

# Adsorption of Congo red dye onto antimicrobial terephthaloyl thiourea cross-linked chitosan hydrogels

Nouf F. El-Harby, Shaimaa M. A. Ibrahim and Nadia A. Mohamed

## ABSTRACT

Adsorption capacity of three antimicrobial terephthaloyl thiourea cross-linked chitosan hydrogels for Congo red dye removal from its aqueous solution has been investigated for the first time in this work. These hydrogels were prepared by reacting chitosan with various amounts of terephthaloyl diisothiocyanate cross-linker. The effect of the hydrogel structural variations and several dye adsorption processing parameters to achieve the best adsorption capacity were investigated. The hydrogels' structural variations were obtained by varying their terephthaloyl thiourea moieties content. The processing variables included initial concentration of the dye solution, temperature and time of exposure to the dye. The adsorption kinetics and isotherms showed that the sorption processes were better fitted by the pseudo-second-order equation and the Langmuir equation, respectively. On the basis of the Langmuir analysis Congo red dye gave the maximum sorption capacity of 44.248 mg/g. The results obtained confirmed that the sorption phenomena are most likely to be controlled by chemisorption process. The adsorption reaction was endothermic and spontaneous according to the calculated results of adsorption thermodynamics.

**Key words** | adsorption isotherms, adsorption kinetics, adsorption thermodynamics, Congo red dye, cross-linked chitosan

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## INTRODUCTION

Colored organic effluents originating from the textile, paper, plastic, leather, food, and mineral processing industries constitute undesirable wastewater that aggregates pigments or dyes, which can cause serious water pollution problems (Vakili *et al.* 2014). A very small amount of dye in water is highly visibly displeasing and hinders light penetration, thus disturbing the biological process in water bodies, and can be toxic to water creatures. Hence, the removal of color from process or waste effluents becomes environmentally important. Physical, chemical and biological methods are known for dye removal from wastewater, such as precipitation, adsorption, flocculation, reverse osmosis and ultra-filtration (Kansal *et al.* 2010). These techniques are nondestructive, since they only transfer the non-biodegradable matter into sludge (Kansal *et al.* 2010). In comparison with other techniques, adsorption is probably one of the simplest, rapid, convenient, low-cost and effective physical processes for the removal of dyes from wastewaters, especially those which are practically unaffected by conventional biological wastewater treatments (Gök *et al.* 2010; Sismanoglu *et al.* 2010).

Biopolymers have gained importance in environmental biotechnology due to their very good adsorption capacity towards dyes and metal ions (Yoshida & Takemori 1997; Jin & Bai 2002; Guibal 2004). Other useful features of biopolymers include their abundance, non-toxicity, hydrophilicity, biocompatibility, biodegradability and antibacterial property (Kumar 2000).

Chitosan is one of the world's most plentiful and low-cost biopolymers that possess several properties as an ideal adsorbent for removing pollutants from wastewater. Chitosan or poly-(1 →4)-2-amino-2-deoxy-b-D-glucose is a biopolymer that can be chemically expressed as a non-toxic, heterogeneous, linear, cationic and biodegradable polysaccharide with high molecular weight (Riva *et al.* 2011). Many researchers have investigated the adsorption performance of different forms of chitosan (Vakili *et al.* 2014). Adsorption ability of chitosan powder, obtained from shrimp waste, to remove food dyes (acid blue 9 and yellow 3) from aqueous solution using a batch method has been investigated (Dotto & Pinto 2011). The effects of the

pH, contact time and stirring rate were elucidated and the obtained results showed that the adsorption capacity increased with time increase and with pH decrease.

Although chitosan shows a great potential, it suffers from drawbacks such as inadequate mechanical properties (Chatterjee et al. 2009a), low acid stability, low solubility in neutral solutions (Zhou et al. 2009), low porosity, low thermal resistance (Crini & Badot 2008) and low surface area (Setthamongkol & Salaenoi 2012; Alhwaige et al. 2013). Therefore, modification is an effective solution to produce a product with the desired properties to overcome the limitations of chitosan. Modification of chitosan is easier than that of other polysaccharides because of its reactive functional groups, including amino and hydroxyl groups (Rinaudo 2006). Applying physical and chemical modifications leads to enhancing the mechanical properties and adsorption capacity of chitosan (Acharyulu et al. 2013). Cross-linking, impregnation, and grafting are methods used for chemical modification of chitosan (Vakili et al. 2014).

It is well known that chitosan is readily soluble in dilute acid solution. So its dissolution tendency in the acid effluent can severely limit its use as an adsorbent for dye removal (Chiou & Li 2002). To overcome this behavior, chitosan can be modified by cross-linking the polymer chains to prevent dissolution as well as to improve the mechanical resistance and reinforcement of the chemical stability of chitosan in acidic solutions. All of these features are important for an adsorbent to be effective (Vakili et al. 2014). To date, the most common cross-linkers used for modifying chitosan for dye adsorption are glutaraldehyde (Mirzaei et al. 2013), epichlorohydrin (Jing et al. 2013), ethyleneglycol diglycidyl ether (Hsien et al. 2013) and tripolyphosphate (Mengatto et al. 2013).

Four super-porous hydrogels have been prepared by cross-linking chitosan with different concentrations of terephthaloyl thiourea moieties (Mohamed & Al-mehbad 2013). Their structures have been proven using elemental analysis, Fourier transform infrared (FTIR) spectra, scanning electron microscopy (SEM), and X-ray diffraction. These hydrogels showed a greater antibacterial activity against *Bacillus subtilis*, *Staphylococcus aureus* and *Escherichia coli* and a higher antifungal activity against *Aspergillus fumigatus*, *Geotrichum candidum* and *Candida albicans* than that of the parent chitosan. They were more potent in the case of Gram-positive bacteria than Gram-negative bacteria. Increasing the degree of cross-linking in the hydrogels resulted in a stronger antimicrobial activity (Mohamed & Al-mehbad 2013). Congo red dye is one of the most important azo dyes and its discharge into water streams from various

printing and dyeing processes of textile, paper, leather, rubber and plastics is aesthetically unacceptable and causes a serious environmental pollution. It is metabolized to benzidine, a known human carcinogen and the exposure to it can cause some allergic responses (Chen & Zhao 2009). It was selected in this work as a model anionic dye because of its complex chemical structure, high solubility in aqueous solution and its persistence, once it is discharged into the natural environment. In this regard the removal of Congo red dye remainders from the aqueous solution is one of the major global environment concerns. In the present work, and for the first time, the ability of the available basic active sites on terephthaloyl thiourea cross-linked chitosan hydrogels to remove Congo red dye from its aqueous solution has been investigated. Equilibrium, kinetics and thermodynamics of the adsorption of Congo red dye from its aqueous solution onto these hydrogels will be studied.

## EXPERIMENTAL

### Materials

Chitosan, with a degree of deacetylation of 88% and molecular weight of  $2.0 \times 10^5$ , was purchased from Acros Organics, NJ, USA. Congo red dye was purchased from DyStar and used as received without further purification. The UV-visible absorption spectrum of Congo red dye shows characteristic absorption peaks both in UV and visible regions. The concentration of Congo red dye solution was determined at  $\lambda_{\max}$  497 nm throughout the work. The chemical structure of the dye is shown in Figure 1. All other chemicals and reagents, from Aldrich, were of analytical grade and were used as received.

### Synthesis of terephthaloyl thiourea cross-linked chitosan (TTU-chitosan) hydrogels

Three different predetermined amounts of terephthaloyl dichloride were dissolved in 20 mL methylene chloride and

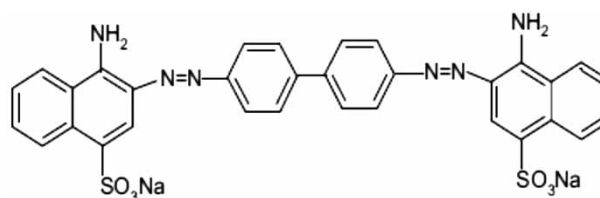
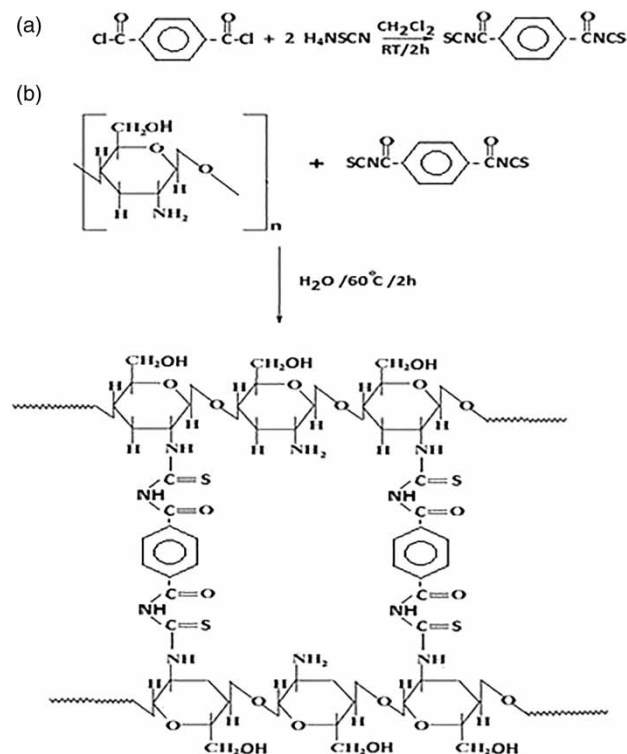


Figure 1 | Structure of Congo red dye

were gradually added to solutions of ammonium thiocyanate of appropriate concentrations in 20 mL methylene chloride. The molar ratio of terephthaloyl dichloride to ammonium thiocyanate was 1:2, respectively. Polyethylene glycol-400 (1 mL) was gradually added to each reaction mixture as a phase transfer catalyst. After stirring for 2 h at room temperature, the white precipitate of the formed ammonium chloride was removed by filtration. Each filtrate (cross-linker, terephthaloyl diisothiocyanate, Figure 2(a)) was added to a chitosan solution (3.22 g, 20 mmol, in 200 mL of 1% acetic acid). The reaction mixture was stirred at 60 °C for 2 h and then cooled, and the homogenous cross-linked hydrogels formed (Figure 2(b)) were neutralized with sodium bicarbonate solution to pH 7 to give yellowish white products, which



**Figure 2** | Synthesis of TTU-chitosan hydrogels.

**Table 1** | Synthesis of TTU-chitosan hydrogels having different degree of cross-linking and their elemental analyses

Samples	Terephthaloyl dichloride (mmol)	Ammonium thiocyanate (mmol)	Chitosan (mmol)	Elemental analyses (%)			
				C	H	N	S
TTU-chitosan-1	1.25	2.50	20	45.5	6.1	8.8	3.3
TTU-chitosan-2	2.50	5.00	20	45.8	5.7	9.1	5.5
TTU-chitosan-3	10.00	20.00	20	46.4	4.7	9.7	10.7

were submerged in methanol for 24 h for dewatering. The dewatered hydrogels were filtered and dried at 60 °C to constant weights. The ratios of the reactants were varied as shown in Table 1 to give three products which were designated as TTU-chitosan-1, TTU-chitosan-2, and TTU-chitosan-3 of increasing degree of cross-linking, respectively (Mohamed & Al-mehbad 2013). It is worth mentioning that TTU-chitosan-3 in this work has already been reported previously as TTU-chitosan-4 (Mohamed & Al-mehbad 2013). The particles of the finely powder prepared hydrogels were spherical in shape with an average diameter of ~0.5 mm as determined with an electronic microvernier caliper.

### Preparation of Congo red dye solution

An accurate weighed quantity of the dye was dissolved in bi-distilled water to prepare a stock solution of a known concentration. The solutions for adsorption tests were prepared from the stock solution to the desired concentrations ranging from 10 to 100 ppm by successive dilutions.

### Sorption and kinetic studies

The adsorption of reactive Congo red dye from its aqueous solution onto the adsorbents was performed using batch equilibrium technique. In each experiment, 100 mL of dye solution of known initial concentration ranging from 10 to 100 ppm was shaken with a certain weight of the adsorbent (100 mg) and the mixtures were then kept in an isothermal shaker at 150 rpm at 25 ± 0.1 °C or 55 ± 0.1 °C until equilibrium was reached. The residual dye concentration was measured at different time intervals up to equilibrium. At different time intervals, approximately 5 mL was taken from the solution and the solid was separated by centrifugation at 6,000 rpm for 10 min using a centrifuge (Hettich, EBA 21, Germany) and the aliquots of supernatant were analyzed by a UV-visible spectrophotometer (Shimadzu UV/Vis1601, Japan) at appropriate wavelength corresponding to the maximum absorption of Congo red dye (497 nm).

The corresponding concentration in the supernatant solution was obtained using a previously constructed calibration graph. These data were used to calculate the adsorption capacity of the adsorbent. A similar procedure was followed for another set of Erlenmeyer flasks containing the same dye concentration without adsorbent to be used as a blank. The amount of adsorption at equilibrium time  $t$ ,  $q_A$  (mg/g), is calculated by

$$q_A = \frac{(C_0 - C_e) \times V}{W} \quad (1)$$

where  $C_0$  and  $C_e$  (mg/L) are the concentrations of dye at initial and at equilibrium time, respectively;  $V$  is the volume of the solution (L);  $W$  is the mass of dry adsorbent used (g).

Langmuir and Freundlich isotherm models were employed to investigate the adsorption process. The effect of contact time was studied to determine the time taken by adsorbents to reach equilibrium with initial dye concentrations of 50 ppm while the other experiment parameters were kept constant.

The effect of temperature (at 25, 35 and 55 °C) on the adsorption of Congo red dye by TTU-chitosan hydrogels was studied, using 100 mg adsorbent and 100 mL of Congo red dye solution of initial concentration of 50 ppm.

The procedures of kinetic experiments were basically identical to those of equilibrium tests. The amount of adsorption at time  $t$ ,  $q_t$  (mg/g), is calculated by

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

where  $C_0$  and  $C_t$  (mg/L) are the concentrations of dye at initial and any time  $t$ , respectively;  $V$  is the volume of the solution (L);  $W$  is the mass of dry adsorbent used (g). The experimental parameters included studying the effect of initial dye concentrations, temperature, cross-linking ratio and contact time on dye removal.

## RESULTS AND DISCUSSION

Chitosan was modified with terephthaloyl diisothiocyanate via reacting of both the isothiocyanate groups with the amino groups of chitosan (Figure 2). The amount of terephthaloyl diisothiocyanate (Figure 2(a)) with respect to chitosan was varied as described in Table 1 to produce three terephthaloyl thiourea cross-linked chitosan

hydrogels (Figure 2(b)) designated as TTU-chitosan-1, TTU-chitosan-2, and TTU-chitosan-3 of increasing degree of cross-linking, respectively, based on their sulfur contents which were determined by elemental analyses (Table 1). The structure of the TTU-chitosan hydrogels was emphasized by their FTIR spectra and the microstructures of TTU-chitosan-1 and TTU-chitosan-3 hydrogels' surface were previously investigated by SEM (Mohamed & Al-mehbad 2013) as presented in Figure 3. This figure shows that the hydrogels have a channel-like surface and an extremely porous structure. While the two examined hydrogels have a similar surface appearance, the distribution and the size of their pores are different. The distribution of porosity became more uniform and dense with increasing degree of cross-linking (TTU-chitosan-3 hydrogel). This result might be attributed to the increase of the equilibrium water content of the TTU-chitosan-3 hydrogel, which led to more pores (Mohamed & Al-mehbad 2013). The microporous surface structure of the hydrogels could lead to high surface areas with low diffusion resistance in the matrix; the pore size of TTU-chitosan-3 hydrogel is approximately 80  $\mu\text{m}$ , whereas it is approximately 180  $\mu\text{m}$  for TTU-chitosan-1 hydrogel.

### Adsorption kinetics

Adsorption kinetics study is important for designing adsorption systems and selecting optimum operating conditions for adsorption. The adsorption kinetic experiments of Congo red dye onto cross-linked TTU-chitosan hydrogels were performed with constant dye concentration of 50 ppm, adsorption temperature at 25 °C and the other experiment

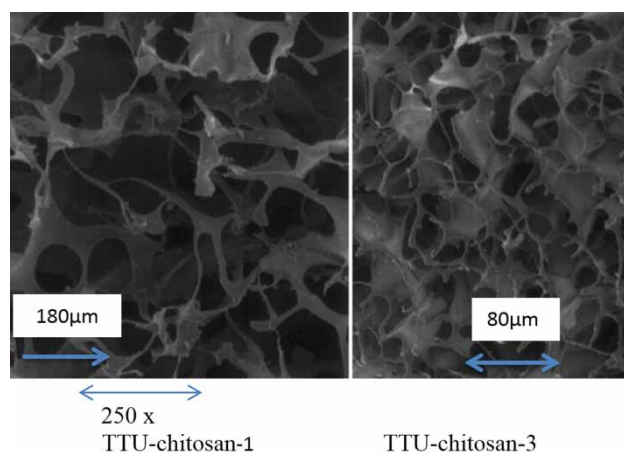
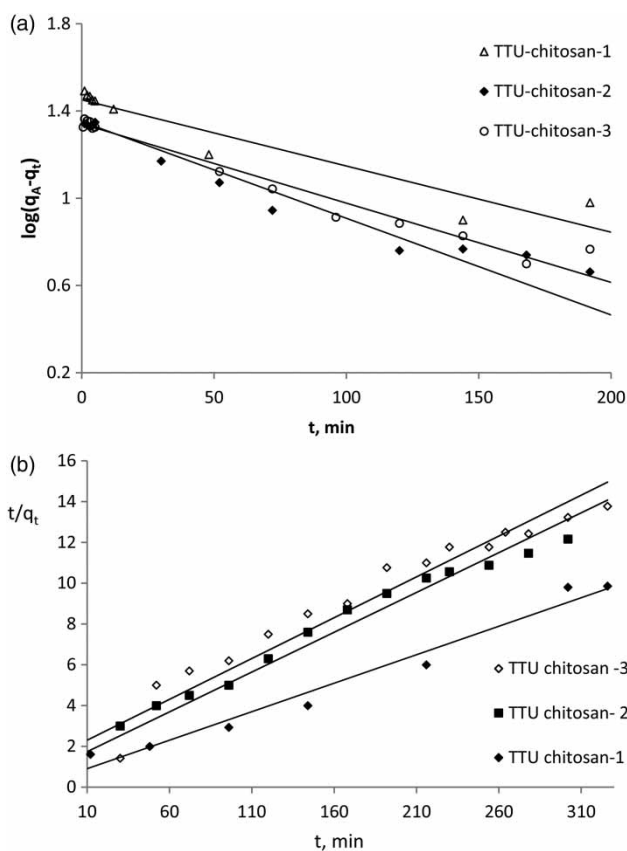


Figure 3 | Scanning electron micrographs of TTU-chitosan hydrogels (Mohamed & Al-mehbad 2013).



**Figure 4** | Pseudo-first-order kinetics (a) and pseudo-second-order kinetics (b) for Congo red dye adsorption onto cross-linked chitosan samples (dye concentration = 50 ppm) at 25 °C.

parameters were kept constant. The results of adsorption are shown in Figure 4(a) and 4(b). Also, Table 2 lists different kinetic parameters of the pseudo-first-order and pseudo-second-order rate model for Congo red dye adsorption onto the hydrogel samples at different temperatures.

In order to evaluate the kinetic mechanism that controls the adsorption process, pseudo-first-order (Equation (3)), and pseudo-second-order (Equation (4)) models were

employed to interpret the experimental data. The Lagergren rate equation (Lagergren 1898), which is the first rate equation developed for sorption in liquid/solid systems, is based on solid capacity. The pseudo-first-order equation is represented by:

$$\log(q_A - q_t) = \frac{\log q_A - k_1 t}{2.303} \quad (3)$$

where  $k_1$  ( $\text{min}^{-1}$ ) is the pseudo-first-order adsorption rate constant,  $q_t$  is the amount of dye adsorbed at time  $t$  (min), and  $q_A$  denotes the amount adsorbed at equilibrium, both in mg/g. The values of  $k_1$  were calculated from the slope of the linear plots of  $\log(q_A - q_t)$  versus  $t$  (plot is shown in Figure 4(a)). The correlation coefficient,  $R^2$ , values were found to be between 0.9324 and 0.9985, but the calculated  $q_A$  values ( $q_{A,\text{cal}}$ ) did not agree with the experimental data ( $q_{A,\text{exp}}$ ) (Table 2).

The pseudo-second-order equation can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_A^2} + \frac{t}{q_A} \quad (4)$$

where  $k_2$  ( $\text{g}/(\text{mg}\cdot\text{min})$ ) is the adsorption rate constant of pseudo-second-order. The slope and intercept of the linear plots of  $t/q_t$  versus  $t$  yield the values of  $q_A$  and  $k_2$  for Equation (4) (plot is shown in Figure 4(b)). Compared with the results obtained for the pseudo-first-order adsorption model, the  $R^2$  values for the pseudo-second-order kinetic model were found to be higher than 0.9608, and the calculated  $q_A$  values ( $q_{A,\text{cal}}$ ) were also closer to the experimental data ( $q_{A,\text{exp}}$ ) (Table 2). In other words, the calculated correlations are closer to unity for the second-order kinetics model. These results revealed that the adsorption behavior of Congo red dye onto cross-linked chitosan samples followed the pseudo-second-order kinetic model.

**Table 2** | Kinetic model constants and correlation coefficients for adsorption of Congo red dye onto cross-linked chitosan samples

samples	t (°C)	Pseudo-first-order model					Pseudo-second-order model				
		$q_{A,\text{exp}}$ (mg/g)	$q_{A,\text{cal}}$ (mg/g)	$k_1 \times 10^{-3}$ ( $\text{min}^{-1}$ )	$R^2$	S.D. (%)	$q_{A,\text{cal}}$ (mg/g)	$k_2 \times 10^{-3}$ ( $\text{g}/(\text{mg}\cdot\text{min})$ )	$R^2$	S.D. (%)	
TTU-chitosan-1	25	31.400	4.1787	26.024	0.90460	12.474	35.842	1.6200	0.98795	1.2859	
	55	36.066	4.4379	30.860	0.98010	12.581	37.175	1.7980	0.99070	0.25609	
TTU-chitosan-2	25	24.817	3.8636	10.133	0.92270	12.075	25.810	1.1207	0.98700	0.21945	
	55	31.888	4.3903	18.194	0.98830	12.372	34.014	1.6600	0.99470	0.65207	
TTU-chitosan-3	25	23.668	3.8240	8.2900	0.97250	11.978	25.111	0.93600	0.97400	0.35838	
	55	29.858	4.3619	24.412	0.95040	12.207	33.670	1.3930	0.96080	1.1606	



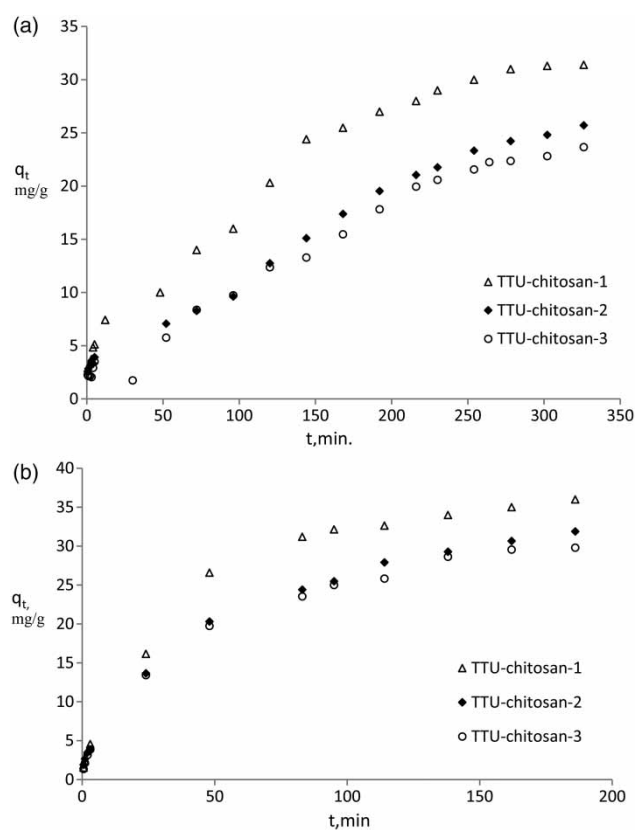
Normalized standard deviation, S.D. (%), is used to find the most applicable model that could describe the kinetic study of adsorption of dye on the investigated samples. The S.D. (%) was calculated using Equation (5) (Zhou *et al.* 2011):

$$\text{S.D.}(\%) = 100 \times \sqrt{\frac{[(q_{t,\text{exp}} - q_{t,\text{cal}}/q_{t,\text{exp}})]^2}{N - 1}} \quad (5)$$

where  $N$  is the number of data points,  $q_{t,\text{exp}}$  is the experimental values and  $q_{t,\text{cal}}$  is the calculated value by the above two models. Based on the values of S.D. (%) given in Table 2, it is clear that, of the two models, the pseudo-second-order equation model is better in describing the adsorption kinetics of Congo red dye onto hydrogel samples at different temperatures.

### Effect of contact time

Effect of contact time was studied by placing 100 mg of hydrogel in a flask containing 100 mL of 50 ppm concentration of Congo red dye solution. The contents of the flask were agitated on a shaker at 150 rpm and temperatures of 25 and 55 °C. Samples were taken at time intervals for the analysis of residual dye concentration in solution. Figure 5(a) and 5(b) show the amount of dye adsorbed at time  $t$ ,  $q_t$  (mg/g), as a function of contact time at 25 and 55 °C, respectively. It can be seen from this figure that the adsorption capacity of Congo red dye on TTU-chitosan hydrogels increased by increasing of time. Figure 5(a) shows the adsorption for Congo red dye onto chitosan samples at 25 °C. It can be noted that the equilibrium was not reached until 200 min. This could be because Congo red dye has a large molecular weight, so transport of the external and internal mass of Congo red dye onto the adsorbents may be difficult (Dotto *et al.* 2016). On the other hand, Figure 5(b) indicates that the shorter adsorption equilibrium time for Congo red dye adsorption by TTU-chitosan hydrogels was obtained at 55 °C. This increasing temperature may produce a swelling effect within the internal structure of TTU-chitosan hydrogels, which facilitates the penetration of dye molecules into their internal structure. Increasing dye removal by chitosan hydrogel with increasing temperature, due to the high diffusion capability of the long-chain branched structure of the dye molecules, has recently been reported (Subramani & Thinakaran 2017).



**Figure 5** | The variation of adsorption capacity with adsorption time for Congo red dye onto chitosan samples (dye concentration = 50 ppm) at temperatures: (a) 25 °C and (b) 55 °C.

### Effect of cross-linking content

The results of Congo red dye adsorption by TTU-chitosan hydrogels having various cross-linking contents are shown in Figure 5(a) and 5(b) and Table 3. The results obtained revealed that: (i) TTU-chitosan-1 adsorbent has higher dye uptake rate (more than 90% removal at temperature 55 °C) and higher adsorption capacity than that of TTU-chitosan-3 and TTU-chitosan-2 adsorbents; (ii) the dye removal efficiency by TTU-chitosan-2 was quite close to that of TTU-chitosan-3 under the same experimental conditions; (iii) in Figure 5(a), at temperature 25 °C and at time 326 min, increasing the content of terephthaloyl thiourea moieties from 1 to 2 moles may cause a significant decrease in  $q_t$  (18%), but increasing cross-linker content to form TTU-chitosan-3 leads to a slight decrease in  $q_t$  at the same time (7.7%).

In general, cross-linking improves the mechanical resistance and reinforces the chemical stability of chitosan in acidic solutions, modifies hydrophobicity, and stabilizes the chitosan at extreme pH (Vakili *et al.* 2014). However,

**Table 3** | Adsorption isotherm parameters for adsorption of Congo red dye onto cross-linked chitosan samples

samples	t (°C)	Langmuir isotherm model				Freundlich isotherm model		
		q <sub>max</sub> (mg/g)	K <sub>L</sub> (L/mg)	R <sup>2</sup>	R <sub>L</sub>	K <sub>F</sub> (mg/g)	1/n	R <sup>2</sup>
TTU-chitosan-1	25	42.735	0.87700	0.96740	0.031730	1.9570	0.52550	0.67160
	55	44.248	0.76610	0.97290	0.036200	4.4390	0.49180	0.50990
TTU-chitosan-2	25	36.101	0.21500	0.99910	0.11789	2.3650	0.44600	0.87530
	55	38.760	0.43510	0.95690	0.061950	3.6197	0.55520	0.26000
TTU-chitosan-3	25	36.630	0.85600	0.95160	0.032480	4.4464	0.08390	0.05060
	55	37.736	0.52680	0.98940	0.051730	3.2772	0.48440	0.76000

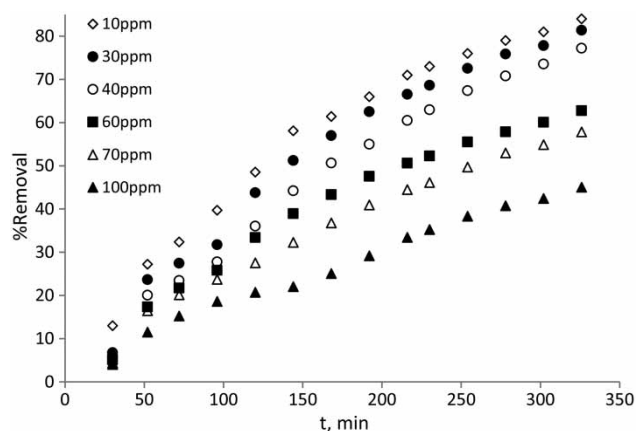
cross-linking also decreases the number of free and available amino groups in the chitosan backbone, and hence, the possible ligand density and polymer reactivity. So, cross-linking may cause a significant decrease in dye uptake efficiency and adsorption capacities, especially in chemical reactions involving amine groups. This is because the amino groups of the polymers are much more active than the hydroxyl groups and can be more easily attacked by cross-linkers. Consequently, these functional groups are no longer available for complex formation, and dye adsorption capacity decreases (Vakili *et al.* 2014). In previous studies, the activity of chitosan has been related to the interaction between NH<sub>3</sub><sup>+</sup> groups of chitosan and the electronegative charges on the dye surfaces (Chiou & Li 2002; Crini & Badot 2008; Vakili *et al.* 2014). So, the decrease in adsorption capacity from TTU-chitosan-1 to TTU-chitosan-3 may be due to the decrease of electrostatic interaction between adsorbents and dye anions. The incorporation of terephthaloyl thiourea moieties into chitosan allowed the synthesis of hydrogels with CO-NH- amide group, which cannot be easily protonated. Since the electron withdrawal by carbonyl group makes the nitrogen of the amide group a much poorer source of electrons than that of the amine group, electrons are less available for sharing with a hydrogen ion, and therefore amide is a much weaker base than amine. However, the increase in the cross-linking ratio does increase the steric hindrance for dye molecule to diffuse through the adsorbent, which led to decreasing of the dye uptake (Guibal 2004).

In the case of TTU-chitosan-2 and TTU-chitosan-3, a slight decrease in adsorption capacity is observed for Congo red dye even though there is an absence of amine groups in TTU-chitosan-3 (Figure 5(a) and 5(b)). It has been reported that the amount adsorbed by the adsorbent depends on its porosity (Chatterjee *et al.* 2009b; Seredych *et al.* 2009). Therefore, the possible reason for this unexpected result, when terephthaloyl thiourea content rose, from TTU-

chitosan-1 to TTU-chitosan-3, is that the equilibrium water content of the hydrogels increased, which led to more pores in hydrogels. The microporous surface structure of the hydrogels could lead to high surface area with low diffusion resistance in the matrix. This expectation may be supported by SEM photos (Figure 3). The pore size of the freeze-dried hydrogels is approximately 80 μm for TTU-chitosan-3 hydrogel, whereas it is approximately 180 μm for TTU-chitosan-1 hydrogel (Mohamed & Al-mehbad 2013). Furthermore, this may be due to the high quality of the distribution of porosity, which became more uniform and dense with increasing concentration of terephthaloyl thiourea moieties incorporated into the hydrogel (TTU-chitosan-3) (Figure 3). These results revealed that the prepared TTU-chitosan hydrogels are effective adsorbents for removing Congo red dye from its aqueous solution. Finally, the differences in the adsorption capacities of the dye molecule studied were due to the nature of functional groups present in the chitosan hydrogels and their molecular pore size.

### Effect of initial dye concentration

The effect of initial concentration of the dye on the efficiency of the cross-linked hydrogels for dye removal was studied by placing 100 mg of TTU-chitosan samples in a series of flasks containing 100 mL of Congo red dye solution of varying concentrations (10–100 ppm). The contents of the flasks with TTU-chitosan-1 and TTU-chitosan-2 were equilibrated on the shaker at 150 rpm at temperature of 55 and 25 °C for 186 min and 326 min, respectively. After adsorption, the residual concentration of the dye was determined. The results are illustrated in Figures 6 and 7. An increase in initial dye concentration leads to decrease in the adsorption capacity of dye on TTU-chitosan samples. The degradation ratio decreased with further increase in the dye concentration because the active sites on the hydrogel surface were covered by dye molecules (Zhu *et al.* 2009).



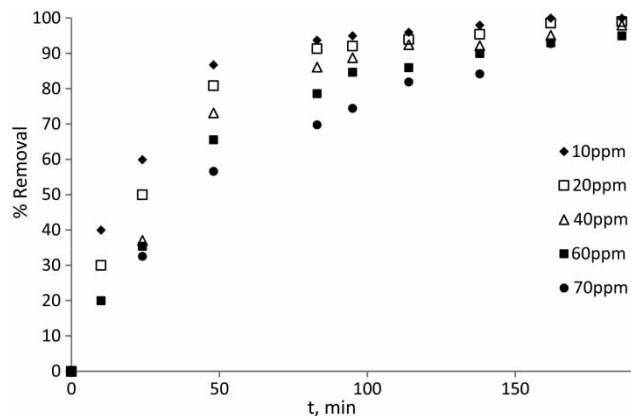
**Figure 6** | The effect of Congo red dye concentration on % dye removal by TTU chitosan-2 sample at 25 °C.

Another possible reason was that a high dye concentration shielded the visible light (Liu *et al.* 2006).

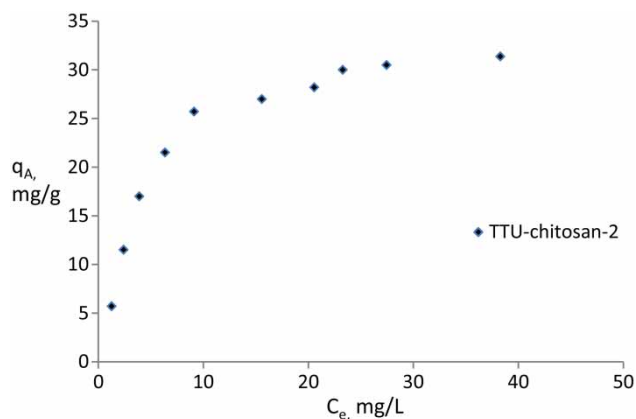
### Adsorption isotherms

The equilibrium relationship between the quantity of adsorbate per unit of adsorbent ( $q_A$ ) and its equilibrium solution concentration ( $C_e$ ) at a constant temperature is known as the adsorption isotherm. Adsorption isotherms describe how pollutants interact with sorbent materials and, so, are critical in optimizing the use of adsorbents. In order to optimize the design of an adsorption system to remove dye from solutions, it is important to establish the most appropriate correlation for the equilibrium curve.

The adsorption isotherm for Congo red dye onto TTU-chitosan-2 hydrogel at 25 °C is shown in Figure 8. This figure shows that the equilibrium data of the adsorption



**Figure 7** | The effect of Congo red dye concentration on % dye removal by TTU chitosan-1 sample at 55 °C.



**Figure 8** | Adsorption isotherms for Congo red dye onto TTU-chitosan-2 hydrogel at 25 °C.

process correspond to the monolayer chemisorption process (Sadeghi-Kiakhani *et al.* 2013). The Langmuir isotherm, which has been successfully applied to many other real sorption processes, can be used to explain the sorption of dye into chitosan and its cross-linked polymers (Chiou & Li 2002; Wang & Wang 2008; Hsien *et al.* 2013; Mahmoud 2017; Zhou *et al.* 2017). The adsorption isotherms for Congo red dye onto TTU-chitosan hydrogels at 25 and 55 °C plotted by the two models, Freundlich and Langmuir isotherms, are shown in Figure 9(a) and 9(b) and Figure 10(a) and 10(b), respectively.

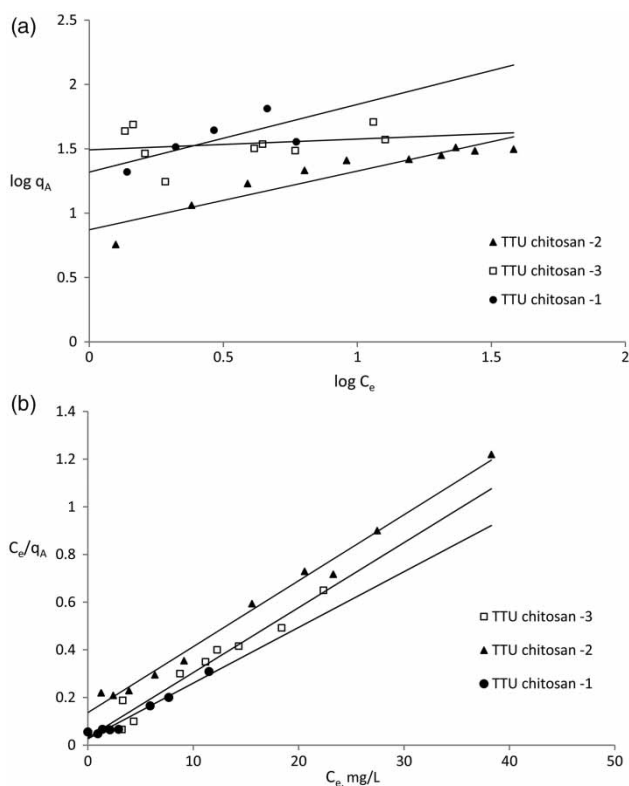
The linear form of the Langmuir isotherm is expressed in Equation (6):

$$\frac{C_e}{q_A} = \frac{1}{q_{\max} \cdot K_L} + \frac{C_e}{q_{\max}} \quad (6)$$

where  $q_A$  is the amount of dye adsorbed at equilibrium (mg/g), and  $C_e$  is the equilibrium concentration of dye in solution (mg/L). The monolayer sorption capacity,  $q_{\max}$  (mg/g), and  $K_L$  are constants related to the energy of the adsorption (L/mg). A plot of ( $C_e/q_A$  versus  $C_e$ ) results in a linear graphical relation with slope  $1/q_{\max}$  and intercepts  $1/(q_{\max} \cdot K_L)$  indicating the applicability of the above model for different samples as shown in Figures 9(b) and 10(b). The Langmuir isotherm constants along with correlation coefficients are reported in Table 3. The essential characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter, such as the separation factor or equilibrium factor ( $R_L$ ) used in Equation (7) (Mahmoud *et al.* 2013):

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (7)$$

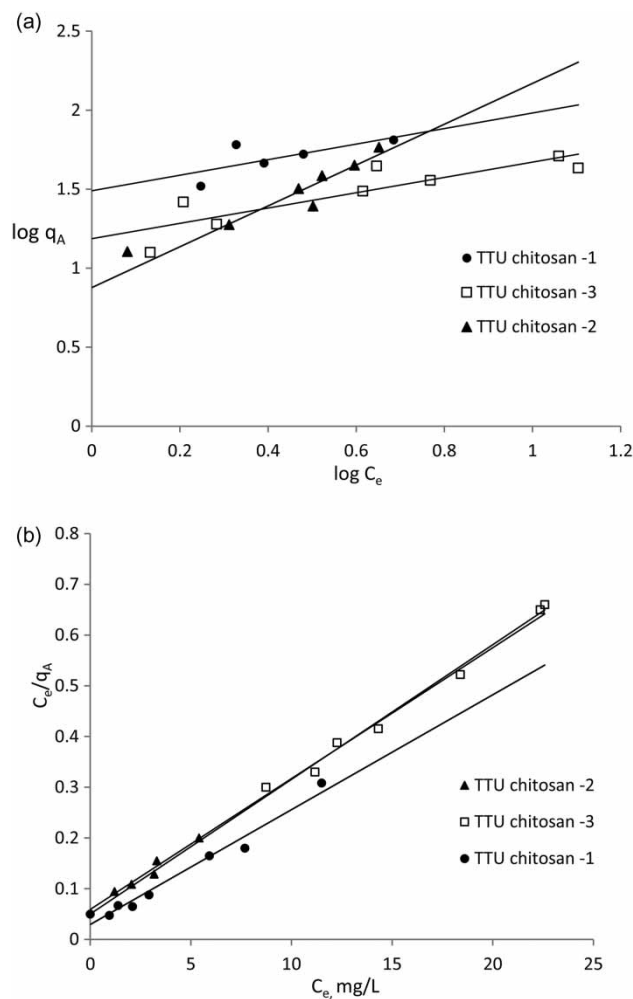




**Figure 9** | Adsorption isotherms for Congo red dye onto cross-linked chitosan hydrogels at 25 °C: (a) Freundlich isotherms; (b) Langmuir isotherms.

where  $C_0$  is the initial concentration of the adsorbate in solution. This parameter indicates that the isotherm will be shaped according to the following adsorption characteristics:  $R_L > 1$  unfavorable;  $R_L = 1$  corresponds to linear;  $0 < R_L < 1$  is favorable and  $R_L = 0$  is irreversible. It can be seen in Table 3 that the  $R_L$  values were in the range of 0.03173–0.11789. So, the experimental equilibrium data were better described by the Langmuir isotherm model, indicating the homogeneous nature of the sample surface and demonstrating the formation of monolayer coverage of dye molecule on the outer surface of adsorbent.

On the basis of the Langmuir analysis, the maximum monolayer sorption capacity (mg/g)  $q_{max}$  is calculated and listed in Table 3 for different cross-linked chitosan hydrogels at 25 and 55 °C. It is clear that at 25 and 55 °C,  $q_{max}$  value was higher for TTU-chitosan-1 hydrogel than other cross-linked samples at the same condition. This may be due to increasing freely protonated amino groups on the TTU-chitosan-1 hydrogel particle available for adsorption of dye molecules. However, in Table 3, it is clear that, with increasing degree of cross-linking, TTU-chitosan-2 and TTU-chitosan-3 improved the selectivity and the capacities. In other words, in the present work increasing the content of terephthaloyl



**Figure 10** | Adsorption isotherms for Congo red dye onto cross-linked chitosan hydrogels at 55 °C: (a) Freundlich isotherms; (b) Langmuir isotherms.

thiourea moieties does not cause high decrease in  $q_{max}$  value comparing with previous studies, using cross-linker epichlorohydrin for removing of Reactive red dye (Chiou & Li 2002). Also, this may be attributed to the regular distribution of porosity with increasing concentration of terephthaloyl thiourea moieties incorporated into the TTU-chitosan-3 hydrogel as mentioned before.

The linear form of the Freundlich expression is represented by Equation (8):

$$\ln q_A = \ln K_F + \frac{1}{n} \ln C_e \quad (8)$$

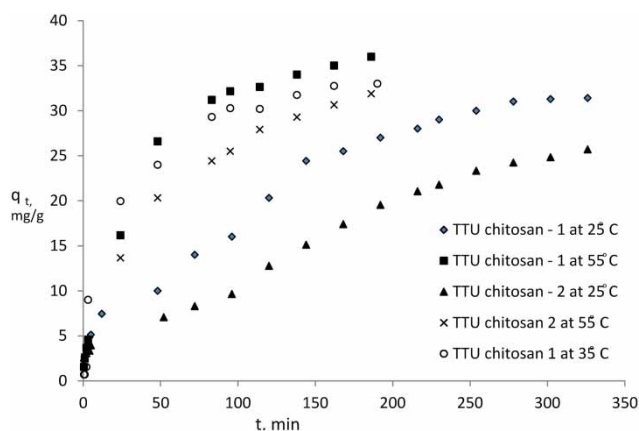
where  $q_A$  (mg/g) is the amount of dye adsorbed at equilibrium,  $C_e$  (mg/L) is its equilibrium solution concentration at a constant temperature,  $K_F$  and  $n$  are empirical constants that can be related to the adsorption capacity and the

adsorption intensity, respectively. The isotherm parameters for modeling the experimental results with the Freundlich equation are shown in Table 3. The  $1/n$  values indicate the type of isotherm to be irreversible ( $1/n = 0$ ), favorable ( $0 < 1/n < 1$ ), or unfavorable ( $1/n > 1$ ) (Mahmoud *et al.* 2013). As given in Table 3,  $1/n$  values were lower than unity, which shows the favorable uptake of the dye process by Freundlich isotherm model.

The correlation coefficient ( $R^2$ ) (Table 3) was  $>0.95$  and  $>0.05$  by applying Langmuir and Freundlich isotherm models, respectively. These results indicate that the data yield a better fit with the Langmuir isotherm model. Also, the Langmuir equation yields a straight line with a better fit of the experimental data than the Freundlich equation over the whole concentration range studied (Figures 9 and 10). Based on the values of correlation coefficients listed in Table 3, we can conclude that the Langmuir isotherm model yields a better fit with the experimental data for Congo red adsorption than the Freundlich isotherm. It indicated that Congo red was adsorbed mainly in the form of monolayer coverage on the surface of the adsorbent.

### Effect of temperature

Temperature is an important parameter for the adsorption process. A plot of the Congo red dye uptake as a function of time at different temperatures (25, 35 and 55 °C) is shown in Figure 11. The results reveal that increasing the temperature led to increasing values of adsorption capacity. This indicates that the temperature played an important role in the adsorption of Congo red dye onto cross-linked TTU-chitosan samples. Increasing the values of adsorption



**Figure 11** | The effect of temperature on adsorption capacity for Congo red dye onto TTU-chitosan samples at various time intervals (dye concentration = 50 ppm).

capacity by increasing the temperature may be attributed to increase in the mobility of the large dye ions as well as production of a swelling effect within the internal structure of the hydrogel, which facilitates the penetration of Congo red dye molecules into the internal structure of TTU-chitosan hydrogel. This result is also in agreement with the adsorption of Congo red dye on activated carbon prepared from coir pith (Namasivayam & Kavitha 2002), and on *N,O*-carboxymethyl-chitosan (Wang & Wang 2008).

However, adsorption of the dye from its aqueous solutions was completed in approximately 250 min at 25 °C, in 190 min at 35 °C and in 150 min at 55 °C. This suggests that the equilibrium time becomes shorter with increasing temperature. This result may be because the higher temperature increases the reaction rate and decreases the particle density, which forms larger pore size, making it is easier for dye molecule to diffuse (Chiou & Li 2003). In Table 2, increasing temperature leads to increasing the rate constants and the equilibrium adsorption capacity ( $q_A$ ). Therefore, the adsorption capacity should largely depend on the chemical interaction between the functional groups on the adsorbent surface and the adsorbate, and should increase as the temperature rises. This can be explained by an increase in the diffusion rate of the adsorbate into the pores, which indicates a kinetically controlling process. At higher temperatures the adsorbent might contribute to the adsorption of Congo red dye, so diffusion is an endothermic process (Hasan *et al.* 2008).

### Adsorption thermodynamics

For further evaluation of the effect of temperature on Congo red dye adsorption, the adsorption thermodynamics was studied. Thermodynamic parameters of standard free energy change ( $\Delta G^\circ$ ), standard enthalpy change ( $\Delta H^\circ$ ), and standard entropy change ( $\Delta S^\circ$ ) of Congo red adsorption on the cross-linked TTU-chitosan-1 sample were calculated at different temperatures, 25, 35 and 55 °C. The values of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  were estimated according to the Gibbs free energy, Equations (9)–(11) (Raymond 1998; Ngah & Liang 1999; Jain & Bhatnagar 2002):

$$\Delta G^\circ = -RT \ln K_D \quad (9)$$

$$\ln K_D = \text{constant} - \frac{\Delta H^\circ}{RT} \quad (10)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (11)$$

where  $R$  is the universal gas constant (8.314 J/(mol K)),  $T$  is the absolute solution temperature (K), and  $K_D$  is the

variation of the thermodynamic equilibrium constant, which can be calculated from the ratio of the equilibrium adsorption capacity ( $q_A$ ) to the equilibrium concentration of Congo red solution ( $C_e$ ), i.e.  $K_D = q_A/C_e$ . The values of  $K_D$  were  $876.4 \times 10^{-3}$ ,  $811.2 \times 10^{-3}$  and  $726.6 \times 10^{-3}$  for temperature 25, 35, and 55 °C, respectively.

The value of standard enthalpy of adsorption,  $\Delta H^\circ$ , for Congo red on TTU-chitosan-1, obtained from the slope of the plot between  $\ln K_D$  versus  $1/T$ , was 5.014 k J/mol (figure not shown,  $R^2 > 0.99$ ). A positive value of  $\Delta H^\circ$  suggests that the interaction of Congo red adsorbed by TTU-chitosan-1 is endothermic, which is supported by the increasing adsorption of Congo red with the increase in temperature. The negative values of  $\Delta G^\circ$  ( $-17.365$ ,  $-18.117$ , and  $-19.618$  kJ/mol at 25, 35, and 55 °C, respectively), indicate that the adsorption reaction is a spontaneous process and more favorable at high temperature, as previously reported (Hasan *et al.* 2008). On the other hand, the positive value of  $\Delta S^\circ$  (0.0751 kJ/(mol K)) showed the increasing of randomness at the solid/solution interface during the sorption of Congo red dye on adsorbent, relating to the increase of the adsorbent surface heterogeneity (Cao *et al.* 2014).

### Adsorption mechanism

In order to confirm that chemisorption of Congo red dye by TTU-chitosan samples is the predominant mechanism, activation energy ( $E_a$ ) and sticking probability ( $S^*$ ) values were calculated using a modified Arrhenius-type equation related to surface coverage ( $\theta$ ) (Mahmoud *et al.* 2016):

$$S^* = (1 - \theta)e^{-E_a/RT} \quad (12)$$

The  $S^*$  is a function of the adsorbate/adsorbent system under investigation; its value lies in the range  $0 < S^* < 1$  and is dependent on the temperature of the system. The value of  $\theta$  can be calculated from Equation (13):

$$\theta = \left[ 1 - \frac{C_e}{C_o} \right] \quad (13)$$

The  $E_a$  was calculated from the slope of the plot of  $\ln(1-\theta)$  vs.  $1/T$  (not shown). The magnitude of the activation energy gives an idea about the type of adsorption, which is mainly physical or chemical. The value of  $E_a$  for the adsorption of Congo red dye on cross-linked chitosan samples was

found to be 324.6 kJ/mol, suggesting that chemisorption was the predominant mechanism involved.

It has been reported that the solution at a pH below the point of zero charge ( $pH_{pzc}$ ) made the surface of the sorbent positively charged, which can attract anions from the solution (Mahmoud *et al.* 2016). The  $pH_{pzc}$  (pH at the surface has a net zero charge) of the cross-linked chitosan samples was determined by the potentiometric titration method (figure not given) (Mustafa *et al.* 2004). The  $pH_{pzc}$  value of the chitosan samples was found to be 6.7. So, below pH 6.7 most of the free amino groups were protonated. These protonated amino groups are attracted to anionic dye molecules. So, an electrostatic attraction exists between the positively charged surface of the adsorbent and the negatively charged Congo red dye (which is due to the presence of two  $SO_3$  groups on each molecule, Figure 1).

The above results revealed that the adsorption capacity of TTU-chitosan-1 was higher than the other adsorbents and could successfully remove more than 90% of the dye. This may be due to the strong adsorption affinity of TTU-chitosan-1 toward the dye, which is probably due to its larger pore size coupled with electrostatic forces of attraction involved between  $NH_3^+$  groups of adsorbent and the electronegative charges on the dye surfaces.

Finally, the previous observations showed that the chemisorption mechanism is based on the electrostatic interactions between the dye molecules and the synthesized chitosan hydrogel samples.

### Comparison with other adsorbents

To get an idea about the efficiency of the investigated cross-linked chitosan hydrogels, a comparison of the maximum adsorption capacities of Congo red dye over TTU-chitosan adsorbent in this work with those of other dyes using different cross-linked chitosan adsorbents reported in the literature is shown in Table 4 (Guibal *et al.* 2003; Cestari *et al.* 2004; Cestari *et al.* 2008; Morais *et al.* 2008; Xing *et al.* 2009; Zhua *et al.* 2010; Feng *et al.* 2011). This table shows that the developed terephthaloyl thiourea cross-linked chitosan hydrogels possess higher adsorption capacity (for Congo red dye) than that of other reported cross-linked chitosan adsorbents. This reflects the potential utility for TTU-chitosan adsorbent in Congo red dye removal. In this study, an environmentally friendly chitosan was modified with efficient synthesis of hydrogels via ionic cross-linking method. The prepared TTU-chitosan hydrogels 1, 2, and 3 could efficiently adsorb dye at 55 °C with  $q_{max}$  values of 44.3, 38.7, and 37.7 mg/g, respectively. Results

**Table 4** | Comparison of adsorption capacity of different dyes with different cross-linked chitosan adsorbents

No.	Cross-linking reagent	Dye	Adsorption capacity (mg/g)	Reference
1	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	Reactive blue15	29.370	Zhua <i>et al.</i> (2010)
2	Epichlorohydrin	Methyl green	33.700	Xing <i>et al.</i> (2009)
3	Glutaraldehyde	Reactive red	7.5000	Cestari <i>et al.</i> (2004)
4	Glutaraldehyde	Methyl orange	7.0000	Morais <i>et al.</i> (2008)
5	Glutaraldehyde	Acid black one	37.000	Guibal <i>et al.</i> (2003)
6	Glutaraldehyde	Direct blue 71	14.000	Guibal <i>et al.</i> (2003)
7	Glutaraldehyde	Congo red	24.180	Feng <i>et al.</i> (2011)
8	Glutaraldehyde	Indigo carmine	0.61300	Cestari <i>et al.</i> (2008)
9	Glutaraldehyde	Reactive yellow	9.0000	Cestari <i>et al.</i> (2004)
10	TTU-chitosan-1	Congo red	44.250	Present study
11	TTU-chitosan-2	Congo red	38.700	Present study
12	TTU-chitosan-3	Congo red	37.700	Present study

indicated that the synthesized cross-linked chitosan samples are promising adsorbents for the removal of Congo red dye from its aqueous solutions.

### Desorption and reuse results

Desorption and reuse are important in terms of costs and economic feasibility of the adsorption process. The Congo red dye desorption was possible with NaOH, where the dye was desorbed in 140 min. These findings confirm the results obtained previously that electrostatic interactions are involved in the dye adsorption. The chitosan sample reuse was possible for Congo red dye for three times, maintaining no change in adsorption capacity. Finally, it can be concluded that TTU-chitosan hydrogels are efficient adsorbents in Congo red dye removal. Their nature does not change even if they are used for three times.

### CONCLUSION

Congo red dye adsorption from aqueous solution by three cross-linked chitosan hydrogels containing various contents of terephthaloyl thiourea moieties (TTU-chitosan-1, TTU-chitosan-2 and TTU-chitosan-3) has been investigated. The factors influencing adsorption capacity of these hydrogels, such as the amount of cross-linker, initial concentration of the Congo red dye solution, time of attack with dye and adsorption temperature, for anionic dye were studied. The results showed that TTU-chitosan-1 adsorbent has a higher dye uptake rate and higher adsorption capacity than those

of TTU-chitosan-3 and TTU-chitosan-2 adsorbents. On the other hand, increasing the concentration of Congo red dye led to decrease in the percent removal of dye from aqueous solution, whereas increasing adsorption time or adsorption temperature led to increasing adsorption capacity. The adsorption kinetics and isotherms showed that the sorption processes were best fitted by the pseudo-second-order equation and the Langmuir equation, respectively. The results indicated that chitosan cross-linked by terephthaloyl thiourea moieties was an attractive candidate for removal Congo red dye from its aqueous solution. Cross linked chitosan samples can be reused three times for Congo red dye removal, maintaining the same adsorption capacity. However, the positive values of  $\Delta H^\circ$  and  $\Delta S$  indicated an endothermic and increasing disorder of the system, respectively, whereas the negative value of  $\Delta G^\circ$  suggested the adsorption reaction is a spontaneous process.

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