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ADSORPTION POTENTIAL FOR A MIXTURE OF CHEMICALLY AND THERMALLY TREATED CLAYS TO REMOVE ORANGE G DYE FROM WASTE-WATER

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ABSTRACT

This study examined the adsorption behavior of anionic dye (orange G) from aqueous solution onto the raw and activated a mixture of illite, kaolinite and chlorite clays from area of Zorbatiya (east of Iraq).The chemical treatment involved alkali and acid activation. The alkali activation obtained by treated the raw clay (RC) with 5M NaOH (ACSO) and the acid activation founded by treated it with 0.25M HCl (ACH) and 0.25M H_2SO_4 (ACS). The thermal treatment carried out by calcination the produce activated clay at 750°C for acid activation and 105°C for alkali activation. Batch adsorption method was used to study the adsorption of orange G dye onto raw and activated clays. The impact of different factors related to the adsorption process was studied such as: agitation time, clay dosage, solution pH, starting OG dye concentration, temperature and ionic strength. The adsorption process was described by using Langmuir, Freundlich, Temkin and Dubinin-Raduchkevish isotherm models. Thermodynamic functions like change in enthalpyΔH°, change in entropy ΔS° and change in Gibbs free energy ΔG°were estimated based on Van't Hoff equation.

Keywords: Adsorption of OG dye, raw clay, alkali and acid activated clays.

جهد ألإمتزاز لمزيج من ألاطيان ألمنشطة كيميائيا وحراريا لإزالة صبغة ألمثيل ألبرتقالي من مياة ألصرف الصحي

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الخلاصة

تمت دراسة سلوك إمتزاز الصبغة الانيونية (المثيل البرتقالي) من المحلول المائي على الطين العادي ومزيج من أطيان ألايليتو الكاؤليتو الكلورايت المفعلة من منطقة زرباطية (شرق العراق)، وتضمنت المعاملة الكيميائية بالقاعدة والحامض، اذ تم التنشيط بالقاعدة بمعاملة الطين العادي بمحلول 5 مولار من هيدروكسيد الصوديوم والتنشيط بالحامض تم باستخدام 0.25 مولار بحامض الهيدروكلوريك و0.25 مولار حامض الكبريتيك، بينما تمت المعاملة الحرارية بكلسنة الاطيان المنشطة بالحامض بدرجة حرارة 750م، في حين كانت 105م للطين المنشط بالقاعدة، واستخدمت طريقة الوجبة للامتزاز لدراسة امتزز صبغة المثل البرتقالي على سطح الطين الخام والاطيان المنشطة بالحامض والقاعدة، وتم دراسة تأثير مختلف العوامل على عملية الامتزاز مثل زمن الرج ووزن الطين ودرجة حامضية المحلول والتركيز الابتدائي لصبغة المثيل البرتقالي ودرجة الحرارة والقوه الايونية، وجرى وصف عملية الامتزاز باستخدام نماذج متساوي درجة حرارة الامتزاز لنكماير وفرندلش وتمكن وودوبنترادش كفيج والدوال الثرموديناميكية مثل التغير في الانثالبي ΔH° والتغير في الانتروبي ΔS° والتغير في الطاقه الحرة لكبس ΔG° والتي تم تقديرها بالاستناد الى معادلة فانت هوف.

الكلمات المفتاحية: إمتزاز صبغة المثيل البرتقالي، الطين الخام، الاطيان المفعلة بالقاعدة والحامض.

INTRODUCTION

The purity of water has damaged due to arrival of effluents such as heavy metals industrial dyes, etc. from industries such as paper, leather, textiles, plastics and food to water reservoirs, that leads to generation of disorders, hypertension, hemolytic, mutagenic, carcinogenicity etc. **(Ghaedi *et al*., 2014)**. For this reason it is needed to treat the dye-containing waste-water before its discharge to aquatic ecosystem using an economic, efficient and fast way.

The decolorizing of water that proceeds during the using different technique such as solvent extraction, chemical precipitation, reverse osmosis, nano-filtration and ozonation have many disadvantage **(Ahmad *et al*., 2014)**. These technique yielding of secondary sludge, inconvenience and have a high operational costs **(Ghaedi *et al*., 2015)**.Generally adsorption recognized as an important technique for treatment the waste-water. The cost-effective and simple adsorption method with a high adsorption capacity are of a high interest **(Hajati *et al*., 2015)**. This released to the uses of a large number of substances as adsorbents in the adsorption process. Various materials have been used for removal different pollutants, including the uses of banana stalk **(Bello & Ahmad 2012a)**, oil palm ash **(Foo & Hameed 2009a)**, spent tea leaves **(Hameed 2009a)**, de-oiled soya **(Mittal *et al*., 2005)**, activated carbon and clays **(Zakaria *et al*., 2009)**.

In recent years the use of soil clay materials to replace commercially available adsorbents has attracted much attention due to their low cost **(Adeyemo *et al*., 2017)**, ecofriendly nature, lack of toxicity and ready availability. Highlight to activated and modified the clays in order to improved its surface property and to increases the mechanical stabilities the give these materials a broad range of applications **(Chen *et al*., 2011)**. According to academic source there are three or four main groups of clays include illite kaolinite chlorite and montmorillonite-smectite **(Adeyemo *et al*., 2017)**. The aim of this paper was to study the adsorption potential for a mixture of chemically and thermally treated clays to remove orange G dye from waste-water.

MATERIALS AND METHODS

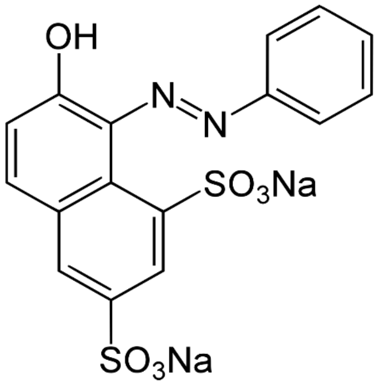
Materials

Orange G dye

Orange G is an anionic or acid dye, it is a sulfonatedazo dye, it is used in silk, wool products and dyeing, also can dye paper and manufacturing ink, used in wood and biological dyeing. This dye having the IUPAC name as (disodium; 7-hydroxyl-8-phenyl diazenyl naphthalene-1,3-disulfonic acid) **(Kumar & Mishra 2015)**. OG has organic carbon within the aromatic metallic rings which are resistant to biodegradation due to azo bonding **(Iyandic 2018)**. It has a harmful effects to animals and human beings and aquatic life **(Sarwa & Verma 2013)**. This dye used in this work was provided from Fluka, (Table 1) shows the chemical and physical properties of OG dye.

A stock solution of 1000 mg/L was prepared by dissolving 1g of OG in1liter distilled water, then this solution used for prepared working solution by diluting to obtain the desired concentrations.

Table (1): Chemical and physical properties of OG dye**.**

Specification		Chemical structure
Molecular formula	$C_{16}H_{10}N_2Na_2O_7S_2$	
Solubility	95% ethanol, water	
Color	Orange	
Maximum absorption	476nm	
Molar mass	452.37g/mol	
Nature	Anionic dye, acidic	
C.I. number	16230	

Clays

The raw clay used in the study was collected from Zorbatiya area (east of Iraq). The clay has the following composition: SiO_2 19.6%, Al_2O_3 3.8%, Fe_2O_3 4.5%, CaO 15.2%, MgO 3.4%, K_2O 1.3%, Na_2O 12.8%, TiO_2 0.6%, P_2O_5 0.1%, SiO_3 1.2%, Cl 14.8%, MnO 0.38% and L.O.I. 19.6%. The clay mineral analysis of this clay showed that this clay is a mixture of illite, kaolinite and chlorite **(Al-Dabbagh 2018)**.

The acidification of the clays was performed by using 37% hydrochloric acid and 98% sulfuric acid supplied by Fluka, also alkali activated of clay was carried out using 99% sodium hydroxide supplied by BDH.

Methods

Raw clay

30 g of the raw clay was mixed with 100 mL distilled water, the mixture was shaking for one hour at room temperature, then filtered by using Buckner funnel and oven dried at 120°**C** for 7 hr, then allowed to cool and keep in a dry place. The obtained clay labeled as RC.

Activation with NaOH, HCl and H_2SO_4

The activated clay with NaOHa volume of 70 mL from 5 M NaOH was added to five grams pretreated raw clay under 800 rpm mechanical stirring for 4 hr to yield a homogenous suspension, by using centrifugation at 5000 rpm, the product was separated, washed with distilled water several times and dried at 105°**C** for 4 hr. The result sample marked as ACSO.

To prepare acid activated clay with HCl 20 g of the raw clay was mixed with 67 mL 0.25 M HCl by using a thermo stated shaker type (Gallenkamp, England) for 2 hr. The resulting clay was filtered by using a Buckner funnel, the residue slurry washed with distilled water until it becomes neutral. The prepared sample was dried at 120°**C** for 2 hr, the activated clay was calcinate in muffle furnace type (BS32C, Korea) at 750°**C** for 4 hr. The obtained clay labeled as ACH.

The acid activated clay with H_2SO_4 carried out by mixing 20 g of raw clay with 200 mL 0.25 M H_2SO_4 in a shaking water bath for 6 hr at 70°**C**, then the sample was allowed to stand for fourteen hours in solution. Finally, the precipitate was filtered and washed for many times with distilled water till reaching a natural pH. The sample was dried at 120°**C** for 2 hr, then calcinate at 750°**C** for 4 hr. The obtained clay marked as ACS.

Batch adsorption studies

Batch experiments were carried out to study the adsorption of OG on RC, alkali and acid activated clays ACSO, ACH, ACS. A known quantity of the clay was added to 20 mL dye solution in 100 mL Erlenmeyer flask. The mixture was agitated by using a shaker with water bath type (JTYS-1000, China) at pre- determined speed, time and temperature. Centrifugation with 1000 rpm was used for 5 min to separate the supernatant, the residual OG dye concentration was determined by UV-Vis –Spectrophotometer model(Shimadzu UV 1800, Japan) at λ_{max} = 476 nm.

The removal percentage R% and the amount of the OG dye adsorbed at equilibrium Q_e in (mg/g) were calculated by using equations:

$$R\% = 100 \left[\frac{C_i - C_e}{C_i}\right] \text{-----------------} (1)$$

$$Q_e = \frac{V}{M} [C_i - C_e] \text{----------------} (2)$$

Where C_i,C_e are the starting concentration and the concentration at equilibrium (mg/L), V is the volume of the working solution (L) and M is the mass of the clay (g).

Optimum conditions

Influence of adsorption time

The influence of adsorption time on the removal efficiency carried out at various adsorption time (5-60) minute, with 100mg/L starting concentration at 288 K, PH=7, clay dosage = 0.2 g/ 50mL and agitation speed 150 rpm, as shown in (Figure 1). It is found that the adsorption reaches equilibrium after 30 min for all clay samples. According to this statistic, adsorption was found to be rapid within the first minutes of adsorbent/ adsorbate interaction. This can be explained by the fact that the amount of active sites accessible on the surface of the adsorbent material at the beginning of the adsorption is much higher than that of the sites remaining after a certain period of time.Furthermore, the ACS sample has interesting basal spacing that favors the phenomenon of adsorption **(Ayari *et al*., 2019)**. The optimum time chosen for all experiments was 36 minute. Similar fact was obtained by **(Gode & Pehlivan 2005)**.

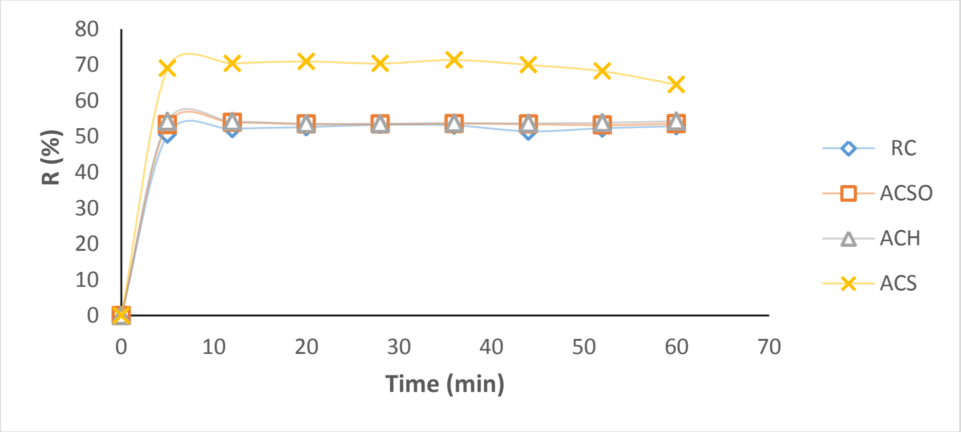


Figure (1): Influence of adsorption time on removal (100 mg/L) OG dye using RC, ACSO, ACH and ACS as adsorbents.

Influence of clay dosage

The impact of clay dosage on removal of OG dye was tested using different quantities of clay (0.025, 0.05 , 0.1, 0.15, 0.2, 0.3, and 0.5 g) in 20 mL of 100 mg/L OG dye at 288 K, pH=7 and shaking speed (150 rpm). As seen in (Figure 2), the removal efficiency increased with increasing the clay dosage for all samples till reaches a constant values at clay dosage equal to 0.2 g, then the removal kept constant. Increasing the R% may be resulted from the abundance of more available adsorption sites. Unless too much adsorbent has been applied to the dye solution, the transport of dye ions to the active adsorption sites would also be reduced, thereby reducing the efficiency of adsorption **(Seey & Kassim 2012)**.Therefore 0.2 g of clay was selected as the optimum weight for the further experiments. The same results was found by **(Rostami *et al*., 2018)**.

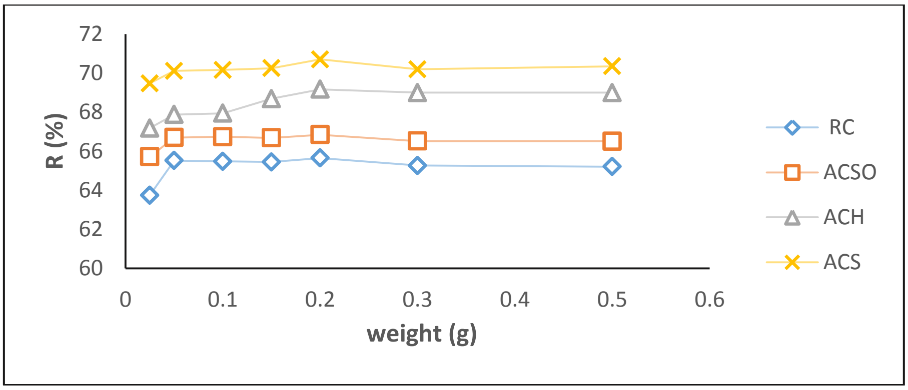


Figure (2): Influence of clay dosage on the removal efficiency of OG dye using RC, ACSO ACH and ACS as adsorbents**.**

3. Influence of Ph:

Batch experiments were performed for the adsorption of OG dye onto the clay samples by varying the pH levels from 2.17 to 11.24 a fixed adsorption time of 36 min, starting OG concentration 100 mg/L at 288 K and agitation speed 150 rpm as shown in (Figure 3), it is evident that the removal efficiency of OG increased in acidic medium pH=2.17 to 5 and reaches to 66.89 for RC and 67.2, 67.85, 69.03 for ACSO, ACH, ACS. As the pH increase there is a decrease in the R% reaches to 66.13 for RC and 66.33, 67.14, 67.93 for ACSO, ACH, ACS. The higher values of R% noticed in the acidic solution may be related to the electrostatic attractions between the negative charge of the functional groups of the OG dye and a positive charged of clay surfaces also the H^+ acts a bridging ligand between the OG and the clay surfaces. The abundance of OH^- ions in the simple solution also creates a competitive environment which causes anionic OG ions to decrease adsorption in the adsorption sites **(Shariati *et al*., 2011)**. Similar reported pH values was found by **(Ogunmodede *et al*., 2015)**.

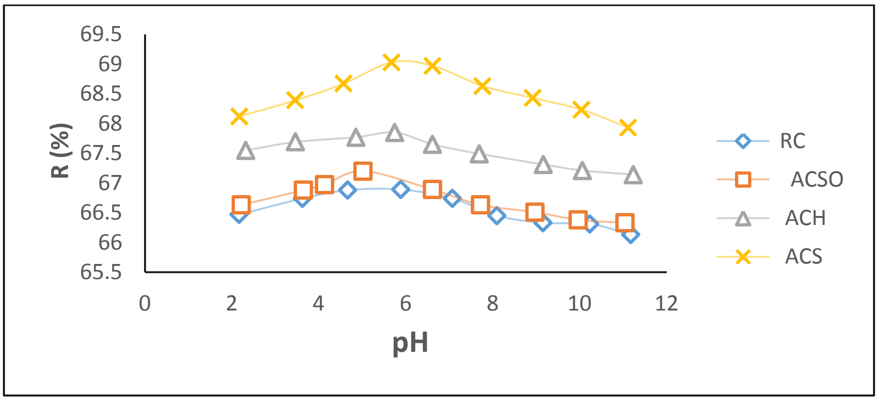


Figure (3): Influence of PH on adsorption of OG dye onto RC, ACSO, ACH and ACS as adsorbent.

Influence of initial OG dye concentration

Influence of varying starting concentration of OG dye on the adsorption process investigated with the use of various initial OG concentrations (50, 75, 100, 150 and 200 mg/L) at 288K, PH=7, clay weight (0.2 g/20 mL), shaking time 36 min and agitation speed (150 rpm). As noticed in (Figure 4) the removal efficiency increased from 9.82 for RC and 10.42, 13.24, 18.46 for ACSO, ACH, ACS to 62.23 for RC and 72.52, 78.68, 85.92 for ACSO, ACH, ACS when the starting concentration increased from 50 to 200 mg/L. It might suggest that increasing the initial concentration of the dye leads to an increase in the mass gradient between the solution and the adsorbent surface and therefore acts as a driving force to move the dye molecules from the bulk solution to the surface particles. **(Ogunmodede *et al*., 2015)**.The same results was noticed by **(Fernandes *et al*., 2020)**.

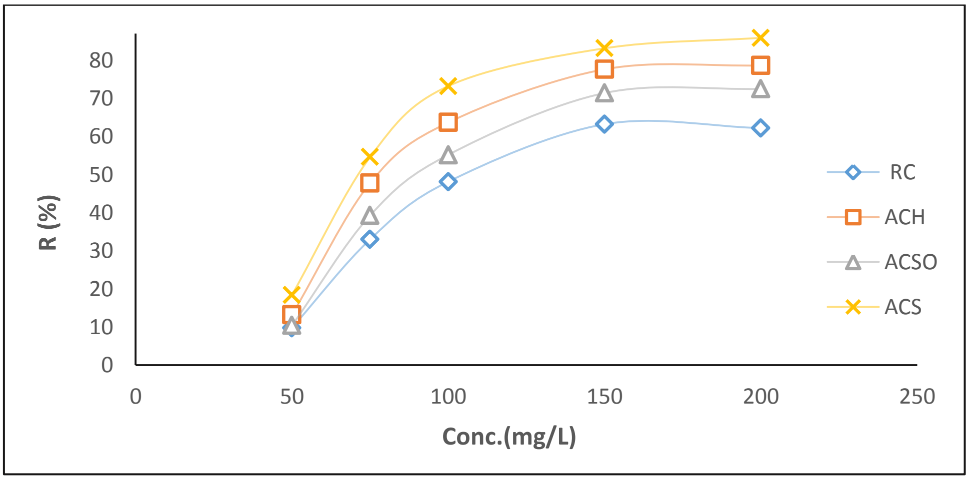


Figure (4): Removal efficiency of OG dye as a function of concentrations using RC, ACSO, ACH and ACS as adsorbents**.**

Influence of temperature

Temperature effect was tested for initial OG dye (100 mg/L) at temperature range (288-328 K), clay dosage (0.2g /20 mL), PH=7, shaking time 36 min and agitation speed (150 rpm), the findings results are seen in (Figure 5).The results showed that the R% for all samples decrease with increases thetemperature from 288 to 328 K, thus suggested that the adsorption of OG dye on the clay samples can be imparts an exothermic naturefor the adsorption process. It means that when the temperature rise the adsorption forces betweenthe dye moleculesand the active sites of the clay samples surfaces are weaken **(Bendaho *et al*., 2017)**. Similar result was found by **(Dawood 2010)**.

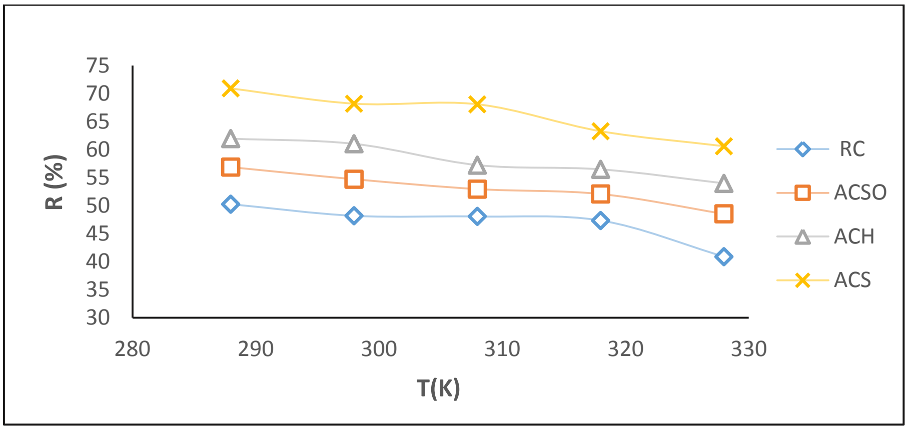


Figure (5): Influence of temperature on adsorption of OG dye onto RC, ACSO, ACH and ACS as adsorbents.

Influence of solution ionic strength

The effect of ionic activity on the adsorption of OG dye was tested by adding sodium chloride salt within the range 0.2-1.0 mg/L, OG concentration is 100 mg/L, clay dosage 0.2 g, pH=7, shaking time equal to 36 min at 288K and shaking speed (150 rpm). The presence of salts in water can contribute to high ionic strength and effective to the efficiency for adsorption process. As seen in (Figure 6), the change in salt concentration NaCl has a significant effect on the range of acidic OG dye adsorption. In aqueous solution, the escalates of ionic strength may result in the compression of the diffuse double layer on the clays. It eases the electrostatic attraction and consequently participated to the adsorption **(Aki *et al*., 2013)**. In the case of RC, NaCl prevented the adsorption of OG dye on mixed clay due to the competition between chloride ions and anionic dye **(Tamimi *et al*., 2018)**.

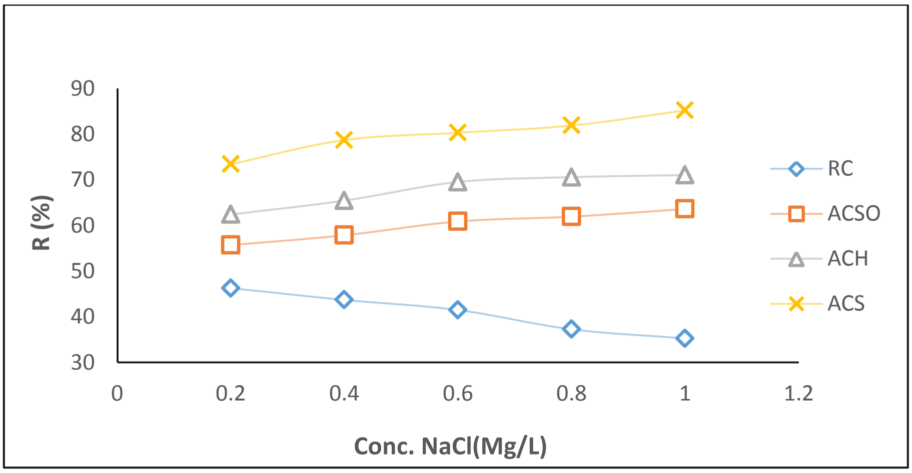


Figure (6): Influence of ionic strength on the adsorption OG dye onto RC, ACSO, ACH and ACS as adsorbents.

RESULTS AND DISCUSSION

Adsorption isotherm

The experiments of isotherm were carried out at five temperatures in the range of (288, 298, 308, 318 and 328K), clay dosage 0.2 g/20 mL, shaking time 36 min for all types of clay, pH=7, shaking speed 150 rpm and the concentration of OG dye in the range of (50, 75, 100, 150 and 200 mg/L).

Langmuir adsorption isotherm

The Langmuir isotherm model postulation the maximum adsorption agrees to a saturated monolayer of solute molecular on the adsorbent surface. Linear form of Langmuir model is **(Bouatay *et al.*, 2014)**.

$$\frac{C_e}{Q_e} = \frac{1}{Qm.k_L} + \frac{1}{Qm}.C_e \text{-------------} (3)$$

Where:C_e is the equilibrium concentration for OG dye (mg/L). And Q_e is the amount of adsorbate per gram of adsorbent at equilibrium (mg/g).

The values of Q_m (mg/g) andk_L (L/mg) are the Langmuir constants associated to adsorption capacity, and rate of adsorption were resolute from the linear plot of specific adsorption C_e/Q_e against C_e. (Figures 7, 8, 9 and 10) show the Langmuir isotherm plots for the adsorption of OG dye onto RC ACSO, ACH and ACS respectively.

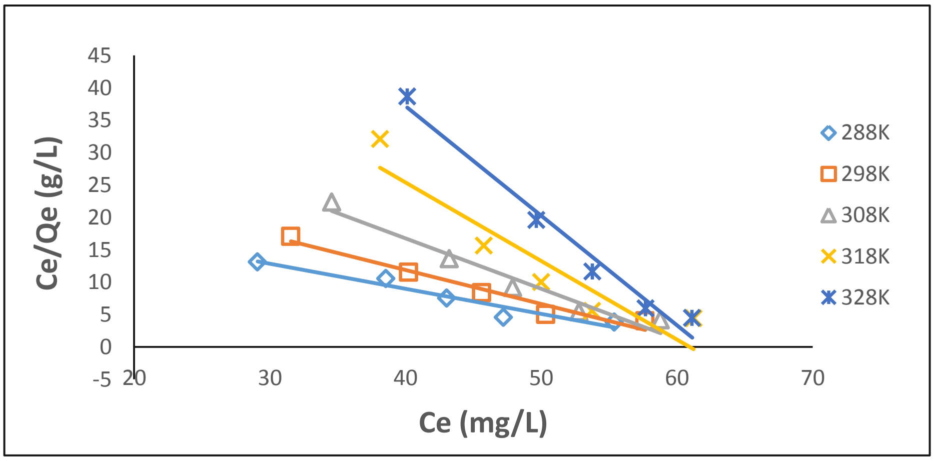


Figure (7): Langmuir isotherms for OG dye onto RC at different temperatures.

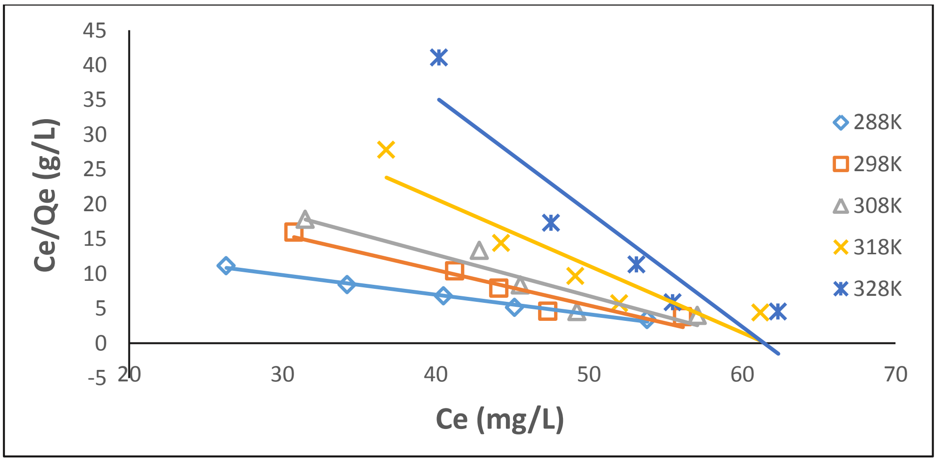


Figure (8): Langmuir isotherms for OG dye onto ACSO at different temperatures.

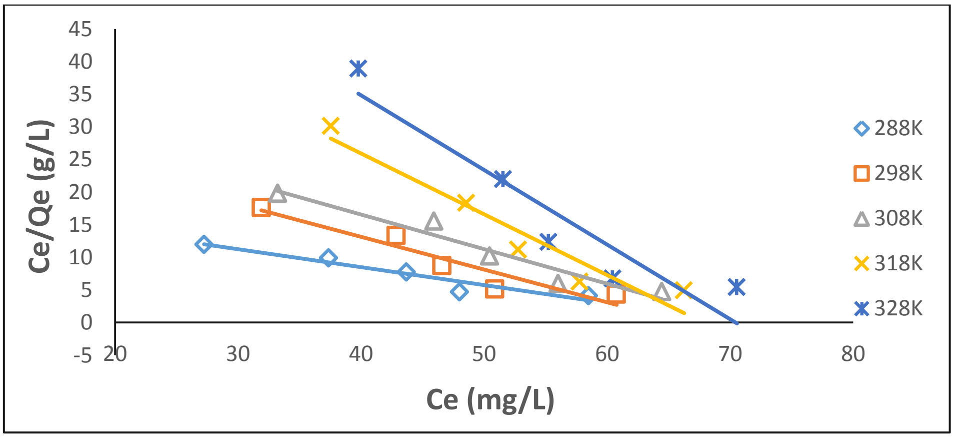


Figure (9): Langmuir isotherm for OG dye onto ACH at different temperatures.

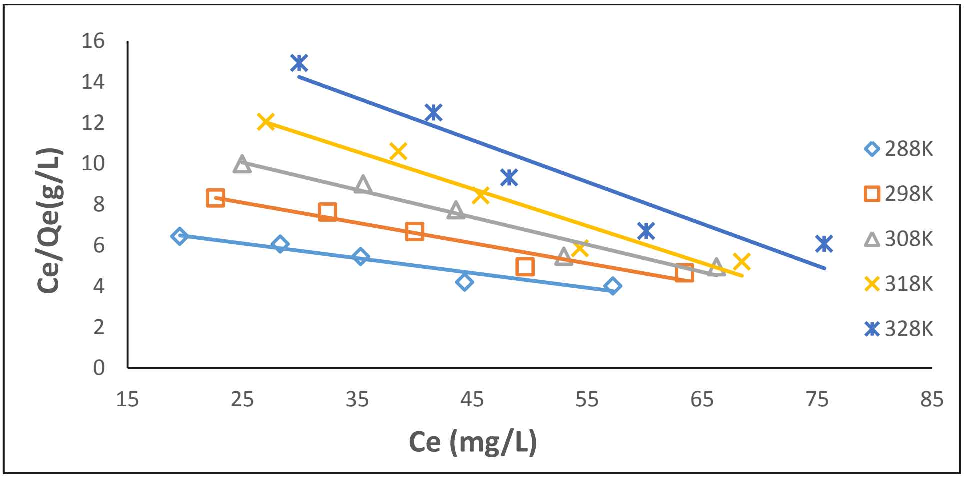


Figure (10): Langmuir isotherm for OG dye onto ACS at different temperatures.

The values of Langmuir constants Q_m and K_L and the correlation coefficients R^2 are shown in (Table 2). The values of R^2 lies between 0.8616, 0.8471, 0.8780 and 0.9026 to 0.9324, 0.9898, 0.9313 and 0.9450 for RC, ACSO, ACH and ACS respectively. At different temperatures the values of monolayer capacity Q_m arranged as ACS>ACH>ACSO>RC, this indicated that the adsorption capacity for acid and alkali activated clay is higher than raw clay. The same result was noticed by **(Sarma *et al*., 2018)**.

The separation factor R_S can be calculated from the equation:

$R_S = 1/1 + K_L C_S$ ------------ (4)

(Table 2) shows the values of separation factor R_s for the adsorption of 50 mg/L OG dye onto clay samples at different temperatures. The calculated R_s values are lies between o and 1 indicate that the adsorption process is favorable.

Freundlich adsorption isotherm

Freundlich model assumes OG dye adsorption takes place on sites with various adsorption energies or at heterogeneous clay surfaces, and can be applied to multilayer adsorption **(Gbaji*et al*., 2019)**.It usually written as **(Miyah*et al*., 2017)**:

$\ln q_e = \ln K_{Fr} + \ln(C_e)/n$------------------ (5)

Where K_{fr} and n are freundlich constants related to adsorption capacity and adsorption intensity respectively. The values of these constants were estimated from the intercept and slope of the plot between Ln q_e vs Ln C_e. (Figures 11, 12, 13 and 14), these values are illustrate in (Table 2). The values of n identify the favorability of the sorption process.

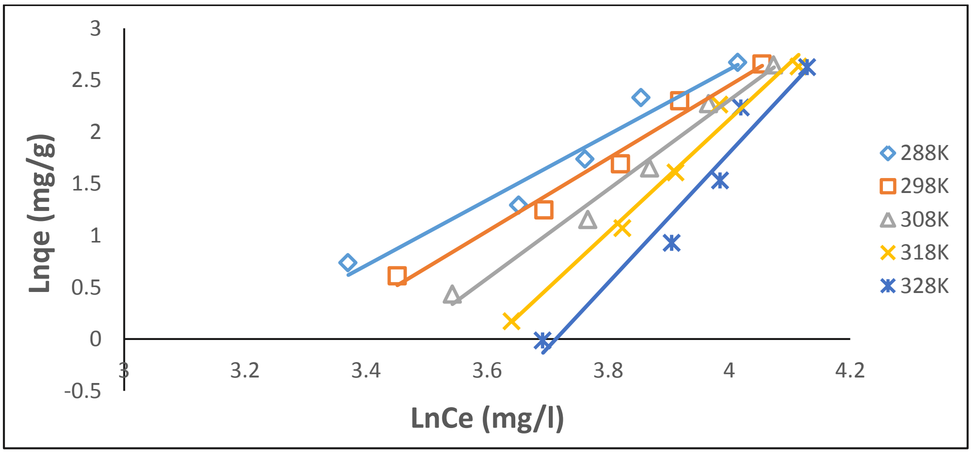


Figure (11): Freundlich isotherm plot for OG dye onto RC at different temperatures.

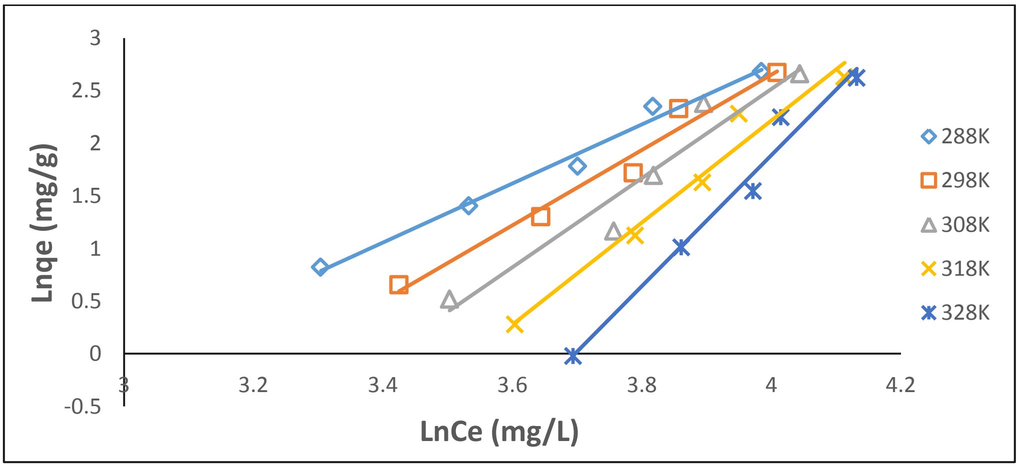


Figure (12): Freundlich isotherm plot for OG dye onto ACSO at different temperatures.

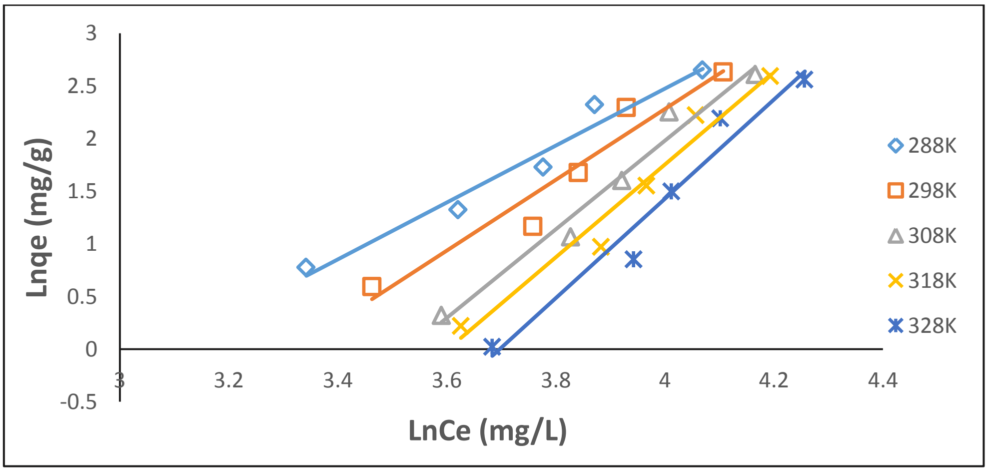


Figure (13): Freundlich isotherm plot for OG dye onto ACH at different temperatures.

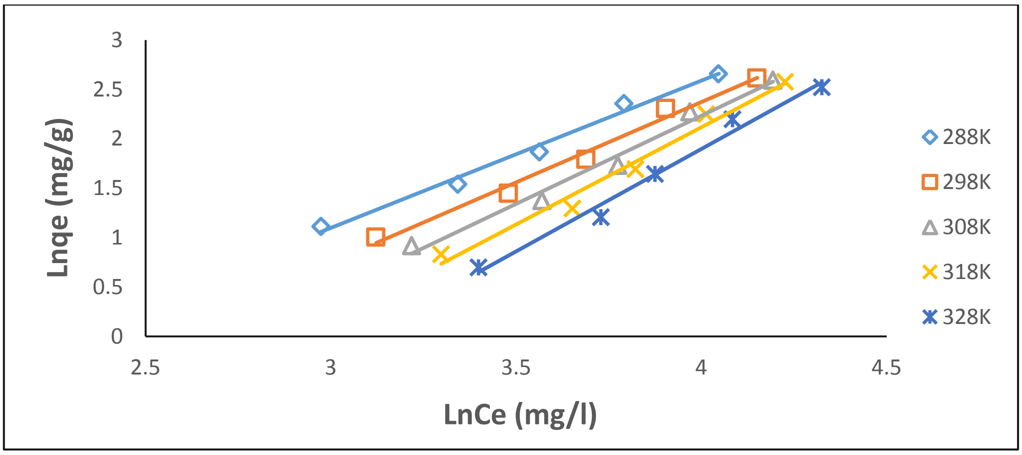


Figure (14): Freundlich isotherm plot for OG dye onto ACS at different temperatures**.**

(Table, 2) shows that the values of n<1 that indicates cooperative adsorption. The value of R^2 lies between 0.9511-0.9832, 0.9317-0.9859, 0.9368-0.9694 and 0.9768-0.9878 for RC, ACSO, ACH and ACS respectively, these values show a reasonable fit to Freundlich model plots for the adsorption of OG dye onto different clay samples, which predicted that the adsorption process carried out on a heterogeneous surface and this process is reversible **(Sejie & Nadiye-Tabbiruka 2016)**. The similar results was found by **(Nadiye-Tabbiruka *et al.*, 2018)**.

Temkin isotherm

This model based on the effect of the indirect dye- clay interactions on sorption leads to, linearly decreasing the heat of adsorption with the surface coverage. The linear equation for this isotherm was expressed as equation **(Bouatay *et al.*, 2014)**.

$qe = B_T LnA_T + B_T(LnCe)$ ----------- (6)

The values of B_T can be calculated from the equation:

$B_T = \frac{RT}{b_T}$ ---------- (7)

A_T = Equilibrium binding constant (L/g), B_T is the Temkin coefficients (J/mol) b_T is Temkin constant related to heat of adsorption, R= gas constant (8.314 J.mol^{-1}.K^{-1}), T= absolute temperature (K).

The constants A_T and b_T evaluated from the intercept and slope of the linear plot of q_e vs. LnC_e (Figures 15, 16, 17 and 18).

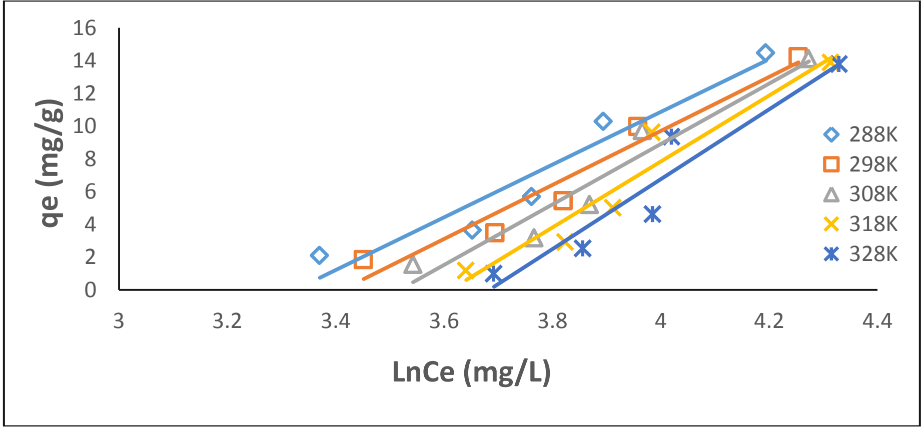


Figure (15): Temkin isotherm plot for adsorption OG dye onto RC at different temperatures.

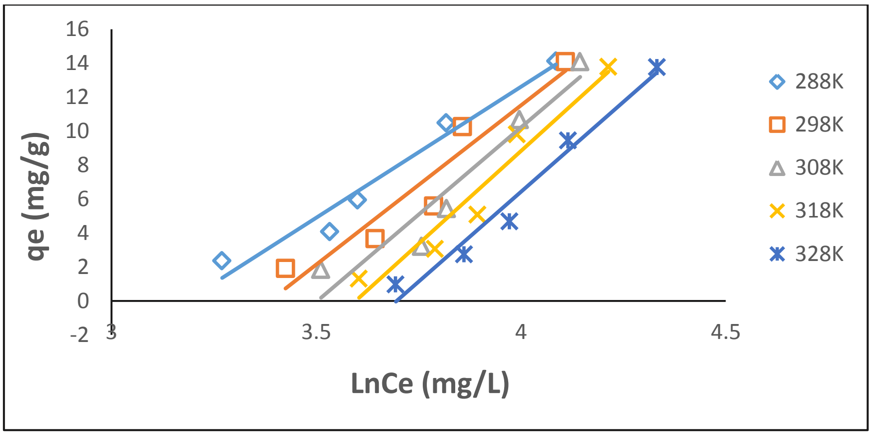


Figure (16): Temkin isotherm plot for adsorption OG dye onto ACSO at different temperatures.

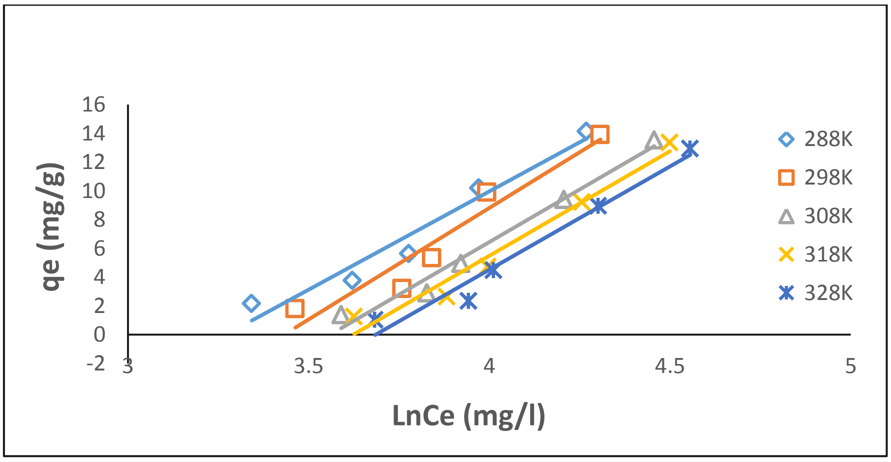


Figure (17): Temkin isotherm plot for adsorption OG dye onto ACH at different temperatures.

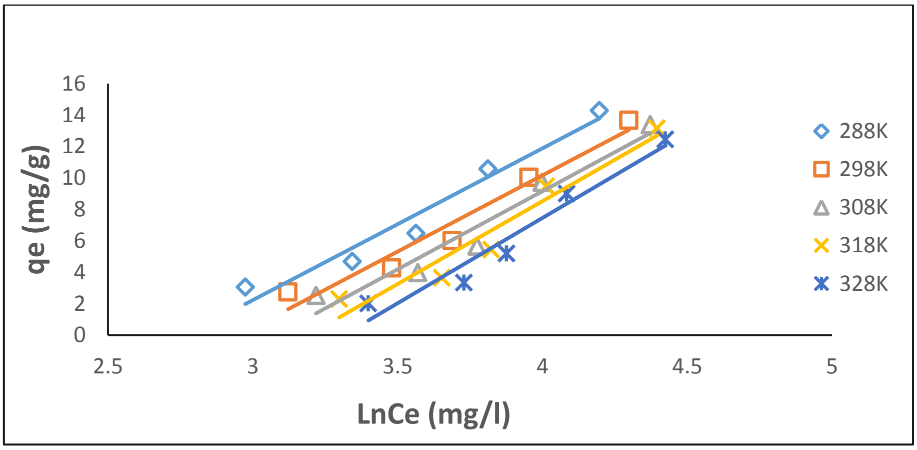


Figure (18): Temkin isotherm plot for adsorption OG dye onto ACS at different temperature.

(Table, 2) shows the Temkin constants for the adsorption of OG dye onto RC, ACSO, ACH and ACS at different temperatures. In this Table increasing in temperature leads to decreases in the values of A_T that indicates the adsorption process is an exothermic, the values of B_T are less than 8 kJ/mol suggesting a weak interaction between OG dye ions and clay surface indicating that the adsorption process is likely physi-sorption. The values of correlation coefficient lies between 0.9103-0.9460, 0.9112-0.9692, 0.9223-0.9779 and 0.9343-0.9544 for RC, ACSO, ACH and ACS respectively. The highest values of R^2 relatively predicted a uniform distribution for the binding energies a rises during the adsorption of OG dye onto clays samples **(Okoli *et al*., 2015)**.

Dubinin-Radushkevich (D-R) isotherm:

The Dubinin-Radushkevich isotherm was applied to study the adsorption on micro porous materials based on the potential theory of adsorption. The linear form of D-R model written as **(Emeniru *et al*., 2015)**.

$Lnq_e = LnK_{D-R} - BƐ^2$----------------------- (8)

Where B: activity coefficient related to the mean adsorption energy ($mole^2/KJ^2$), K_{D-R}: maximum adsorption capacity (mg/g), Ɛ: is Polanyi potential calculated by using the equation $Ɛ=RT\ Ln\ [1+1/C_e]$ --------- (9).

The adsorption energy E (J/mole) is calculated by

$E= \frac{1}{(2B)^{0.5}}$ ------------ (10)

(Figures, 19, 20, 21 and 22) refer to plot of Lnq_e against $Ɛ^2$ for adsorption of OG dye onto RC, ACSO, ACH and ACS respectively at different temperatures.

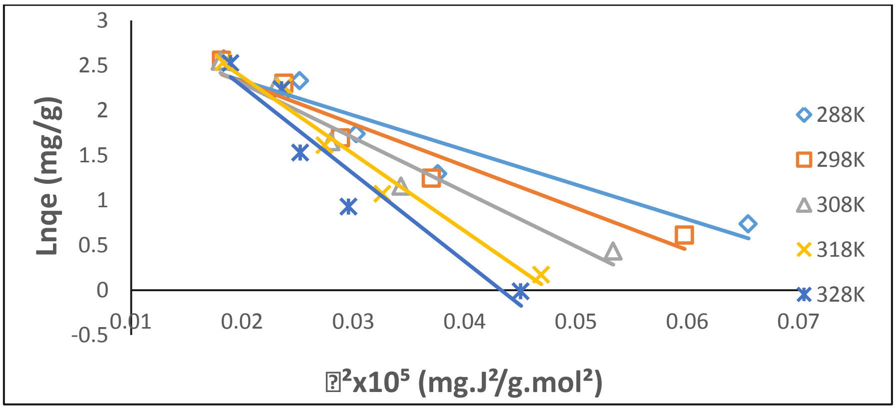


Figure (19): D-R isotherm for the adsorption of OG dye onto RC at different temperatures.

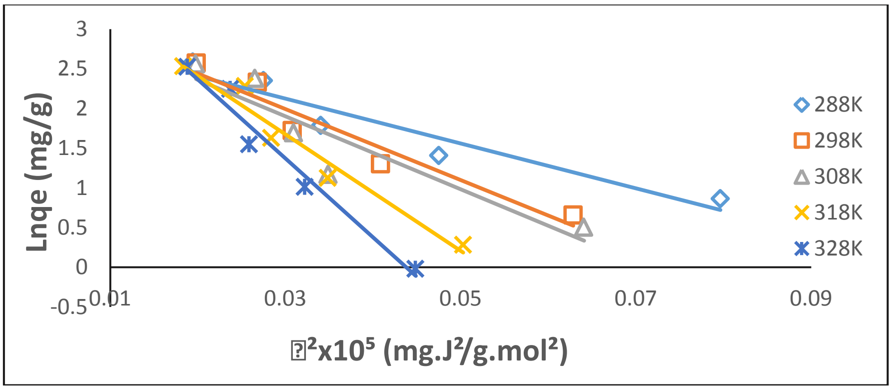


Figure (20): D-R isotherm for the adsorption of OG dye onto ACSO at different temperatures.

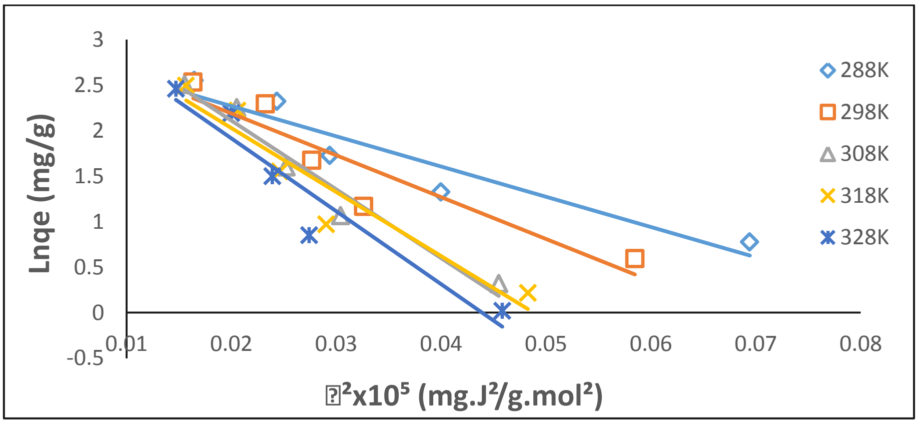


Figure (21): D-R isotherm for the adsorption of OG dye onto ACH at different temperatures.

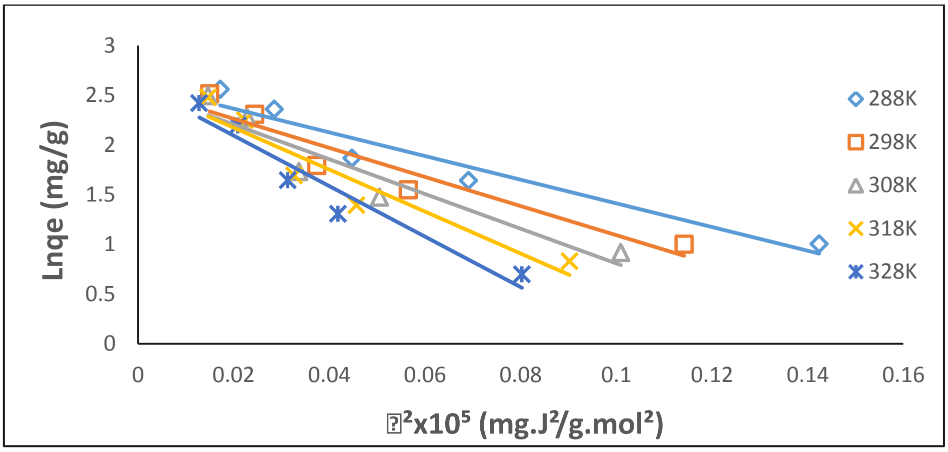


Figure (22): D-R isotherm for the adsorption of OG dye onto ACS at different temperatures.

As shown in (Table, 2) the values of R^2 lies between 0.9041-0.9662, 0.9019-0.9632, 0.9037-0.9552 and 0.9194-0.9797 for RC, ACSO, ACH and ACS clays, this values indicate a good fitting for the adsorption of OG dye onto four types of clays. At all temperatures the highest values of mean free energy (E) were (0.1174, 0.1307, 0.1216 and 2.082 kJ/mol) for RC, ACSO, ACH and ACS respectively (less than 8kJ/mol). The low values of mean free energy predicting that the adsorption of OG dye onto four types of clays is Physi-sorption in nature **(Dada *et al*., 2012)**. From the values of correlation coefficient, the following order to fit the isotherm: Freundlich>Temkin>Dubinin-radushkevich>Langmuir. It was obvious that Freundlich isotherm described better the dye uptake with the higher correlation coefficient R^2 values for the RC, ACSO, ACH and ACS samples in comparison with that of the other adsorption isotherm model.

Table (2): Equilibrium isotherms data for the adsorption of OG dye onto RC, ACSO, ACH and ACS at different temperatures.

	Langmuir					Freundlich		
adsorbent	Temperature (K)	Q_m (mg/g)	K_L (L/mg)	R^2	R_S	n	K_{Fr} (mg/g)	R^2
RC	**288**	2.5799	0.0158	0.9298	0.5586	0.3172	0.0025	0.9556
	298	1.9113	0.0159	0.9255	0.5571	0.2847	0.0014	0.9777
	308	1.2833	0.0162	0.9324	0.5524	0.2325	0.0004	0.9832
	318	0.8264	0.0164	0.8616	0.5494	0.1838	0.0002	0.9803
	328	0.5730	0.0162	0.9267	0.5524	0.1593	0.0001	0.9511
ACSO	**288**	3.5387	0.0154	0.9898	0.5649	0.3564	0.0113	0.9859
	298	1.9573	0.0164	0.9170	0.5494	0.2795	0.0035	0.9715
	308	1.6801	0.0163	0.8885	0.5509	0.2362	0.0016	0.9317
	318	1.0417	0.0162	0.8471	0.5524	0.2059	0.0008	0.9643
	328	0.6059	0.0163	0.8573	0.5509	0.1607	0.0002	0.9757
ACH	**288**	3.6390	0.0141	0.9195	0.5865	0.3704	0.0132	0.9643
	298	1.9940	0.0151	0.8942	0.5698	0.2975	0.0057	0.9368
	308	1.8892	0.0140	0.9313	0.5882	0.2380	0.0011	0.9694
	318	1.0736	0.0147	0.9212	0.5763	0.0070	0.0004	0.9632
	328	0.8744	0.0142	0.8780	0.5847	0.2122	0.0002	0.9550
ACS	**288**	13.8880	0.0091	0.9235	0.6872	0.6701	0.0340	0.9878
	298	10.1010	0.0093	0.9315	0.6825	0.6151	0.0160	0.9861
	308	7.4626	0.0099	0.9450	0.6688	0.5605	0.0074	0.9813
	318	5.5187	0.0107	0.9295	0.6514	0.5081	0.0032	0.9768
	328	4.8804	0.1059	0.9026	0.1588	0.4821	0.0016	0.9828

	Temkin					Dubinin-radushksvich			
adsorbent	Temperature (K)	B_T (J/mol)	b_T	A_T (L/g)	R^2	B (mol^2/kJ^2)	E (kJ/mol)	K_{D-R} (mg/g)	R^2
RC	**288**	19.3970	123.44	0.0348	0.9249	39.8330	0.1174	3.1634	0.9041
	298	20.5150	120.76	0.0318	0.9460	48.0380	0.1020	3.3113	0.9140
	308	23.3970	109.44	0.0285	0.9345	62.2420	0.0896	3.5842	0.9147
	318	27.5710	95.89	0.0257	0.9268	88.1990	0.0753	4.1784	0.9662
	328	28.4520	95.84	0.0240	0.9103	99.9870	0.0707	4.3082	0.9193
ACSO	**288**	17.1760	139.40	0.0397	0.9615	29.2540	0.1307	3.0342	0.9019
	298	21.5860	114.77	0.0329	0.9112	46.2580	0.1039	3.4119	0.9234
	308	24.3920	104.98	0.0297	0.9154	47.2730	0.1028	3.3454	0.9372
	318	25.6690	102.98	0.0270	0.9405	75.6780	0.0812	3.9688	0.9565
	328	29.1330	93.60	0.0242	0.9692	102.130	0.0699	4.4529	0.9632
ACH	**288**	16.8060	142.47	0.0365	0.9506	34.4090	0.1216	2.9966	0.9345
	298	19.2590	128.64	0.0312	0.9223	47.4350	0.1026	3.1756	0.9522
	308	21.7460	117.75	0.0271	0.9779	77.8090	0.0801	3.7042	0.95520
	318	21.5620	122.61	0.0258	0.9436	72.2310	0.0832	3.5082	0.9037
	328	21.4050	127.39	0.0241	0.9273	82.2230	0.0779	3.5944	0.9087
ACS	**288**	10.6690	224.42	0.0601	0.9544	11.5330	0.2082	2.6038	0.9250
	298	10.8410	228.53	0.0501	0.9539	15.2640	0.1809	2.5888	0.9217
	308	11.2920	226.77	0.0440	0.9455	18.2240	0.1656	2.5892	0.9369
	318	11.9120	221.94	0.0394	0.9343	21.9330	0.1509	2.6302	0.9797
	328	11.7300	232.48	0.0354	0.9464	26.4330	0.1375	2.6417	0.9194

Adsorption thermodynamic

The thermodynamic parameters for the adsorption of OG dye were evaluated by using the following equations:

$\Delta G^{\circ} = -RT \ Ln \ K_{eq}$ --------------- (11)

$K_{eq} = [\frac{C_i - C_e}{C_e}] [\frac{V}{M}]$ --------------------- (12)

$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ ----------------- (13)

And $LnK_{eq} = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{R} \cdot \frac{1}{T}$ --------------- (14)

Where: T: is absolute temperature (K), K_{eq}: is the ability of adsorbate to retain and the measure of its movement within solution, R: is the perfect gasconstant (8.314 J.K⁻¹mol⁻¹),C_i and C_e: initial and equilibrium concentrations for OG dye solution (mg/L), M: the weight of the adsorbent (g), V: the volume solution of adsorbate in (L) **(Bendaho *et al.*, 2017)**. The values of ΔH° and ΔS° can be estimated from the slope and intercept of the linear Vant's Hoff plot of LnK_{eq} vs. 1/T (Figures 23, 24, 25 and 26).

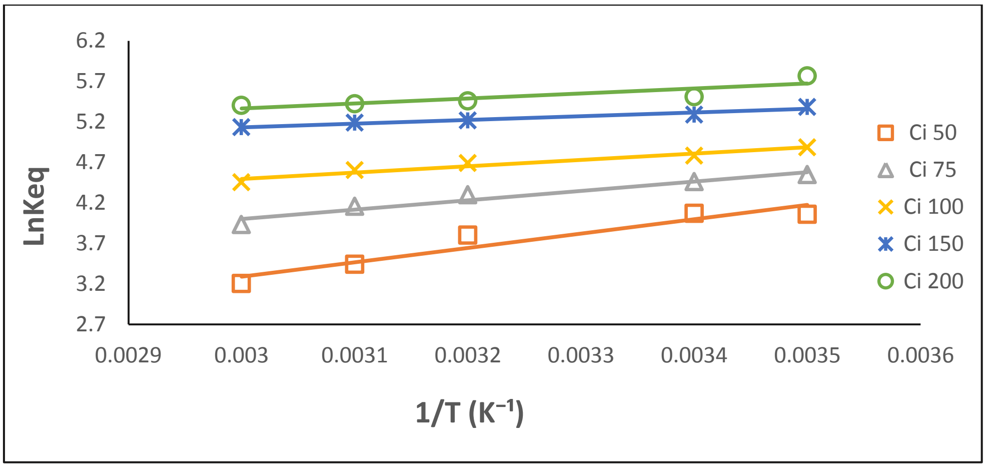


Figure (23): Van't Hoff plots for the adsorption of OG dye onto RC.

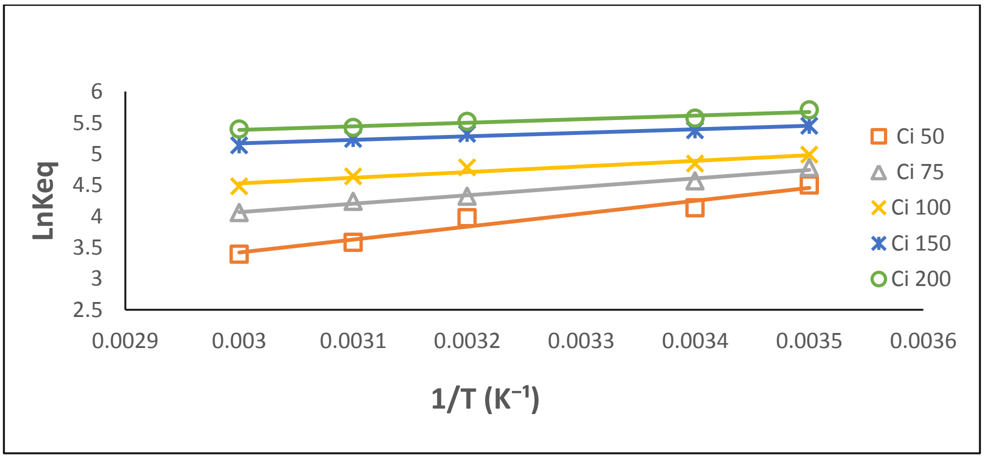


Figure (24): Van't Hoff plots for the adsorption of OG dye onto ACSO.

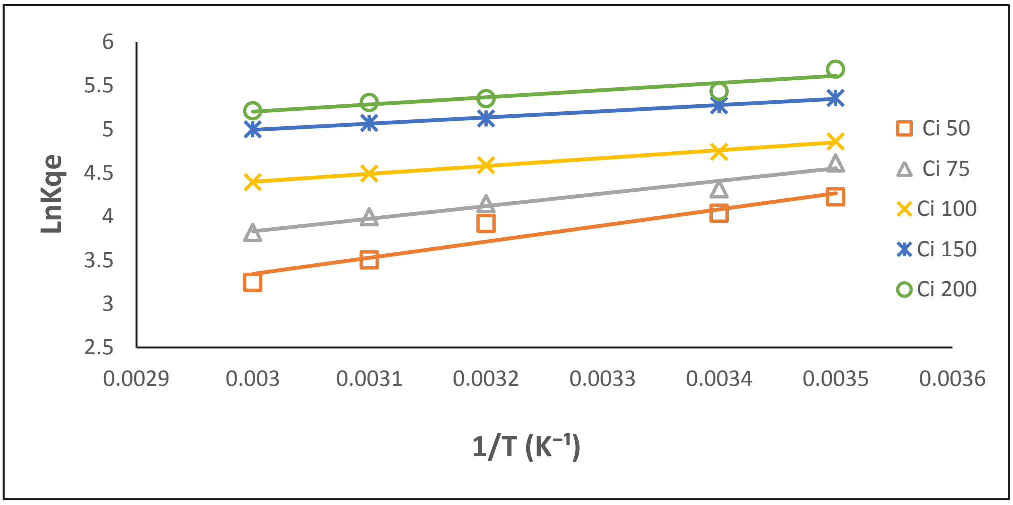


Figure (25): Van't Hoff plots for the adsorption of OG dye onto ACH.

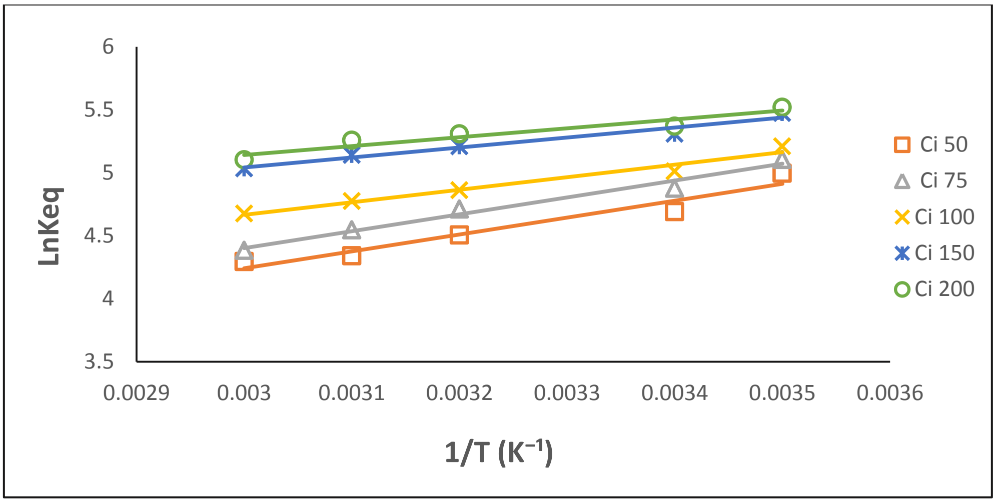


Figure (26): Van't Hoff plots for the adsorption of OG dye onto ACS.

(Table, 3) shows the thermodynamic parameters ($\Delta G^{\circ}, \Delta H^{\circ}$ and ΔS°) for the adsorption of OG dye onto four types of clays at different temperatures. In this Table the negative values of ΔG° confirm the spontaneous and thermodynamically favorable characteristic for the adsorption of OG dye onto the clays samples at low temperatures and the negative values of ΔH° indicating that the adsorption of OG dye onto clays is exothermic the positive values of ΔS° represents the adsorption of OG dye onto RC, ACSO, ACH and ASC is reversible **(Akbartabar *et al.*, 2017)**, and occurs with a good affinity of OG dye towards the clay samples, that leads to an increased at the solid/liquid interfere during dye adsorption onto the clay samples and it remain randomly on the each surface **(Al-Timimi *et al.*, 2016)**.

Table (3): Thermodynamic parameters for the adsorption of OG dye onto RC, ACSO, ACH and ACS.

	C_i(mg/L)	(-)ΔH(kJ/mol)	(+)ΔS(J/mol.K)	(-) ΔG(kJ/mol)				
				288K	298K	308K	318K	328K
RC	**50.0**	17.2016	16.7152	10.194	10.080	9.7291	9.0927	8.7331
	75.0	9.5985	17.5099	10.891	11.049	11.003	10.988	10.724
	100.0	6.4767	17.9499	11.698	11.844	12.008	12.176	12.144
	150.0	3.8292	31.1708	12.889	13.103	13.355	13.716	13.994
	200.0	2.6195	37.0022	13.325	13.648	13.975	14.338	14.732
ACSO	**50.0**	19.5728	16.7660	10.771	10.248	10.175	9.4700	8.705
	75.0	11.2712	17.8834	11.444	11.310	11.055	11.210	11.063
	100.0	7.5089	23.4512	11.945	11.993	12.250	12.268	12.218
	150.0	4.7140	28.8354	13.044	13.328	13.627	13.852	14.011
	200.0	3.5318	34.3185	13.420	13.803	14.143	14.340	14.717
ACH	**50.0**	17.9166	18.4263	10.596	10.005	10.041	9.2566	8.852
	75.0	12.0029	20.7816	11.043	10.694	10.621	10.568	10.408
	100.0	7.4892	24.9137	11.635	11.748	11.744	11.880	11.983
	150.0	5.9065	32.1169	12.830	13.062	13.116	13.411	13.629
	200.0	2.2811	32.8419	13.141	13.463	13.696	14.031	14.212
ACS	**50.0**	12.7428	19.2585	12.083	11.868	11.794	11.738	11.466
	75.0	11.1540	21.4318	12.224	12.082	12.063	12.021	11.952
	100.0	8.2787	28.1088	12.477	12.414	12.451	12.625	12.751
	150.0	6.5839	32.1593	13.105	13.156	13.341	13.592	13.729
	200.0	5.8637	33.0600	13.215	13.307	13.591	13.902	13.914

CONCLUSION

In this article we can concluded that:

1. The percentage removal for OG dye onto raw and activated clays were varied with clay dosage, agitation time, starting dye concentration, temperature, ionic strength and initial pH, the adsorption process was carried out 0.2 g clay dosage, equilibrium time was 36 min, pH 5, the adsorption process increased when increase the dye concentration from 50 to 200 mg/L, when the temperature increased from 288K to 328K the adsorption decrease and for ionic strength when the concentration of sodium chloride increased, the adsorption increased for ACSO, ACH and ACS and decreased for RC.
2. The adsorption isotherm models indicates the adsorption of OG dye onto four types of clays was fitted with Freundlich isotherm model.
3. The maximum mono layer capacity Q_m that estimated from Langmuir model increased from RC to ACS respectively, this indicates that the activation leads to increase the adsorption capacity for ACSO, ACH and ACS clays.
4. The values of thermodynamic parameters suggested that the adsorption of OG dye onto clays is spontaneous, exothermic and reversible.
5. From the isotherm models analysis and experimental data we can concluded the removal efficiency of color pollutants from water for the alkali and acid activated clay is more than raw clay.
6. It is recommended to apply this clay as adsorbent to remove other types of dyes and other environmental pollutants such as phenols, heavy metals and toxic organic compounds.

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