Textile & Leather Review

ISSN 2623-6281 | www.tlr-journal.com | 10.31881/TLR

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Manindra Nath Roy, Md. Tofazzal Hossain, Md. Zahid Hasan, Khairul Islam, Md. Rokonuzzaman, Md. Azharul Islam, Shahjalal Khandaker, M Mahbubul Bashar

How to cite: Roy MN, Hossain MT, Hasan MZ, Islam K, Rokonuzzaman M, Islam MA, Khandaker S, Bashar MM. Adsorption, Kinetics and Thermodynamics of Reactive Dyes on Chitosan Treated Cotton Fabric. Textile & Leather Review. 2023; 6:211-232. https://doi.org/10.31881/TLR.2023.030

How to link: https://doi.org/10.31881/TLR.2023.030

Published: 15 May 2023

Adsorption, Kinetics and Thermodynamics of Reactive Dyes on Chitosan Treated Cotton Fabric

Manindra Nath ROY[1,2], Md. Tofazzal HOSSAIN[2,3], Md. Zahid HASAN[1,4], Khairul ISLAM[1], Md. ROKONUZZAMAN[1], Md. Azharul ISLAM[1], Shahjalal KHANDAKER[3], M Mahbubul BASHAR[1*]

[1]Department of Textile Engineering, Mawlana Bhashani Science and Technology University, Tangail, Bangladesh

[2]Department of Textile Engineering, Northern University, Dhaka, Bangladesh

[3]Department of Textile Engineering, Dhaka University of Engineering & Technology, Gazipur, Bangladesh

[4]Department of Knitwear Engineering, BGMEA University of Fashion and Technology, Dhaka, Bangladesh

**bashar.te@mbstu.ac.bd*

Article

https://doi.org/10.31881/TLR.2023.030

Received 23 March 2023; Accepted 04 May 2023; Published 15 May 2023

ABSTRACT

The adsorption performance, kinetics, and thermodynamic parameters of reactive dyes on chitosan-treated cotton fabric are described in this research. The batch experiment was carried out to investigate the influence of pH, time, temperature, dye concentration, and material to liquid ratio of Remazol Red RR and Remazol Yellow RR, two widely used reactive dyes. The adsorption of red and yellow dyes was observed at λ_{max} 517 and 419 nm respectively. For both Remazol Red RR and Remazol Yellow RR reactive dyes with starting dye concentrations of 0.0667 and 40 mg/L, the greatest dye adsorption was reported at pH 11 (0.0009 and 0.1284 mg/g) and pH 4 (0.0004 and 0.1038 mg/g). The adsorption performance was investigated using the Langmuir and Freundlich isotherms. The adsorption behaviours of the two reactive dyes closely matched to the Langmuir adsorption isotherm (R^2>0.98) than Freundlich isotherm (R^2>0.92). The pseudo-second-order kinetic model (R^2>0.99) was followed by the dyeing kinetics of modified cotton sample. Thermodynamic investigation was covered with enthalpy change (ΔH^o), Gibbs free energy (ΔG^o) and entropy change (ΔS^o) where all the values were reported positive confirming that the adsorption process was non-spontaneous, endothermic and the higher affinity of reactive dye on chitosan treated cotton.

KEYWORDS

reactive dye, chitosan, surface modification, cotton fibre, adsorption isotherm, dyeing kinetics, thermodynamic properties

INTRODUCTION

Cotton is an ancient and exoteric natural cellulosic fiber, has one of the highest usage rates in the textile business [1]. It is composed of about 96% cellulose which is poly (1,4-β-D-anhydroglucopyranose [2,3]. The highest popularity of cotton is due to its wearing comfort, skin friendly and biodegradability [4]. In general, cellulose fibre contains negative surface charge (ζplateau =-11mV) and at higher pH, this negative charge affects the reduced anionic dyes adsorption significantly [5–7]. To increase the dye adsorption, a large amount of electrolytes, for example, sodium sulphate (40-100g/L) are normally applied [8–10]. This lavish amount of salt and unexhausted dyes in wastewater causes a dilemma for the biosphere [11,12]. Diverse approaches are being developed to

reduce the usage of salt in reactive dyeing and enhance dye fibre affinity. These new technologies of dyeing are mainly concerned with three approaches: firstly, the alternative dyeing techniques; secondly, the dyes modification; and thirdly the surface modification of cellulosic fibre [12–14]. To enhance the dye ability of cotton fibre for reactive dyeing, surface modification is drawing the attention of researchers in current times. Several investigations have been made to modify the cellulosic fibre surface frequently, but the introduction of the cationic group, mainly amino derivatives in the fibre surface, is a very popular choice [15,16].

Recently, chitosan, has gained more popularity regarding this issue [17–19]. It's a linear biopolymer polysaccharide comprised of frequently dispersed β-(1-4)-linked D-glucosamine and N-acetyl-D-glucosamine [20]. After alkaline de-acetylation of chitin (poly-(1-4)-2-acetoamido-2-deoxy-β-D-glucose), chitosan is obtained [21,22].

When cotton fibre oxidizes with hydrogen peroxide, it creates aldehyde group in their structure, and chitosan is applied after oxidation (pre-treatment of cotton), then it creates a cross-link between the cotton aldehyde group and the chitosan amino group [23]. This addition of chitosan with cellulose increases the cationic sites in the fibre surface, and anionic reactive dye is easily absorbed on the fabric surface without using electrolytes [24,25]. The oxidation and chitosan grafting onto cellulose are shown in Figure 1.

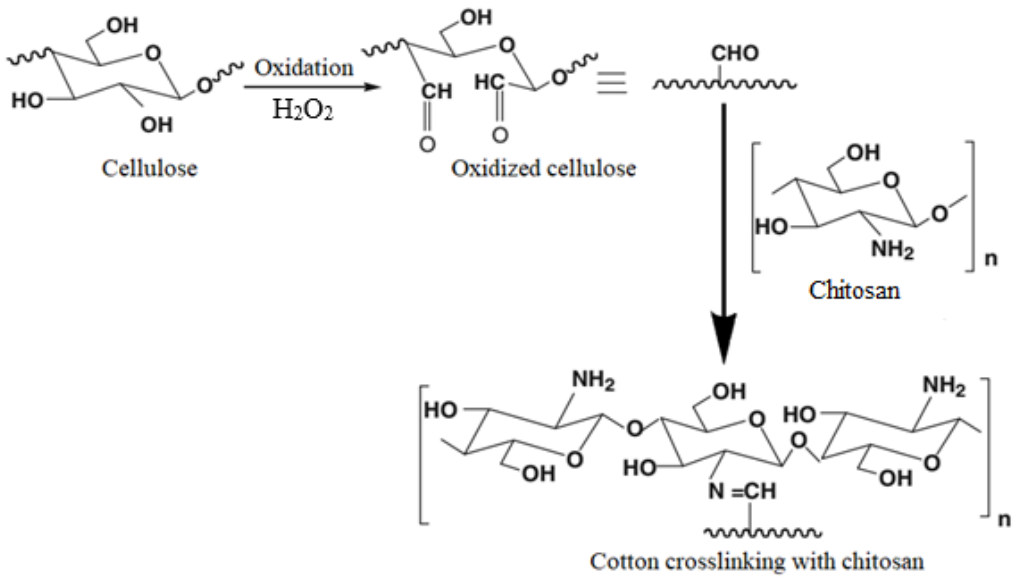


Figure 1. Oxidation of cellulose and subsequent grafting of chitosan into its surface

A substantial amount of research have been conducted for improving the dyeability of cotton fibre treated with chitosan [17,19,23,26–30]. Although the adsorption behaviour of reactive dyes on cellulose is already established [31]. Chairat has investigated the lac dyeing adsorption kinetics of

cotton [32]. He and Xie analysed reactive dye adsorption behaviour on magnetic chitosan-coated cotton [33].

From the above literatures it is evident that chitosan had used for several uses for instance, flame retardancy, UV protection, antimicrobial properties, dye encapsulation, dyed with turmaric extracts and multifunctional activity. However, to the best of our knowledge, the adsorption phenomena and dyeing kinetics of chitosan treated cotton with reactive dyes have not been studied yet. Here in, we have attempted to explore thermodynamic parameters and the adsorption isotherms of chitosan treated cotton fabric dyed with reactive dyes. The adsorption behaviour was analysed by adopting the models of Langmuir and Freundlich (L&F) adsorption isotherm, and kinetics and thermodynamics parameters were experimented in respect of pseudo-first order (PFO) and pseudo-second order (PSO) kinetic models.

EXPERIMENTAL

Materials

The knitted 100% cotton single jersey grey fabrics of 170 GSM were collected from a local factory and subsequently scoured and bleached. The chitosan (deacetylation >75%) was obtained from the Institute of Radiation and Polymer Technology (IRPT), Bangladesh Atomic Energy Commission, Dhaka, Bangladesh. Remazol Red RR (RRedRR) and Remazol Yellow RR (RYellowRR) reactive dye in commercial grade was utilized without purification. The reagents and chemicals that were used in this experiment is mentioned in Table 1.

Table 1. Reagents CAS registry number, suppliers and purity of the reagents

Reagents/chemicals	CAS registry no.	Suppliers	Purity
RRedRR	N/A	DyStar	Commercial grade
RYellowRR	N/A	DyStar	Commercial grade
Sodium Hydroxide	1310-73-2	Sigma-Aldrich	98%
Hydrogen Per-oxide	7722-84-1	Sigma-Aldrich	98%
Sequestering agent	N/A	N/A	Commercial grade
Wetting agent	N/A	N/A	Commercial grade
Peroxide stabilizer	N/A	N/A	Commercial grade
Detergent	N/A	N/A	Commercial grade

Scouring and bleaching of grey cotton fabric:

The typical scouring and bleaching recipe is mentioned in Table 2. As per the mentioned recipe, degreasing and bleaching of grey cotton fabric were processed in a sample dyeing machine. Immediately after that the sample was thoroughly washed and fully dried in air and used for further processing steps.

Table 2. Reagents for scouring and bleaching

Reagents/chemicals	Amount (g/L)
Sodium Hydroxide	2
Hydrogen Per-oxide	4
Sequestering agent	1
Wetting agent	1
Peroxide stabilizer	1
Detergent	1
pH	10-11
M:L ratio	1:20
Time, min	60
Temperature, ^{o}C	90

Pre-treatment of cotton using chitosan

To prepare 1(w/v)% chitosan solution, 10% acetic acid was used as the solvent and 5 g of cotton cloth that had been thoroughly cleaned, bleached, and scrubbed was soaked in a 3 (v/v)% chitosan solution for 30 minutes. The swollen cotton fabric was passed through a padding mangle maintaining wet pick-up 80%. The sample was treated for 1 minute at 130 °C after 5 minutes of drying at 80 °C. The sample was then dried in the air, cleaned with water, and placed in a sealed polybag for further research.

Characterization of chitosan treated fabric

FT-IR (Fourier transform infrared spectroscopy) was used to examine the surface chemistry of cotton fabric that had been treated and untreated. The FT-IR spectra of different cotton fabrics were obtained at 4 cm^{-1} spectral resolution using an FTIR spectrometer with KBr pellet using FT-IR 4700 (Jasco Corp., Japan). To examine the surface's morphology, a field emission scanning electron microscope (FE-SEM) was employed with Sigma 300 (ZEISS, Germany). The adsorption data of different stages were measured with the help of a UV-Visible spectrophotometer (UV-600; Shimadzu, Japan).

Adsorption experiment

The adsorption of RRedRR and RYellowRR reactive dyes was investigated on 0.25 g cotton fabric at material to liquid ratio (MLR) 1:20. The experiment was conducted on a closed vessel in an IR sample dyeing machine at 60 °C. A UV-Visible spectrophotometer was deployed to determine the absorbance. A mass-balance relationship equation, Eq. (1) was used to compute the dye uptake quantity of cotton (mg/g) per gram at any time (qt) [6,34].

$$\mathbf{q_t} = (\mathbf{C_0} - \mathbf{C_t})\frac{\mathbf{V}}{\mathbf{W}} \quad (1)$$

Here C_0 denotes the concentration of initial dye (mg/L), and C_t denotes the dye concentration after a time t (mg/L), V denotes dye solutions volume (mL), and finally W (g) express chitosan pretreated cotton weight.

The L&F adsorption isotherm model were employed to analyse adsorption isotherms. The Langmuir isotherms assumed that sorption deals with specific homogenous sites and have been applied to many sorption processes. The following equation is used to express the linear form of Langmuir isotherm [35–38]:

$$\frac{C_e}{q_e} = \frac{1}{q_m}C_e + \frac{1}{q_m K_L} \quad (2)$$

Where q_m denotes the maximal dye absorption per unit weight of fiber (mg/g) which, at a high equilibrium dye concentration C_e(mg/L), creates a full monolayer covering on the fiber surface q_e, expresses the adsorbed amount of dye per unit weight of fibre (mg/g) at equilibrium, and K_L denotes Langmuir constant refers the adsorption energy (L/mg). The intercepts and slopes of the straight lines derive from C_e/q_e versus C_e are used to compute the values of q_m and K_L [39,40].

The Freundlich isotherm depicts equilibrium on a heterogonous surface and monolayer capacity is not assumed in this case. Following equation describes the linear isotherm:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (3)$$

Where K_F indicates the adsorption capacity and n indicates the adsorption intensity (Freundlich constant) that were deliberated from the slopes and intercepts of the linear plot of $\log q_e$ versus $\log C_e$

[41]. The magnitude of the 1/n shows the adsorption favourability. Adsorption process suitability is expressed by the values of 1/n between 0~1.

The R_L factor is being used to verify the feasibility and favourability of the Langmuir isotherm model. It is determined by the below mentioned Equation 4 [32,42]:

$$R_l = \frac{1}{(1+K_L C_o)} \quad (4)$$

Where C_o denotes solution initial dye concentration (mg/L), and K_L indicates Langmuir constant (L/mg). If R_L >1, then the isotherm is unfavourable; if R_L=1, then linear; if 0<R_L<1, then favourable; and if R_L=0, then the isotherm is irreversible [43].

Adsorption Kinetics

To investigate the adsorption kinetics of reactive dye on chitosan treated cotton, the PFO and PSO kinetic models were employed to study the experimental data. The Langergren equation is the simple kinetic equation for the analysis of PFO kinetic models [35,36,44]. The equation is (linear form)-

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} (\text{linear form}) \quad (5)$$

The PSO kinetic model is on the basis of the adsorption equilibrium capacity that can be demonstrated by the below equation [45].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (\textit{linear form}) \quad (6)$$

Where k_1(min^{-1}), and k_2(g/mg/min) signify the rate constant of PFO, and PSO kinetic models, respectively. Here, q_e and q_t denote the capacity of adsorption (mg/g) of reactive dye on chitosan treated cotton at equilibrium and contact time t.

Applicability of the PFO kinetic model to suit the experimental data is indicated by a straight line of log(q_e-q_t) versus t. The intercept and slope of this line were used to derive k_1, the first order constant and q_e, equilibrium adsorption. Also, the applicability of PSO kinetic model can be determined by the straight line of $\frac{t}{q_t}$ and t. Here k_2, the second-order constant, and q_e were calculated from the slope and intercept of this $\frac{t}{q_t}$ versus t line.

Thermodynamics

The thermodynamic parameters of the adsorption process are enthalpy ΔH^o, free energy ΔG^o, and entropy ΔS^o was be determined by using Van`t Hoff equation.

$$\ln K_d = \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (7)$$

Where T is the temperature (K), R (8.314 J/mol) indicates the gas constant, and K_d (ml/g) denotes the distribution coefficient of adsorption process. The distribution coefficient (K_d) was obtained using the following equation.

$$K_d = \frac{C_0 - C_t}{C_t} \times \frac{V}{M} \quad (8)$$

Where C_0 (mg/L) expresses dye initial concentration, and C_t (mg/L) denotes the concentration of dye after time t, V (mL) denotes dye solutions volume, and m (g) express chitosan treated cotton fabric weight.

The Gibbs free energy ΔG^0, was obtained from the value of (ΔH^0) and (ΔS^0).

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

This ΔH^0 indicates the reaction is either exothermic or endothermic nature while ΔG^0 provides information about the spontaneous nature and affinity of dye to the fiber [46].

RESULTS AND DISCUSSION

FT-IR analysis of chitosan treated fabric

The FT-IR spectroscopy illustrated in Figure 2 shows the proof of chemical interaction in between chitosan and cellulosic polymer. The hydroxyl group (–OH) broad absorption band was noted at 3220 cm^{-1} wavenumbers. Likewise, the –NH absorption of the amide group overlapped in the same region and was difficult to identify separately due to the broadness of the –OH group present in cellulose. But the characteristic new peak at 1365 cm^{-1} appeared as a consequence of C-N stretching vibration for amide III [47]. Another new peak was observed at 1570 cm^{-1} for bending vibration of the N-H bond of the amide II group [48]. Furthermore, a strong absorption band was observed at 1745 cm^{-1} for cotton fabric treated with chitosan signifying the Schiff base (C=N double bond) formation between the carbonyl group of cellulose and the amino group of chitosan [3]. However, the stretching band of

carbonyl (-C=O) carbon was overlapped with the water absorption peak at 1640 cm^{-1} of cellulose fibre [49]. The fundamental base peaks of cellulose are obviously observed in the 1020-1160 wavenumber region responsible for different C-O backbone peaks of the cellulose ring [5]. In addition, different absorption bands of amide group, C-N group and cellulosic backbone peaks and –OH stretching vibrations were also confirmed in the dyed sample of chitosan treated fabric (supplement, Figure 1). Finally, the surface chemistry study of untreated cotton, chitosan modified cotton, chitosan and chitosan treated cotton fabric after dyeing showed the sufficient chitosan incorporation into cellulose polymer.

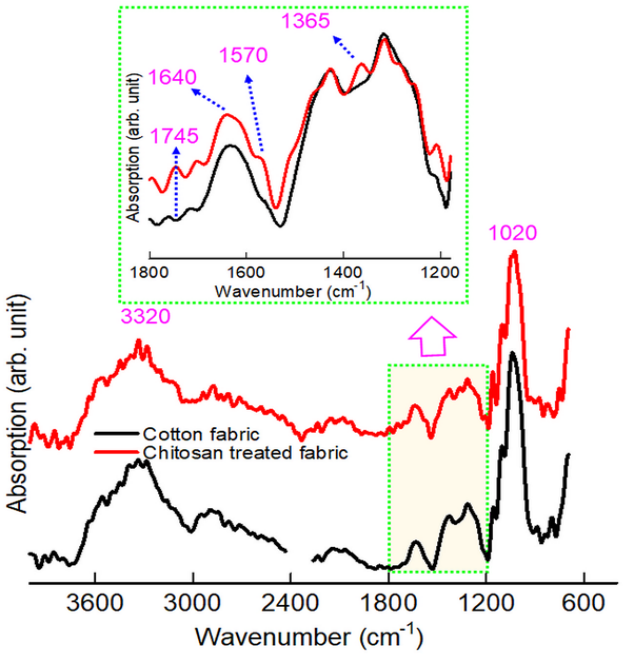


Figure 2. FT-IR absorption spectra of chitosan treated cotton fabric and cotton fabric. The inset shows the different absorption bands for the chemical interaction of chitosan with cellulose

Surface morphology of chitosan treated cotton fabric

A scanning electron microscope (SEM) was deployed to study the surface morphology of both the treated and untreated cotton fabric to demonstrate the morphological change in cotton fibre due to chitosan treatment. Figure 3 shows the surface morphology of pristine cotton and chitosan treated cotton fibre with elemental mapping from SEM-EDX stud. The pristine cotton fibre exhibited comparatively smooth surface whereas chitosan treated cotton fibre showed deposition of chitosan polymer on the surface (Figure 3(b)). Consequently, chitosan incorporation resulted the rough surface with numerous tiny grains than the untreated cotton fabric which conforms the previous studies

[50,51]. Furthermore, the elemental mapping of untreated and chitosan treated cotton fabric were also shown in Figure 3 (c) and (d).

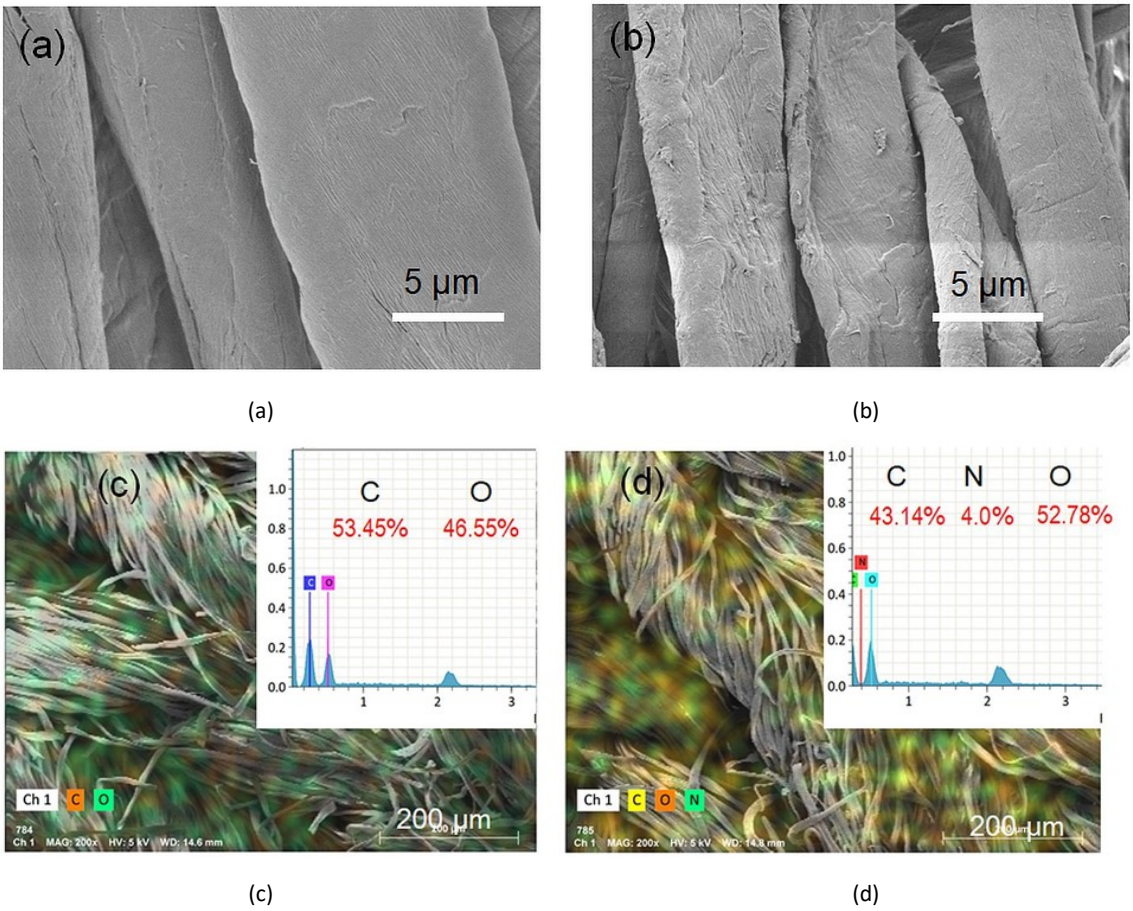


Figure 3. The SEM images of (a) pristine cotton fabric with smooth surface, (b) Chitosan treated cotton fabric showing chitosan particles in the fabric surface, SEM-EDX elemental mapping of (c) pristine cotton fabric and (d) chitosan treated fabric with nitrogen concentration 4.0%

The pristine cotton fibre surface was only confined with carbon and oxygen whose elemental proportions were 53.45% and 46.55% for carbon and oxygen atom respectively. On the contrary, the presence of nitrogen atom originated from chitosan was 4.0% confirmed by the SEM-EDX study in chitosan treated cotton fabric specifying the successful incorporation of chitosan into the cellulose matrix.

Adsorption and kinetic and thermodynamics studies

The effect of initial dye concentration

The reactive dye adsorption phenomenon on chitosan treated cotton is influenced by the initial dye concentrations. The Figure 4 demonstrates the effect of various dye concentration (1-47 g/L). It was

observed that chitosan treated cotton fabric showed the saturation point at 33 g/L and 40 g/L for RRedRR and RYellowRR respectively. The uptake of dye increased as the dye concentration was raised until the saturation point was reached. This occurred as a result of the concentration gradient's enhanced driving force [6]. At initial dye concentration, maximum dye adsorbed per gram of cotton for 33 g/L was 0.1552 mg/g and for 40 g/L was 0.0903 mg/g at 60 °C about 60 minutes at pH 6.6 for RRedRR and RYellowRR respectively.

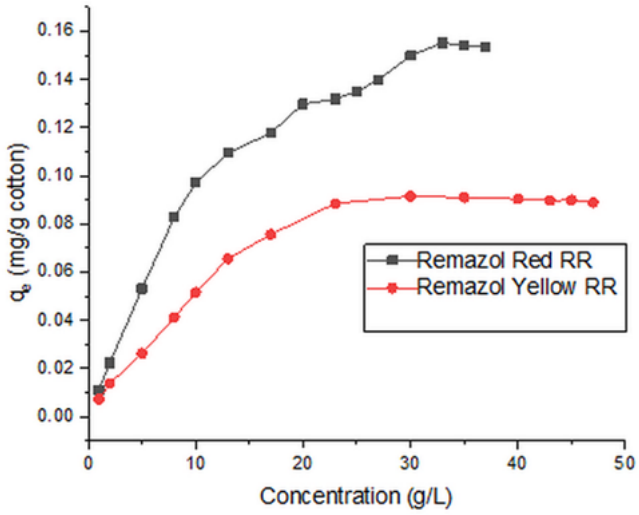
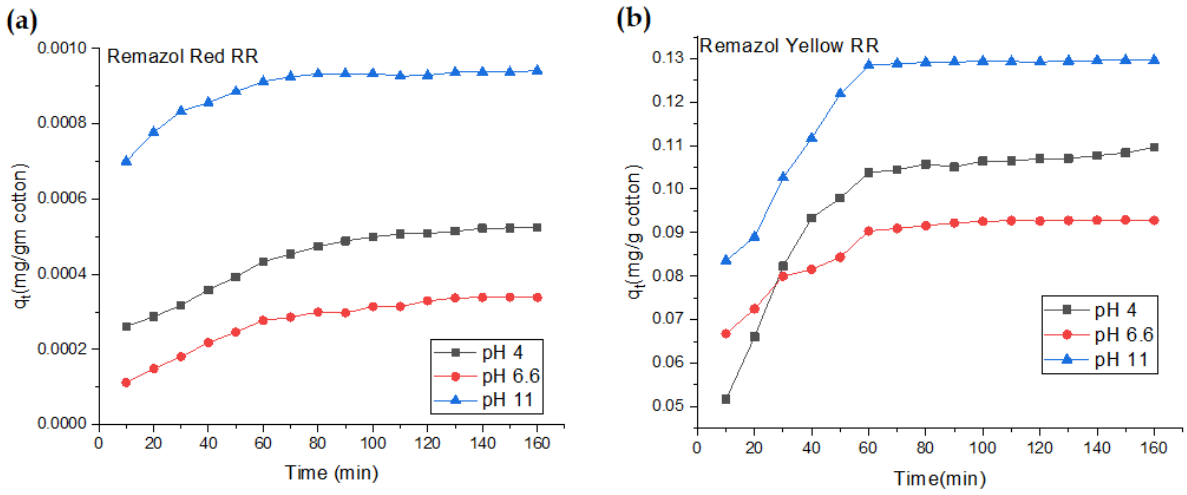


Figure 4. The effect of dye concentrations of chitosan treated cotton fabric

The effect of pH

The pH effect on the chitosan treated cotton of reactive dye was studied at 60 °C for 60 minutes. The Fig. 5 represents the dye adsorption onto chitosan treated cotton fabric for various pH (4, 6.6 and 11) against different time interval. The maximum dye adsorption was obtained at pH 11 accounting 0.0009 and 0.128 mg/g for RRedRR and RYellowRR dye respectively. At neutral pH value the dye adsorption was decreased significantly. A slight increasing trend of dye adsorption was found at pH 4. The similar phenomena were observed in case of both the dyes used in this study. The neutral (pH 6.6) dye exhibited less adsorption than the acidic (pH 4) dye bath while the highest adsorption was achieved at alkaline (pH 11) conditions. This result suggested that after chitosan grafting, the chemical nature of cotton fibre was changed slightly which resulted the higher dye adsorption at acidic (pH 4) dye bath than the neutral (pH 6.6) conditions. However, the alkaline condition (pH 11) showed the highest dye adsorption which is typical for reactive dyes for cotton fibre [52]. Moula A.T.M.G. et al. observed the

same phenomenon in their research where higher dye adsorption of cotton fabric was observed at alkaline pH [40].

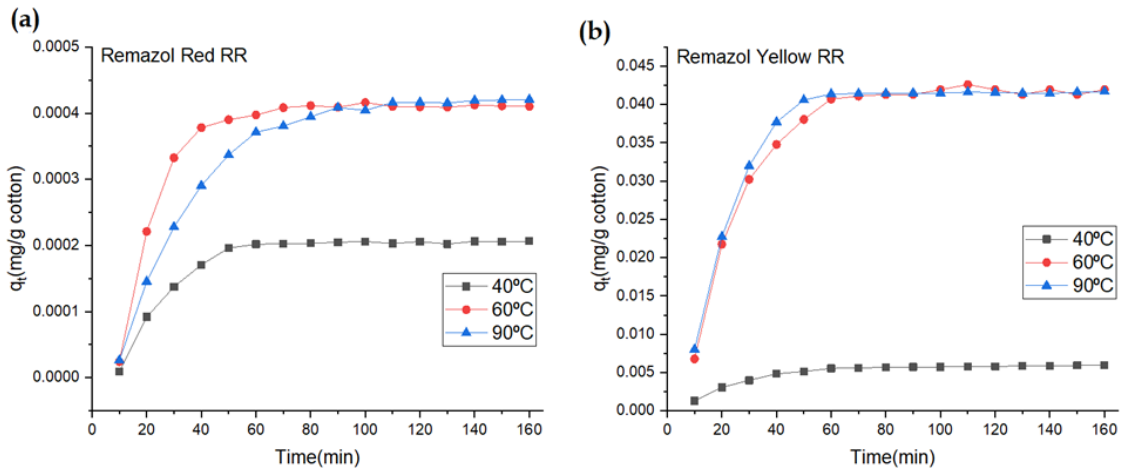


(a) (b)

Figure 5. The adsorption of chitosan treated cotton fabric at various pH conditions of the (a) RRedRR, and (b) RYellowRR reactive dyes

The effect of dyeing temperature

The effect of dyeing temperature was experimented at 40 °C, 60 °C and 90 °C with initial dye concentration 0.0667 mg/L (RRedRR) and 40 mg/L (RYellowRR) and pH 6.6 which is mentioned in Figure 6. It was revealed that the greater dye adsorption was observed at 60 °C for RRedRR and RYellowRR dyes. However, a slight variation was obtained in case of yellow dye. The maximum dye absorption for RRedRR was found 0.00042 mg/g cotton at 90 °C and 0.0419 mg/g cotton at 60 °C . But at 60 minutes, the maximum adsorption of RRedRR was about 0.0407 mg/g cotton for 60 °C, and at 40 ℃ the minimum was about 0.0055 mg/g cotton. The dye adsorption difference between 90 °C and 60 °C is very slight, 0.0006mg. At higher temperatures, dye is absorbed more because of the high mobility of the dye particle in the solution, while the internal fibre structure at high temperatures leads to more dye absorption [53]. The differences in dye adsorption between 60 minutes and 160 minutes are 0.000005, 0.00002, and 0.00004 mg/g cotton for RRedRR. Almost same phenomena was observed in case of RYellowRR dye. Quite a similar tendency was observed for wool dyeing with acid dye radiated with ultrasound. Dye take up and adsorption were increased with the uplifting of dyeing temperature [54].

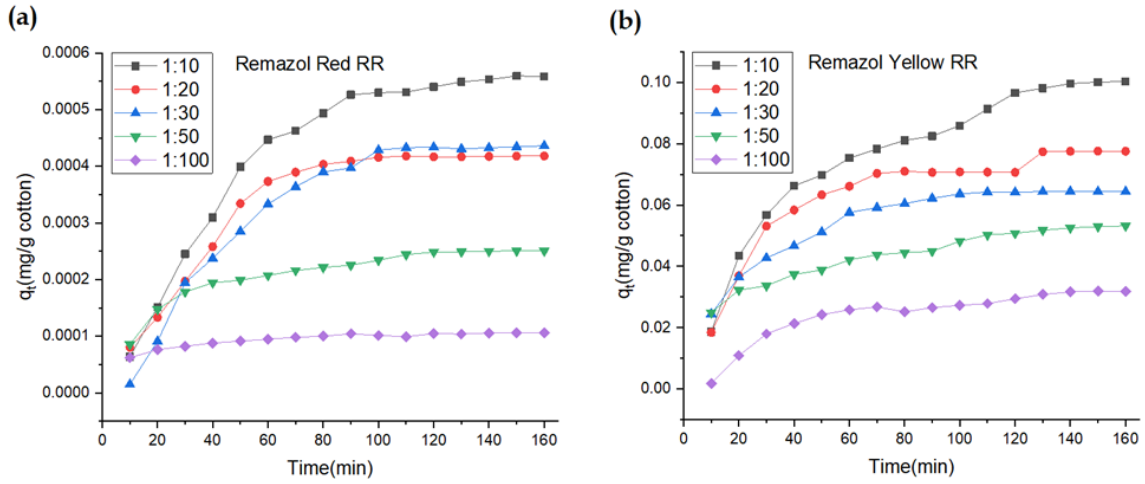


(a) (b)

Figure 6. The effect of temperature against different time of (a) RRedRR and (b) RYellowRR dyes

Effect of material to liquor (MLR) ratio

The effect of MLR on dye adsorption of chitosan treated cotton fabric with RRedRR and RYellowRR is shown in Figure 7. The amount of dye transferred from solution to the chitosan treated fabric is largely influenced by the liquor ratio. The result suggested that while the MLR increases, the dye adsorption on chitosan treated cotton fabric decreases; and maximum dye adsorption for RRedRR and RYellowRR was 0.00045 mg/g and 0.0753 mg/g at 1:10 ratio respectively. This was happened as a large liquor ratio needed more energy for the movement of the dye particle, and it showed less affinity to the fibre due to the significant distance while in case of shorter material to liquor ratio, the dyeing equilibrium reached rapidly [40,55].



(a) (b)

Figure 7. The effect of liquor ratio of (a) RRedRR, and (b) RYellowRR at 60 °C on chitosan treated fabric

Adsorption isotherms

The adsorption isotherm of chitosan treated cotton fabric was studied for the dyeing conditions of pH 6.6, MLR 1:20, initial dye concentration 0.0667 mg/L (RRedRR) and 40 mg/L (RYellowRR) at 60 °C following the Langmuir Equation 2 and Freundlich isotherms Equation 3. The Figure 8 illustrates the L&F adsorption isotherms and the parameters are described in Table 3.

Table 3. Isotherm parameters for RRedRR and RYellowRR dyes

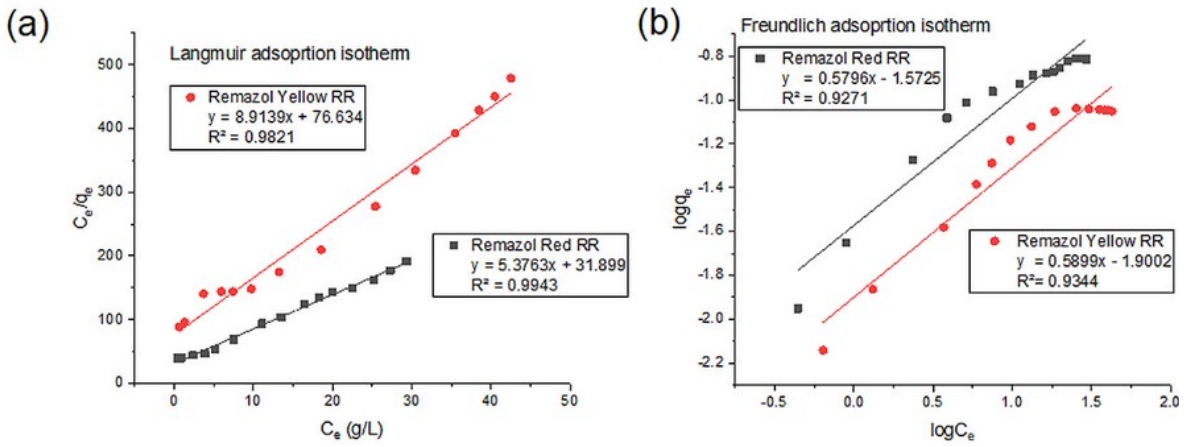
Dyes	Langmuir isotherm			Freundlich isotherm		
	q_m (mg/g)	K_L (L/mg)	R^2	K_F (L/mg)	1/n	R^2
RRedRR	0.1860	0.1685	0.994	0.0268	0.5796	0.927
RYellowRR	0.1122	0.1163	0.982	0.0126	0.5899	0.934

The result suggested that the adsorption isotherm of chitosan treated cotton fabric followed the Langmuir isotherm model exhibiting coefficients of multiple correlations (R^2>0.98-0.99). The data revealed that the dye adsorption on chitosan treated cotton fabric followed the monolayer adsorption which might directed by the amino group present in chitosan polymer. The maximum monolayer adsorption capacity of Red RR and Yellow RR Remazol dyes were 0.1860 and 0.1122 mg/g respectively. In addition, the favourability and feasibility of the Langmuir isotherm model are also determined by the R_L factor Equation 4, and the results are presented in Table 4.

Table 4. Determination of favorability and feasibility of Langmuir isotherm model

Dyes	C_o (g/L)	K_L (L/mg)	R_L
RRedRR	0.0667	0.1685	0.988
RYellowRR	40	0.1163	0.176

It was noticed that R_L ranged between 0 and 1, signifying that the Langmuir isotherm model was favorable and feasible for both RRedRR and RYellowRR dyes.



(a) (b)

Figure 8. (a) Langmuir and (b) Freundlich adsorption isotherms of Remazol dyes (Red RR and Yellow RR) on chitosan treated cotton fabric

Adsorption kinetics studies

The adsorption kinetics of chitosan treated cotton fabric of RRedRR and RYellowRR were analysed by the Equation 8 and Equation 9 for PFO and PSO kinetic models respectively. The parameters are reported in Table 5.

Table 5. The adsorption kinetics parameters of chitosan treated cotton fabric

Dyes		Pseudo-first order			Pseudo-second order			
		q_e (mg/g)	K_1	R^2	q_e (exp)	q_e (mg/g)	K_2	R^2
RRedRR	40 °C	20160.44	0.0327	0.5650	0.00020	0.00021	895.41	0.9978
	60 °C	28721.03	0.0142	0.6195	0.00041	0.00042	783.83	0.9994
	90 °C	1221.8	0.0444	0.9584	0.00042	0.00048	106.24	0.9949
RYellowRR	40 °C	268.287	0.0306	0.9594	0.0059	0.0066	9.3732	0.9955
	60 °C	77.321	0.0211	0.7224	0.0420	0.0460	1.7038	0.9920
	90 °C	99.907	0.0361	0.7271	0.0416	0.0447	2.4461	0.9932

PSO kinetic model was supported by the experimental data. The calculated equilibrium adsorption values were in line with the PSO kinetic model in different temperatures for both the dyes. In addition, the correlation co-efficient was found 0.99 which was in good agreement with PSO kinetics. On the contrary, the data did not match with the PFO kinetic model due to higher difference of correlation from unity. This results supported the adsorption of acid dye on wool fibre suggesting the presence of amino functional group from chitosan on the cotton fabric [54,56-61].

Thermodynamics studies

Thermodynamic parameters like enthalpy change (ΔH°), Gibbs free energy (ΔG°), and entropy change (ΔS°) for RRedRR and RYellowRR were determined using Equation 7 and 9 at 40 °C, 60 °C, and 90 °C respectively. The thermodynamic parameters are tabulated in Table 6.

Table 6. Thermodynamic parameters of RRedRR and RYellowRR dyes for the adsorption on chitosan treated cotton fabric

Dye	Temperature (°C)	ΔG° (KJ)	ΔH° (KJ)	ΔS° (J/K)
RRedRR	40	13.48	21.11	0.025
	60	13.10		
	90	12.59		
RYellowRR	40	20.86	45.58	0.082
	60	19.61		
	90	17.95		

The free energy (ΔG^o) of the system was found positive indicating that the adsorption of RRedRR and RYellowRR require external heat energy thereby the process of adsorption of both type of dyes is non-spontaneous. The heat of enthalpy of RRedRR and RYellowRR dyes was obtained 21.11 and 45.58 KJ respectively confirming that the adsorption process was endothermic in nature. The positive value of entropy ΔS° also indicated that the chitosan-treated cotton had a high affinity for the reactive dye [62-64]. An opposite finding was observed on silk dyeing with turmeric extracts where the dyeing process was exothermic active energy for adsorption was 94.90 kj/mol [38].

Plausible mechanism of dyeing of chitosan treated cotton fabric

The adsorption performance of reactive dye on cotton depends on adsorption time, temperature, material to liquor and pH. At higher pH and high temperature with higher adsorption time and lower material to liquor ratio reactive show better exhaustion using salt. But the adsorption rate seems off or negligible after certain times which indicates the Langmuir adsorption.

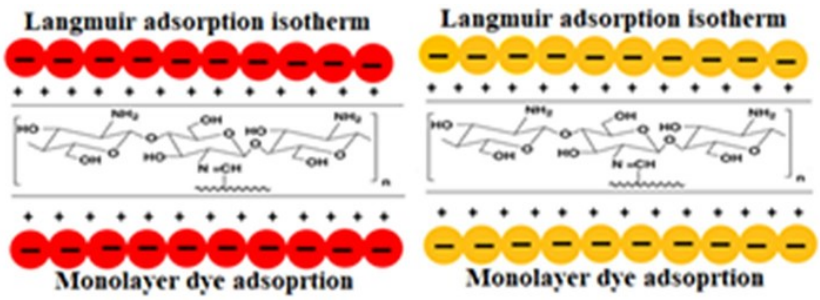


Figure 9. The mechanism of RRedRR (red circle) and RYellowRR (yellow circle) dyes adsorption on chitosan treated cotton fabric satisfying the monolayer adsorption of Langmuir adsorption isotherm

Langmuir adsorption depends on the specific sites in the solid, on which often only a limited number dye molecules are deposited on the fabric surface as a monolayer deposition and after this monolayer deposition no dye particles are transferred to fabric. This known as equilibrium time. Due to chitosan treatment cotton fibre demonstrated amino functional group confirmed by the FT-IR study and elemental mapping analysis. This amino functional cation acted as active sites for anionic dyes like RRedRR and RYellowRR. The schematic of such dyeing mechanism is illustrated in Fig. Consequently, the number of active sites that are accessible determines how much colour the cotton fibres will absorb. In the equilibrium situation, the dye molecules initially adsorbed on the surfaces of the most accessible places, however when the dye must gradually penetrate the less accessible areas, adsorption becomes more challenging.

CONCLUSIONS

In this study we have attempted to investigate the adsorption isotherms, thermodynamics and kinetics of RRedRR and RYellowRR commercial dyes on chitosan treated cotton knit fabric. The modification entailed the successful incorporation chitosan polymer on the cotton fibre surface. The chitosan modified cotton exhibited a protein-like structure due to the attachment of the amino functional group of chitosan. The microstructural chitosan particles were observed in the cotton fibre and 4% nitrogen was associated in the surface of cotton fibre that was confirmed by SEM and SEM-EDX elemental mapping analysis. Consequently, the adsorption isotherms of both RRedRR and RYellowRR dyes followed the Langmuir adsorption isotherm model closely. The maximum dye adsorptions were 0.1552 mg/g and 0.0903 mg/g of cotton for RRedRR and RYellowRR respectively. Reactive dye adsorption kinetics on chitosan treated cotton followed the PSO kinetic model. The enthalpy (ΔH°) value of reactive dye on chitosan pretreated cotton was found to be 21.11 KJ (RRedRR) and 45.58KJ (RYellowRR), and entropy ΔS° value 0.025 J/K (RRedRR) and 0.082 J/k indicate the process is endothermic and have a good affinity to the chitosan pretreated cotton. The current study validated the dyeing mechanism and improvement of dyeing technique of chitosan modified cotton fabric.

Author Contributions

Conceptualization – Roy MN and Bashar MM; methodology – Roy MN, Islam K, Khandaker S and Bashar MM; formal analysis – Hossain MT, Hasan Z, Rokonuzzaman M and Islam MA; investigation – Roy MN and Hossain MT; resources – Bashar MM, Rokonuzzaman M and Islam MA; writing-original draft preparation – Roy MN, Hossain MT and Bashar MM; writing-review and editing – Hasan Z, Islam K, Rokonuzzaman M, Islam MA and Khandaker S; visualization – Roy MN, Khandaker S and Bashar MM; supervision – Bashar MM. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

Funding

This research was funded by University Grants Commission (UGC), Bangladesh through the Research Cell of Mawlana Bhashani Science and Technology University for the fiscal year 2019-2020. The specific research grants number is 3631108.

Acknowledgements

We thank Institute of Radiation and Polymer Technology of Bangladesh Atomic Energy Commission, Dhaka, Bangladesh and Sparkle Knit Composite Ltd for the kind gifts of chitosan and knit fabric for the experimentation. The authors also gratefully acknowledge the experimental support of Jashore Science and Technology University, Jashore, Bangladesh for FT-IR, FE-SEM and EDX study.

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