

Removal of Reactive Yellow 160 from Industrial Wastewater onto Modified Sand (Sand of Larache city beach, Morocco)

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Abstract

The aim of this research paper is to investigate the removal of Reactive Yellow 160 (RY160) from industrial wastewater onto Modified Sand (MS). The adsorbent was characterized by infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDXA). The effects of significant parameters such as adsorbent dose, pH, initial dye concentration, contact time, temperature were examined. It was revealed that the removal rate percentage was equal to 92.6%, the maximum adsorption capacity appeared at pH 1, and the optimal contact time for the removal of RY160 onto MS was 120min. Adsorption kinetics, isotherms and thermodynamic parameters were studied. The finding shows that the Langmuir isotherm and the Pseudo-second order kinetic model described well the adsorption process. The thermodynamic study disclosed that the adsorption of RY160 onto MS is exothermic and spontaneous with a physisorption nature.

Keywords: Modified Sand, Reactive Yellow 160 (RY160), Adsorption, wastewater treatment, Industrial dyes.

1. Introduction

Several dyes and their break-down products are toxic for living organisms because dyes are not easily degradable and are generally not removed from wastewater by conventional wastewater treatment systems; this makes it difficult to remove dyes from effluent [1,2]. Synthetic dyes [3], which are extensively used in the textile industry [3], represent a major environmental problem. Due to inefficiency of the industrial dyeing process, 10-15% of the dyes are lost in the effluents of textile units, rendering them highly colored [4,5]. The efficient removal of dyes from textile industry effluents is still a major environmental challenge [6]. In addition, exposure to dyes will impede light transmission, decrease transparency of waters, retard photosynthetic activity and inhibit the growth of biota [7]. Furthermore, it is hard to biodegrade due to its synthetic and complex aromatic molecular structure [8]. Adsorption is a major industrial separation technique for the purification of effluent media [9]; it has the merits of high efficiency, cost-effective, simple operation and environmental friendliness [10].

The potential of sand was assessed for the removal of different types of dyes, metal ions and used as a filter in the production of tap water. Sand can be used as a substrate or carrier for its stability, high hardness, and strength, but its adsorption capacity is very poor [11].

In the present research, sand was selected as an adsorbent but as it's reported in the literature that the sand has a low capacity of adsorption, it's was modified and used as a bio-adsorbent for the removal of reactive yellow 160 (RY 160 Figure 1) from industrial wastewater. Isotherms, kinetics, thermodynamics and equilibrium studies are investigated to understand the behavior of our adsorbent onto azo dyes [3].

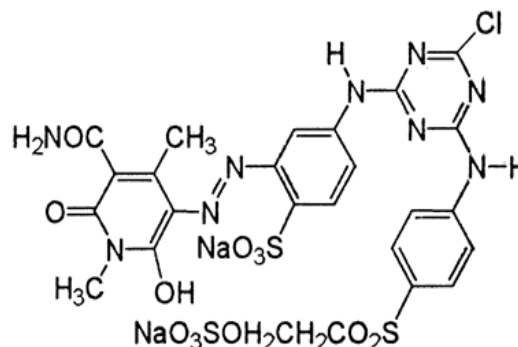


Figure 1. Chemical structure of reactive yellow 160 (Single azo class).

2. Materials and methods

2.1. Preparation of adsorbent

The sand samples were taken from the shallow waters of Larache city beach, Morocco. Sulfuric acid H_2SO_4 , Sodium hydroxide NaOH and hydrochloric acid HCL were from Sigma-Aldrich and all other chemicals used were of analytical quality. It is first necessary to remove all the impurities present in the sand samples by intensive washing, after drying at a temperature of $105^\circ C$ overnight, the sand samples were sustained at a particle size of $200\ \mu m$, sand modification was applied by the addition of sand in sulfuric acid (H_2SO_4 , 40%) during 4 hours. The final product was washed several times by water distilled, and finally dried at a temperature of $105^\circ C$ during one night [12]. To characterize our adsorbent and defined the functional groups, we used an infra-red spectrophotometer (FT-IR) of type JASCO FT/IR-410. The structure of modified sand was evaluated by X-ray diffraction (XRD) type Bruker D8 Advance ECO. The surface morphology, the adsorbent elements localization and the qualitative detection was examined by the scanning electron microscope (SEM) supplied with energy dispersive X-ray analysis (EDXA). The adsorbed quantities measurements of Reactive yellow 160 (RY160) on our adsorbent were carried out in an analysis wavelength λ_{max} : 413 nm [13] by using a spectrophotometer UV of the type JASCO V-360 with a preliminary calibration of the instrument spectrophotometer to detect the parameters effect on the adsorption process.

2.2. Batch adsorption experiments

The optimal conditions for the removal of reactive yellow 160 (RY160) by modified sand (MS) were discovered by investigating every parameter influencing the adsorption process. The optimal adsorbent amount was defined by mixing various quantities of MS from 10mg to 260mg with 30ml of dye solution for 90 min in a temperature of $24^\circ C$, with an initial dye concentration of 50mg/l and neutral pH under continuous stirring at 150 rpm. The effect of pH was studied by fixing all the parameters except the pH of the dye solution (1 to 11), it's was adjusted by using NaOH and HCL, with a contact time of 90min in a temperature of $24^\circ C$, initial dye concentration of 50mg/l, adsorbent dose of 70mg under continuous stirring at 150 rpm. The effect of initial dye concentration (10mg/l to 300mg/l) was conducted by using 70mg as an adsorbent dose under continuous stirring at 150 rpm with a temperature of $24^\circ C$ for 90min at a neutral pH. Various time intervals (10min to 300min) were used to define the absorbance variations under the following conditions: initial dye concentration of 50mg/l under continuous stirring at 150 rpm, with a temperature of $24^\circ C$ and 70mg as an adsorbent dose at a neutral pH. The recognition of the adsorption phenomena during the removal of RY160 by MS require a temperature study at different degrees from $25^\circ C$ until $85^\circ C$ by applying 70mg as an adsorbent dose, initial dye concentration of 50mg/l at neutral pH under continuous stirring at 150 rpm. After centrifugation, the final concentrations of the dye are given, the amount adsorbed (q_e) and the removal percentage (R%) of the dye are calculated by equations (1) and (2):

$$\text{Amount adsorbed}(q_e) = \frac{C_0 - C_e}{M} * V \quad (1)$$

$$\text{Removal}(\%) = \frac{C_0 - C_e}{C_0} * 100 \quad (2)$$

White C_0 is the initial dye concentration in solution (mg/l), C_e is the final dye concentration in solution (mg/l), M is the adsorbent mass (g) and V is the solution volume.

3. Results and discussion

3.1. Characterization of adsorbent

To characterize our adsorbent (MS) we used an infra-red spectrophotometer (FT-IR), the characteristic bands of sand (S) are shown in Figure 2 and compared with the characteristic bands of the modified sand (MS). Sand (S) main bands are $3400\ cm^{-1}$ (strong and broad stretching vibration band of -OH associated with alcohols and phenols), $2872\ cm^{-1}$ (strong asymmetric stretching vibration band of C-H bond of the alkane groups), $2132\ cm^{-1}$ (weak stretching band of the alkyne groups), $1794\ cm^{-1}$ (strong stretching band of the acid group -C=O), $871\ cm^{-1}$ (stretching vibration of Si-O) [14] and $692\ cm^{-1}$ (twisting vibration of Si-O-Si) [14]. There are two characteristic bands separate between S and MS can be attributed to the modification by the strong acid H_2SO_4 : $3608\ cm^{-1}$ (variable and thin stretching band of free O-H bond of alcohols and phenols) and $3548\ cm^{-1}$ (intense stretching band of O-H bond of the acid group).

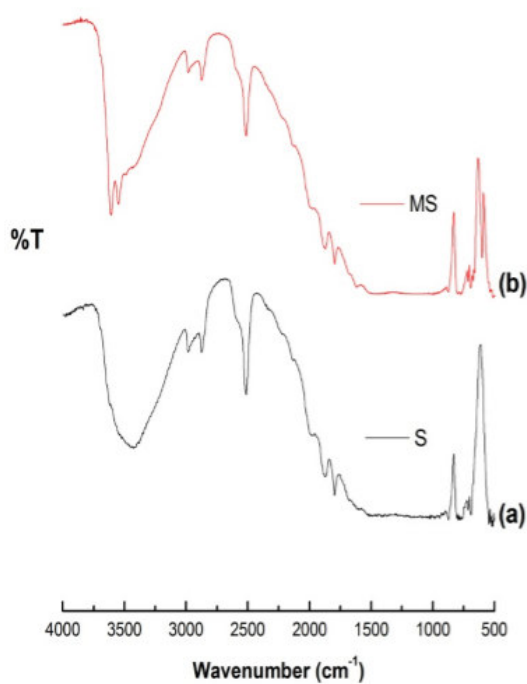


Figure 2. FT-IR spectra of sand (a) and modified sand (b).

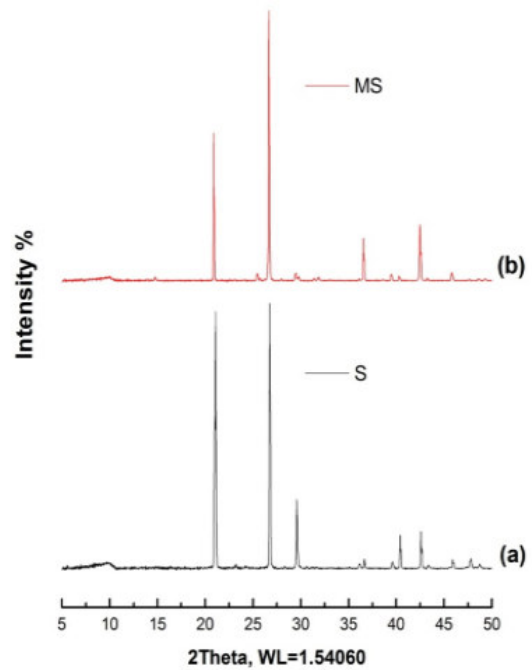
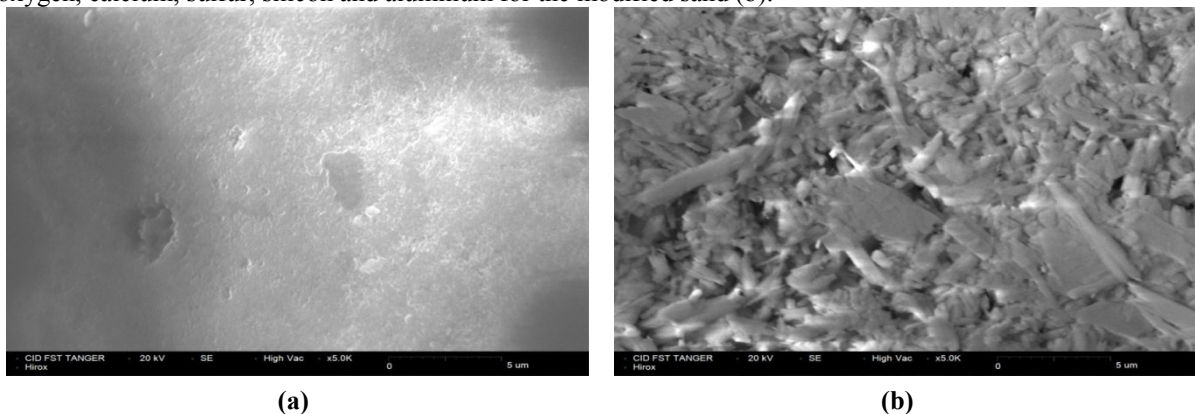


Figure 3. XRD diffractograms of sand (a) and modified sand (b).

The diffractograms of the sand (S) and the modified sand (MS) are indicated in Figure 3. The sand (S) has characteristic peaks in $2\theta=21^\circ$; 26.8° ; 29.6° ; 40.5° and 42.8° representing the crystalline structure of quartz, on the other hand modified sand (MS) shows characteristic peaks in $2\theta=21^\circ$; 26.8° ; 36.7° and 42.5° representing the crystalline structure of quartz and silicalite ($\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}(\text{SO}_4)$) due to the modification with sulfuric acid H_2SO_4 .

Figure 4 represent the SEM micrographs of sand (S) and modified sand (MS). We can notice the smooth morphology of the sand (a). On the contrary, at the modified sand level (b) a porous morphology appears caused by the chemical modification. The elemental analysis by energy dispersive X-ray analysis (EDXA) on both samples (Figure 5), sand (S) and modified sand (MS), revealed the presence of elements such as oxygen, carbon, silicon, calcium, fluorine, sodium, aluminum and magnesium for the sand (a), and the presence of oxygen, calcium, sulfur, silicon and aluminum for the modified sand (b).



(a) (b)
Figure 4. SEM micrographs of sand (a) and modified sand (b).

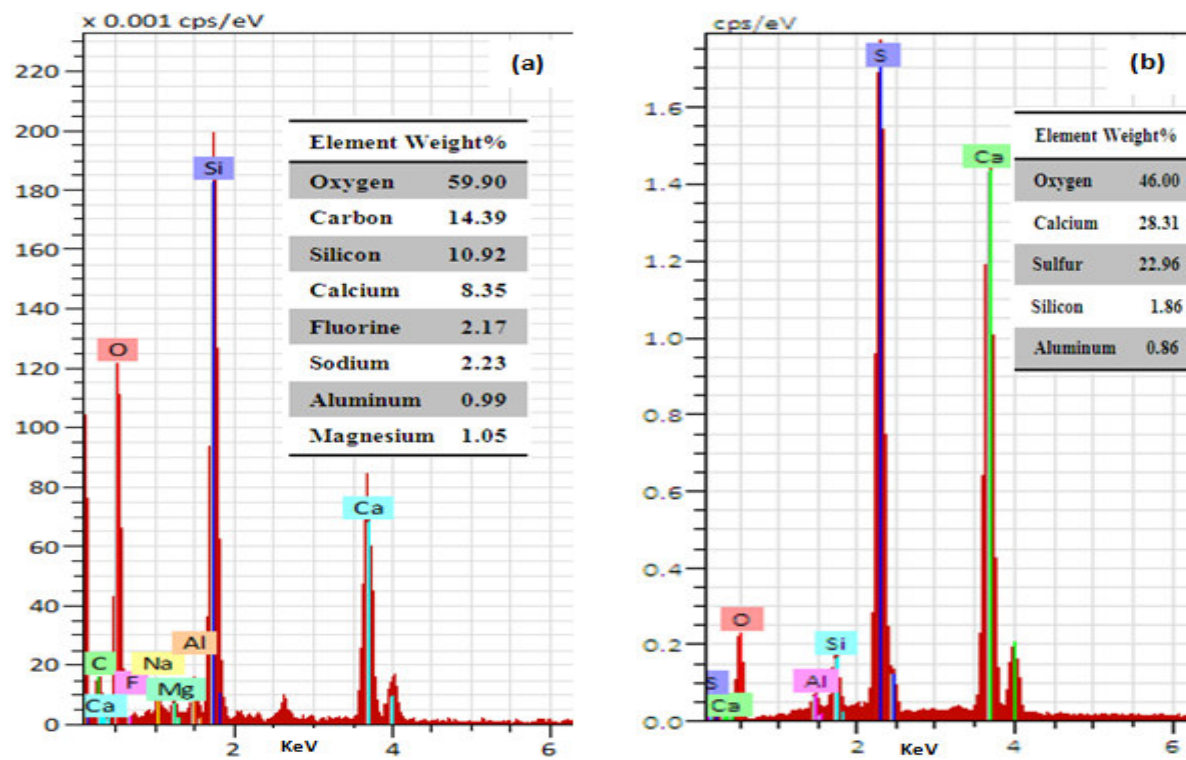


Figure 5. EDXA diffractograms of the sand (a) and the modified sand (b).

3.2. Effect of operational parameters

3.2.1. Effect of pH

The pH controls the surface charge and surface properties of the adsorbent surface as well as degree of ionization. It represents a major part in the removal of anionic dyes from water and industrial wastewater. Figure 6 presents the variation of the adsorption capacity in function of the pH of the dye solution.

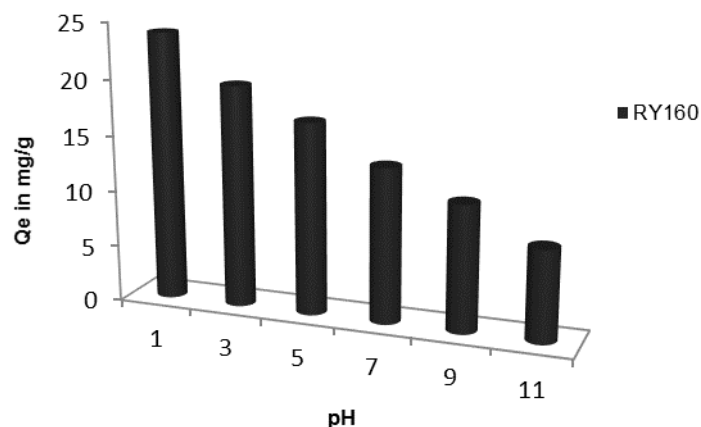


Figure 6. The effect of pH on the adsorption of RY 160 onto the modified sand (MS). (Time=90 min; Temperature=24°C, Initial dye concentration =50mg/l; Adsorbent mass=70mg; Stirring=150 rpm).

According to the Figure 6, the maximum adsorption capacity occurred at pH 1 due to the neutralization of the OH^- groups by the hydrogen ions and favors the adsorption of reactive yellow 160 (RY160). At higher pH, the presence of larger number of OH^- hinders the retention of RY 160 because of the increase in negatively charged sites which create an electrostatic repulsion and a competition between the OH^- and the active sites of the dyes (R-SO_3^-).

3.2.2. Effect of adsorbent dose

The effect of adsorbent dose was studied by using different amounts of modified sand (MS) from 10 mg to 260 mg for the same volume of the dye solution and the same experimental conditions. Figure 7 discuss the removal rate (R%) in function of the adsorbent mass. The removal rate (R%) increase with increasing the adsorbent amount until reaching the equilibrium state, it's can be clarified by the increase in the adsorbent specific surface area and consequently more active sites are available for the adsorption of the dye. At 160 mg/30 ml of modified

sand dosage, the removal rate of RY 160 was found to be 92.6% and this dose was taken as the optimal adsorbent dose.

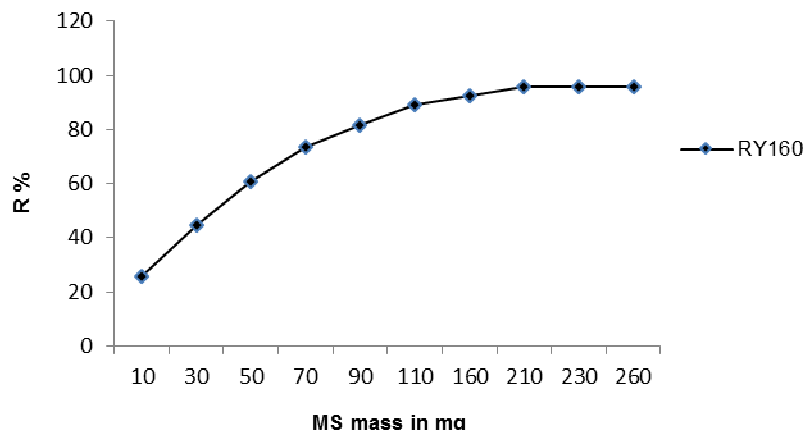


Figure 7. Effect of adsorbent amount (MS) on the adsorption of dye reactive yellow 160 (RY160). (Time=90 min; Temperature=24°C, Initial dye concentration =50mg/l; Stirring=150 rpm and pH~7).

3.2.3. Effect of initial dye concentration

The effect of initial dye concentration was evaluated by varying the initial concentration of RY 160 from 10 mg/l to 300mg/l under identical operating conditions. Results are presented in Figure 8. The initial dye concentration of the solution provides the necessary driving force to overcome the mass transfer resistance for the adsorbate between the solution and solid phases. Rising the initial dye concentration conduct to the rise up of the adsorption capacity due to the driving force of the concentration gradient. The optimal initial dye concentration for the removal of reactive yellow 160 (RY160) by modified sand (MS) was in the range of 150 mg/l to 200 mg/l (Figure 8).

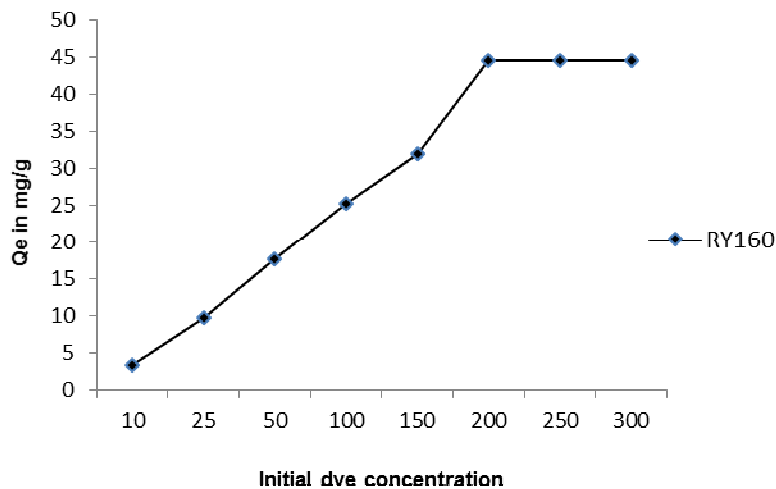


Figure 8. Effect of initial dye concentration on the adsorption of reactive yellow 160 (RY160) onto modified sand (MS). (Time=90 min; Temperature=24°C, Adsorbent mass=70mg; Stirring=150 rpm and pH~7).

3.2.4. Effect of contact time

The effect of contact time on the adsorption of RY 160 by modified sand (MS) is crucial to settle the optimal contact time affined to the saturation state. The optimal contact time proportional to the adsorption balance is 120 min (Figure 9).

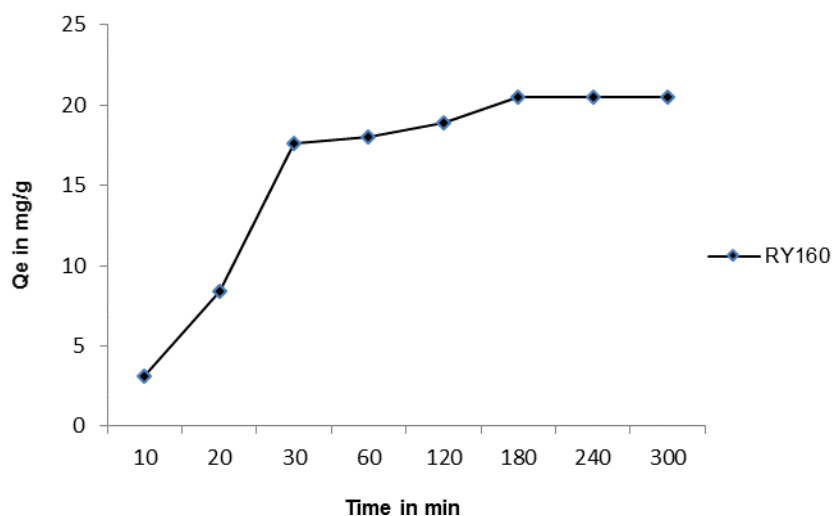


Figure 9. Effect of contact time on the adsorption of reactive yellow 160 (RY160) onto the modified sand (MS). (Temperature=24°C, Initial dye concentration =50mg/l, Adsorbent mass=70mg; Stirring=150 rpm and pH~7).

3.2.5. Effect of temperature

In order to understand the adsorption process and the different phenomena which take a place during the dye fixation on the modified sand surface, it's necessary to define the optimal temperature for the adsorption process. The temperature has a major effect on the solution viscosity and consequently affects the adsorption capacity. Figure 10 shows the evolution of the adsorption capacity versus the temperature, it's quite clear that the increase in temperature adversely affects the removal of dyes, the optimal temperature for the removal of reactive yellow 160 (RY160) by the modified sand (MS) is equal to 25°C (Figure 10).

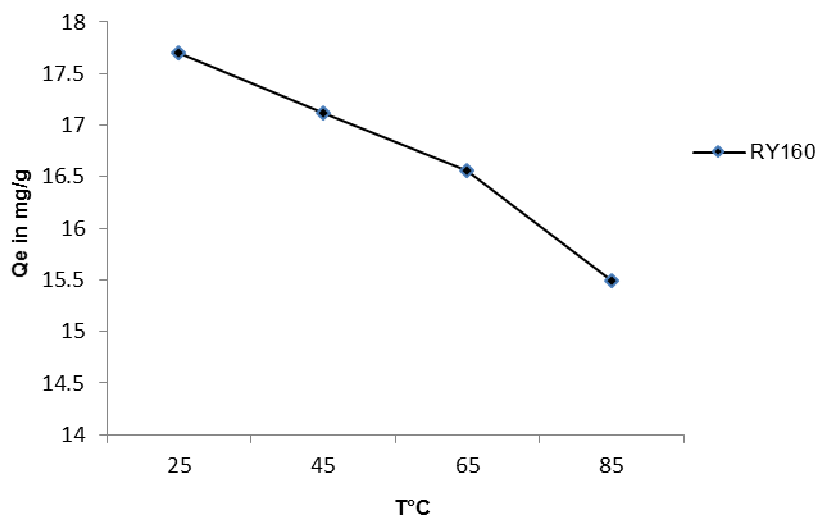


Figure 10. Effect of temperature on the adsorption of reactive yellow 160 (RY160) onto modified sand (MS). (Time=90 min, Initial dye concentration =50mg/l, Adsorbent mass=70mg; Stirring=150 rpm and pH~7)

3.3. Adsorption isotherm models

To model our adsorption process we must examine the different isotherms and select the model which represents the highest correlation coefficient, each isotherm represents a hypothesis which describes the adsorption process.

- Langmuir model [15, 16] is valid for a monolayer sorption with a homogeneous distribution of the sorption sites and sorption energies (uniform adsorption on the surface). Dimensionless constant called equilibrium parameter R_L [17] represents the main characteristics of Langmuir isotherm. The linearized expression of Langmuir model is given by the equation (3) and the equation (4) represents the equilibrium parameter R_L :

$$q_e = Q_0 K_L C_e / (1 + K_L C_e) \quad (3)$$

$$R_L = 1 / (1 + K_L C_e) \quad (4)$$

The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Where q_e , C_e , Q_0 and K_L are the amount of solute adsorbed at equilibrium (mg/g), the concentration of adsorbate at equilibrium (mg/l), maximum adsorption capacity (mg/g) and Langmuir constant (L/mg), respectively. (Figure 11, (a)).

- The Freundlich model [18] is based on the hypothesis of energy surface heterogeneity and the adsorption is not limited to the formation of a monolayer with a non-uniform distribution of adsorption heat on the adsorbent surface, the empirical equation of this model is presented in the form :

$$\ln Q_e = \ln K_f + \ln C_e / n_f \quad (5)$$

With K_f is the relative adsorption capacity of the adsorbent and n_f is the dependence degree of adsorption on the adsorbate equilibrium concentration (Figure 11, (b)).

- Temkin model assumes that the adsorption energy of the molecules is reduced with the coverage ratio of the surface [19]. The linear transform is given by the equation (6):

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (6)$$

$$B_1 = RT / b$$

Where

K_T is the Temkin isotherm equilibrium binding constant (l/g), B_1 is the constant related to heat of sorption (J/mol), b is the Temkin isotherm constant, R and T are the universal gas constant (8.314 J/mol/K) and the absolute temperature (K), respectively. (Figure 11, (c)).

- Dubinin–Radushkevich (DRK) isotherm [18] is basically used to formulate the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The empirical form is given by the equation (7). The DRK isotherm constant ε is given by the equation (8). This model used mostly to differentiate between physical and chemical adsorption of metal ions with its mean free energy E per molecule of adsorbate, calculated by the relation (9).

$$q_e = (q_s) \exp(-K_{ad} \varepsilon^2) \quad (7)$$

$$\ln q_e = \ln(q_s) - (K_{ad} \varepsilon^2) \quad (7)$$

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (8)$$

$$E = \left[\frac{1}{\sqrt{2B_{DR}}} \right] \quad (9)$$

Where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g); q_s is the theoretical isotherm saturation capacity (mg/g); K_{ad} and B_{DR} are the DRK isotherm constant (mol^2/kJ^2) and ε is the DRK isotherm constant. R , T and C_e indicates the gas constant (8.314J/mol. K), absolute temperature (K) and adsorbate equilibrium concentration (mg/l), respectively. (Figure 11, (d)).

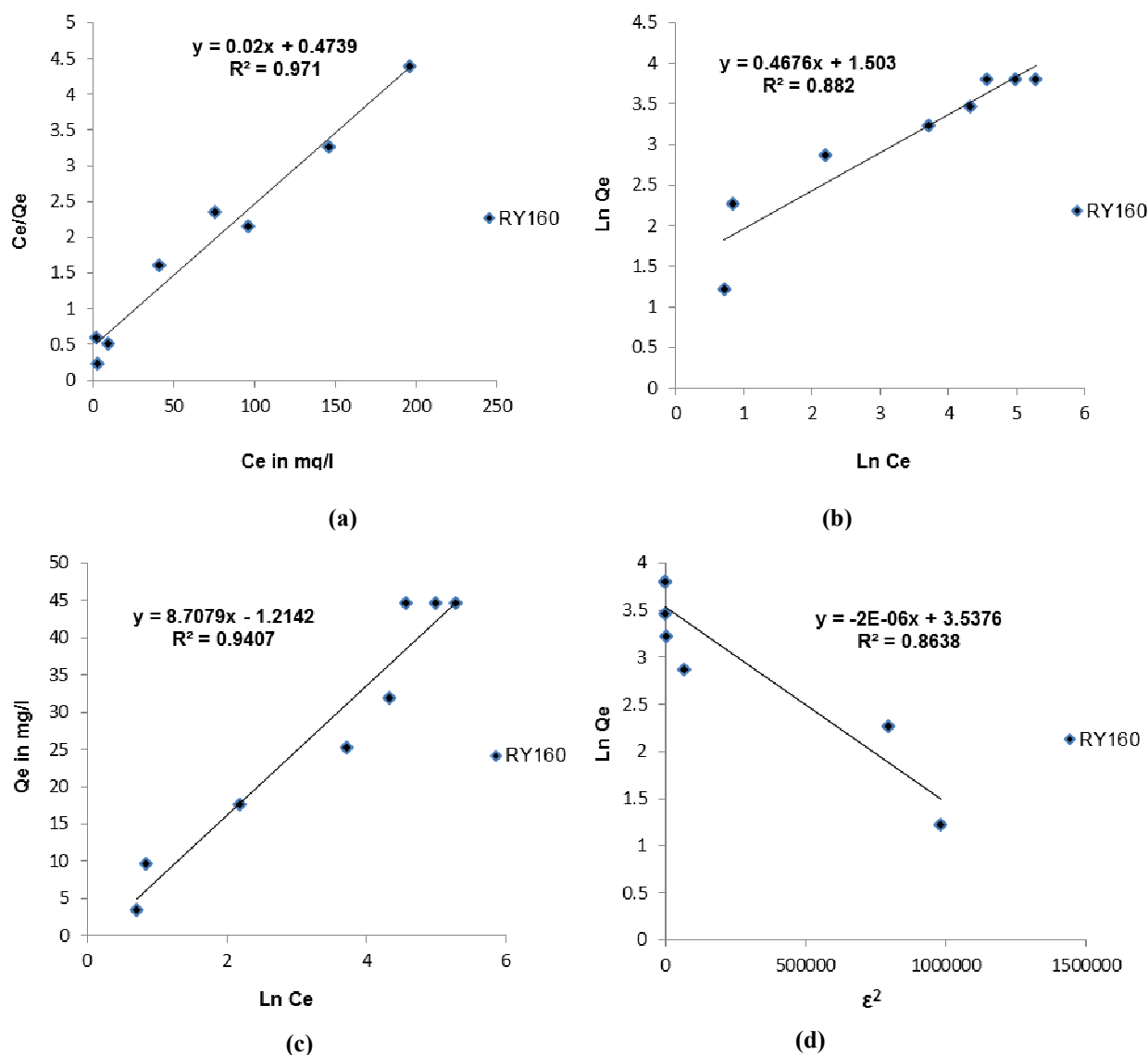


Figure 11. Isotherms plot for the adsorption of RY160 onto MS. Langmuir isotherm (a), Freundlich isotherm (b), Temkin isotherm (c) and Dubinin–Radushkevich isotherm (d). (Time=90 min; Temperature=24°C, Adsorbent mass=70mg; Stirring=150 rpm and pH~7).

Table 1. Adsorption isotherms parameters of RY 160 onto MS. (Time=90 min, Temperature=24°C, Adsorbent mass=70mg; Stirring=150 rpm and pH~7).

	R^2	Q_0 (mg.g ⁻¹)	K_L (L.mg ⁻¹)	R_L
Langmuir parameters	0.971	50	0.042202996	0.108-0.921
	R^2	K_f (mg.g ⁻¹)	n	
Freundlich parameters	0.882	4.495154325	2.138579983	
	R^2	b	K_T (L.g ⁻¹)	B_1 (J.mol ⁻¹)
Temkin parameters	0.9407	284.5200335	0.869848166	8.707900001
	R^2	K_{ad} (mol ² /kJ ²)	Q_s (mg.g ⁻¹)	E (KJ.mol ⁻¹)
Dubinin-Radushkevich parameters	0.8638	0.004957504	34.38429777	10.04276882

From the finding of Figure 11 and Table 1, it's quite clear that the Langmuir isotherm is the best fitting model with the highest correlation coefficient ($R^2=0.971$) compared with other models, Langmuir isotherm describe better the adsorption process with a monolayer sorption which means a homogeneous distribution of the sorption sites and sorption energies on the surface of our adsorbent.

3.4. Adsorption kinetic models

Chemical kinetics is the study of rates of chemical processes and factors that influence them in the attainment of

equilibrium in a reasonable amount of time. Various kinetics models are employed in this study to have an obvious perspective of the adsorption kinetics behavior of reactive yellow 160 (RY 160) onto the modified sand (MS).

3.4.1. Lagergren equation (The pseudo first order model)

For many adsorption processes, the pseudo-first order kinetics was found to be suitable for only the initial 20 to 30 minutes of interaction time and not for the whole range of contact time. K_1 and q_e can be evaluated from the graph of $\ln(q_e - q_t)$ versus t (Figure 12, (a)), if a straight line, and hence the adsorption follows a pseudo first order kinetics model, sorption kinetics model [19] is expressed by:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (10)$$

The linear form of the previous equation is:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (11)$$

Where q_e is the component amount adsorbed at equilibrium (mg/g), q_t is the component amount adsorbed at time t (mg/g) and k_1 is the equilibrium rate constant of pseudo first order kinetics (1/min) and t is the contact time (min).

3.4.2. Ho and Mckay equation (The pseudo second order model)

If the adsorption system follows a pseudo-second order kinetics, then the rate limiting step may be chemical adsorption involving valence forces through sharing or exchange of electrons between the adsorbent and sorbate, then a plot of t/q_t versus t (Figure 12, (b)) would be linear and k_2 and q_e can be determined from the intercept and gradient of the graph. One of the advantages of the pseudo-second order equation for estimating q_e values is its small sensitivity to the influence of random experimental errors and its applicability to a wider time interval mainly the entire adsorption process. Based on equilibrium adsorption, the pseudo-second-order kinetics equation [20] is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (12)$$

The linearization of the preceding equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (13)$$

Where k_2 : the reaction speed constant of second order adsorption in (g/mg/min), q_e : the component amount adsorbed at equilibrium in (mg/g), q_t : the component amount adsorbed at time t (mg/g), t : contact time in (min).

3.4.3. Morris Weber equation (The intraparticle diffusion model)

According to this model, the plot of uptake, q_t , versus the square root of time ($t^{1/2}$) (Figure 12, (c)) should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate-controlling step [21]. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and this further show that the intraparticle diffusion is not the only rate-limiting step, but also other kinetics models may control the rate of adsorption, all of which may be operating simultaneously. Weber and Morris equation used to investigate the components molecules transporting possibility by the adsorbent particles. The intraparticle diffusion model [22] is given by the equation (14), this model contains a parameter C presenting the boundary layer thickness, the value of C gives an idea about the boundary layer thickness, as more the ordinate at the origin value is bigger, the effect of the boundary layer is more significant.

$$q_t = k_i t^{1/2} + C \quad (14)$$

q_t is the amount adsorbed at time t (mg/g), K_i is the intraparticle diffusion constant (mg/g.min^{1/2}), t is contact time in (min) and C is the boundary layer thickness obtained by the intersection of the line with the Y-axis.

3.4.4. Elovich equation

Elovich equation is also used successfully to describe second order kinetics assuming that the actual solid surfaces are energetically heterogeneous, but the equation does not propose any definite mechanism for adsorbate-adsorbent. It has extensively been accepted that the chemisorptions process can be described by this semi-empirical equation [23]. The linear form of this equation [24] is given by:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \ln(t) \quad (15)$$

Where α and β are the initial adsorption speed (mg/g.min) and the desorption constant (g/mg), respectively. Tracing $q_t = f(\ln(t))$ (Figure 12, (d)), the values of α and β can be defined.

According to the results from Figure 12 and Table 2, we can conclude that the best fitting model is the Pseudo-second order model which represents the higher correlation coefficient $R^2 = 0.9769$ for the adsorption of reactive

yellow 160 (RY160) onto the modified sand (MS).

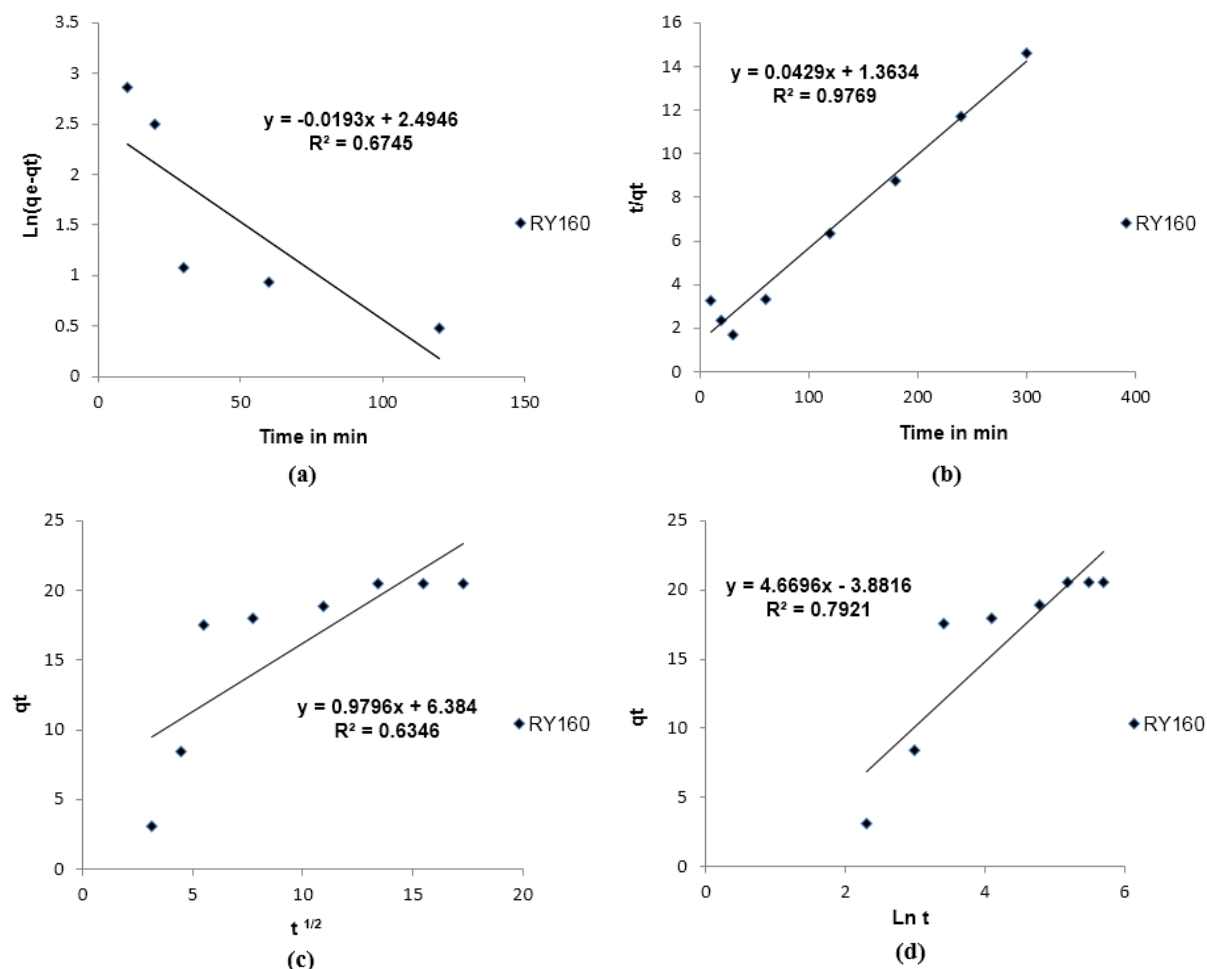


Figure 12. Kinetics plot for the adsorption of RY160 onto MS. The pseudo first order model (a), pseudo second order model (b), intraparticle diffusion model (c) and Elovich model (d). (Time=90 min, Temperature=24°C, Adsorbent mass=70mg; Stirring=150 rpm and pH~7).

Table 2. Kinetics constants for the adsorption of RY160 onto MS. (Time=90 min, Temperature=24°C, Adsorbent mass=70mg; Stirring=150 rpm and pH~7).

$Q_{e,exp} = 20.52 \text{ (mg.g}^{-1}\text{)}$	R^2	$Q_{e,cal} \text{ (mg.g}^{-1}\text{)}$	$K_1 \text{ (min}^{-1}\text{)}$
Pseudo first order rate constants	0.6745	12.11688579	0.0193
	R^2	$Q_{e,cal} \text{ (mg.g}^{-1}\text{)}$	$K_2 \text{ (g.mg}^{-1}.\text{min}^{-1}\text{)}$
Pseudo-second order rate constants	0.9769	23.31002331	0.001349867
	R^2	$C \text{ (mg.g}^{-1}\text{)}$	$K_{int} \text{ (mg.g}^{-1}.\text{min}^{-1/2}\text{)}$
Intra-particle diffusion constants	0.6346	6.384	0.9796
	R^2	$\alpha \text{ (mg.g}^{-1}.\text{min}^{-1}\text{)}$	$\beta \text{ (g.mg}^{-1}\text{)}$
Elovich constants	0.7921	2.033634296	0.214151105

3.5. Thermodynamic study

The importance of the thermodynamic study is in the detection of the various parameters like the standard enthalpy ΔH° (kJ/mol), standard entropy ΔS° (J/mol.K) and the standard free energy ΔG° (kJ/mol) which gives a clear definition of the adsorption process during the practical application [25].

Equations (16), (17) and (18) are used to define the thermodynamic parameters [18].

$$\ln K_d = \Delta S^\circ / R - \Delta H^\circ / RT \quad (16) \quad K_d = (C_0 - C_e) * V / (C_e * m) \quad (17) \quad \Delta G^\circ = -RT \ln K_d \quad (18)$$

With T is the temperature in Kelvin, R is the gas constant (8.314 J/mol.K) and K_d is the distribution coefficient calculated by the equation (17), C_0 is the initial dye concentration in solution (mg/l), C_e is the equilibrium concentration (mg/l), m is the adsorbent mass (g), V is the solution volume and Q_e is the quantity adsorbed per

unit adsorbent mass at equilibrium (mg/g).

The plot of $\text{Ln}K_d$ as a function of $1/T$ allows us to determine ΔS° and ΔH° (Figure 13). The values of the different thermodynamic parameters are shown in Table 3.

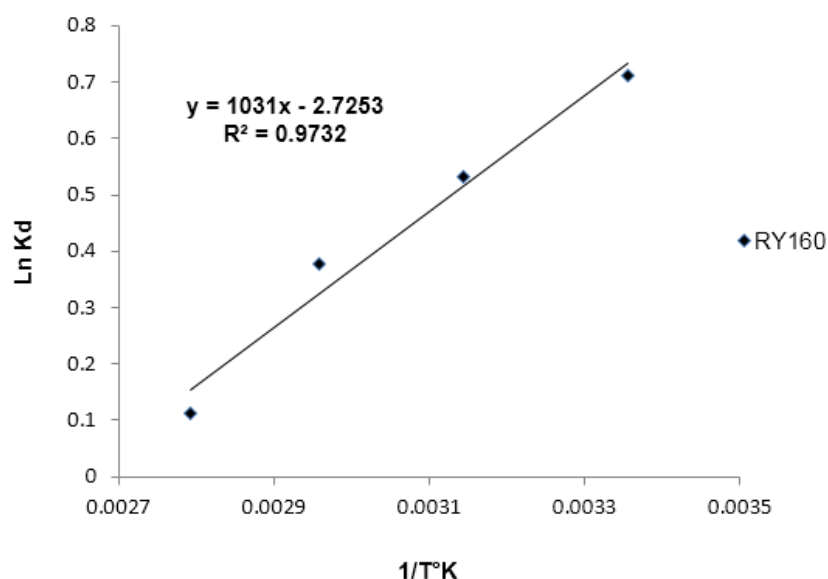


Figure 13. The plot of $\text{Ln}K_d$ as a function of $1/T$ for the calculation of the thermodynamic parameters ΔS° and ΔH° of dye (RY160) adsorption onto modified sand (MS). (Time=90 min, Initial dye concentration =50mg/l, Adsorbent mass=70mg; Stirring=150 rpm and pH~7)

Table 3. Thermodynamic parameters ΔH° , ΔS° and ΔG° relating to the reactive yellow 160 adsorption onto modified sand (MS). (Time=90 min, Initial dye concentration =50mg/l, Adsorbent mass=70mg; Stirring=150 rpm and pH~7)

Temperature (°K)	ΔG° (kJ.mol ⁻¹)	ΔH° (kJ.mol ⁻¹)	ΔS° (J.mol ⁻¹ .K ⁻¹)
298	-1.76006262	-8.571734	-22.6581442
318	-1.4057237		
338	-1.0573553		
358	-0.33672206		

From the negative value of the standard entropy ΔS° we can say that the adsorption is happening with an increase in the order to the solid-solution interface [26] and that the dye molecules distribution order on the adsorbent is important compared to that in the solution. The negative value of the standard enthalpy ΔH° indicates that the adsorption process is exothermic [18]. In general, the variation in the enthalpy due to chemisorption is about 40 to 120 kJ/mol [27]. It is more important than the enthalpy due to physisorption (<40kJ/mol) [27]. Numerically, it appears that the adsorption of reactive yellow 160 onto modified sand (MS) is of physical nature ($\Delta H^\circ = -8.571734$ kJ/mol). However, the pseudo-second order kinetics obtained is based on an adsorption capacity which rather provides for the validity of the chemisorption which could control the kinetics [28]; the adsorption phenomenon is mainly physical because of the low adsorption activation enthalpy [29]. Negative ΔG° values obtained at all temperatures (Table 3) indicated the feasibility and the spontaneous nature of RY160 adsorption onto MS [30,31].

4. Conclusion

From the results of this research paper we can conclude that the modified sand (MS) represents a logical choice for the treatment of the industrial wastewater charged with anionic dyes due to the simple process of modification, its economical viability and a removal rate of 92.6%. The optimal adsorbent mass is 160 mg/30 ml of modified sand dosage for a maximum removal rate of 92.6%.

- The acidic medium (pH=1) represents the best middle to achieve the maximum adsorption capacity.
- The optimal initial dye concentration for the removal of reactive yellow 160 (RY160) by modified sand (MS) was in the range of 150mg/l to 200 mg/l.
- The optimal contact time proportional to the adsorption balance is 120 min.
- At 25°C, we obtained the maximum adsorption capacity for the removal of RY 160 onto MS.
- Langmuir isotherm describes better the adsorption process with a monolayer sorption.
- The Pseudo-second order model is the best fitting model for this adsorption process.

- The analysis of the thermodynamic parameters suggested that the adsorption process is exothermic and spontaneous and basically physical because of the very low adsorption activation enthalpy.

Sand is a naturally available material and its modification (MS) might supply a non-toxic process for the removal of anionic toxic dyes and specially the reactive yellow 160 (RY160) from wastewater by adsorption process.

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