask from which desired concentrated solutions were prepared for adsorption study. Malachite Green in solution was analyzed at predetermined $\lambda_{\text{max}} = 617 \text{ nm}$ and at optimum pH 4.0. All the chemicals were used in this present study of analytical reagent grade.

Fig. 1. Structural formula of Malachite Green.

2.3 Determination of equilibrium time

For determination of equilibrium time, 0.0015 g UBTL (425-500 μm in diameter size) was taken in 25 mL of about $110 \text{ mg}\cdot\text{L}^{-1}$ MG solution in each of the adsorption bottles. Before addition of UBTL, pH of MG solution was adjusted at predetermined optimum pH 2.0 by drop-wise addition of $0.05 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 or $0.05 \text{ mol}\cdot\text{L}^{-1}$ NaOH solutions. All bottles were shaken in a thermostated mechanical shaker (NTS-4000 EYELA, Japan) at constant temperature of 30°C . The bottles were individually taken out from the shaker after 15, 45, 60, 120, 240 and 360 minutes of shaking. After adsorption, the UBTL was separated from the mixtures. The separated solutions were diluted as required concentration within the calibration limit and pH of the diluted solutions were adjusted at 4.0 before measuring their absorbance using UV-vis spectrophotometer (Model 1800A, Shimadzu) at 617 nm, due to the construction of calibration curve at pH 4.0. The amounts of MG adsorbed on to UBTL at different contact times were calculated using the following Eq. 1,

$$q_t = (C_i - C_t) \times \frac{V}{W} \quad (1)$$

where C_i and C_t are the concentrations of MG ($\text{mg}\cdot\text{L}^{-1}$) at zero time and at time t , respectively. V is the volume of solution in liter and W is the weight of the dry UBTL in g. The amount adsorbed is plotted against the contact time as shown in Fig. 2 from where equilibrium time was found to 24 hours.

2.4 Determination of adsorption isotherms at different temperatures

To determine adsorption isotherms at optimum pH, 7 bottles containing each of 0.0015 g UBTL into 25 mL MG solution of various concentrations ranging from 25 to 900 mg·L⁻¹ of MG solutions, have been shaken at 30°C for 24 hours which was the equilibrium time determined in last section. After adsorption, the residual concentrations of MG in each bottles, were analyzed by UV-vis spectrophotometer using same procedure described. The amount adsorbed was calculated for different initial concentrations of MG and respective equilibrium concentration was determined to construct the adsorption isotherm. To obtain adsorption isotherms at optimum pH for different temperatures, similar experiments were repeated at temperatures 35, 40 and 50°C. Each temperature was controlled within ± 0.5 °C. Adsorption isotherms at different temperatures are shown in Fig. 3.

2.5 Determination the effect of electrolyte

To establish the adsorption mechanism, the effect of electrolyte on the adsorption of MG on UBTL was determined. Two separate adsorption experiments at initial pH 2.0 using fixed initial concentration of 97.623 mg·L⁻¹ of MG at 30°C, were performed with different amounts of NaCl and NaNO₃ keeping other parameters constant. Experimental results are presented as amount adsorbed of MG on UBTL as a function of electrolytes concentration.

3. Results and Discussion

3.1 Estimation of equilibrium time

The equilibrium time for an adsorption process occurs when rate of adsorption and desorption is equal. The amount adsorbed is being steady value with time after reaching equilibrium. Estimation of equilibrium time is very important for construction of adsorption isotherm. Fig. 2 shows the variation of amount adsorbed of MG on UBTL with contact time. From this figure, the equilibrium time was determined at minimum change of amount adsorbed with time which is about 24 hours.

3.2 Adsorption isotherm

Adsorption isotherms are used to study the interaction between the adsorbent surface and the adsorbate molecules. The amount of MG adsorbed at equilibrium with the equilibrium concentration of MG on UBTL at different temperature and pH 2.0 are presented in Fig. 3. Different isotherm model equations such as Langmuir, Freundlich, Temkin, D-R, Harkin-Jura, Halsey, Elovich-Larionov and Flory-Huggens were used to verify their applicability to evaluate the nature of adsorption.

Langmuir Isotherm

The Langmuir isotherm assumes monolayer surface coverage on equivalent sites [21]. The Langmuir isotherm model has been successfully applied to many adsorbate pollutants adsorbed on different adsorbents such as tamarix aphylla leaves [22], citrullus lanatus rind [23], raw moroccan clay [24] and chemically modified silica gel [25]. The linear form of the Langmuir isotherm equation is given by Eq. 2,

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (2)$$

where, C_e (mg·L⁻¹) is the equilibrium concentration of MG, q_e (mg·g⁻¹) is the amount of MG adsorbed at equilibrium, q_m (mg·g⁻¹) and b (L·mg⁻¹) is Langmuir constant related to adsorption efficiency and the rate of adsorption. The linear plot of C_e/q_e vs C_e is shown in Fig. 4 and the values of q_m and b were determined from the slope and the intercept of the plots for different temperatures and are presented in Table 1. It shows that the adsorption capacity (q_m) of UBTL for MG is 109.89 mg·g⁻¹ at 30°C which is increased to 588.24 mg·g⁻¹ at 50°C.

Fig. 2. Change of amount adsorbed of MG on UBTL with time for the initial concentration of $110.012 \text{ mg}\cdot\text{L}^{-1}$ at pH 2.0 and $(30\pm 0.2)^\circ\text{C}$.

Fig. 3. Adsorption isotherms of MG on UBTL for different temperature at pH 2.0.

Separation factor. The feasibility of the adsorption isotherm is described by the essential characteristics of the Langmuir isotherm which can be expressed in terms of dimensionless constant called separation factor, R_b [26] by the Eq. 3 as

$$R_b = \frac{1}{1 + bC_o} \quad (3)$$

The values of R_b indicate the nature of the adsorption isotherm to be unfavorable ($R_b > 1$), favorable ($0 < R_b < 1$), linear ($R_b = 1$) or unfavorable ($R_b = 0$). A plot of the calculated R_b values vs C_o at different temperature is presented in Fig. 5. The R_b values for the adsorption of MG onto UBTL lies between 0 to 1, indicating that the adsorption is a favorable [27].

Fig. 4. Linear plot of Langmuir isotherm for the adsorption of MG on UBTL at pH 2.0 for different temperatures.

Fig. 5. Effect of initial concentration of MG on on dimensionless separation factor, R_b at pH 2.0 and different temperatures.

Freundlich Isotherm

The Freundlich isotherm equation assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and are not equally available. The Freundlich isotherm is expressed by the Eq. 4 [28],

$$\ln q_e = \ln k_f + 1/n \ln C_e \quad (4)$$

where, k_f ($\text{mg}\cdot\text{g}^{-1}$) and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. A plot of $\ln q_e$ vs $\ln C_e$ is shown in Fig. 6 and the values of k_f and n were calculated from the intercept and the slope of the plot and are presented at Table 1. The values of $n > 1$ indicate the favorable adsorption process [29].

Temkin isotherm

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy [30]. The Temkin isotherm is generally given by the following Eq. 5,

Fig. 6. Freundlich isotherm for the adsorption of MG on UBTL at pH 2.0 for different temperatures.

Fig. 7. Temkin isotherm for the adsorption of MG solution on UBTL at pH 2.0 for different temperatures.

$$q_e = \frac{RT}{b_T} \ln(k_T C_e) \quad (5)$$

where, T is the absolute temperature (K), R is the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), k_T is the equilibrium binding constant ($\text{L}\cdot\text{mg}^{-1}$) corresponding to the maximum binding energy and b_T is the variation of adsorption energy ($\text{kJ}\cdot\text{mol}^{-1}$). The linear form of this model is given by Eq. 6 as follows [31].

$$q_e = B \ln k_T + B \ln C_e \quad (6)$$

where $B = RT/b_T$ is the Temkin constant related to the heat of adsorption ($\text{J}\cdot\text{mol}^{-1}$). The values of k_T and B were calculated from the intercept and the slope of the linear plot of q_e vs $\ln C_e$ as shown in Fig. 7. The values are presented in Table 1 where the values of B indicated that the heat of adsorption increases with temperature. So, the adsorption process is endothermic [32].

Dubinin-Radushkevich (D-R) isotherm

Dubinin-Radushkevich have reported a isotherm model where adsorption occurs on both homogenous and heterogeneous surfaces [33]. It is applied to estimate characteristics porosity and apparent free energy of adsorption. The linear form of the D-R isotherm is given as Eq. 7,

$$\ln q_e = \ln q_{\text{DR}} - \gamma \varepsilon^2 \quad (7)$$

where, q_{DR} is the D-R adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$), γ is the activity coefficient ($\text{mol}^2\cdot\text{k}^{-1}\cdot\text{J}^{-2}$) related to the mean free energy of adsorption and ε is Polanyi potential which is calculated by Eq. 8 as

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (8)$$

The linear plot of $\ln q_e$ vs ε^2 is shown in Fig. 8 and the values of γ and q_{DR} were determined from the slope and the intercept of the plot and are presented in Table 1. The value of γ decreases with increasing of temperature due to strengthening of adsorbate-adsorbent interaction for the above system [34].

The mean free energy of adsorption, E ($\text{kJ}\cdot\text{mol}^{-1}$) can be calculated from the Eq. 9,

$$E = -\frac{1}{\sqrt{2\gamma}} \quad (9)$$

The E values indicate the adsorption type, physical adsorption ($E < 8 \text{ kJ}\cdot\text{mol}^{-1}$) or chemical ion exchange ($E = 16 \text{ kJ}\cdot\text{mol}^{-1}$) or particle diffusion mechanism ($E > 16 \text{ kJ}\cdot\text{mol}^{-1}$) [35]. The adsorption energy, E was found between $0.302\text{--}0.341 \text{ kJ}\cdot\text{mol}^{-1}$ which implies that the adsorption of MG on UBTL is controlled by physical in nature.

Harkin-Jura isotherm

The Harkin-Jura isotherm describes the multilayer adsorption system with the existence of a heterogeneous pore distribution in adsorbent surface [36]. The Harkin-Jura adsorption isotherm model is presented by Eq. 10,

$$\frac{1}{q_e^2} = \frac{B_{HJ}}{A_{HJ}} - \frac{1}{A_{HJ}} \log C_e \quad (10)$$

where, B_{HJ} and A_{HJ} are the Harkin-Jura isotherm constants. The values of B_{HJ} and A_{HJ} are obtained from the intercept and slope of the plot of $1/q_e^2$ vs $\log C_e$ as shown in Fig. 9 and values are presented in Table 1.

Fig. 8. D-R isotherms for adsorption of MG on UBTL for different temperatures.

Fig. 9. Harkin-Jura isotherm for adsorption of MG on UBTL for different temperatures.

Halsey isotherm

The Halsey adsorption isotherm model mainly describes the multilayer adsorption system for the adsorbate at a relatively large distance with a heterogeneous porous nature of adsorbent surface [37]. The Halsey adsorption isotherm is given by Eq. 11,

$$\ln q_e = \left(\frac{1}{n_H} \right) \ln k_H - \left(\frac{1}{n_H} \right) \ln C_e \quad (11)$$

where, k_H and n_H are the Halsey constants. The values of k_H and n_H were calculated from the slope and the intercept of the linear plot of $\ln q_e$ vs $\ln C_e$, respectively as shown in Fig. 10 and the values are presented in Table 1. The experimental data are not applicable to the Halsey adsorption equation.

Elovich-Larionov isotherm

Elovich-Larionov isotherm describes the adsorption of non electrolytes from solution on solid surface. This isotherm can be expressed by Eq. 12 as [38-39],

$$\ln \left(\frac{q_e}{C_e} \right) = \ln(k_E q_E) - \left(\frac{1}{q_E} \right) q_e \quad (12)$$

where, k_E is the Elovich-Larionov isotherm constant and q_E is the maximum MG concentration on UBTL surface ($\text{mg} \cdot \text{g}^{-1}$). The values of q_E and k_E were obtained from the slope and the intercept of the plot of $\ln(q_e/C_e)$ vs q_e , respectively shown in Fig. 11 and the values are give in Table 1.

Fig. 10. Halsey isotherm for adsorption of MG on UBTL for different temperatures at pH 2.0.

Fig. 11. Elovich-Larionov isotherm for adsorption of MG on UBTL for different temperatures.

Flory-Huggins isotherm

Flory-Huggins model describes the degree of surface coverage nature of the adsorbate onto the adsorbent. The linear form of Flory-Huggins model is presented by Eq. 13 as [40],

$$\ln \frac{\theta}{C_0} = \ln k_{FH} + \alpha_{FH} \ln(1 - \theta) \quad (13)$$

where, $\theta = (1 - C/C_0)$ is the surface coverage of the adsorbent by the adsorbate, α_{FH} is the number of adsorbate occupying in adsorption sites, K_{FH} is Flory-Huggins equilibrium constant. The values of K_{FH} and α_{FH} are determined from the intercept and the slope of the plot as $\ln(\theta/C_0)$ vs $\ln(1 - \theta)$, respectively shown in Fig. 12 and presented in Table 1.

Table 1. Comparison of the parameters derived from different isotherm models for different processing temperatures at pH 2.0.

Isotherm Model	Parameters	Temperatures (°C)			
		30	35	40	50
Langmuir	$q_m (\text{mg} \cdot \text{g}^{-1})$	109.890	250.000	357.143	588.235
	$b \times 10^3 (\text{L} \cdot \text{mg}^{-1})$	6.046	3.779	7.203	7.759
	$R^2 (-)$	0.995	0.996	0.998	0.998
Freundlich	$K_f (\text{L} \cdot \text{mg}^{-1})$	3.018	3.497	15.481	24.138
	$1/n$	0.533	0.616	0.465	0.477
	$R^2 (-)$	0.943	0.967	0.962	0.952
Temkin	B	24.056	51.623	76.273	126.422
	A	0.061	0.046	0.077	0.080
	$R^2 (-)$	0.979	0.984	0.986	0.984
Dubinin-Radushkevich	$q_m \times 10^3 (\text{mol} \cdot \text{g}^{-1})$	1.100	2.471	2.768	4.795
	$r (\text{mol}^2 \cdot \text{k}^{-1} \cdot \text{J}^{-2})$	5.5	6.1	4.4	4.3
	$E (\text{kJ} \cdot \text{mol}^{-1})$	0.302	0.286	0.337	0.341
	$R^2 (-)$	0.966	0.984	0.980	0.982
Harkin-Jura	B_{HJ}	2.75	2.70	4.00	3.33
	A_{HJ}	416.67	1000	10000	16666.67
	$R^2 (-)$	0.679	0.664	0.744	0.705
Halsey	n_{H}	-1.88	-1.62	-2.15	-2.10
	$k_{\text{H}} \times 10^2$	12.53	13.16	0.28	0.12
	$R^2 (-)$	0.943	0.967	0.962	0.953
Elovich-Larionov	q_E	53.76	135.14	144.93	250.00
	$k_E \times 10^3$	14.54	7.86	26.38	24.76
	$R^2 (-)$	0.872	0.923	0.947	0.926
Flory-Huggins	$K_{\text{FH}} \times 10^6 (\text{mg} \cdot \text{g}^{-1})$	2.39	2.80	12.75	18.22
	$\alpha_{\text{FH}} (-)$	-194.75	-127.8	-45.74	-28.93
	$R^2 (-)$	0.998	0.996	0.981	0.991

3.3 Thermodynamics of adsorption

The maximum amount adsorbed of MG on UBTL was determined from the best fitted Langmuir plots for different temperatures at pH 2.0. Fig. 13 shows the variation of amount adsorbed with temperature known as adsorption isobar which indicated that the amount adsorbed increased with increasing temperature i.e. the process is endothermic.

The Langmuir constant values, b for MG adsorption on UBTL were also calculated for different temperatures by using Langmuir equation. These were used to calculate the thermodynamic parameters: ΔG_{ads} , ΔS_{ads} and ΔH_{ads} by using Eq. 13 and 14 [41-42] as a plot of $\ln b$ vs. $1/T$ as shown in Fig. 14.

Fig. 12. Flory-Huggins isotherm for adsorption of MG on UBTL for different temperatures.

$$\ln b = \frac{\Delta S_{\text{ads}}}{R} - \frac{\Delta H_{\text{ads}}}{RT} \quad (13)$$

$$\Delta G_{\text{ads}} = -RT \ln b \quad (14)$$

where, R is the molar gas constant ($8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), T is the absolute temperature (K), b is Langmuir constant ($\text{L}\cdot\text{g}^{-1}$), ΔG_{ads} is the adsorption free energy ($\text{kJ}\cdot\text{mol}^{-1}$), ΔH_{ads} is the adsorption enthalpy ($\text{kJ}\cdot\text{mol}^{-1}$) and ΔS_{ads} is the adsorption entropy ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$). The values ΔH_{ads} and ΔS_{ads} were estimated from the slopes and intercepts of the plot of $\ln b$ versus $1/T$ as shown in Fig 14. Again, ΔG° value is computed by using Eq. 14. The values of ΔG_{ads} , ΔH_{ads} and ΔS_{ads} of MG adsorption on UBTL at different temperatures are presented in Table 2. The positive values of ΔG_{ads} and ΔH_{ads} indicated the adsorption of MG was non-spontaneous and endothermic at pH 2.0. The positive values of ΔS_{ads} indicated that the fragmentation of large MG molecules might occur during adsorption process.

3.4 Effect of electrolytes and adsorption mechanism

The effect of electrolytes on the adsorption of MG onto UBTL was carried out to identify the involvement of protonation/deprotonation mechanism or electrostatic force of attraction between MG and UBTL. The batch adsorption experiments were performed in presence of two electrolytes (NaCl and NaNO_3) with different concentrations for a same concentration of MG. A plot of equilibrium amount adsorbed, q_e vs concentration of electrolytes is presented in Fig. 15.

Fig. 13. Adsorption isobar for adsorption of MG on UBTL at pH 2.0

Fig. 14. A plot of $\ln b$ vs $1/T$ for adsorption of MG on UBTL at pH 2.0

Table 2. The thermodynamic parameters for MG adsorption on UBTL at pH 2.0 for different temperatures.

Temperature (K)	ΔH_{ads} $\text{kJ}\cdot\text{mol}^{-1}$	ΔG_{ads} $\text{kJ}\cdot\text{mol}^{-1}$	ΔS_{ads} $\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$
303		+ 10.45	
313	+ 10.35	+ 10.34	-22.13
323		+ 10.47	

The figure shows that at pH 2.0, the amount adsorbed is exponentially decreased with the increase of electrolyte (NaCl) concentration which supports the involvement of protonation mechanism in the adsorption due to the faster competitive adsorption of negative electrolytes (NaCl) than that of the neutral MG molecule to the positive site of UBTL surface as shown in Fig. 16. Same figure shows that the amount adsorbed is exponentially increased with increasing the concentration of NaNO_3 electrolytes. This observation might be due to the formations of positive site on NO_3^- ions after adsorption on positive UBTL surface by delocalization of lone pair of electrons on rest two

Fig. 15. Variation of equilibrium amount adsorbed (q_e) with concentration of electrolytes for the adsorption of MG on UBTL at initial pH 2.0 and $30\pm 0.2^\circ\text{C}$.

Fig. 16. Proposed mechanism for the adsorption of MG on UBTL based on the effect of two electrolytes at pH 2.0.

oxygen atoms of NO_3^- ions. MG exists in MG^+ and MG^0 form at lower pH. As a result, the positive sites of MG repelled by positive sites of adsorbed NO_3^- ions but partially attract the neutral MG to surface. As a result, the amount adsorbed of neutral MG increased with increasing the concentration of NO_3^- ions on the less positive UBTL surface as shown in Fig. 16.

4. Conclusions

The results of this investigation showed that the equilibrium adsorption of MG on UBTL follows Langmuir comparatively better than other isotherms. The maximum adsorption capacity was found $110 \text{ mg}\cdot\text{g}^{-1}$ at 30°C , which was increased with increasing temperature. Thermodynamics parameters: ΔG_{ads} , ΔH_{ads} and ΔS_{ads} of the adsorption suggested that the adsorption is endothermic and less spontaneous. The value of activation energy for the adsorption of MG on UBTL indicated that the process is controlled by physical in nature.

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