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

Saba A. Saeed¹, Dunya E. AL-Mammar²
¹Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq, sabaadil314@yahoo.com
²Prof. Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq. dunya.almamar@yahoo.com

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 H₂SO₄ (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 enthalpy ΔH°, 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.
تجه الإتمام لمزيج من الأطعمة المنشطة كيميائيًا وحاريًا لإزالة صبغة المثيل البرتقالي من مباني الصرف الصحي

صبي عامل سعي - نتيا عبيان العمار
اسم الكيمياء، كلية العلوم، جامعة بغداد، بغداد، العراق
sabaadil314@yahoo.com

أستار، قسن الكيوياء، كلية العلوم، جاهعت بغذاد، بغداد، العراق
dunya.almamar@yahoo.com

الخلاصة
تتم دراسة سلوك إمتزاز الصباغ الألبوني (المثيل البرتقالي) من المحالل الماني على الطين العادي ومزيج من أطعمة الأليلو الكاتاليتو الكلورات المفعة من منطقة زرباطية (شرق العراق)، وتضمنت المعاملة الكيميائية بالقاعدة والحاض، إذ تم التنظيف بالقاعدة بعملية الطين العادي بحلول 5 ملاير من هيدروكسي الصوديوم والتشنج بالحامض تم باستخدام 25 ملايرا بحامض الهيدروكسيكولونيك و25 ملايرا حامض الكبريت إلتي، بينما تمت المعاملة الحرارية بمستوى الأطعمة المنقحة بالحامض بدرجة حرارة 750م، في حين كانت 105م للطين المنشط بالقاعدة، واستخدمت طريقة الوجبة الامتزاز لدراسة إمتزاز صباغ المثيل البرتقالي على سطح الطين الخام والأطعمة المنقحة بالحامض والقاعدة، وتم دراسة تأثير مختلف العوامل على عملية الامتزاز مثل زمن الزيت ووزن الطين ودرجة حامضية المحلول والتركيز الابتدائي لصبغة المثيل البرتقالي ودرجة حرارة الحموضة والقوة الألبوني، وجرى وصف عملية الامتزاز باستخدام نماذج متشابه درجة حرارة الامتزاز لتكسر وفرنذش وتمك وودينبرادش كفج بالدواويندومدوميكية مثل الزيت في الألبوني 
الزيتي، والتنوع في الطاقة الحرية لركس، والغيث في التشنج في الألبوني 
الزيتي، والتنوبي في الطاقة الحرية لركس، والغيث في التشنج في الألبوني 
الزيتي، والتنوبي في الطاقة الحرية لركس، والغيث في التشنج في الألبوني

الكلمات المفتاحية: إمتزاز صباغ المثيل البرتقالي، الطين الخام، الأطعمة المنقحة بالقاعدة والحاض،
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_{2}Na_{2}O_{7}S_{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$_2$O$_3$ 3.8%, Fe$_2$O$_3$ 4.5%, CaO 15.2%, MgO 3.4%, K$_2$O 1.3%, Na$_2$O 12.8%, TiO$_2$ 0.6%, P$_2$O$_5$ 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$_2$SO$_4$**

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$_2$SO$_4$ carried out by mixing 20 g of raw clay with 200 mL 0.25 M H$_2$SO$_4$ 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 $\lambda_{\text{max}} = 476$ 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:

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

$$Q_e = \frac{V}{M} \left( C_i-C_e \right) \quad (2)$$

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](image)

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 the temperature from 288 to 328 K, thus suggested that the adsorption of OG dye on the clay samples can be imparts an exothermic nature for the adsorption process. It means that when the temperature rise the adsorption forces between the dye molecules and 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 escalation 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).

\[
\frac{C_e}{Q_e} = \frac{1}{Q_m k_L} + \frac{1}{Q_m} C_e \quad \text{------------- (3)}
\]

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) and \(k_L\) (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:

\[ R_s = \frac{1}{1 + K_L C_0} \]  

(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 0 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 (Gbajiet al., 2019). It usually written as (Miyahet al., 2017):

\[ \ln q_e = \ln K_F + \ln(C_e) \]  

\[ n \]  

(5)
Where $K_f$ 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).

$$q_e = B_T \ln A_T + B_T(LnC_e) \quad \quad (6)$$

The values of $B_T$ can be calculated from the equation:

$$B_T = \frac{R \cdot T}{b_T} \quad \quad (7)$$

$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 as it 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 microporous materials based on the potential theory of adsorption. The linear form of D-R model written as (Emeniru et al., 2015).

\[
\ln q_e = \ln K_{D-R} - B \xi^2
\]

Where $B$: activity coefficient related to the mean adsorption energy (mole²/KJ²), $K_{D-R}$: maximum adsorption capacity (mg/g), $\xi$: is Polanyi potential calculated by using the equation

\[
\xi = RT \ln \left[ \frac{1}{1 + C_e} \right]
\]

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

\[
E = \frac{1}{(2B)^{0.5}}
\]

(Figures, 19, 20, 21 and 22) refer to plot of $\ln q_e$ against $\xi^2$ 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.
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.

| Adsorbent | Temperature (K) | Langmuir | Freundlich | Dubinin-Radushksvich |
|-----------|----------------|----------|------------|----------------------|
|           |                | $Q_m$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $n$ | $K_F$ (mg/g) | $R^2$ | $B_T$ (L/mol) | $b_T$ | $A_T$ (L/g) | $R^2$ | $B$ (mol²/kl²) | $E$ (kJ/mol) | $K_{D-R}$ (mg/g) | $R^2$ |
| RC        | 288            | 2.5799   | 0.0158     | 0.9298 | 0.5586 | 0.3172 | 0.0025 | 0.9556 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 |
|           | 298            | 1.9113   | 0.0159     | 0.9255 | 0.5571 | 0.2847 | 0.0014 | 0.9777 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 |
|           | 308            | 1.2833   | 0.0162     | 0.9324 | 0.5524 | 0.2325 | 0.0004 | 0.9832 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 |
|           | 318            | 0.8264   | 0.0164     | 0.8616 | 0.5494 | 0.1838 | 0.0002 | 0.9803 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 |
|           | 328            | 0.5730   | 0.0162     | 0.9267 | 0.5524 | 0.1593 | 0.0001 | 0.9511 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 |
| ACSO      | 288            | 3.5387   | 0.0154     | 0.9898 | 0.5649 | 0.3564 | 0.0113 | 0.9859 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 |
|           | 298            | 1.9573   | 0.0164     | 0.9170 | 0.5494 | 0.2795 | 0.0035 | 0.9715 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 |
|           | 308            | 1.6801   | 0.0163     | 0.8885 | 0.5509 | 0.2362 | 0.0016 | 0.9317 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 |
|           | 318            | 1.0417   | 0.0162     | 0.8471 | 0.5524 | 0.2059 | 0.0008 | 0.9643 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 |
|           | 328            | 0.6059   | 0.0163     | 0.8573 | 0.5509 | 0.1607 | 0.0002 | 0.9757 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 |
| ACH       | 288            | 3.6390   | 0.0141     | 0.9195 | 0.5865 | 0.3704 | 0.0132 | 0.9643 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 |
|           | 298            | 1.9940   | 0.0151     | 0.8942 | 0.5698 | 0.2975 | 0.0057 | 0.9368 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 |
|           | 308            | 1.8892   | 0.0140     | 0.9313 | 0.5882 | 0.2380 | 0.0011 | 0.9694 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 |
|           | 318            | 1.0736   | 0.0147     | 0.9212 | 0.5763 | 0.0070 | 0.0004 | 0.9632 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 |
|           | 328            | 0.8744   | 0.0142     | 0.8780 | 0.5847 | 0.2122 | 0.0002 | 0.9550 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 |
| ACS       | 288            | 13.8880  | 0.0091     | 0.9235 | 0.6872 | 0.6701 | 0.0340 | 0.9878 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 |
|           | 298            | 10.1010  | 0.0093     | 0.9315 | 0.6825 | 0.6151 | 0.0160 | 0.9861 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 |
|           | 308            | 7.4626   | 0.0099     | 0.9450 | 0.6688 | 0.5605 | 0.0074 | 0.9813 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 |
|           | 318            | 5.5187   | 0.0107     | 0.9295 | 0.6514 | 0.5081 | 0.0032 | 0.9768 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 |
|           | 328            | 4.8804   | 0.1059     | 0.9026 | 0.1588 | 0.4821 | 0.0016 | 0.9828 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 | 0.9249 |
Adsorption thermodynamic

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

\[ \Delta G^o = -RT \ln K_{eq} \quad \text{(11)} \]

\[ K_{eq} = \left( \frac{C_i - C_e}{C_e} \right) \frac{V}{M} \quad \text{(12)} \]

\[ \Delta G^o = \Delta H^o - T \Delta S^o \quad \text{(13)} \]

And \( \ln K_{eq} = \frac{\Delta S^o}{R} \cdot \frac{\Delta H^o}{R} \cdot \frac{1}{T} \quad \text{(14)} \)

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 gas constant (8.314 J.K\(^{-1}\).mol\(^{-1}\)), \( C_i \) 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 \( \Delta H^o \) and \( \Delta S^o \) can be estimated from the slope and intercept of the linear Vant’s Hoff plot of \( \ln K_{eq} \) 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 $\Delta S^\circ$) for the adsorption of OG dye onto four types of clays at different temperatures. In this Table the negative values of $\Delta G^\circ$ 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 $\Delta H^\circ$ indicating that the adsorption of OG dye onto clays is exothermic the positive values of $\Delta S^\circ$ 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_0 (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.
REFERENCES
1. Mittal, A., Krishnan, L. & Gupta, V. K. (2005). Removal and recovery of malachite green from waste water using agriculture waste material De-oiled soya. *Separation and Purification Technology*, 43, 125-133.
2. Adeyemo, A. A., Adeoye, I. O. & Bello, O. S. (2017). Adsorption of dyes using different types of clay: a review. *Applied Water and Science*, 7, 543-568.
3. Dada, A. O., Olalekan, A. P., Olatunya A. M. & Dada, O. (2012). Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms studies of equilibrium sorption of Zn*+2 onto phosphoric acid modified rice husk. *IOSR Journal of Applied Chemistry*, 3, 38-45.
4. Hameed, B. H. (2009a). Spent tea leaves a new non-conventional and low cost adsorbent for removal of basic dye of methylene blue. *Journal of Hazardous Materials*, 161, 753-759.
5. Okoli, C. A., Onukwuli, O. D., Onyesolu, C. F. O. & Okoye, C. C. (2015). Adsorptive removal of dyes from synthetic wastewater using activated carbon from tamarind seed. *European Scientific Journal*, 11, 190-221.
6. Bendaho, D., Driss, T. A. & Bassou, D. (2017). Adsorption of acid dye onto activated Algerian clay. *Bulletin of the Chemical Society of Ethiopia*, 31(1), 51-62.
7. Emeniru, D. C., Onukwuli, O. D., Wodu, P. D. & Okoro, B. I. (2015). The equilibrium and thermodynamics of methylene blue uptake onto ekowe clay. *International Journal of Engineering and Applied Sciences*, 2(5), 17-25.
8. Rostami, E., Norouzbeigi, R. & Kelishami, A. R. (2018). Thermal and chemical modification of bentonite for adsorption of anionic dye. *Advanced in Environmental Technology*, 1, 1-12.
9. Gbaji, E. G. O., Hikon, B. N., Sheckhar, N. G., Yerima, E. A., Mavis, O., Ekirigwe, O. & Ayodeji, A. F. (2019). Synergetic study of hydroxyl iron (III) and kaolinite composite for the adsorptive removal of phenol and cadmium. *International Journal of Environmental Chemistry*, 3(1), 30-42.
10. Ayari, F., Manai, G., Khelifi, S. & Trablesi-Ayadi, M. (2019). Treatment of anionic dye aqueous solution using Ti, HDTMA and Al/Fe pillared bentonite. *Journal of Saudi Chemical Society*, 23, 294-306.
11. Bouatay, F., Dridi, S. & Mhenni, M. F. (2014). Valorization of Tunisian pottery clay onto basic dyes adsorption. *International Journal of Environmental Researches*, 8(4), 1053-1066.
12. Gode, F. & Pehlivan, E. (2005). Adsorption of Cr (III) ions by Turkish brown coals. *Fuel Processing Technology*, 86, 875-884.
13. Sejie, F. P. & Nadiye-Tabbiruka, M. S. (2016). Removal of methyl orange (MO) from water by adsorption onto modified local clay (kaolinite). *Physical Chemistry*, 6(2), 39-48.
14. Sarma, G. K., SenGupta, S. & Bhattacharyya, K. G. (2018). Adsorption of monoazo dyes (crocein orange G and procion red MX5B) from water using raw and acid-treated montmorillonite K10. *Water Air and Soil Pollution*, 229, 312, 1-17.
15. Dawood, G. S. (2010). Removal of orange (G) dye from aqueous solution by adsorption on bentonite. *Tikrit Journal of Pure Science*, 15(1), 231-234.
16. Akbartabar, I., Yazdanshenas, M. E., Tayebi, H. A. & Nasirizadeh, N. (2017). Physical chemistry studies of acid dye removal from aqueous media by mesoporousnano composite. *Physical Chemistry Research*, 5(4), 659-679.
17. Fernandes, J. V., Rodrigues, A. M., Menezes, R. R. & Neves, G. D. (2020). Adsorption of anionic dye on the acid-functionalized bentonite. *Materials*, 13(36), 1-19.
30. Foo, K. Y. & Hameed, B. H. (2009a). Value-added utilization of oil palm ash: a superior recycling of the industrial agricultural waste. *Journal of Hazardous Materials*, 172, 523-531.

19. Ahmad, M. A., Ahmad, N. & Bello, O. S. (2014). Adsorptive removal of malachite green dye using durian seed-based activated carbon. *Water Air and Soil Pollution*, 225(20), 1-18.

20. Ghaedi, M., Ansari, A., Habibi, M. & Asghari, A. (2014). Removal of malachite green from aqueous solution by zinc oxide nanoparticle loaded on activated carbon. *Journal of Industrial and Engineering Chemistry*, 20(1), 17-28.

21. Ghaedi, M., Mazaheri, H., Hajati, S. & Purkait, M. K. (2015). Application of central composite design for simultaneous removal of methylene blue and Pb\(^{2+}\) ion by walnut wood activated carbon. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 123, 402-409.

22. Ghaedi, M., Pakniat, M., Mahmoudi, Z., Hajati, S. & Daneshfar, A. (2014). Synthesis of nickel sulfide nanoparticles loaded on activated carbon as a novel adsorbent for the competitive removal of methylene blue and safranine-o. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 135, 479-490.

23. Tamimi, M., Bougdour, N., Alahaine, S., Sennaoui, A. & Assabbane, A. (2018). A study of the removal cationic and anionic dyes in aqueous solution by a new natural clay. *International Journal of Engineering Technologies and Management Research*, 5(10), 64-74.

24. Aki, M. A., Youssef, A. M. & Al-Awadhi, M. M. (2013). Adsorption of acid dyes onto bentonite and surfactant-modified bentonite. *Journal of Analytical and Bio analytical Techniques*, 4(4), 1-7.

25. Nadiye-Tabbiruka, M. S., Lungani, L., Chaloba, S. & Damba, W. (2018). Investigation of methyl orange adsorption from water using acid activated makoro clay. *American Journal of Material Science*, 8(4), 73-78.

26. Al-Dabbagh, N. O. F. (2018). *Mineralogy and Geochemistry of Injana and Mukdadiya Formations (Upper Miocene-Pliocene) in Zorbiatiya area, east Iraq*. M.Sc. Thesis, University of Baghdad, Iraq.

27. Bello, O. S. & Ahmad, M. A. (2012a). Preparation and characterization of activated carbon derived from rubber seed coat. *Bulgarian Journal of Science Education*, 21, 389-395.

28. Ogunmodede, O. T., Ojo, A. A., Adewole, E. & Adebayo, O. L. (2015). Adsorptive removal of anionic dye from aqueous solutions by mixture of kaolin and bentonite clay. *Iranica Journal of Energy and Environment*, 6(2), 147-153.

29. Sarwa, P. & Verma, S. K. (2013). Decolourization of orange G dye microalgae *Acutodesmus obliquus* strain PSV2 isolated from textile industrial site. *International Journal of Applied Sciences and Biotechnology*, 1(4), 247-252.

30. Al-Timimi, R. J. M., Jassim, H. S. & Suleiman, G. M. (2016). Adsorption of folic acid on Iraqi bentonite and kaolin from aqueous solution. *Iraqi Journal of Medicine Science*, 14(1), 25-32.

31. Zakaria, R. M., Hassan, I., El-Abd, M. Z. & El-Tawil, Y. A. (2009). *Lactic Acid Removal from Wastewater by Using Different Types of Activated Clay*. 13\(^{th}\) International Water Technology Conference (IWTC), Hurghada, 13, 403-416.

32. Hajati, S., Ghaedi, M. & Yaghoubi, S. (2015). Local cheap and nontoxic activated carbon as efficient adsorbent for the simultaneous removal of cadmium ions and malachite green. *Journal of Industrial and Engineering Chemistry*, 21, 760-767.
33. Ivandic, S. (2018). Degradation of Orange G Through Persulfate Activated Nanoscalezerovalent Iron Composites and Boron Doped Diamond Electrodes. Chemical Engineering Undergraduate Honors Thesis, University of Arkansas. USA.

34. Shariati, S., Fraji, M., Yamani, Y. & Rajabi, A. A. (2011). Fe$_3$O$_4$ magnetic nanoparticles modified with sodium dodecyl sulfate for removal of safranin O dye from aqueous solutions. *Desalination*, 270, 160-165.

35. Seey, T. L. & Kassim, M. J. N. M. (2012). Acidic and basic dyes removal by adsorption on chemically treated mangrove barks. *International Journal of Applied Science and Technology*, 2(3), 270-276.

36. Kumar, U. & Mishra, V. K. (2015). Degradation of orange G dye by immobilized bacillus sp. S2. *Journal of Industrial Pollution Control*, 31(2), 271-278.

37. Miyah, Y., Lahrichi, A., Idrissi, M., Anis, K., Kachkkoul, R., Idrissi, N., Lairini, S., Nenov, V. & Zerrouq, F. (2017). Removal of cationic dye “Crystal Violet” in aqueous solution by the local clay. *Journal of Materials and Environmental Sciences*, 8(10), 3570-3582.

38. Chen, Y. M., Tsao, T. M. & Wang, M. K. (2011). Removal of Crystal Violet and Methylene Blue from Aqueous Solution Using Soil Nano-Clays. International Conference on Environment Science and Engineering, IPCBEE, IACSIT Press, Singapore, 8, 252-254.