

Removal of Reactive Yellow 135 from Wastewater of Textile Industry onto Chitosan Extracted by Hydrothermo-Chemical Method.

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Abstract

The capabilities of chitosan for removing anionic dyes as reactive yellow 135 from wastewater of textile industry were examined. The chitosan was extracted from shrimp co-products "*Pandalus Borrealis*" by the hydrothermo-chemical method in two steps. The bio-adsorbent obtained was characterized by infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDXA). Operational parameters studied were pH, contact time, adsorbate and adsorbent concentrations with a removal rate percentage of 98% and a maximum adsorption capacity of 69.244 mg/g at pH 1.9. Adsorption kinetics for the removal of reactive yellow 135 onto chitosan followed pseudo-second-order kinetics model. The examination of the isotherm data showed that the Freundlich isotherm model is the best fitting model.

Keywords : Chitosan, Reactive Yellow 135 (RY135), Adsorption, Wastewater treatment, Industrial dyes, Textile industry.

1. Introduction

Synthetic dyes [1], which are extensively used in the textile industry [1], represent a major environmental problem. Several dyes and their break-down products are toxic for living organisms because dyes are not easily degradable, undergo transformations, and have great environmental, public health, and economic impacts [2] and are generally not removed from wastewater by conventional wastewater treatment systems; this makes it difficult to remove dyes from effluent [3,4].

The chitosan presents itself as an economically viable alternative [5] to effluents treatment by the adsorption technique. It is a biodegradable glucosamine polymer [6] produced by deacetylation of chitin [7] from crustacean's shells [8].

Conventional technologies treat dyes effluents like membrane separation, electrodeposition, ion exchange, chemical precipitation, and solvent extraction are used a lot in the industry but due to the high operating cost and inefficiency in removing trace quantities of dyes from waste streams create a huge problem for dyes industry. On the contrary, adsorption is an effective and economical method among the physicochemical treatments [9].

The objective of this research is to determine the feasibility of using chitosan produced from northern shrimp "*Pandalus Borealis*" by the hydrothermo-chemical method in the laboratory scale for the removal of anionic dyes as reactive yellow 135 (RY 135) from the wastewater of textile industry.

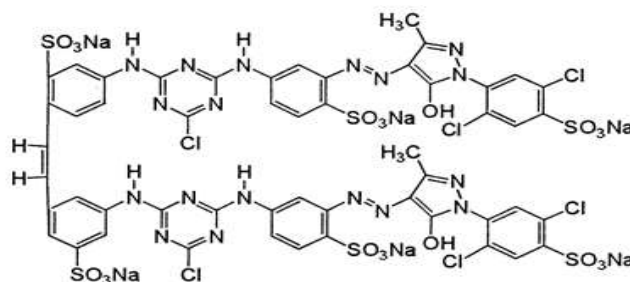


Figure 1. Chemical structure of reactive yellow 135 (Azo class).

2. Materials and methods

2.1. Preparation of bio-adsorbent

Chitosan with a deacetylation degree of 85% was extracted by Hydrothermo-Chemical way [10] starting from northern prawns "*Pandalus Borealis*". Sodium hydroxide NaOH, hydrochloric acid HCL were from Segma-Aldrich and all other chemicals used were of analytical quality.

The Hydrothermo-Chemical method [10] followed to the chitosan extraction based on two parts a demineralization in acidic medium HCl 2M for 2.5 h at a temperature of 50°C and a simultaneous deproteination/deacetylation in basic medium NaOH 12.5M for 2 h at a temperature of 110°C with a solid/liquid ratio of 1:10 (dry carapace weight/volume of diluted solution), the optimal experimental conditions are quoted in Table 1.

Table 1. Optimal experimental conditions to extract chitosan by the Hydrothermo-Chemical method.

Step	Temperature (°C)	Digestive Solution	Time (h)	DD(%)
Demineralization	50	2 M HCl	2.5	-
Deproteination/Deacetylation	110	12.5 M NaOH	2.0	90

To characterize our bio-adsorbent and determine the functional groups we used an infra-red spectrophotometer of type JASCO FT/IR-410 on potassium bromide pastilles KBr with 2% of chitosan extracted by Hydrothermo-Chemical way in the laboratory scale. The obtained spectrum was recorded between 4000 cm^{-1} and 400 cm^{-1} . Then we used the X-ray diffraction type Bruker D8 Advance ECO to know the structure of our chitosan, the Scanning Electron Microscope (SEM) gives us an idea about the morphology surface of our adsorbent equipped with an energy dispersive X-ray analysis EDXA allows a qualitative detection and the localization of the elements present in the bio-adsorbent.

In order to define the adsorbed quantities measurements of the reactive yellow 135 removal by the chitosan, we used a Spectrophotometer UV of the type JASCO V-360 with a preliminary calibration of the instrument spectrophotometer with a maximum analysis wavelength λ_{max} : 421 nm.

2.2. Batch adsorption experiments

Several parameters are studied to define the optimal conditions which influence the adsorption process of reactive yellow 135 onto chitosan. The optimal adsorbent amount was specified by mixing various quantities of chitosan from 1.5 mg to 100mg with 30ml of dye solution for 90 min in a temperature of 24°C, with an initial dye concentration of 50mg/l and neutral pH under continuous stirring at 150 rpm. The pH of the solution was adjusted from 1.9 to 11.25 by using NaOH and HCL with an adsorbent mass of 20 mg, initial dye concentration of 50 mg/l, with a temperature of 24°C under continuous stirring at 150 rpm for 90 min to study the optimal pH which gives the maximum adsorption capacity. The effect of initial dye concentration (10mg/l to 350mg/l) was conducted by using 20mg as an adsorbent dose under continuous stirring at 150 rpm with a temperature of 24°C for 90min at a neutral pH. To establish the adsorption kinetics during the adsorption process, the absorbance variations were given at different time intervals between 10min to 360min with an adsorbent mass of 20 mg, initial dye concentration of 50mg/l, with a continuous stirring at 150 rpm in a temperature of 24°C at neutral pH. After centrifugation, the final concentrations of the dye are given, the amount adsorbed (q_e) and the removal rate percentage (R%) of the dye are calculated by equations (1) and (2):

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

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

Where 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 the bio-adsorbent

In order to determine the functional groups of chitosan, FT-IR spectroscopy was used in the range of 4000 cm^{-1} and 400 cm^{-1} . The major bands of chitosan prepared (Figure 2) by the hydrothermo-chemical method in the laboratory scale are: 3465 cm^{-1} (Elongation of the N-H and O-H bonds), 2881 cm^{-1} (Stretching vibration of C-H bonds in the CH_2 or CH_3 groups), 1376 cm^{-1} (The C-H bond deformation vibration in the CH_3 group), 1423 cm^{-1} and 1446 cm^{-1} (The C-H bond deformation vibration in the CH_2 group), 1643 cm^{-1} (Valence vibration of C=O (amide 1)), 1562 cm^{-1} (Deformation Vibration of connection N-H (amide 2)), 1315 cm^{-1} (Valence vibration of the connection C-N), 1076 cm^{-1} and 1149 cm^{-1} (Valence vibration of connection C-O-C), and finally 1029 cm^{-1} (Valence vibration of connection C-O-H) [10].

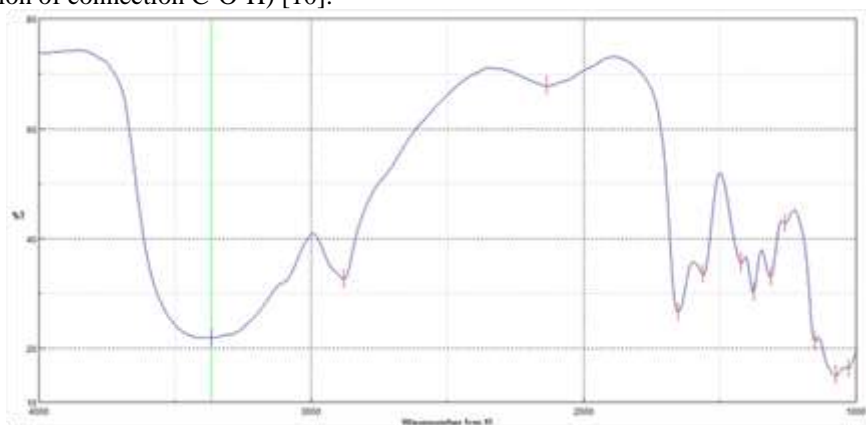


Figure 2. Infra-red spectrum of the chitosan extracted by hydrothermo-chemical method from shrimp "*Pandalus Borealis*" co-products.

Figure 3 represents the X-Ray diffractograms of Chitosan (Cs). The bio-adsorbent (Cs) shows characteristic peaks in $2\theta=9.2^\circ$; 12.5° ; 19.8° ; 26.03° and 39.4° that caused by diffraction from (010) and (100) planes and (020) planes of the crystalline lattice [11]. SEM micrograph of chitosan is presented in Figure 4 with a smooth morphology without any porous structure.

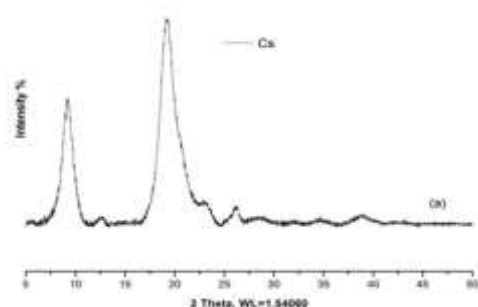


Figure 3. X-ray diffractogram of the chitosan (Cs) (a).

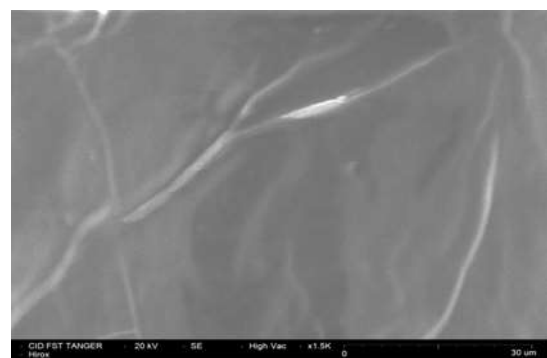


Figure 4. SEM micrograph of chitosan (Cs).

Figure 5 illustrate the quantitative elemental composition of chitosan (a) which proved the presence of elements with different element weight percentages such as carbon 49.99%, oxygen 39.36%, nitrogen 10.65%.

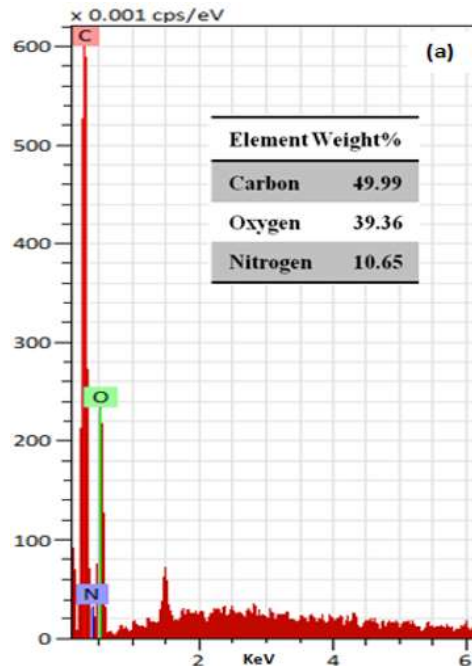


Figure 5. EDXA diffractogram of chitosan (a) with different element weight percentages (a).

3.2. Effect of operational parameters

3.2.1. Effect of pH

Figure 6 presents the variation of the adsorption capacity in function of the pH of the dye solution (RY135), the chitosan surface contains amine groups, -NH_2 , which is easily protonated to form -NH_3^+ , in acidic solutions which lead to a high electrostatic attraction between the positively charged sites of the chitosan (R-NH_3^+) and the negative active sites of the dye reactive yellow 135 (R-SO_3^-). Figure 6 shows that the maximum adsorption capacity 69.24 mg/g takes place with a very acidic medium (pH 1.9).

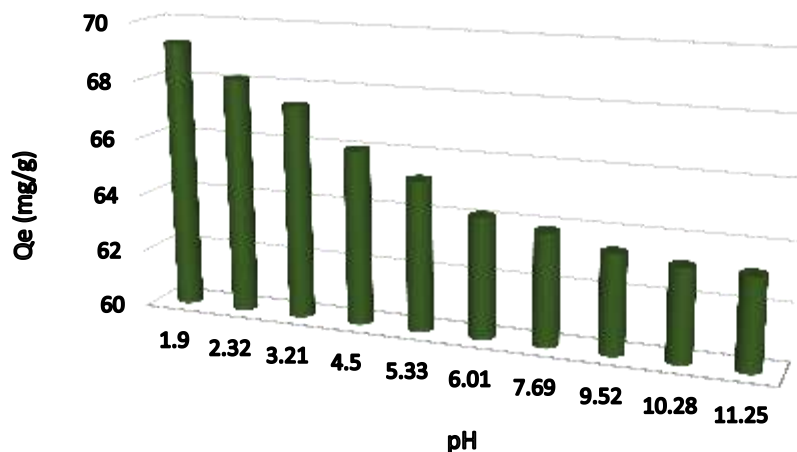


Figure 6. The effect of pH on the adsorption of RY 135 onto the chitosan (Cs). (Time=90 min; Temperature=24°C, Initial dye concentration =50mg/l; Adsorbent mass=20mg; Stirring=150 rpm).

3.2.2. Effect of adsorbent dose

The effect of adsorbent amount used for the elimination of dye (RY 135) onto chitosan (Cs) is presented in Figure 7. The removal rate percentage (R%) increases with the increase in the adsorbent amount until reaching the equilibrium state due to the expansion of the adsorbent specific surface and the availability of several sites of adsorption. The optimal adsorbent amounts to attain the maximum elimination rate 98.5% for the reactive yellow 135 onto chitosan is 70 mg.

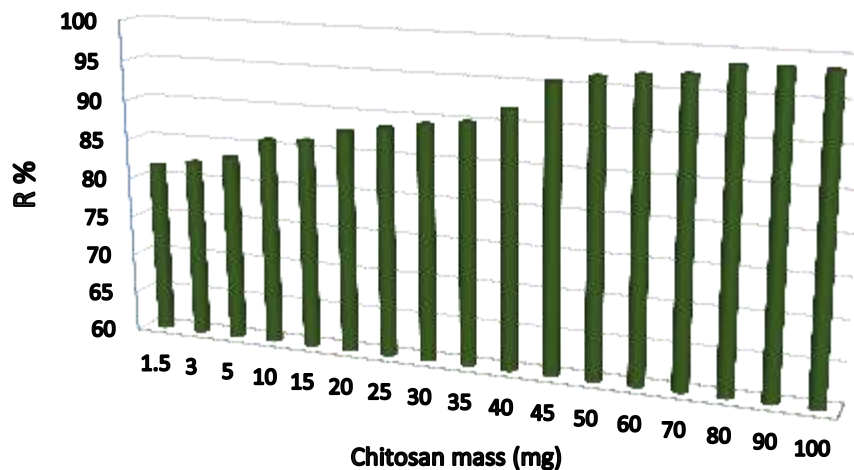


Figure 7. Effect of adsorbent amount (C_s) on the adsorption of dye reactive yellow 135 (RY135). (Time=90 min; Temperature=24°C, Initial dye concentration =50mg/l; Stirring=150 rpm and pH~7).

3.2.3. Effect of initial dye concentration

The effect of initial dye concentration was assessed by varying the initial concentration of RY 135 from 10mg/l to 350mg/l under uniform operating conditions. Figure 8 presents the evolution of the adsorption capacity versus the initial dye concentration, we can observe from this figure that the adsorption capacity rises up with the rising of the initial dye concentration until arrived at a constant value of 400mg/g, this elevation caused by the increase in the motive force of the concentration gradient [12]. The optimal initial dye concentration for the removal of reactive yellow 135 onto chitosan is 300mg/l.

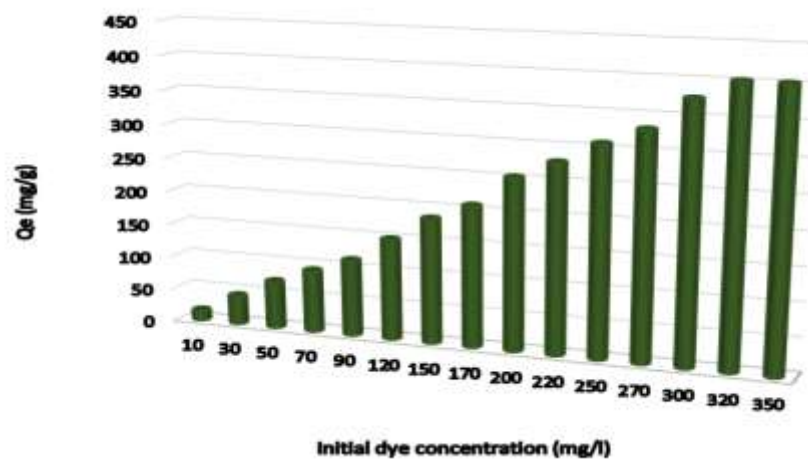


Figure 8. Effect of initial dye concentration on the adsorption of reactive yellow 135 (RY135) onto chitosan (C_s). (Time=90 min; Temperature=24°C, Adsorbent mass=20mg; Stirring=150 rpm and pH~7).

3.2.4. Effect of contact time

To define the optimal contact time related to the maximum adsorption capacity of reactive yellow 135 onto chitosan, a function of adsorption capacity versus contact time from 10min to 360min is plotted (Figure 9). The optimal contact time commensurate to the adsorption balance is 240min.

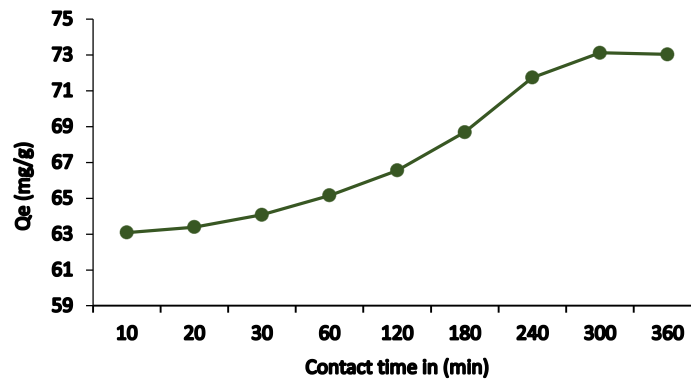


Figure 9. Effect of contact time on the adsorption of reactive yellow 135 (RY135) onto chitosan (Cs). (Temperature=24°C, Initial dye concentration =50mg/l, Adsorbent mass=20mg; Stirring=150 rpm and pH~7).

3.3. Adsorption isotherm models

Adsorption isotherm models are decisive to describe and understand several phenomena during the adsorption process of reactive yellow 135 (RY135) onto chitosan (Cs). The most frequent models used in several research papers are Langmuir and Freundlich isotherm models, each model represents a hypothesis. The uniform adsorption on the adsorbent surface is presented by the Langmuir model [13, 14] which is adequate for a monolayer sorption with a homogeneous distribution of the sorption sites and sorption energies, expressed by a linear equation (3) and a specific dimensionless constant (4) called equilibrium parameter R_L [15].

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \quad (3) \qquad R_L = \frac{1}{1 + K_L C_e} \quad (4)$$

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 10, (a))

The hypothesis of energy surface heterogeneity is offered by the Freundlich model expressed by equation (5) which clarified that the adsorption is not limited to the formation of a monolayer with a non-uniform distribution of adsorption heat on the adsorbent surface [16].

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

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 10, (b)).

To investigate the applicability of Langmuir, Freundlich isotherm models for the adsorption of reactive yellow 135 onto chitosan a linear plot of C_e/Q_e against C_e , $\ln Q_e$ versus $\ln C_e$ are plotted respectively and the values of Q_0 , K_L , R_L , K_f , n_f and R^2 (correlation coefficient values of all isotherm models) are enumerated in Table 2.

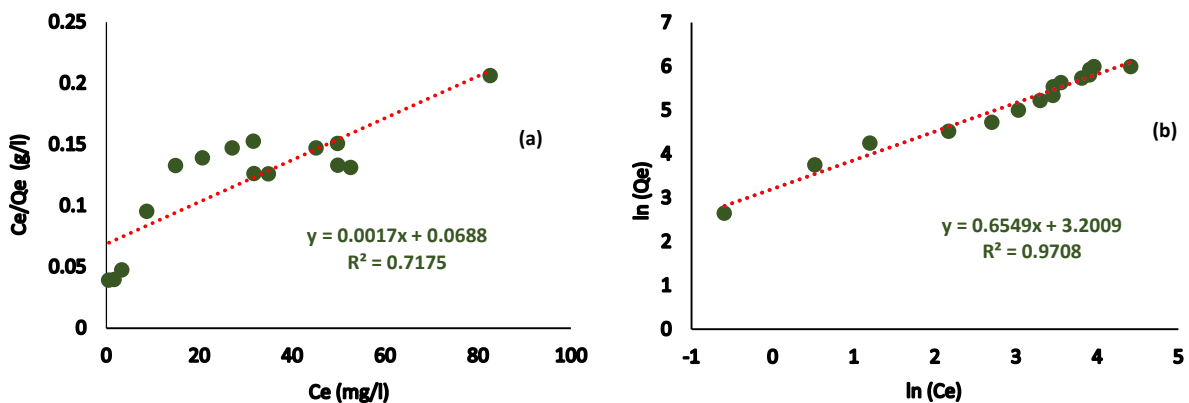


Figure 10. Isotherms plot for the adsorption of RY135 onto Cs. Langmuir isotherm (a), Freundlich isotherm (b). (Time=90 min; Temperature=24°C, Adsorbent mass=20mg; Stirring=150 rpm and pH~7).

Table 2. Adsorption isotherms parameters of RY 135 onto Cs. (Time=90 min, Temperature=24°C, Adsorbent mass=20mg; Stirring=150 rpm and pH~7).

	R^2	$Q_0(\text{mg}\cdot\text{g}^{-1})$	$K_L(\text{L}\cdot\text{mg}^{-1})$	R_L
Langmuir parameters	0.717	588.235	0.025	0.329-0.986
	R^2	$K_f(\text{mg}\cdot\text{g}^{-1})$	n_f	
Freundlich parameters	0.971	24.555	1.527	

From the results of Figure 10 and Table 2 we can conclude that the best fitting isotherm model is the Freundlich model due to the higher correlation coefficient $R^2=0.971$ which means that there is a heterogeneity of surface energy with a nonuniform distribution of the adsorption heat on surface and the adsorption of reactive yellow 135 onto chitosan is not limited to the formation of monolayer.

3.4. Adsorption kinetic models

To review the control mechanisms of the adsorption process, such as chemical reactions, controlling the diffusion and mass transfer, several kinetic models are applied to examine the experimental data. The pseudo first order and the pseudo second order kinetics models are employed to describe the various phenomena during the adsorption process of reactive yellow 135 (RY135) onto chitosan (Cs) to achieve the balance in a moderate time.

3.4.1. Lagergren equation (The pseudo first order model)

The pseudo first order model is generally used to describe the phenomena occurring during the first minutes of the adsorption process presented as follows [17]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (6)$$

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

After integration by applying conditions, $q_t=0$ at $t=0$, then equation (17) becomes:

$$q_t = q_e (1 - e^{-k_1 t}) \quad (7)$$

The linearization of the previous equation gives [18]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

One traces $\ln(q_e - q_t) = f(t)$, one obtains a line which gives k_1 and q_e (Figure 11, (a)).

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

Contrary to the pseudo first order model, the pseudo second order model is applicable to a broader time interval (generally the entire adsorption process). The pseudo-second-order model is given by the following expression [19, 20]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (9)$$

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

$$q_t = \left(\frac{k_2 q_e^2 t}{k_2 q_e t + 1} \right) \quad (10)$$

The linearization of the previous equation gives [19, 20]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (11)$$

One traces $t/q_t=f(t)$, one obtains a line which gives k_2 and q_e (Figure 11, (b)).

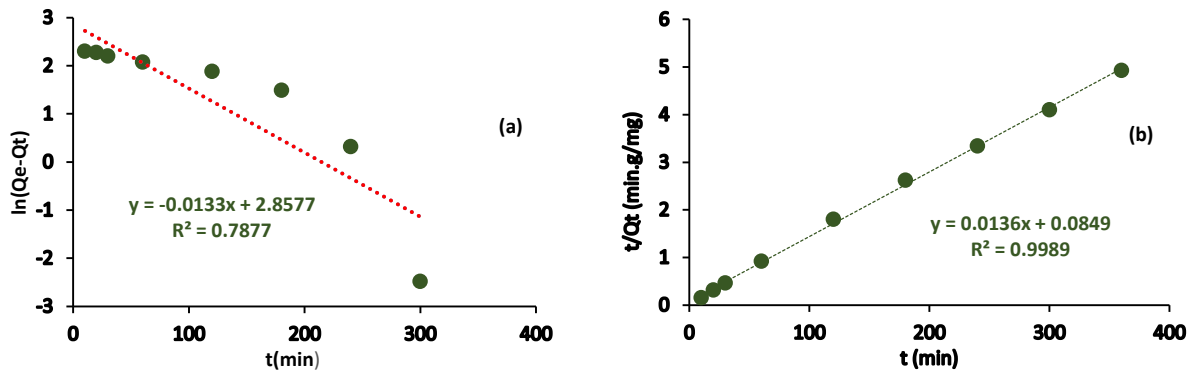


Figure 11. Kinetics plot for the adsorption of RY135 onto Cs. The pseudo first order model (a), pseudo second order model (b). (Time=90 min, Initial dye concentration =50mg/l, Temperature=24°C, Adsorbent mass=20mg; Stirring=150 rpm and pH~7).

Table 3. Kinetics constants for the adsorption of RY135 onto Cs. (Time=90 min, Initial dye concentration =50mg/l, Temperature=24°C, Adsorbent mass=20mg; Stirring=150 rpm and pH~7).

$Q_{e,exp} = 73.114 \text{ (mg.g}^{-1}\text{)}$	R^2	$Q_{e,cal} \text{ (mg.g}^{-1}\text{)}$	$K_1 \text{ (min}^{-1}\text{)}$
Pseudo first order rate constants			
	0.7877	17.421	0.0133
	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			
	0.9989	73.529	0.0022

According to the finding of Figure 11 and the Table 3, the best fitting kinetic model is the pseudo second order with the higher correlation factor $R^2=0.9989$. We can deduce that the pseudo second order model is the one that best described the adsorption process of reactive yellow 135 (RY135) onto chitosan (Cs), we also see that the adsorbed amount calculated $(Q_e)_{cal}=73.529 \text{ (mg/g)}$ by this model is closer to the quantity adsorbed experimentally $(Q_e)_{exp}=73.114 \text{ (mg/g)}$ which confirm the hypothesis of the pseudo second order kinetic model which say that the rate limiting step may be chemical adsorption involving valence forces through sharing or exchange of electrons between the adsorbent and sorbate.

4. Conclusion

Chitosan extracted by the hydrothermo-chemical method has demonstrated high efficiency in removing reactive yellow 135 (RY135) from wastewater of the textile industry with a maximum removal rate of 98.5% and a maximum adsorption capacity of 69.24 mg/g which took place with a very acidic medium (pH 1.9). The optimal initial dye concentration for the removal of reactive yellow 135 onto chitosan is 300mg/l with an optimal contact time of 240 min. The isotherm data shows that the Freundlich model represents the suitable isotherm model for the adsorption of (RY135) onto (Cs) which indicates that there is a heterogeneity of surface energy with a nonuniform distribution of the adsorption heat on surface and the adsorption is not limited to the formation of monolayer. From the kinetics data, we can conclude that the pseudo second order model described better the adsorption process and the rate limiting step may be chemical adsorption involving valence forces through sharing or exchange of electrons between the adsorbent (Cs) and sorbate (RY135).

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