



Cross-Linked Chitosan Terephthaldehyde for Removal of Congo red: Synthesis, Characterization, and Adsorption Studies

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Abstract

A cross-linked chitosan (denoted as TCCS) was synthesized by dissolving chitosan in acidic aqueous solution and addition of minimum amount of terephthaldehyde as cross-linker, the synthesized polymer was characterized by Fourier-transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). TCCS was used as an adsorbent to remove the organic dye congo red (CR) from aqueous solutions. The effects of contact time, pH, adsorbent weight, and initial dye concentration were studied. The results indicated the 0.02 g of TCCS can remove more than 98% of CR from 25 ml aqueous solution with 40 ppm solution after 60 min with no significant effect observed with changing the pH. Langmuir, Freundlich, and Temkin isotherm models were implemented to on the experimental data, the best fit was with Langmuir isotherm model, the correlation coefficient (R^2) value for this isotherm was (0.998), while for Freundlich, and Temkin isotherms the R^2 values were 0.8824 and 0.933 respectively. The results of the kinetic studies revealed that the adsorption of CR on TCCS is a pseudo-second order process, with R^2 value of 0.9982, and the calculated adsorption capacity (q_e) values for this model 49.26 mg/g, which is very close to the experimental result (49.04 mg/g). The thermodynamic parameters indicated that the adsorption of CR on TCCS is spontaneous with negative ΔG values, endothermic with positive ΔH and positive ΔS which indicates that the disorder of the CR molecules increases at the adsorbent-solution interface.

Keywords: Water Treatment; Adsorption; Congo Red; Chitosan; Terephthaldehyde. .

1. Introduction

Growth of the traditional textile industry in many developing countries, gradually increased year by year. During the dyeing process in the conventional textile industry, an amount of synthetic dyes remain which can permeate the fabric and they are with high resistance to oxidizing agents, biodegradation and photo-degradation treatment.[1] Since organic dyes are employed as coloring agents for textiles, cosmetics, and polymers, they are used in a wide range of industrial processes.[2]

Congo red is one of the most common synthetic dyes used in the textile industry. It is a group of benzidine-based anionic diazo dyes with high toxicity and irritant properties to eye and skin contact. At a high level of contamination, it could induce some respiratory problems and even could be a carcinogenic agent to humans. Consequently, Congo red removal from wastewater of the textile industry is a necessity in order to avoid environmental issues (Figure 1).[3]

In order to remove the dye contamination from wastewater, various technologies have been developed including filtration, coagulation, electrochemical

oxidation, chemical oxidation, membrane filtration, adsorption or biosorption, reverse osmosis, ozonation, microbiological treatment and many other processes.[4-7]

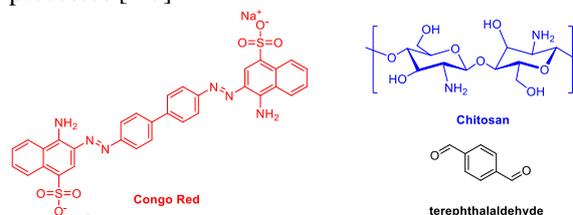


Figure 1: Chemical structures of Congo red, Chitosan and terephthaldehyde

Therefore, several natural material-based adsorbents such as active carbon [8], natural polymers [9, 10], synthetic polymers [11], biological biomasses [12] have been tested for treating dye-laden wastewater, but they are either costly or inefficient, impeding their application. One of the preferred and broadly utilized approach in water treatment is adsorption technique due to its relatively easy application and cost-effectiveness. [13]

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Accordingly, to overcome these disadvantages, it is necessary to develop efficient adsorbents such as chitosan; one of the most recent preferred choice in variety of applications and natural biopolymer. It is an amino polysaccharide consisting of N-acetyl D-glucosamine and D-glucosamine (both acetylated and deacetylated units), It has biocompatible, biodegradable, and non-toxic properties with presence of free amino group allows chemical modification to construct desired polymeric networks with improved adsorption efficiency and mechanical strength (Figure 1). [14, 15] these properties support it to attract many researchers in the field of water treatment to use chitosan and its derivatives and composites as adsorbents for the removal of water pollutants [16-18]. Also, various chitosan-based crosslinked composites, [19, 20] one of them is terephthalaldehyde has been reported as a good crosslinking agent in crosslinked chitosan hydrogel for the selective removal of organic dyes. So according to our survey, our aim of this study is utilization of ultrasound wave-induced synthesis of crosslinked chitosan hydrogels using terephthalaldehyde/glutaraldehyde as crosslinking agents to develop new material for eco-friendly application as efficient adsorbent for the removal of Congo red from aqueous solution.

Experimental:

Materials

All used chemicals are purchased from known companies of chemicals HiMedia and other commercial sources and they used without further purification.

Preparation of chitosan-Terephthalaldehyde hydrogels

Chitosan (2.0 g) was dissolved in 100 mL of 1% aqueous acetic acid solution under continuous stirring at room temperature for 3 h. terephthalaldehyde (0.1 g) was dissolved in 5.0 mL of ethanol and added to the chitosan solution in drop-wise with vigorous stirring until the viscous gel was formed. The product was then dried at 50 °C and grinded by manual mortar. chitosan-terephthalaldehyde hydrogel is characterized by FTIR (Tensor II, Bruker, Germany), SEM [Quanta 450 FEI scanning electron microscope (voltage 25 kV, spot size 2 and magnification range 3621–6888 x with 5.0 – 10.0 μm scale bar)] and other studies such as swelling analysis, determination of amine content and adsorption studies.

Swelling analysis

To determine the synthesized hydrogel swelling capacity; 0.03 g of hydrogel was soaked in water (15 ml) at room temperature for 12 h to assure reaching the equilibrium, then, the water was removed from the surface by blotting the samples with filter paper and

sample was then weighed immediately. The swelling percentages of the hydrogel was calculated as follows [21]:

$$E_{sw} = [(W_e - W_o) / W_o] 100 \quad (1)$$

Where, E_{sw} is the swelling percentage of the gel at equilibrium.

W_e denotes the weight of the gel when the swelling equilibrium is reached and

W_o is the initial weight of the gel.

Determination of Amine Content

The amine content of the chitosan and the hydrogels was determined by using the acid-base titration method [17]. Chitosan or chitosan hydrogel (0.1 g) was placed in a flask containing 30 mL of 0.05 N HCl solution and kept for equilibrium for 15 h, the solution was then titrated against 0.05 M NaOH in the presence of phenolphthalein as indicator to determine the amount of unreacted HCl from which amine content was calculated.

Adsorption studies

The adsorption experiment of Congo red dye from aqueous solution was conducted by shaking suspensions of a fixed weight of TCCS (0.02 g) in 25 ml of different concentrations of aqueous Congo red (CR) solution followed by filtration and then the absorbance was measured at 492 nm using the UV-Vis spectrophotometer (Shimadzu-1800, Japan) to determine the dye concentration. The amount of the dye adsorbed by the adsorbent was calculated by using the following equation [18]:

$$q_e = \frac{(C_0 - C_e) V}{W} \quad (2)$$

Where q_e is the amount of dye at equilibrium (mg/g), V is the volume of the dye solution (L)

C_0 is the initial concentration of dye (mg/L)

C_e is the final concentration of dye at equilibrium after adsorption and

W is the dry weight of the adsorbent TCCS (g).

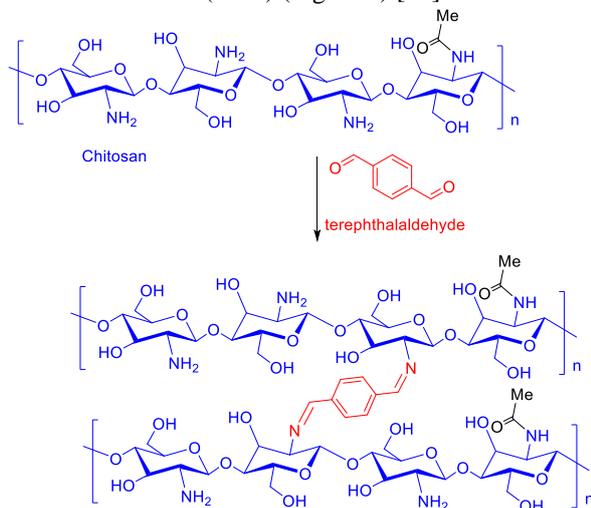
The time required for equilibrium was determined by running experiments at different time intervals, the time of the other experiments was set accordingly. The pH was adjusted by using 0.1 M HCl solution and 0.1M NaOH solution. The thermodynamic parameters were studied by running adsorption experiments at different temperatures (298, 308 and 318 K).

Results and discussion

Terephthalaldehyde cross-linked chitosan (TCCS) was synthesized via a simple one pot reaction, Addition of dissolved chitosan to terephthalaldehyde (minimum quantity) to become viscous hydrogel which then was dried to the solid product (Figure 1).

The mechanism of formation of this hydrogel is depicted in Scheme 1 via formation imine bond between the chitosan and terephthalaldehyde via

condensation reaction between the carbonyl groups of the terephthalaldehyde and the amino groups of the chitosan. The new structure of terephthalaldehyde cross-linked chitosan (TCCS) was confirmed by FT-IR spectroscopy with SEM. FT-IR spectrum of TCCS revealed presence of main characteristic absorption band at 1637 cm^{-1} (C=N) (Figure 2).[22]



Scheme 1: Cross-linking of Chitosan with terephthalaldehyde

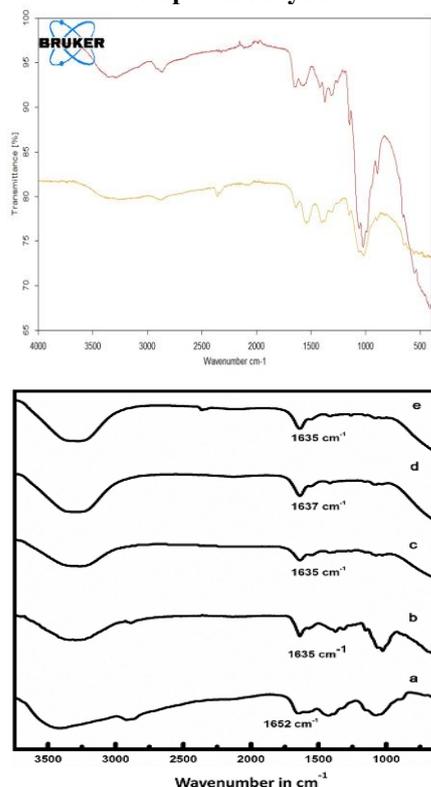


Figure 2: FT-IR spectra of chitosan (CS) and TCCS with different % of cross linker terephthalaldehyde (CST 1-V).[22]

The morphology of the TCCS surface was studied by using SEM, Figure 3 shows the SEM micrographs of

TCCS. The chitosan surface seems reasonably smooth, but the TCCS surface appears rough and jagged, with small visible randomly distributed pockets, demonstrating that the structural change and cross-linking affect the smoothness of the surface.

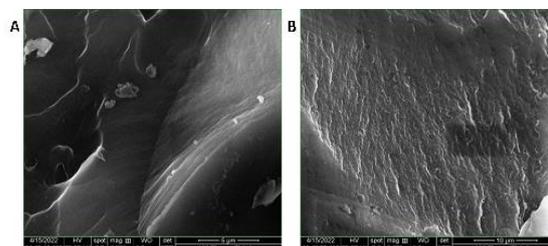


Figure 3: SEM micrographs of TCCS.

It is well known that many of cross-linked chitosans can capture water molecule from the wet media, in other words they behave as hydrogels, in this context TCCS was found to be able to accommodate water inside its network, the swelling analysis indicated that swelling percentage of the gel at equilibrium was found to be 543.66%. The estimation of amine content by acid base titration method showed that the number of amino groups in the polymeric chain of TCCS is less than it in the chitosan itself, in TCCS the amine content was found to be 0.2 mmol/g while for chitosan 2.25 mmol/g, this reduction confirms the transformation of the amino groups to imine groups by condensation with the aldehydic carbonyl of the cross-linker, furthermore, the availability of the amino groups to be exposed to the acid decreased significantly due to the folding of the polymeric chains in the cross-linked form.

Effect of contact time on CR adsorption

The time profile tells how fast the adsorption process is and how long it takes to reach the maximum removal efficiency, the point at which the process has reached equilibrium and no significant changes in removal efficiency will be observed.

In the present study, portions of a fixed weight of TCCS (0.02 g) were treated with CR solution (25 ml, 40 ppm), Figure 4 A illustrates the results of measuring the removal efficiency at various time intervals. The adsorption of CR on TCCS takes 60 minutes to reach the equilibrium point.

Effect of adsorbent weight

The effect of the adsorbent weight was investigated by the treatment of addition of CR solutions (25 ml, 40 ppm) with different weights of TCCS (from 0.01 to 0.06 g) in 25 mL 40 ppm CR aqueous solution at 298 K for 60 min. The result is shown in Figure 4 B, the optimum weight is 0.02 g, below this weight the mass of the adsorbent is not enough to reach the maximum removal efficiency, on the other hand, above this weight the decrement in the removal efficiency could be attributed to the decrement of the adsorption centers which are exposed to the solution.

Effect of pH of medium on CR adsorption

The pH of the CR aqueous solution has a significant impact on the adsorption process and the removal efficiency, CR solutions with fixed concentrations and varying pH values (2–10) were treated with a fixed weight of TCCS. Figure 4 C displays the results, which show that changing the pH values has no influence on the adsorption process and that removal efficiency values (R percent) are quite near. This implies that adjusting the pH has no effect on the electrostatic characteristics of the TCCS surface, and that the mechanism of CR adsorption on TCCS is mostly dependent on π - π interactions between the modified polymer's phenyl rings and those of CR molecules.

Effect of initial dye concentration

The effect of the initial CR concentration on the removal efficiency was studied, different CR concentrations (30, 40, 50, 60 and 70 ppm) were treated with 0.02 g of the adsorbent. Slight gradual decrements in the removal efficiency values with increasing CR concentration were observed, the maximum and minimum removal efficiency values were found to be 98.08% and 84.23% for the 40 ppm and 70 ppm concentrations respectively. The opposite proportion between the removal percentage and the initial CR concentration was observed, it relates to the ratio of the numbers of the CR molecules at the initial concentrations to the adsorption centers on the TCCS surface, at the low CR concentrations the number of the free adsorption centers is relatively higher than in the case with higher dye concentration, so the removal percentage for the lower concentrations will be higher and vice versa. It was also observed that the adsorption capacity increases with increasing the initial dye concentration, the maximum adsorption capacity value at the equilibrium point was 73.70 mg/g for the 70 ppm (25 ml) solution at 298 k, higher values were recorded at higher temperatures. Figure 4 D illustrates the results.

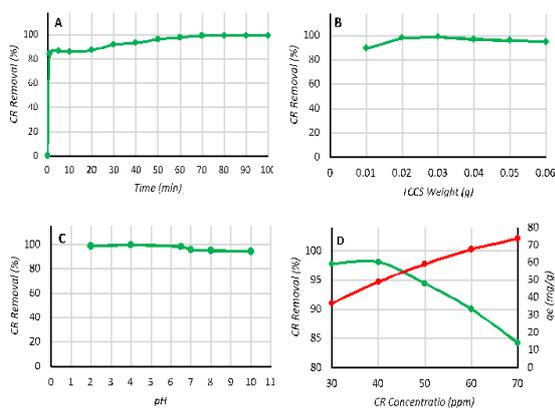


Figure 4: Effect of contact time (A), TCCS weight (B), pH (C) and initial CR concentration on the dye removal (%).

Adsorption isotherms

It is important to understand how the CR being adsorbed on the surface of TCCS, accordingly, the experimental equilibrium data were fitted to different isotherm models including Langmuir [23], Freundlich [24], and Temkin [25] as shown in Figures 5, 6 and 7 respectively, Table 1 demonstrate the obtained data, from the values of correlation coefficient (R^2) we can conclude that the adsorption of CR on TCCS obeys Langmuir isotherm ($R^2 = 0.998$).

According to the Langmuir isotherm, the molecules of CR form a monolayer on the adsorbent's homogenous surface (TCCS in this case). Equation (3) express the linearized Langmuir isotherm (3):

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b} \quad (3)$$

where C_e is the equilibrium liquid phase concentration (mg/L), q_e is the amount of sorbent adsorbed per unit weight of adsorbent (mg/g); Q_0 is the maximum adsorption capacity, and b is the Langmuir constant related to the rate of adsorption. From the slope and intercept values of Langmuir adsorption isotherm (Figure 5) the values of Q_0 and b were calculated from the slope and intercept values, they were found to be $Q_0 = 77.50$ mg/g, and $b = 1.42$ L/mg. Another characteristic constant that can be calculated for Langmuir adsorption model is the separation constant R_L , this dimensionless constant is also called the equilibrium constant, it indicates

the favorability and degree of feasibility of the adsorption process can be determined from the Langmuir adsorption model b calculating the separation constant (R_L), when ($R_L = 0$) the adsorption is irreversible; when ($R_L > 1$) the adsorption is unfavorable; when ($R_L = 1$) the adsorption is linear; when ($0 < R_L < 1$) adsorption is favorable. The R_L is expressed by equation 4:

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

where b (L/mg) is the Langmuir constant and C_0 (mg/L) is the initial highest concentration of the adsorbate (CR). In this case, the R_L was found to be 0.0099 indicating that the adsorption of CR on TCCS happens as a favorable process.

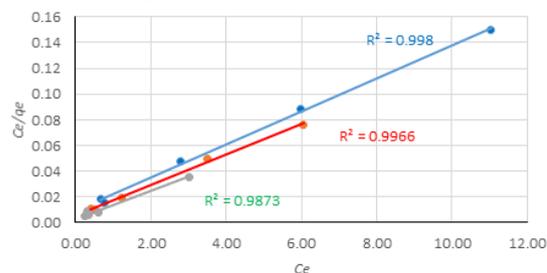


Figure 5: Langmuir isotherm plot for adsorption of CR on TCCS.

The Freundlich isotherm model was also implemented in the experimental equilibrium data, it is expressed in equation 5:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

where K_f and n are the Freundlich constants, K_f represents the adsorption capacity in mg/g and n represents the adsorption intensity on the heterogeneous surface. Freundlich isotherm model assumes that the adsorption is not limited to the formation monolayer on the surface of the adsorbent. This model is obtained by plotting $\log q_e$ versus $\log C_e$, Figure 6, the K_f and n values were calculated from the intercept slope respectively.

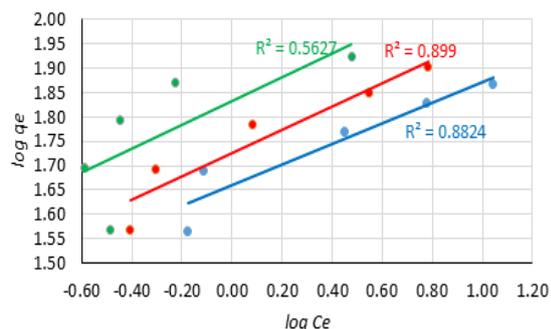


Figure 6: Freundlich isotherm plot for adsorption of CR on TCCS.

Furthermore, the Temkin isotherm was also implemented on the experimental equilibrium data, this model suggests that the interactions between the adsorbent and the adsorbate make the heat of adsorption of all molecules in the formed layer decreases linearly with the surface coverage. The linear form of Temkin isotherm model is represented in equation 6:

$$q_e = B \ln K_t + B \ln C_e \quad (6)$$

where B is constant which is related to the heat of adsorption, and K_t is Temkin isotherm constant (L/mg). Plotting q_e versus $\ln C_e$, gives the Temkin isotherm, Figure 7, the values of the constants were determined from the slope and intercept values.

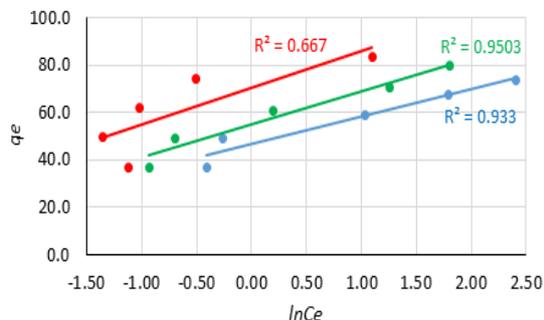


Figure 7: Temkin isotherm plot for adsorption of CR on TCCS.

Adsorption kinetics

The kinetics of the adsorption of CR on the surface of TCCS have been studied by implementing the experimental data on Lagergren pseudo-first order and Ho pseudo-second order models, at different time intervals the amount of CR adsorbed on the TCCS have been calculated according to equation 7. Lagergren pseudo-first order and Ho pseudo-second order models are represented by equations 8 and 9 respectively.

$$q_t = \frac{(C_0 - C_t) V}{W} \quad (7)$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.302} t \quad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

where q_e and q_t is the amount of CR (mg/g) adsorbed on TCCS equilibrium and at time t respectively, V is the volume of the dye solution (L), W is the mass of TCCS (g), C_0 is the initial CR concentration and C_t is the concentrations of CR at time t , k_1 (min^{-1}) and k_2 (mg/g min) are the pseudo-first order and pseudo-second-order rate constants. The graphical representations of the Lagergren pseudo-first order and Ho pseudo-second order models are shown in Figures 8 and 9 respectively, Table 2 illustrates the obtained results. The R^2 values for the pseudo-first order model was found to be 0.8625, in contrast for the pseudo-second order model the R^2 values were 0.9982, which means that the adsorption of CR on TCCS obeys the pseudo-second order model. Furthermore, the theoretical values of q_e that obtained from the pseudo-second order model are very close to the experimental values ($q_{e,exp}$) at 40 ppm.

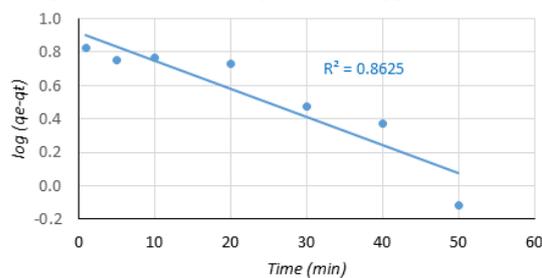


Figure 8: Lagergren first-order kinetic plot for the sorption of CR on TCCS.

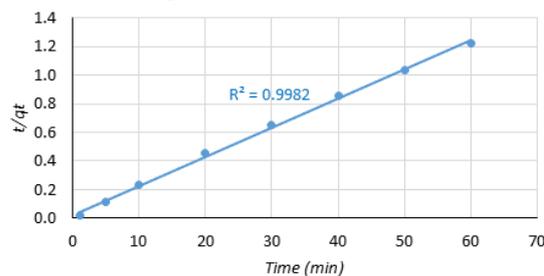


Figure 9: Second-order kinetic plot for the sorption of CR on TCCS.

3.8. Adsorption thermodynamic parameters

To determine the thermodynamic parameters such as free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) for the adsorption of CR on TCCS, equations 10, 11, and 12 have been used:

$$K_c = \frac{C_{Ae}}{C_e} \quad (10)$$

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (11)$$

$$\Delta G = \Delta H - T\Delta S \quad (12)$$

where K_c is the equilibrium constant, C_{Ae} is the weight of CR adsorbed on TCCS per liter of the solution at equilibrium (mg/L), C_e is the equilibrium concentration of the dye in the solution (mg/L), T is the absolute temperature (K), and R is the universal gas constant (8.314 J/mol K).

From the plot of $\ln K_c$ versus $1/T$, Figure 10, the ΔS and ΔH values were calculated from the slope and intercept of the linear curve according to equation 11, then the ΔG values were determined from the obtained results according to equation 12.

Table 3 illustrates the calculated thermodynamic parameters, the negative ΔG values indicate a spontaneous adsorption process, the variation of the ΔG values with increasing the temperature comes in line with the experimental results which showed that at a higher temperature the amount of CR adsorbed on TCCS increases. The positive ΔH and ΔS values indicate that the process is endothermic with increasing the disorder of molecules at the adsorbent-solution interface.

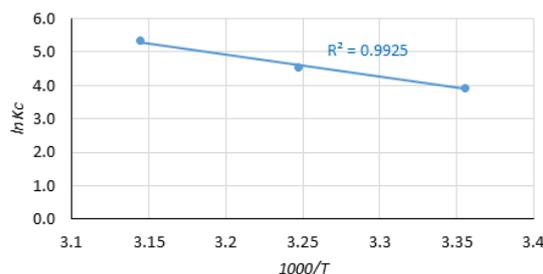


Figure 10: Plot of $\ln K_c$ vs. $1/T$ for CR adsorption on TCCS.

Table 1: Parameters of the Langmuir, Freundlich and Temkin isotherm models.

Langmuir isotherm		Freundlich isotherm			Temkin isotherm				
Q_0 (mg/g)	B (L/mg)	R_L	R^2	K_f (mg/g) (L/mg) ^{1/n}	n	R^2	K_t (L/mg)	B	R^2
77.52	1.417	0.0099	0.998	45.8352	4.737	0.882	4.062	11.503	0.933

Table 2: Kinetic parameters for pseudo-first order and pseudo-second order.

Pseudo-first order			$q_{e,exp}$ (mg/g) ($C_0 = 40$ ppm)
k_1 (min ⁻¹)	q_e (mg/g)	R^2	
0.0389	8.30	0.8625	49.04
Pseudo-second order			
k_2 (mg/g min)	q_e (mg/g)	R^2	
0.0162	49.26	0.9982	

Table 3: Thermodynamic parameters for adsorption of CR on TCCS.

Temperature	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol/K)
298	-9.7516	55.4344	0.2187
303	-11.6711		
308	-14.1326		

Conclusion

A terephthaldehyde cross-linked chitosan (TCCS) has been synthesized by adding the minimum amount of the cross-linker to the acidic aqueous solution of chitosan, the polymer has been characterized using FT-IR, SEM, and swelling with amine content analysis. The synthesized polymer was used as an efficient adsorbent for the removal of Congo red dye from aqueous solution. The variation of pH has no significant effect on the removal efficiency. The maximum adsorption capacity 73.70 mg/g was recorded for the 70 ppm concentration, however, for the 40 ppm with which the maximum removal

efficiency (98.08%), the adsorption capacity was found to be 49.04 mg/g. The adsorption process obeys Langmuir model and the kinetic studies indicated that it is pseudo-second-order. The calculated thermodynamic parameters indicated that the adsorption is spontaneous and endothermic.

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