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# Adsorption of Janus Green by Flint Clay from Aqueous Solution at Different Temperatures

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**Abstract.** The study includes a demonstration of the removal of janus green dye from aqueous solutions by an available and inexpensive surface, which is flint clay. The effect of several conditions on the adsorption process was applied, including contact time, adsorption dose, size of adsorbent surface particles, initial concentration of dye, and temperature. Analyze the study data dynamically and found that it follows the pseudo-second order model. It also analyzed the equilibrium data and found it to follow the Langmuir isotherm model. The thermodynamic functions of the dye adsorption process were calculated and found to be a not easy-to-occur and irregular process of an endothermic nature of the type of physical adsorption.

**Keywords:** Flint clay, Adsorption, Janus green dye.

## 1 Introduction

The process of discharging residues of dyes from various industries into water bodies is a serious and big problem due to the difficulty of dealing with the complexity of installing these dyes in industrial wastewater.This leads to significant impacts on living organisms and the environment due to being toxic. In addition, the pigments can form a large stain that blocks light from life in water bodies, causing their degradation [To solve this environmental problem, include coagulation , ,electrochemical , chemical oxidation , aerobic and anaerobic microbial degradation and membrane separation process However, the efficiency of these methods did not reach high levels due to their limitations and defects [2]

Adsorption technology is considered an effective dye removal technique in which dye molecules are attached to the surface of the adsorbent materials. Therefore, there is interest in using the inexpensive and available dye removal materials to adsorb the dyes [3].

Where these cheap materials are found and available in nature or may come from industrial and agricultural waste, it may be usable as adsorbent materials that can be disposed of after using them in adsorption because they are cheap.A wide variety of materials such Activated carbon [4] ,Zeolite [5] ,algea [6] and clay [7].

Clay materials consist of an inorganic layered structure suitable to contain organic site particles due to their ability to cation exchange and high area/weight ratio , Part of the structural $Si^{4+}$ , $Al^{3+}$or $Mg^{2+}$ A symmetrical substitution of positive ions with less valence can occur, giving the slurry plates a negative charge that is neutralized by inorganic ions present between these plates ($Na^+$, $K^+$,$Ca^{2+}$) which are absorbed at the external surface of the clays .These moist cations are interchangeable and induce parallel clumping of the clay layers, resulting in a clay structure with an interlayer distance of about 1-2 nm , This distance provides enough space to exchange with a large group of organic and organic ions according to a simple ion exchange mechanism [8].

In one study it involved adsorption of direct blue dye (DB71) onto flint clay from its aqueous

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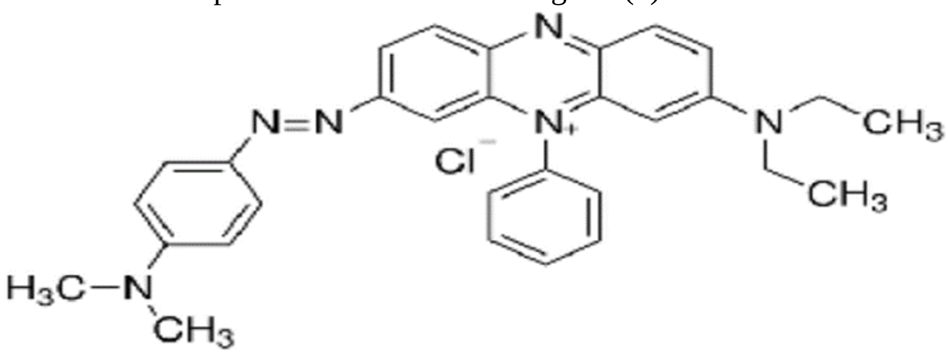
solution. Factors affecting the batch system adsorption process were also studied, including contact time, pH, adsorbent dose, and temperature. The study data follow the Langmuar and Freundlicisothermate models according to the value of the correlation coefficient. A thermodynamic study was also conducted, and it was found that the automatic adsorption process and endother nature mic of dyes on flint clay [9].

In another study, cheap adsorbents were used, including two types of clays, atapulgite (AT) and clays (FLN) to adsorb the (R (6G)) dye from an aqueous solution, and several factors were tested, including the effect of the pH where the amount of adsorption increases with increasing the pH values of all Clay species, the effect of contact time was studied and the best time was at (30 minutes) for (AT) and (40 minutes) for (FLN), and the results showed that the percentage of removal at equilibrium for (R (6G)) using clay ( AT =88% and FLN = 85%). Equilibrium data composed are compatible with the S-shape according to Gilles' classification, and also follow the Freundlich isotherm model [10].This study aimed to evaluate the absorbability potential of flint clay as an absorbent for removing Janus Green B (JG) dyes.

## 2 Materials and Methods:

The adsorbate

Janus green The cationic dye, was used without further purification , Janus Green (JG) dye is[ 3-diethylamino -7-(4- dimethylaminophenylazo)-5-phenyl-phenazinium chloride,3-(diethylamino)-7-((p- (dimethylamino)phenyl)azo)-5-phenylphenazinium chloride] . The dye used in this study has a chemical composition as shown in the figure (1).



A solution of concentration (100 mg / L) of JG dye was prepared by dissolving a certain amount in double distilled water. This solution was further diluted to the desired concentrations to obtain the test solutions. The absorbance of solutions was measured at the wave length 611nm with Shimadzu UV -Vis. Spectrophotometer- 1800.

The clay

The adsorbent used in this study was Flint clay and obtained from the General Company for Geological Survey and Mining. The particle size between(75-150-212) micrometer . This Flint clay was used in all experiments and analysis.

Table 1. The specification of flint clay .

| Constituents | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | CaO | MgO | L.O.I |
|---|---|---|---|---|---|---|---|

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| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Wt % | 38-45 | 35-41.5 | 1.4-3 | 0.5-1.96 | 0.2 | 0.1 | 13.4-15.1 |

Adsorption Experimental

The quantity of (JG) dye adsorbed on the surface flint clay, $q_e$ (mg/g), was determination

$q_{e=}V_{sol}(\frac{C_0 - C_e}{m})$ …………... (1)

Where, $C_o$ = initial concentration(mg /L) , $C_e$ = equilibrium concentration (mg /L) for (JG ) dye , m is the clay mass in grams (g) and V is the solution volume in liters (L)

The percentage of JG dye adsorption was calculated by equation (2) :-

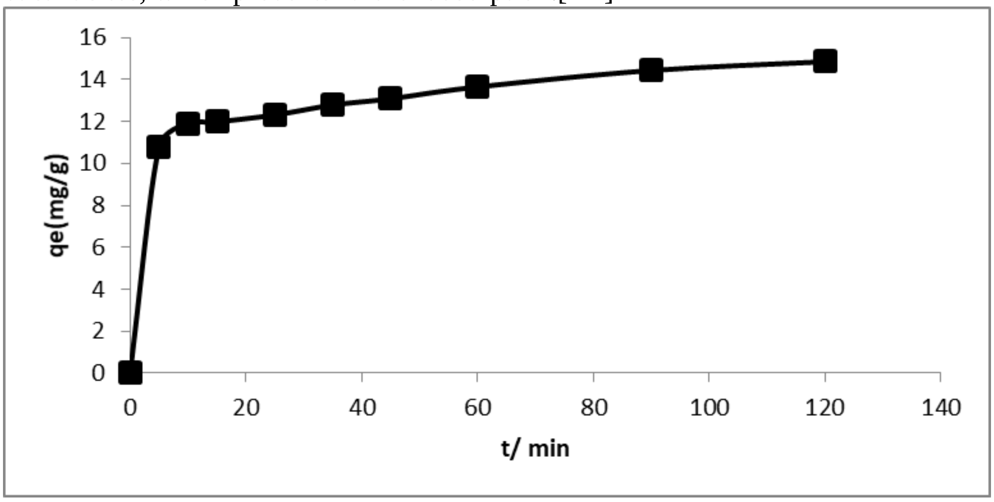
$A\% = \frac{C_0 - C_t}{C_0} * 100$ ………. (2)

Where A% Percentage removal of the adsorbate [ 6 ]

## 3 Results and Discussion

Effect of Time on Adsorption

The time required for the adsorption of a JG dye on the flint clay to reach its equilibrium state is ( 90 min ) as shown in Figure (2). This is due to the saturation of most of the active adsorption sites and the absence of vacant sites, which prevents further adsorption.[11 ]




Effect of Clay Weight on Adsorption

The effect of flint clay weight was studied using different weights between (0.005 , 0.007 , 0.01 , 0.013 , 0.015) g of clays , the maximum amount of adsorption using both types of clays was found (0.015 ) g as shown in figure ( 3 ) , As the higher the dose of adsorbent surface, the amount of adsorbed dye increases in order to provide more active sites vacant for adsorption, and this corresponds to other studies. [12]

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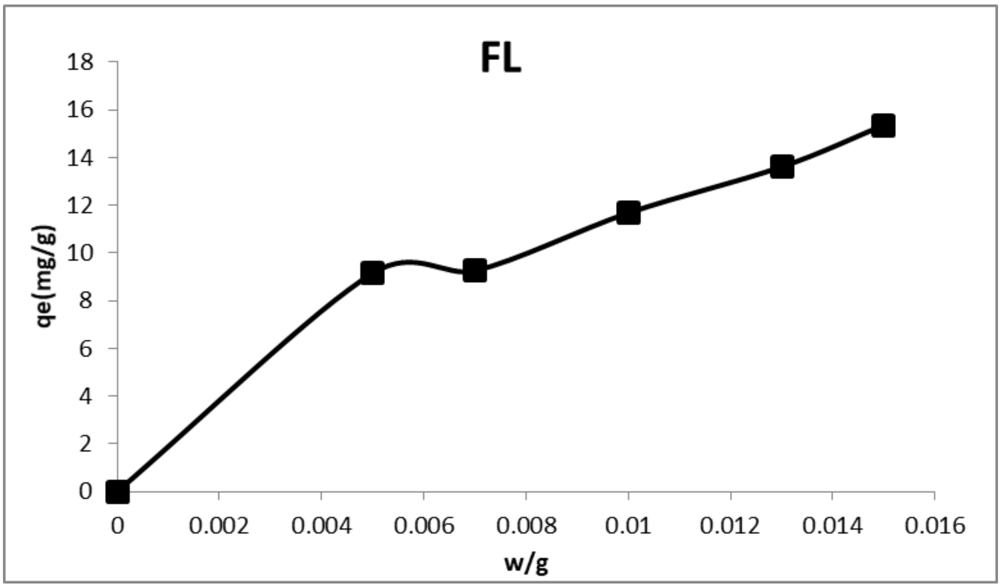
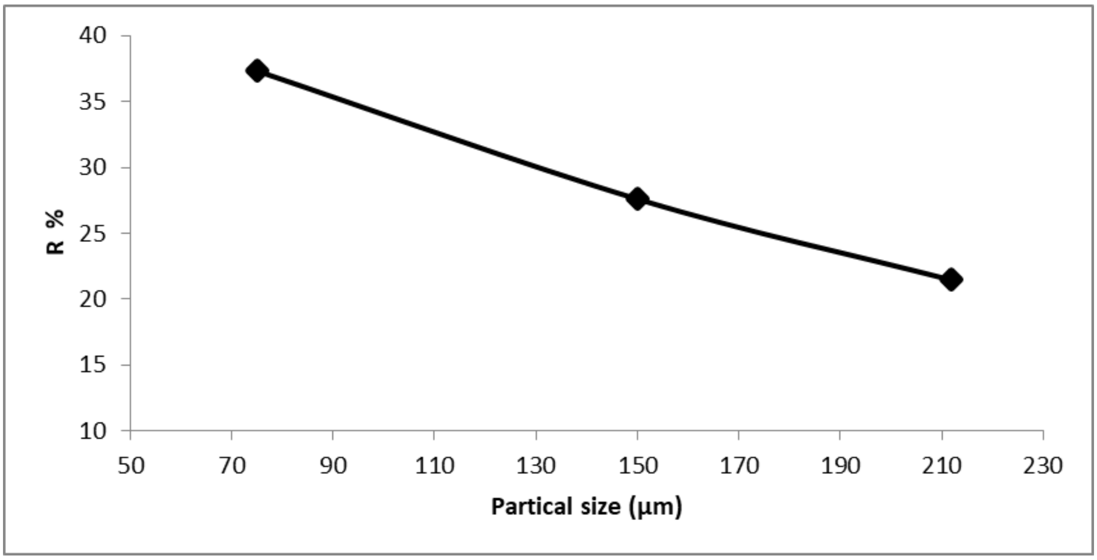



Figure (3) Effect of clay weight on adsorption

Effect of Clay particalsize on dye Adsorption

The effect of flint clay partical size was studied using different partical size between (75-150-212) µm of clays , the maximum percent of removel using of clay was found (75) µm as shown in figure (4) , From the results of this study, we note that the amount of adsorbed JG dye increases with the decrease in the partical size of the clay surface , because the smaller the partical size of the clay , the greater the surface area of the clay, and thus this leads to an increase in the number of active sites vacant for adsorption through association with the adsorbent JG dye molecules.[13 ]




Kinetic study

The kinetic study provides information on the mechanism of occurrence of adsorption of a JG dye on the flint clay. Among these kinetic models are the psedo first order and the psedo second order which represented by the equations (3) and (4):

Pseudo-first-order : ln(qe – qt) = lnqe – k1t ……………(3)

Pseudo-second-order : $\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{t}{q_e}$ ……………(4)

Where qt (mg.g-1) is the adsorption quantity of dye at time t, k1 (min-1) is the rate constant

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of pseudo-first order model and and k2 (g.mg-1.min) is the rate constant of pseudo-second order model. According to the convergence of practical and theoretical values of the adsorption quantities and the best-fit model was chosen according to values of the regression coefficient (R2) of the linear plots for both kinetic model equations [14-16]

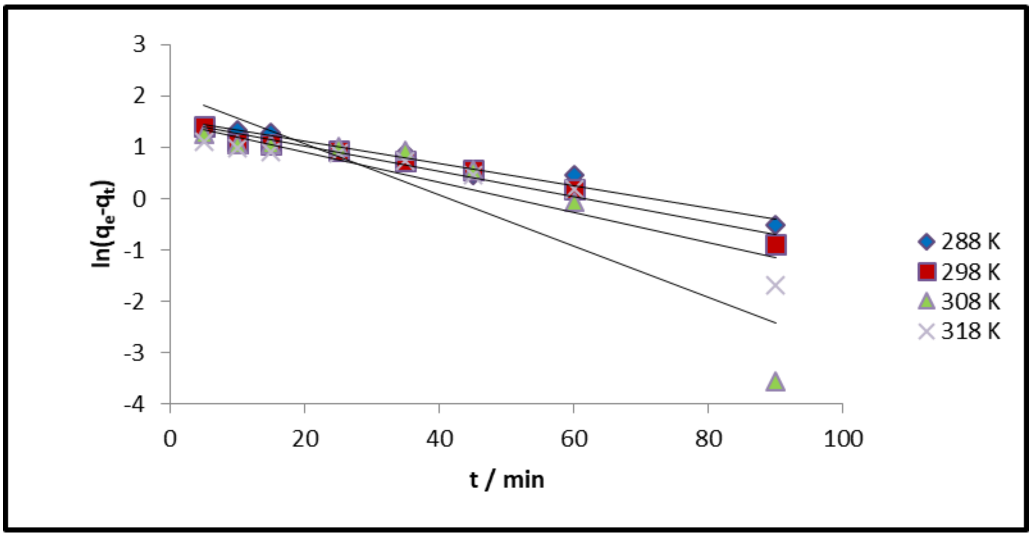


Figure (5) pseudo-first order for ( JG ) adsorption on flint cla

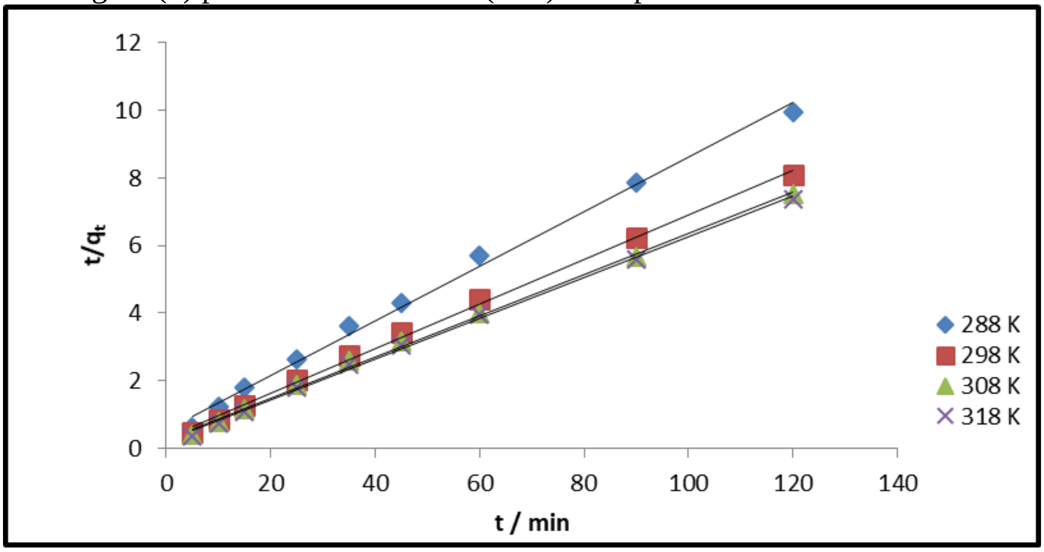


Figure (6) pseudo-second order for ( JG ) adsorption on flint clay

Table 2 . kinetic parameters for adsorption of (JG) dye onto flint clay surface based on Pseudo (first and second ) order equations

| Model kinetic | Parameter | Temperature / K | | | |
|---|---|---|---|---|---|
| | | 288 | 298 | 308 | 318 |
| Pseudo-first order | $K_1(min^{-1})$ | 0.0217 | 0.0244 | 0.0499 | 0.0295 |
| | $q_e$(mg/g) | 4.7105 | 4.4974 | 7.8255 | 4.4673 |
| | $R^2$ | 0.9690 | 0.9641 | 0.7996 | 0.8661 |
| Pseudo-second order | $K_2$(mg/g.min) | 0.0117 | 0.0143 | 0.0135 | 0.0160 |
| | $q_e$(mg/g) | 12.3915 | 15.1515 | 16.4203 | 16.5837 |
| | $R^2$ | 0.9949 | 0.9975 | 0.9970 | 0.9977 |

Adsorption Isotherm

The study of adsorption isotherms provides information to describe the interaction of

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adsorbent materials with adsorption surfaces. This is necessary to give an evaluation of the efficiency of the adsorption process.
Freundlich Isotherm Model [17]

The Freundlich isotherm was determined according to the following equation (linear form ):-
$ln\ q_e = ln\ lnk_f + \frac{1}{n} ln\ lnC_e$ ..............(5)

Where kf equal the adsorption capacity and (1/n) equal the adsorption intensity .Kf and 1/n Values can be determined from the linear plot of ln (qe) vs. ln(Ce) figure ( 7 ).

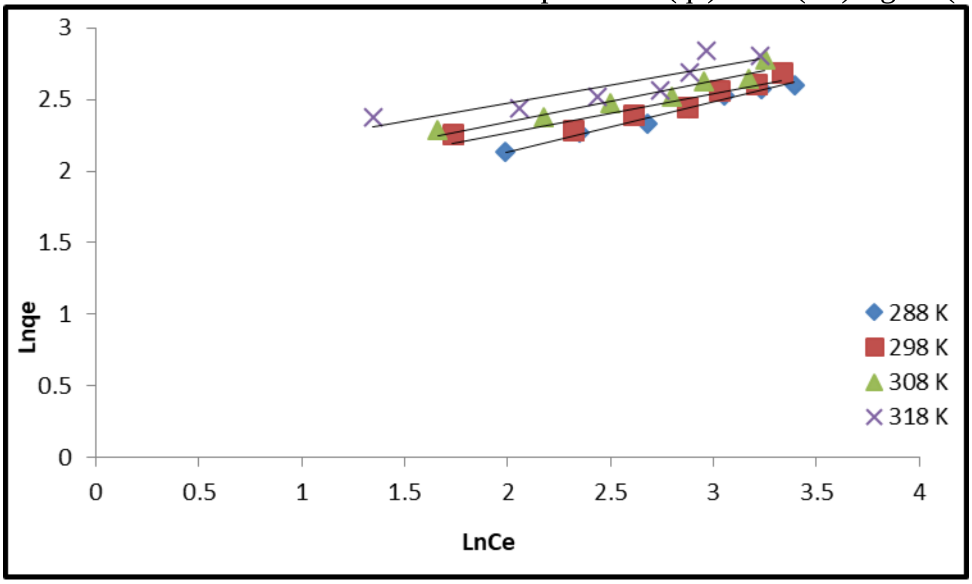


Figure (7) Freundlich isotherms for (JG) adsorption on flint clay

Langmuir Isotherm Model [18]

The Langmuir isotherm can be determined according to the following equation (linear form ) :-
$\frac{C_e}{q_e} = \frac{1}{q_{max}\ K_L} + \frac{C_e}{q_{max}}$ ...............(6)
where $q_m$ equal the adsorption efficiency and$k_L$ equal the energy of adsorption.

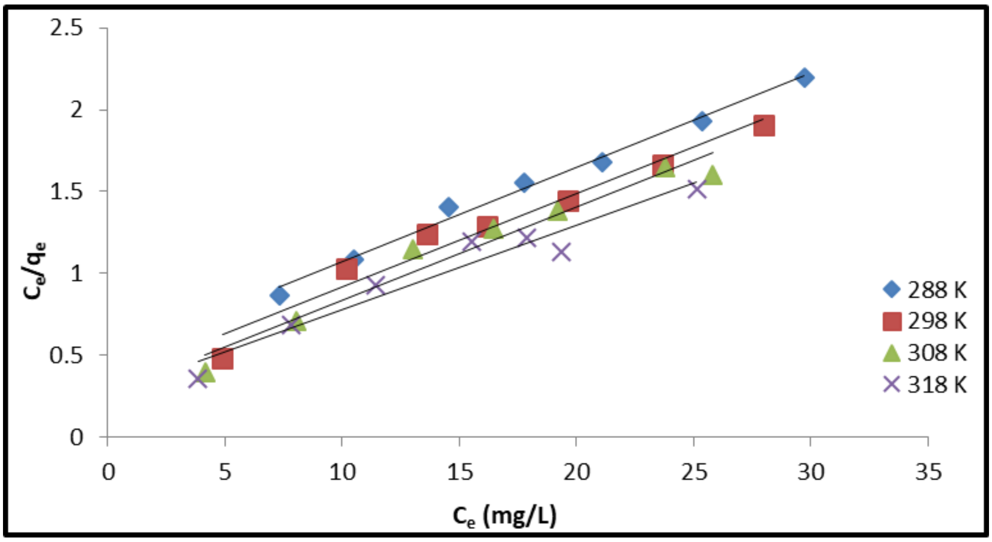


Figure (8) Langmuir isotherms for (JG) adsorption on flint clay

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Table 3. Freundlich , Langmuir isotherm constants for adsorption of ( JG ) dye onto Flint clay.

| Model isotherm | Parameter | Temperature / K | | | |
|---|---|---|---|---|---|
| | | 288 | 298 | 308 | 318 |
| Freundlich isotherm | $K_F$ (L. $g^{-1}$) | 4.2206 | 5.5672 | 5.9180 | 7.1915 |
| | n | 2.8752 | 3.6509 | 3.5112 | 3.9952 |
| | $R^2$ | 0.9846 | 0.8944 | 0.9289 | 0.8066 |
| Langmuir isotherm | $K_L$(L.$mg^{-1}$) | 0.1174 | 0.0595 | 0.1631 | 0.1960 |
| | $q_m$(mg/g) | 17.3310 | 17.4216 | 18.4501 | 19.4552 |
| | $R^2$ | 0.9914 | 0.9641 | 0.9628 | 0.9402 |

Table 3 ,show the Freundlich isotherm does less suitable to the JG dye adsorption experiments, according to the values of the R2 correlation coefficient, which was ≥ 0.8066, The data from adsorption studies are best described by The Langmuir isotherm ( R2 ≥ 0.9402 ). Therefore, the adsorption of JG dye by flint clay in more suitable with the Langmuir isotherm model which mean the JG dye adsorption occurs in a Homogeneous system with active site occupations and visible forces of interaction between absorbed particles. [19,20]

Thermodynamic study[21]

by Vant Hoff -Arrhenius' equation:

$\ln k_{eq} = \frac{-\Delta H}{RT}$ + Constant ……………(7)

Where ΔH = change of Enthalpy and ΔS = change of entropy ,which could be calculated using (Figures 7 and 8). Where: keq =equilibirium constant of adsorption . Gibbs free energy change is also calculated using the following equation at 310.5 K:

$\Delta G = \Delta H - T\Delta S$ ……………(8)

The reaction rate of the adsorption process can be calculated as follows:

$\Delta G = -RT \ln K$ ……………(9)

Table 4. Thermodynamic study and parameters of JG dye adsorption on clay

| **T / K** | $k_{eq}$ | **ΔG ( kJ.mol$^{-1}$)** | **ΔH ( kJ.mol$^{-1}$)** | **ΔS ( J.mol$^{-1}$.K$^{-1}$)** |
|---|---|---|---|---|
| 288 | 0.6819 | 0.9165 | 9.8479 | 31.0 |
| 298 | 0.7880 | 0.5901 | | 31.1 |
| 308 | 0.9370 | 0.1666 | | 31.4 |
| 318 | 0.9883 | 0.0309 | | 30.8 |

Table ( 4 ) show the data of physical constants which conclude that the JG dye adsorption process occurred not easily for the positive values of ΔG which and decreased with increase in temperature , meanwhile values of ΔH are positive , less than 40kJ/mol indicate that the adsorption is involves physical adsorption phenomena and suggest that the adsorption process is endothermic while the positive values of ΔS shows the increasing random movement of the JG dye on the flint adsorbent surface, which supports the scenario of physical adsorption process.[22]

## 4 Conclusions

Flint clay showed normal efficient at JG dye removal, with maximum adsorption capacity of 15 mg/g . Considering these results, was effective at improving clay adsorption capacity, proving the advantage of its application.psedo second order model and Langmuir model presented the best adjustments, showing the tendency for a monolayer and uniform adsorption. Thermodynamic analysis indicated that the adsorption of the dye onto Flint clay was endothermic , physical adsorption , more random and nonspontaneous.

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