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# Adsorption of Naphthol Green B Dye on to Ca-Montmorillonite and Nano-Composite Ca-Montmorillonite Clay

**Hadeel Adnan Al-musawi**[1], **Dunya Edan Al-Mammar**[2]

[1,2] Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq.

e-mail: Hadeeladnan89@yahoo.com, dunya.almamar@yahoo.com

**Abstract**

In this work Iraqi Ca-montmorillonite clay was converted to Fe-Ca-montmorillonite nano composite for enhancing the adsorption capacity of the clay for adsorbing the anionic dye Naphthol Green B using batch method for adsorption. The equilibrium adsorption parameters which affects the removal efficiency of the dyes including clay dose, starting dye concentration, pH of the dyes solutions, time of adsorption and temperature were studied for the both clays. The adsorption isotherms at optimum operating conditions were described using various adsorption isotherm models such as: Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms and the values of the adsorption constants for these isotherms were evaluated. The equilibrium data were fitted by Freundlich isotherm .The values of the mean free energy calculated from Dubinin-Radushkevich isotherm show that the adsorption of NGB dye onto both clays was physi-sorption. The values of the $\Delta G_{Ad}$, $\Delta H_{Ad}$ and $\Delta S_{Ad}$ suggest that the adsorption process of NGB dye is spontaneous, exothermic occurs with increasing in the disorder.

**Keywords:** Adsorption, Naphthol Green B dye, Ca-Montmorillonite clay, isotherm, nano Ca-Montmorillonite.

## Introduction

The sorption of dye is an important field for the controlling and coloration the wastewater. For this purpose using materials that have good sorption capacity, good dye ability, less-cost, good color-fastness and have a less problems in the treatment of wastewater was almost an important issue. First approach to enhance color eliminate is to copolymerize or graft the initial fiber polymers with a powerful dye sites. As examples are a cationic-treatment of a cellulose, anionic-treatment of polyester when no/low salt cellulose dyeing with acid/reactive dyes and basic dyes used for dyeing polyester. A cationic treatment of cellulose used quaternary ammonium to cellulose to supply attractiveness to anionically charged dyes, e.g. acid, direct and reactive dyes [1, 2, 3]. Anionic treatment for polyester adds a co-monomer with sulfonate to the polyester chain, for this reason polyester thus produced will attract cationically charged basic dyes [4,5]. The other approach to enhance the adsorption of dye is to used sorbent physically into the polymer matrix to make a composite. Since the strong dye adsorption ability of the sorbent, textiles construct from that composite shall have a good dye adsorption ability [6, 7]. Our obvious study used nanoclay to yield nano-composite clay also investigate adsorption capability of nanoclay for removal acid dye. Nanoparticles have a good application in the textiles because their small size which supply the large surface area, which is important characteristic for good adsorbent. The using of nanoclay for other nanoparticles is due to its commercial availability with reasonable prices quality and consistent quality. In this study we selected Ca-montmorillonite that have one octahedral sheet and two tetrahedral sheets (2:1) Figure (1) shows the structure of montmorillonite. There are two silica, tetrahedral, sheets in the top and bottom, while in the middle; an aluminum octahedral sheet. Using nanoclay as adsorbent can not only enhane the adsorption capability for the adsorption of dye, but also enhance the service ability and mechanical of the substance [8]. The morphology of montmorillonite clay is platelet, with a thickness of < 1 mm and width from 100 nm to 1 µm. Because of large aspect ratio, clay has a huge surface area [9]. Studying the sorption of dye onto nanoclay is not only used for coloration and removal of color from wastewater, but also useful for studying the sorption characteristic to cationic, anionic and non-ionic chemicals. The adsorption of dye on clay and nanoclay have been studied by many researcher in last years for wastewater cleaning [10], especially for anionic dyes [11].

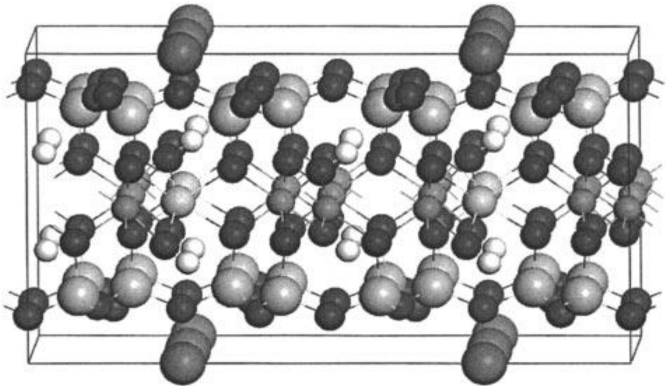

**Figure 1: The structure of montmorillonite clay.**

## Materials and Methods

### Experimental part:

Clay preparation: montmorillonite clay used in this work was provided by state company for mining industries. Its CEC equal to 65 meq/100g. This clay consist of the following oxides (by weight) $SiO_2$: 52.122%, $Al_2O_3$: 12.781%, $Fe_2O_3$: 4.089%, CaO: 7.66%, $Na_2O$: 0.622%, $K_2O$: 0.567%, MgO: 3.044%, $TiO_2$: 0.874%, MnO: 0.026%, $P_2O_5$: 0.458% and LOI: 16.11%. The clay was washed using distilled water for many times then it was dried at 100°C. 10g of clay was suspensied with 500ml distilled water and stirred for 3hours. 0.2M $Fe(NO_3)_3.9H_2O$ was stirred vigorously with $Na_2CO_3$ till the molar ratio reaches 1:1 for $[Na^+]/[Fe^{3+}]$, then this solution was dropping into the clay solution and shaking for 3hr. The produce clay was filtered and washed for several times with distilled water, then dried for two days at 100°C and kept in a dry place.

### Preparation of Naphthol Green B solution

Naphthol Green B, an ionic or acidic dye was donate by Fluka chemicals M.W=878.45 g/mol, absorption maxima=716 nm, C.I. number=10005, its water soluble dye with molecular formula $C_{30}H_{15}FeN_3Na_3O_{15}S_3$. Figure (2) shows the chemical structure for NGB dye. 1000ppm a stock solution of NGB dye was prepared. This solution used to prepare different concentrations of (5, 10, 20, 30 and 40) ppm.

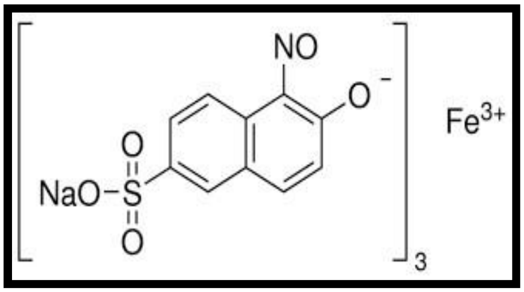

**Figure 2: Chemical formula for Naphthol Green B**

**Apparatus:** Spectrophotometer measurements was done for dye using uv-vis spectrophotometer [UV-1800] Shimadzu, Japan. pH measurements was obtained using pH-meter type EUTECH pH700 singapore made. A mechanical shaker type JTYS-1000, China, was used for shaking the working solutions.

**Methods:** Batch sorption experimental were carried out in 100ml flask at temperature range (288, 298, 308, 318 and 328) K using initial concentration of NGB dye ranged (5, 10, 20, 30 and 40) ppm shaking with 0.1g of clay for 60 min as shaking time, the agitation speed is 150 rpm and pH=7. The suspend solution was separated using centrifuge, then the final concentration of the dye at equilibrium $C_e$(mg/L) determined. The amount of the adsorbed NGB dye $Q_e$(mg/g) was calculated as:

$$Q_e = \frac{C_o - C_e}{Wt} * V \qquad (1)$$

Where $C_0$ is the initial NGB dye concentration (mg/L), $C_e$ is the NGB dye concentration at equilibrium (mg/L), V is volume of the solution (L) and W is weight of the clay (g).

The removal of NGB dye percentage R% was estimated:

$$R\% = \frac{Co - Ce}{Co} * 100 \qquad (2)$$

## Results and Discussion

### Optimization

### Influence of adsorption time

The influence of the adsorption time on the removal efficiency of 20 mg/L NGB dye has been assigned by changing the adsorption time from 5 to 90 min at 298K, pH: 7, adsorbent dose: 0.2g/50ml and agitation speed 150rpm. Figure (3) shows the effect of adsorption time on the uptake of NGB dye. There is a smooth and continues increasing until reaching to the saturation after 60 min [12]. These suggest the possible of the formation of mono coverage of NGB dye on the surface of the two clays. At first the adsorbate species moved from the bulk liquid phase to the surface of adsorbent particles, then the dye species move within the micro and macro-pores of adsorbent particles. Similar fact was observed by T.A. Khan et al [13]. Since the percentage removal reaches maximum values when the adsorption time is 60 min, so the optimum adsorption time was selected 60 min.

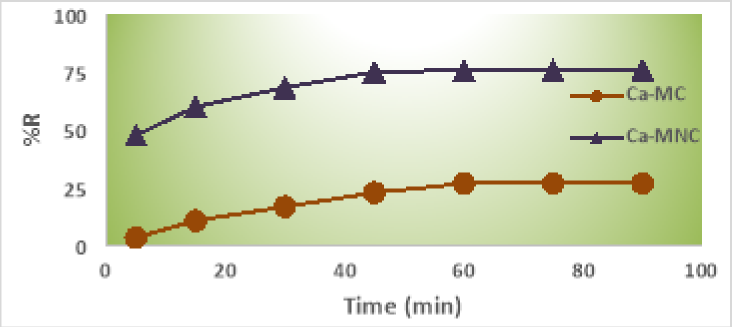

**Figure 3: Influence of adsorption time on removal of (20mg/L) NGB dye using Ca-MC and Ca-MNC as adsorbents.**

### Influence of clay dosage

The influence of clay dosage on NGB dye removal was studied by using various amounts of clay (0.05, 0.1, 0.15, 0.2, 0.3, 0.4 and 0.5g) into 25ml of 20mg/L NGB dye at 298K, pH: 7 and shaking speed (150rpm). The removal were shown in Figure (4), the removal efficiency increased from (38%) (72%) to (60%) (90%) respectively for Ca-MC and Ca-MNC as the clay dose increased from 0.05g to 0.1g. An increase in the adsorbent amount leads to reduce the removal efficiency for the dye till reaches 53%, 82% values for 0.5g of Ca-MC and Ca-MNC. Increasing the removal efficiency may be explained due to the increase in the active functional groups that resulted to more available adsorption sites. After 0.1g of clay the reduction in the removal percentage with the increasing of the amount of clay may be due to the patiticle aggregation, that resulting from a high adsorbent mass [14]. Therefore (0.1g) of clay were selected as optimum weight for the further experiments.

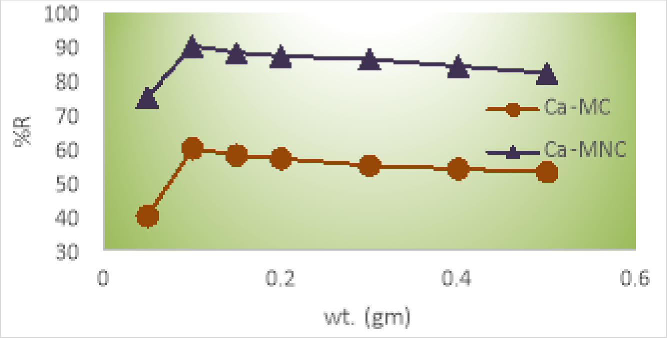

**Figure 4: Influence of clay dosage on the removal efficiency of NGB dye onto Ca-MC and Ca-MNC.**

### Influence of initial pH

To optimize the pH for the maximum percentage removal the experiments were carried out by maintaining the clay amount 0.1g/25ml of 20mg/L NGB dye solution at different pH range 1.5 to 11.4, adsorption time: one hour, at 298K and agitation speed 150rpm. Figure (5) represented the varying of the percentage removal as a function of pH for the adsorption of NGB dye onto Ca-MC and Ca-MNC. It is evident that as the pH value increase from 1.5-3.5 the removal increased from 60%, 80% to 70%, 93% for Ca-MC and Ca-MNC respectively, after that the removal efficiency start to decreases from 66%, 87% to 30%, 53% for Ca-MC and Ca-MNC respectively as the pH value increase from 5.5-11.4.

It is logical to assume that the adsorption of the anionic dye, NGB can be promoted under the acidic conditions, where the positive charge density on the surface of adsorbent is great. Due to the electrostatic attraction between positively charged clay surfaces and negatively charged functional groups of NGB dye, higher removal be established at the acidic range, furthermore the hydrogen ion ($H^+$) acts as a bridging ligand between the clay wall and the NGB dye. At lower pH the increasing of ($H^+$) concentration in the clays surfaces acquires positive charge by the adsorbing ($H^+$), that leads to increasing the adsorption of NGB dye. When the clay surfaces in acidic range are positively charged, a strong electrostatic-attraction recognize between the clay surfaces and NGB anions that leading to maximum removal for the NGB dye. On the other hand, when pH value increased (basic range), there are increasing in the number of negatively charged sites, that not favoring for the adsorption of NGB dye anions because of the electrostatic repulsion [15]. Similar pH trends were reported by other researches [16].

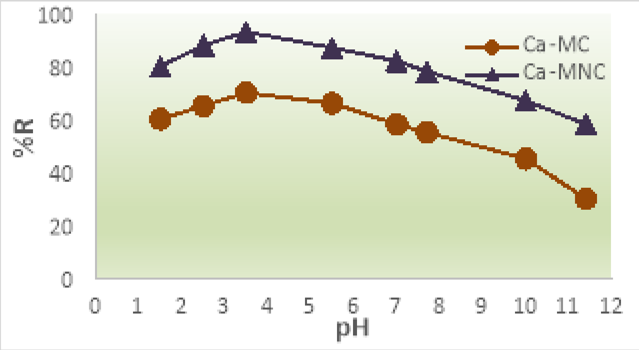

**Figure 5: Influence of pH on adsorption of NGB dye onto Ca-MC and Ca-MNC as adsorbents.**

### Influence of initial NGB dye concentration

In order to demonstrate influence of the initial NGB dye concentrations, different initial NGB dye concentrations ranging from (5, 10, 20, 30 and 40 mg/L) were used at 298K, pH: 7, clay weight (0.1 g/25 ml), shaking period 60 min and agitation speed 150 rpm. Figure (6) shows at low concentration of NGB dye 5ppm, the removal efficiency increases from 20%, 73% to 27.5%, 79% for both Ca-MC and Ca-MNC respectively, it may attributed to the ratio of number of active sites that available per unit NGB dye concentration was small due to increased competition for active sites. At low dye concentration the sorption is highly dependent on the initial NGB dye concentration, because it provides necessary driving force to overcome all mass transfer resistances of the dye between solid and aqueous phase. As the initial NGB concentration reaches 40ppm NGB concentration the removal efficiency decreases from 30%, 79% to 21%, 70% for both Ca-MC and Ca-MNC respectively, that may be due to the demand for active sites is more but there are a limited active sites on the surfaces. Similar result was obtained by G.V.K. Mohan et al [17].

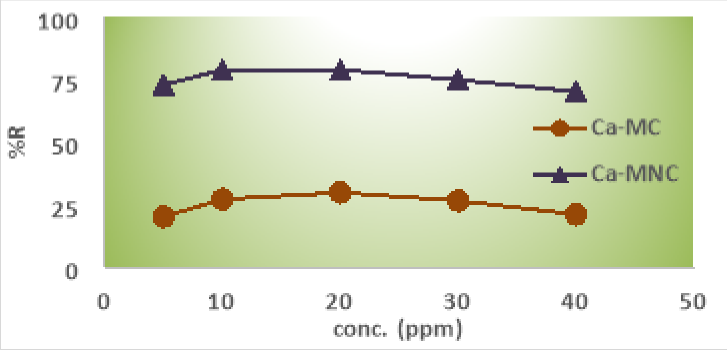

**Figure 6: Removal efficiency of NGB dye as a function of concentrations using Ca-MC & Ca-MNC as adsorbent.**

### Influence of temperature

The influence of temperature was studied for initial NGB dye (20mg/L) at temperatures rang (288-328K), clay dose (0.1g/25ml), pH (7) for one hour and agitation speed (150rpm). Figure (7) shows the influence of temperature on the adsorption process of NGB on the surface of Ca-MC and Ca-MNC. The results show that the removal efficiency decreases with increasing of temperature for two clays, therefore the adsorption process can be classified as an exothermic process. So, high temperature may decrease the adsorption forces between the NGB dye and the active sites on the clay surface [18].The same result was obtained by V. Vimonses et al [19].

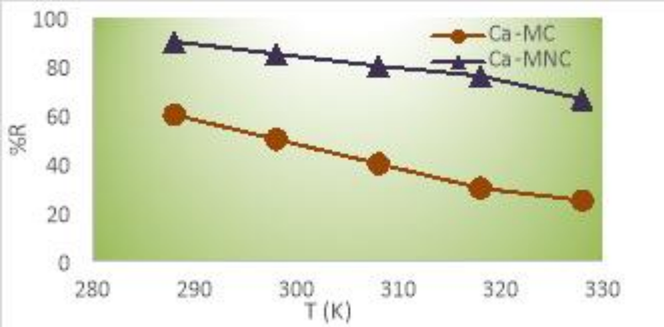

**Figure 7: Influence of temperature on adsorption of NGB dye onto Ca-MC&Ca-MNC.**

## Adsorption isotherm

Adsorption isotherm is the most important information, which indicates how molecules are dispersed between the solid phase and liquid phase when the adsorption reaches equilibrium. Figures (8a&b) show the adsorption isotherm of NGB dye onto Ca-MC and Ca-MNC at different temperatures.

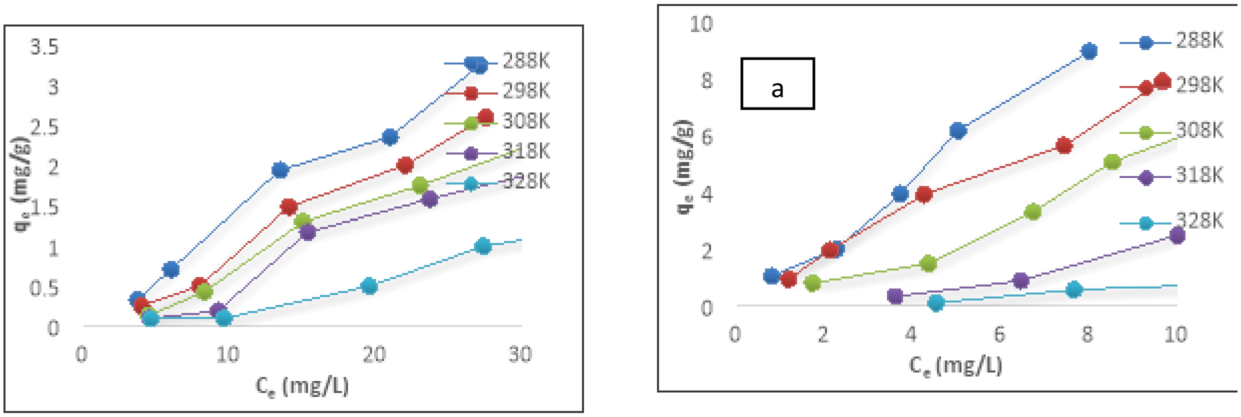

**Figure 8: Adsorption isotherms of NGB dye onto a-Ca-MC b- Ca-MNC at different temperatures.**

Figures (8a&b) show the adsorption isotherms of NGB onto Ca-MC and Ca-MNC were S-type isotherm, indicating that the adsorbent is possibly mesoporous. This type represent the adsorption process when the solid has a high affinity for the solvent [20].

Adsorption data explain the performance of adsorbent and adsorption isotherms and the equilibrium distribution of a solute between adsorbent and solution, will provide the ability to estimate the adsorbent efficiency and costs. Four most common isotherm equations namely, Langmuir, Freundlich, Timken, and Dubinin-Radushkevich isotherms were tested for the adsorption of NGB dye onto both clays.

**Langmuir Adsorption Isotherm:** This model built on the following assumption

1- The adsorption happen at specific homogenous sites in the surface of adsorbent.
2- When this site was occupied by a molecular of a solute, no further adsorption occur at this site.

This model written as:

$$\frac{C_e}{q_e} = \frac{1}{K_L.Q_m} + \frac{1}{Q_m}.C_e \qquad (3)$$

Where: $C_e$ = the equilibrium concentration of SO dye (mg/L), $q_e$= the amount of material adsorbed per gram of the adsorbent at equilibrium (mg/g), $q_m$= maximum monolayer coverage capacity (mg/g) and $K_L$ = Langmuir isotherm constant (L/mg). The values of $Q_m$, $K_L$ was obtain from the slope and intercept of the plot between $C_e/q_e$ and Ce as shown in Figures (9a&b). The values of ($Q_m$ and $K_L$) are listed in Table (1).

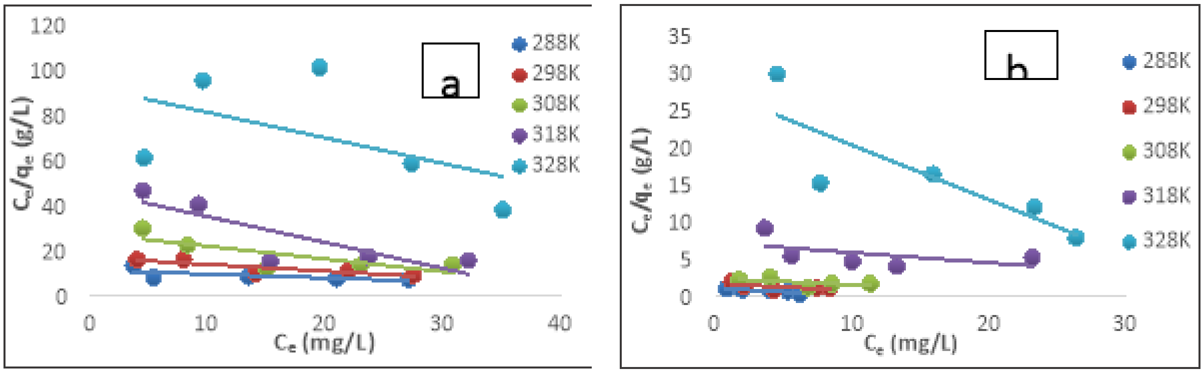

**Figure 9: Langmuir isotherms of NGB dye on a-Ca-MC b- Ca-MNC at different temperatures.**

**Table 1: Langmuir constants for adsorption of NGB dye onto Ca-MC and Ca-MNC at different temperatures.**

| | Temperature (K) | $Q_m$ (mg/g) | $K_L$ (L/mg) | $R^2$ |
|---|---|---|---|---|
| **Ca-MC** | 288 | 5.8309 | 0.0155 | 0.4651 |
| | 298 | 3.3783 | 0.0178 | 0.7358 |
| | 308 | 1.7736 | 0.0206 | 0.6364 |
| | 318 | 0.8735 | 0.0247 | 0.7030 |
| | 328 | 0.8862 | 0.0122 | 0.2813 |
| **Ca-MNC** | 288 | 9.1324 | 0.1072 | 0.8850 |
| | 298 | 11.0864 | 0.0565 | 0.4922 |
| | 308 | 12.0334 | 0.0362 | 0.3524 |
| | 318 | 7.2992 | 0.0193 | 0.2767 |
| | 328 | 1.3599 | 0.0267 | 0.7112 |

The values of ($R^2$) lies between 0.2813 to 0.7358 and 0.2767 to 0.8850 for Ca-MC and Ca-MNC respectively, The marked increasing in the values of monolayer capacity $Q_m$ at different temperatures for Ca-MNC (9.1324, 11.0864, 12.0334, 7.2992, 1.3599mg/g) relative to Ca-MC (5.8309, 3.3783, 1.7736, 0.8735, 0.8862mg/g) indicated the formation Fe-nano composite clay enhanced uptake of NGB dye onto Ca-MC. Similar result was obtained by I. Belbachir and B. Makhoukhi [21].

The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter $R_S$, which is a dimensionless constant referred to as a separation factor or an equilibrium parameter. The value of $R_S$ expressed in the following equation:

$$R_S=1/(1+K_LC_o) \qquad (4)$$

Table (2) shows the values of $R_s$ for 5mg/L NGB dye at different temperatures. As shown in this table the values of separation factor $R_s$ for the adsorption of NGB dye onto both clays lies between 0 and 1 indicating that the adsorption processes are favorable.

**Table 2: Dimensionless equilibrium parameter for the adsorption of NGB dye onto Ca-MC and Ca-MNC at $C_o$ 5 mg/L.**

| **Temperature (K)** | | **288** | **298** | **308** | **318** | **328** |
|---|---|---|---|---|---|---|
| **Ca-MC** | $R_S$ | 0.9280 | 0.9182 | 0.9066 | 0.8904 | 0.9425 |
| **Ca-MNC** | $R_S$ | 0.6510 | 0.7800 | 0.8467 | 0.9124 | 0.8822 |

**Freundlich Isotherm:** Frundlish model confine to describe homogeneous system. The linearized frundlish equation written by:

$$\text{Ln } q_e = \text{Ln } K_{Fr} + (1/n) \text{ Ln } C_e \qquad (5)$$

The constant $K_{Fr}$ is an approximate in the dictator of the adsorption capacity, while 1/n represents the adsorption intensity of the adsorbate towards the adsorbent or heterogeneity, both of these parameters was obtained from intercept and slope of the plots of Ln $q_e$ versus Ln $C_e$, Figures (10a&b) on the basis of the linear of Freundlich equation (5). The parameters (n and $K_{Fr}$) values are listed in Table (3).

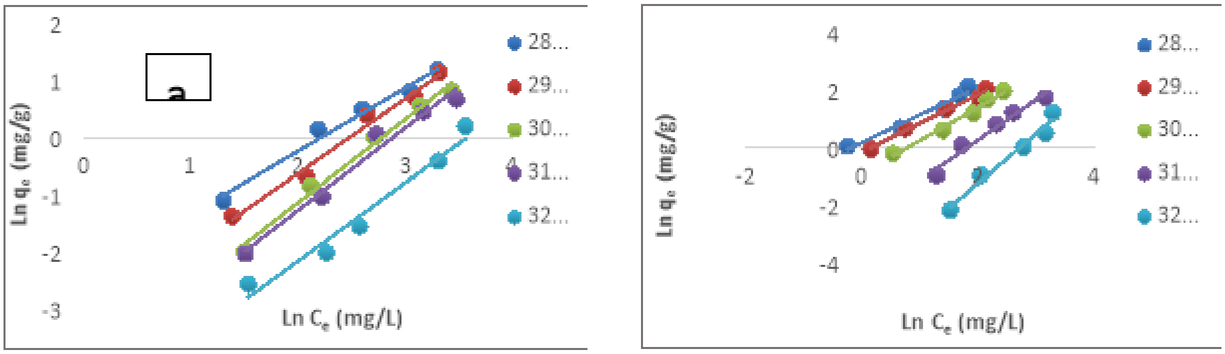

**Figure 10: Freundlich isotherm plot of NGB dye onto a-Ca-MC b-Ca-MNC at different temperatures.**

**Table 3: The values of Freundlich isotherm constants at different temperatures for the adsorption of NGB dye onto both clays.**

| | **Temperature(K)** | **Slope (1/n)** | **n** | **Intercept $\text{Ln}K_{Fr}$** | **$K_{Fr}$ (mg/g)** | **$R^2$** |
|---|---|---|---|---|---|---|
| **Ca-MC** | **288** | 1.1019 | 0.9075 | -2.4330 | 0.0877 | 0.9822 |
| | **298** | 1.3059 | 0.7657 | -3.2300 | 0.0395 | 0.9832 |
| | **308** | 1.4553 | 0.6871 | -4.0380 | 0.0176 | 0.9884 |
| | **318** | 1.4373 | 0.6957 | -4.1371 | 0.0159 | 0.9767 |
| | **328** | 1.3686 | 0.7306 | -4.8861 | 0.0075 | 0.9643 |
| **Ca-MNC** | **288** | 0.9707 | 1.0301 | 0.1873 | 1.1888 | 0.9676 |
| | **298** | 1.0056 | 0.9944 | -0.1427 | 0.8670 | 0.9868 |
| | **308** | 1.1621 | 0.8605 | -0.8997 | 0.4066 | 0.9872 |
| | **318** | 1.4107 | 0.7088 | -2.5216 | 0.0803 | 0.9677 |
| | **328** | 1.7239 | 0.5800 | -4.6466 | 0.0095 | 0.9737 |

As shown in Table (3) the values of n was<1which indicates cooperative adsorption. The highest values of $R^2$ were 0.9789 and 0.9766 for Ca-MC and Ca-MNC respectively. From the values of $R^2$ it can be observed that the experimental data fit the Frundlich model adequately, the applicability of this model to the experimental data predict monolayer coverage on heterogeneous adsorbent surface (surface with various active sites affinities) [22]. The same result was obtained by K.A.S. Al-Saade et al [23].

**Temkin Isotherm**: Temkin model describes the adsorption characteristics of heterogeneous surfaces. The model postulates a uniform distribution of binding energies over all the entire exchangeable sites on the clay surface which dependent also on the functional groups of the adsorbent surface and that the heat of adsorption of ions or molecules in the layer decreases linearly with surface coverage due to the adsorbent-adsorbate interactions. This model is written as:

$$q_e = B_T \ln A_T + B_T (\ln C_e) \qquad (6)$$

Where; $A_T$: is the equilibrium binding constant ($L.g^{-1}$), $B_T$: is the Temkin isotherm constant related to the heat of adsorption (J/mol), $b_T$: is Temkin isotherm constant, R: is the gas constant (8.314 J. $mol^{-1}$. $K^{-1}$) andT: is the absolute temperature (K). The values of $B_T$ and $A_T$ can be estimated from the slope and intercept of the linear Temkin equation (6) and Figures (11a &b). The characteristic parameters of this isotherm at various temperatures are represented in Table (4).

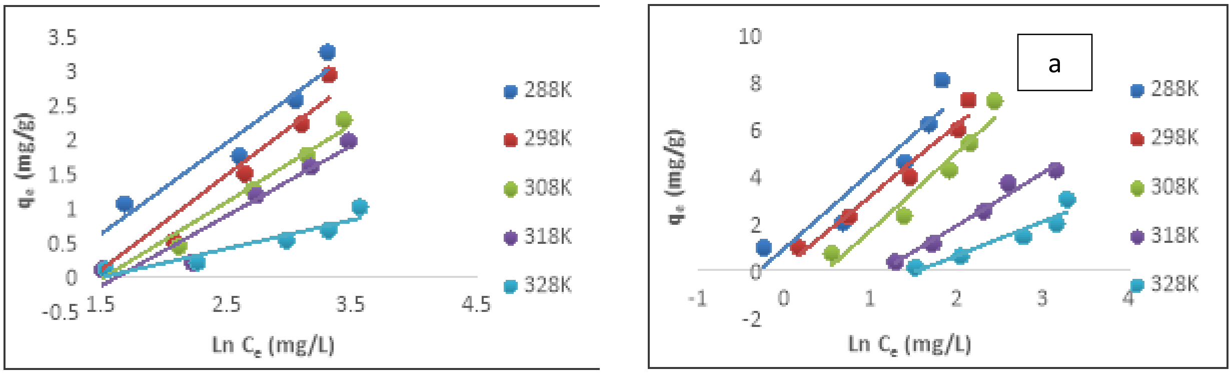

**Figure 11: Temkin isotherm of NGB dye onto a-Ca-MC b-Ca-MNC at different temperatures.**

**Table 4: Temkin isotherm constants for the adsorption of NGB dye onto Ca-MC and Ca-MNC at different temperatures.**

| | **Temperature (K)** | **$B_T$(J.mol$^{-1}$)** | **$b_T$** | **Intercept** | **$A_T$ (L/g)** | **$R^2$** |
|---|---|---|---|---|---|---|
| **Ca-MC** | **288** | 1.3175 | 1818.0956 | -1.3559 | 0.3573 | 0.9594 |
| | **298** | 1.3762 | 1800.2993 | -1.9672 | 0.2394 | 0.9213 |
| | **308** | 1.1181 | 2290.2352 | -1.7138 | 0.2161 | 0.9655 |
| | **318** | 1.0193 | 2593.7918 | -1.6673 | 0.1948 | 0.9179 |
| | **328** | 0.4171 | 6537.9813 | -0.6419 | 0.2146 | 0.8921 |
| **Ca-MNC** | **288** | 3.1980 | 748.7279 | 0.9571 | 1.3458 | 0.8767 |
| | **298** | 3.0063 | 824.1266 | 0.1671 | 1.0571 | 0.9635 |
| | **308** | 3.3039 | 775.0573 | -1.5943 | 0.6175 | 0.9403 |
| | **318** | 2.2203 | 1190.7634 | -2.5219 | 0.3214 | 0.9720 |
| | **328** | 1.4444 | 1887.9756 | -2.2488 | 0.2109 | 0.8989 |

As shown in Table (4) the values of $A_T$ is decreased with increasing temperature for Ca-MC and Ca-MNC, which reveals that the adsorption process is an exothermic process. Low values of $B_T$ indicates a weak interaction between adsorbent and adsorbate, consistent with physical interface between the two surfaces. The Table (4) reports $B_T$ values less than 8kJ/mol suggesting a weak interaction between NGB ions and the clay surface thus indicating that the adsorption process is likely a physi-sorption. The highest values of $R^2$ were 0.9594 and 0.9720 for Ca-MC and Ca-MNC respectively. Which indicate a good fitting for adsorption of NGB dye on the two clays with Temkin isotherm model. The plot with relatively a high values of $R^2$ predict a uniform distribution of binding energies during the adsorption of NGB dye onto clay surfaces [24].

**Dubinin - Radushkevich (D-R) isotherm:** This isotherm generally related the porous structure of the adsorbent and the mean free energy of the adsorption process per mole sorbate as it transferred to the surface of the solid from an infinite distance in the bulk of solution. Also this isotherm applied to express the mechanism of adsorption with a Gaussian energy distribution onto heterogeneous surface. The linear form of D-R isotherm equation:

$$\ln q_e = \ln K_{D\text{-}R} - B\,\varepsilon^{2} \qquad (7)$$

where $\varepsilon$: is Polanyi potential. $q_e$: is the quantity adsorbed per unit mass of adsorbent at equilibrium (mg.g$^{-1}$). $K_{D\text{-}R}$: is the theoretical adsorption saturation capacity (mg.g$^{-1}$). $C_e$: is the equilibrium concentration of adsorbate (mg/L). B: is the Dubinin-Radushkevich isotherm constant (mol$^2$.kJ$^{-2}$) related to sorption energy E (free energy change when 1 mole of ion is transferred to the surface of the solid from infinity in solution) was calculated from the constant B using equation (8):

$$E = 1/\,(2B)^{1/2} \qquad (8)$$

The magnitude of E is used in predicting the type of adsorption mechanism. If the value is less than 8 kJ mol$^{-1}$ the adsorption is physical in nature due to weak Vander Waals forces and if it is between 8 - 16 kJmol$^{-1}$ the adsorption is due to an exchange of ions [25]. Figures (12a&b) show the D-R isotherms for the adsorption of NGB dye onto Ca-MC and Ca-MNC at different temperatures and Table (3.74) shows the D-R isotherm constants for the adsorption of NGB dye onto both clays.

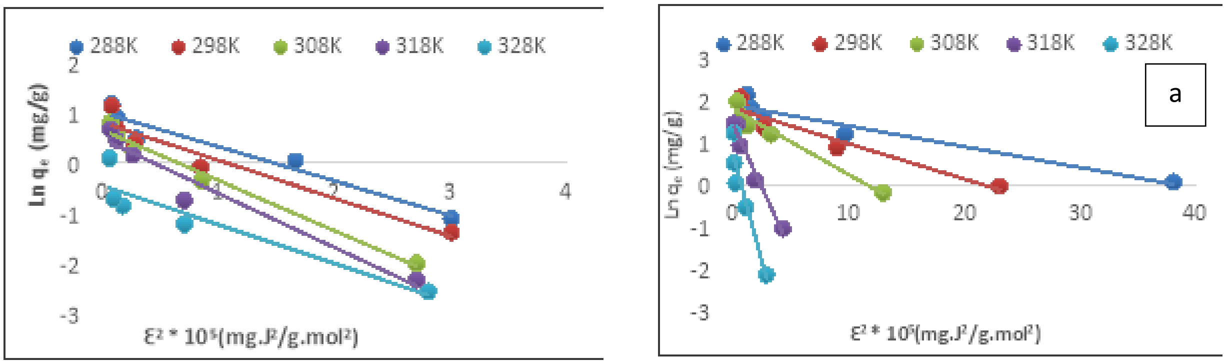

**Figure 12: D-R isotherm for the adsorption of NGB dye onto a-Ca-MC b- Ca-MNC at different temperatures.**

**Table 5: D-R isotherm constants for the adsorption of NGB dye using Ca-MC and Ca-MNC at different temperatures.**

| | **Temperature (K)** | **B mol$^2$ kJ$^{-2}$** | **E J/mol** | **$K_{D\text{-}R}$(mg/g)** | **$R^2$** |
|---|---|---|---|---|---|
| **Ca-MC** | **288** | 0.6802 | 0.8575 | 2.7286 | 0.9441 |
| | **298** | 0.7507 | 0.8169 | 2.2304 | 0.9283 |
| | **308** | 0.9981 | 0.7078 | 1.9143 | 0.9786 |
| | **318** | 1.0777 | 0.6811 | 1.6051 | 0.9500 |
| | **328** | 0.7542 | 0.8143 | 0.6030 | 0.8301 |
| **Ca-MNC** | **288** | 0.0495 | 3.1847 | 6.5738 | 0.9328 |
| | **298** | 0.0844 | 2.4390 | 6.1343 | 0.9327 |
| | **308** | 0.1556 | 1.7953 | 6.0008 | 0.9623 |
| | **318** | 0.6002 | 0.9132 | 4.2405 | 0.9723 |
| | **328** | 1.0229 | 0.6993 | 2.1089 | 0.9136 |

As listed in Table (5) the highest $R^2$ values are 0.9786 and 0.9723 for Ca-MC and Ca-MNC respectively. . Which indicate a good fitting for adsorption of NGB dye on the two clays with D-R isotherm, the adsorption energy (E) values at all temperature for both clays were less than 80kJ/mol, as the highest value was (0.8575, 3.1847 J/mol) for Ca-MC and Ca-MNC respectively. The low values of the adsorption energy predicted that the adsorption of NGB onto the both clays is physi-sorption in nature. Same results was found by M.I. Din et al [26].

From the values of the correlations coefficient, the following order to fit the isotherm: Freundlich>Temkin>Dubinin-Radushkevich>Langmuir, which indicate that Freundlich model was found to have the highest correlation values and hence the best fit, therefore this model confirms the formation of multi-layer.

**Thermodynamic Study of Adsorption:** In understanding the effect of temperature on the adsorption, it is important to study the thermodynamic parameters of adsorption, enthalpy change $\Delta H_{Ad}$, entropy change $\Delta S_{Ad}$ and Gibbs free energy change $\Delta G_{Ad}$. The distribution - coefficient $K_{DI}$ (mL.g$^{-1}$) for the adsorption process at each temperature calculated from the equation:

$$K_{DI} = \frac{C_{in} - C_e}{C_e}\,[V/m] \qquad (9)$$

Where $C_{in}$ and $C_e$ are the initial and equilibrium of the adsorbate concentration (mg L$^{-1}$), m: is the weight of adsorbent (g), V: is the volume of adsorbate solution (L).

$$\Delta G_{Ad} = -RT\ln K_{DI} \qquad (10)$$

$\Delta H_{Ad}$ and $\Delta S_{Ad}$ have been calculated according to Van't Hoff equation [27]:

$$\text{Ln } k_{DI} = \frac{\Delta S_{Ad}}{R} - \frac{\Delta H_{Ad}}{RT} \qquad (12)$$

The plot of ln $K_{DI}$ against 1/T (in Kelvin) should be linear as show in Figures (13a&b). The values of $\Delta H_{Ad}$ and $\Delta S_{Ad}$ are estimated from the slope and intercept of the Van't Hoff equation. The obtained results are given in Table (3.15).

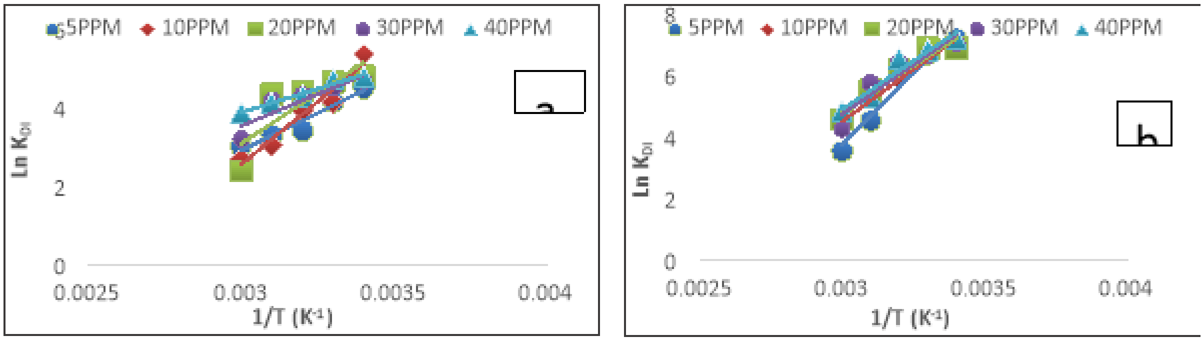

**Figure 13: Van't Hoff plots for the adsorption of NGB dye onto a-Ca-MC b-Ca-MNC.**

**Table 6: Thermodynamic parameters for the adsorption of NGB dye onto Ca-MC and Ca-MNC.**

| $C_o$ (mg/I) NGB | | $-\Delta H_{Ad}$ (kJ/mol) | $-\Delta S_{Ad}$ (kJ/K.mol) | $-\Delta G_{Ad}$(kJ/mol) | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | **288K** | **298K** | **308K** | **318K** | **328K** |
| **Ca-MC** | **5** | 31.7594 | 0.0710 | 10.7840 | 10.2909 | 8.7686 | 8.7330 | 8.2360 |
| | **10** | 53.4265 | 0.1389 | 12.8735 | 10.3756 | 10.1124 | 8.0723 | 6.2786 |
| | **20** | 42.8287 | 0.1027 | 11.5024 | 11.5477 | 11.3254 | 11.4677 | 4.8857 |
| | **30** | 26.9489 | 0.0514 | 11.2010 | 11.1769 | 11.0888 | 11.1095 | 8.7620 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **40** | 20.1356 | 0.02813 | 11.4617 | 11.7226 | 11.0138 | 10.9323 | 9.7500 |
| **Ca-MNC** | **5** | 78.3029 | 0.2037 | 17.2016 | 16.6090 | 15.7946 | 12.0348 | 8.8700 |
| | **10** | 53.5280 | 0.1210 | 16.6078 | 16.8733 | 15.1936 | 14.0168 | 11.8284 |
| | **20** | 56.5401 | 0.1315 | 16.5226 | 17.0452 | 15.8945 | 14.5974 | 11.4022 |
| | **30** | 52.8454 | 0.1182 | 16.9025 | 16.4420 | 16.5083 | 15.2351 | 11.6680 |
| | **40** | 52.0140 | 0.1152 | 17.2949 | 16.9701 | 16.5254 | 13.7612 | 13.2778 |

The results obtained in Table (6) indicates that the values of the change in Gibbs free energy (ΔG) were negative at all tested temperatures (288-328) K, verifying that the adsorption of NGB dye onto Ca-MC and Ca-MNC was spontaneous and thermodynamically favorable at low temperature (not requiring external energy from outside of the system) [28]. As temperature increased from 288 to 328 K, ΔG increases (decreasingly negative), this may be because of the presence of electrostatic attraction between the clay and the dye, with increased temperature the electrostatic attraction weakened. The negative ΔH values indicate that the adsorption of NGB dye onto Ca-MC and Ca-MNC was an exothermic process [29]. Furthermore, the negative values of ΔS indicate that the degrees of freedom decreased at the solid – liquid interface during the adsorption of NGB dye onto Ca-MC and Ca-MNC. Therefore adsorption leads to a reduction in the disorder of the adsorption system [30].

## Conclusion

The ability of Iraqi Ca-montmorillonite clay and Fe-Ca-montmorillonite nano composite have been investigated to removal anionic dye NGB dye by using batch method for adsorption. The removal efficiency of this dye is varied with adsorption time, adsorbent amount, starting dye concentrations and temperatures. The contact time was optimized at 60 min for adsorption of NGB dye onto Ca-MC and Ca-MNC, the best removal efficiency was found for 20mg/L of NGB dye. The best adsorbent dosage was 0.1g of Ca-MC and Ca-MNC, the optimum pH for favorable adsorption was 3.5 and the adsorption favorited at low temperature. For identification of shape and curvature of adsorption isotherms S type noticed for the adsorption of NGB dye onto both clays that explained a high affinity between the solid and solvent. Among different adsorption isotherm models used the adsorption of NGB dye onto both clays best fit with Frundlich isotherm. The values of the mean free energy E calculated from Dubinin-Radushkevich show that the adsorption of NGB dye onto both clays was physi-sorption. The marked increasing in the values of monolayer capacity $Q_m$ at different temperatures for the adsorption of NGB dye onto both clays indicated that the formation of Fe-nano composite clay enhanced the uptake of these dyes. The values of $\Delta G_{Ad}$, $\Delta H_{Ad}$ and $\Delta S_{Ad}$ suggest that the adsorption process is spontaneous, exothermic occurs with increasing in the disorder for NGB dye.

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