Preparation of cationic cotton through reaction with different polyelectrolytes

Jeferson Correia · Fernando Ribeiro Oliveira · Rita de Cássia Siqueira Curto Valle · José Alexandre Borges Valle

Abstract Cationization of cotton fabrics was performed by exhaustion procedure utilizing four different reagents provided with quaternary ammonium groups: poly diallyldimethylammonium chloride (PDDACl), poly acrylamide-co-diallyldimethylammonium chloride (PAcD), poly[bis(2-chloroethyl) ether-alt-1,3-bis[3-(dimethylamino)propyl]urea] quaternized (P42) and 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC). Pretreated samples were dyed using Reactive Red 195 dye. The cationic fabrics were analyzed by colorimetric and fastness properties, zeta potential, SEM, FTIR and an estimate of the bactericidal effect. Cationic cotton treated with PDDACl and CHPTAC showed a higher affinity for the reactive dye, with color strength (K/S) values varying from 41 to 48, against 32 for conventional dyeing. P42 presented competitive results with K/S of 27–28. The cationic dyeing considerably reduced the amount of effluent, especially for the CHPTAC samples, which requires a single washing bath for complete removal of unfixed dye. The PDDACl and P42 samples presented bactericidal activity.


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Graphic abstract
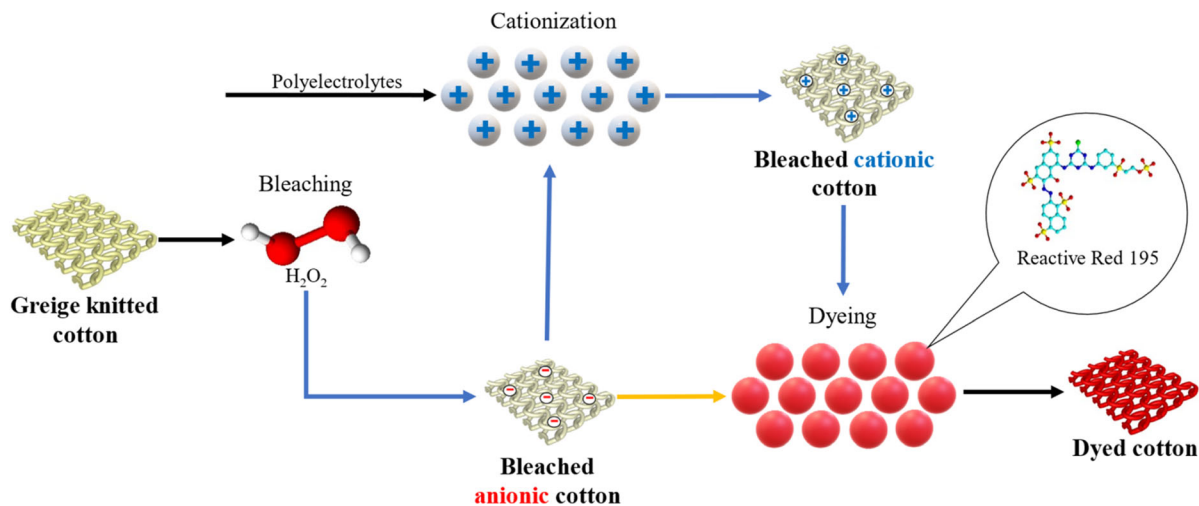
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Introduction

Cellulosic fibers, such as cotton, are essential materials in the textile industry, because of the high availability and low price and its many applications (Fu et al. 2013; Arivithamani and Giri Dev 2018). The cotton fabric is usually dyed with reactive dyes, which is considered the most important class of dyeing for cellulosic fibers (Shen et al. 2019). However, the major limitation of this process is that only 70–80% of the reactive dye is exhausted due to the anionic behavior of both cellulosic fibers and reactive dyes (Arivithamani et al. 2014). To overcome the limited affinity between reactive dyes and cotton fabrics, additional electrolytes are essential for conventional dyeing. Hence, cotton dyeing consumes a lot of chemical inputs, water and energy, which results in a large amount of effluent (Helmy et al. 2017).

The anionic behavior of the cellulosic fabrics can be changed by introducing new cationic groups that increase the affinity for reactive dyes (Micheal et al.

2002; Arivithamani and Giri Dev 2018; Abdelileh et al. 2019). Cationization of cotton has been extensively researched with the use of anionic dyes because they have a better affinity to materials with positive surface charges. One of the benefits of cationization is the elimination of the salt feed from conventional processes. It is estimated that the cationic process can reduce at least 70% of the concentration of salt in the reactive dyeing effluent (Arivithamani and Giri Dev 2018). Therefore, many authors refer to cationization as a salt-free or low-salt process (Chattopadhyay 2001; Ma et al. 2015, 2020; Arivithamani and Giri Dev 2017a; Sadeghi-Kiakhani and Safapour 2018; Dong et al. 2020). Even after extensive research and advancement in the field, cationization encounters barriers to industrial-scale applications due to nuisance odor (Farrell et al. 2015), high costs (Aktek and Millat 2017), toxicity (Farrell and Hauser 2013) and limited commercial availability of the reagents (Hasani et al. 2009). The cationization process has still not seen a significant industrial recognition beyond niche markets. The technique still needs to be improved to meet the industrial requirements.

The cationization of cotton has been researched for more than 50 years (Correia et al. 2020) but has grown especially at the beginning of the 2000s, after the after process improvement by Hauser and Tabba (2001). Besides, cationic cellulose is widely applied in other fields, such as papermaking (Gao et al. 2016; Odabas

et al. 2016, 2017; Aguado et al. 2018), cosmetics (Bujak et al. 2020), adsorbents (Pei et al. 2013; Lawchoochaisakul et al. 2021), flocculants (Yan et al. 2009; Sirviö et al. 2011) and antimicrobial agents (Chaker and Boufi 2015; Kumar et al. 2016). Cationic agents are also used to prepare fabrics with functional properties, such as UV protection, hydrophobicity, and conductive textiles (Wang and Hauser 2010; Kamal Alebeid and Zhao 2015; Sahito et al. 2015, 2016; Abd El-Hady et al. 2020; Liu et al. 2020).

The most common way to prepare cationic cotton fiber is by incorporating quaternary ammonium groups into the cellulose molecule (Roy Choudhury 2014; Aktek and Millat 2017). CHPTAC is the most common reagent for cotton cationization applied in textile dyeing (Hauser and Tabba 2001; Wang et al. 2009, 2018; Fu et al. 2013; Acharya et al. 2014; Arivithamani and Giri Dev 2016, 2017b, 2018; Abdelileh et al. 2019). However, CHPTAC faces some concerns over the safety of the product (Farrell and Hauser 2013; Farrell et al. 2015). Some researchers studied novel cationic agents to overcome the concerns regarding the use of CHPTAC.

Farrell et al. (2017) used various quaternary ammonium compounds for cotton cationization using reactive and disperse dyes. The long-chain cationic agents increased the hydrophobicity of the cotton, making it dyeable with disperse dye. Dong et al. (2020) improved the dye uptake, dyeing levelness, and color fastness for fabrics cationized with the polyelectrolyte 2-(N, N-dimethylamino) ethyl methacrylate. Ma et al. (2015) prepared cationic cotton with 2-methacryloyloxyethyltrimethyl ammonium chloride. The proposed method increased about 24% the fixation of the reactive dyes into cationic cotton, besides reducing the chemical oxygen demand, color, and nitrogen content of the effluent.

Chitosan, a biopolymer derived from chitin, is an example of a possible natural substitute for cationization of cotton as it has been studied by many researchers (Chattopadhyay 2001; Ibrahim et al. 2010; Oliveira et al. 2017; Sadeghi-Kiakhani and Safapour 2018; Pan et al. 2020). Other studies include keratin, betaine, and ovalbumin as natural cationic agents (Arivithamani et al. 2014; Ma et al. 2016; Giacomini et al. 2020).

In this paper, four cationic reagents with quaternary ammonium groups were used for cationization of cotton: Poly diallyldimethylammonium chloride (PDDACl), Poly acrylamide-co-diallyldimethylammonium chloride (PAcD), Poly[bis(2-chloroethyl) ether-alt-1,3-bis[3-(dimethylamino)propyl]urea] quaternized, also known as Polyquaternium-2 (P42) and 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC). Figure 1 presents the molecular structure of each polyelectrolyte.

P42 and PAcD are polymers with potential as novel cationic agents for the pretreatment of cotton. PAcD, also known as PAD, PAADDA or P(AAm-co-DADMAC) (Lian et al. 2016; Qi et al. 2018; Ao et al. 2018) is a copolymer provided with a quaternary ammonium group. One of the PAcD copolymer monomers is diallyldimethylammonium chloride, the same PDDACl forming monomer. Some recent publications already testified PDDACl's capacity as a cationic agent (Kim et al. 2016; Peng et al. 2016; Helmy et al. 2017; Oliveira et al. 2017; Bessa et al. 2019; Meng et al. 2021). PDDACl has been recently researched as a cationic agent for textiles due to the low cost and environmentally safe properties. PDDACl is the first polymer approved by the United States Food and Drug Administration (USFDA) for
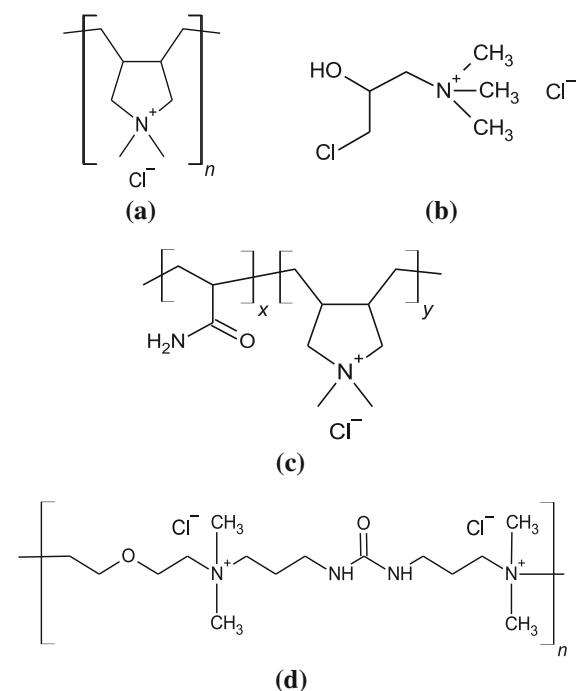

Fig. 1 Molecular structure of the polyelectrolytes used in the present paper: **a** PDDACl, **b** PAcD, **c** CHPTAC and **d** P42

use in the treatment of potable water (Helmy et al. 2017).

As CHPTAC is the most common cationic agent for textiles, it will be used in the present paper for reference purposes. PDDACl has a smaller number of publications regarding dyeing processes. Jareansin et al. (2019), Helmy et al. (2017), and Meng et al. (2021) prepared cationic cotton fabrics with the PDDACl's monomer diallyldimethylammonium chloride and dyed with acid or reactive dyes. The polymer PDDACl has been used as a cationic agent with meta-aramid and a blended fabric composed of 50% polyester and 50% cotton to dye using acid dyes (Oliveira et al. 2017; Bessa et al. 2019). The novelty of this paper is concentrated on the other two cationic agents: PAcD and P42.

The application of PAcD has become a research focus due to several advantages, such as high positive charge density, safety, and stability of the cation unit (Lian et al. 2016). Recently, PAcD has been researched for the development of drug carriers nanogels and nanofiltration membranes (Sana et al. 2019; Scheepers et al. 2021). Qi et al. (2018) prepared hydrogel using PAcD to adsorption of methyl orange dye in aqueous solutions, for wastewater treatment. PAcD has been researched in different fields but the application of PAcD as a cationic agent for textile fabrics has not been reported.

P42 is a water-soluble polymer and has been used as a conditioning agent for skin and hair care products (Chen et al. 2016). It has two quaternary ammonium groups in its molecule structure. Hence, it may be a candidate for cotton cationization. P42 has antimicrobial efficacy and non-toxic behavior reported (Kumar et al. 2016). A sustainable approach with plasma treatment and cationization of cotton at the greige stage using P42 was recently reported by the same research group (Correia et al. 2021). In the present paper, cationization was performed on bleached cotton as bleaching is the conventional pretreatment for textile dyeing.

The present paper focuses on the comparison between four cationic agents. The fabrics were treated using cationic agents at 20 or 40 g L^{-1}. The surface of the cotton fabrics was characterized by Fourier Transform Infrared (FTIR) spectroscopy, Scanning Electron Microscopy (SEM) and zeta potential. Besides, the bactericidal efficacy was estimated and the mechanism for cationization was proposed.

Materials and methods

Materials

A 100% greige cotton single jersey knitted fabric (weight = 160 gsm) was used in this paper and was supplied from Pemgir Malhas, Brusque, Brazil. PDDACl solution (20 wt% in H$_2$O), PAcD solution (10 wt% in H$_2$O) and P42 solution (62 wt% in H$_2$O) were purchased from Sigma-Aldrich. Commercial CHPTAC solution (65 wt% in H$_2$O) was supplied from Werken Química (Brazil). C.I. Reactive Red 195 was the dye used in this paper. The supplementary material contains additional information about the dye, among auxiliary chemicals used.

Pretreatment and dyeing of cotton

Bleaching, cationization and dyeing of greige cotton fabric were performed by exhaustion method, in a TC 2200 dyeing machine (Texcontrol) with 250 mL steel cannons. All assays were performed with a material-to-liquor ratio of 1:10. The greige cotton fabric was initially submitted to bleaching process. A solution containing 1 g L^{-1} of nonionic detergent, 8 mL L^{-1} of NaOH 50% solution, 1 g L^{-1} of peroxide stabilizer and 10 mL L^{-1} of H$_2$O$_2$ 35% solution. The solution and the greige cotton were heated at 2 °C min^{-1} until 95 °C, remaining at that level for 45 min. After that, bleached cotton was washed using 1 g L^{-1} of non-ionic detergent solution at 60 °C and 10 min. The bleaching process scheme can be seen in Fig. 2a.

The cationization and dyeing procedure occurred according to the recipe provided by the CHPTAC supplier. The cationization process scheme can be seen in Fig. 2b. Cationization was performed from a solution containing 2 g L^{-1} of nonionic detergent, 20 or 40 g L^{-1} of cationic agent and 10.5 or 13.5 mL L^{-1} of NaOH 50%, respectively. The solution was mixed with the fabric sample and inserted into the equipment, heated at 3 °C min^{-1} until 75 °C, maintaining at that level for 25 min. Two wash baths were then carried out. The first was done by adding a neutralizing solution to the fabric, containing 0.5 g L^{-1} of formic acid 85% and remaining at 35 °C for 5 min. In the second, the fabric was subjected to washing with deionized water.

The reactive dyebaths were prepared by dissolving 2 g L^{-1} of leveling agent and 0.4%owf (over weight

Fig. 2 a bleaching process. Solution A: nonionic detergent, NaOH, peroxide stabilizer and H2O2. Solution B: nonionic detergent. **b** cationization process. Solution A: cationic agent, non-ionic detergent and NaOH 50%. Solution B: Formic acid. Solution C: deionized water. **c** dyeing process. Solution A: equalizing agent, dye and NaCl (only in conventional dyeing). Solution B: alkalizing agent. Solution C: deionized water. Solution D: Formic acid and anionic detergent. Solution E: deionized water
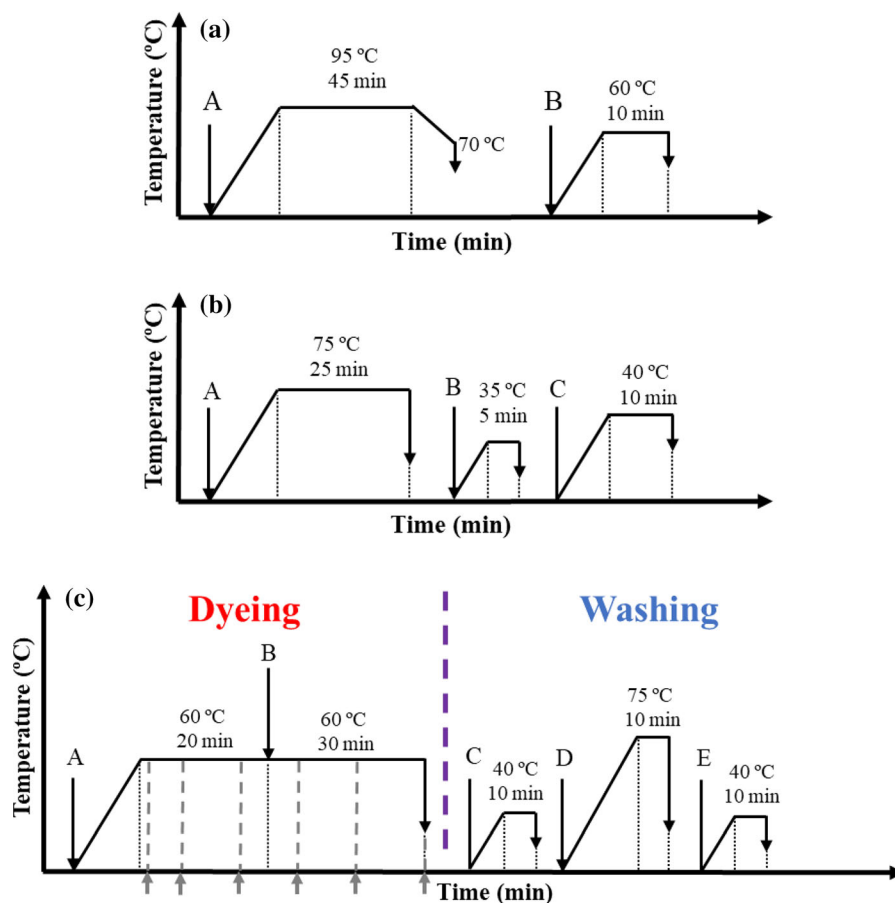
of fiber) of dye. For the dyeing of the non-cationic sample, 60 g L^{-1} of NaCl was also added. The dyeing occurred at 3 °C min^{-1} until 60 °C, maintaining that level for 50 min. After 20 min, 4.7 $g.L^{-1}$ of an alkalizing agent composed of sodium hydroxide and sodium carbonate was added. Following the dyeing, washing was carried out by adding the fabric with deionized water at 40 °C and 10 min. The second washing bath was made with 1.2 g L^{-1} formic acid 85% solution and 1.0 g L^{-1} of anionic detergent, maintained at 75° C for 10 min. The last washing bath was made with deionized water at 40 °C for 10 min. The samples dried at room temperature after each bleaching, cationization or dyeing step. The dyeing process scheme can be seen in Fig. 2c.

The arrows pointing up in Fig. 2c indicate data collection intervals. After the bath dyeing temperature stabilized at 60 °C, fabric samples were collected at intervals of 2, 8, 28, 38 and 50 min. The effect of time on dyeing was assessed by measuring the color

properties in the fabric. All samples were submitted to washing after dyeing.

In the competitive dyeing test, all samples treated with the same cationic concentration were dyed simultaneously into a single bath. The material-to-liquor ratio was still 1:10, considering the sum of the mass of all fabric samples. The objective of this experiment is to estimate the competitiveness of the pretreatments with anionic dye. Therefore, the dyed samples were submitted to rinse with water after the dyeing, without the washing procedure indicated in Fig. 2c. Besides, it was not possible to perform the conventional dyeing due to the absence of salt in the dyebath.

Measurement of color properties

Color measurements of the textile samples were performed on a Datacolor 500 reflectance spectrophotometer (Datacolor International, illuminant D65, 10°

standard observer). The values were an average from four readings taken at different points with the sample folded. The color strength (K/S) was measured using the Kubelka–Munk equation (Eq. 1):

$$K/S = \frac{(1-R)^2}{2R} \qquad (1)$$

where R is the reflectance, K is the absorption coefficient, and S is the scattering coefficient. The final value was calculated by a sum of 10 nm intervals from the wavelength of 360–700 nm (Fu et al. 2013).

The whiteness of the fabric was measured by the Berger degree (Puebla 2006), and colorimetric coordinates by the CIELab color space. The whiteness and color deviation (ΔE) were calculated using Eq. 2 and Eq. 3:

$$Whiteness = Y + 3.448 \cdot Z - 3.904 \cdot X \qquad (2)$$

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 (\Delta b^*)^2} \qquad (3)$$

where X, Y, and Z are the coordinate values of the tristimulus system. ΔE is the CIELab color difference between the sample and the control. ΔL^*, Δa^* Δb^* denotes the difference between the pairs of samples at the CIELab color space (Arivithamani et al. 2014; Nakpathom et al. 2017).

The levelness in dyed fabrics was calculated using the Relative Unlevelness Index (RUI), as shown in Eq. 4 and Eq. 5. For calculating RUI, ten randomly selected locations on each sample had the reflectance measured in the visible wavelength region (390–700 nm) at 10 nm intervals. The RUI takes account of the reflectance measured over the visible spectrum, with a correction function that considers the human vision sensitivity (Chong et al. 1992).

$$S_\lambda = \frac{\sqrt{\sum_{i=1}^{n} (R_i - \overline{R})^2}}{n-1} \qquad (4)$$

$$RUI = \sum_{\lambda=390}^{700} \left(\frac{S_\lambda}{\overline{R}}\right) V_\lambda \qquad (5)$$

where S_λ is the standard deviation of reflectance measured at a specific wavelength, n is the number of measurements at each wavelength. R_i and $\overline{R}$ are the reflectance values of, respectively, the ith measurement and the mean. V_λ is the photopic relative luminous efficiency function, these data are tabulated

in the work of Guild (1932). The visual appearance of levelness followed the suggested interpretation of the RUI values listed in Table 1.

One-way ANOVA and Tukey's test were performed in the color properties of the fabric samples. P-values lower than 0.05 indicate that the terms are statistically significant. The analysis was performed using BioEstat 5.3 (Ayres et al. 2007).

Washing fastness tests were performed according to ISO 105-C06, procedure C1S, using a TC 2200 dyeing machine (Texcontrol). Rubbing fastness tests were performed according to ISO 105-X12 using a Rubbing Fastness Tester of the brand Kimak, CA-11 model. The color change was rated according to the appropriate grey scale value, using a Datacolor 500 reflectance spectrophotometer for measurement.

Liquid phase dye concentrations were measured with a UV-M51 transmittance spectrophotometer (BEL Engineering), with a 1.0 cm optical path quartz cuvette. The values were an average from three readings. A scan was also performed to verify the wavelength of maximum absorption in the UV–Visible region, followed by the creation of a calibration curve for absorbance conversion in concentration according to Beer's law.

Surface characterization

Streaming potential measurements on fabrics were performed with an electrokinetic analyzer (SurPASS, Anton Paar GmbH, Austria) using a measuring cell for solid samples (glass cylinder cell with filter disc 25 μm). 500 mg of cotton was used for each sample. Before starting the measurement, the samples were thoroughly rinsed with the measuring electrolyte. A 10^{-3} mol L^{-1} KCl solution was used as the background electrolyte and the pH of this aqueous solution was adjusted with 0.1 M HCl and 0.1 M NaOH.

The zeta potential of the dye solution was determined by Zetasizer Nanosizer ZS (Malvern Instruments). 0.01 g of dye was diluted in 20 mL of deionized water. The solution was placed in the equipment under magnetic agitation. The solution pH was varied with the addition of NaOH 0.1 M and HCl 0.5 M.

The morphology of the pretreated fabrics was characterized by a scanning electron microscope (JSM-6390LV, Jeol, Japan), using high vacuum system, secondary electron detector, operating with

Table 1 Interpretation of RUI values (Chong et al. 1992)

RUI	Grade of levelness	Visual appearance
< 0.2	Excellent	Unlevelness not detectable
0.2–0.49	Good	Noticeable unlevelness under close examination
0.5–1.0	Poor	Apparent unlevelness
> 1.0	Bad	Conspicuous unlevelness

an acceleration voltage of 8 kV and 15–17 mm of working distance. The SEM samples were sputtered with gold before the observation.

The identification of the functional groups present in the fabric surface was performed using a Fourier Transform Infrared spectrometer with a built-in ATR crystal (Carry 660, Agilent, USA). The FTIR spectra were obtained using a resolution of 4 cm^{-1} and with an average of 32 scans per sample.

Estimative of the bactericidal efficacy

A simplified version of the Petrifilm Aerobic Count (AC) method was used to qualitatively evaluate the bactericidal efficacy of the cationic cotton fabrics. Petrifilm AC (3M, USA) is a ready to use product, containing culture media, cold water-soluble gelling agent and triphenyl tetrazolium chloride, an indicator that colors bacterial colonies red. This product can be used for the enumeration of aerobic bacteria growth over a surface (Fritz et al. 2015; Sjollema et al. 2018).

1 mL of underground water was pipetted between the two foils of the Petrifilm AC plate. After 1 min interval for spreading the water, the fabric samples (size 1 × 2 cm) were placed. Then, the top foil was lowered and the spreader was gently applied over the entire surface to distribute the water evenly. The Petrifilm plates were incubated at 35 °C for 48 h (3M 2020). The control sample consists of a Petrifilm plate without the fabric, to assure the microbiological growth with the raw underground water.

The simplification of the method consists of using raw underground water as a source of bacteria, instead of a bacterial solution. Since the bacteria concentration was unknown and there were multiple sources of microorganisms, it was not possible to enumerate the bacterial colonies. Therefore, only a qualitative estimative of the bactericidal efficacy was performed.

Results and discussion

Fabric samples were classified by the type of cationic agent, followed by the concentration in g L^{-1}. The non-cationic sample was pretreated only by bleaching, which is considered the conventional process to dye cotton fabrics. The non-cationic fabrics were dyed with or without feeding salt in the process. When the non-cationic sample was dyed without feeding of salt, it was identified by WS. The following sections present the properties of fabrics and baths.

Dyeing, color and fastness properties

The CIELab coordinates, K/S and whiteness degree of undyed cotton are in Table 2. The K/S non-cationic sample is 0.73 ± 0.08 while the whiteness degree is 75 ± 3. Cationization treatments did not produce substantial changes in the coloristic properties of the samples. Statistical analysis indicates small variations in colorimetric properties, but imperceptible to the human eye. This is corroborated by the statistical analysis of the whiteness degree, which indicated that all samples are equal.

Table 2 also presents the color and colorimetric coordinates for dyed samples. From comparison with the undyed cotton, it is noticeable the increment in coordinate a*, characteristic of red color. The lowest value was obtained for the Non-cationic (WS) sample due to the limited interaction between bath and fiber. Conventional dyeing (referred to as Non-cationic sample) reproduced the value of 50.1 ± 0.4 for a* coordinate, slightly above that compared to samples cationized with P42 and PDDAC1. The best results were obtained for the commercial CHPTAC. Photographs of dyed samples are available in the supplementary material.

Conventional dyeing was used as a control sample. Two colors can be optically distinguished by the human eye if $\Delta E \geq 1$. When $\Delta E > 3$ is perceived as a significant color deviation and has commercial

Table 2 Colorimetric properties of undyed and dyed cotton

Undyed cotton

Sample	L*	a*	b*	K/S	Whiteness degree
Non-cationic	94.4 ± 0.1[a,b]	− 0.1 ± 0.1[a]	3.5 ± 0.6[a]	0.73 ± 0.08[a, b]	69 ± 3[a]
P42-40	94.4 ± 0.1[a,b]	− 0.05 ± 0.04[a]	3.3 ± 0.1[a]	0.70 ± 0.02[a, b]	70.2 ± 0.5[a]
P42-20	94.5 ± 0.2[a,b]	− 0.04 ± 0.04[a]	3.2 ± 0.1[a]	0.67 ± 0.04[b]	70.6 ± 0.8[a]
PAcD-40	94.5 ± 0.1[a,b]	− 0.06 ± 0.01[a]	3.2 ± 0.1[a]	0.66 ± 0.02[b]	70.8 ± 0.5[a]
PAcD-20	94.6 ± 0.1[a]	− 0.06 ± 0.02[a]	3.2 ± 0.1[a]	0.65 ± 0.03[b]	71.0 ± 0.6[a]
CHPTAC-40	94.6 ± 0.2[a]	− 0.05 ± 0.01[a]	3.06 ± 0.05[a]	0.64 ± 0.02[b]	71.6 ± 0.3[a]
CHPTAC-20	94.37 ± 0.09[a,b]	− 0.07 ± 0.07[a]	3.3 ± 0.5[a]	0.72 ± 0.08[a, b]	70 ± 2[a]
PDDACl-40	94.1 ± 0.3[b]	− 0.13 ± 0.05[a]	3.4 ± 0.2[a]	0.79 ± 0.04[a]	68.9 ± 0.3[a]
PDDACl-20	94.2 ± 0.4[a,b]	− 0.12 ± 0.03[a]	3.3 ± 0.2[a]	0.74 ± 0.06[a, b]	69.8 ± 0.8[a]

Dyed cotton

Sample	L*	a*	b*	ΔE	RUI	K/S	Washing fastness	Rubbing fastness Dry	Wet	Color[g]
Non-cationic	59.7 ± 0.3[a]	50.1 ± 0.4[a,f]	− 6.9 ± 0.4[a]	–	0.25	32 ± 1[a]	3/4	5	4	
Non-cationic (WS)	76.2 ± 0.9[b]	30.0 ± 0.7[b]	− 7.9 ± 0.1[b]	26.0	0.23	6.8 ± 0.7[b]	1/2	5	4	
P42-40	61 ± 1[a]	46 ± 1[c]	− 6.3 ± 0.4[a,c]	4.0	0.34	28 ± 3[a]	2/3	5	3	
P42-20	61.7 ± 0.5[a]	46.0 ± 0.6[c]	− 6.8 ± 0.3[a]	4.5	0.53	27 ± 1[a]	2	5	3/4	
PAcD-40	70.2 ± 0.6[c]	37 ± 1[d]	− 8.5 ± 0.2[b,d]	16.7	0.43	12.2 ± 0.7[b]	1	5	3/4	
PAcD-20	72.7 ± 0.5[d]	35 ± 1[d]	− 8.6 ± 0.1[d]	20.2	0.35	9.7 ± 0.5[b]	1	5	3/4	
CHPTAC-40	55.7 ± 0.5[e,f]	54.5 ± 0.6[e]	− 5.6 ± 0.3[e]	6.1	0.34	48 ± 2[c]	3/4	5	4/5	
CHPTAC-20	57.2 ± 0.2[e]	52.6 ± 0.2[a,e]	− 6.1 ± 0.3[c,e]	3.7	0.26	41.2 ± 0.5[c]	3	5	5	
PDDACl-40	55 ± 2[f]	49 ± 2[f]	− 9.2 ± 0.2[d]	5.6	1.63	45 ± 7[c]	5	5	3	
PDDACl-20	54 ± 1[f]	50 ± 2[a,f]	− 8.9 ± 0.36[d]	6.2	1.54	48 ± 6[c]	3	5	3	

[a–f] data that share the same letters, in the same column, are considered statistically equals. [g] Before fastness tests

restrictions (Choudhury 2015). According to Table 2 the color deviation changed substantially with the cationic agent.

The K/S values for dyed cotton are available in Table 2. The best K/S values were obtained for the cationic agents CHPTAC and PDDAC1. K/S values for CHPTAC was 48 ± 2 and 41.2 ± 0.5, for PDDACl was 45 ± 7 and 48 ± 6, respectively for 40 and 20 g L^{-1} of cationic agent. These values are statistically equal. Results were above those obtained for the conventional dyeing (K/S = 32 ± 1). The pretreatment with P42 enabled dyeing with coloristic properties equal to conventional dyeing, but with results inferior to CHPTAC and PDDACl.

Cationic cotton treated with PAcD resulted in poor K/S. Statistical analysis indicated no difference in K/S values for samples PAcD-20, PAcD-40 and Non-cationic (WS). It was expected that the cationic treatment would increase the dye-fiber affinity. In contrast, the steric hindrance in the PAcD molecule may have caused a barrier in dye assembly to the fiber. Steric hindrance is the inability of a molecule to participate in a reaction due to the difficulty of approach caused by the physical presence of the surrounding ligands (McMurry 2011).

According to the correlation between the RUI values in Table 2 and the grade of levelness indicated in Table 1, most of the dyeings presented good

levelness. Sample P42-20 exhibited poor levelness, while PDDACl-40 and PDDACl-20 resulted in bad levelness. Conspicuous unlevelness in samples treated with PDDACl is probably attributed to a strong interaction between dye and cellulose. A strong interaction occurs between the dye molecule and the cationic site at the external surface of the fiber. Therefore, the diffusion of the dye into the fiber pores is limited as most of the molecules interact with the external surface of the fiber.

The statistical analysis indicated no difference between the K/S of the dyed samples pretreated with 20 or 40 g L^{-1} of cationic agent. This is related to the concentration of cationic sites in the fabric. Cotton pretreated with 20 g L^{-1} of cationic agent is enough for providing cationic sites for dyeing with Reactive Red 195 dye. Therefore, 40 g L^{-1} of the cationic agent means a waste of chemicals.

Washing and rubbing fastness

The color fastness of the dyed cotton fabric against washing and rubbing are presented in Table 2. Cationization performed by PDDACl, at 40 g L^{-1} provided excellent washing fastness, superior to conventional dyeing (Non-cationic sample). CHPTAC-40 present the same washing fastness as conventional dyeing, while samples PDDACl-20 and CHPTAC-20 decreased a half degree. Samples treated by P42 decreased more substantially the washing fastness, with a decrease of 1 and 1.5 degrees below the conventional dyeing. This indicates that the dye-fiber interaction was more intense for samples treated by CHPTAC and PDDACl.

The PAcD did not show good washing fastness and presented the lowest fastness classification, lower than non-cationic sample dyed without feeding of salt. In this case, the dye interacted with treated cotton by weak forces, such as Van Der Waals, which was removed during the washing test.

The greater concentration of cationic sites enhanced the interactions between fiber and dye. Cationic cotton presented better washing fastness when treated by 40 g L^{-1} of cationic agent. This can be observed comparing each concentration of cationic agents P42, CHPTAC and PDDACl.

The dry rubbing fastness of treated fabrics was equal in all samples. Wet rubbing fastness for CHPTAC cationic cotton was superior to the Non-cationic sample. A slight decrease in wet rubbing fastness was observed for cationic cotton treated by PDDACl, P42 and PAcD. The cationization process probably forms a layer on the surface of the cotton. Once solubilized in water, this layer may be removed under the action of rub, carrying dye molecules. Therefore, a larger amount of cationic agent could form a thicker layer, being more susceptible to removal by rubbing. This is the probable reason for CHPTAC and P42 presented better wet rubbing fastness at 20 g L^{-1}.

Similar results were obtained by other researchers. Bessa et al (2019) considered that the pretreatment with PDDACl allowed dyed cationic cotton knitted fabric with almost the same level of rubbing and washing fastness when compared with the conventional dyeing. Cotton pretreated with CHPTAC and dyed with reactive dye by Arivithamani and Giri Dev (2018) exhibited excellent color fastness properties. The washing and dry rubbing fastness were as good as the conventional dyed fabric, while the wet rubbing fastness improved when used cationic cotton.

Dyeing and washing baths

The exhaustion and washing baths data for each cationic cotton are presented in Fig. 3. For comparisons, conventional dyeing (Non-cationic sample) is present in each graph. Non-cationic (WS) curve is presented only in the PAcD sample because both reproduced similar values. Three washing baths were performed, to reproduce common dyeing industry practices. By the summation of the amount of dye in each bath, the total residual dye mass was calculated and shown in Fig. 3e. Photographs of each bath, wavelength scan and calibration curve necessaries for measurement of Reactive Red 195 concentration are available in the supplementary material.

CHPTAC and PDDACl resulted in a higher reduction of dye concentration in each bath. For CHPTAC, a single washing bath is enough for dye removal. In PDDACl cationic samples, a small concentration of dye is present also in the third wash (2.9 ± 0.5 and 4.0 ± 0.2 mg L^{-1}, respectively for 40 or 20 g L^{-1} of PDDACl).

The cationic agent P42 presented similar results in comparison with the conventional dyeing, but with a higher waste of dye than CHPTAC or PDDACl. The total mass of residual dye in the baths was
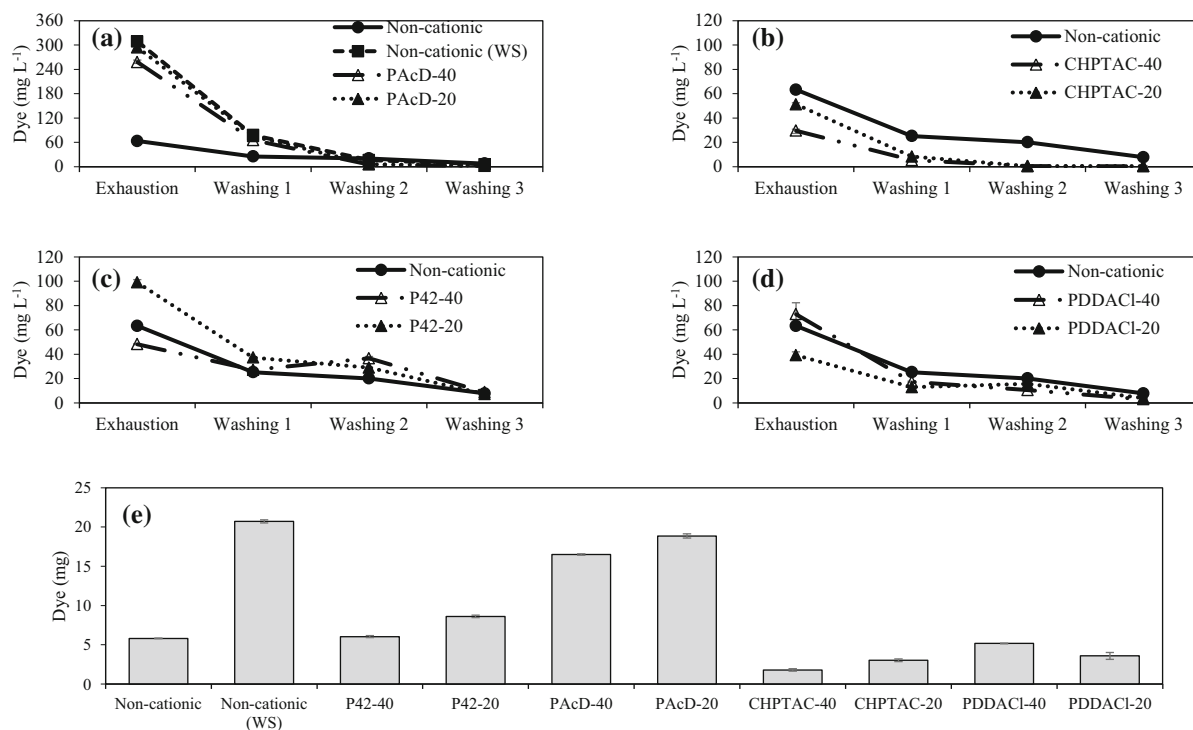
Fig. 3 **a–d** dye concentration in the exhaustion and washing baths. **e** total mass of residual dye (summation of the exhaustion and washing baths)

6.04 ± 0.5 mg and 8.4 ± 0.1 mg for P42-40 and P42-20, respectively, which were close to the conventional dyeing (5.8 ± 0.2 mg). The total mass of dye in the effluent was smaller when 40 g L^{-1} of the cationic agent was used, except for PDDACl. In this case, the high concentration of cationic reagent may have increased the steric hindrance.

Effect of dyeing time

The progression of the dyeing process was evaluated for samples pretreated with the cationic agent at 20 g L^{-1}. Figure 4 shows the color strength of the fabric, the dye concentration and the pH of the dyebath. According to Fig. 4c, there is a sudden pH change between 18 and 28 min due to the addition of alkali. Most of the samples had significant properties variation after changing the pH.

The fabric pretreated with P42 showed the greatest variation due to the addition of alkali. The dyeing stabilized quickly, with K/S at 17–19 at the beginning of the dyeing. After the addition of alkali, more dye molecules interacted with the fabric, resulting in a

40% increase in color strength. Then there was a gradual decrease in K/S and part of the dye weakly attached to the fiber returned to the dyebath.

The PDDACl-20 sample showed an intense affinity with the dye at the beginning of the process. According to Figs. 4a, b, at the second minute of dyeing, there was a high color strength and a low concentration of dye in the bath. Then, some dye returns from the fabric to the dyebath. At the beginning of the process, there may be some NaOH in the fabric, not removed in the cationization process. This residual may cause a difference between the pH of the dyebath and the fabric so that the dye would quickly interact with the cotton. After a few minutes, the system is balanced and is part of the return to the dyebath. After a few minutes, the system reaches equilibrium and some of the dye returns to the dyebath. The high alkalinity of the bath increased the affinity of the dye to the fabric.

According to Table 2, the pretreatment with PDDACl resulted in dyeing with conspicuous unlevelness. This can also be seen in Fig. 4a. The treatment with PDDACl showed a relative deviation of 5–33% from the average. The greatest deviation occurs in the
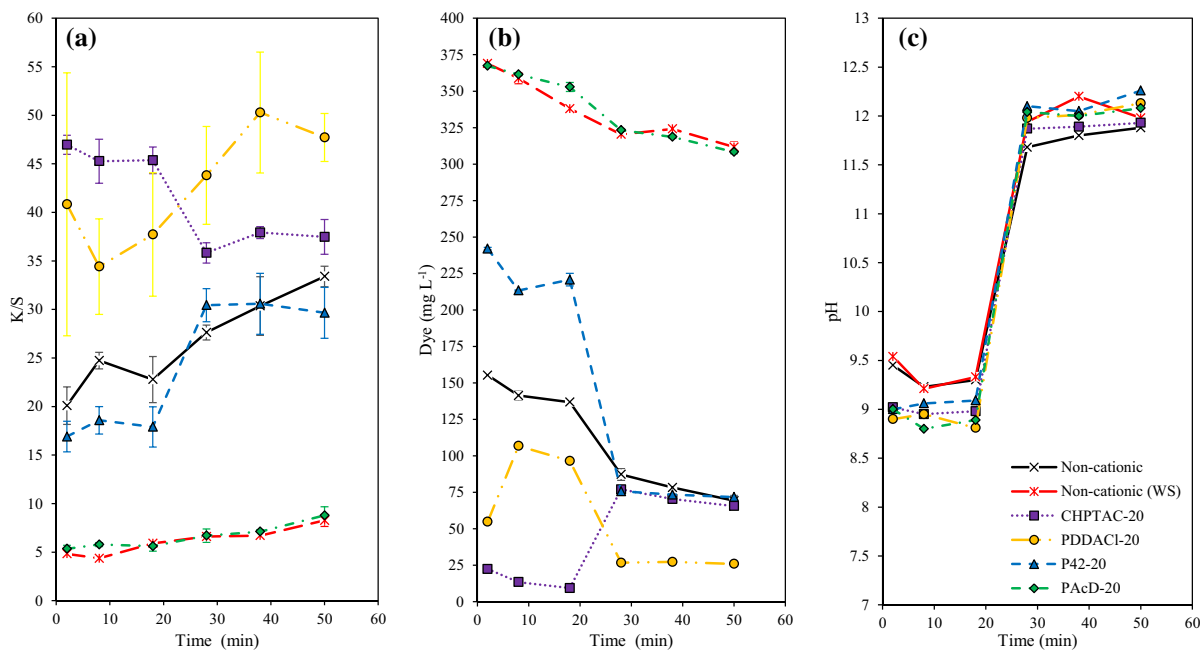
Fig. 4 Variation of color strength, dye concentration and pH in the dyebath throughout the dyeing process

first measurement, caused by an instantaneous dye-fiber interaction. This may also be related to the presence of residual NaOH in the treated tissue.

In conventional dyeing (Non-cationic sample), there is a slight increase in the K/S values at the firsts ten minutes of the dyeing. The dye uptake increases gradually after the addition of alkali, up to a K/S value of 33 ± 1. The Non-cationic and P42 samples presented similar behavior over time. Electrostatic repulsion and steric hindrance are the probable causes for the limited dye-fiber interaction for samples PAcD-20 and Non-cationic (WS), consequently resulting in low K/S.

The exhaustion of the CHPTAC pretreated sample increased quickly. The maximum K/S was observed in the first minutes of the dyeing. Then it drops significantly after 18 min. It occurred due to the rise in pH. This effect was only observed with the CHPTAC pretreatment. This may be related to the competitiveness between the dye molecule and the new nucleophilic groups added in the bath. The weakly fixed dye molecules return to the dyebath after pH elevation, which raises the dye concentration in the liquid phase as shown in Fig. 4b.

According to Acharya et al. (2014), alkali is only necessary for cotton cationized with lower

concentrations of CHPTAC. The authors found that alkali addition increased the exhaustion of Reactive Blue 235 dye with cotton pretreated with CHPTAC solution at a concentration in the range 4.4–13.1 g L^{-1}. However, the addition of alkali decreased the exhaustion with cotton pretreated at a concentration between 17.5 and 35.0 g L^{-1}. The author considers this effect is related to the unfixed or weakly fixed CHPTAC molecules that return to the dyebath after the addition of alkali.

Competitive dyeing

Table 3 shows the color properties of competitive dyeing for cationic cotton treated with 20 or 40 g L^{-1} of cationic agent. Photographs of dyed samples are available in the supplementary material. With this experiment is possible to evaluate the affinity that the Reactive Red 195 has with each cationic sample. Each sample competes for the fixation of the dye, which migrates primarily to the fabric with the highest affinity. In this sense, PDDACl cationized cotton presented the highest affinity, observed by the best K/S for 20 and 40 g L^{-1}.

The cationic agent P42 stood out, obtaining the second highest K/S, at 20 g L^{-1}. At 40 g L^{-1} P42 lost

Table 3 Properties of the competitive dyeing: CIELab coordinate, color, K/S and ΔE between samples treated with 20 and 40 g L^{-1} of the cationic agent

20 g L^{-1}				
Sample	L*	a*	b*	Color
Non-cationic (WS)	78.6 ± 0.9	21 ± 1	− 7.3 ± 0.6	
P42	48 ± 1	49 ± 1	− 3.8 ± 0.6	
PAcD	76.7 ± 0.5	23.4 ± 0.5	− 8.3 ± 0.2	
CHPTAC	58.7 ± 0.8	48 ± 2	− 7.7 ± 0.5	
PDDACl	43.7 ± 0.7	52 ± 1	− 4.1 ± 0.8	

40 g L^{-1}				
Sample	L*	a*	b*	Color
Non− cationic (WS)	62.6 ± 0.6	39.1 ± 0.6	− 9.0 ± 0.1	
P42	56 ± 2	45 ± 2	− 7.7 ± 0.8	
PAcD	62 ± 2	39 ± 2	− 8.5 ± 0.2	
CHPTAC	54.3 ± 0.5	49 ± 1	− 7.0 ± 0.2	
PDDACl	44 ± 4	51 ± 2	− 5 ± 3	

Comparison between samples			
Sample	K/S		ΔE
	20 g L^{-1}	40 g L^{-1}	
Non-cationic (WS)	5.0 ± 0.4	22 ± 1	24.2
P42	75 ± 9	39 ± 8	9.6
PAcD	6.0 ± 0.3	24 ± 4	22.0
CHPTAC	34 ± 3	46 ± 3	4.5
PDDACl	111 ± 7	113 ± 37	1.4

competitiveness, the K/S was lower than CHPTAC-40 and PDDACl-40. This indicates that low concentrations of reagent P42 may produce more intense color dyes than the commercial cationic agent.

The ΔE in Table 3 refers to the color deviation between the pairs of samples treated with 20 and 40 g L^{-1} of cationic agent. The PDDACl presented higher competitiveness at both concentrations and the low ΔE indicates that the concentration of 20 g L^{-1} is sufficient for the cationic sample preparation. The PAcD sample had a high ΔE value, caused by the substantial increase in color strength for 40 g L^{-1}. This is an indication that increasing the concentration of PAcD may increase the dyeing properties.

Characterization

According to Table 2, the color properties were almost the same for dyed fabrics regardless of the concentration of the cationic agent. Therefore, the characterization was performed for fabrics treated with the cationic agent at 20 g L^{-1}. The cationic fabrics were characterized through Zeta potential and FTIR spectroscopy.

Zeta potential

The incorporation of cationic functional groups causes changes in the superficial charge of the fabric and one way to represent this process is through zeta potential. Figure 5 contains the relation between zeta potential and pH for each undyed sample. The zeta potential of the Reactive Red 195 dye solution is also present. All

Fig. 5 Zeta potential as a function of solution pH, for cationic and non-cationic cotton fabrics and Reactive Red 195 dye solution
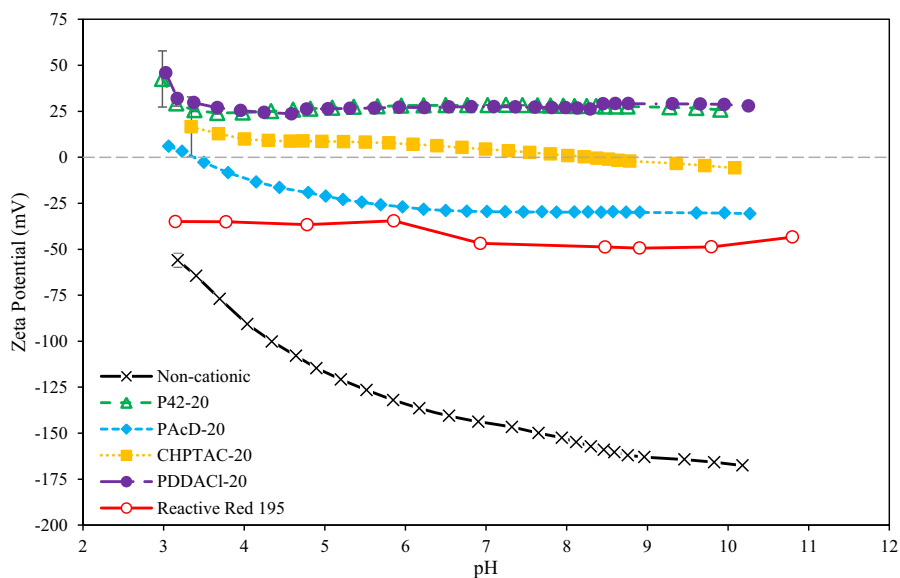
cationic agents substantially increased the zeta potential of the cotton fabric.

The surface of the Reactive Red 195 dye is negatively charged at a solution pH of 3–11. The zeta potential of the Reactive Red 195 dye solution varied from around − 34 to − 50 mV. The surface of the Non-cationic sample is also negatively charged across the analyzed pH range. The interaction of the dye and fiber is limited as both have anionic behavior.

The pH value where the zeta potential is equal to zero is called isoelectric point. At this condition, the number of cationic and anionic charges is even (Wakelyn et al. 2006). The isoelectric point of samples CHPTAC-20 and PAcD-20 were, respectively, around 8.2 and 3.4. Below these values, the fabrics show a positive surface charge and above it behave negatively charged. That is the probable reason why the dye-fiber interaction decreased after the alkali addition. The isoelectric point of the CHPTAC-20 was close to the pH at the beginning of the dyeing (around 9), as shown in Fig. 4. After the addition of alkali, the pH of the dyebath raised to around 12.

The dyeings were performed above pH 9. However, the PAcD-20 samples must be dyed at pH below 3.4 so that the positive surface charge would attract the anionic dye. The inadequate pH is another reason for the low dye-fiber interaction, besides the steric hindrance. The PAcD cationic agent may be useful for dyeing at low pH, which is applicable to acid dyebaths (Mahapatra 2016).

The higher the zeta potential, the greater the number of cationic charges present on the cotton surface, which increases the interaction between the anionic dye and the fiber. The highest zeta potential results were obtained for P42 and PDDACl cationic fabrics. The high zeta potential for P42 is attributed to the presence of two ammonium quaternary groups in each repeating unit of the polymer (Zhang et al. 2015; Arivithamani and Giri Dev 2017b). The repeating unit of the PDDACl polymer has only one ammonium quaternary group. However, the repeating unit is considerably smaller than P42 and PAcD.

As shown in Table 2, the dye-fiber interaction of the P42-20 sample was lower than PDDACl-20 and CHPTAC-20 samples. However, the zeta potential of the P42-20 samples was basically the same as the PDDACl-20 and higher than CHPTAC-20 sample. The reason for the lower dye-fiber interaction is probably due to the steric hindrance caused by the deposition of the P42 molecule into the cotton surface.

The zeta potential is a function of the surface chemical composition of the fiber, the type of the cationic agent and the concentration of the cationization process. Cai et al. (2018) measured the zeta potential for cationic ramie fibers. The authors performed the analysis solely at pH 7, varying the CHPTAC concentration between 0 and 20 g L^{-1} and bath temperature of 40 or 60 °C. The temperature had no effect on zeta potential, but the zeta potential increased sharply with increasing the concentration of
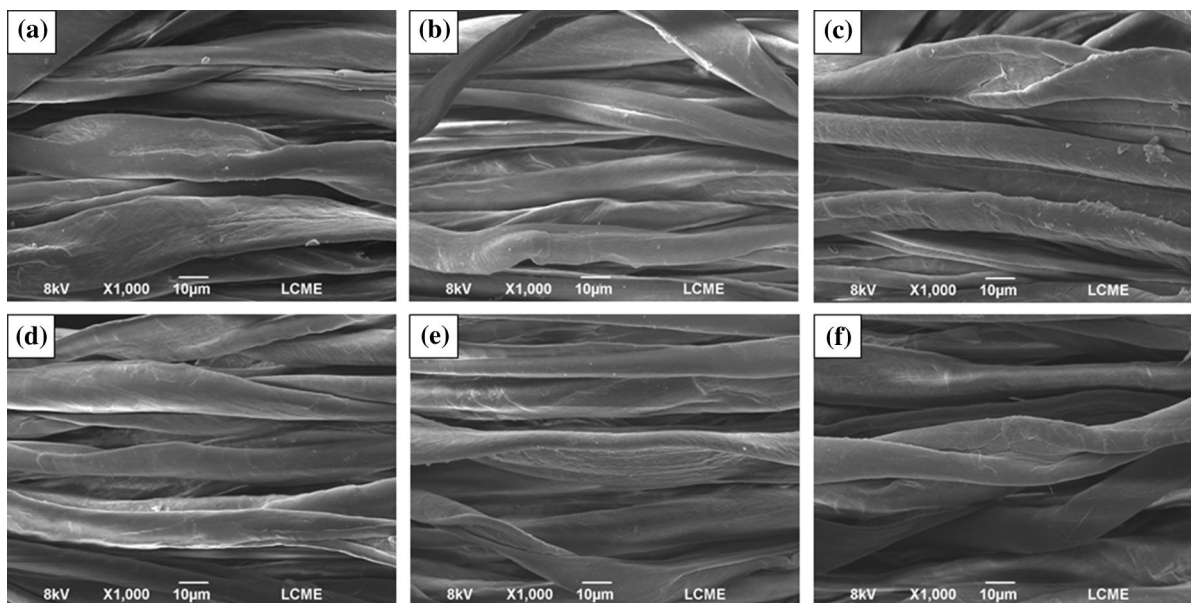
Fig. 6 SEM photographs of the **a** greige cotton, **b** Non-cationic, **c** CHPTAC-20, **d** P42-20, **e** PDDACl-20 and **f** PAcD-20
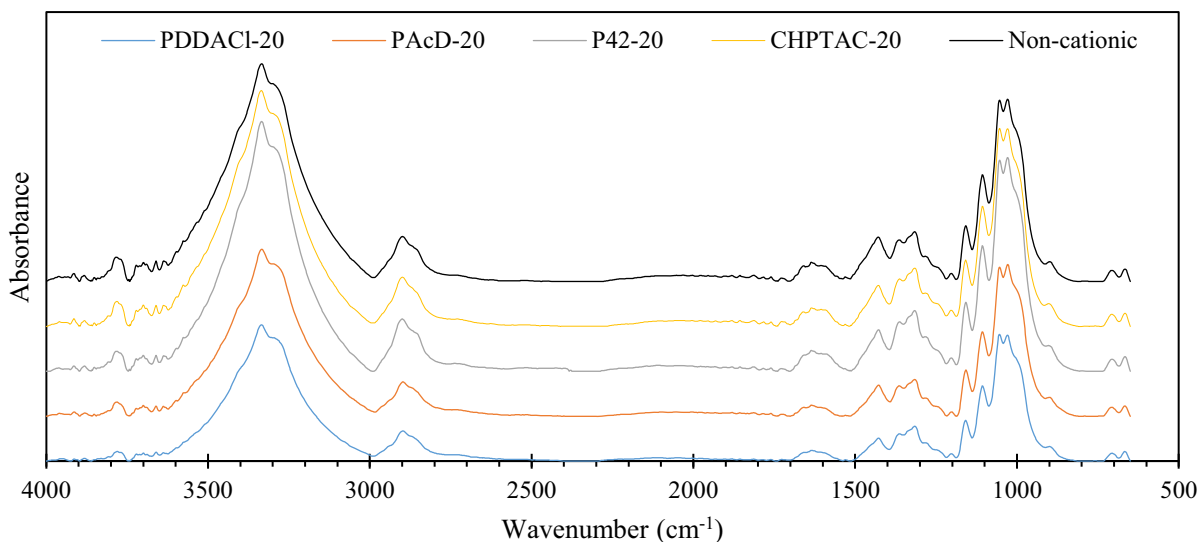

Fig. 7 FTIR spectra of the non-cationic fabric and after cationization using 20 g L^{-1} of each cationic agent

CHPTAC. After 14 g L^{-1}, however, a stable zeta potential value was obtained.

SEM

Figure 6 shows the SEM images of the (a) greige, (b) non-cationic and (c–f) cationic samples at 1000X magnification. The comparison between each sample indicates that no remarkable morphological difference could be observed. Small particles were detected over the greige cotton and CHPTAC-20 fabrics, which may be related to some impurities. For CHPTAC-20 fabric, it could be also related to the cationic agent deposition.

**Table 4** FTIR absorption bands obtained in this paper and comparison with the data available in the literature

FTIR signal (Wavenumber, cm^{-1})		Functional group	References
This paper	Literature		
3600–3000	3570–2955	O–H stretching	Molina et al. (2020)
2980–2800	3000–2800	C–H stretching	Chung et al. (2004)
1674–1538	1650–1633	O–H bending of adsorbed water	Chung et al. (2004)
	1627	N–H asymmetric deformations	Abdelileh et al. (2019)
	1571	N–H symmetric deformations	Abdelileh et al. (2019)
1436	1430	C–H or C–OH bending vibrations	Molina et al. (2020)
1392–1275	1400–1300	–CH and –CH$_2$ bending vibrations	Molina et al. (2020)
1155–1020	1160–1130	C–O–C stretching	Abdelileh et al. (2019)

(1)

(2)
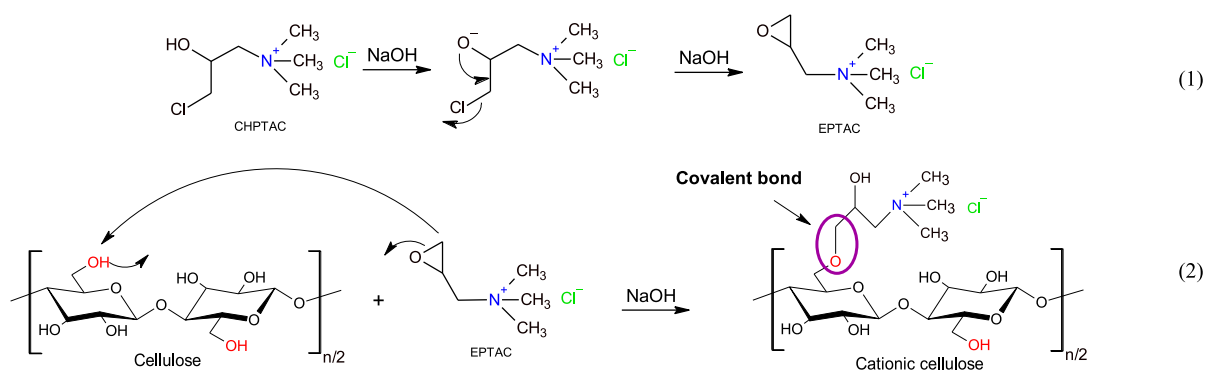
Scheme 1 Cationization of cellulose with CHPTAC
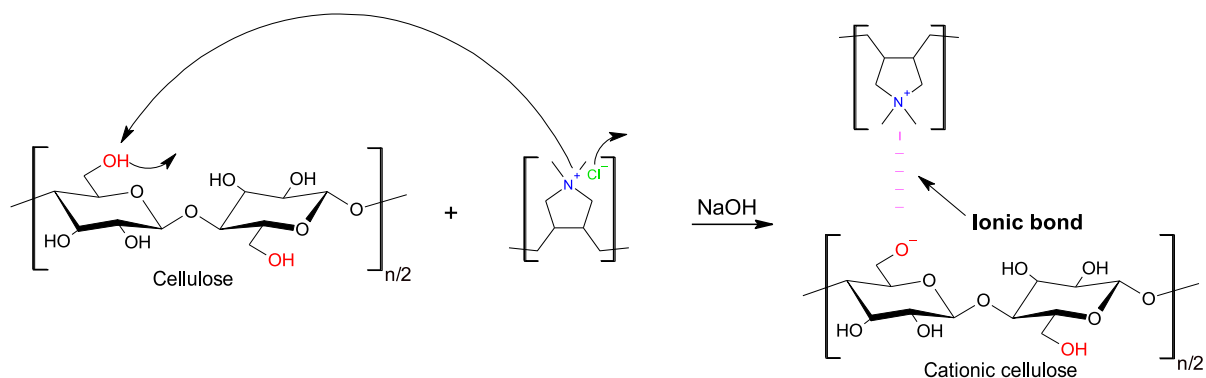
**Scheme 2** Cationization of cellulose with PDDACl

Based on the micrographs, it can be concluded that the surface morphology was basically unaffected after the pretreatment. This conclusion is in accordance with other published works, which indicate that cationization does not change the surface morphology significantly (Abdelileh et al. 2019; Ma et al. 2020).

FTIR

The FTIR spectra of the fabrics before and after cationization with 20 g L^{-1} of cationic agent are represented in Fig. 7. The spectra are nearly identical, with minor differences. The spectra show the
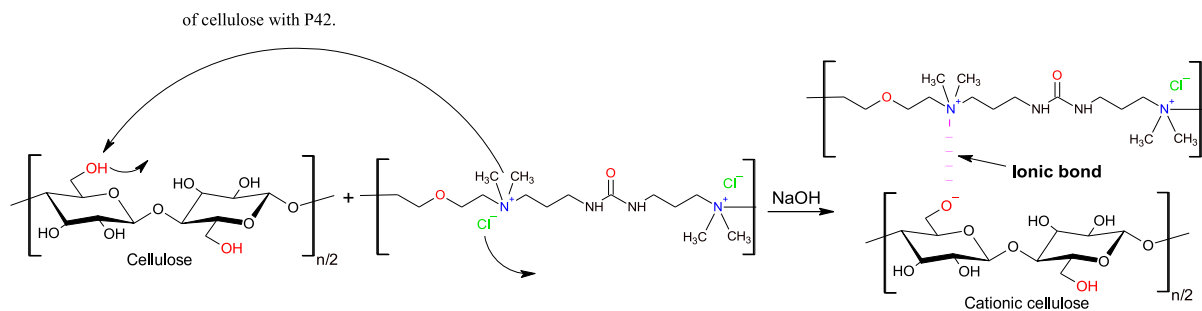
Scheme 3 Cationization of cellulose with P42
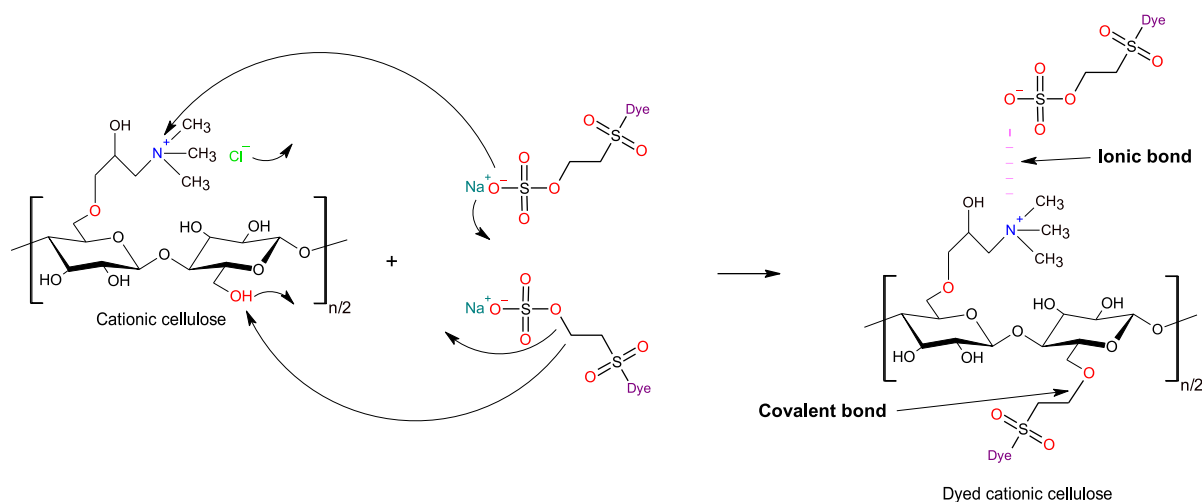
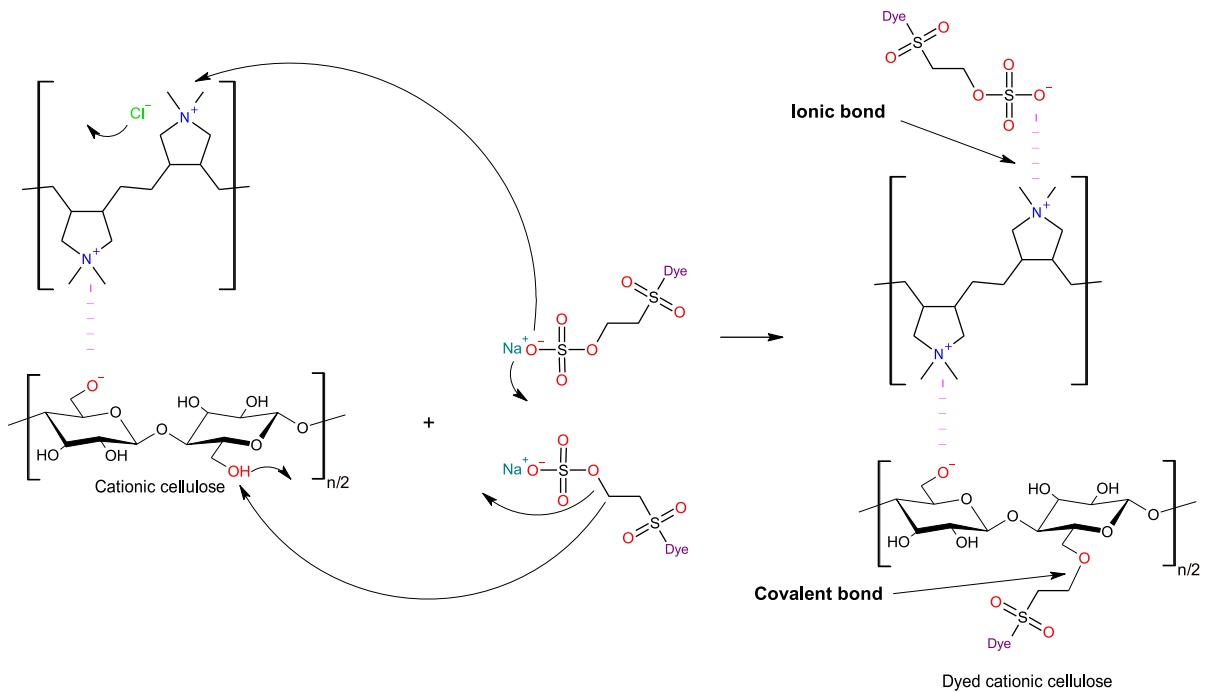**Scheme 4** Fixation of Reactive Red 195 on cotton cationized with CHPTAC

characteristic absorption bands of cellulose, the main component of the cotton fabric. The cationic agents have functional groups that are not in cellulose, but the quantity was too small to be detected in the spectra.

Table 4 shows the absorption peaks of the spectra. The peaks were compared with the data available in the literature. Although the peaks were characteristic of the bands of cellulose, which may be overlapped those belonging to the cationic agent. The spectra show a broad peak at 1674–1538 cm^{-1}. Absorption bands between 1650 and 1633 cm^{-1} are usually attributed to O–H vibrations of the adsorbed water (Chung et al. 2004). These bands are near the characteristic bands of N–H deformations (1627and 1571 cm^{-1}), which are present in the molecule of the cationic agents.

Mechanism for cationization and dyeing

Pretreatments with PDDACl, P42 and CHPTAC significantly altered the behavior of the dyeing process. Therefore, the mechanism of cationization and cationic dyeing is proposed in Schemes 1, 2, 3, 4, 5 and 6. The cationic agent tends to interact with the primary cellulosic hydroxyl groups because they are more accessible and reactive (Wakelyn et al. 2006). The cellulose reacts with the cationic agents by different mechanisms.

The mechanism of cationization of cotton with CHPTAC was already discussed by some researchers (Hauser and Tabba 2001; Wang et al. 2009; Farrell et al. 2015; Arivithamani and Giri Dev 2016, 2017b). In the presence of NaOH, the CHPTAC is firstly converted into 2,3-epoxypropyl trimethylammonium chloride (EPTAC). The EPTAC is very reactive so it

Scheme 5 Fixation of Reactive Red 195 on cotton cationized with PDDACl
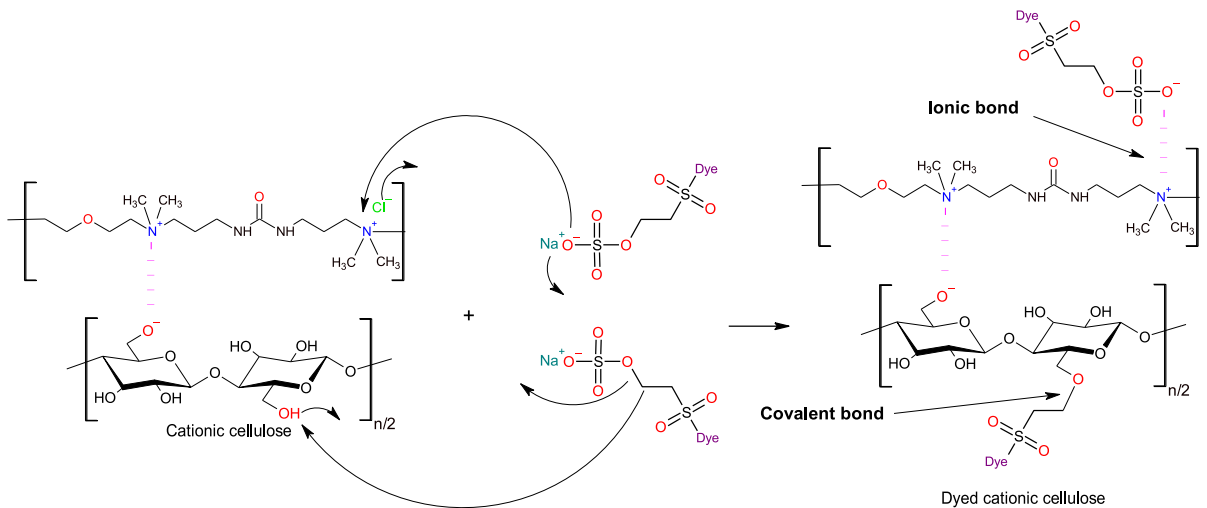
Scheme 6 Fixation of Reactive Red 195 on cotton cationized with P42

forms a covalent bond with the cellulose anion. The reaction mechanism is shown in Scheme 1.

Despite the efforts dedicated to the literature review, no publication was found regarding the mechanism of cationization with PDDACl or P42. Jareansin et al. (2019) published the mechanism for

cationization with diallyldimethylammonium chloride, the monomer of PDDACl. However, the authors used potassium persulfate as an initiator to create the cellulose radical and the PDDACl polymer. In the present work the PDDACl polymer was directly applied and without the initiator.
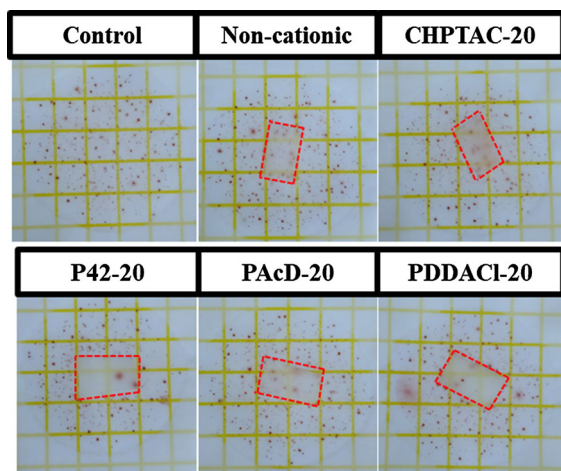
Fig. 8 Estimative of the bactericidal effect using a simplified methodology of the Petrifilm AC

The mechanism proposed for the cationization of cotton with PDDACl and P42 are similar and are presented in Schemes 2 and 3, respectively. The quaternary ammonium groups of the polyelectrolytes interact with the cellulose anion to form an ionic bond. By ionic exchange, the chlorine ion is removed so that the oxygen binds with the cationic nitrogen.

The fixation of the Reactive Red 195 dye on cationic fiber can be achieved by an ionic bond between the cationic nitrogen and the oxygen anion from the vinyl sulfone reactive group (Arivithamani and Giri Dev 2017b). Considering that cationization may not occur completely, dye fixation can also occur through the conventional dyeing mechanism. In that case, the non-cationic cellulose can be fixed with a covalent bond between the oxygen anions and the dye (Fu et al. 2013). The dyeing mechanisms are proposed in Schemes 4, 5 and 6.

The cationization using CHPTAC differs from the other cationic agents because it involves the formation of EPTAC. The EPTAC fixes to cellulose through the epoxy group, this represents an advantage in the mechanism because the cationic nitrogen remains available for binding with the dye. In the case of PDDACl and P42, the cationic nitrogen has the function of binding the cellulose and the dye. P42 has two cationic nitrogen atoms in its monomeric unit, so it is possible to interact between molecule, dye and cationic agent. In the case of PDDACl, the monomer unit has only one nitrogen. Therefore, the interaction

of the dye with PDDACl must occur in monomers that are not bonded to the cellulose.

Bactericidal effect

The importance of bactericidal and antiviral properties of textile materials reached a new level after the outbreak of the COVID-19 pandemic. The functionalization of the fabrics with antimicrobial activity is expected to be an essential practice soon (Valle et al. 2021). Therefore, an estimative of the bactericidal efficacy was evaluated according to Fig. 8. The red dots are colonies of microorganisms. The control samples testified that the raw underground water had enough microorganisms to perform the tests. The fabric samples are delimited by the red lines. It can be visualized that the number of colonies onto the samples P42-20 and PDDACl-20 are smaller. Therefore, it is estimated that these samples have higher bactericidal than samples CHPTAC-20 and PAcD-20.

Since the microorganism concentration and the presence of contaminants are unknown, a standardized test is necessary for a more precise and quantitative bactericidal analysis. However, the estimative provided by this test is in accordance with other published results. Polymers containing quaternary ammonium groups have a remarkable bactericidal effect (Lu et al. 2021). According to Kumar et al. (2016), P42 exhibits significant antimicrobial efficacy against *Staphylococcus aureus*. Besides, the research accomplished by Kim et al. (2016) indicated an inhibition rate of *Staphylococcus aureus* and *Escherichia coli* growth close to 100% for cotton fabrics treated with PDDACl.

Conclusions

This research brings the possibility of using novel cationic agents with potential for industrial application, especially for PDDACl that presented results similar to the commercial reagent CHPTAC. P42 also produced results compatible with conventional dyeing. Besides, the P42 molecule provides a great marketing alternative as it is used in the cosmetics sector, while cationization with CHPTAC has a considerable toxicity factor. These processes, however, need to be optimized to increase dye uniformity using PDDACl and P42.

There were small variations in colorimetric properties when increasing the concentration of cationic agent from 20 to 40 g L^{-1}. Therefore 20 g L^{-1} was considered a more adequate concentration as it saves cationic agent. Otherwise, the PAcD cationic agent did not enhance the dye-fiber affinity at either concentration. The poor results for cationic cotton treated by PAcD are related to the isoelectric point of the sample. The PAcD-20 sample requires a dyebath pH below 3.4 for the dye-fiber interaction to be effective.

As presented in the materials section, all reagents are previously solubilized in water and PAcD has the lowest concentration of all. Increasing the dosage of PAcD may increase dye exhaustion. In this sense, PDDACl shows promising results, as it presented results comparable to the commercial cationic agent, with a low concentration: 20% in H_2O against 65% of CHPTAC. Besides, PDDACl and P42 presented bactericidal activities.

The pH is a fundamental control factor for the dyeing of cationic fabrics. The samples cationized with P42 and PDDACl benefited from the higher pH due to the cellulose ionization, which increases the interaction with the cationic group. However, the opposite occurred with the CHPTAC as the higher pH in the dyebath increased the anionic charge onto the fabric surface.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Human and animal participants This paper does not contain any studies with human participants or animals performed by any of the authors.

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