



## Triaminoguanidine-modified cationic cotton for salt-free dyeing with enhanced leveling performance

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Received: 18/9/2023  
Accepted: 23/10/2023

**Abstract:** The chemically modified cellulose Triaminoguanidyl-modified (TAGu-MC) was synthesized and fully characterized by using a variety of suitable techniques, including scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, and elemental analysis. The synthesized (TAGu-MC) was applied for acid dye uptake from aqueous dye solutions, including 2-(4-Sulfo phenyl azo)-1,8-dihydroxy-3,6 naphthalene disulfonic acid trisodium salt (SPADNS). Significant variables such as pH effect, temperature effect, the initial concentration, the contact time were investigated to confirm the ideal adsorption conditions. The outcomes demonstrate that cellulose fiber cationization is a powerful and promising strategy for improving the adsorption of acid dyes was adsorption capacity 140 (mg/g).

**keywords:** Triaminoguanidine hydrochloride, SPADNS dye

### 1. Introduction

Substantial quantity of harmful and dangerous chemicals are produced as a result of ongoing industrialization and urbanization, which cannot be thrown into the environment, which is already under stress. An ecosystem is negatively impacted by rising global pollution levels and human activity. Many industrially manufactured compounds, including dyes, pigments, and other aromatics, are extremely poisonous and pose a serious threat to the environment. The second-largest industry in the world and one of Egypt's fastest-growing industrial sectors, the textile industry generates a significant quantity of trash throughout the dyeing, printing, and finishing operations [1-4]. Additionally, plenty of dyes used in the textile industry include hazardous such heavy metals, formaldehyde, and aromatic amines. These substances pose a threat to both human health and the environment [5-8]. For instance, even in little levels, dangerous heavy metals like lead and cadmium can bioaccumulate in organisms and eventually find their way into the food chain. Aromatic amines have been linked to cancer-causing effects and other medical problems. It is critical to regulate and reduce the concentration of these chemicals in dye effluent in order to preserve human health.

Implementing numerous methods is necessary for the difficult process of treating dye wastewater. The most common approach for treating dye wastewater is physical-chemical treatment. This procedure combines physical processes like sedimentation, flocculation, and filtering with chemical ones like coagulation and oxidation. These techniques have drawbacks since they are more expensive, less adaptable, less effective, and conflict with other wastewater components and waste management. It is not always successful to remove colors from wastewater using traditional methods. Currently, a variety of processes, including photocatalytic oxidation, radiation, magnetic separation, adsorption, and membrane separation, have the potential to treat dye wastewater [9-11]. Cotton dyeing has a significant negative influence on the environment. Reactive dyes, which are anionic in nature and brilliant, come in a variety of colors and have a high wash-fastness, making them the dye of choice for cotton fabrics.

Hence, it is necessary to balance the repelling interactions between the dye's negative charges and the negative charges generated on the surface of the fiber, which calls for a substantial amount of electrolytes,

such as sodium chloride or Glauber's salt [12]. In normal dyeing methods, about 60% of the dye is used up when Glauber's salt is added. Because they are neither used up nor destroyed during the dyeing process, the electrolytes stay in the dyebath. Reactive dyeing also needs an alkali to produce enough cellulose anions for fixation of dye molecules. But the many hydroxyl ions significantly hydrolyze the reactive dyes. Consequently, reactive dyeing causes environmental pollution by releasing a brightly colored, saline dyebath [13-14].

Due to the low exhaustion and inadequate color fixation, the expense of the dyeing process as a whole is considerably higher, even though the direct cost of using salt to dye cotton garments may be rather inexpensive. Price is significantly influenced by the amount of water and energy required to cleanse the dyebath and remove the hydrolyzed dye from the fabric [15]. Therefore, it is crucial to find procedures that reduce or completely remove the need for salt during the dyeing process. Many research efforts have tried to boost the affinity of anionic dyes toward cotton fabric by generating positively charged sites to cotton [16]. This is commonly referred to as cationization. Addition of positively charged sites makes it attainable for an electrostatic attraction to occur between the negatively charged dye molecules and the fiber, obviating the necessity for electrolytes in the cotton dyeing process and boosting the amount of dye exhausted and the fabric's color yield. On cationized cotton, complete depletion can be attained without the use of salt. The textile industry benefits immensely from cationic cotton's capability to be dyed faster, more efficiently, and with less environmental impact than conventionally dyed cotton, while also achieving higher color yields and fastness qualities [17]. According to the authors, cationization of cotton surface significantly enhances the amount of anionic dyes that are adsorbed ECR and SPADNS [18].

Herein, cotton fabrics are cationized using triaminoguanidine by utilizing a variety of experimental approaches. The newly produced triaminoguanidine modified cellulose chelating fibers (TAGu-MC) was characterized.

This research sought to create an N-donor

modified cellulose adsorbent for the removal of SPADNS dye in light of these findings and the coordination chemistry features of TAGu-MC. Periodic acid was used to oxidize cellulose before it was condensed with triaminoguanidine to create functionalized cellulose. (TAGu-MC).

## 2. Materials and methods

### Materials

Cotton, sodium periodate, Triaminoguanidine hydrochloride, 2-(4-Sulfo phenyl azo)-1,8 di hydroxy -3,6 naphthalene disulfonic acid trisodium salt (SPADNS), ethanol, triethylamine were purchased from Sigma Aldrich. All chemicals were used as obtained.

### 2.2. The method of preparation of the TAGu-MC

The following step-by-step instructions were applied to generate the modified cellulose by (TAGu-MC):

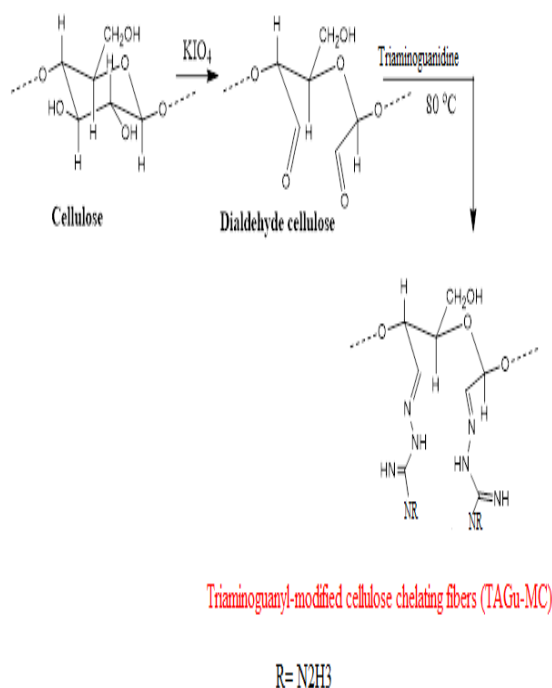
#### 2.2.1. Periodate oxidation of cotton fabrics.

In the following process, the cotton fiber was oxidized by sodium periodate. In the absence of light and at room temperature, sodium periodate (0.5 g) was dissolved in distilled water (100 ml), and then cotton fabric (0.5 g) was added to the solution. For two hours, the vessel was gently swirled at an average speed of 60 r/min. The cotton sample was immersed in 0.1 M glycerol solutions for 30 minutes after the oxidation was finished to eliminate any unreacted oxidant, and it was subsequently rinsed with cold distilled water to return it to its neutral state. The sample was then finished drying in a regular dryer.

#### 2.2.2. Cationization of the Cotton fiber by Triaminoguanidine .

Triaminoguanidine solution was prepared by dissolving (0.2g) of Triaminoguanidine in 100 ml of ethanol, then adding drops of triethylamine and oxidized cotton (DAC). It was stored in a flat bottomed three necked flask. Nitrogen gas was continuously purged through the agitated solution at a temperature of 100 °C during the reaction period. 3 hours were spent stirring the reaction, and it proceeded for an additional 15 minutes at room temperature. Subsequently, HCl (0.1 N) was used to wash the reaction product on stirrer for two hours without heating. The cationized cotton was

dried in its entirety.



**Scheme 1:** preparation of Triaminoguanyl-modified cellulose chelating fibers (TAGu-MC)

### 2.2.3-Characterization of present samples

Utilizing a Perkin Elmer 240 C Elemental Analytical Instrument (USA), the C, H, and N elemental percent composition for the untreated cotton and cationized cotton samples were calculated. To observe the surface morphology of the samples, a scanning electron microscope (SEM) (FEI Quanta-200 FEI Company- The Netherlands) is used. Before examinations, the fibers were sputtered and covered with gold. Spectrophotometer Libra S12 was used to measure the residual concentrations of SPADNS at max = 510 nm using Perkin-Elmer Bio UV-visible (LANBDA XLS, USA) Spectrometer.

### 2.2.4. Sorption studies using batch method

TAGu-MC chelating fibers were quantitatively absorbed for the investigated residual dyeing utilizing batch technique. As long as the temperature was kept at 25 °C, 50 mL of residual dyeing solution containing metal ions was employed along with 0.03 g of the modified cellulose for all of the experimental stages. Three hours at 25 °C were spent studying the sorption isotherm with dye concentrations ranging from 40 to 150 mg L<sup>-1</sup>.

The beginning residual dyeing concentration was 150 mg L<sup>-1</sup>, the study temperature ranged from 25 to 45 °C, contact period was three hours, shaking frequency was 150 rpm, and pH was five. To assign various thermodynamic characteristics, these variables were used. The assigned metal ions' initial concentration was 50 mL of 150 mg/L, pH 5 at 25 °C, and the kinetic parameter was examined while the interaction time ranged from 10 to 120 minutes.

$$q_e = (C_o - C_e) v/w \quad \text{Eq. 1}$$

Where the sorption capacity is  $q_e$  (mg/g), the initial and equilibrium concentrations of the assigned ions are  $C_o$  and  $C_e$ , respectively, correspondingly.  $V$  (L) volume of utilized solution in which the weight of modified cellulose is  $W$  (g).

## 3. Results and Discussion

### 3.1. Characterization of the polymeric samples

#### 3.1.1. Elemental analysis

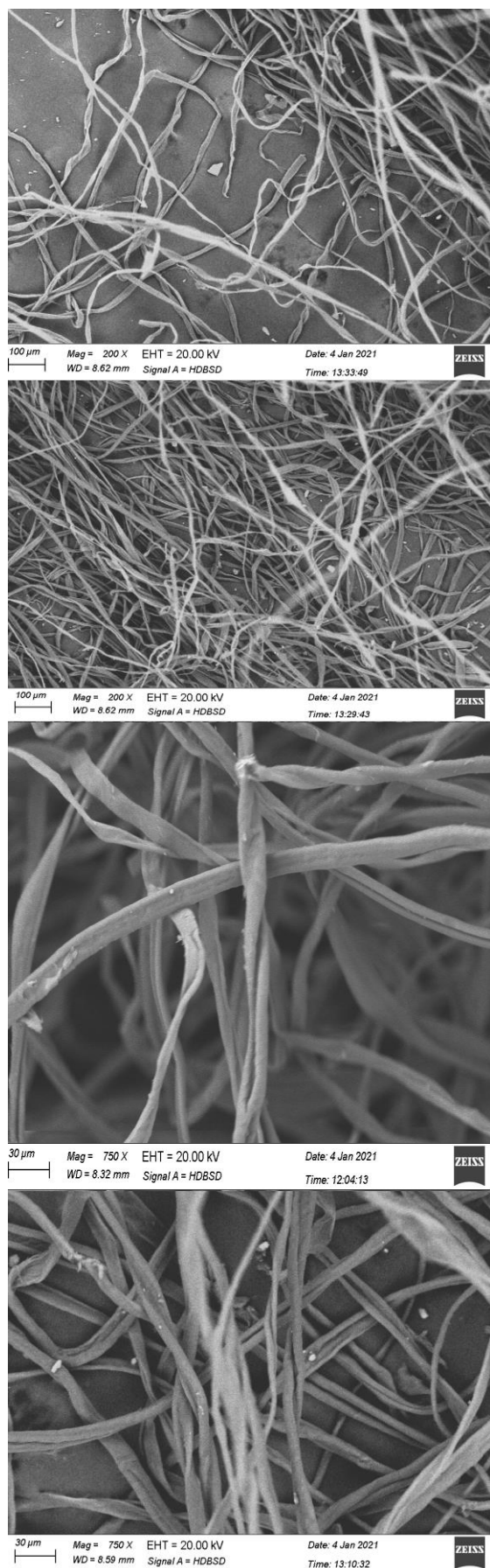
Table 1 shows the results gathered from the elemental analysis of native cellulose and TAGu-MC. The results show that when aminoguanidine is oxidized and then condensed, nitrogen is produced in substantial amounts. This investigation confirms the generation of cellulose aldehyde-guanyl Schiff's base.

**Table 1:** Elemental analysis of cellulose and TAGu-MC.

Fibers	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Cellulose	43.5	7.12	-----
TAGu-MC	49.7	12.3	26.4

#### 3.1.2. Scanning electron microscope

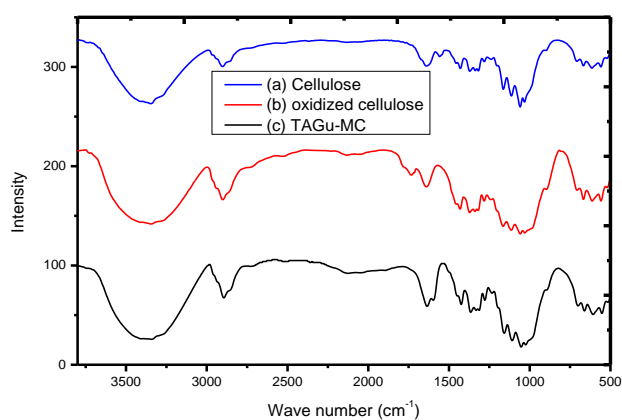
SEM images of both native and modified cellulose have been displayed (Fig. 1) by scanning electron microscope. It is straightforward to recognize rough and narrow streaks on the oxidized cellulose's outermost layer (Fig. 1a), which can be attributed to the periodate's impact on the cellulose fibers during oxidation [19]. Furthermore, the chemical reaction between the triaminoguanidine and the oxidized cellulose may be responsible for the rougher surface that TAG-MC detected



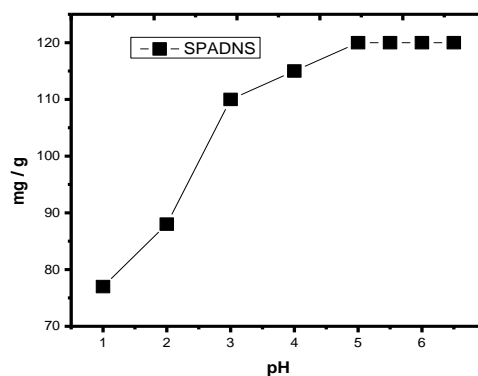
**Fig.1:** SEM photos of (a, b) oxidized cellulose, (c, d) Triaminoguananyl-modified cellulose

### 3.1.3. Infra red spectra

Utilizing UV-vis absorption spectroscopy, the progressive steps in the generation of Gu-MC as chelating fibers were identified, and the results are displayed in Fig. 2. Unmodified cellulose's UV-vis spectra (Fig. 2a) exhibited three distinct peaks at around  $1070\text{--}1150\text{ cm}^{-1}$ ,  $1240\text{--}1410\text{ cm}^{-1}$ , and  $3450\text{--}3100\text{ cm}^{-1}$  due to the stretching vibrations of O–H, C–O, and O–H. Upon selective oxidation by periodate, the spectra of the dialdehyde cellulose displayed a clear peak at about  $1725\text{ cm}^{-1}$ , This is related to the newly developed stretching of the aldehyde group. vibrations [20] (Fig. 2b). The spectrum of the produced TGu-MC (Fig. 2c) after treatment with triaminoguanidine correlates to the Schiff base's azo-methane group, which formed between the dialdehyde groups of the oxidized cellulose and the amino group of the triaminoguanidine, and a new peak at roughly  $1620\text{ cm}^{-1}$ . As a result, the Gu-MC's IR spectrum as a finished product (Fig. 2c) demonstrates that cellulose aldehyde-triaminoguananyl Schiff's base was formed.



**Fig.2:** FT-IR spectra of (a) native cellulose, (b) oxidized cellulose, (c) TAGu-MC



**Fig 3:** Effect of pH on the removal of SPADNS

### 3.2. Optimization studies

#### 3.2.1-Effect of pH

The dye uptake is affected by pH [21], as shown in figure 3. This trend could be explained in the terms of protonation for nitrogen atom of the Triaminoguanidine moiety under strong acidic medium, and almost all imino groups of the Triaminoguanidine moiety of TAGu-MC are existed in positively charged forms. However, by raising the pH to around 5, the uptake of the target metal ions showed a significant increase in the pH range from 2 to 5

#### 3.2.2. Adsorption kinetics:

An essential factor in the analysis of sorption effectiveness is contact time. 0.1 g of (TAGu-MC) material was used as the adsorbent dose, and it was added to a series of bottles containing 50 ml of 250 mg/l at various adsorption intervals between 60 and 120 min to study the contact time parameter. solutions with adsorbed metal ions, its shown that 90 mins is the best time for adsorption that after that the adsorption is constant.

The Effect of initial concentration on the adsorption capacity The sort of interaction between the adsorbed dyes solution and chelating fibers is best explained by the sorption isotherm research. A very basic theoretical model for monolayer sorption onto a surface with a limited number of identical sorption sites is the Langmuir model. The calculated experimental results are shown in table (2). The Langmuir model has the highest correlation coefficient values and best fits the derived experimental data.

Fiber	Langmuir isotherm constants		
	$K_L(L/g)$	$q_m(mg/g)$	$R^2$
TAGu-MC	$17 \times 10^{-2}$	140	0.978

**Table 2:** Thermodynamic studies for the sorption of targe dye solution on TAGu-MC sorbent.

System	Kc			-ΔG°ads (kJ/mol)			ΔH°ads (kJmol <sup>-1</sup> )	ΔS°ads (Jmol <sup>-1</sup> K <sup>-1</sup> )
	293 K	303 K	313 K	293 K	303 K	313 K		
SPADNS.TA Gu-MC	229	216	189	14.6	15.45	12.25	-25.6	34.39

**Table 3:** Comparison of equilibrium time of various adsorbents for dye sorption.

Adsorbates	Adsorbents	Sorption capacity (mg/g)		Reference
CV dye		Nonacomposite	28.2	22
		Red mud	60.5	23
		Activated carbon	67.1	24
SPADNS	TAGu-MC	55.4		Present study

#### 3.2.1.The effect of temperature on the sorption capacity of TAGu-MC sorbent towards the target dye

In order to ascertain the thermodynamic properties of the metal ion adsorption process on the TAGu-MC sorbent, studies were conducted at four different temperatures. Important parameters like the target dye's Gibbs free energy (Gadsn), heat of enthalpy (H), and entropy of sorption (S)

were calculated using TAG-Mc sorbent. Eq. 2 was used to calculate the thermodynamic equilibrium constant (Kc). $Kc = C_{adsn} / C_e$  Eq. 2

Cadsn represent the concentration of sorbed metal ions on to the active center of the chelating fibers at equilibrium (mg/g) and Ce is the equilibrium concentration in (mg/L)

$$\Delta G^{\circ}_{adsn} = -RT \ln KC \quad Eq. 3$$

$$\ln KC = (\Delta S^{\circ} / R) - (\Delta H^{\circ}_{adsn} / RT) \quad Eq. 4$$

where 8.314 J. mol<sup>-1</sup> K<sup>-1</sup> (or R) is the universal gas constant. The slope (Hoadsn/R) and intercept (Soadsn/R) of the plot of ln can be used to determine the values of Hoadsn and Soadsn. Kc versus 1/T as evaluated. We can infer from the G°adsn results that the sorption process by TAGu-MC occurs spontaneously at room temperature because the negative sign of G°adsn is what is expected. We can infer from the results of H°adsn that the sorption process by TAGu-MC is exothermic in nature at room temperature. This is because H°adsn has a negative sign. We can infer that the metal's desire to arrange itself is what is causing the reduction of the negative charge of S°ads values. many reported literatures displayed a similar behavior[22].

#### 4. Conclusions

Utilizing a variety of experimental approaches, the new triaminoguanyl-modified cellulose chelating fibers (TAGu-MC) were created and described. Thermodynamic analyses showed that the adsorption was spontaneous and exothermic in nature at all temperatures examined. Additionally, the Langmuir isotherm model accurately predicted the experimental results and guaranteed the metal ion monolayer adsorption.

#### 5. References :

- 1 J.H. Qiu, Y. Feng, X.F. Zhang, M.M. Jia, J.F. Yao, (2017) Acid-promoted synthesis of UiO-66 for highly selective adsorption of anionic dyes: Adsorption performance and mechanisms, *J. Colloid Interf. Sci.* **499**, 151-158,.
- 2 R. Yang, D.W. Li, A.M. Li, H. Yang, (2018). Adsorption properties and mechanisms of palygorskite for removal of various ionic dyes from water, *Appl. Clay Sci.* **151**, 20-28,
- 3 I. Belbachir, B. Makhoukhi (2017), Adsorption of Bezathren dyes onto sodic bentonite from aqueous solutions, *J. Taiwan Inst. Chem. E.* **75**, 105-111,.
- 4 Y. Zhao, Y. Chen, J. Zhao, Z.R. Tong, S.H. Jin, (2017) Preparation of SA-g-(PAA-co-PDMC) polyampholytic superabsorbent polymer and its application to the anionic dye adsorption removal from effluents, *Separation and Purification Technology* **188**, 329-340,.
- 5 J.H. Qiu, Y. Feng, X.F. Zhang, M.M. Jia, J.F. Yao, (2017) Acid-promoted synthesis of UiO-66 for highly selective adsorption of anionic dyes: Adsorption performance and mechanisms, *J. Colloid Interf. Sci.* **499**, 151-158,.
- 6 R. Yang, D.W. Li, A.M. Li, H. Yang, (2018) Adsorption properties and mechanisms of palygorskite for removal of various ionic dyes from water, *Appl. Clay Sci.* **151**, 20-28,.
- 7 I. Belbachir, B. Makhoukhi, (2017) Adsorption of Bezathren dyes onto sodic bentonite from aqueous solutions, *J. Taiwan Inst. Chem. E.* **75**, 105-111,.
- 8 Y. Zhao, Y. Chen, J. Zhao, Z.R. Tong, S.H. Jin, (2017). Preparation of SA-g-(PAA-co-PDMC) polyampholytic superabsorbent polymer and its application to the anionic dye adsorption removal from effluents, *Separation and Purification Technology* **188**, 329-340,.
- 9 K.X. Cui, B. Yan, Y.J. Xie, H. Qian, X.G. Wang, Q.X. Huang, Y.H. He, S.M. Jin, H.B. Zeng, (2018) Regenerable urchin-like Fe<sub>3</sub>O<sub>4</sub>@PDA-Ag hollow microspheres as catalyst and adsorbent for enhanced removal of organic dyes, *J. Hazard. Mater.* **350**, 66-75,.
- 10 Y.Y. Wang, L.L. Zhu, X.H. Wang, W. R. Zheng, C. Hao, C.L. Jiang (2018), Synthesis of aminated calcium lignosulfonate and its adsorption properties for azo dyes, *J. Ind. Eng. Chem.* **61**, 321-330,.
- 11 N. Ghaemi, P. Safari, (2018) Nanoporous SAPO-34 enhanced thin-film nanocomposite polymeric membrane: Simultaneously high water permeation and complete removal of cationic/anionic dyes from water, *J. Hazard. Mater.* **358**, 376-388,.
- 12 Acharya, Sanjit. (2012) "Cationization of Cotton Fabric for Improved Dye Uptake." PhD diss.
- 13 Blackburn, R. S., & Burkinshaw, S. M. A (2002) greener approach to cotton dyeings with excellent wash fastness. *Green Chemistry*, **4**(1), 47-52,.
- 14 Acharya, S., Abidi, N., Rajbhandari, R., & Meulewaeter, F. (2014) Chemical cationization of cotton fabric for improved dye uptake. *Cellulose*, **21**, 4693-4706,.
- 15 Blackburn, R. S., & Burkinshaw, S. M. A (2002) greener approach to cotton dyeings with excellent wash fastness. *Green Chemistry*, **4**(1), 47-52.
- 16 Kanik, M., & Hauser, P. J. Printing (2004) cationized cotton with direct dyes. *Textile research journal*, **74**(1), 43-50.
- 17 Blackburn, R. S., & Burkinshaw, S. M. (2003). Treatment of cellulose with cationic, nucleophilic polymers to enable reactive dyeing at neutral pH without electrolyte addition. *Journal of Applied Polymer Science*, **89**(4), 1026-1031,
- 18 Shateri Khalil-Abad, M., Yazdanshenas, M. E., & Nateghi, M. R (2009). Effect of cationization on adsorption of silver

- 
- nanoparticles on cotton surfaces and its antibacterial activity. *Cellulose*, **16**, 1147-1157,.
- 19 Siddiqua, U.H.; Ali, S.; Iqbal, M.; Hussain, T. (2017) Relationship between structures and dyeing properties of reactive dyes for cotton dyeing, *J. Mol. Liq.* **241**, 839–844,.
- 20 Siddiqua, U.H.; Ali, S.; Iqbal, M.; Hussain, T. (2017) Relationship between structures and dyeing properties of reactive dyes for cotton dyeing. *J. Mol. Liq.* **241**, 839–844,.
- 21 Acharya, S.; Abidi, N.; Rajbhandari, R.; Meulewaeter, F. (2014) Chemical cationization of cotton fabric for improved dye uptake. *Cellulose*, **21**, 4693–4706,.
- 22 Kim, J. Y.; Choi, H. M. (2014) Cationization of periodate-oxidized cotton cellulose with choline chloride *Cellulose Chemistry and Technology*, **48(1–2)**, 25–32.
- 23 Gholami, M., Vardini, M. T. & Mahdavinia, G. R. (2016). Investigation of the effect of magnetic particles on the Crystal Violet adsorption onto a novel nanocomposite based on  $\kappa$ -carrageenan-g-poly(methacrylic acid). *Carbohydr. Polym.* **136**, 772–781
- 24 Hamidzadeh, S., Torabbeigi, M. & Shahtaheri, S. J. (2015) Removal of crystal violet from water by magnetically modified activated carbon and nanomagnetic iron oxide. *J. Environ. Heal. Sci. Eng.* **13**, 1–7.