Sys Rev Pharm 2020; 11(3): 495 – 502
A multifaceted review journal in the field of pharmacy
E-ISSN 0976-2779 P-ISSN 0975-8453

Adsorption, Thermodynamic and DFT Studies of Removal RS Dye on the Iraqi's Clay from Aqueous Solutions

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Article History: *Submitted: 25.01.2020* *Revised: 24.02.2020* *Accepted: 19.03.2020*

ABSTRACT

The removal of dye (RS) anionic (Benzene sulfonic acid, 4-hydroxy-3-((2-hydroxy-1-naphthalenyl)) azo monosodium salt) on flint clay in aqueous solution was investigated by using a system of the batch for different concentrations from the dye. The temperature, pH, contact time, adsorbent dose, was studied beneath the batch adsorption method. Data adsorption equilibrium appropriate with isotherm Langmuir and Freiundlich, when the correlation coefficient utilized to clarify the better model for the fitting isotherm. The thermodynamic constants like ΔH°, ΔS°, and ΔG°. Thermodynamic analyses specified for the sorption of the dyes on to Alhusaenat clay (Baghdad Governorate in Iraq) was spontaneous as well as endothermic. Density Functional Theory (DFT) was studied the dye structure used Gaussian 09 and predicted the active site in a molecule by total electron density (TED) and electrostatic surface potential (ESP).

Keywords: Adsorption, Dye RS, DFT, Langmuir model, Thermodynamic

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DOI: 10.5530/srp.2020.3.63

INTRODUCTION

The control of environmental pollution has been a troubling matter in many countries and the problem in the environmental pollution is wastewater pollution, as well as air pollution [1] On the market, was have a much for 100,000 various synthetic dyes parameter, resulted in more than 700,000 tons annually worldwide [2]. Bad effects are obtained by wastewater pollution on the supplies of public water, which can reason problems on health like diarrhea [3]. The textile wastewaters were caused the Major pollutants, which must be high acidity, heat, and other soluble substances textile wastewater formed the major pollution that came from dyeing as well as finishing processes [4-5]. Many treatment processes included physical, chemical, and biological have been employed to treat various municipal and industrial wastewaters, for example, chemical [6]. Biological, food [7]. Peanut hulls [8], maize bran [9]. Many researchers offered that the possibility occurs for the utilizing of strongly concentrated sunlight for the removal of the dye from the wastewater [10-11]. Industrial facilities take clean water from nature and re-contaminated water into water sources where these industrial pollutants affect the physical properties of natural water such as the intensity, color, and taste [12], own attracted the awareness of some realizations for the removal of the dye. By the studied work, the capability for flint clay to take off the anionic dye, the considered adsorption has been shown. The contact time influences, the concentration of initial dye as well as the quantity of color elimination were examined. The experimental data of equilibrium were adjusted by using Freundlich as well as Langmuir equations to investigate the perfect isotherm correlation. Density functional theory (DFT) [13] has provided a very useful framework for developing new criteria for rationalizing, predicting, and eventually understanding many aspects of chemical processes [14]. Varieties of chemical concepts, which are now widely used as descriptors of chemical reactivity, e.g., electronegativity hardness or softness quantities, etc., appear naturally within DFT. The effects of solvent ions, surface structure and adsorption of metal atoms, or sites or vacancies for oxides, active liquid-phase adsorption, and solubility are some of the omitted parameters to be included in the field [15].

EXPERIMENTAL SECTION

The adsorbent substance

The dye RS reagent is organic reagent, which belongs to aromatic azo dyes, which is used widely as complexing agent in the determination of many metal ions (Al, Ca, Fe, V, Y, Uo_2, La, Zn, and Ti) by different techniques such as spectrophotometry, polarography, potentiometry, and it is used in inks, and textiles industry. Voltammetry [16-17] λmax= 500 nm The RS stock solution was intended by resolving carefully from weight dye in distilled water to the 50 ppm concentration. The solutions work prepared by resolving the stock solution in precise ratios to various primary concentrations by range 5-50 ppm. This reagent has many other names such as Acid chrome violet K, Acid Alizarin violet N, Pontachrome violet SW chromatid violet R, Brasilian chrome violet B, Diamond Corinth N, Magracrom violet N, Omega chrome Dark violet D, as well as Yodochrome violet B, etc.

Table 1. RS chemical name and characteristics

Chemical Name	Benzene sulfonic acid,4-hydroxy-3-((2-hydroxy-1-naphthalenyl)) azo Monosodium salt
Physical Appearance	Reddish–Violet crystals
Molecular Formula	$C_{16}H_{11}N_2O_5SNa$
Molecular Weight (g. mole^{-1})	366.33
UV–VIS (λmax)	501nm In water
Melting point	>300 c◦
Solubility	Water, ethanol-soluble
Toxicity	Mutagenicity

Alhussainiyat clay (Baghdad-Iraq)

The adsorbent used in this study was Hussainiyat clay and get from the public company for Mining as well as Geological survey, Industry Ministry as well as mineral Baghdad, Iraq. The Hussainiyat rock was crushed and sifted in the average particle size 150-200 micrometer. The sample was washed with distilled water and subsequently dried at 25 ◦C. This Hussainiyat clay used in experiments and analysis [18].

Table 2. The specification of flint

Constituent	SO3	Al2O3	Fe2O3	TiO2	CaO	MgO	SiO3	L.O.I
Wt. %	<0.7	11.22%	29.48%	0.80%	<2.0%	0.2%	20.28%	10.14%

The bath mode adsorption study of the effect

The solution of this work was prepared by resolving in a volumetric flask a carefully weighted dye in distilled water at a 0.050 gm in 1000 ml of water concentration to give 50 ppm for dye. A series of diluted solutions of dye were prepared in the range from 5.0-50.0 ppm. Various parameters like temperature, dye concentration as well as clay dose were studies. Solution dye 100 mL and 0.5 gm of clay in 250 mL conical flask were rambunctious at 200 rpm in the water bath equipped with a shaker at the time were already determined in advance. Adsorbate solution was centrifuged at 3000 rpm and for 15min. The sample concentration is computed by the spectrophotometric investigation. The quantity of RS adsorbed was measured from the next Eq. [19-20].

$q_e = C_0\text{-}Ce/m * V$ ---------- (1) $R\% = (C_0\text{-}C_t)/C_0 * 100$ ---------- (2)

That C_0 and Ce are the primary, equilibrium concentrations in mg/L unit of DB71 in solution, respectively. q_e is a quantity of RS adsorbed into the adsorbent at the equilibrium time (mg/g), m(g) the weight of clay, while V (L), the solution volume given for the test. The λ max 500 nm, the spectrum for 25 mg/L RS adsorption was shown in (Figure 1). The calibration curve was established as a function of RS dye concentrate on at pH7 (Figure 2).

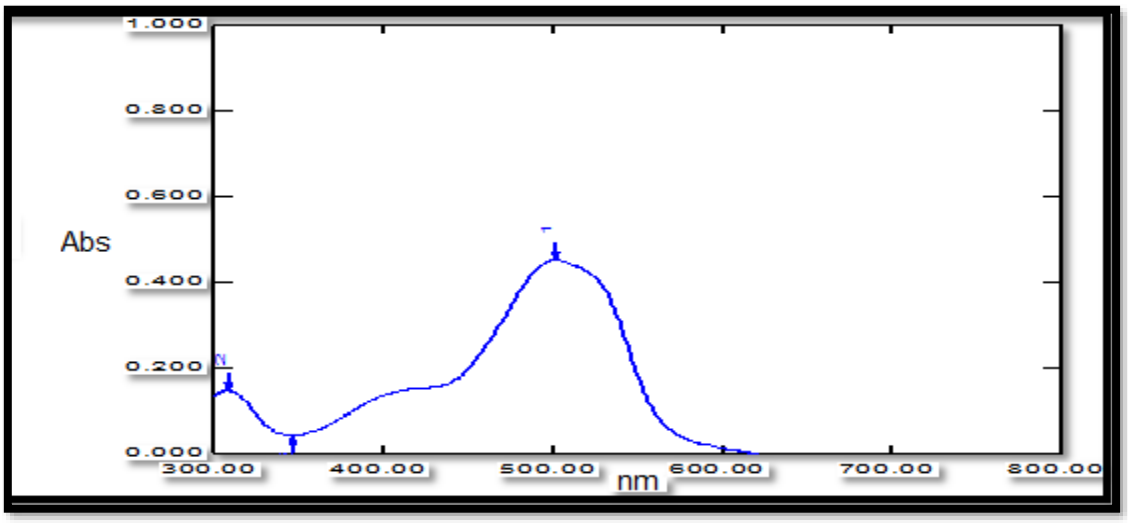


Figure 1: The scan spectrum curve of RS dye.

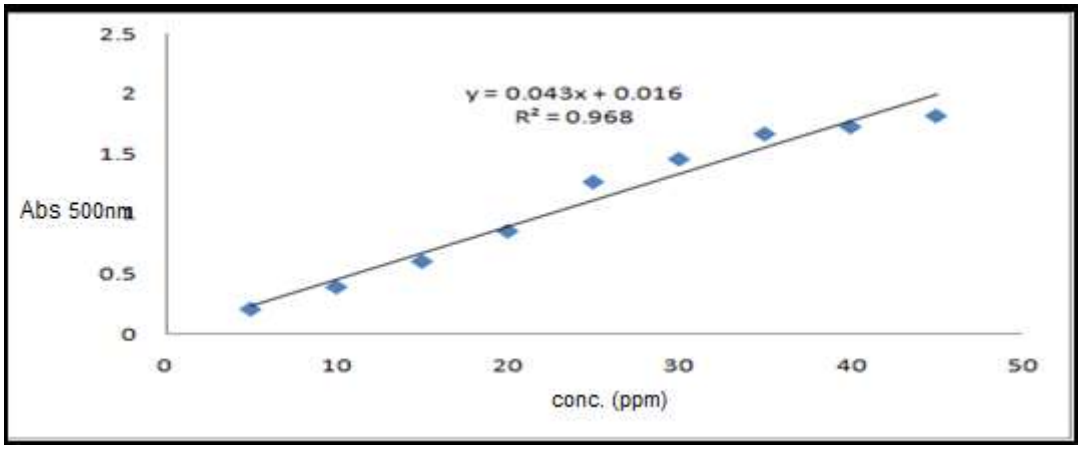


Figure 2: The calibration curve of RS dye at different pH.

Effect of variable parameters

The experiments were accomplished in shaking conical flasks with 100 mL dye at a constant temperature shaker. The amount of adsorbent of the solution was kept constant. A sample of 10mL was careful with down at every 5 min until the equilibrium of the adsorption process has been reached. The study of adsorption was conducted from 20-45 ◦C. The rang of the adsorbent amount used in this experiment between 0.1 to 0.6 g/ L.

Calculations models

The calculations were done by using DFT with the B3LYP hybrid functional [19,20] in vacuum using the Gaussian 09 program [21]. The triple-z basis set 6-311G (d,p) basis set for all atoms (C, H, N, O) used. Also, the charges for the electrostatic potential (ESP) is determined to measure the maps of the molecular electrostatic potential (MEP). These maps were used to determine the delocalization of electrons in the molecular surface [22]

RESULTS AND DISCUSSION

Effect of agitation time (equilibrium time)

An influence on this factor by the quantity in RS adsorbed on the unit from adsorbent was obtained at constant pH as well as concentration. Table 2 and Figure 3 given the results of equilibrium time to dye in 25 ppm at 20 ºC and pH= 7 were illustrated in table 2 and Figure 3.

Table 3. Values of q_e with Time of 25 ppm of RS PH=7

Time, min	*Q*e, mg g-1
5	1.95
10	1.92
15	1.96
20	1.99
25	2.10
30	2.23
35	2.45
40	2.78
45	2.66

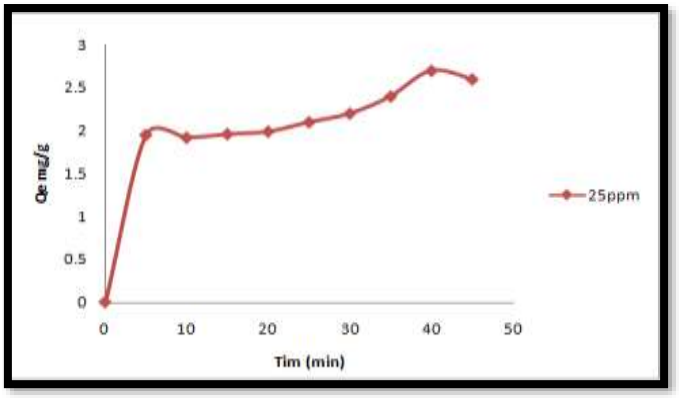


Figure 3: Influence of contact time.

The results in (Figure 3) shows that the fast adsorption was obtained at 5 min and gradually increasing with growing contact time up to 45 min, after this time, no improvement in the dye adsorbed amount. Therefore, the 45 min is the constant time as the prefect contact time [23] Dosage influence:

The adsorbent dosage influence on the elimination of RS dye was examined at different amounts of Flint clay while keeping the primary concentration from dye at 25 ppm as well as the contact times 45 min are fixed. The results are explained in (table 4) and (Figure 4). Removal of dye on clay was taken from dosage for 0.1-0.6 g.

Table 4. The quantities of R percentage as well as w (g)

W (g)	R%
0.1	18.64
0.2	17.76
0.3	27.35
0.4	25.58

0.5	30.77
0.6	28.80

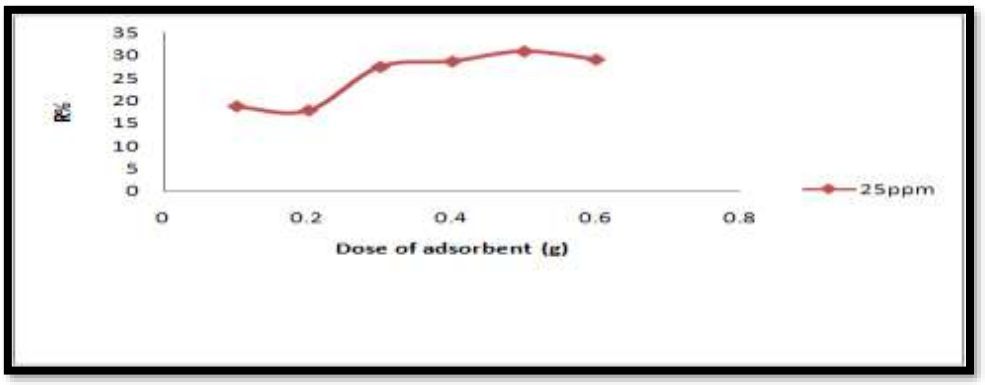


Figure 4: The adsorbent dosage influence.

The R% for the elimination of the increases dye was increased with the dose of adsorbent but after the value of 0.5 gm. (Figure 4) shown. The change that produces form the high availability of the commutable sites or the increasing the area of surface wherever the adsorption happened

Thermodynamic analysis

The effect of various temperatures on RS adsorption by ALhusseniat clay was accomplished using (20, 25, 30, 35and 40 °C). The calculated of thermodynamic parameters like entropy change ΔS^o, enthalpy change ΔH^o as well as Gibbs free energy change ΔH^o,ΔG^o, according to Van't Hoff equation (equation (3)), the equilibrium constant has been calculated of the Eq 3,4. $K_{eq} = \frac{qe}{Ce}$ against the temperature [24]. The result is shown in (Figure 5)

$$\ln K_{eq} = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad \text{----------(3)}$$

$$G^\circ = -RT \ln K_{eq} \quad \text{----------(4)}\Delta$$

where R represents the gas constant and K_{eq} is the constant of adsorption equilibrium. The ln K_{eq} plot versus 1/T (in Kelvin) must be linear. The Van't Hoff plot slope is equal to $\frac{-\Delta H^o}{RT}$, as well as the intercept is equal to $\frac{\Delta S^o}{R}$. ΔH^o and ΔS° gained are given in (Table 6). The adsorption efficiency increase with increasing temperature. This observation is quite common and suggests that the adsorption is endothermic. Therefore, enthalpy was found in positive values. The positive amounts of entropy given the randomness increasing; the negative Gibbs free energy amounts showed the adsorption model was spontaneous nature [25-26]

Table 5. Amounts of 1/T and ln Keq for the RS adsorption for C0= 25ppm

T (K)	1/T	$Ce_{(mg/l)}$	$Q_{e\ (mg/g)}$	ln K_{eq}
293	0.00341	19.86	1.628	2.96
298	0.00336	15.65	1.930	2.12
303	0.00330	15.34	1.944	2.07
308	0.00325	14.94	2.014	2.007
313	0.00329	14.27	2.14	1.394

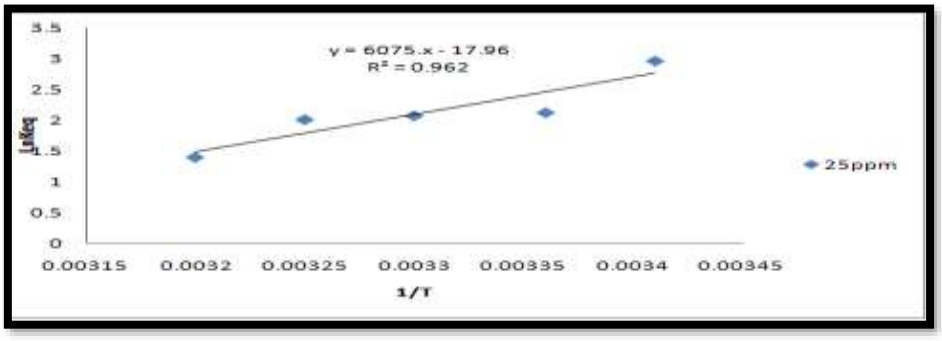


Figure 5: Van't Hoff plot of RS adsorption.

Table 6. Thermodynamic study and parameters of RS adsorption on clay at 25 ppm, 0.5g, and PH 7

ΔH° KJ.mol^{-1}	ΔS° J.mol^{-1} K^{-1}	ΔG° KJ.mol^{-1}				
35.48	91.24	20°C	25°C	30°C	35°C	40°C
		-7.211	-5.253	-5.215	-5.139	-3.628

The isotherm of adsorption

The isotherm of adsorption is the maximum paramount information that shows how molecules are divided between the solid phase and the liquid phase when the adsorption arrived for the equilibrium. The most popular isotherm type, Langmuir and Freundlich, were checked to RS dye. (Table 7) appeared the data, and (Figure 7) shown the isotherm of adsorption take the shape at one of the five types I to V of the classification originally nag proposed by Brunauer. Deming, Deming .is S-type, shows that the possibly adsorbent is mesa porous or is not porous as well as contains the adsorption with maximum energy [27-28].

Table 7. The values of q_e mg/g and C_0 (ppm)

mg/L	Ce mg/L	Q_e mg/g
5	3.02	1.27
10	3.62	1.76
15	6.16	1.83
20	8.44	1.900
25	15.6	1.930
30	18.44	2.73
35	20.5	2.99
40	25.77	3.78
45	30.6	4.22
50	33.90	4.99

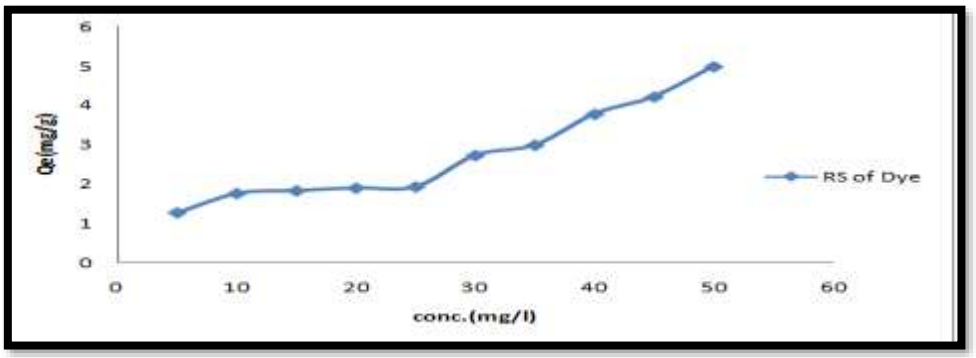


Figure 6: The adsorption isotherms of RS dye.

The experimental data obtained (Table 8) are also tested according to the linear form of the Freundlich equation [(equation 5]. The linear plots of log q_e versus log *Ce* are shown in (Figure 7), which offer the application for the Freundlich isotherm. The amounts of $\frac{1}{n}$ and Kf is obtained from the slope as well as the intercept of the plots and are seen in (Table 8) [29-30].

$$\text{Log } Q_e = \log Kf + \frac{1}{n} \log Ce \quad \text{---------- (5)}$$

Where *Qe* is the solid-phase concentration at equilibrium (mgg^{-1}), Ce is the equilibrium of dye in solution (mgL^{-1}), $\frac{1}{n}$ is constants combining the parameters that influence the capacity of adsorption additionally K_f is the adsorption intensity.

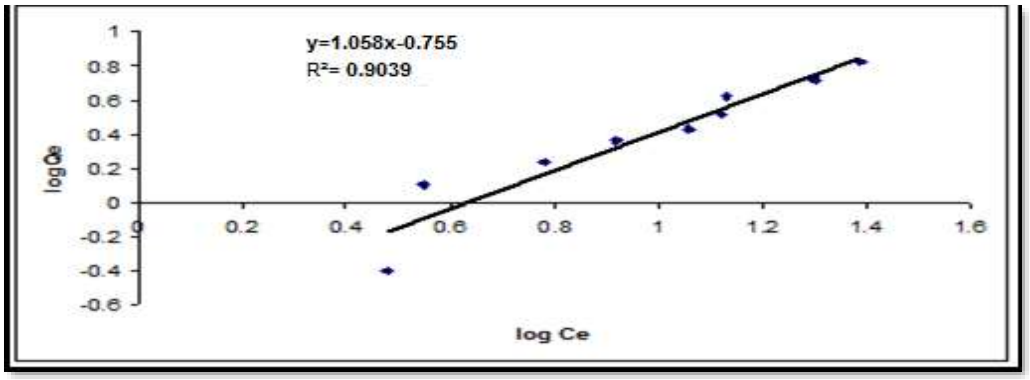


Figure 7: The Freundliech model of a linear plot.

The Langmuir model was applied successfully for many real sorption processes. It is expressed by the following relation equation [Eq. 6].

$$\frac{Ce}{Qe} = \frac{1}{Qm\ kL} + \frac{Ce}{Qm} \quad \text{---------- (6)}$$

The Q_m and k_L are Langmuir constants in connection with the efficiency of adsorption and energy of adsorption, Sequentially [31]. The plots linear for $\frac{Ce}{Qe}$ against C_e show the application of the Langmuir isotherms (Figure 8). The amounts of Q_m and k_L were obtained from the slope as well as intercepts additionally appear in (Table 8).

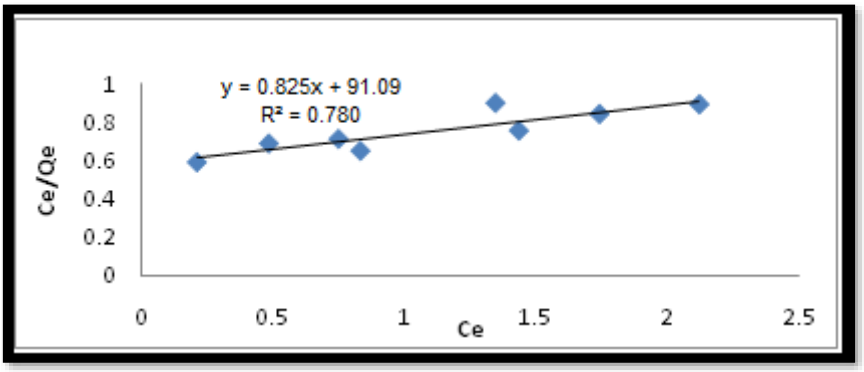


Figure 8: The linear plot of Langmuir isotherm.

R_L called separation factor. An essential characteristic of Langmuir isotherm can be expressed by a dimensionless constant, which is calculated by using the [Eq. 7]

$R_L = 1/1+K_L C_0$ ---------- (7)

R_L values show that the isotherm type was irreversible (R= 0), suitable ($0 < R_L < 1$) , liner ($R_L = 1$) or unsuitable ($R_L > 1$. values of n > 1 appear suitable adsorption circumstances [32]. The R_L value is established to be between zero and one as well as emphasize that the outstanding process of adsorption is suitable. The R2 coefficient was more than 0.9 for Freundlich isotherm and showing the beneficial amounts of its constants. Freundlich isotherm model was explained better by the present system [33].

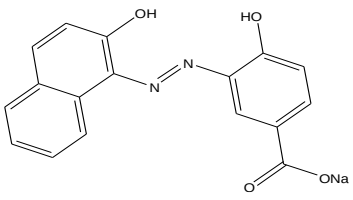
Table 8. The Freundlich and Langmuir parameters for the adsorption

Freundlich parameter	T (°C)	1/n	K_F	R^2	
	20	0.14	0.708	0.9039	
Langmuir parameter	T (°C)	q_L	K_L	RL	R^2
	20	0.716	0.5 21	0.355	0.765

Quantum chemical

Theoretical calculations were used to perform optimization structurer of the RS dye and the active adsorption site. The HOMO (High Occupied Molecular Orbital) and LUMO (Low Occupied Molecular Orbital), HOMO-LUMO orbitals and the optimized structure of RS dye have been shown in Table 8. Almost symmetrical on all atoms where green color refers to HOMO orbital (donate electron orbital) and red color to LUMO orbital (accept electron orbital). This suggests that most parts in the molecular orbitals of the RS dye can actively interact with Hussainiyat clay orbitals either via electron donation to the appropriate orbitals of the clay or electron acceptance from suitable occupied clay orbitals. The electron density was known as total electron density (TED); denoted sites by a red color were as a negative, which refers to the electronegativity of N and O atoms within the RS dye molecule, it's an electrophilic attack, while the blue region indicates the best positive area that can accept electrons from the donor compound [34-35] The electrostatic surface (ESP) potential as a direction of adsorption sit of molecules with the clay. Table 10 shows the TED and ESP of the dye.

Table 9. Molecular orbitals distribution (HOMO, LUMO, and HOMO-LUMO) and 3D structure of RS dye.

2D	3D
	 N: blue; O: red; Na: violet; C: gray; H: white
HOMO	LUMO

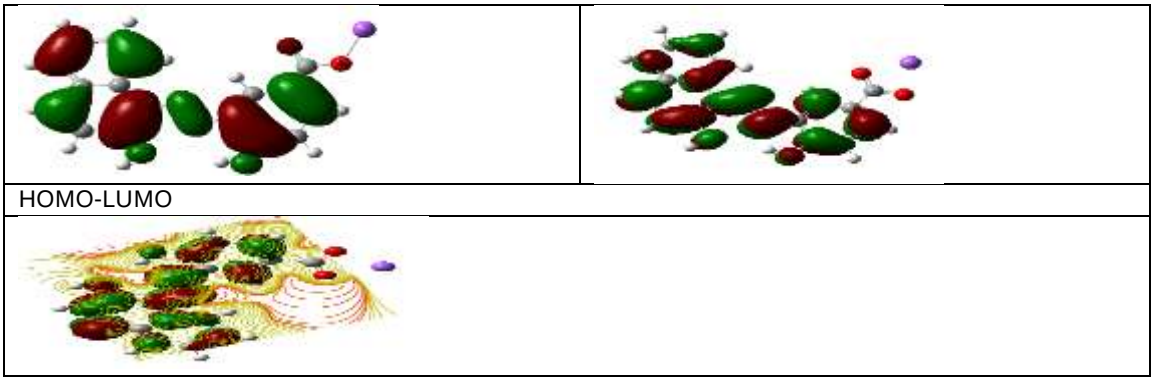
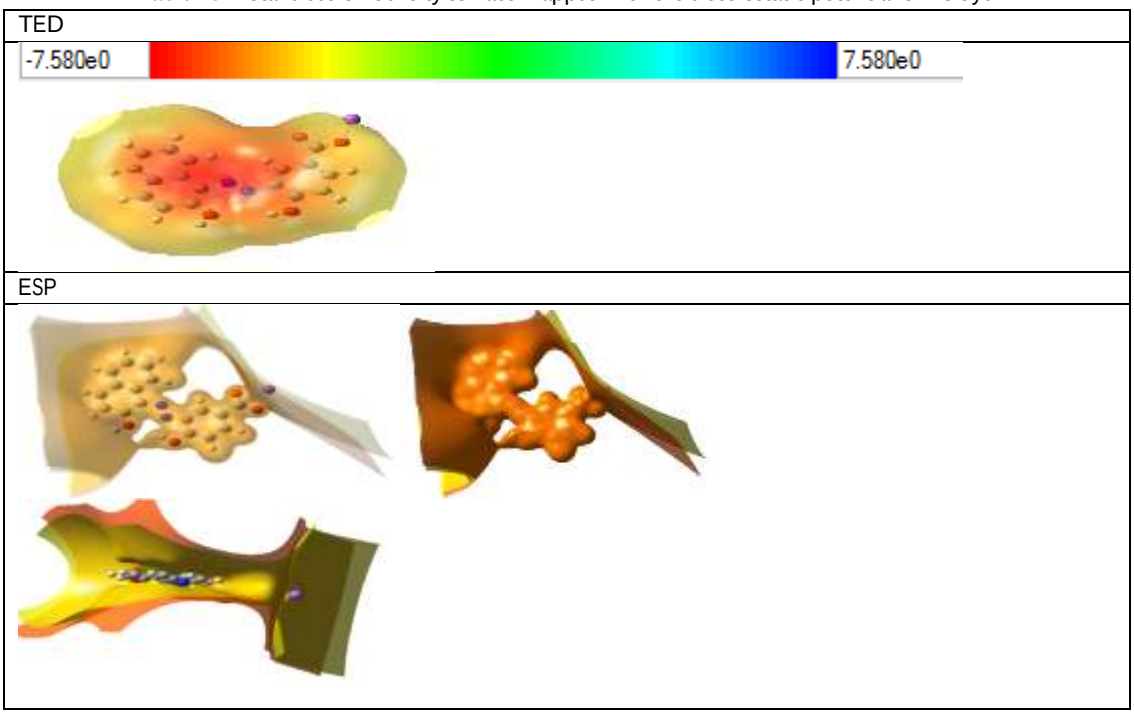


Table 10. Total electron density surface mapped with the electrostatic potential of RS dye.



CONCLUSIONS

The most important results can give from the previous resulted and discussion may be formulated as in the following paragraphs: The system of adsorption could be studied by (the physical adsorption). Thermodynamic analyses explain that the dye adsorption onto clay was spontaneous as well as endothermic this proved by the results of the amount of ΔG° as well ΔH°. For the equilibrium adsorption, RS dye was better adjusted to the Freundlich isotherm. DFT results indicated to RS dye molecules contain a good position site for adsorption onto clay by infracts its electrons with the clay; these results were proved with the experimental data.

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