UNIVERSIDADE FEDERAL DE SANTA CATARINA
CENTRO TECNOLÓGICO
PROGRAMA DE PÓS-GRADUAÇÃO EM ENGENHARIA QUÍMICA

Jeferson Correia

Cationic dyeing in chemical textile processing of cotton fabric

FLORIANÓPOLIS
2021

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Tese submetida ao Programa de Pós-graduação em Engenharia Química da Universidade Federal de Santa Catarina para a obtenção do título de Doutor em Engenharia Química.
Orientador: Prof. Dr. José Alexandre Borges Valle.
Coorientadores: Prof.ª Dr.ª Rita de Cassia Siqueira Curto Valle, Prof. Dr. Fernando Ribeiro Oliveira.

Florianópolis

2021

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Correia, Jeferson
Cationic dyeing in chemical textile processing of cotton fabric / Jeferson Correia ; orientador, José Alexandre Borges Valle, coorientadora, Rita de Cassia Siqueira Curto Valle, coorientador, Fernando Ribeiro Oliveira, 2021.
178 p.

Tese (doutorado) - Universidade Federal de Santa Catarina, Centro Tecnológico, Programa de Pós-Graduação em Engenharia Química, Florianópolis, 2021.

Inclui referências.

1. Engenharia Química. 2. Cationização. 3. Tingimento catiônico. 4. Tingimento sem sal. 5. Tecido de algodão. I. Valle, José Alexandre Borges. II. Valle, Rita de Cassia Siqueira Curto. III. Oliveira, Fernando Ribeiro IV. Universidade Federal de Santa Catarina. Programa de Pós Graduação em Engenharia Química. V. Título.

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O presente trabalho em nível de doutorado foi avaliado e aprovado por banca examinadora composta pelos seguintes membros:

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Prof. Dr. José Alexandre Borges Valle
Orientador

Florianópolis, 2021.

Ao professor e amigo Fernando Ribeiro Oliveira, um ser humano especial, que dedicou muitas horas para o desenvolvimento deste trabalho e recebeu o chamado de Deus logo antes da conclusão.

AGRADECIMENTOS

Agradeço primeiramente à Deus, que me deu a vida, família e saúde, condições essenciais para que eu tivesse condições de superar todo e qualquer desafio.

Aos meus queridos pais, Edson e Maristela, que dedicaram suas vidas por mim e meus irmãos. Me apoiaram e me encorajaram durante todo o doutorado e em tudo que fiz na vida.

Aos meus familiares, avós, irmãos, tios e primos, pelos diversos momentos felizes que passamos juntos. Dois deles já estão me observando do céu: meu avô Dionísio e minha avó Therezinha, me lembro deles com muito orgulho, sempre me incentivaram a conquistar tudo que almejei.

À minha amável companheira, Viviana, por todo o amor envolvido. Sempre muito compreensiva, simpática e bem-humorada, me ajudou a superar vários desafios. Foi fundamental para a conquista do doutorado.

Ao meu orientador Prof. Dr. José Alexandre Borges Valle e minha coorientadora Prof.ª Dr.ª Rita de Cassia Siqueira Curto Valle, por toda orientação e conhecimentos transmitidos, fundamentais para o meu desenvolvimento. Ao meu coorientador Prof. Dr. Fernando Ribeiro Oliveira (*in memoriam*), que muito me ensinou e me surpreendeu com sua simpatia. Aos três posso dizer que, de orientadores, se tornaram bons amigos.

Aos professores Dr. José Heriberto Oliveira do Nascimento, Dr. António Pedro Garcia de Valadares Souto (*in memoriam*), Dr.ª Cristiane da Costa, Dr. Manuel Jose Lis Arias e Dr. Fabricio Maestá Bezerra, por comporem a banca examinadora de qualificação e defesa, contribuindo com a melhoria do trabalho.

Aos professores Dr.ª Kavita Mathur, Dr. Mohamed Bourham e Dr. Abdel-Fattah M. Seyam, pelos valorosos ensinamentos e orientação durante a realização de pesquisa na Universidade Estadual da Carolina do Norte (NCSU).

Aos colegas Karine T. Rainert, Samara M. Behling e Raphael Baraldi pelo auxílio e troca de ideias durante o desenvolvimento da pesquisa.

À Central de Análises do EQA pela realização das análises de potencial zeta e FTIR.

À CAPES, pelo suporte financeiro, concedido através da minha bolsa de doutorado sanduíche do programa PRINT-CAPES/UFSC.

Ao Instituto do Meio Ambiente de Santa Cataria, pelo apoio institucional fundamental para a realização do doutorado. Aos colegas servidores por estarem sempre à disposição de me auxiliar.

À Universidade Federal de Santa Catarina (UFSC), à NCSU e ao Programa de Pós-graduação em Engenharia Química, por proporcionar o suporte estrutural e acadêmico que me permitiu realizar esse trabalho.

À Werken Química, em especial ao sócio proprietário Jefferson Zomignan, por disponibilizar os reagentes e a estrutura laboratorial, além de compartilhar os conhecimentos adquiridos pela empresa acerca da cationização de algodão.

À Dr.ª Daniela Bresolin e ao LINDEN pelas análises de potencial zeta em soluções.

Gratidão a todos que, direta ou indiretamente, contribuíram para a realização deste trabalho, muitíssimo obrigado!

O vigor físico é bom,
o vigor intelectual melhor ainda,
mas, muito acima de ambos,
está o vigor do caráter.
(Theodore Roosevelt)

RESUMO

Da crescente necessidade de reduzir o consumo de água e o uso de insumos químicos no processamento de substratos têxteis, surgiu uma nova técnica que aumenta a eficácia do tingimento: a cationização da celulose que modifica quimicamente a molécula, tornando-a fortemente catiônica. O objetivo do trabalho é avaliar as diferentes técnicas de cationização de fibras de algodão, aplicando agentes catiônicos inovadores. Uma molécula típica de agente catiônico contém quaternário de amônio e um grupo reativo que interage com a celulose através de ligações covalentes. A cationização é dependente da concentração de NaOH e do agente catiônico, pH, temperatura, tempo e relação de banho. Neste trabalho foram utilizados quatro agentes catiônicos: cloreto de 3-cloro-2-hidroxipropil trimetil amônio (CHPTAC), cloreto de poli dialil dimetil amônio (PDDACl), cloreto de poliacrilamida-co-dialildimetilamônio (PAcD) e Poliquaternário-2 (P42). Os reagentes P42 e PAcD foram considerados agentes catiônicos inéditos para a área têxtil. Não foi encontrada publicação na literatura que relaciona o uso do P42 e PAcD como cationizantes de tecidos. Os tecidos catiônicos foram tintos utilizando corantes da classe reativa e ácida. As amostras de tecido foram analisadas através de propriedades colorimétricas, solidez à cor, potencial zeta, atividade bactericida, Espectroscopia no Infravermelho por Transformada de Fourier (FTIR), Microscopia de Força Atômica (AFM) e Espectroscopia Fotoeletrônica por Raios X (XPS). Também foi investigado o processo de cationização assistido por tratamento com plasma atmosférico. Os tecidos tratados com os agentes cationizantes CHPTAC, PDDACl e P42 foram tintos sem adição de sal e obtiveram força colorística (K/S) igual ou superior ao tingimento convencional. Além disso, enquanto o processo convencional exige 3 banhos de lavação consecutivos, no tingimento com tecido cationizado com CHPTAC um único banho é suficiente para remoção do corante não fixado à fibra. A amostra cationizada com PDDACl apresentou K/S de 45±7 e 48±6, respectivamente para 40 e 20 $g.L^{-1}$ de agente catiônico, em tingimento com corante Vermelho Reativo 195. Para o CHPTAC, os valores de K/S foram 48±2 para 40 $g.L^{-1}$ e 41.2±0.5 para 20 $g.L^{-1}$. Esses resultados foram superiores ao tingimento convencional, com K/S=32. O agente catiônico P42 apresentou resultados compatíveis com o tingimento convencional, com K/S de 28±3 e 27±1, respectivamente para 40 e 20 $g.L^{-1}$. Os agentes catiônicos PDDACl e P42 apresentaram resultados promissores, as amostras tratadas com estes reagentes apresentaram atividade bactericida. A cationização aumentou consideravelmente a interação entre a fibra e o corante ácido, entretanto a fixação do corante à fibra foi menor com o tingimento catiônico. A maior parte do corante ácido retornou à fase liquida após a realização do ensaio de solidez à lavagem. O tratamento com plasma alterou pouco as propriedades dos tecidos catiônicos e tintos. Foi observado o incremento da solidez à luz em algumas amostras tratadas com plasma. Entretanto, basicamente, o efeito da cationização prevaleceu sobre o plasma. A cationização se mostrou promissora por possibilitar o tingimento com cores mais intensas, além de reduzir a carga de efluentes geradas e eliminar a alimentação de sal no processo de tingimento.

Palavras-chave: Cationização. Tingimento catiônico. Tingimento sem sal. Tecido de algodão.

RESUMO EXPANDIDO

Introdução

O tingimento da fibra de algodão é massivamente realizado por meio dos corantes reativos e diretos. Dentre estes dois tipos, os corantes reativos são os mais utilizados pois conferem ao tecido melhores propriedades de brilho, tonalidades e solidez à lavagem. Entretanto, essas duas classes de corante possuem interação limitada com a fibra de algodão, por causa do caráter aniônico presente tanto no corante, quanto na celulose. Para compensar a baixa afinidade entre os corantes reativos e a fibra de algodão, a indústria têxtil utiliza grandes quantidade de sal nos banhos de tingimento (entre 30 e 100 $g.L^{-1}$). Em termos de uso de insumos químicos, um processo convencional de tingimento de malha de algodão pode resultar em um consumo de 300 a 1200 g de insumos químicos e 80 L de água para tingir um único quilograma de tecido.

A cationização faz parte do rol de novas tecnologias que visam diminuir o consumo de água e insumos químicos. A cationização modifica quimicamente a molécula de celulose, principal constituinte do algodão, tornando-a fortemente catiônica. A fibra de algodão, que originalmente é carregada negativamente, após essa funcionalização passa a ter cargas superficiais positivas, o que facilita uma interação com corantes aniônicos. A utilização deste tipo de corante pode trazer à fibra de algodão cores mais intensas e brilhantes utilizando a mesma quantidade de corante do processo convencional. Além disso, traz benefícios ao processo de tingimento principalmente pela eliminação da utilização de álcalis, barrilha e sal, insumos essenciais para o tingimento com os corantes de classe reativa.

A interação eletrostática entre fibra e corante funciona da mesma forma que um imã. Quando cargas do mesmo sinal estão próximas estas se repelem, é o que acontece com a celulose e os corantes aniônicos. No caso da fibra catiônica a celulose passa a ter cargas positivas, próxima ao corante aniônico as cargas opostas se atraem. Portanto, a cationização resulta em um tingimento têxtil com maior afinidade entre corante e fibra. Para a indústria têxtil isso significa maior efetividade, possiblidade de produzir tecidos tintos utilizando menor quantidade de corante para produção de cores mais intensas e vivas. Além disso, significa ganho de competitividade, pois reduz o gasto de tempo de processo, energia e volume de efluente gerado.

O desenvolvimento de alternativas sustentáveis e economicamente viáveis é altamente apreciado pela indústria de processamento têxtil. O Brasil possui considerável representatividade no setor têxtil. O país é o quarto maior produtor mundial de malhas e é o único país ocidental com a cadeia têxtil completa. O Brasil processa desde a produção das fibras, como a plantação do algodão, fiações, tecelagens, beneficiadoras, confecções, desfiles de moda e comercialização.

Este trabalho foca em diferentes técnicas de cationização de algodão, com uso de agentes cationizantes inovadores. A tese foi estruturada na forma de coletânea de artigos científicos e está dividida em seis capítulos: introdução, revisão da literatura, artigo 2, artigo 3, artigo 4, conclusões gerais e sugestões para trabalhos futuros. Os resultados indicam uma economia grande na quantidade de efluentes gerados e possibilitam a utilização novos cationizantes.

Objetivos

Este trabalho tem como objetivo avaliar diferentes técnicas de cationização de fibras de algodão, com agentes catiônicos inovadores e aplicação no tingimento com corante reativo e ácido.

Metodologia

O trabalho foi dividido em 4 artigos científicos. O artigo 1 consistiu numa revisão da literatura e apresenta o estado da arte do processo de cationização. No artigo de revisão também são indicadas as tendencias para o futuro da cationização de algodão, baseado na avaliação crítica do estado da arte.

No artigo 2 o tecido de algodão foi cationizado com CHPTAC e tinto com corante ácido e reativo. Quatro diferentes pré-tratamentos foram realizados: alvejamento (amostra S-B), cationização (amostra S-C) e uma combinação de ambos em uma única ou duas etapas (amostras S-BC1 e S-BC2, respectivamente). Os tecidos tiveram suas propriedades colorimétricas mensuradas e foram caracterizados por FTIR, enquanto o efluente líquido foi avaliado em virtude da concentração de corante.

No artigo 3 foram testados 4 agentes cationizantes: cloreto de 3-cloro-2-hidroxipropil trimetil amônio (CHPTAC), cloreto de poli dialil dimetil amônio (PDDACl), cloreto de poliacrilamida-co-dialildimetilamônio (PAcD) e Poliquaternário-2 (P42). As amostras pré-tratadas foram tintas com corante Vermelho Reativo 195. As propriedades colorísticas foram mensuradas e as amostras caracterizadas por FTIR e potencial zeta. Além disso foi avaliada a atividade bactericida dos tecidos catiônicos e proposto o mecanismo de cationização.

O tratamento com plasma e a cationização foram utilizados no artigo 4 em amostras de algodão cru. O plasma foi aplicado no tecido uma única vez (antes da cationização) ou duas vezes (antes da cationização e do tingimento). Os tecidos foram submetidos ao tingimento com corante Vermelho Reativo 195 e Azul Ácido 260. As propriedades colorimétricas foram mensuradas para todos os tecidos. As amostras têxteis foram caracterizadas por sua morfologia, por meio do AFM, e composição química superficial, por FTIR e XPS.

A metodologia dos artigos 3 e 4 foram definidas com base nos resultados obtidos no artigo 2. O processo de tratamento proposto por alvejamento seguido de cationização em duas etapas foi utilizado no artigo 3 pois a amostra apresentou o maior grau de brancura no artigo 2 (amostra S-BC2). Esse procedimento visou evitar ao máximo as interferências na medição da cor e na presença de impurezas do algodão. Para o artigo 4, foi selecionada a amostra cationizada sem alvejamento do artigo 2 (amostra S-C), pois o objetivo foi justamente avaliar o uso do plasma em processos de cationização com tecido de algodão cru.

Resultados e discussão

Todas as amostras que receberam pré-tratamento, no artigo 2, estavam aptas para o tingimento, porém observou-se algumas variações nas propriedades colorimétricas. O tingimento com o corante reativo apresentou maior valor de força colorística para amostra S-C, cujo K/S foi 41±2. Esse maior valor está relacionado a coloração do substrato. A amostra S-C foi cationizada sem processo de alvejamento, logo as ceras e outras impurezas não foram removidas e conferiram uma coloração amarelada para a amostra.

O tingimento convencional com Vermelho Reativo 195 apresentou K/S igual a 32±1. Os tecidos cationizados com CHPTAC e PDDACl apresentaram os maiores valores de K/S após o tingimento. Os valores de K/S após o tingimento foram 48±2 e 41,2±0,5 se cationizado com CHPTAC e 45±7 e 48±6, se cationizado com PDDACl, utilizando respectivamente 40 ou 20 $g.L^{-1}$ de cationizante. Todos estes valores são estatisticamente iguais. O agente cationizante P42 apresentou K/S igual a 28±3 e 27±7, utilizando 40 ou 20 $g.L^{-1}$ de cationizante, respectivamente. Estes valores são estatisticamente iguais ao tingimento convencional.

O cationizante PAcD não apresentou resultados satisfatórios, provavelmente por não ser suficiente para cationizar o tecido de algodão. A amostra tratada com PAcD a 20 $g.L^{-1}$, possui ponto isoelétrico igual a 3.4, logo, a amostra é aniônica em soluções de pH acima deste valor. Os tingimentos foram realizados em pH>8.5. Todos os outros tecidos catiônicos apresentaram caráter catiônico em toda faixa de pH. A amostra de algodão convencional é completamente aniônica, independente do pH da solução.

Os processos de cationização e alvejamento realizados de forma conjunta ou em duas etapas pouco influenciaram as características do tecido tinto após o tingimento com corante reativo. A análise estatística não identificou diferenças significativas nas propriedades colorimétricas das amostras S-BC1 e S-BC2 tintos com corante reativo. Além disso o desvio da cor (ΔE) entre as duas amostras foi de 0,8. De uma forma geral, as diferenças nos tecidos são imperceptíveis quando o ΔE é menor que 1,0; exceto quando os avaliadores são profissionais treinados.

Os tecidos cationizados com PDDACl e CHPTAC obtiveram maior interação com os corantes, seja ácido ou reativo. Isto resultou em menor quantidade de corante retornando ao banho de tingimento ou lavagem. Para o tecido cationizado com CHPTAC, o corante está presente na fase líquida somente no banho de esgotamento (no fim do processo) e na primeira lavagem. Considerando a cationização com PDDACl, utilizado no tingimento com Vermelho Reativo 195, a menor concentração de corante foi encontrada no terceiro banho de lavagem (2,9±0.5 e 4.0±0.2 mg.L^{-1} para os tecidos cationizados a 40 e 20 g.L^{-1}, respectivamente).

Os tecidos catiônicos obtiveram K/S em torno de 4 a 9 vezes maior que o tingimento com o tecido alvejado. Este aumento é atribuído à coloração dos substratos variável com o tipo de pré-tratamento e ao aumento da interação corante e fibra. Também foi observado uma expressiva redução de corante na fase líquida. A redução da concentração do corante Acido Azul 260 ao final do esgotamento e nos banhos de lavagem foi acima de 80 % quando foi utilizado tecido catiônico. Em contrapartida, a interação não foi suficiente para fixação completa do corante. A solidez a lavagem resultou em valores entre 1 e 2 devido à grande parte do corante ácido retornar aos banhos após a execução deste teste.

As análises de FTIR indicaram pouca modificação dos grupos químicos presentes na superfície após os tratamentos. Os espectros das amostras indicaram majoritariamente a presença de bandas características da estrutura da celulose. Entretanto, nas amostras tratadas com plasma e cationizadas com P42, foi observado uma banda de absorção próxima de 1572 cm^{-1}, relacionado a presença de amida secundária. Este grupo funcional está presente no agente P42. As análises de XPS, efetuadas no artigo 4, indicaram o aumento do teor de oxigênio na amostra após os tratamentos com plasma e cationização. O teor de oxigênio aumenta em consequência da remoção das ceras presentes no algodão cru.

Considerações finais

A cationização do tecido de algodão incrementou consideravelmente a interação com o corante reativo e ácido. A força colorística dos tecidos catiônicos tintos com corante Vermelho Reativo 195 aumentou 28-50 % quando utilizado os cationizantes PDDACl ou CHPTAC. Além disso, a quantidade de efluente gerado durante o tingimento é menor ao utilizar o tecido catiônico. Utilizando CHPTAC, um único banho de lavagem foi suficiente para remoção do corante não fixado à fibra.

Com as condições estudadas, o reagente PAcD não apresentou resultados satisfatórios para que seja utilizando com cationizante têxtil. O tecido cationizado com 20 g.L^{-1} de PAcD se comporta como catiônico em solução de pH<3,4, porém o tingimento ocorreu em meio básico. Outra explicação à baixa interação do tecido cationizado com PAcD e a fibra está relacionada à baixa concentração do reagente. Todos os reagentes foram utilizados em 20 ou 40 g.L^{-1}, porém o PAcD foi fornecido com 20 % do reagente em água, a maior diluição entre todos.

A cationização melhorou substancialmente a interação corante-fibra, quando utilizados, P42, CHPTAC e PDDACl. Mas o processo precisa ser aprimorado para tingimento do algodão com corante ácido. Durante o teste de solidez à lavagem, a maior parte do corante ácido não estava fortemente fixada e retornou ao banho.

O tratamento com plasma possibilitou uma melhora da solidez à luz de algumas amostras de tecidos tintos, provavelmente devido ao aumento da reatividade da fibra. Entretanto, de uma forma geral, o tratamento com plasma influenciou pouco nas propriedades tintoriais dos tecidos. O efeito de cationização prevaleceu sobre o tratamento plasma.

Esta pesquisa traz a possibilidade de utilização de dois novos agentes cationizantes. O PDDACl que apresentou resultados comparáveis ao reagente comercial CHPTAC. O P42 também produziu resultados satisfatórios. O P42 é uma molécula de baixa toxicidade utilizada na formulação de cosméticos. A questão da segurança é um dos fatores mais importante da cationização pois o reagente CHPTAC possui restrições comerciais devido à sua toxicidade. Além disso os tecidos cationizados com PDDACl e P42 apresentaram propriedades bactericidas.

Palavras-chave: Cationização. Tingimento catiônico. Tingimento sem sal. Tecido de algodão.

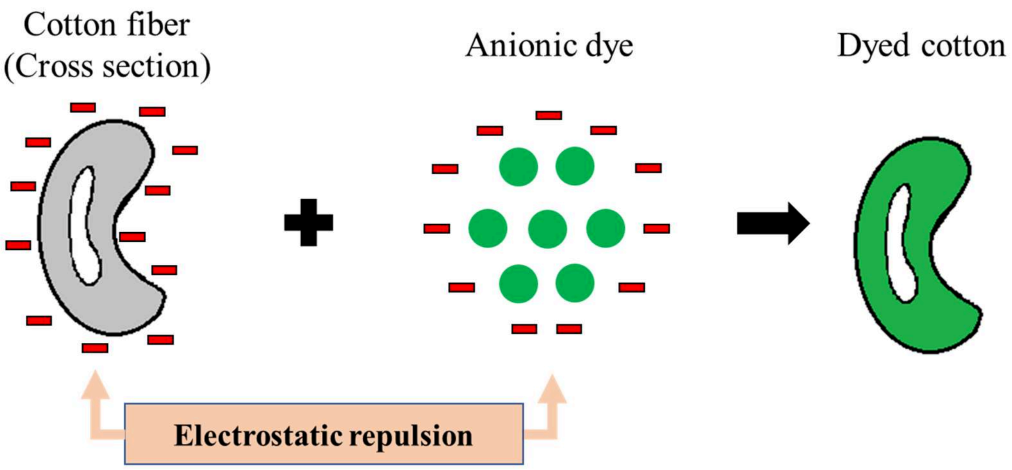
ABSTRACT

From the increasing necessity to reduce water consumption and the use of chemical inputs in the processing of textile substrates has emerged a new technique that increases dyeing efficiency: the cationization of cellulose that chemically modifies the molecule, making it strongly cationic. The objective of this work is to evaluate the different cationization techniques of cotton fibers, applying innovative cationic agents. A typical cationic agent molecule contains quaternary ammonium and a reactive group that interacts with cellulose through covalent bonds. The cationization is dependent on the NaOH and cationic agent concentration, pH, temperature, time and material-to-liquor ratio. Four cationic agents were used: 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC), poly diallyldimethylammonium chloride (PDDACl), poly acrylamide-co-diallyldimethylammonium chloride (PAcD) and Polyquaternium-2 (P42). The reagents P42 and PAcD were considered unprecedented cationic agents for the textile sector. No publication was found in the literature regarding the use of P42 and PAcD as cationic agents for fabrics. The cationic fabrics were dyed using reactive and acid dyes. The fabric samples were analyzed by colorimetric properties, color fastness, zeta potential, bactericidal activity, Fourier Transform Infrared Spectroscopy (FTIR), Atomic Force Microscopy (AFM), and X-Ray Photoelectronic Spectroscopy (XPS). The cationization process assisted by treatment with atmospheric plasma was also investigated. The fabrics treated with the cationic agents CHPTAC, PDDACl and P42 were dyed without the feeding of salt and obtained color strength (K/S) equal to or greater than the conventional dyeing. Besides, while the conventional process requires three consecutive washing baths, in the CHPTAC cationic process, a single bath is sufficient for the removal of the dye non-fixed to the fiber. The cationic fabric treated with PDDACl presented K/S of 45±7 and 48±6, respectively for 40 and 20 $g.L^{-1}$ of cationic agent, when dyed with Reactive Red 195 dye. For CHPTAC, the K/S values were 48±2 for 40 $g.L^{-1}$ and 41.2±0.5 for 20 $g.L^{-1}$. These results were superior to conventional dyeing, with K/S=32. The cationic agent P42 presented results similar to the conventional dyeing, with K/S of 28±3 and 27±1, respectively for 40 and 20 $g.L^{-1}$. The cationic agents Poly diallyldimethylammonium chloride (PDDACl) and Polyquaternium-2 (P42) presented promising results, the samples treated with these reagents showed bactericidal activity. The cationization considerably increased the interaction between the fiber and the acid dye, however, the fixation of the dye to the fiber was lower with cationic dyeing. Most of the acid dye returned to the liquid phase after carrying out the washing fastness test. The plasma treatment little changed the properties of the cationic and the dyed fabrics. An increase in light fastness was observed in some samples treated with plasma. However, the effect of cationization prevailed over plasma. The cationization was promising because it allows the dyeing with more intense colors, besides reducing the effluent load generated and eliminating the feeding of salt in the dyeing process.

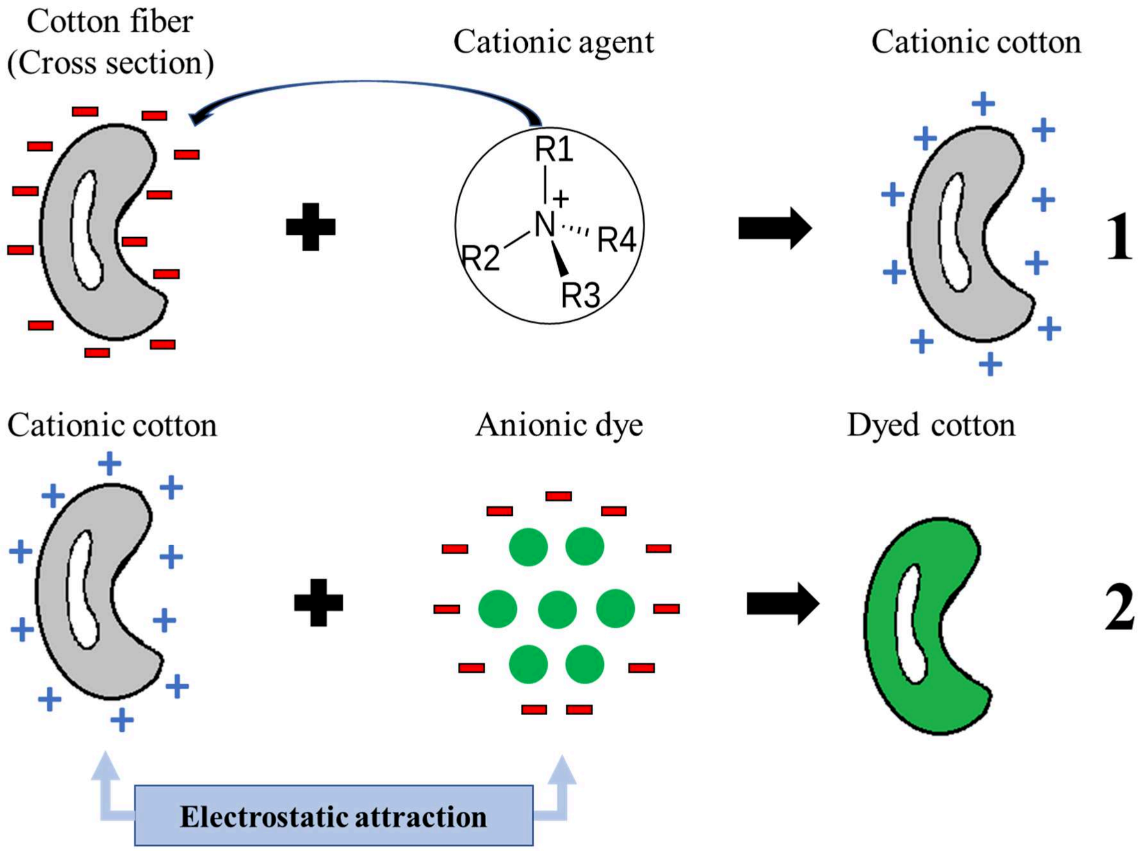
Keywords: Cationization. Cationic dyeing. Salt-free dyeing. Cotton fabric.

GRAPHICAL ABSTRACT

CONVENTIONAL DYEING



CATIONIC DYEING



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LIST OF ABBREVIATIONS AND ACRONYMS

AAHTAPC	1-acrylamido-2-hydroxy-3-trimethylammoniumpropane chloride
AC	Aerobic Count
AFM	Atomic force microscopy
ATR	Attenuated total reflection
ANOVA	Analysis of variance
BCHDAC	Benzyl (3-chloro-2- hydroxypropyl) dimethylammonium chloride
BSA	Bovine serum albumin
C.I.	Color Index
CA	Cationic agent
CHPCDAC	3-chloro-2- hydroxypropyl cocoalkyldimethylammonium chloride
CHPDDAC	3-chloro-2- hydroxypropyl dimethyldodecylammonium chloride
CHPDODAC	3-chloro-2- hydroxypropyl dimethyloctadecylammonium chloride
CHPTAC	3-chloro-2-hydroxypropyl trimethylammonium chloride
CO	Cotton
CONAMA	National Environment Council
CPS	Counts per second
DADMAC	Diallyldimethylammonium chloride
DBD	Dielectric barrier discharge
DI	Deionized
DMC	2-methacryloyloxyethyltrimethyl ammonium chloride
DOI	Digital Object Identifier
E	Exhaustion
EP	Epichlorohydrin
EPO	European Patent Office
EPTAC	2,3-epoxypropyl trimethylammonium chloride
Eq.	Equation
F	Fixation
FTIR	Fourier transform infrared spectroscopy
IARC	International Agency for Research on Cancer
ISO	International Organization for Standardization
K	Absorption coefficient

KH	Keratin hydrolysate
MTLR	Material-to-liquor ratio
N	Nitrogen
NA	Not available
NCSU	North Carolina State University
NMM	N-oxiranylmethyl-N-methylmorpolinium chloride
owb	Over weight of bath
owf	Over weight of fiber
P42	Poly[bis(2-chloroethyl)ether-alt-1,3-bis[3-(dimethylamino)propyl]urea] quaternized
PA	Polyamide
PAcD	Poly acrylamide-co-diallyldimethylammonium chloride
PDDACl	Poly diallyldimethylammonium chloride
PDMAEMA	2-(N,N-dimethylamino)ethyl methacrylate
R	Reflectance
Ref.	Reference
RMS	Root mean square
RUI	Relative unlevelness index
S	Scattering coefficient
T	Temperature
TH	Thiourea
UFSC	Federal University at Santa Catarina
USA	United States of America
WIPO	World Intellectual Property Organization
WS	Without salt
wt	Weight
XPS	X-ray photo electronic spectroscopy

LIST OF SYMBOLS

K/S	Color strength
X	Tristimulus value corresponding to the red color
Y	Tristimulus value corresponding to the green color
Z	Tristimulus value corresponding to the blue color
ΔE	Color deviation
R^2	Coefficient of determination
L^*	Lightness coordinate
a^*	Red/green coordinate
b^*	Yellow/blue coordinate
p	P-value
S_λ	Standard deviation of reflectance measured at a specific wavelength
i	Order of the measurement
$\overline{R}$	Mean of the reflectance
V_λ	Photopic relative luminous efficiency function
λ	Wavelength

CONTENTS

1 INTRODUCTION

The conventional method of dyeing cotton generally uses, besides the dyes, the following chemical inputs: sulfate or sodium chloride, sodium hydroxide, sodium carbonate, acetic acid, surfactant, and chelating agent. In terms of chemical quantity, a conventional cotton dyeing process result in a consumption of 300 to 1200 g of chemical inputs (GHALY et al., 2013) and up to 80 L of water per kilogram of fabric (ROSA et al., 2014). The conventional process has a limited affinity between the fiber and the dyes and it is estimated that only 60-70 % of the dye is exhausted, when reactive dyes are applied (MA et al., 2015). Therefore, it generates a considerable amount of effluent composed of non-reacted chemical inputs and hydrolyzed dye (ACHARYA et al., 2014; ARIVITHAMANI; GIRI DEV, 2017a).

The growing need to reduce water consumption and the use of chemicals in textile substrate processing has led to new technologies that increase dyeing effectiveness. One is the cationization of cellulose that chemically modifies the cellulose molecule, making it strongly cationic (AKTEK; MILLAT, 2017; HAUSER; TABBA, 2001; LI et al., 2019; ROY CHOUDHURY, 2014). Cotton fiber, which is originally negatively charged, after this functionalization behaves with positive surface charges, which increases the interaction with anionic dyes (ARIVITHAMANI; GIRI DEV, 2018). This type of dyeing can bring to cotton fiber more intense and brighter colors. Besides, it brings benefits to the dyeing process mainly by eliminating the use of alkali, soda ash (Na_2CO_3) and salt, essential inputs for dyeing with reactive class dyes.

Anionic dyes, such as reactive and direct dyes are often used for cotton dyeing. Reactive dyes are predominantly used for dyeing cotton due to their high washing fastness, brilliancy and wide range of shades (WANG et al., 2009). However, these two dye classes often have a low affinity for cotton fabrics (HELMY; HAUSER; EL-SHAFEI, 2017). Thus, conventional dyeing of cotton with these classes of dyes requires the presence of electrolytes, which can neutralize negative charges on the cotton surface and increases the dye-uptake in cellulose (LIU; YAO, 2011). The most common electrolytes used for industrial reactive dyeing of cotton are the salts NaCl or Na_2SO_4 (ARIVITHAMANI; DEV, 2017; LIU; YAO, 2011), in concentrations of 30-100 $g.L^{-1}$ (WANG et al., 2009).

One of the great triumphs of cationization is the elimination of the salt feed from conventional processes. Many authors name the cationization process as salt-free or low-salt dyeing (ARIVITHAMANI; GIRI DEV, 2016; CHATTOPADHYAY; CHAVAN; SHARMA, 2007; DONG et al., 2020). A high concentration of salts elevates the water density, reduces the solubility of oxygen gases, affects the microorganisms, thus is undesirable in effluents (AHSAN et al., 2019; SALMANIKHAS; TIZGHADAM; RASHIDI MEHRABADI, 2016). Water desalination processes are unfeasible because of the high cost (NI et al., 2018). Separation of salt from effluents increases the dyeing cost by 10 % (ARIVITHAMANI; GIRI DEV, 2018). Therefore, a viable alternative for companies is the reduction of salt in dyeing processes.

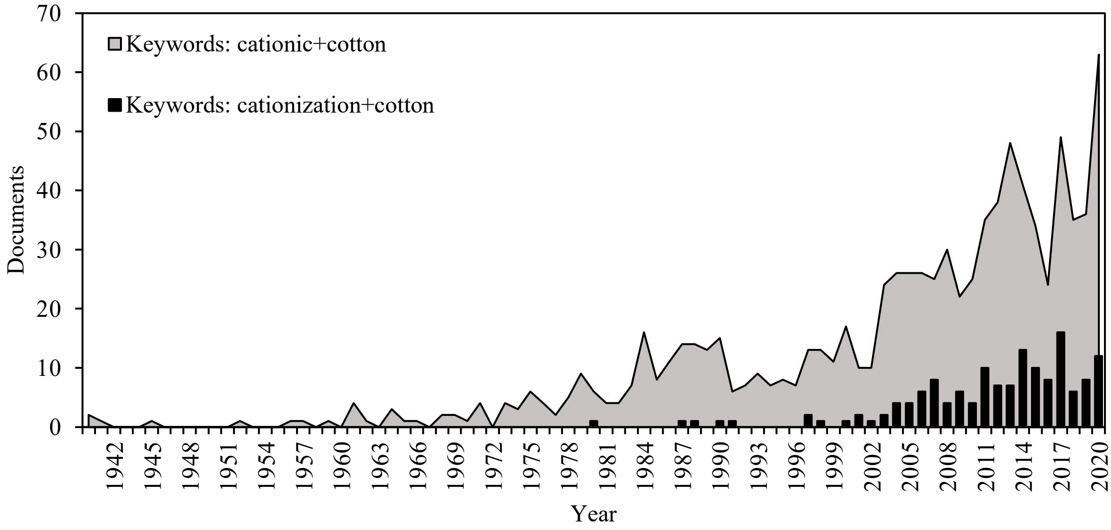
Considering the competitiveness of the market, the greatest benefit of this technology is to achieve a reduction in water, energy, and chemicals in the dyeing process (BESSA et al., 2019; FARRELL; HAUSER, 2013). Cationic cotton helps address market demands and improve inventory and cost efficiencies. It enables to dye fabrics utilizing one-third to one-half the typical amount of dye required in traditional dyeing (COTTON INCORPORATED, 2018).

Several authors have studied cotton cationization as an alternative for lower cost or more sustainable dyeing over the years. Figure 1 shows the historical increase in the number of publications in the Scopus database, searched with keywords “cationic”, or “cationization”, and “cotton”. There has been a considerable number of publications for over 50 years. Even after extensive research, cotton cationization still faces structural problems that make it difficult to use. Cationic cotton has still not seen considerable industrial recognition aside from niche markets. This happens because of the concerns about the safety of cationic agents, cost of cationization, lack of results in large scale procedures and lack of methodology to transition from a conventional to a cationic cotton dyeing (FARRELL; ORMOND; GABLER, 2015). The cationization process still needs improvement before achieving industrial-scale use.

The development of alternatives that are environmentally and economically viable is highly appreciated by the Brazilian textile processing industry. Brazil has great representation in the textile sector as it is considered the fourth-largest producer of knitwear in the world. Brazil is the only western country with a complete textile chain, that is, it operates from fiber production, such as cotton growth, through spinning, weaving, processing, clothing, fashion shows and strong retail sales (BRAZILIAN TEXTILE AND APPAREL INDUSTRY ASSOCIATION, 2018).

In this context, the cationization process can minimize the environmental impacts caused by the chemical processing of the cotton fabric. This is especially important in the regions with higher production of this textile substrate. The region of Vale do Itajaí, in Santa Catarina, is considered the largest producer of knitted cotton in Latin America (BRAZILIAN TEXTILE AND APPAREL INDUSTRY ASSOCIATION, 2013). Consequently, industries can reach a new competitive technological level, as it will result in a productivity gain of the textile industry and production of fabrics with more brightness and intense colors. All this with reduced consumption of inputs and water and reduction of dyes and salts in the generated effluent.

Figure 1 – Historical series of the number of publications indexed by Scopus database, using "cationic", or “cationization”, and "cotton" as search keywords.



Source: the author.

1.1 OBJECTIVES

This work aims to evaluate the different cationization techniques for cotton fibers, with novel cationic agents and application in dyeing with reactive and acid dye. To achieve the general objective, specific objectives defined are listed below:

i. Proceed with a literature review, to identify the state of the art of the cationization process. Moreover, evaluate the physical and chemical modifications on cotton substrates before and after the application of cationization.
ii. Propose novel cationic agents for textiles.
iii. Pretreat the greige cotton knitted fabric by different combinations of cationization or bleaching.
iv. Prepare functional fabrics with cationization and plasma treatment.
v. Dye the cationic fabrics with reactive and acid dyes.
vi. Measure the color and the fastness properties of the fabrics.

vii. Evaluate the chemical, physical and morphological properties of dyed and non-dyed fabrics through Fourier transform infrared spectroscopy (FTIR), zeta potential, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).
viii. Estimate the bactericidal activity of the cationic fabrics.
ix. Compare the proposed process with conventional dyeing, regarding water consumption, effluents generation and proprieties of the dyed textile products.
x. Propose the mechanism for cationization.

1.2 STRUCTURE OF THESIS

The thesis is structured as a collection of four scientific manuscripts. Therefore, the work was divided into six chapters: (1) Introduction, (2) Literature review, (3) manuscript 2, (4) manuscript 3 (5) manuscript 4 and (6) general conclusions and suggestions for future research. A list of references used in this work is provided at the end of the thesis. The Appendix A contains the image of the first page of the review paper (manuscript 1). Appendix B, C and D contains supplementary material for manuscripts 2, 3 and 4, respectively. Appendix E contains the images of some equipment used in this research.

The manuscript 1 is a literature review, which presents an overview of the current state of the art regarding cotton cationization. It provides knowledge about the cationic agents and the cationization process variables used by many researchers. It also presents indicators to evaluate cationization and dyeing efficacy, the market for cationic cotton, challenges and prospects of the cationization process.

The literature review was published as a review paper by the Cellulose Journal, entitled "Cationization of cotton fiber: an integrated view of cationic agents, processes variables, properties, market and future prospects". The DOI of the paper is https://doi.org/10.1007/s10570-020-03361-w.

Manuscript 2, entitled "Cationization as an alternative method to develop new bright colors and decrease the effluent load in cotton dyeing process" brings three different procedures for cotton cationization. These procedures can be used in industrial processes and vary according to the quality criteria adopted by the company. This work also compared reactive and acid dyes for dyeing of cotton. Acid dye is widely used for the dyeing of cationic fibers, such as polyamide, but has no application for dyeing of cellulosic fibers.

From manuscript 2, the fabrics with the highest whiteness degree among the cationic samples were prepared by the procedure of bleaching followed by cationization in two separated steps (referred to as sample S-BC2). Therefore, to avoid color and impurities interferences, this procedure was adopted for the pretreatment of fabrics in manuscript 3.

Manuscript 3 has the title “Preparation of cationic cotton through reaction with different polyelectrolytes” and aims to increase the cationization process from the research of novel cationic agents, some of them not yet present in the scientific literature. The originals cationic agents were tested and compared with the commercial agent CHPTAC, which is already used in some industrial applications. The samples were characterized by FTIR and zeta potential. Besides, the bactericidal efficacy of the treated fabric was estimated. The mechanism for cationization was proposed too.

Manuscript 4 regards the research period developed at North Carolina State University (NCSU, Raleigh, USA) as a result of the sandwich doctorate program, sponsored by the PRINT-CAPES/UFSC program. The manuscript was entitled “Surface functionalization of greige cotton knitted fabric through plasma and cationization for dyeing with reactive and acid dyes”. In this work, plasma treatment and cationization were used to prepare greige cotton for dyeing. The cationic agent P42 was used due to the novelty of the research and to the good results described in manuscript 3. CHPTAC was also used for comparisons as it is the most popular cationic agent of the textile sector. The fabrics were characterized by XPS, FTIR and AFM.

2 LITERATURE REVIEW

The literature review approaches the state of the art in the process of cationization of textile fibers, with emphasis on cotton. The articles used for this review were mainly collected from the Scopus and Science Direct databases.

2.1 CATIONIZATION OF CELLULOSE FIBERS

Cationization is a chemical process that provides cationic sites to the cellulose fibers. After the treatment, the fiber becomes positively charged. Therefore, this modification increases the electrostatic attraction between the fibers and the anionic dyes. Most dyes used for the dyeing of cellulose fibers are anionic (ARIVITHAMANI et al., 2014; IBRAHIM; EL-SAYED; AMEEN, 2010).

Cellulose is the major component of cotton, as shown in Table 1. While in contact with water, negative charges accumulate on the cotton surface due to the partial ionization of hydroxyl groups of cellulose (ACHARYA et al., 2014). Thus, in the conventional dyeing process, cotton fibers have electrostatic repulsion to most commercially available dyes, such as reactive and direct dyes, which are negatively charged (AKTEK; MILLAT, 2017). The efficiency of the process is increased by using high concentrations of electrolytes in the dyebath and extended dyeing times at elevated temperatures. Therefore, several washing cycles are necessary after dyeing to eliminate the dye that did not react with the fiber. For this reason, dyeing cotton fabrics with direct and reactive dyes consume a large amount of energy and natural resources (ARIVITHAMANI; GIRI DEV, 2017a; FARRELL; FU; ANKENY, 2017).

By introducing cationic groups into the cotton fibers, the ionic attractions between cationized cotton and anionic dyes result in increased dye uptake, due to the electrostatic attraction. The most common methodology for cationization is to introduce amino groups into the fiber (ROY CHOUDHURY, 2014). Quaternary or tertiary amino groups bind to cellulose to provide nucleophilic groups, which show greater attraction for anionic dye resulting in the interaction of dye-fiber without the addition of salt (AKTEK; MILLAT, 2017).

Cationic fiber also enables anionic dyeing at neutral pH. Dyeing cationic cotton results in greater exhaustion of dye and higher color strength. The strong dye-fiber interaction, resulting from cationic cellulose, allows dyeing with minimal rinsing and after-washing. Furthermore, a fiber with good dye affinity may continue to exhibit those strong colors and brightness in later use, after consecutive washes (ROY CHOUDHURY, 2014).

Table 1 – Composition of typical cotton fibers.

Component	Composition (% dry weight)	
	Typical	**Range**
Cellulose	95	88-96
Protein	1.3	1.1-1.9
Pectic substances	0.9	0.7-1.2
Ash	1.2	0.7-1.6
Wax	0.6	0.4-1.0
Total sugars	0.3	0.1-1.0
Organic acids	0.8	0.5-1.0
Pigment	Trace	NA[a]
Others	1.4	NA

Source: Wakelyn et al. (2006).
Note: [a] data not available.

2.1.1 Cationic agents

Several authors researched the introduction of amine quaternary groups into the cellulose structure for the cationization of cotton. A typical form of the cationic agent is a molecule containing quaternary ammonium and a reactive group that interacts with cellulose. Cationic agents can be grouped into polymer or monomeric based agents. A list of reagents studied for fiber cationization is shown in Table 2.

Hauser and Tabba (2001) studied the effect of commercially CHPTAC (3-chloro-2-hydroxypropyl trimethylammonium chloride), available as a 65 % solution in water, in cationization of cotton fabrics with direct and reactive dyes. In comparison with conventional dyeing, the color strength values (K/S) of cationic fabric dyed with reactive and direct dyes were increased by approximately 50 %. The color fastness of the cationic dyeing was equal or superior in comparison with untreated cotton.

Acid dyes are typically applied to fibers with positive charges, such as wool, silk and polyamide fibers in an acidic bath. Although, it has a low affinity to cellulosic fibers due to repulsions forces between the negative charges of the cellulosic fibers and the acid dye molecules (REHAN et al., 2020). However, according to Hauser and Tabba (2001), cationization with CHPTAC also allowed the dyeing of cellulosic fabric with acid dyes. The authors compared cationic cotton and nylon dyed with different acid dyes. The results showed that K/S values were almost the same for both types of fabric. However, the color fastness considerably decreased for acid-dyed cationic cotton. Acid dyes are widely used by the textile market for producing fabrics with intense and bright shades. Besides, acid dyes are also considered easier to dye than other classes (PATIL; MAITI; ADIVAREKAR, 2019).

A fabric composed of 50 % polyester and 50 % cotton was cationized using poly diallyldimethylammonium chloride (PDDACl) and chitosan by Oliveira et al. (2017). The cationic fabric was dyed using acid dyes. The best K/S value was 43 for the sample treated by PDDACl, this value was approximately 20 % higher than cationic fabric treated with chitosan and around 280 % higher than the untreated sample. Comparing treated with non-treated samples, no significant variation on the whiteness degree was found; this means that the cationization process does not change the base color of the fabric.

According to Farrell and Hauser (2013), most of the chemicals used for the cationization of cotton have some toxicity issues. Therefore, chitosan has been studied in the textile dyeing process because it represents an environmentally sound and non-toxic practice to increase dye uptake. Chatha et al. (2016) measured the properties of dyeing cotton cationized by chitosan. The authors concluded that pretreatment increased color strength along with a significant improvement in the washing fastness.

Dong et al. (2020) grafted 2-(N,N-dimethylamino)ethyl methacrylate (PDMAEMA) onto the cotton fabric. The results showed that the cotton fabric was successfully grafted. The dyeing with reactive dye presented excellent dye uptake, fixation yield, K/S value, dyeing levelness, and color fastness.

Hasani et al. (2009) prepared two epoxy reagents, N-oxiranylmethyl-N-methylmorpolinium chloride (NMM) and 2-oxiranylpyridine, for cationization of the cotton linter. CHPTAC was also used in cationization tests for comparison. The authors observed the dependence between the nitrogen content in cellulose and water retention. The higher the amount of nitrogen, the greater the water retention into the cotton. Better water retention, consequently, resulted in raised adsorption of the acid dye methyl orange to the fiber. NMM exhibited higher reactivity for cellulose than CHPTAC and 2-oxiranylpyridine.

Wang and Lewis (2002) researched cationic cotton fabrics treated with 1-acrylamido-2-hydroxy-3-trimethylammoniumpropane chloride (AAHTAPC) using a pad–bake process. The treated fiber was dyed with several reactive dyes without the addition of salt or alkali. The cationization increased dye-fiber affinity. The reactive dyes were almost completely exhausted when used with cationic cotton. The dyeings were uniform on the surface, but some dyeings exhibited ring dyeing (a fault in which the dye did not diffuse completely to the interior of the fiber). Ring dyeing is associated with the molecular weight of the cationic agent. High molecular cationic agents cannot penetrate cellulose pores, therefore the cationization is restricted to the external surface of the fiber.

Ma et al. (2016) treated cotton fabric with betaine (N,N,N-trimethyl glycine) as a cationic agent, using a pad–dry–bake pretreatment process. The cationic fabrics were applied in salt-free dyeing of reactive dyes. The increase in dye fixation of Reactive Red 195, Reactive Yellow 145 and Reactive Blue 19 on cationic fabrics were 6.7 %, 9.5 %, and 7.7 %, respectively. Dye fixation on the cationic fabrics in the absence of salt improved with good light fastness. However, some wash and wet rub fastness could not remain as good as that of the conventional dyeing.

Cotton fabrics were cationized using 2-methacryloyloxyethyltrimethyl ammonium chloride (DMC). Modified and unmodified cotton was dyed with Reactive Blue 19, Reactive Red 195 Reactive Yellow 145. The fixation of dye in modified cotton was 23-24 % higher than those obtained using the conventional dyeing method in the presence of inorganic salt. The wastewater parameters, chemical oxygen demand, color and ammonia-nitrogen content of the cationic cotton dyeing method were considerably lower than those of the conventional dyeing (MA et al., 2015).

Liu and Yao (2011) prepared cationic cotton with two pretreatment solutions. Initially, epichlorohydrin was used for epoxidation of the cotton fibers. Then the fabric was treated with a solution containing thiourea to bind amino groups to the cellulose. The epichlorohydrin acted as a crosslinking agent between the thiourea and the cotton fibers. The cationic samples were dyed using reactive dyes. The cationic dyed fabrics presented higher K/S, levelness, washing and rubbing fastness.

Farrell et al. (2015) cationized cotton using various alkyl chlorohydrin quaternary ammonium compounds, in conjunction with the traditional reagent CHPTAC. The cationic samples were dyed using reactive and disperse dyes. The K/S of reactive dyeings were higher for samples pretreated by molecules with low molecular weights, BCHDAC and CHPTAC. This happens due to the higher nitrogen ratio of these molecules. The authors also found a possibility to dye cotton with disperse dyes. Cationic cotton treated by long-chain compounds (CHPDDAC, CHPCDAC, and CHPDODAC) readily exhausted almost all disperse dye. This is related to the increased hydrophobicity of cotton treated by long-chain compounds. Disperse dyes are often used for dyeing of hydrophobic fibers, such as polyester and polyamide (MATTHEWS, 2018).

Table 2 – Cationic agents and methods of application used for the pretreatment of cotton.

(to be continued)

Cationic Agent	Method for cationization	Reference
3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC)	Pad-batch	(FAROUK; SHARAF; ABD EL-HADY, 2013; FARRELL; ORMOND; GABLER, 2015; FU et al., 2013; HAUSER; TABBA, 2001; KAMAL ALEBEID; ZHAO, 2015; KANIK; HAUSER, 2002)
	Exhaustion	(ABDELILEH et al., 2019; ACHARYA et al., 2014; ARIVITHAMANI; DEV, 2017; ARIVITHAMANI; GIRI DEV, 2016, 2017a, 2017b, 2018; MA et al., 2017; SHATERI KHALIL-ABAD; YAZDANSHENAS; NATEGHI, 2009)
	Pad-bake	(FARRELL; FU; ANKENY, 2017; WANG et al., 2009)
	Pad-dry	(NAKPATHOM et al., 2017; REHAN et al., 2017)
	Pad-dry-cure	(GIACOMINI; DE SOUZA; DE BARROS, 2020)
	Exhaustion, pad-batch, pad-steam	(HASHEM, 2006)
	Pad-batch, exhaustion, pad-steam, and pad-dry-cure	(HASHEM; HAUSER; SMITH, 2003)
Poly diallyldimethylammonium chloride (PDDACl)	Exhaustion	(JAREANSIN; SUKAAM; KUSUKTHAM, 2019; OLIVEIRA et al., 2017)
	Pad-dry-bake	(HELMY; HAUSER; EL-SHAFEI, 2017)
	Pad-dry-cure	(ABD EL-HADY; SHARAF; FAROUK, 2020)

Table 2 – Cationic agents and methods of application used for the pretreatment of cotton.

(continuation)

Cationic Agent	Method for cationization	Reference
Diallyldimethylammonium chloride (DADMAC)	Pad-batch	(FAROUK; SHARAF; ABD EL-HADY, 2013)
Chitosan	Exhaustion	(CHATHA et al., 2016; IBRAHIM; EL-SAYED; AMEEN, 2010)
	Pad-dry-cure	(GIACOMINI; DE SOUZA; DE BARROS, 2020)
	Pad-dry, pad-batch, pad-steam, and pad-dry-steam	(HOUSHYAR; AMIRSHAHI, 2002)
2-(N,N-dimethylamino)ethyl methacrylate (PDMAEMA)	Exhaustion	(DONG et al., 2020)
Ovalbumin	Pad-dry-cure	(GIACOMINI; DE SOUZA; DE BARROS, 2020)
Bovine serum albumin (BSA)	Exhaustion	(SAHITO et al., 2015)
N-oxiranylmethyl-N-methylmorpolinium chloride (NMM)	Exhaustion	(HASANI et al., 2009)
2-oxiranylpyridine	Exhaustion	(HASANI et al., 2009)
1-acrylamido-2-hydroxy-3-trimethylammoniumpropane chloride (AAHTAPC)	Pad-bake	(WANG; LEWIS, 2002)
Betaine	Pad-bake	(MA et al., 2016)
2-methacryloyloxyethyltrimethyl ammonium chloride (DMC)	Exhaustion	(MA et al., 2015, 2020)
Epichlorohydrin/thiourea (EP/TH)	Exhaustion	(LIU; YAO, 2011)
Benzyl (3-chloro-2- hydroxypropyl) dimethylammonium chloride (BCHDAC)	Pad-bake	(FARRELL; FU; ANKENY, 2017)

Table 2 – Cationic agents and methods of application used for the pretreatment of cotton.

(conclusion)

Cationic Agent	**Method for cationization**	**Reference**
3-chloro-2- hydroxypropyl dimethyldodecylammonium chloride (CHPDDAC)	Pad-bake	(FARRELL; FU; ANKENY, 2017)
3-chloro-2- hydroxypropyl cocoalkyldimethylammonium chloride (CHPCDAC)	Pad-bake	(FARRELL; FU; ANKENY, 2017)
3-chloro-2- hydroxypropyl dimethyloctadecylammonium chloride (CHPDODAC)	Pad-bake	(FARRELL; FU; ANKENY, 2017)

Source: the author.

2.1.1.1 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC)

Among all the cationic agents, CHPTAC has been the most preferred for cotton cationization and has shown potential for industrial scale-up (ARIVITHAMANI; GIRI DEV, 2018). The synthesis procedure for CHPTAC is published by Seong and Ko (1998). CHPTAC is also known by their commercial names Glytac A, Quat-188, CA200, and CR2000.

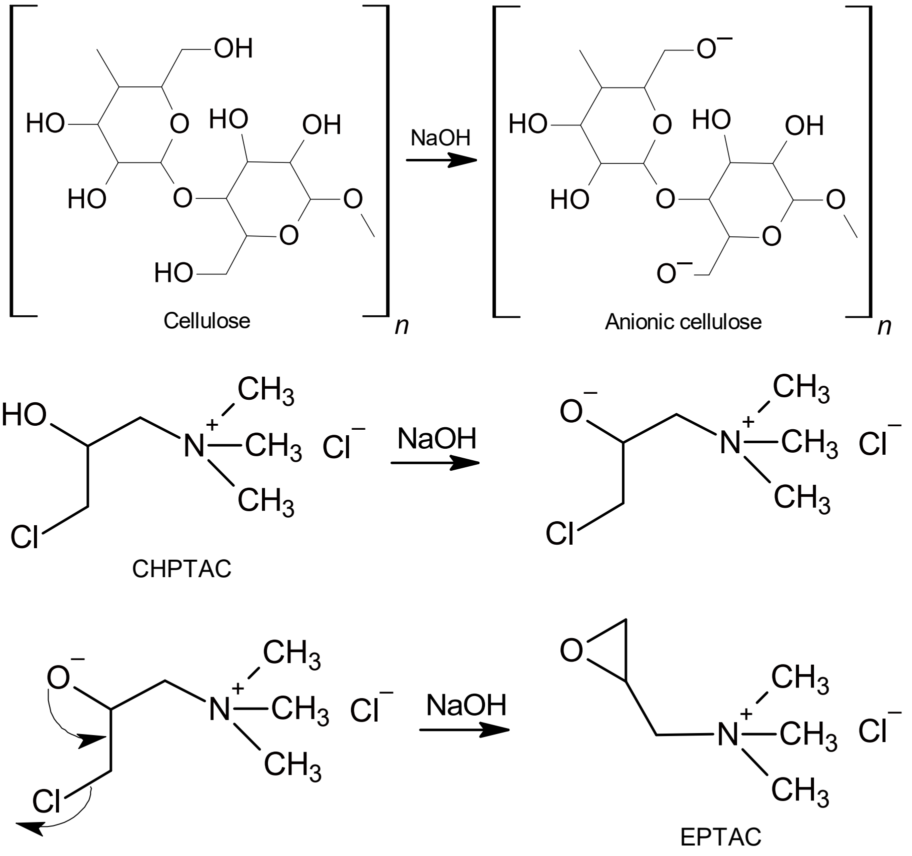
A great advantage of the CHPTAC is the size of the molecule. It is easier to penetrate the fiber pores if the molecule has low molecular weight. Therefore, dyeings with cotton treated with CHPTAC tends to present a uniform dyeing. The cross-section optical microscope images performed by Arivithamani and Giri Dev (2017b) and Ma et al. (2017) indicated that the dyes penetrated satisfactorily in the cotton when treated with CHPTAC.

CHPTAC itself does not react with cellulose. Firstly, it converts into 2,3-epoxypropyl trimethylammonium chloride (EPTAC), also identified as glycidyl trimethylammonium chloride, by reacting with alkali. Then EPTAC reacts with the hydroxyl groups on cotton fiber under alkaline conditions to form cationized cotton. In the presence of alkali, CHPTAC is converted to EPTAC, at the same moment occurs the dissociation of the cellulose hydroxyl group (FARRELL; HAUSER, 2013). The reaction is shown in Scheme 1 (ARIVITHAMANI; GIRI DEV, 2016; FARRELL; ORMOND; GABLER, 2015; HAUSER; TABBA, 2001; WANG et al., 2009).

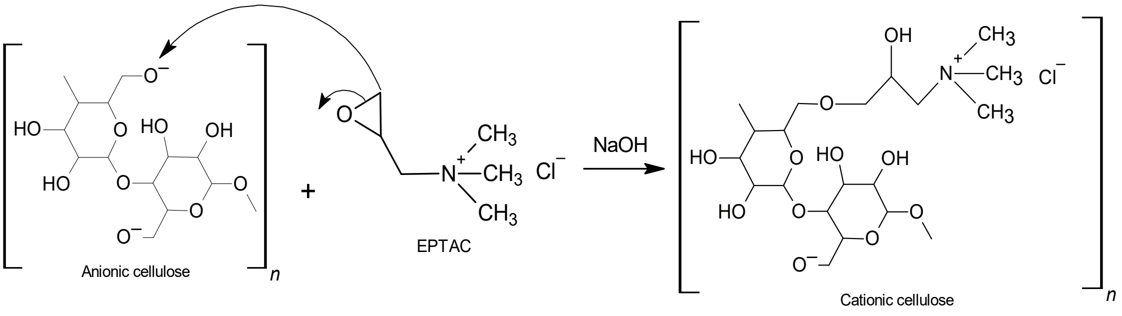
The EPTAC reacts with the primary hydroxyl group of ionized cellulose under alkaline conditions to form the cationized fiber. The reaction mechanism is presented in Scheme 2 (ARIVITHAMANI; GIRI DEV, 2016). Each repeating unit of the cellulose molecule has one primary and two secondary hydroxyl groups, which can undergo chemical reactions. However, the primary hydroxyl groups are more accessible and reactive than the secondary groups (WAKELYN et al., 2006).

CHPTAC is a moderately nontoxic chemical reagent, but to proceed with cellulose reaction, it must be firstly converted into EPTAC, which presents carcinogen properties (ROY CHOUDHURY, 2014). Therefore, to minimize exposure, EPTAC solutions should never be handled or transported. Cationization processes should be designed to introduce CHPTAC and the alkali required for EPTAC conversion, followed by its subsequent reaction with the cellulose. The overall cationization process should be designed in a quantity that EPTAC is consumed to the maximum by fiber, to ensure minimal EPTAC release to the environment (FARRELL; HAUSER, 2013).

Scheme 1 – Formation of anionic cellulose and conversion from CHPTAC to EPTAC.



Scheme 2 – Cellulose reaction with EPTAC in an alkaline solution.



2.1.1.2 *Poly diallyldimethylammonium chloride (PDDACl)*

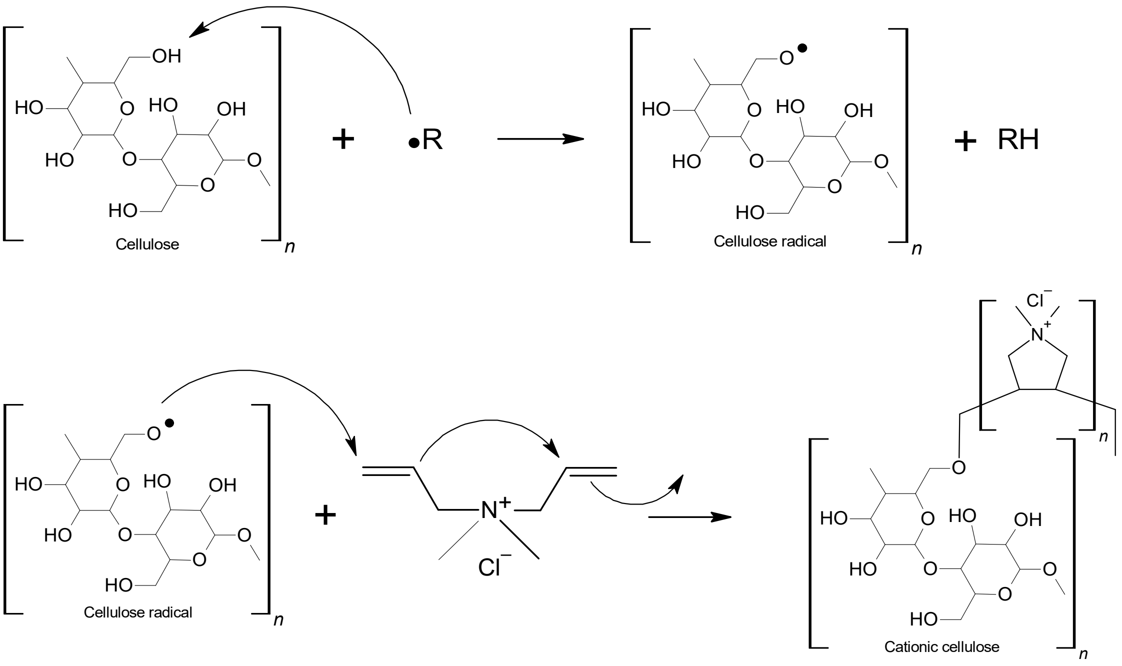
Poly diallyldimethylammonium chloride (PDDACl), usually abbreviated as PDDA, PDADMAC and Poly-DADMAC is a well-known cationic polyelectrolyte. Research interest for PDDACl is related to applications in different fields, such as papermaking, wastewater treatment, mineral processing, food and medical industry (ZHANG et al., 2003). It does not have the same acceptance as CHPTAC for cationization of fibers, but recent research indicates that this polyelectrolyte has potential as an environmentally-safe cationic agent (BESSA et al.,

2019; HELMY; HAUSER; EL-SHAFEI, 2017; JAREANSIN; SUKAAM; KUSUKTHAM, 2019; KIM et al., 2016; OLIVEIRA et al., 2017).

PDDACl is considered as an environmentally friendly and low-cost polyelectrolyte (LIU et al., 2018; WANG et al., 2013). It is the first polymer approved by United States Food and Drug Administration for use in potable water treatment (HELMY; HAUSER; EL-SHAFEI, 2017). Environmental and human health studies destined for the United States Environmental Protection Agency testified that diallyldimethylammonium chloride (DADMAC), the monomer of PDDACl, has low toxicity and is readily biodegradable (DADMAC HPV COMMITTEE, 2004). This report was issued for the High Production Volume Challenge Program, which provides hazard information for the chemicals produced or imported into the United States of America (BISHOP et al., 2012).

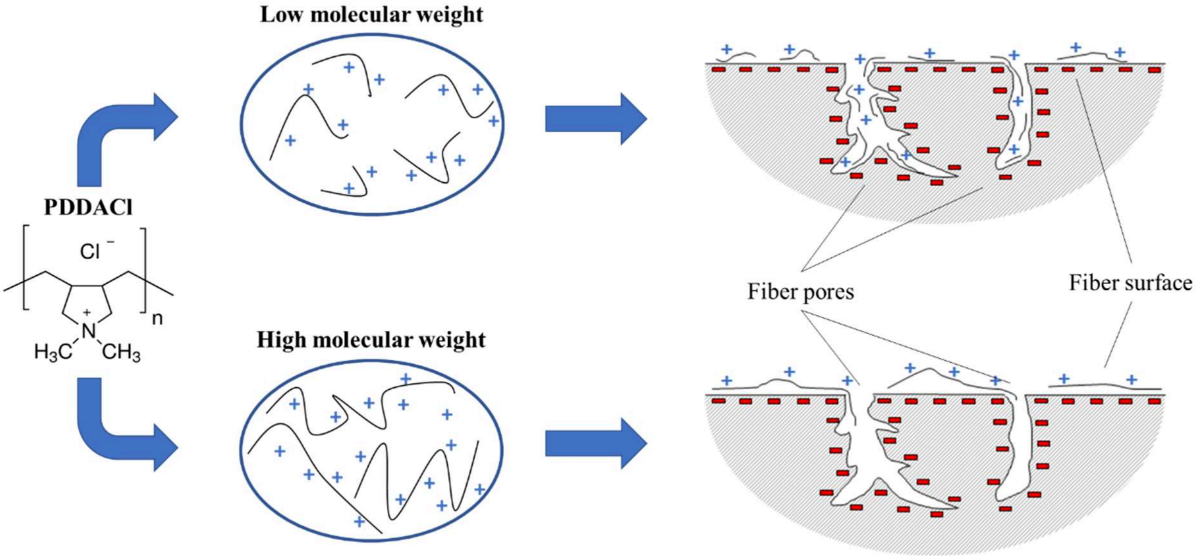
The cellulose mechanism for cationization with DADMAC was published by Jareansin et al. (2019). Potassium persulfate was used as an initiator to create cellulose radicals. The initiator creates a radical in the hydroxyl bonded to the primary carbon of cellulose. The cationization mechanism is explained in Scheme 3. The initiator has the same function as the epoxy group in the CHPTAC cationization process shown in Scheme 1. The formation of PDDACl and binding to cellulose occurs from the interaction with hydroxyl radicals.

Scheme 3 – Mechanism of cellulose reaction with diallyldimethylammonium chloride.



Considering the polymer structure of PDDACl, its fiber penetration is limited by the size of the molecule. Thus, the degree of polymerization is a particularly important property for determining the effectiveness of cellulose cationization. Zhang et al. (2016) used PDDACl with different molecular weights for the accessibility evaluation of cellulose fiber charges. Fiber charges strongly depended on the molecular weight of the polyelectrolyte. A higher fiber charge was detected using PDDACl with low molecular weight. However, the charge was nearly unchanged when the molecular weight varied from 100 to 600 kg.mol^{-1}. This suggests that above 100 kg.mol^{-1}, PDDACl is not filled into the cellulose pores and the interaction is restricted to the external surface, as illustrated in Figure 2.

Figure 2 – Schematic illustration of surface deposition and pores penetration by high and low molecular weight PDDACl.

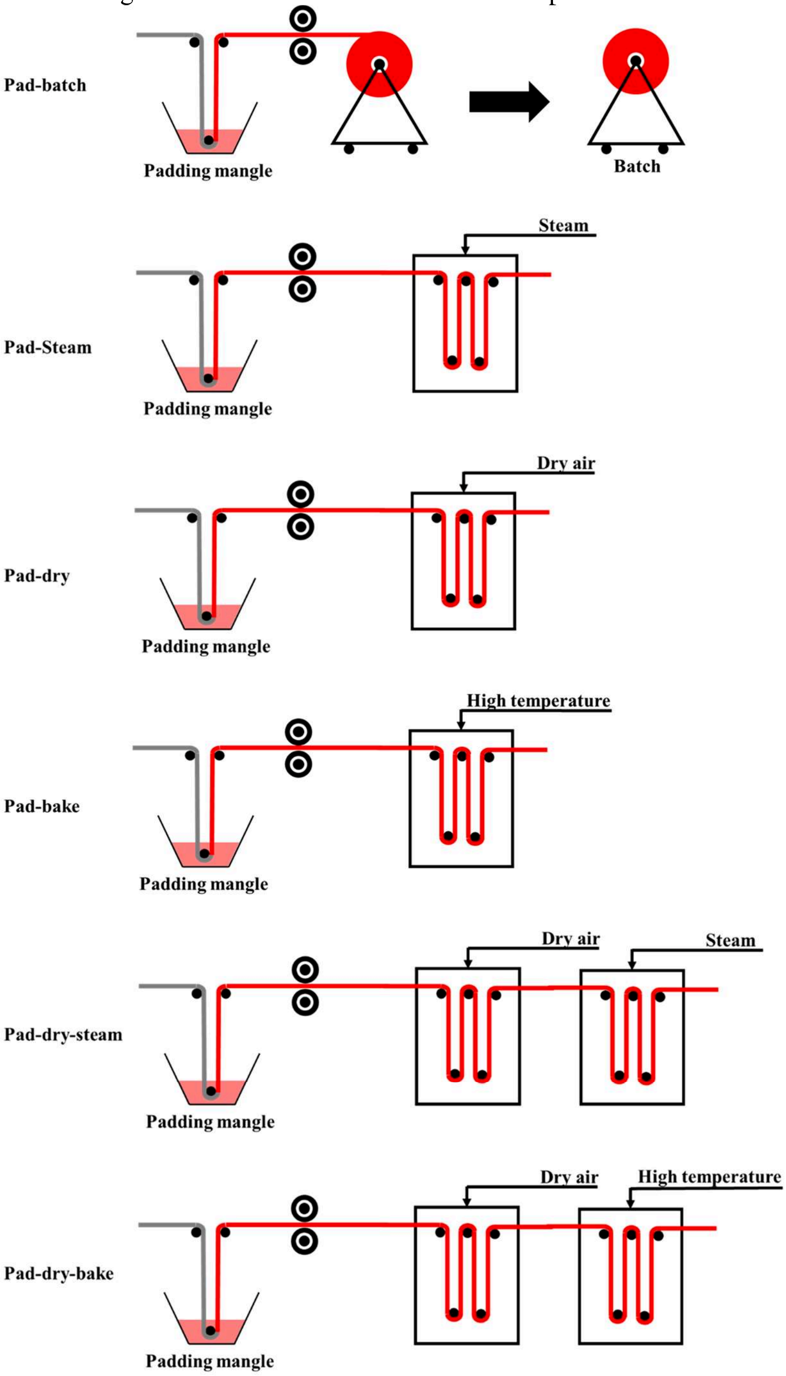


Source: the author.

2.1.2 Methods for fiber cationization

The method used by each author for the pretreatment of cotton is available in Table 2. Among them, exhaustion is a discontinuous process considered the conventional system of dyeing as most of the industries follow this process (ARIVITHAMANI; GIRI DEV, 2018). However, continuous and semi-continuous processes are used mainly in the treatment before the dyeing. Therefore, various processes are used for the cationization of fibers. A brief explanation of each method is also given in Figure 3. Pad-batch is a sequence of operations involving padding and batching without intermediate drying. The padded fabric is rolled in a batch, wrapped by plastic sheets, and stored with slow rotation to allow the dye to fix at room temperature. In pad-steam, the fabric is padded and steamed for fixation of the chemicals. Pad-dry is like the pad-steam method, the difference consists in using dry air instead of steam. Pad-bake is like pad-dry but involves chemical fixation at high temperatures. Pad-dry-steam and pad-dry-bake, as the names suggest, are associations between pad-dry, pad-steam and pad-bake. Pad-dry-cure, also presented in Table 2, is reciprocal to the pad-dry-bake method (HASHEM; HAUSER; SMITH, 2003; MATTHEWS, 2018; ROY CHOUDHURY, 2014).

Figure 3 – Different methods used for the pretreatment of fabrics.



Source: the author.

Houshyar and Amirshahi (2002) treated cotton fabric with chitosan using five different techniques, consisting of exhaustion, pad-dry, pad-batch, pad-steam, and pad-dry-steam methods. The exhaustion method was carried out in a laboratory dyeing machine at 60 °C during 5 min. The pad-dry method was carried out by padding with 110 % pick up and dried at 150 °C for 3 min. In the pad-batch method, cotton was padded with 110 % pick up and batched for 30 min, while in the pad-steam method samples were padded with 110 % pickup and steamed during 30 min at 110 °C. The pad-dry-steam method padded samples with 110 % pick up, dried at 150 °C for 3 min and steamed at 100 °C for 30 min. The authors concluded that the pad-dry method ensured the highest dye uptake with a slight reduction of light and wash fastness.

Hashem (2006) developed a one-stage process of scouring, bleaching or desizing with cationization. CHPTAC was the cationic agent used. Three methods were used: exhaustion, cold pad-batch and pad-steam. The authors have found that the cationic agent was compatible with the enzymatic desizing agent diastase. However, the CHPTAC was incompatible with the chemical desizing agents, specifically ammonium persulfate and potassium peroxydiphosphate. Besides, CHPTAC was also incompatible with hydrogen peroxide. The combination of CHPTAC and hydrogen peroxide hindered the effect of cationization and bleaching. However, cationization and scouring with NaOH was performed without incompatibility.

Arivithamani et al. (2014) fixed KH into cotton fabric by an esterification reaction. In a round-bottom flask was prepared a solution with cotton, KH, and toluene as solvent. The solution was heated to boiling. During this process, the esterification reaction takes place, water was eliminated from the reaction and it was evaporated from the flask. To avoid a reverse esterification reaction, the evaporated water continuously removed from the process was condensed and collected. The process ended when it stopped the formation of water.

Ma et al. (2016) cationized cotton fabric with betaine through the pad-dry-bake method. It was prepared a solution containing 8 wt% of anhydrous betaine, hydrochloric acid (1 mol of betaine per mol of acid) and 5 wt% of dicyandiamide. The fabric was dipped in the solution at a material to liquor ratio of 1:10 and padded to 90 % pickup. Then the fabrics were dried at 80 °C during 3 min and baked at 150 °C during 40 s. The cationic treatment improved the fixation of the dye, maintaining the washing and rubbing fastness at satisfactory levels.

According to some authors (FU et al., 2013; MANDAL, 2017), among the higher temperature application methods, the cold pad-batch is possibly the most efficient method to provide uniform cationization of cotton because heat may cause the migration of reactants, which results in non-uniform cationization

2.1.3 Cationization process variables

The cationization variables must be optimized for achieving higher dye fixation. Understanding all the parameters involved, the treatment can be evaluated comprehensively. Table 3 contains a list and range of values for the variables used in various cationization studies carried out by the exhaustion method.

Table 3 – List of variables used for cotton cationization, by exhaustion method, used by different authors: cationic agent (CA), CA and NaOH dosage, temperature (T), time and material-to-liquor ratio (MTLR).

CA	**CA dosage**	**NaOH ($g.L^{-1}$)**	**T (°C)**	**Time (min)**	**MTLR**	**Ref.**[c]
PDDACl, Chitosan	5 %owf[a]	-	30-70	10-40	1:200	(a)
Chitosan	0.5-2.0 %owf	15	50	30	NA[b]	(b)
DMC	10-60 $g.L^{-1}$	-	60	40	1:20	(c)
CHPTAC	5-40 $g.L^{-1}$	1-4	50-90	5-20	1:20	(d)
CHPTAC	80 $g.L^{-1}$	24	80	30	1:20	(e)

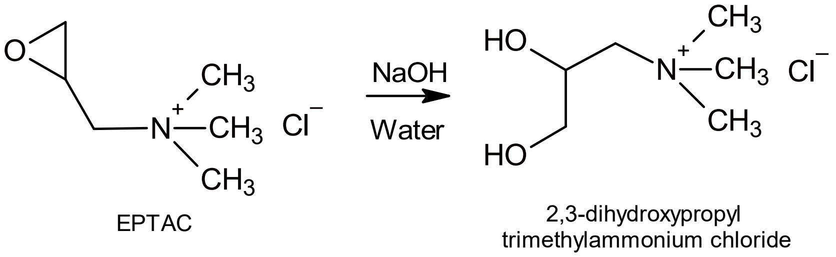
Source: the author.

Note: [a] Expressed in percentage over weight of fiber, [b] data not available, [c] reference: (a) Oliveira et al. (2017), (b) Chatha et al. (2016), (c) Ma et al. (2020),(d) Ma et al. (2017), (e) Arivithamani and Dev (2017).

Although some authors prefer to represent the concentration of the cationic agent in percentage over weight of fiber (owf), according to Table 3 the concentration evaluated varies from 5 to 80 grams per liter of solution. It was observed a strong correlation between cationic agent dosage and reactive dye fixation. An addition of a high concentration of cationic agent could achieve a higher cationization degree of cotton, as well as high dye exhaustion and the percentage of the total dye fixed on the cationized cotton (CHATHA et al., 2016; MA et al., 2017).

The alkali concentration is a parameter that needs to be optimized for the cationization process. For example, a low mole ratio of NaOH to CHPTAC result in a low formation of EPTAC, consequently, it decreases the fiber cationization. On the contrary, an increase in the mole ratio led to the hydrolyzed form of EPTAC, a diol namely as 2,3-dihydroxypropyl trimethylammonium chloride, as shown in Scheme 4. The diol form is stable, therefore it does not react with the cotton fabrics and results as an effluent at the end of the cationization process (FARRELL; HAUSER, 2013; HAUSER; TABBA, 2001).

Scheme 4 – Hydrolysis mechanism for EPTAC.



Ma et al. (2017) studied the effect of NaOH concentration in the fixation of Reactive Red 195 dye on cationic cotton. When the concentration of NaOH was 1, 2, 3, and 4 g.L^{-1}, the dye fixation was 45.94, 70.53, 96.74 and 96.18 %, respectively. The fixation of the reactive dye did not increase when the NaOH dosage rose from 3 to 4 g.L^{-1}. Therefore, they found 3 g.L^{-1} as the optimal concentration for NaOH. According to Hashem, Hauser and Smith (2003), the optimal NaOH:CHPTAC molar ratio for the cationization process is 1.8.

According to Table 3, the temperature used in cationization by the exhaustion method can vary from 30 to 90 ºC. Cationization of cotton by CHPTAC is an etherification reaction, dehydration of an alcohol group to form ether, so that increasing the temperature is beneficial for the retention of cationic groups on cotton (MA et al., 2017).

The material-to-liquor ratio was 1:20, except for the research developed by Oliveira et al. (2017), which used a considerably higher amount of liquor. According to Mandal (2017), the nitrogen fixation efficiency tends to decrease with increasing liquor ratio because the hydrolysis reaction of the cationic agent is more favorable with higher amount of water. Besides, a higher bath ratio rises the energy costs for temperature elevation and increases the amount of effluent.

Exhaustion is a discontinuous process for fiber cationization. However, there are also some continuous or semi-continuous processes. For example, Hauser and Tabba (2001) used a foulard to pad cotton fabric with a solution consisting of 50 g.L^{-1} of a 65 % CHPTAC solution and 36 g.L^{-1} of a 50 % sodium hydroxide solution, at 100 % wet pick-up. Wang and Lewis (2002) used a pad–bake process with 50 g.L^{-1} AAHTAPC, 30 g.L^{-1} sodium hydroxide, 90 % wet pick-up and baked at 125 °C for 6 min.

Nakpathom et al. (2017) used CHPTAC to prepare cationic cotton and dyed using purple corncob. The concentration of CHPTAC varied between 5-150 g.L^{-1} and NaOH was added to achieve the molar ratio of 1:2.6 (CHPTAC:NaOH). The fabric samples were padded to 100 % pick up. The addition of NaOH occurred immediately before proceeding with the padding bath to avoid the hydrolysis of the CHPTAC. Then, the cotton fabric was neutralized using 1.5 g.L^{-1} of acetic acid during 30 min, rinsed with water and air-dried. The authors obtained optimum K/S values for cotton pretreated with 125 g.L^{-1} CHPTAC and dyed at 100°C and pH 9, during 30 min.

2.1.4 Characterization of cationic fiber

As exemplified in the mechanism described in Scheme 1 – Scheme 3, the cationization process occurs from the incorporation of cationic elements to the fiber, mainly quaternary ammonium compounds, which positively charge the surface of the fiber. Thus, a good indicator of the efficiency of the cationization process is the nitrogen content incorporated in the fiber. Table 4 contains the percentage of nitrogen in cationic cotton researched by some authors, using different methods and reagents concentrations. The nitrogen content analyses were performed using an elemental analyzer by Kanik and Hauser (2002) and Fu et al. (2013), while Wang et al. (2009), Hashem (2006) and Ma et al. (2017) measured with the Kjeldahl method.

For reference purposes, the percentage of nitrogen in a non-cationized sample is 0.01 % (KANIK; HAUSER, 2002). According to Table 4, the percentage of nitrogen increased up to 0.65 %, depending on the variables and the process used. It is observed a strong and positive dependence on the concentration of CHPTAC. Considering that is the nitrogen incorporated in the fiber that guarantees the affinity with anionic dyes, the bigger its quantity the better the fixation to the fiber occurs.

Some authors characterized the nitrogen content using X-ray photoelectronic spectroscopy (XPS) (LIU; YAO, 2011; OLIVEIRA et al., 2017). The analysis indicated that the atomic percentage of nitrogen for a cationic fabric composed of 50 % polyester and 50 % cotton treated with PDDACl (concentration of 5 %owf and temperature of 50 ºC) was 3.7 %. Moreover, XPS analysis of cotton fabric cationized by epichlorohydrin and thiourea revealed a nitrogen atomic percentage of 3.35 %. For both cases, the nitrogen content in the untreated sample was null.

Kim et al. (2016) performed a qualitative analysis to validate the deposition of PDDACl and chitosan. The authors assessed the color of dyed fabrics with Coomassie Brilliant Blue dye. The color strength of the fibers regards the number of polyelectrolytes attached to the fibers. Therefore, the stronger color after dyeing means more affinity to the fiber surface. Coomassie Brilliant Blue dye is often used for protein detection due to its anionic character and affinity with protonated amino groups (GEORGIOU et al., 2008). The stronger color was obtained for samples pretreated with cationic agents PDDACl and chitosan.

Table 4 – Percentage of nitrogen (N) in cotton cationized with CHPTAC obtained by different processes and authors.

CA ($g.L^{-1}$)	**NaOH ($g.L^{-1}$)**	**Process**	**N (%wt)**	**Reference**
Untreated	-	-	0.01	(KANIK; HAUSER, 2002)
50	31.0	Pad-batch	0.12	(KANIK; HAUSER, 2002)
75	46.5		0.17	
100	62.0		0.23	
30	3	Exhaustion	0.0839	(MA et al., 2017)
100	40	Exhaustion	0.21	(HASHEM, 2006)
		Pad-steam	0.23	
		Pad-batch	0.22	
8.0 %owb[a]	1.8 %owb[a]	Pad-bake	0.65	(WANG et al., 2009)
100	60	Pad-batch	0.22	(FU et al., 2013)
150	90		0.26	
200	120		0.3	

Source: the author.
Note: [a] Expressed as a percentage over weight of bath.

According to the conventional cationization procedure proposed by Hashem (2006), the exhaustion, pad-steam and pad-batch methods presented a small difference in the nitrogen quantity fixed, although the pad-steam process obtained the best result.

Fourier-transform infrared spectroscopy (FTIR) can also confirm the fixation of the cationic agent into cellulose. A peak between 1000-1400 cm^{-1} may correspond to the presence of quaternary ammonium groups, while a peak at 1200 cm^{-1} may correspond to C-N stretching vibration (ARIVITHAMANI; DEV, 2017; ZHANG et al., 2015).

As cationization induces a positive charge at the surface of cotton, due to the presence of a quaternary ammonium group, it is expected an increment in the zeta potential of cationic cotton. As observed by Arivithamani and Giri Dev (2017b), the cotton fabric showed a zeta potential of -6 mV and -4 mV at pH 7 and 6, whereas the cationic cotton fabric showed a zeta potential of +1.3 mV and +2.2 mV for a pH of 7 and 6 respectively. Zhang et al. (2015) obtained similar results: the zeta potential of modified cellulose was +13.8 mV, in contrast to -5.2 mV that corresponds to original cellulose.

The surface morphology of cationic cotton fiber was evaluated through scanning electron microscopy. Based on the micrographs, the surface of the cationic fibers was slightly rougher compared with that of the non-cationic, but the cationization process almost not influenced the structure of the cotton so that it was considered suitable for dyeing application (MA et al., 2017; WANG et al., 2009).

During the cationization, the intermolecular interactions between the chains are affected due to the penetration of the polyelectrolyte molecules. This is responsible for a slight change of the thermal profiles of cationic fabrics (ARIVITHAMANI; GIRI DEV, 2016). A thermogravimetric analysis made by Ma et al. (2017) indicated that the stability of the non-cationic cotton was slightly better, a significant weight loss happened at 320 °C for non-cationic cotton, against 305 °C for the treated sample. Thermal profiles from Arivithamani and Giri Dev (2016) indicated a significant weight loss of around 350 °C 390 °C for cationic and non-cationic cotton, respectively.

X-ray diffraction analysis was used to study the effect of cationization on crystal structural changes. The results showed that the X-ray spectra of the cotton before and after cationization are almost equal. It demonstrated that cationization occurred just on the surface of the fiber; it did not affect its crystal structure (WANG et al., 2009).

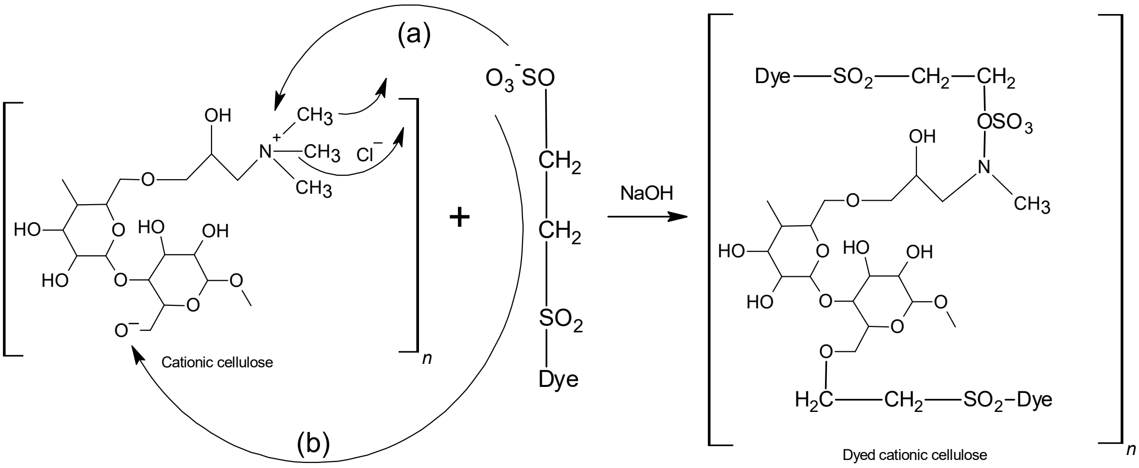
2.2 DYEING OF CATIONIC FIBERS

Cationization of cotton has been widely researched with the use of direct and reactive dyes because they have a high affinity to materials with positive surface charges. For dyeing with reactive dyes, it can not only increase the dye uptake but also eliminate the use of salt. (FU et al., 2013).

The cationic cotton fabric contains cationic sites called quaternary ammonium group, which creates a strong positive potential in the dyebath. Thus, anionic dye molecules move from the dyebath solution to the cationic cotton fabric by ionic attraction (ARIVITHAMANI; GIRI DEV, 2018).

As an example, Scheme 5 shows the reaction mechanism between cationic cotton and a vinyl sulphone based reactive dye (ARIVITHAMANI; GIRI DEV, 2017b). According to the scheme, the dye molecule can bind to the cellulose in two ways. In (a), the reactive group interacts with the ammonium quaternary and causes the breakdown of two N-CH_3 bonds. In (b) is presented the conventional cellulose dyeing mechanism, in which the reactive group reacts with the ionized oxygen of the primary carbon of the cellulose. Primary hydroxyl groups are more accessible and reactive than secondary groups (WAKELYN et al., 2006).

Scheme 5 – Reaction mechanism between cationic cellulose and a vinyl sulphone based reactive dye (a). In (b) is shown the conventional dyeing.



Wang and Lewis (2002) investigated the use of salt in a dyebath containing a commercial anionic reactive dye (Procion Red H-E3B) and cationic cotton. The exhaustion was almost complete in the absence of salt, but the exhaustion drops to 94.6 % after adding 20 $g.L^{-1}$ of sodium sulfate. This unfavorable effect occurs because the sulfate anions have a significant affinity for cationic cellulose, so they compete with dye anions for the quaternary sites in the modified fiber.

Alkalis are often used to obtain the alkaline medium because a higher pH increases the exhaustion and fixation (reaction) of the dye to the fiber. Therefore, the use of Na_2CO_3 is very common in conventional dyeing processes. Fu et al. (2013) investigated the influence of Na_2CO_3 in the dyeing process with cationic fabrics. With the increase of Na_2CO_3 concentration, both K/S and dye uptake of non-cationic cotton increased gradually from 5 to 20 $g.L^{-1}$. The results also revealed that, for cationic cotton fabrics, eliminating the use of Na_2CO_3 decreased both the K/S and dye uptake, but increasing the concentration did not influence the K/S and dye uptake values significantly. Thus, 5 $g.L^{-1}$ Na_2CO_3 appears to be an effective concentration for dyeing cationic cotton fabrics.

Various properties of dyed fibers are presented in Table 5. Through the comparison between non-cationic and cationic fiber, it is observed that the cationization increased the color strength values (K/S). The increase in color intensity in dyed fabrics occurred due to the greater interaction between the dye and the cationic fiber, resulting in higher percentages of exhaustion and fixation. Exhaustion (E) refers to the amount of dye migrating from the bath to the fiber surface. The fixation (F) is related to strong dye-fiber interactions, measured by the color difference of the fabric before and after soaping. It is observed in Table 5 that the cationization increased both percentages of exhaustion and dye fixation.

Washing and rubbing fastness area measured on a scale of 1 to 5, where 5 represents the maximum fastness (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2010, 2016), that is, no color changes were detected after washing or rubbing (dry and wet). In the case of light fastness, the scale ranges from 1 to 7, which 7 being the maximum fastness, according to ISO 105 B2 (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2013).

There was little interference of cationization in the fastness properties of cotton dyed with reactive dyes. For washing fastness, a slight improvement was observed for four dyes: Sumifix Supra Yellow 3RF, Reactive Gold Yellow B-3RD, Reactive Blue 19 and Reactive Yellow 145 (LIU; YAO, 2011; WANG; LEWIS, 2002; WANG et al., 2009). Cationization altered light fastness for Reactive Yellow 145, Reactive Blue 19 and Reactive Red 195 (MA et al., 2020; WANG et al., 2009).

The dry rubbing fastness slightly increased for cationic cotton dyed with Reactive Yellow 145 (WANG et al., 2009) and decreased with Reactive Blue B-RV dyes (LIU; YAO, 2011). Wet rubbing fastness increased for cationic cotton dyed with Reactive Gold Yellow B-3RD (LIU; YAO, 2011). However, a slight loss of wet rubbing fastness occurred for cationic fabrics dyed with Reactive Blue B-RV, Reactive Red 195 and Reactive Yellow 145 (LIU; YAO, 2011; MA et al., 2020; WANG et al., 2009). The loss may be related to the hydrophilic character of the cationic agent. In the wet rubbing fastness, the water acts as a lubricant and removes the cationic sites at the surface of the fabric (NAIKWADE et al., 2017).

The decrease in the fastness properties is also related to the tendency to the ring dyeing in cationic fabrics. Due to strong attraction forces, both fixed and unfixed dye can be present on the surface of the cationic fiber. This effect is more evident when dyeing deep shade fabrics (NAIKWADE et al., 2017). According to Wang and Lewis (2002), ring dyeing can be decreased with anionic surfactants added to the dyebath. The anionic surfactants interact with surface cationic sites so that the dye would penetrate deeper inside the fiber.

Considerable improvements in washing fastness were observed using direct dyes with cationic cotton, increasing from 2 to 4-5 for both dyes tested (HAUSER; TABBA, 2001). The improvement also occurred for light fastness in cationic fabric dyed with Direct Red 80 dye. The rubbing fastness, however, did not change with cationization.

Cationization is also effective for other natural cellulosic fibers. Tests made by Naikwade et al. (2017) resulted in improved dye exhaustion and fixation on ramie fiber, with no loss of fastness. Cationic treatment improved performance, with 89 % and 98 % for exhaustion and fixation, respectively. Besides, K/S values were higher for cationic fibers, with good color uniformity and similar for the untreated fiber.

Table 5 – Comparisons of color strength (K/S), exhaustion (E) and dye fixation (F), washing, light and rubbing fastness from different research papers.

(to be continued)

Dye[a]	Fiber+CA[b]	K/S	E (%)	F (%)	Fastness				Ref.[c]
					Wash	Light	Rubbing		
							Dry	Wet	
Procion Red H-E3B	CO+AAHTAPC	20	99.9	93.0	4-5	5	NA	NA	(a)
2 %owf	CO	12	86.3	84.4	4-5	5	NA	NA	(a)
Sumifix Supra Yellow 3RF	CO+AAHTAPC	NA	99.7	94.2	4-5	5	NA	NA	(a)
2 %owf	CO	NA	97.1	82.7	4	5	NA	NA	(a)
Reactive Gold Yellow B-3RD	CO+EP/TH	8.94	NA	NA	5	NA	4	4	(b)
2 %owf	CO	7.86	NA	NA	4-5	NA	4	3-4	(b)
Reactive Blue B-RV	CO+EP/TH	8.37	NA	NA	5	NA	4	3	(b)
2 %owf	CO	6.88	NA	NA	5	NA	3-4	3-4	(b)
Reactive Blue 19	CO+DMC	11.5	99.9	96.8	4	7	4-5	4	(c)
3 %owf	CO	9.7	81.1	67.2	4	6-7	4-5	4	(c)
Reactive Red 195	CO+DMC	11.3	99.7	97.3	4	3-4	4	3	(c)
2 %owf	CO	8.5	91.0	79.2	4	2-3	4	3-4	(c)
Reactive Blue 19	CO+CHPTAC	9.1	NA	84	4	5-6	4	3-4	(d)
3 %owf	CO	7.9	NA	80	3-4	5-6	4	3-4	(d)

Table 5 – Comparisons of color strength (K/S), exhaustion (E) and dye fixation (F), washing, light and rubbing fastness from different research papers.

(conclusion)

Dye[a]	**Fiber+CA**[b]	**K/S**	**E (%)**	**F (%)**	**Fastness**				**Ref.**[c]
					Wash	**Light**	**Rubbing**		
							Dry	**Wet**	
Reactive Yellow 145	CO+CHPTAC	4.5	NA	85	4-5	4-5	4-5	3-4	(d)
1 %owf	CO	4	NA	81	4	4	4	4	(d)
Direct Blue 78	CO+CHPTAC	13.99	NA	NA	4-5	4-5	NA	5	(e)
2 %owf	CO	8.67	NA	NA	2	4-5	NA	5	(e)
Direct Red 80	CO+CHPTAC	20.11	NA	NA	4-5	4	NA	5	(e)
2 %owf	CO	14.16	NA	NA	2	2	NA	5	(e)

Source: the author.

Note: [a] The percentage below refers to the quantity of each dye, over weight of fiber. [b] In cases where the cationic agent (CA) is not present, it means that the fiber was not cationic. [c] References: (a) Wang and Lewis (2002), (b) Liu and Yao (2011), (c) Ma et al. (2020), (d) Wang et al. (2009) and (e) Hauser and Tabba (2001).

2.3 APPLICATION OF CATIONIC AGENTS IN FUNCTIONAL FABRICS

The application of cationic agents is not restricted to the interaction with dyes. Cationization can also be used to increase functional properties of the fabric, such as antimicrobial activity. Other applications are related to UV protection, water repellency and production of conductive fabrics.

2.3.1 Antimicrobial activity

The textile substrates are considered as possible vectors of transmission of diseases (PACHIAYAPPAN; PRAKASH; KUMAR, 2020). Cellulosic fibers have a high retain moisture rate, which creates an environment that enables microorganism growth onto fabric (ALY et al., 2007). For this reason, antimicrobial behavior can be an important property desired mainly for textiles applied in the health area (KIM et al., 2016). Quaternary ammonium compounds, often used for cationization, are also widely used in antimicrobial applications (LIU et al., 2014). In general, they are bacteriostatic, fungistatic, at very low concentrations (<500 µg/ml), with Gram-positive bacteria being particularly sensitive (<10 µg/ml) (MCDONNELL, 2017).

Chitosan has been studied by many researchers as a natural polymer for antimicrobial treatment of cellulose fibers (ALY et al., 2007; EL-SHAFEI et al., 2008; KIM et al., 2016; RAHMAN BHUIYAN et al., 2017; REHAN et al., 2017). Chitosan is considered a potential antimicrobial substance and has very interesting properties such as good biocompatibility, biodegradability, non-toxicity, and availability in abundance (QIN; LI; GUO, 2020).

Kim et al. (2016) assessed the antimicrobial activity of cotton pretreated with chitosan and PDDACl by the layer-by-layer deposition technique. The gram-negative bacteria *Escherichia coli* and gram-positive bacteria *Staphylococcus aureus* were tested. PDDACl on cotton fibers presented an excellent effect on the inhibition rate of microorganisms growth (almost 100 %) and the inhibition rate of chitosan was close to 50 %. The combination of PDDACl and chitosan layers presented a synergistic effect and enhanced antimicrobial activity.

Farrell et al. (2017) compared fabrics treated with different hydrophobic alkyl quaternary ammonium compounds, reported in Table 2. All pretreatment resulted in antimicrobial activity. The control sample, nontreated cotton, presented an increment in inoculum concentration after 24 hours. All pretreatment resulted in a 99 % reduction in inoculum concentration, except for pretreatment with CHPTAC, which reduced 89 %.

Rehan et al. (2017) prepared antimicrobial cotton gauze by reacting it with CHPTAC and impregnating silver nanoparticles. The pretreated samples presented an inhibition effect above 95 %. The results also indicated that the pretreatment with CHPTAC (without silver nanoparticles) resulted in 73 % and 67 % inhibition effect on samples, respectively for *Escherichia coli* and *Staphylococcus aureus*. A similar methodology was proposed by Shateri Khalil-Abad et al. (2009), who used CHPTAC to enhance the uptake of silver nanoparticles. It was observed that the silver content on cationic cotton was up to three times higher than the conventional cotton.

2.3.2 Other functional properties

Kamal Alebeid and Zhao (2015) used CHPTAC and TiO_2 nanoparticles to prepare functional fabrics with ultraviolet (UV) protection. The CHPTAC can increase the interaction with TiO_2, which has negative charges. The pretreated fabrics presented enhanced UV protection. The fabrics were dyed using Reactive Yellow 176. The K/S of the pretreated and dyed samples did not change significantly. These results may be related to the opposite effect of CHPTAC and TiO_2. While CHPTAC increases the charge of the fabric, the TiO_2 nanoparticles tend to decrease due to the anionic character.

Sahito et al. (2015) investigated cationization as a way to increase the conductivity of electronic textiles (e-textiles). Bovine serum albumin (BSA) was used as a cationic agent. The cationic cotton was then treated with graphene oxide to increase conductivity. The cationization increased 67 % of the graphene oxide uptake in the cotton fabric.

Abd El-Hady et al. (2020) functionalized cotton fabric for hydrophobic and UV protective properties. The fabrics were pretreated with a solution containing 20 $g.L^{-1}$ of PDDACl, using the pad-dry-cure method. Then the cationic fabrics were immersed in an anionic solution containing ZnO/SiO_2 nanocomposites. The proposed method successfully increased the UV protection. Besides, the coated surface became hydrophobic due to the deposition of ZnO/SiO_2 nanocomposites.

In a similar work, Farouk et al. (2013) proposed a method to prepare multifunctional fabrics. The fabric was prior treated with cationic agents CHPTAC and DADMAC. The cationic fabrics were treated with TiO_2 and SiO_2 nanoparticles. The pretreated fabrics presented antimicrobial activity for gram-negative (*Pseudomonas aeruginosa* and *Escherichia coli)* and gram-positive bacteria (*Staphylococcus aureus* and *Bacillus subtilis*). The pretreatment with TiO_2 and SiO_2 nanoparticles enhanced the UV protection. Besides, stearic acid was coated in cotton fabric to achieve water repellency.

2.4 MARKET

There is a significant demand for cationic agents from the dyeing industry. This market is mainly controlled using CHPTAC, thanks to the advances of researchers over the years to enable the development of a reliable product in a robust process. This factor maintained the sales of CHPTAC as a popular cationic agent in the dyeing industry (ARIVITHAMANI; GIRI DEV, 2018). The popularity of the cationic agent is driven by its cost. The purchase cost of the two main cationic agents, CHPTAC and PDDACl, is shown in Table 6. The values were obtained from three random Chinese suppliers on April 3, 2020. The CHPTAC reagent had the highest average cost per solution. However, it represents a 22–28 % discount when the percentage of pure CHPTAC is considered.

Table 6 – Price of cationic reagents CHPTAC and PDDACl, obtained by three random suppliers.

Supplier	**Price range (USD dollars per ton)**	
	CHPTAC, purity: 69 %	**PDDACl, purity: 40 %**
A	\$1,500.00 – \$1,600.00	\$1,100.00 – \$1,500.00
B	\$1,200.00 – \$1,300.00	\$950.00 – \$1,200.00
C	\$1,300.00 – \$1,600.00	\$900.00 – \$1,050.00
Average (solution)	\$1,333.33 – \$1,500.00	\$983.33 – 1,250.00
Average (pure reagent)	\$1,932.36 – \$2,246.38	\$2,458.32 – \$3,125.00

Source: the author.

The market for cationic cotton has seen a resurgence in industrial interest because of the rise in the cost of reactive dyes and the push for more economical and sustainable cotton coloration processes (FARRELL; ORMOND; GABLER, 2015). Cationic cotton attracts attention in niche markets because it improves the K/S using the same amount of dye and produces less effluent (ARIVITHAMANI; GIRI DEV, 2016; DONG et al., 2020). Cotton Incorporated surveyed the main cationic cotton suppliers (COTTON INCORPORATED, 2018). Cotton Incorporated is a not-for-profit company that provides resources to help companies develop cotton products. The list is presented in Table 7. The major players in the market are in China and the USA.

Table 7 – List of cationic cotton suppliers.

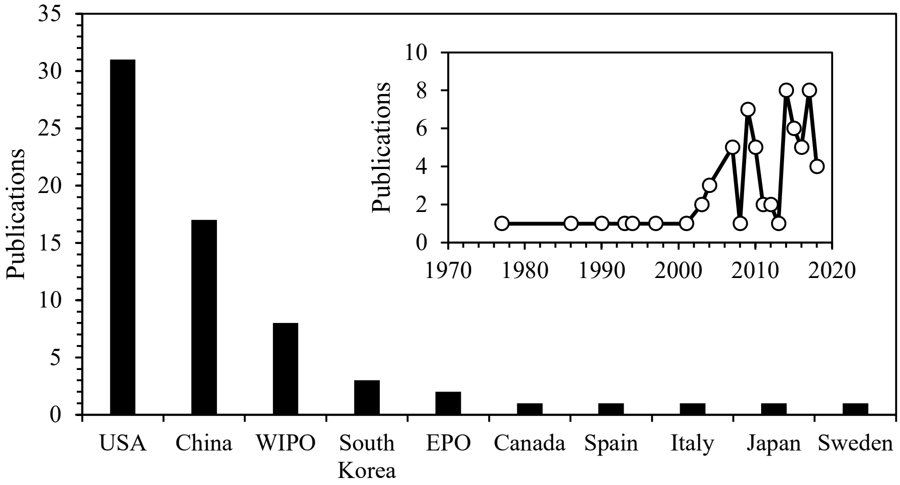
Company	**Category**	**Country**
Bros Eastern Co., Ltd	Fibers and yarns	China
Hill Spinning Mill		USA
Huafu Fashion Co., Ltd.		China
Tintoria Piana U.S., Inc.		USA
Colorzen Inc.		USA
Jiangyin Hengliang Textile Co., Ltd.	Knit	China
Sj Textile Limited		Vietnam
Textil Oceano		Peru
Thai Sin Dee Trading Co., Ltd.		Thailand
Rich Dragon Group International Ltd.		China
Well Dyeing Factory Ltd.		China
G Tech Material Co., Ltd.		Thailand
Cone Denim	Woven	USA
Inman Mills		USA
Kipaş Mensucat A.Ş		Turkey
Lu Thai Textile Co., Limited		China
Nien Hsing Textile Co., Ltd.		Taiwan

Source: Cotton Incorporated (2018).

Driven by competition, industrial protection for cationization processes has been growing especially in the last 10 years. In Figure 4 is shown the number of patent publications available in Espacenet, searched with keywords “cationic cotton” or “cotton cationization” and “cotton” in textile classification. Espacenet is a patent database maintained by the European Patent Office that offers free access to over 110 million documents (EUROPEAN PATENT OFFICE, 2020).

The USA has 31 published patents and is the country with the most publications, followed by China with 17. Both are responsible for 73 % of the entire number of patents. The expressiveness of these countries can also be seen in the list of suppliers. According to Table 7, six companies are from China and five from USA, corresponding to 64 % of suppliers.

Figure 4 – Number of patent publications per year and country or international institution. Related to cationic cotton and cotton cationization, indexed by Espacenet database.



Source: the author.
Note: WIPO and EPO are international institutions. WIPO is the World Intellectual Property Organization and EPO is the European Patent Office.

2.5 CHALLENGES OF CATIONIZATION AND FUTURE PERSPECTIVES

According to Farrel and Hauser (2013), three main concerns hinder the expansion of cotton cationization on an industrial scale: the safety of the predominant cationization reagent CHPTAC, lack of large scale cationization demonstrations, and environmental hazards. For Arivithamani and Dev (2017), the major limitation is because cationization was commonly applied by batch processes, but most of the industries adopt the exhaustion method of dyeing. Thus, the authors propose the application of cationic agents by exhaustion technique followed by reactive dyeing. This is more like the usual practices already adopted by the industry and would enable it to use this process without modification of the existing setup.

Increasing concerns have been expressed over how the industry can adapt to this trend and still achieve energy savings (HASHEM, 2006). Cationization requires an extra pretreatment step which may lead to extra cost (AKTEK; MILLAT, 2017). In this sense, Ma et al. (2017) proposed a combinative methodology for scouring, bleaching, and cationization of cotton. All these processes are under alkaline conditions. If combined into one, alkali dosage, treatment time, consumed energy and water, and the overall cost will be greatly reduced. Cationization is shown to be incompatible with bleaching. However, good results were achieved when scouring and bleaching were first carried out in one bath, and then followed by cationization.

A great concern about industrial cationization is the nuisance odor that remains in the cationic fabric after treatment. This reduces market acceptance of the product. According to

Farrel, Ormond and Gabler (2015), when alkali and CHPTAC are mixed in solution to form the reactive EPTAC, trimethyl amine is liberated. It is presumed that trimethyl amine is already present in the commercial product and is released upon pH increase by the addition of alkali. Volatile trimethyl amine can be easily detected in the processes and is highly undesirable because of the resemblance to a dead fish odor.

The most common cationic agent faces some safety criticism, CHPTAC is currently classified as a Carcinogen Category 3, while EPTAC is classified as a Carcinogen Category 2. This classification is given by IARC (International Agency for Research on Cancer) that classifies into four groups based on the existing scientific evidence for carcinogenicity. Category 3 means that there is no evidence at present that it causes cancer in humans. Category 2 means it is probably or possibly carcinogenic to humans (INTERNATIONAL AGENCY FOR RESEARCH ON CANCER, 2015). Besides, in all CHPTAC use scenarios, the principal concern is the conversion of CHPTAC to EPTAC. EPTAC is a known genotoxic carcinogen (FARRELL; HAUSER, 2013). It is important to understand that EPTAC is an intermediate and unstable product that rapidly reacts with cotton cellulose (Scheme 1 and Scheme 2). The EPTAC not fixed to cellulose tends to hydrolyze and converts to a stable form of diol (Scheme 4). EPTAC is commercially available by the name glycidyl trimethylammonium chloride, but due to instability and safety problems, its industrial use is not recommended. To avoid safety concerns, many authors have been researched natural inputs as cationic agents, such as chitosan, ovalbumin, bovine serum albumin and keratin (ARIVITHAMANI et al., 2014; CHATHA et al., 2016; GIACOMINI; DE SOUZA; DE BARROS, 2020; IBRAHIM; EL-SAYED; AMEEN, 2010; OLIVEIRA et al., 2017; SADEGHI-KIAKHANI; SAFAPOUR, 2018; SAHITO et al., 2015).

The literature search indicates the existence of more than 800 papers related to cotton cationization, published for eight decades. Even so, some gaps remain. The number of publications has grown considerably in the last 10 years, due to the need for economical and sustainable alternatives for textile processing. The researchers focused mostly on CHPTAC reagent, but even after years of research, this reagent has not achieved global recognition in the textile industry. The cationization process still needs to be optimized, mainly to be operated at safer levels.

In the coming years, research is expected to focus on cleaner processes. In this group are included the research for sustainable cationic agents. Recent research using PDDACl indicates good process efficiency, coupled with the use of a clean reagent and large-scale supply availability. Therefore, PDDACl is considered a cationic agent promising for future research and the market.

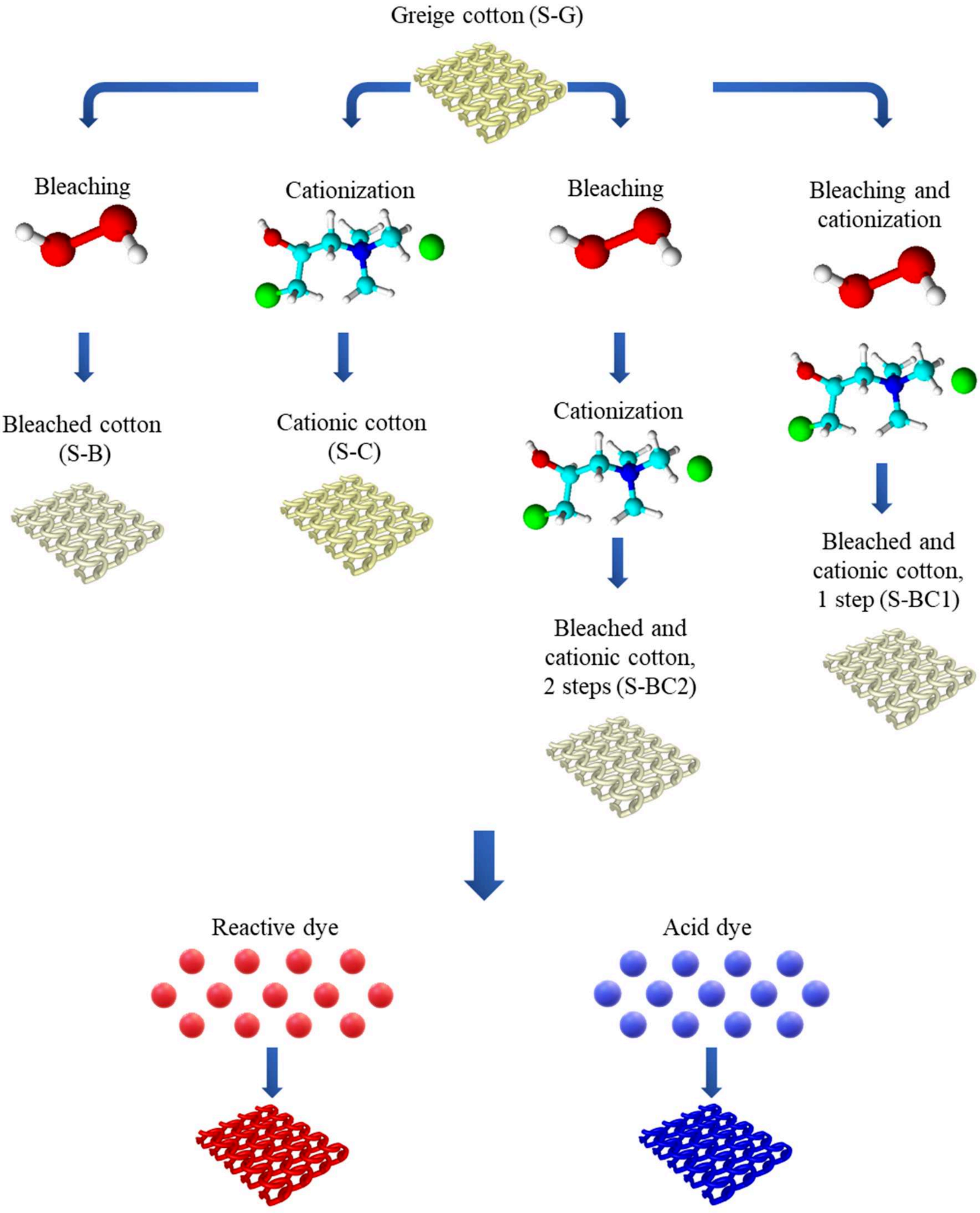
Based on the critical review of the state of the art, it is observed that there are a consistent number of publications. However, the need for a better control of the process and the costs of cationization indicate that the process still needs improvement. Therefore, this work seeks to deal with the previously mentioned challenges, through the research of novel cationic agents and evaluation of cationization in compatibility with the conventional pretreatments of cotton fabrics.

3 CATIONIZATION AS AN ALTERNATIVE METHOD TO DEVELOP NEW BRIGHT COLORS AND DECREASE THE EFFLUENT LOAD IN COTTON DYEING PROCESS

Abstract: The dyeing of cotton with reactive dye requires a high quantity of salt and water, resulting in highly saline-colored effluent loads. Cationization can be used as a chemical treatment to produce positively charged cotton, which has more affinity for uptake anionic dyes. This paper focuses on the cationization of cotton for reactive dyeing without feeding of salt and to dye cotton using acid dyes, which have no affinity for cotton cellulose's. Acid dyes have been typically used to dye natural protein (wool and silk) and synthetic polyamide (nylon) to prepare fabrics with high fastness and brightness. However, the application of acid dyes on cotton requires a previous modification of the cotton fabrics with the cationic groups. The cationic reagent used was 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC). The exhaustion method was employed for bleaching, cationization, and dyeing of greige cotton fabric. Four types of pretreatments were performed using bleaching (S-B) and cationization (S-C) separately and combinations of both in a single (S-BC1) and two separate (S-BC2) steps. The samples were dyed using commercial reactive and acid dyes. Cationic cotton enabled the reactive dyeing with the equivalent color shade as conventional dyeing, besides eliminating the need for feeding salt in the process. The cationization increased the dye exhaustion of acid dyed fabrics, obtaining new and more intense colors. However, the washing fastness needs to be improved for cationic cotton dyed with acid dyes. Cationization presented a promising method for a substantial reduction of the effluent generated and can be an important alternative to create new colors for cotton fabrics.

Keywords: Salt-free dyeing. Low-salt dyeing. Cationic dyeing. 3-chloro-2-hydroxypropyl trimethyl ammonium chloride. Reactive dye. Acid dye. Cellulosic fiber.

Graphical abstract:



3.1 INTRODUCTION

Reactive dyes are usually employed for cotton dyeing due to their excellent properties of tonality, brightness and good color fastness (MA et al., 2016; MAHAPATRA, 2016; NAIKWADE et al., 2017). However, there is a low affinity between the reactive dyes and cotton fibers, due to the anionic character present in both the dye and cellulose. Therefore, a large amount of salt (30-100 $g.L^{-1}$), such as sodium sulfate or sodium chloride, is added to the dyebath to promote cotton dyeing (CHATTOPADHYAY, 2001; WANG et al., 2009).

Salt performs a key function during the dyeing of cotton garments with reactive dyes. Sodium chloride or sodium sulfate dissociates in water to form ion pairs of sodium and chloride or sulfate. The positive charge has the capability of traveling to the fiber-water interface and changes the zeta potential, breaking the barrier to the initial dye-fiber interaction (CHATTOPADHYAY; CHAVAN; SHARMA, 2007; GIACOMINI; DE SOUZA; DE BARROS, 2020). Salts are undesirable in effluents because it is very difficult and expensive to remove from the effluent and cause pollution of the rivers and damage the biological equilibrium (AHSAN et al., 2019; SALMANIKHAS; TIZGHADAM; RASHIDI MEHRABADI, 2016). It is estimated that the separation of salt from effluents increases the dyeing cost by 10 % (ARIVITHAMANI; GIRI DEV, 2018). Even with the addition of large amounts of salt, 30–40 % of the dye is not bonded to the fiber at the end of the dyeing process, resulting in a colored and saline effluent (MA et al., 2015). Besides, multiple rinses and after-washes are employed to remove unfixed dyes from the fabrics (HAUSER; TABBA, 2001).

This paper focuses on the increasingly public pressure for more restrictive environmental legislation. Only a few places in the globe possess environmental regulation for salt discharge in effluents, often referred to as total dissolved solids (ARIVITHAMANI; GIRI DEV, 2018; CENTRAL ARIZONA SALINITY STUDY, 2006; DEY; ISLAM, 2015; ZERO DISCHARGE OF HAZARDOUS CHEMICALS PROGRAMME, 2015). Therefore, many dyeing industries choose not to remove. From the moment it is prohibited the release of salt-containing effluent into rivers, many industries will need to change their processes.

Modifying the cellulose from the cotton fiber is a route to avoid dye-fiber repellency. Cationization is a chemical treatment to produce positively charged cotton. Quaternary or tertiary amino groups are bonded with cellulose to provide nucleophilic groups, which show better attraction for reactive dyes (AKTEK; MILLAT, 2017). Cationization of cotton enables reactive dyeing at neutral pH and without salt feeding (ROY CHOUDHURY, 2014). For that reason, many authors call cationization a salt-free or low-salt process (ARIVITHAMANI; GIRI

DEV, 2017a; CHATTOPADHYAY, 2001; DONG et al., 2020; MA et al., 2015, 2020; SADEGHI-KIAKHANI; SAFAPOUR, 2018).

Acid dyes are water-soluble anionic dyes and are often used to dye fabrics that carry positive charges, such as wool, silk or polyamide and to a small extent acrylics or blends of these fibers. However, it has no application for the dyeing of cotton fibers due to the absence of positive sites (HELMY; HAUSER; EL-SHAFEI, 2017). In this context, cationization may improve the number of positive charges, making possible cotton dyeing by acid dyes obtaining brightness and unique colors to the cotton fiber.

This paper proposes the process of cationization of cotton as an alternative to avoid the use of salt in the reactive dyeing process and to enable acid dyes for cotton. Furthermore, the dyeing of cationic cotton may considerably reduce the amount of effluent generated. Cationization was achieved by treating cotton with the cationic reagent 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC). Four pretreatment routes were performed using bleaching and cationization processes, together or separately. The results were compared to each other regarding color properties and effluent load. The great contribution of this article was to bring a new option: change in the production process to avoid high costs for effluent treatment. With these promising results, it is possible to maintain the quality of the final product with less time and energy spent on dyeing.

3.2 METHODOLOGY

The exhaustion method was employed for bleaching, cationization, and dyeing of greige cotton fabric. The processes were carried out in a dyeing machine (TC 2200, Texcontrol) with stainless steel canisters with a maximum bath capacity of 250 mL. The control is automatic by programming the processing time and bath temperature in the control panel, according to the steps described in the recipe. All tests were performed with a material-to-liquor ratio of 1:10 and the baths were inserted in the equipment at room temperature. (ARIVITHAMANI et al., 2014; NAKPATHOM et al., 2017). The samples were named according to the pretreatment that was performed in the fabric as indicated in Table 8. The samples and processes that were performed in the present work are also presented in the graphical abstract.

Table 8 – Identification of the samples and their respective pretreatment processes.

Sample	Process
S-G	Without pre-treatment (greige cotton)
S-C	Cationization
S-B	Bleaching
S-BC1	Bleaching + cationization, performed in one single process
S-BC2	Bleaching + cationization, performed in two separated processes

Source: the author.

3.2.1 Materials

A commercially 100 % greige cotton single jersey knitted fabric (weight: 160 $g.m^{-2}$) was purchased from Pemgir Malhas, Brusque, Brazil. The chemical products used in this paper are listed in Table 9.

Table 9 – List of chemical products used in this study.

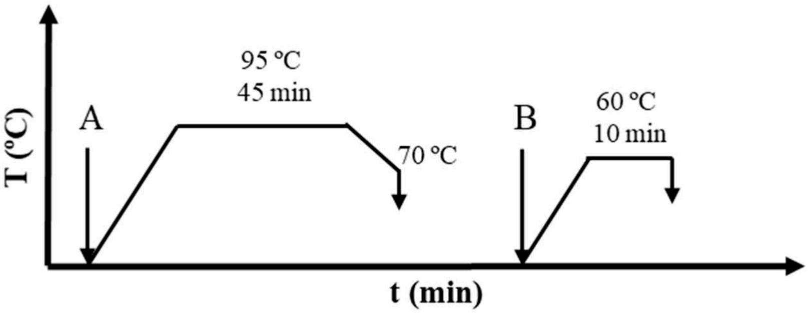
Material	Specification	Source
CHPTAC	Cationic agent, 65 % solution	Werken Química, Indaial, Brazil
Ecodyeing A 230	Non-ionic detergent.	Werken Química, Indaial, Brazil
Stabplex EP 243	Peroxide stabilizer	Werken Química, Indaial, Brazil
Ecodyeing IR 4	Leveling agent	Werken Química, Indaial, Brazil
Formic acid	85 % solution	Werken Química, Indaial, Brazil
Buffer CS 85	Alkalizing agent	Werken Química, Indaial, Brazil
Ecodyeing RW 710	Anionic detergent	Werken Química, Indaial, Brazil
H_2O_2	35 % solution	Neon Comercial Ltda, Suzano, Brazil
NaOH	P.A.	Neon Comercial Ltda, Suzano, Brazil
NaCl	P.A. ACS	Alphatec, São José Dos Pinhais, Brazil
Red Colorsupra PF-3B	Reactive dye	Color Química, Blumenau, Brazil
Blue Colornylon A-R	Acid dye, C.I Acid Blue 260	Color Química, Blumenau, Brazil
IEC detergent	Reference detergent for fastness analysis	Testfabrics Inc., West Pittston, USA

Source: the author.

3.2.2 Bleaching procedure

The fabric was submitted to 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_2O_2 35 % solution. The bath was inserted in the equipment and heated at 2 ºC.min^{-1} up to 95 ºC, kept at this temperature for 45 min. The system was cooled to 70 °C to start the washing using 1 g.L^{-1} of nonionic detergent solution. The samples were then rinsed with water and dried for 24 hours at room temperature. The bleaching process is shown in Figure 5.

Figure 5 – Bleaching process. Solution A: nonionic detergent, NaOH, peroxide stabilizer, and H_2O_2. Solution B: nonionic detergent

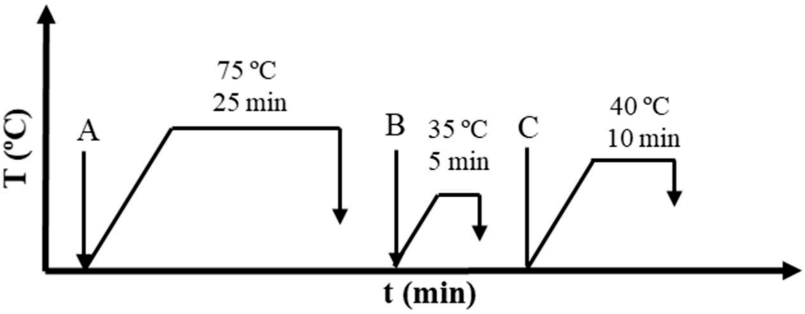


Source: the author.

3.2.3 Cationization of cotton fabric

The cationization process was performed with a solution containing, 20 g.L^{-1} of CHPTAC 65 %, 2 g.L^{-1} of nonionic detergent and 10.5 mL.L^{-1} of NaOH 50 %. The solution was mixed with the fabric sample and inserted into the equipment with circular stirring, being heated at 3 ºC.min^{-1} up to 75 ºC, kept at this temperature for 25 min. Two washing 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 kept at 35 °C for 5 min. In the second, the fabric was washed with deionized water. The cationic fabric samples were then rinsed with water and dried at room temperature for 24 hours. The cationization process is presented in Figure 6.

Figure 6 – Cationization process. Solution A: CHPTAC, nonionic detergent, and NaOH 50 %. Solution B: Formic acid. Solution C: deionized water.

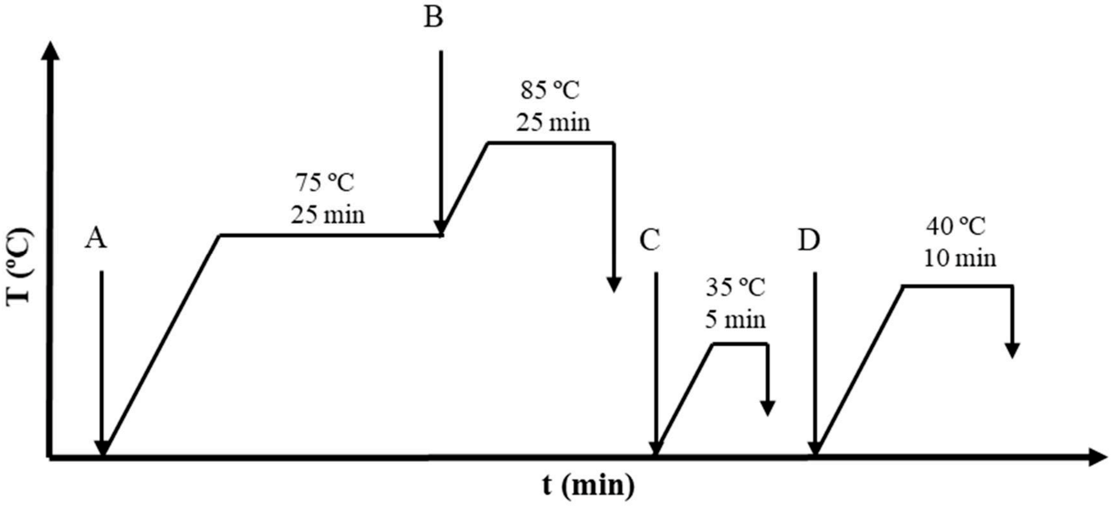


Source: the author.

3.2.4 Cationization and bleaching in a single bath

Cationization and bleaching were also performed simultaneously, in a single bath. Firstly, a solution containing 20 g.L^{-1} of CHPTAC 65 %, 2 g.L^{-1} of nonionic detergent and 10.5 mL.L^{-1} of NaOH 50 % was prepared. The bath was heated at 3 ºC.min^{-1} maintaining at 75 °C for 25 min, then 1 g.L^{-1} of peroxide stabilizer and 10 mL.L^{-1} of H_2O_2 35 % were added and maintained at 95 ºC for 25 min. At the end of the process, the dyebath was cooled to 70 ºC for discharging. The first washing bath was performed with 0.5 g.L^{-1} of formic acid (35 ºC, 5 min) and the second with 0.5 g.L^{-1} of nonionic detergent (60 ºC, 5 min). The process is shown in Figure 7. The cationization process occurred prior to bleaching to avoid the hydrolysis of the CHPTAC (HASHEM, 2006).

Figure 7 – Combined process of cationization and bleaching. Solution A: CHPTAC, nonionic detergent, and NaOH 50 %. Solution B: peroxide stabilizer and H_2O_2. Solution C: formic acid. Solution D: nonionic detergent.

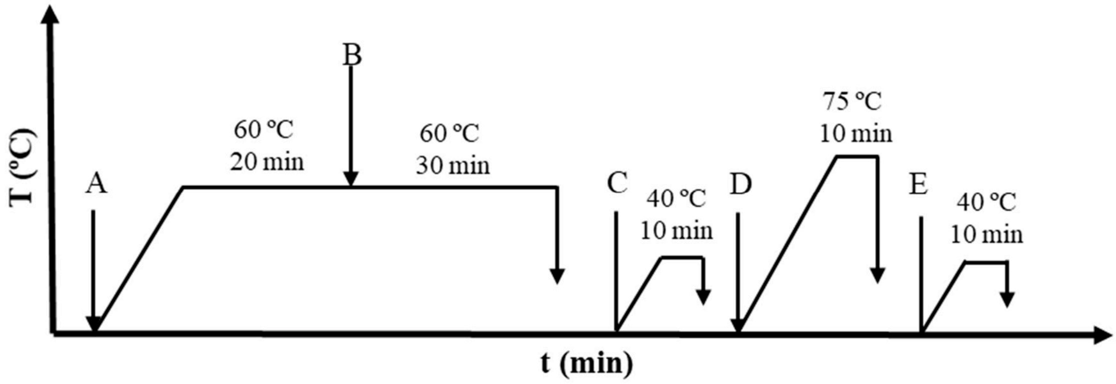


Source: the author.

3.2.5 Dyeing procedure

The recipe for reactive dyeing was provided by the CHPTAC supplier. Reactive dyebaths were prepared by dissolving 2 g.L^{-1} of WK Ecodyeing IR 4 (leveling agent that prevents staining) and 0.4 % owf (over weight 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 60 °C, during 50 min with the gradient of 3ºC.min^{-1}. After 20 minutes, 4.7 g.L^{-1} of the WK Buffer CS 85 alkalizing agent was added. Then a 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 third washing bath was made with deionized water at 40 °C during 10 min. The fabric was then rinsed with water and dried at room temperature for 24 h. The sketching of the dyeing process is shown in Figure 8.

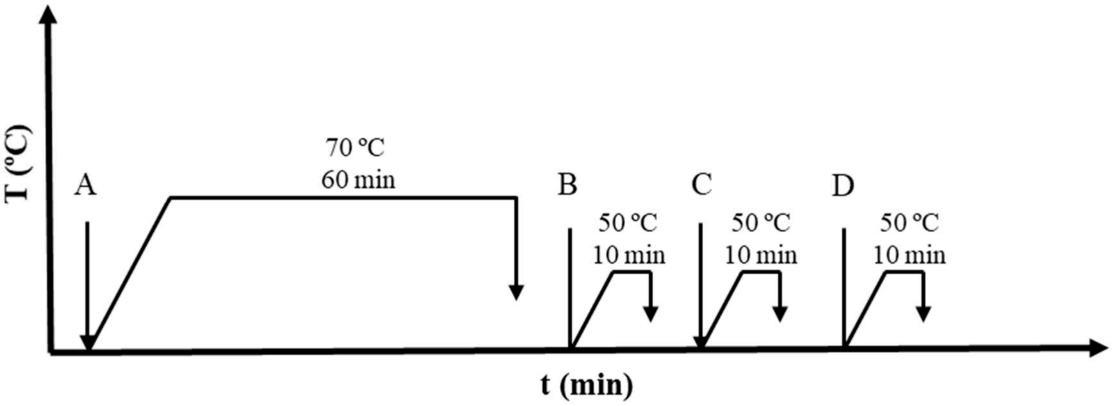
Figure 8 – Reactive dyeing process. Solution A: leveling agent, dye and NaCl (only in conventional dyeing). Solution B: alkalizing agent. Solution C: deionized water. Solution D: Formic acid and anionic detergent. Solution E: deionized water.



Source: the author.

Acid dyebaths were prepared with 0.4 %owf of Acid Blue 260, at pH 4.5. The dyeing occurred at 3 ºC.min^{-1} up to 70 °C, maintaining at that level for 60 min. After exhaustion, three consecutive washes were performed at 50 °C and 10 min with deionized water. 1 g.L^{-1} of anionic detergent was added in the second washing bath. The acid dyeing process is presented in Figure 9.

Figure 9 –Acid dyeing process. Solution A: Acid Blue 260. Solution B and D: deionized water. Solution C: anionic detergent.



Source: the author.

3.2.6 Fabric properties measurement

Color measurements of the textile samples were performed on a reflectance spectrophotometer (Datacolor 500 – Datacolor International) with illuminant D65, 10 ° standard observer. An average value was determined from four measurements taken at different points in the sample. The measurements were taken with the sample folded to minimize the light penetration through the space between the fibers. Color strength (K/S) was calculated using the Kubelka-Munk equation (Eq. 1). The whiteness of the sample was measured by the Berger degree (Eq. 2), and colorimetric coordinates by the CIELab color space. The color deviation (ΔE) and is calculated using Eq. 3.

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

$$Whiteness = Y + 3.448 \cdot Z - 3.904 \cdot X \qquad \text{Eq. 2}$$

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

Where R is the reflectance, K is the absorption coefficient, and S is the scattering coefficient. The K/S considered was calculated by the sum of 10 nm intervals in the wavelength range of 360-700 nm (FU et al., 2013). X,Y, and Z are the coordinate values of the tristimulus system (PUEBLA, 2006). ΔL^*, Δa^* Δb^* denotes the difference between the pairs of samples at the CIELab color space (NAKPATHOM et al., 2017).

Washing fastness tests were performed according to ISO 105-C06, procedure C1S (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2010), using a dyeing machine (TC 2200 – Texcontrol). Rubbing fastness tests were performed according to ISO 105-X12 (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, 2016), using a Rubbing Fastness Tester (CA-11 model – Kimak). The color change was rated according to the appropriate gray scale value, using a reflectance spectrophotometer (Datacolor 500) for measurement. The correlation between the gray scale values and the color deviation of the samples before and after the test is given in the Table 10.

Table 10 - Correlation between the gray scale values and the color deviation.

Gray scale value	Color deviation
5	0.0±0.2
4-5	0.8±0.2
4	1.7±0.3
3-4	2.5±0.3
3	3.4±0.4
2-3	4.8±0.5
2	6.8±0.6
1-2	9.6±0.7
1	13.6±1.0

Source: American Association of Textile Chemists and Colorists (2010)

ATR measurements were made with an Agilent FTIR spectrophotometer (Carry model – Agilent) with a horizontal attenuated total reflectance (ZnSe) accessory. The samples were placed directly on the crystal. The average of 32 scans, in the range of 4000-650 cm^{-1}, and a resolution of 4 cm^{-1} was made for each sample. The sample measurements were divided by the background of the air (e.g., with nothing on the crystal).

3.2.7 Liquid phase measurements

The liquid phase dye concentrations were measured with a transmittance spectrophotometer (UV-M51 – BEL Engineering). A quartz cuvette with a 1.0 cm optical path was used. Three measurements were taken, and the mean value was considered. A wavelength scan was performed to verify the wavelength of maximum absorption in the UV-Visible region, followed by the creation of a calibration curve for conversion of absorbance to concentration, according to Beer's law.

The wavelength of maximum absorbance was 517 nm for reactive and 591 nm for acid dye. The calibration curve correlates the absorbance to the concentration of the reactive and acid dyes in Eq. 4 and Eq. 5, respectively. The calibration curve was performed at pH 4.5 for acid dye and neutral for reactive dye. The coefficient of determination (R^2) indicates a linear relationship between the variables, in agreement with Beer's Law. The wavelength scan and calibration curve are presented in graphic form in the supplementary material (APPENDIX B: Supplementary material for manuscript 2). These data were used to measure the dye concentration in the liquid phase.

$$C\ (mg.L^{-1}) = 58.961 \cdot Abs - 0.1089 \qquad R^2 = 1 \tag{Eq. 4}$$

$$C\ (mg.L^{-1}) = 144.32 \cdot Abs - 1.3192 \qquad R^2 = 0.9991 \tag{Eq. 5}$$

The zeta potential of the dye solutions 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.

3.2.8 Statistical analysis

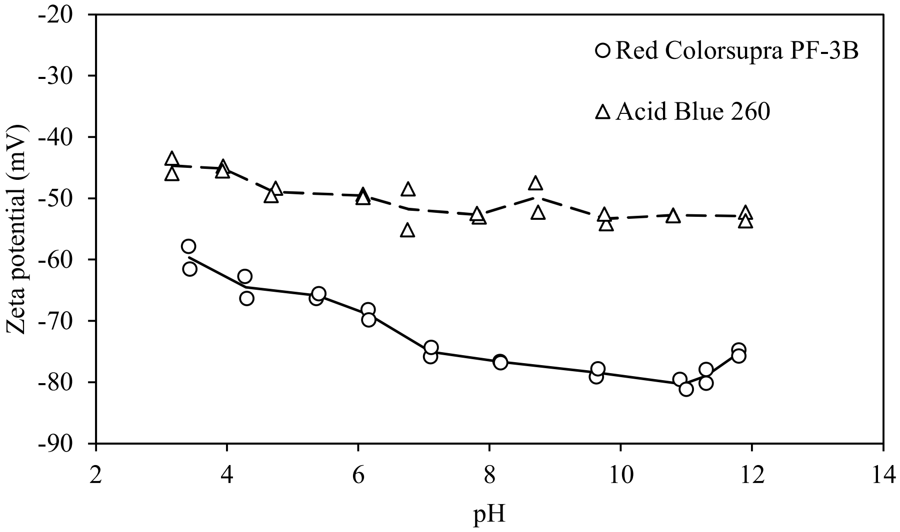
One-way ANOVA and Tukey's test were carried out to find the processes that are significantly different from each other. It was considered statistically significant when $p < 0.05$. The analysis was performed using BioEstat 5.3 (AYRES et al., 2007).

3.3 RESULTS AND DISCUSSION

3.3.1 Zeta potential of the dye solutions

According to Figure 10, the Red Colorsupra PF-3B and Acid Blue 260 dye are anionic. The negative zeta potential across the pH range is a result of the surface chemistry that provides anionic properties to the dyes (RISTIC; RISTIC, 2012). In the conventional dyeing process, the dissociated cotton also has an anionic nature (ARIVITHAMANI; GIRI DEV, 2016; LIU; YAO, 2011). Therefore, the interaction between dye and cotton results in electrostatic repulsion and loss of efficiency in the dyeing process (NAIKWADE et al., 2017).

Figure 10 – Zeta potential as a function of pH for Red Colorsupra PF-3B and Acid Blue 260



Source: the author.

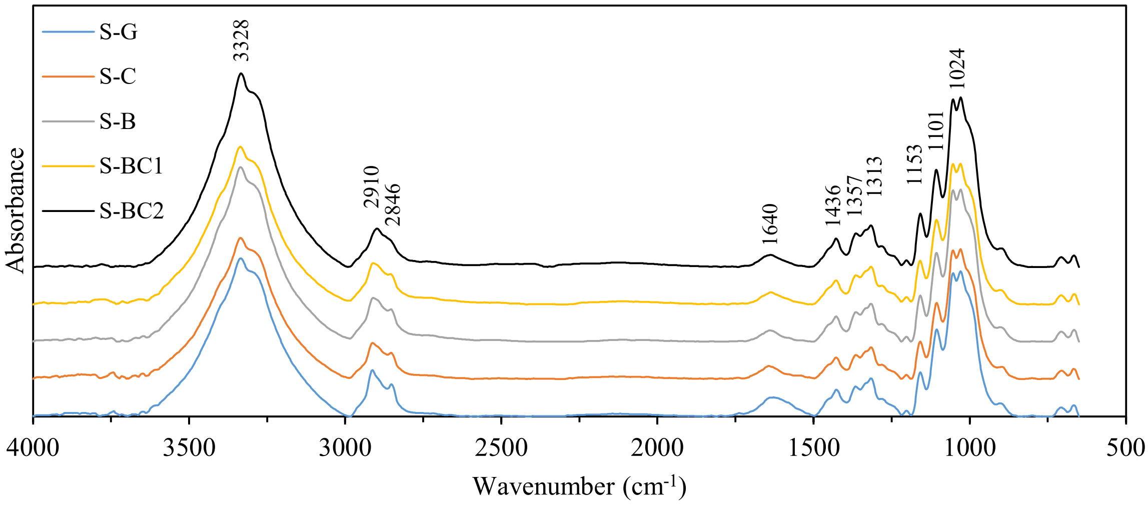
The anionic characteristic is common for most dyes of the reactive and acid classes. This is due to the functional groups present in the dye molecule. These two classes of dyes usually have the sulfonic groups in the molecule, which are responsible for the solubilization of the dye in the dyeing bath (MAHAPATRA, 2016).

3.3.2 Properties of undyed fabric

3.3.2.1 FTIR analysis

The FTIR spectra for the undyed samples are shown in Figure 11. The spectra of untreated and cationic cotton fabrics presented many absorptions bands characteristic of the chemical structure of the cellulose. The broad absorption band that occurred at 3500–3000 cm^{-1} is assigned to O–H stretching. The bands at 2910 and 2846 cm^{-1} appeared due to the presence, respectively, of asymmetric and symmetric H–C–H stretching. These bands are related to impurities of cotton, such as waxes and pectins. The peak at 1640 cm^{-1} was due to the absorbed H_2O. The absorbance at 1436, 1357 and 1313 cm^{-1} are related to C–H deformations (ABDELILEH et al., 2019). The broad intense bands appearing between 1200 and 800 are also common to the cellulosic fabrics, these peaks are assigned to C–O–C asymmetric stretching vibration (CHUNG; LEE; CHOE, 2004; SHATERI-KHALILABAD; YAZDANSHENAS, 2013).

Figure 11 – FTIR spectra of the greige and pretreated cotton.



Source: the author.

The curves had little difference independently of the treatment. This probably occurs because the cotton spectrum peaks overlapped with the peaks related to the cationic treatment. During the cationization process, the CHPTAC is converted to glycidyl trimethylammonium chloride (also known as 2,3-epoxypropyl trimethyl ammonium chloride) before the reaction with cellulose (FARRELL; HAUSER, 2013). The spectra of the glycidyl trimethylammonium chloride contain a characteristic peak for quaternary ammonium salt between 862 and 923 cm^{-1} in cationic starch samples. This peak overlaps with the absorption bands of the cellulose situated between 1200 and 800 cm^{-1}.

3.3.2.2 Colorimetric properties

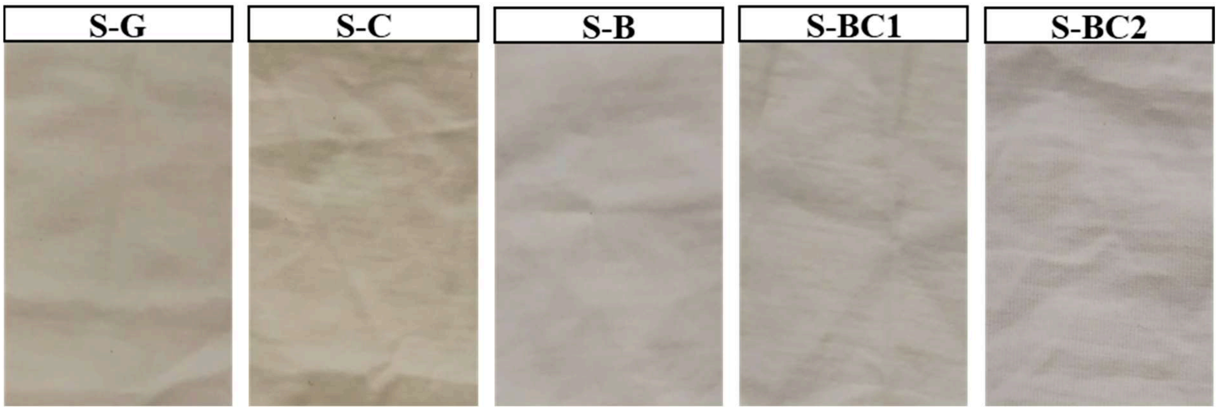
The degree of whiteness, colorimetric CIELab space coordinates (L*, a* and b*) and color strength (K/S) were used to evaluate the undyed samples. The colorimetric properties are shown in Table 11 and the photographs of each sample are shown in Figure 12. The higher the whiteness degree, the lower the K/S value. Samples S-B and S-BC2 achieved the highest whiteness degree, due to the bleaching and cationization processes. Moreover, the high NaOH content in the bleaching process eliminates the waxes and other impurities that cause hydrophobicity and hinders the migration of the dye to the fiber.

Table 11 – Color properties (whiteness measured by Berger Degree, CIELab coordinates and K/S) of undyed fabrics.

Sample	**Whiteness**	**L***	**a***	**b***	**K/S**
S-G	16.1 ± 0.5^{a}	88.36 ± 0.03^{a}	1.60 ± 0.04^{a}	12.9 ± 0.1^{a}	4.22 ± 0.04^{a}
S-C	25.7 ± 0.7^{b}	90.1 ± 0.2^{b}	1.2 ± 0.1^{b}	11.1 ± 0.2^{b}	3.11 ± 0.08^{b}
S-B	70.4 ± 0.9^{c}	94.7 ± 0.3^{c}	-0.02 ± 0.01^{c}	3.3 ± 0.2^{c}	0.66 ± 0.05^{c}
S-BC1	53.6 ± 0.4^{d}	93.53 ± 0.08^{d}	0.04 ± 0.02^{c}	6.38 ± 0.07^{d}	1.31 ± 0.03^{d}
S-BC2	70.6 ± 0.1^{c}	94.6 ± 0.1^{c}	0.02 ± 0.05^{c}	3.22 ± 0.09^{c}	0.65 ± 0.03^{c}

Source: the author.
Note: data that share the same letters, in the same column, are considered statistically equals.

Figure 12 – Photographs of the undyed fabrics. Greige cotton (S-G), Cationization (S-C), Bleaching (S-B), Bleaching + cationization - one single process (S-BC1), Bleaching + cationization - two processes (S-BC2).



Source: the author.

Based on CIELAB values the treated cotton had a little but relevant alteration in red (cf. a*) and yellow (cf. b*) colors after the cationization and bleaching treatments. Bleached samples had the values of the coordinates a* and b* closer to the achromatic point. The value of L* is close to the maximum (100), which indicates that the fabric is white.

The impurities are responsible for the yellowish color of the cotton. Therefore, the greige sample (S-G) resulted in the lowest values of whiteness (Berger degree) and L* coordinate. The removal of impurities by the high concentration of NaOH in the cationization process also gave a higher degree of whiteness; this could be observed comparing samples S-C and S-G. NaOH removes the waxes of the surface of the cuticle of the cotton fiber by saponification. Besides, NaOH facilitates the solubilization of pectin by raising the pH of the dyebath. This process is empowered by the surfactant present in the cationization bath (WAKELYN et al., 2006).

The statistical analysis performed by One-way ANOVA and Tukey's test indicated that there is no significant difference between samples S-B and S-BC2. This indicates that the cationization does not interfere with the degree of bleaching of the samples when performed in two distinct steps.

Statistical analysis indicated a significant difference between S-BC2 and S-BC1. Comparing bleached and cationic fabric samples, the highest whiteness degree was achieved when the process was performed in two steps. The bleaching and cationization performed in a single step removed a smaller amount of impurities, this is due to the shorter bleaching time and the competitiveness of NaOH. In the single-step process, NaOH was added only once, early in the process. Being consumed during cationization, the amount of alkali was lower when the bleaching process starts.

The K/S and reflectance spectrum of the undyed samples are shown in the supplementary material (APPENDIX B: Supplementary material for manuscript 2). All undyed samples exhibited similar behavior. Samples S-B and S-BC2 showed almost the same reflectance in the visible region, which corroborates with the data from Table 11 that did not indicate a significant difference in these samples. The lowest reflectance along the spectrum occurred for sample S-G, followed by S-C and S-BC1. The K/S spectrum presents an inverse behavior to the reflectance curve as it is related to the absorption of the light in the fabric.

3.3.3 Analysis of dyed fabrics with reactive dye

A qualitative analysis can be performed from Figure 13, which shows a large difference in the dyeing of the sample S-G compared to pretreated samples. S-G presented heterogeneous dyeing caused by the presence of impurities that increase the hydrophobicity of the fabric, consequently reducing the dye-fiber interaction. Waves and pectin, responsible for fabric hydrophobicity, were solubilized in the bath after treatment with NaOH. This process increases the hydrophilicity of the fabric, which is essential for the dyeing of cotton. Therefore, the dyeing of the bleached samples was uniform, without staining.

Samples with the acronym WS (without salt) in Figure 13 are referred to conventional dyeing but without the feed of salt. The absence of salt for the dyeing of non-cationic samples reduced the dye-fiber interaction. Salt is important in conventional dyeing to enhance exhaustion by raising the negative zeta potential of cellulose in water, enhancing the affinity with anionic dye in water and disrupting hydration of dyeing sites (HASHEM; HAUSER; SMITH, 2003).

CIELab coordinates and K/S for the dyed samples are shown in Table 12. The color properties were the average from four points collected in the sample surface, but the huge presence of stains made the quantitative analysis impossible for the sample S-G. Therefore, the S-G sample was not subjected to quantitative analysis. In Table 12 is presented the raise of coordinate a*, in comparison with Table 11. Coordinate a* refers to the red coloration in the CIELab color space.

Figure 13 – Photographs of the samples after dyeing with reactive dye.

Source: the author.

Considering only the red coordinate a*, the One-way ANOVA test indicated that there is no significant difference in any of the samples, except for S-B (WS) sample. When considering K/S, One-way ANOVA and Tukey's test indicated no significant difference in the S-B, S-BC1, and S-BC2 samples. The absence of the bleaching process influenced the K/S for the S-C sample after the dyeing process. Through Table 11 it may be seen the higher K/S for the S-C sample also in the undyed fabric.

The non-cationic dyeing, without feeding salt in the process, considerably reduced the dye uptake into the fiber. This is clear by the higher K/S and a* coordinate for dyed sample S-B in comparison with S-B (WS). The difference can be seen in Figure 13 and Table 12. L* coordinate was higher in sample S-B (WS) and closer to the undyed S-B sample, presented in Table 11.

Table 12 – Color properties of the dyed samples with reactive dye.

CIELab coordinates and color strength

Sample	L*	a*	b*	K/S
S-C	56.2±0.6^{a}	46.9±0.5^{a}	-4.0±0.2^{a}	41±2^{a}
S-B	57. 9±0.2^{b}	47.2±0.4^{a}	-6.0±0.1^{b}	34.9±0.8^{b}
S-B (WS)	71.2±0.4^{c}	28.98±0.09^{b}	-4.4±0.1^{c}	10.4±0.3^{c}
S-BC1	57.5±0.2^{b,d}	46.4±0.3^{a}	-4.75±0.05^{d}	36.0±0.8^{b}
S-BC2	56.9±0.6^{a,d}	46.9±0.6^{a}	-5.0±0.2^{d}	37±2^{b}

Color deviation (ΔE)

Sample	S-C	S-B	S-B (WS)	S-BC1
S-B	2.6	-	-	-
S-B (WS)	23.3	22.6	-	-
S-BC1	1.6	1.5	22.1	-
S-BC2	1.2	1.4	22.9	0.8

Source: the author.

Note: data that share the same letters, in the same column, are considered statistically equals.

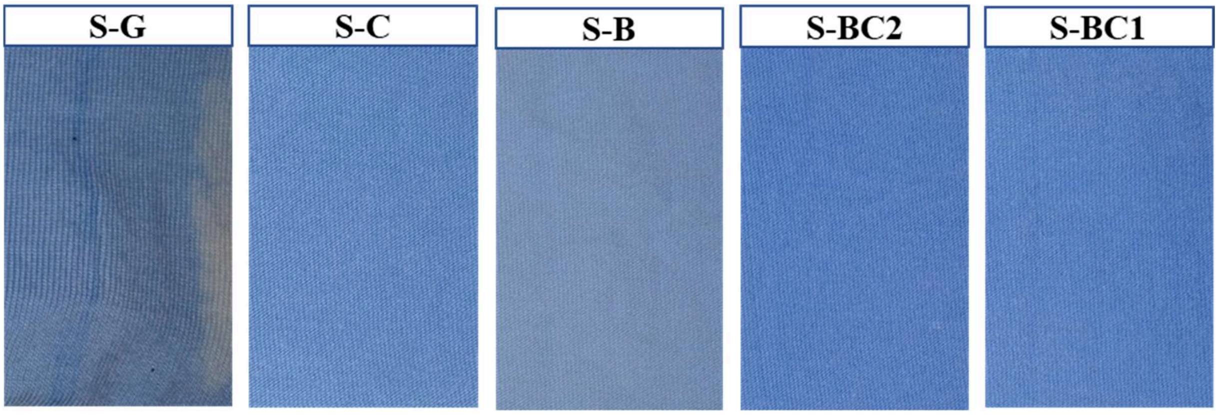
The S-BC1 sample was statistically equal to S-BC2 after reactive dyeing. This affirmation can be corroborated with the ΔE between the color obtained with both processes, which is 0.8. In general, ΔE of 1.0 is the smallest color deviation that the human eye can see. So any ΔE less than 1.0 is normally imperceptible for the human eyes (CHOUDHURY, 2015). This is important for saving time and energy because two processes are carried out in a single bath. When performing cationization and bleaching in a single bath, however, the processes must occur consecutively. The cationic agents are not compatible with oxidative peroxide bleaching ingredients (HASHEM, 2006). Therefore, the bleaching must start after the cationization reaction.

The K/S and reflectance spectrum for samples dyed with reactive dye are shown in the supplementary material (APPENDIX B: Supplementary material for manuscript 2). The reflectance spectrum for all dyed fabric samples was almost the same, indicating that pretreatment processes produced similar dyed fabrics, except for sample S-B (WS). The curves corroborate with the ANOVA statistical test since it is visually perceptible the deviation of the curve corresponding to sample S-B (WS). In all cases, for dyed samples, the highest percentage of reflectance occurred at a wavelength above 660 nm, which corresponds to the visual perception of the red color. The K/S spectrum for the dyed samples showed greater light absorption in the wavelength range of 520-560 nm, corresponding to blue and green.

3.3.4 Analysis of dyed fabrics with acid dye

Figure 14 contains the photographs of fabrics dyed with Acid Blue 260. Like the reactive dyeing, staining was observed for sample S-G. It is visually apparent that samples S-C, S-BC1 and S-BC2 have a higher intensity than S-B. Thus, the cationization increased the fiber affinity also for the acid dye.

Figure 14 – Photographs of the samples after dyeing with acid dye.



Source: the author.

CIELab coordinates and K/S for acid dyed samples are presented in Table 13. As also reported in reactive dyeing, the S-G sample was not considered due to the presence of stains. The increment occurred in the negative part of the b* coordinate, comparing with the undyed samples (Table 11), which corresponds to the blue color in the CIELab color space. One-way ANOVA test indicated that there is no significant difference in any of the K/S samples, except for S-B. Besides, the K/S value for the cationic samples are 4 times higher than the sample solely bleached.

All dyed fabrics were distinguishable for humans because of ΔE ≥ 1. The dyed fabrics presented the same K/S but distinct a* and b* coordinates. This is due to the difference in the undyed fabric sample, which also presents different coordinates. Moreover, the Acid Blue 260 dye may have a different affinity with each treatment.

Table 13 – Color properties of dyed samples with Acid Blue 260.

CIELab coordinates and color strength

Sample	L*	a*	b*	K/S
S-C	63.7 ± 0.4^{a}	-5.4 ± 0.2^{a}	-24.9 ± 0.5^{a}	21.9 ± 0.6^{a}
S-B	78.8 ± 0.4^{b}	-4.67 ± 0.05^{b}	-18.8 ± 0.4^{b}	5.4 ± 0.2^{b}
S-BC1	63.2 ± 0.3^{a}	-3.4 ± 0.1^{c}	-30.6 ± 0.2^{c}	22.6 ± 0.5^{a}
S-BC2	63.3 ± 0.4^{a}	-2.72 ± 0.05^{d}	-31.6 ± 0.4^{d}	22.2 ± 0.7^{a}

Color deviation (ΔE)

Sample	S-C	S-B	S-BC1
S-B	16.3	-	-
S-BC1	6.0	19.7	-
S-BC2	7.2	20.3	1.2

Note: data that share the same letters, in the same column, are considered statistically equals.

The color spectrum of the Acid Blue 260 dyed samples is presented in the supplementary material (APPENDIX B: Supplementary material for manuscript 2). In this case, the reflectance peak in the wavelength region is located between 450-460 nm, corresponding to the reflection range of the blue color. The highest color absorption is in the range of 580-640 nm. The biggest difference between K/S curves is attributed to the sample S-B, which also corroborates the data presented in Table 13.

The functionalization with the polyelectrolyte provided significant results for the dyeing process of cotton fabrics. The dye absorption in the S-B sample was extremely low due to the repulsion between the bleached cotton and the acid dye. The presence of CHPTAC improves electrostatic attraction, achieving colors that are not obtained for cotton with acid dyes.

3.3.5 Fastness properties

Table 14 contains washing and rubbing fastness for reactive and acid dyed fabric samples. Cationic dyed cotton maintained the same fastness levels as conventional cotton, for reactive dyeing. However, a small difference was observed in wet rubbing fastness for samples acid-dyed S-C and S-BC1.

Acid dyeing showed lowest washing fastness level for all samples. This is because the dye molecule did not bond to the cellulose. The cationization process increased the absorption of the acid dye to the fiber, as shown in Table 13, but the process needs to be refined to ensure better fastness levels. A high level of washing fastness is due to more than good electrostatic interactions, it is required a strong bond between the fiber and the dye. Low fastness levels for acid dyeing with cationized cotton were also found by other authors (HAUSER; TABBA, 2001; HELMY; HAUSER; EL-SHAFEI, 2017). Although presenting poor fastness levels, the cationic fabric exhibited greater dye-fiber affinity since the K/S values were higher for cationic samples after washing with the reference detergent.

Table 14 – Fastness properties and K/S after washing procedure of the reactive and acid dyeings.

Reactive dye				
Sample	**Washing fastness**	**K/S**^{a}	**Rubbing fastness**	
			Dry	**Wet**
S-B	2/3	22.21±0.01	5	4/5
S-B (WS)	2/3	9.7±0.3	5	4/5
S-C	2/3	39±1	5	4/5
S-BC1	2/3	31±2	5	4/5
S-BC2	2/3	36.8±0.2	5	4/5
Acid dye				
Sample	**Washing fastness**	**K/S**^{a}	**Rubbing fastness**	
			Dry	**Wet**
S-B	1	5.14±0.05	5	4/5
S-C	1	11.6±0.6	5	4
S-BC1	1	9.1±0.2	5	4
S-BC2	1	9.3±0.4	5	4/5

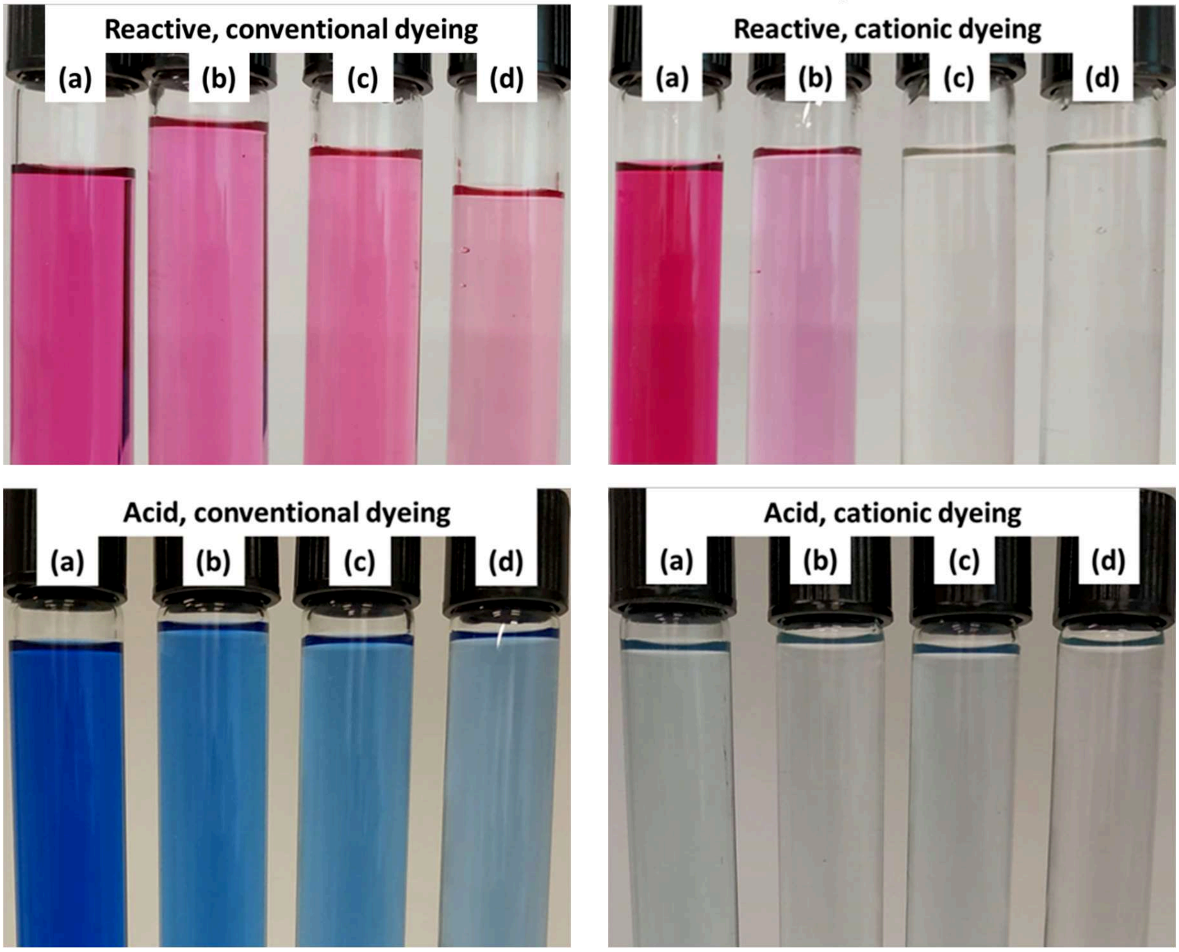
Source: the author.

Note: ^{a}After washing fastness procedure.

3.3.6 Dyeing and washing baths

According to the methodology, the dyeing was followed by three consecutive washing baths, totalizing four baths in the conventional or cationic process. The baths were shown in Figure 15. For reactive cationic dyeing, the presence of dye is not visible from the second wash bath. In the conventional dyeing, even in the third washing bath, the presence of dye is still perceptible. The same behavior occurred for acid dyeing, but in this case, the exhaustion was even better and there was almost an absence of dye into the exhaustion bath, meaning that a higher amount of dye was retained on the fabric.

Figure 15 – Comparison between conventional and cationic dyebaths. (a) Exhaustion bath, (b) first, (c) second and (d) third wash, for reactive red and acid blue dyes.

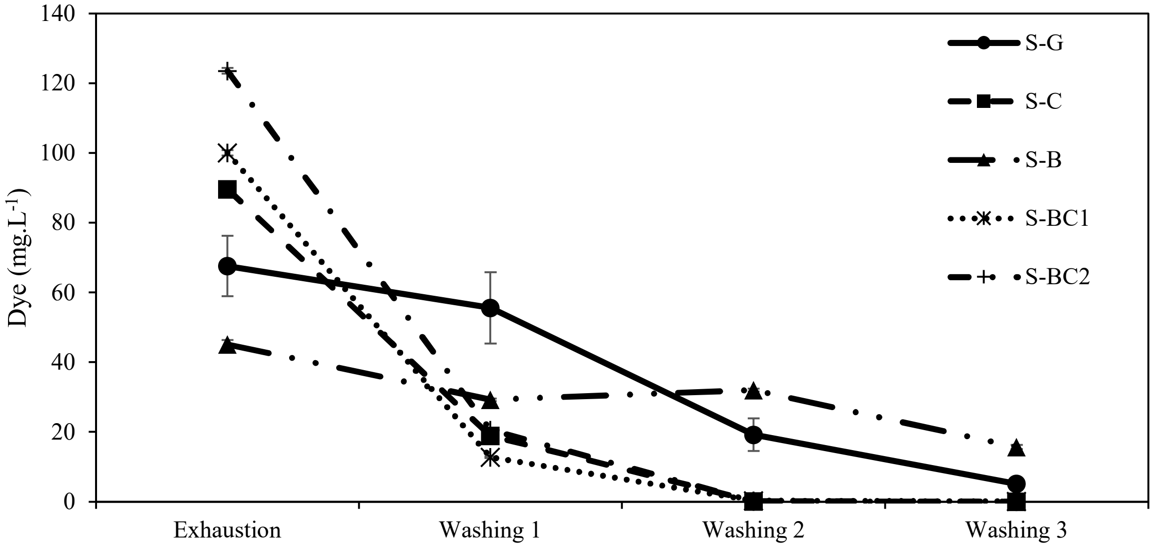


Source: the author.

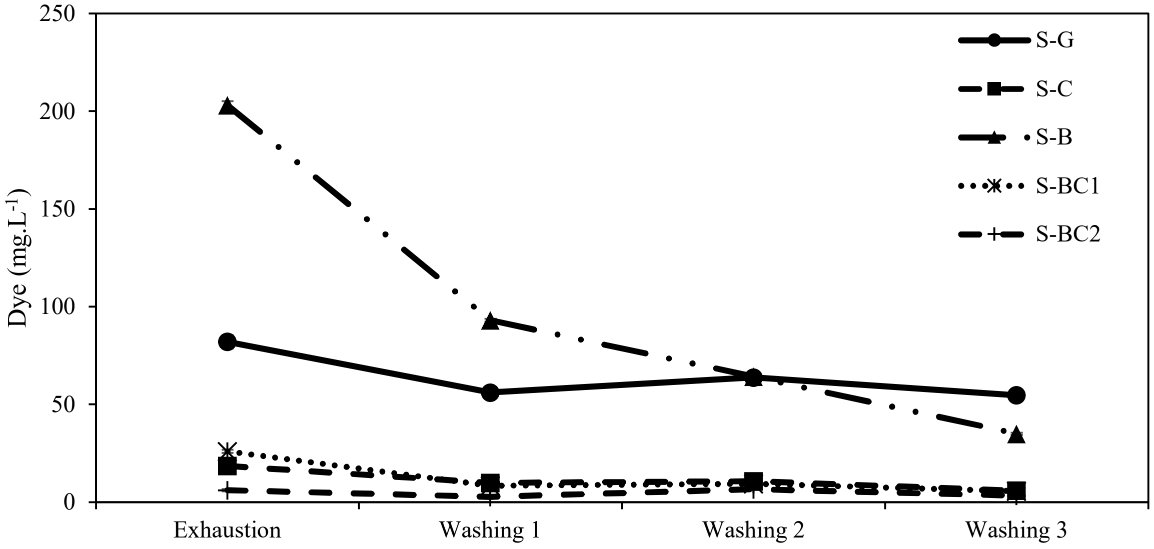
It is possible to identify the effect of the bleaching and cationization processes on the dye concentration of the baths from the analysis of Figure 16. The samples S-G and S-B presented the lowest concentration of dye in the exhaustion bath, respectively 68±9 and 45±1 mg.L^{-1}. Between these two non-cationic samples, S-G resulted in higher dye concentration in the exhaustion bath due to the impurities that confer less wettability and low dye-fiber interaction, which is responsible for the stains shown in Figure 13 and Figure 14.

The high standard deviation for the dyed greige sample (S-G) is remarkable, in Figure 16 (a). Especially in the first wash and exhaustion bath, which represented 13 % and 18% of the mean concentration, respectively. The bleaching and cationization processes are responsible an even dyeing. The greige fabric, as mentioned before, has several impurities, since it is a natural product, its composition varies according to the characteristics of the crop.

Figure 16 – Dye concentration in the exhaustion and washing baths for (a) reactive and (b) acid dyes.



(a)



(b)

Source: the author.

The dye weakly bonded to the fiber was removed with successive washes. For the S-G sample, the dye concentration decreases gradually until it reaches the value of 5.2±0.3 mg.L^{-1} and 54.7±0.3 mg.L^{-1} for reactive and acid dye, respectively. For the sample S-B in Figure 16 (a), it is observed that was an increase at a concentration from 29.3±0.4 to 32.02±0.4 mg.L^{-1}, from the first to the second washing. As shown in Figure 16 (b), the same increase happens for sample S-G, from 56.0±0.7 mg.L^{-1} to 62±2 mg.L^{-1}. These data indicate the importance of performing washing with anionic detergent, as it removes the unfixed cationic agent and solubilizes part of the hydrolyzed and unfixed dye.

The comparison between the graphs from Figure 16 indicates quantitatively what was observed in Figure 15. The cationic samples (S-C, S-BC1, and S-BC2) showed a higher concentration of dye in the exhausting bath. The concentration of dye decreases drastically from the dyebath to the first wash and is practically zero in the consecutive washes. This indicates that a large portion of the dye is weakly retained in the fiber during the exhaustion bath in conventional dyeing. Therefore, the dye is removed after the washing baths.

Cationization highly influenced the absorption of the acid dye in cotton fiber. All cationized samples showed low dye concentration in the exhaustion bath. Table 15 contains the percentage of reduction for dye in each bath, compared to the non-cationized S-B sample with acid dyeing. Cationization reduced the concentration of dyes to above 80 % in all baths.

Table 15 – Dye concentration reduction, in each bath, relatively from the sample S-B dyed with Acid Blue 260.

Sample	Exhaustion	Washing 1	Washing 2	Washing 3
S-BC1	87%	91%	85%	84%
S-BC2	97%	97%	90%	91%
S-C	91%	89%	83%	83%

Source: the author.

The increase in dye fixation on cationic cotton fabric reduces the effluent load in the industrial treatment plant (ARIVITHAMANI; GIRI DEV, 2016). A single wash in the cationized fabric is enough for the removal of the dye weakly bonded to the fiber. Besides, the cationization does not require the use of laundry detergent. Washing with formic acid, however, is advisable to remove the trimethyl amine from the cationization process, responsible for fabric unpleasant odors (FARRELL; ORMOND; GABLER, 2015).

3.4 CONCLUSION

Cationic dyeing produced dyed fabrics with the same color intensity as conventional dyeing. However, cationization presented two main advantages: the reduction of effluent load and the halt of salts fed in the dyeing process. While conventional dyeing requires at least three washing steps, in cationic dyeing a single wash is enough for the removal of the hydrolyzed dye.

The bleaching step is an essential step for the incorporation of the dye into the fiber. The single-step cationization and bleaching process produced a fabric with a lower degree of whiteness, but without a significant difference in the properties of the dyed fabric. This is important because it was possible to produce a dyed fabric with equal characteristics and with one less process, reducing the generated effluent, consumption of inputs, time, and energy.

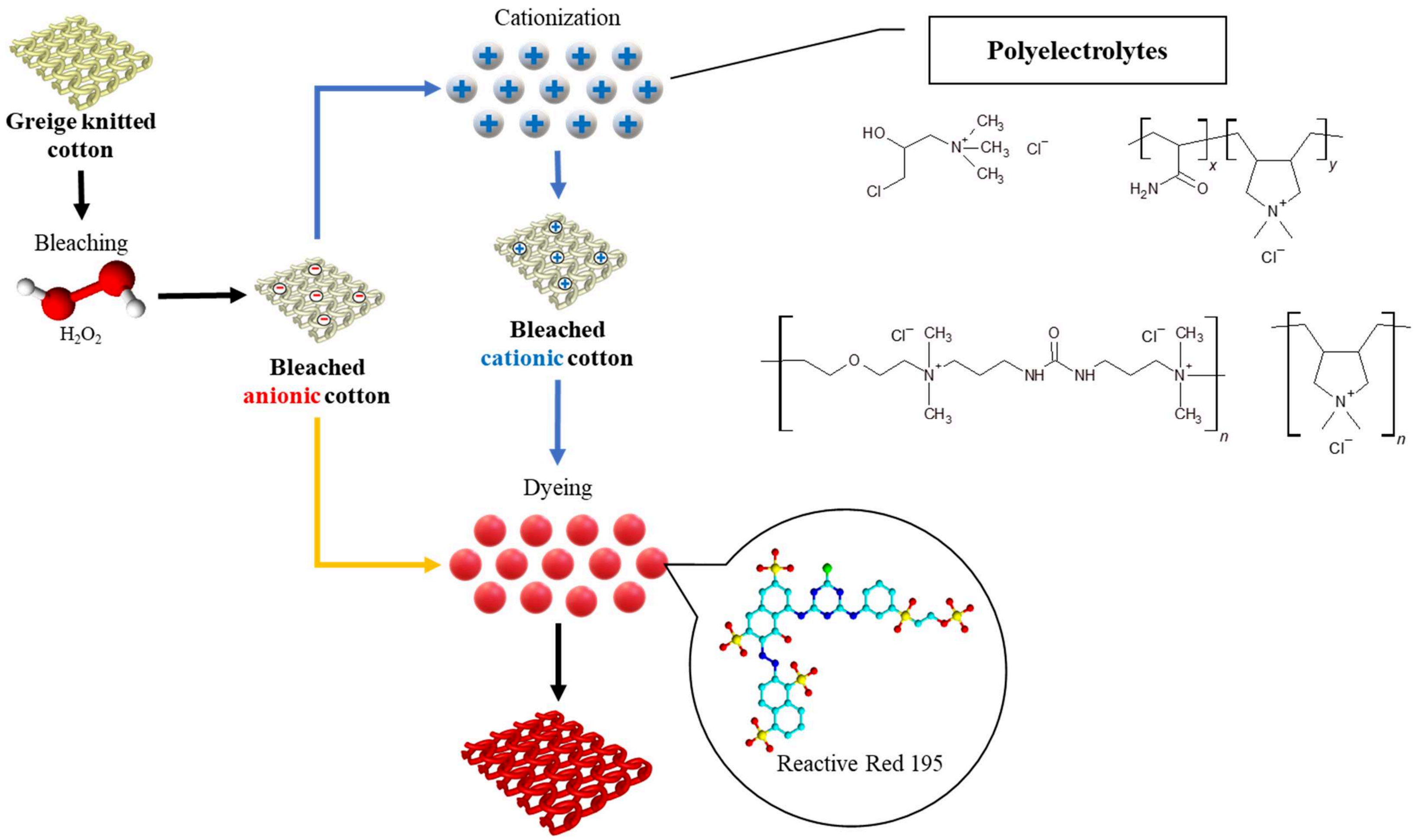
Cationization substantially increased acid dye fixation, opening the possibility of using this class of dye in cotton fiber to develop colors with high brightness. However, the fastness levels achieved with Acid Blue 260 for acid dyes need to be considerably improved to attract the process to an industrial scale.

4 PREPARATION OF CATIONIC COTTON THROUGH REACTION WITH DIFFERENT POLYELECTROLYTES

Abstract: Cationization of cotton fabrics were 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, FTIR and 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 41-48, 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.

Keywords: Cationization. Cationizing agents. Salt-free dyeing. Low-salt dyeing. Poly diallyldimethylammonium chloride. Polyquaternium-2. Poly acrylamide-co-diallyldimethylammonium chloride. 3-chloro-2-hydroxypropyl trimethyl ammonium chloride.

Graphical abstract:



4.1 INTRODUCTION

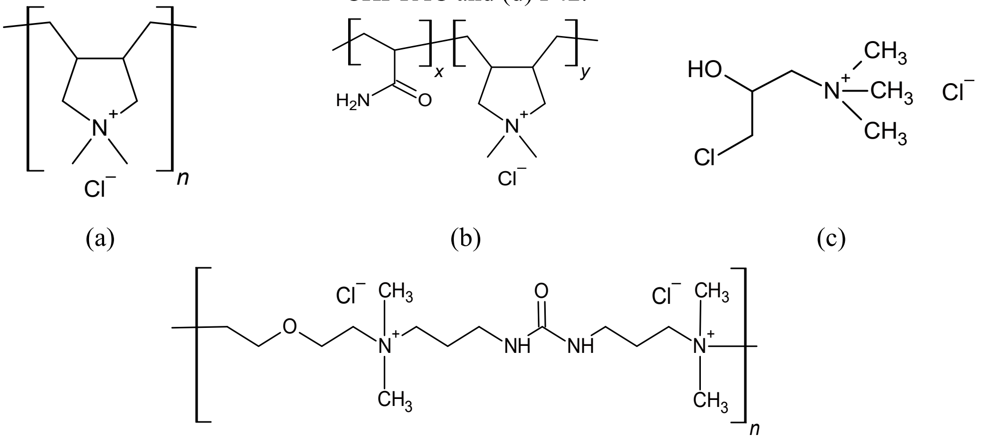
Cellulosic fibers, such as cotton, are essential materials in the textile industry, because of the high availability, low price and extensible applications (ARIVITHAMANI; GIRI DEV, 2018; FU et al., 2013). Cotton fabrics are usually dyed with reactive dyes. Those dye classes have a low affinity for cotton fabrics, thus additional electrolytes are essential for conventional dyeing. Hence, cotton dyeing consumes a lot of water and energy, resulting in a large amount of effluent (HELMY; HAUSER; EL-SHAFEI, 2017).

Chemical modification of cellulosic fabrics is achieved by introducing new functional groups to increase the affinity of cotton fibers for different dye classes (ABDELILEH et al., 2019; ARIVITHAMANI; GIRI DEV, 2018; MICHEAL; TERA; IBRAHIM, 2002). 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 the 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; GIRI DEV, 2018). Therefore, many authors refer to cationization as salt-free or low-salt processes (ARIVITHAMANI; GIRI DEV, 2017a; CHATTOPADHYAY, 2001; DONG et al., 2020; MA et al., 2015, 2020; SADEGHI-KIAKHANI; SAFAPOUR, 2018). Even after extensive research and advancement in the field, cationization encounters barriers to industrial-scale applications due to nuisance odor (FARRELL; ORMOND; GABLER, 2015), high costs (AKTEK; MILLAT, 2017), toxicity (FARRELL; HAUSER, 2013) and limited commercial availability of the reagents (HASANI et al., 2009). The cationization process must improve to satisfy industrial requirements.

The most common way to prepare cationic cotton fiber is by incorporating quaternary ammonium groups into the cellulose molecule (AKTEK; MILLAT, 2017; ROY CHOUDHURY, 2014). 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 17 presents the molecular structure of each polyelectrolyte.

Despite the efforts for research for the state of the art, no papers were found that use PAcD and P42 as cationic agents for textile processes. PAcD, also known as PAADDA or P(AAm-co-DADMAC) (AO et al., 2018; LIAN et al., 2016) is a copolymer provided with quaternary ammonium group. One of the PAcD copolymer monomers is the diallyldimethylammonium chloride, the same forming monomer of PDDACl. Some recent publications already testified PDDACl's capacity as a cationic agent (BESSA et al., 2019; HELMY; HAUSER; EL-SHAFEI, 2017; KIM et al., 2016; OLIVEIRA et al., 2017). CHPTAC is the most common reagent for cotton cationization and will be used in the present paper for comparison.

Figure 17 – Molecular structure of the polyelectrolytes used in the present paper: (a) PDDACl, (b) PAcD, (c) CHPTAC and (d) P42.



(d)

Source: the author.

P42 has potential as a novel cationic agent. It is a water-soluble polymer and has been used as a conditioning agent for skin and hair care products such as soaps, shampoos and hair conditioners. 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 (CHEN et al., 2016; KUMAR et al., 2016).

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 and zeta potential. Besides, the bactericidal activity was estimated and the mechanism for cationization was proposed.

4.2 EXPERIMENTAL

Different samples of cationic cotton were produced by varying the concentration and polyelectrolyte. The samples were dyed with reactive dye and characterized. The graphical abstract summarizes the main stages of the proposed process.

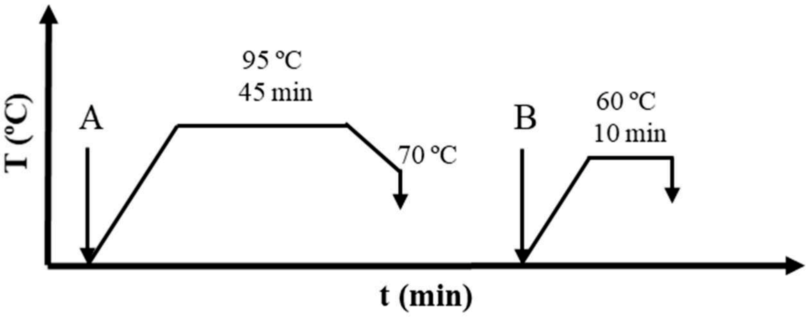
4.2.1 Materials

A 100 % greige cotton single jersey knitted fabric (weight = 160 g.m^{-2}) was used in this paper and was supplied from Pemgir Malhas, Brusque, Brazil. PDDACl solution (20 wt% in H_2O), PAcD solution (10 wt% in H_2O) and P42 solution (62 wt% in H_2O) were purchased from Sigma-Aldrich. A commercial CHPTAC solution (65 wt% in H_2O) 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 (APPENDIX C: Supplementary material for manuscript 3).

4.2.2 Pretreatment and dyeing of cotton fabrics

Bleaching, cationization and dyeing of greige cotton fabrics 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 the bleaching process with a solution containing 1 g.L^{-1} of nonionic detergent, 8 mL.L^{-1} of NaOH 50 %, 1 g.L^{-1} of peroxide stabilizer and 10 mL.L^{-1} of H_2O_2 35 %. The solution was heated at 2 ºC.min^{-1} up to 95 ºC, remaining at that level for 45 min. After that, bleached cotton was washed using 1 g.L^{-1} of nonionic detergent solution at 60 ºC and 10 min. The bleaching process can be seen in Figure 18.

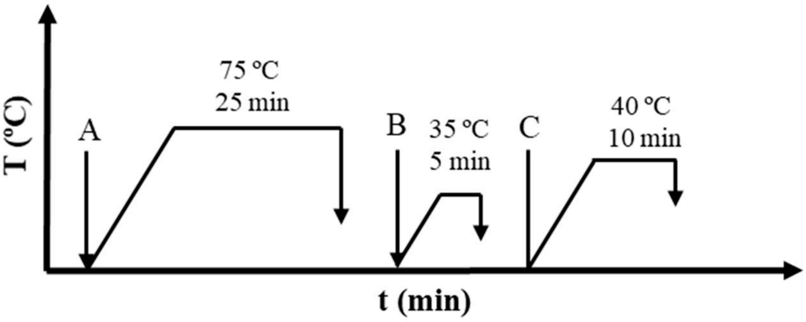
Figure 18 – Bleaching process. Solution A: nonionic detergent, NaOH, peroxide stabilizer and H_2O_2. Solution B: nonionic detergent.



Source: the author.

The cationization and dyeing procedure occurred according to the recipe provided by the CHPTAC supplier. 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 ºC.min^{-1} until 75 ºC, maintaining at that level for 25 min. Two washing 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 washed with deionized water. The cationization process can be seen in Figure 19.

Figure 19 – Cationization process. Solution A: cationic agent, non-ionic detergent and NaOH 50 %. Solution B: Formic acid. Solution C: deionized water.



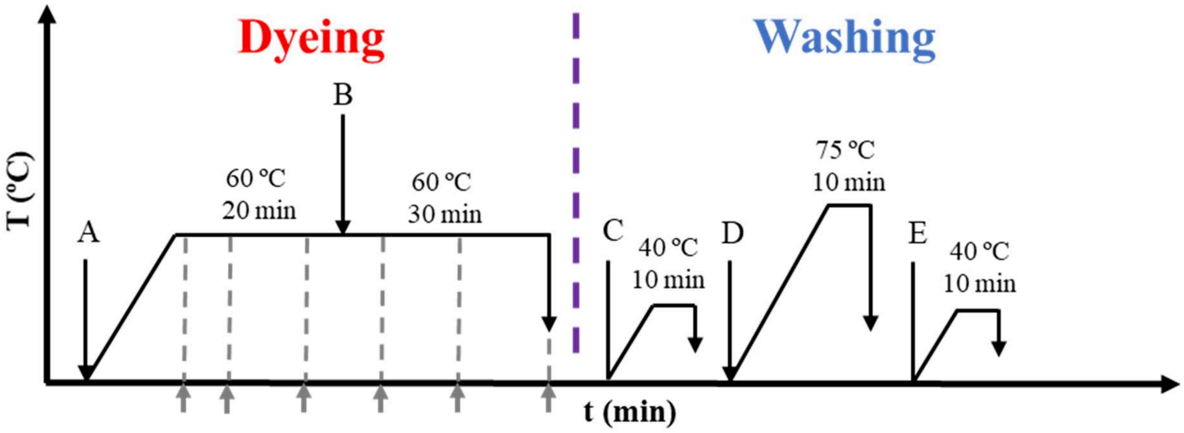
Source: the author.

The reactive dyebaths were prepared by dissolving 2 g.L^{-1} of leveling agent and 0.4 %owf (over weight 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 ºC.min^{-1} up to 60 °C, maintaining at that level for 50 min. After 20 minutes, 4.7 g.L^{-1} of the alkalizing agent was added. After the dyeing, a 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 were dried at room temperature after each bleaching, cationization or dyeing step. The dyeing process can be seen in Figure 20.

The arrows pointing up, in Figure 20, indicate data collection intervals. After the temperature of the dyebath stabilized at 60 ºC, fabric samples were collected at intervals of 2, 8, 28, 38 and 50 minutes. 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, the samples treated with the same cationic agent concentration were dyed simultaneously in 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 Figure 20. Besides, it was not possible to perform the conventional dyeing due to the absence of salt in the dyebath.

Figure 20 – Dyeing process. Solution A: leveling 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.



Source: the author.

4.2.3 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. 6):

$$K/S = \frac{(1-R)^2}{2R} \qquad \text{Eq. 6}$$

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 color deviation (ΔE) is calculated using Eq. 7:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 (\Delta b^*)^2} \qquad \text{Eq. 7}$$

Where ΔE is the CIELab color deviation 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 of the dyed fabrics was calculated using the Relative Unlevelness Index (RUI), as shown in Eq. 8 and Eq. 9. For calculating RUI, ten randomly selected locations of 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; LI; YEUNG, 1992).

$$S_\lambda = \frac{\sqrt{\sum_{i=1}^{n} (R_i - \bar{R})^2}}{n - 1} \qquad \text{Eq. 8}$$

$$RUI = \sum_{\lambda=390}^{700} \left(\frac{S_\lambda}{\bar{R}}\right) V_\lambda \qquad \text{Eq. 9}$$

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 $\bar{R}$ 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 16.

One-way ANOVA and Tukey's test were performed for 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 gray 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 to concentration according to Beer's law.

Table 16 – Interpretation of RUI values.

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

Source: Chong, Li and Yeung (1992).

4.2.4 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 were 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 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.

4.2.5 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 minute interval for spreading the water, the fabric samples (size 1x2 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 untreated underground water.

The simplification of the method consists of using 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.

4.3 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 of 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.

4.3.1 Dyeing, color and fastness properties

The CIELab coordinates, K/S and whiteness degree of undyed cotton are in Table 17. The K/S of non-cationic sample is 0.73±0.08 while the whiteness degree is 75±3. The cationization treatments did not present 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.

In Table 18 are presented the color and colorimetric coordinates for dyed samples. From comparison with Table 17, 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 (APPENDIX C: Supplementary material for manuscript 3).

Table 17 – Colorimetric properties of 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}

Source: the author.

Note: data that share the same letters, in the same column, are considered statistically equals.

The conventional dyeing was used as a control sample. Two colors can be optically distinguished by the human eye if ΔE ≥ 1. When ΔE > 3 is perceived as a significant color deviation and has commercial restrictions (CHOUDHURY, 2015). According to Table 18 and Figure 21, the color deviation changed substantially with the cationic agent.

The K/S values for dyed cotton are available in Figure 21. The best K/S values were obtained for the cationic agents CHPTAC and PDDAC1. The 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 the cationic agent. These values are statistically equal. The results are above the values 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 of the PAcD molecule may have caused a barrier for the interaction with the dye. 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).

Table 18 – CIELab coordinates, color deviation (ΔE) between control and treated samples and Relative Unlevelness Index (RUI).

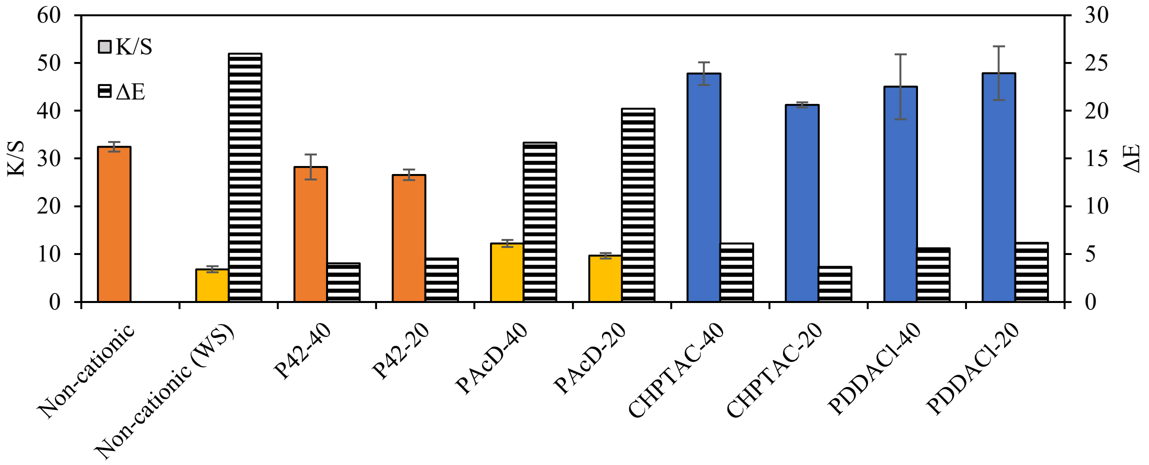
Sample	L*	a*	b*	ΔE	RUI	Color
Non-cationic	59.7 ± 0.3^{a}	$50.1\pm0.4^{a,f}$	-6.9 ± 0.4^{a}	-	0.25	▬
Non-cationic (WS)	76.2 ± 0.9^{b}	30.0 ± 0.7^{b}	-7.9 ± 0.1^{b}	26.0	0.23	▬
P42-40	61 ± 1^{a}	46 ± 1^{c}	$-6.3\pm0.4^{a,c}$	4.0	0.34	▬
P42-20	61.7 ± 0.5^{a}	46.0 ± 0.6^{c}	-6.8 ± 0.3^{a}	4.5	0.53	▬
PAcD-40	70.2 ± 0.6^{c}	37 ± 1^{d}	$-8.5\pm0.2^{b,d}$	16.7	0.43	▬
PAcD-20	72.7 ± 0.5^{d}	35 ± 1^{d}	-8.6 ± 0.1^{d}	20.2	0.35	▬
CHPTAC-40	$55.7\pm0.5^{e,f}$	54.5 ± 0.6^{e}	-5.6 ± 0.3^{e}	6.1	0.34	▬
CHPTAC-20	57.2 ± 0.2^{e}	$52.6\pm0.2^{a,e}$	$-6.1\pm0.3^{c,e}$	3.7	0.26	▬
PDDACl-40	55 ± 2^{f}	49 ± 2^{f}	-9.2 ± 0.2^{d}	5.6	1.63	▬
PDDACl-20	54 ± 1^{f}	$50\pm2^{a,f}$	-8.9 ± 0.36^{d}	6.2	1.54	▬

Source: the author.
Note: data that share the same letters, in the same column, are considered statistically equals.

RUI values are also shown in Table 18. According to Table 16, 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 affinity 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 are 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 the cationic agent. This is related to the concentration of cationic sites in the fabric. Cotton pretreated with 20 g.L^{-1} of the 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.

Figure 21 – K/S and ΔE values for dyed cationic and non-cationic cotton.



Source: the author.
Note: K/S bars with the same color are considered statistically equals.

4.3.1.1 *Washing and rubbing fastness*

The color fastness of the dyed cotton fabric against washing and rubbing are presented in Table 19. The cationization performed by PDDACl, at 40 g.L^{-1} provided excellent washing fastness, superior to conventional dyeing (Non-cationic sample). The CHPTAC-40 sample presented the same washing fastness as the 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 the cationic agent. This can be observed comparing each concentration of cationic agents P42, CHPTAC and PDDACl.

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 higher wet rubbing fastness at 20 g.L^{-1}.

Table 19 – Fastness properties of dyed cotton fabrics, treated by different cationic agents.

Sample	Washing fastness	Rubbing fastness	
		Dry	Wet
Non-cationic	3/4	5	4
Non-cationic (WS)	1/2	5	4
P42-40	2/3	5	3
P42-20	2	5	3/4
PAcD-40	1	5	3/4
PAcD-20	1	5	3/4
CHPTAC-40	3/4	5	4/5
CHPTAC-20	3	5	5
PDDACl-40	5	5	3
PDDACl-20	3	5	3

Source: the author.

Similar results were obtained by other researchers. According to Bessa et al (2019), the pretreatment with PDDACl resulted in 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.

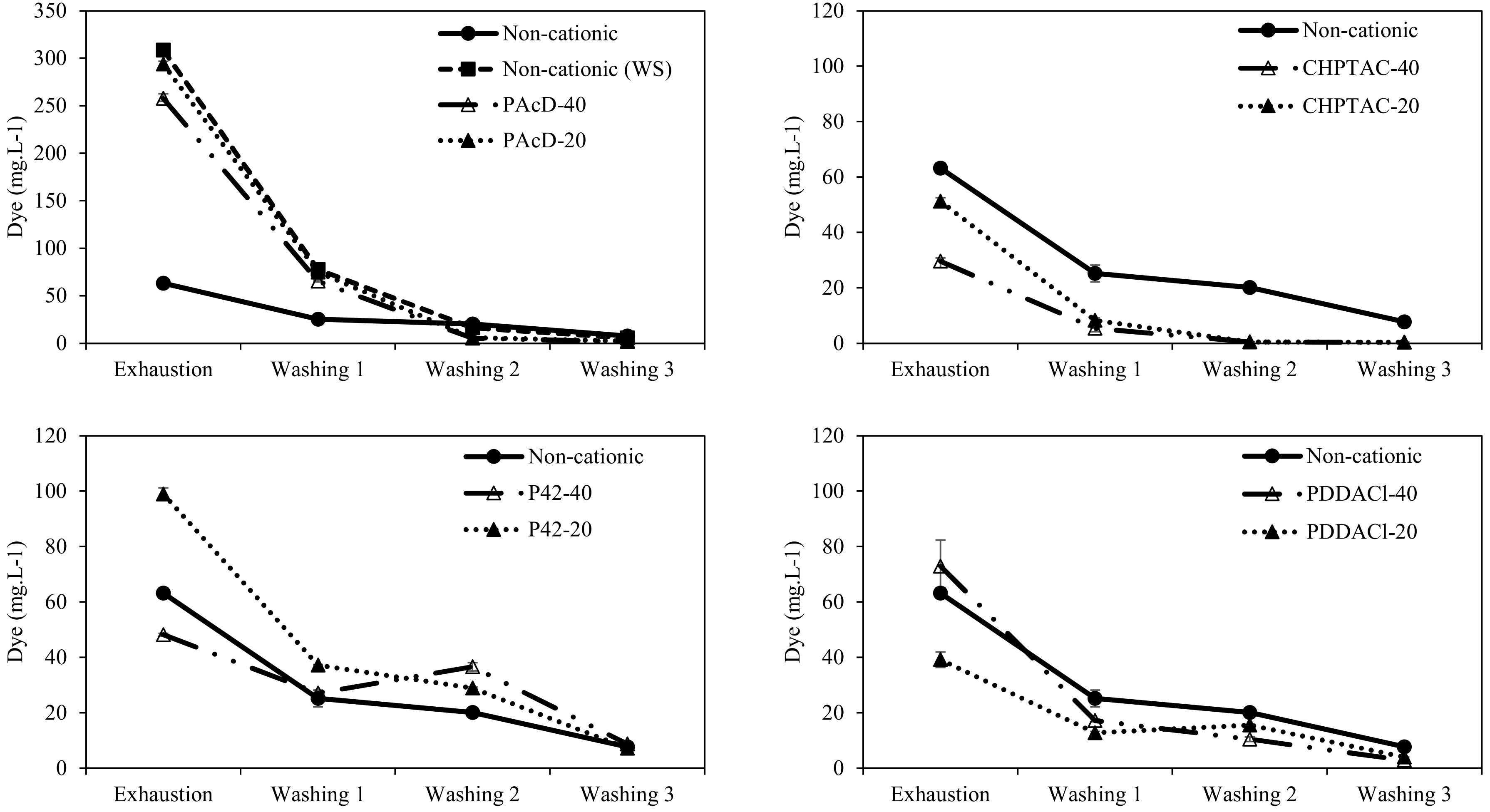
4.3.1.2 Dyeing and washing baths

The exhaustion and washing baths data for each cationic cotton are presented in Figure 22. For comparisons, conventional dyeing (Non-cationic sample) is present in each graph. The curve of the Non-cationic (WS) 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 Figure 23. Photographs of each bath, wavelength scan and calibration curve necessary for the measurement of Reactive Red 195 concentration are available in the supplementary material (APPENDIX C: Supplementary material for manuscript 3).

CHPTAC and PDDACl resulted in a 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).

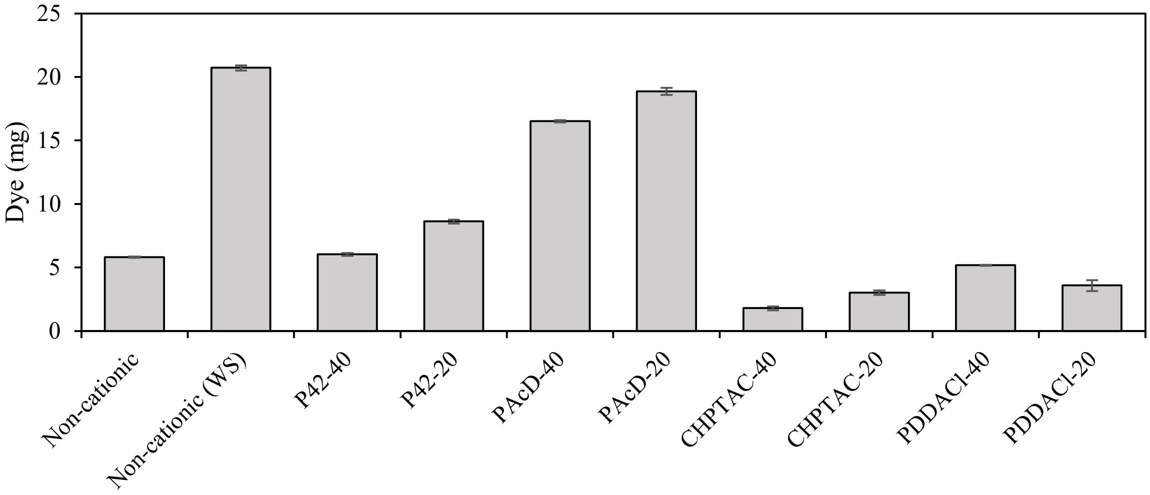
The cationic agent P42 presented similar results in comparison with the conventional dyeing, but with a higher waste of dye than CHPTAC or PDDACl. The total mass of residual dye in the baths was 6.0±0.5 mg and 8.4±0.1 mg for P42-40 and P42-20, respectively, which were very close to the conventional dyeing (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.

Figure 22 – Dye concentration in the exhaustion and washing baths.



Source: the author.

Figure 23 – Total mass of residual dye (summation of the exhaustion and washing baths).



Source: the author.

4.3.1.3 Effect of dyeing time

The progression of the dyeing process was evaluated for samples pretreated with the cationic agent at 20 g.L^{-1}. In Figure 24 is shown the color strength of the fabric, the dye concentration and the pH of the dyebath. According to Figure 24 (c), there is a sudden pH change between 18-28 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 around 18 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 Figure 24 (a) and (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 reaches equilibrium and some of the dye returns to the dyebath. The high alkalinity of the bath increased the affinity of the dye with the fabric.

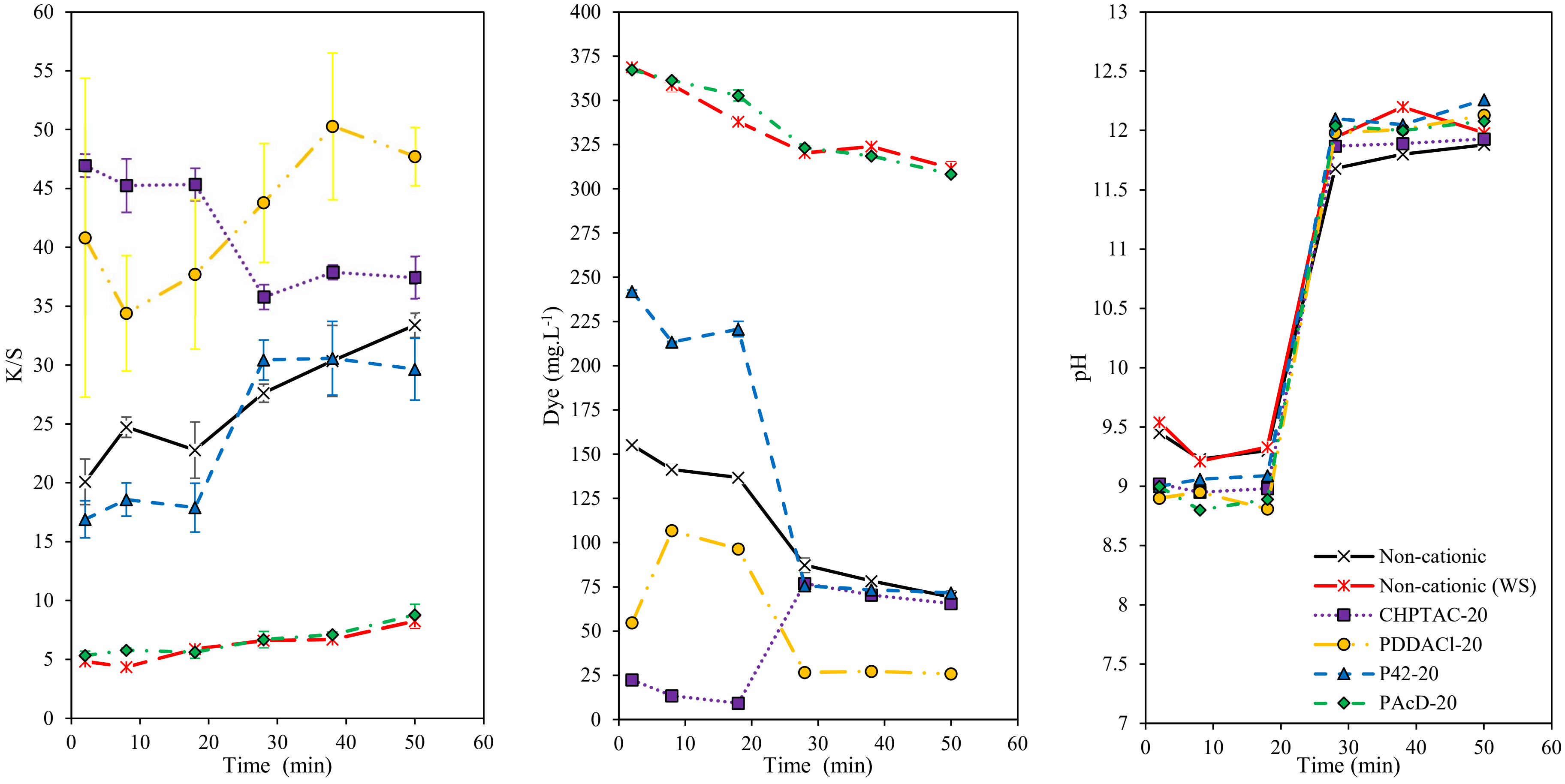
According to Table 18, the pretreatment with PDDACl resulted in dyeing with conspicuous unlevelness. This can also be seen in Figure 24 (a). The treatment with PDDACl showed a relative deviation of 5-33 % from the average. The greatest deviation occurs in the first measurement, caused by an instantaneous dye-fiber interaction. This may also be related to the presence of residual NaOH after the cationization.

In the conventional dyeing (Non-cationic sample), there is a slight increase in the K/S values at the first 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 with the cationic sites of the fabric and the new ions groups added to the dyebath. The weakly fixed dye molecules return to the dyebath after pH elevation, raising the dye concentration in the liquid phase as shown in Figure 24 (b).

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 at a concentration in the range of 4.4-13.1 $g.L^{-1}$. However, the addition of alkali decreased the exhaustion when cotton was pretreated at a concentration between 17.5-35.0 $g.L^{-1}$. 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.

Figure 24 – Variation of (a) color strength, (b) dye concentration and (c) pH in the dyebath throughout the dyeing process.



(a) (b) (c)

Source: the author.

4.3.1.4 Competitive dyeing

Table 20 shows the color properties of competitive dyeing for cationic cotton treated with 20 or 40 g.L^{-1} of the cationic agent. Photographs of dyed samples are available in the supplementary material (APPENDIX C: Supplementary material for manuscript 3). 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. Therefore, 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 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 20 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.

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

Source: the author.

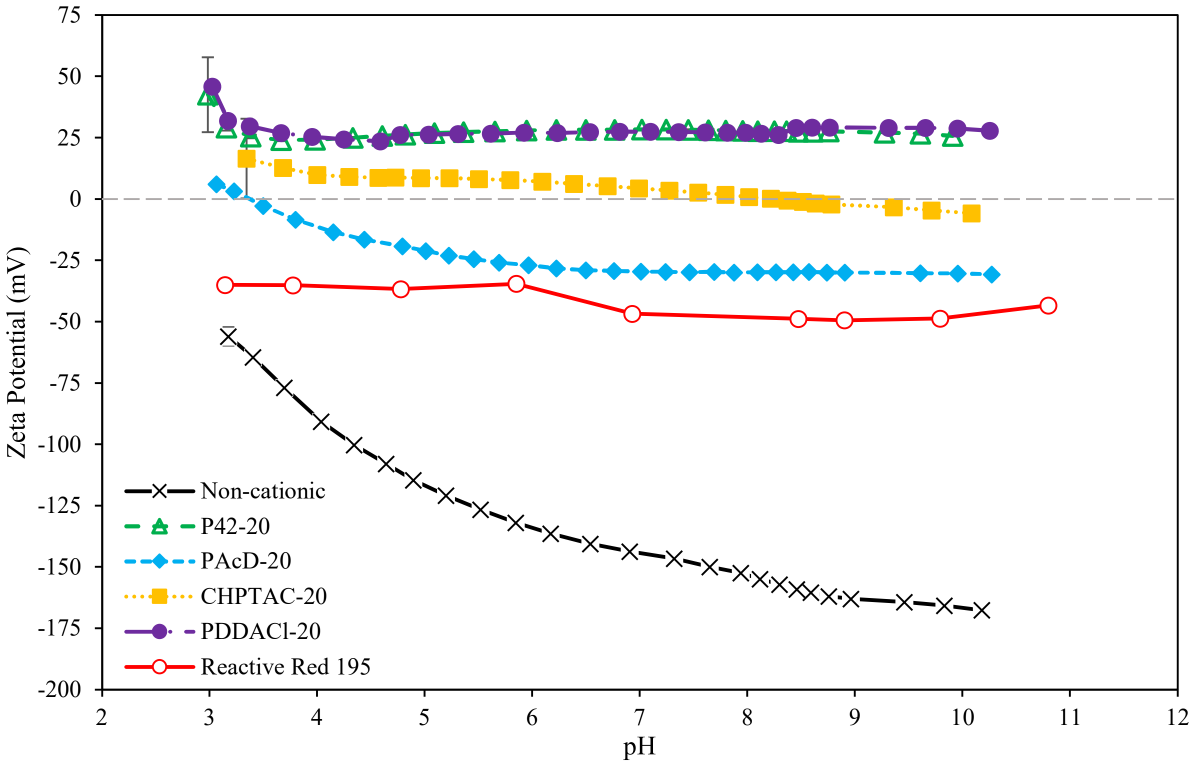
4.3.2 Characterization

According to Table 18 and Figure 21, the color properties were almost the same for dyed fabrics regardless 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.

4.3.2.1 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 25 contains the relation between zeta potential and pH for each undyed sample. The zeta potential of the Reactive Red 195 dye solution is also presented. All cationic agents substantially increased the zeta potential of the cotton fabric.

Figure 25 – Zeta potential as a function of solution pH, for cationic and non-cationic cotton fabrics and Reactive Red 195 dye solution.



Source: the author.

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 are anionic. It is estimated that only 65-70 % of anionic reactive dyes are exhausted in the cotton dyeing process (ARIVITHAMANI; GIRI DEV, 2016).

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 have a positive surface charge and above it behaves 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 Figure 24. After the addition of alkali, the pH of the dyebath raised to around 12.

The dyeings were performed above pH 8.5. 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 (ARIVITHAMANI; GIRI DEV, 2017b; ZHANG et al., 2015). The repeating unit of the PDDACl polymer has only one ammonium quaternary group. However, the repeating unit is considerably smaller than P42 and PAcD.

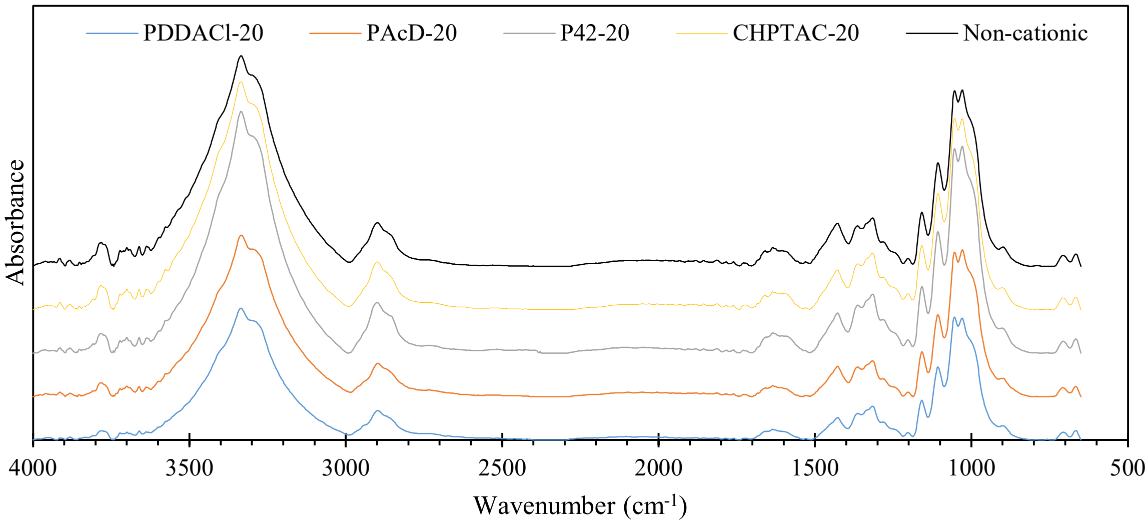
As shown in Table 18 and Figure 21, the dye-fiber interaction of the P42-20 sample was lower than PDDACl-20 and CHPTAC-20 samples. However, the zeta potential of the P42-20 samples was basically the same as the PDDACl-20 and higher than CHPTAC-20 sample. The reason for the lower dye-fiber interaction 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 0-20 $g.L^{-1}$ and bath temperature of 40 or 60 ºC. The temperature did not affect zeta potential. However, the zeta potential increased sharply with increasing the concentration of CHPTAC. Then, above 14 $g.L^{-1}$, a stable zeta potential value was obtained.

4.3.2.2 FTIR

The FTIR spectra of the fabrics before and after cationization with 20 g.L^{-1} of the cationic agent are represented in Figure 26. The spectra are nearly identical, with minor differences. The spectra show the 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.

Figure 26 – FTIR spectra of the non-cationic fabric and after cationization using 20 g.L^{-1} of each cationic agent.



Source: the author.

Table 21 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, some bands may have overlapped those belonging to the cationic agent. The spectra show a broad peak at 1674-1538 cm^{-1}. Absorption bands between 1650-1633 cm^{-1} are usually attributed to O-H vibrations of the adsorbed water (CHUNG; LEE; CHOE, 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.

Table 21 – FTIR absorption bands obtained in this paper and comparison with the data available in the literature.

FTIR signal (Wavenumber, cm^{-1})		Functional group	Reference
This paper	Literature		
3600-3000	3570-2955	O–H stretching	(MOLINA et al., 2020)
2980-2800	3000-2800	C–H stretching	(CHUNG; LEE; CHOE, 2004)
1674-1538	1650-1633	O–H bending of adsorbed water	(CHUNG; LEE; CHOE, 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)

Source: the author.

4.3.3 Mechanism for cationization

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 Scheme 6-12. The cationic agent tends to interact with the primary cellulosic hydroxyl groups because they are more accessible and reactive (WAKELYN et al., 2006). The beginning of the cationization process is the formation of anionic cellulose, this step is the same for each cationic agent and is presented in Scheme 6. Then the anionic cellulose reacts with the cationic agents by different mechanisms.

The mechanism of cationization of cotton with CHPTAC was already discussed by some researchers (ARIVITHAMANI; GIRI DEV, 2016, 2017b; FARRELL; ORMOND; GABLER, 2015; HAUSER; TABBA, 2001; WANG et al., 2009). In the presence of NaOH, the CHPTAC is firstly converted into 2,3-epoxypropyl trimethylammonium chloride (EPTAC). The EPTAC is very reactive so it forms a covalent bond with the cellulose anion. The reaction mechanism is shown in Scheme 7.

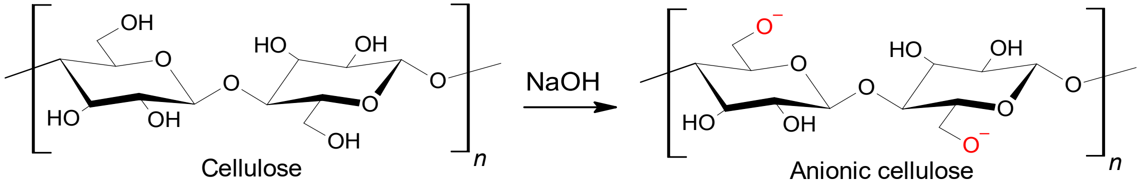
Despite the efforts dedicated to the literature review, no publication was found regarding the mechanism of cationization with PDDACl or P42. Jareansin et al. (2019) published the mechanism for cationization with diallyldimethylammonium chloride, the monomer of PDDACl. However, the authors used potassium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

The mechanism proposed for the cationization of cotton with P42 and PDDACl are similar and are presented in Scheme 8 and Scheme 9. The quaternary ammonium groups of the polyelectrolytes interact with the cellulose anion to form an ionic bond. By nucleophilic substitution, the chlorine atom is removed so that the oxygen binds with the cationic nitrogen.

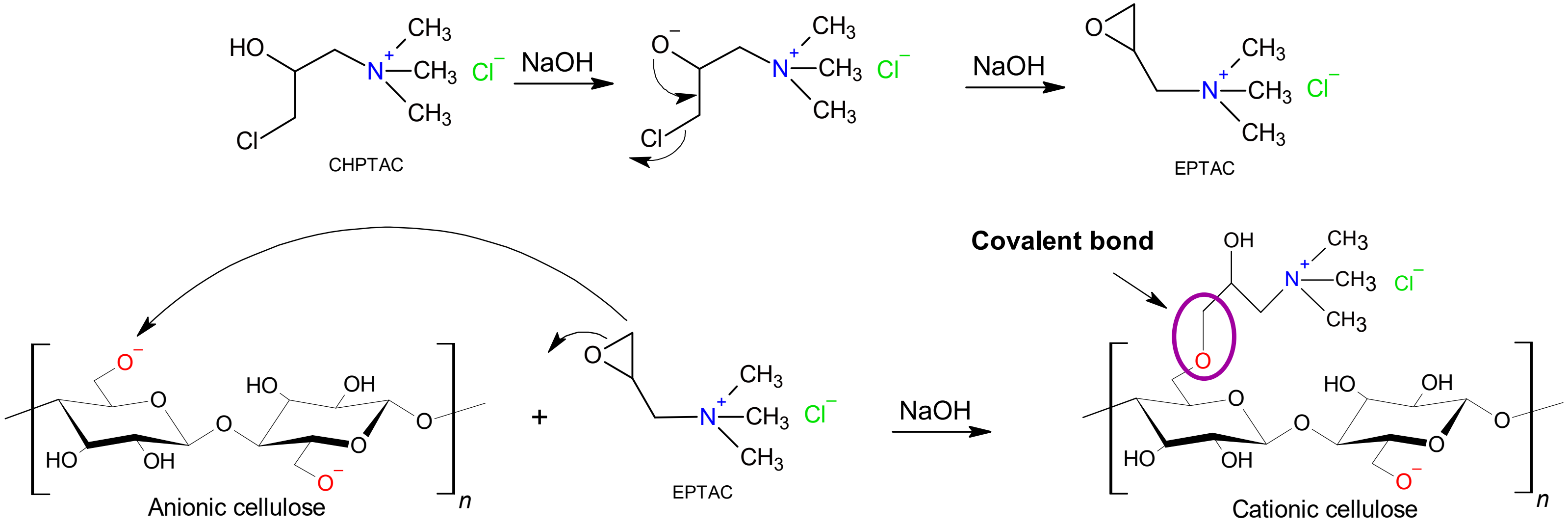
The fixation of the Reactive Red 195 dye on cationic fiber can be achieved by an ionic bond between the cationic nitrogen and the oxygen anion from the vinyl sulfone reactive group (ARIVITHAMANI; GIRI DEV, 2017b). Considering that cationization may not occur completely, the dye fixation can also occur 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 Scheme 10-12.

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 to interact 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.

Scheme 6 – Formation of anionic cellulose in alkaline medium.



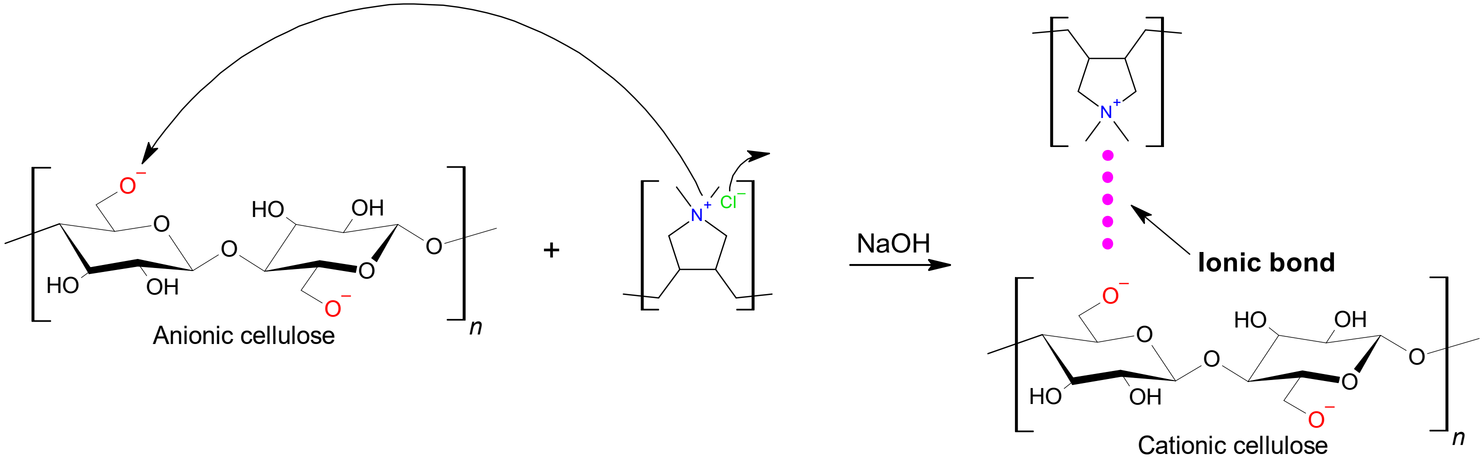
Scheme 7 – Cationization of cellulose with CHPTAC.



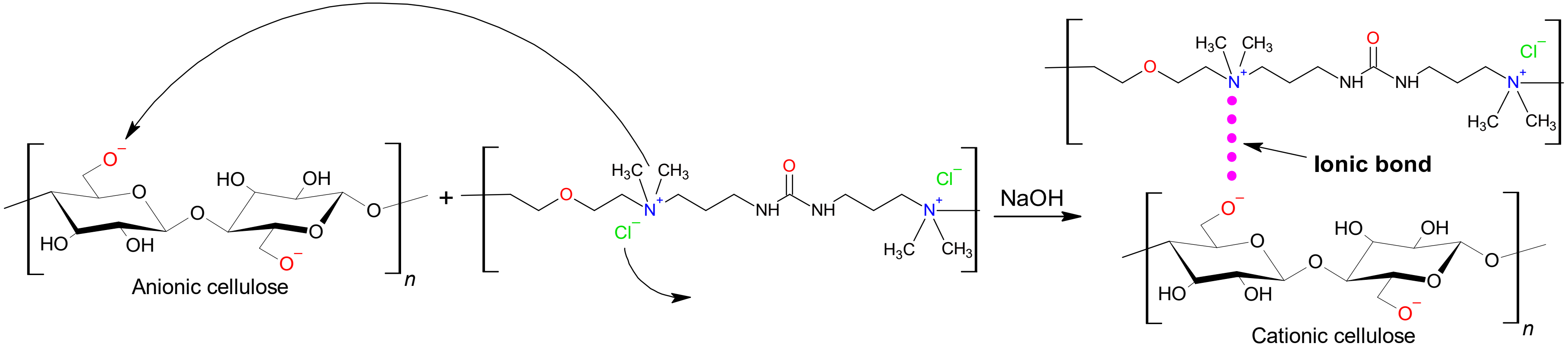
(1)

(2)

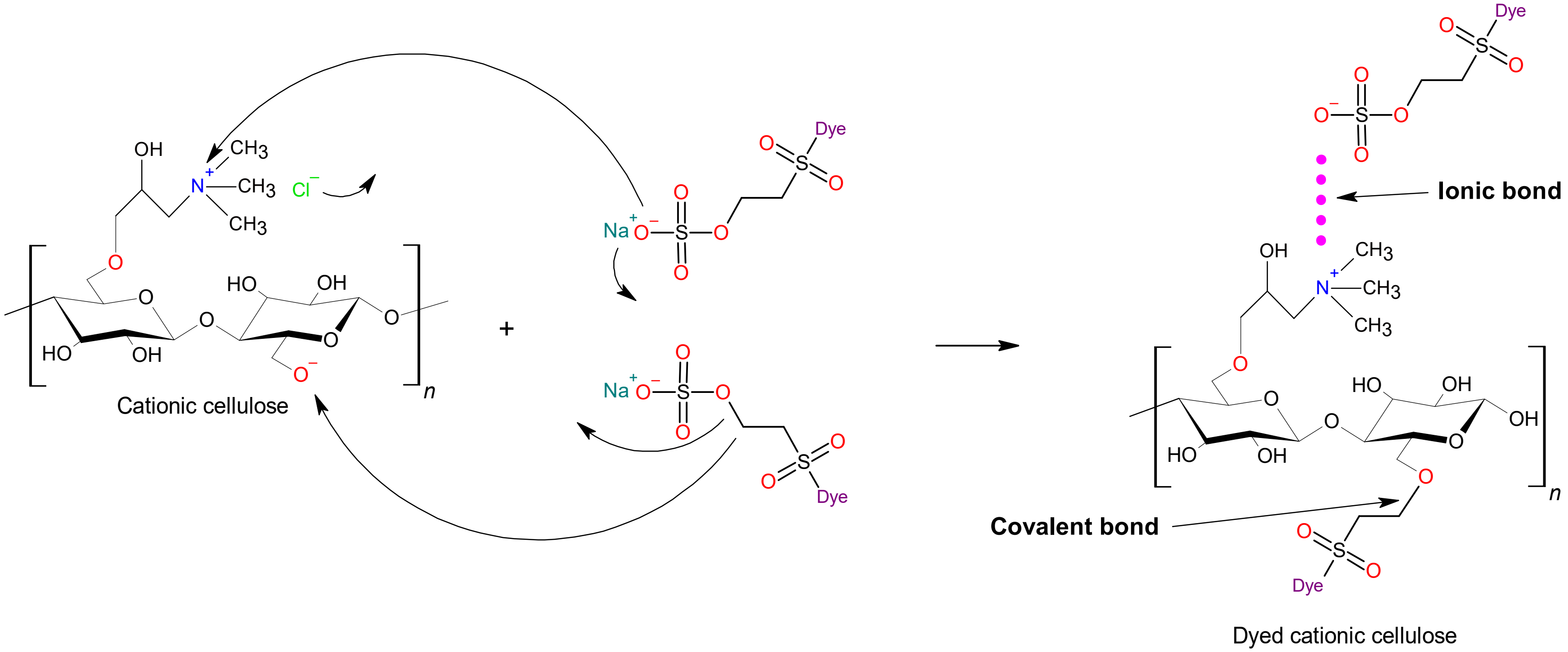
Scheme 8 – Cationization of cellulose with PDDACl.



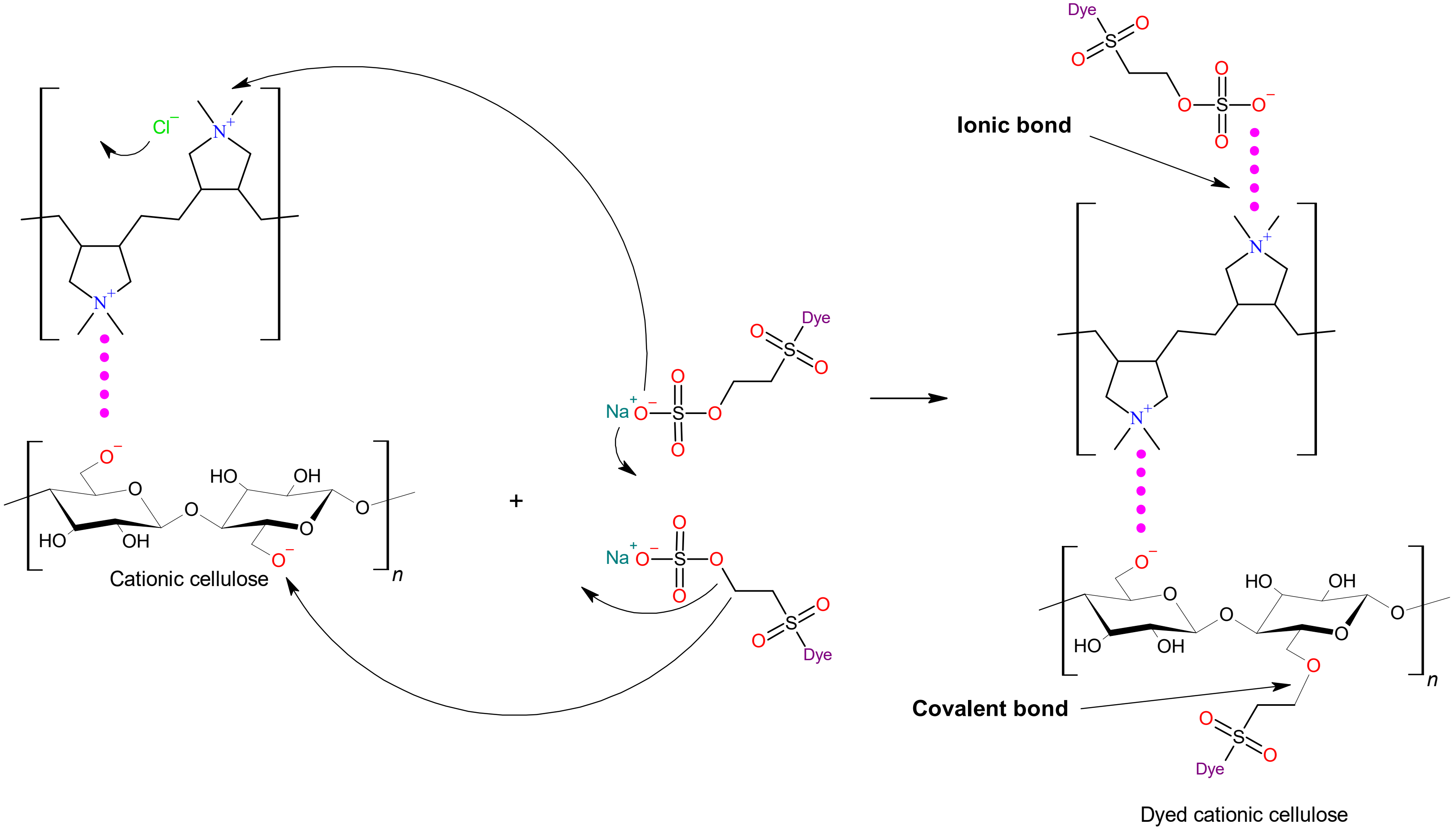
Scheme 9 – Cationization of cellulose with P42.



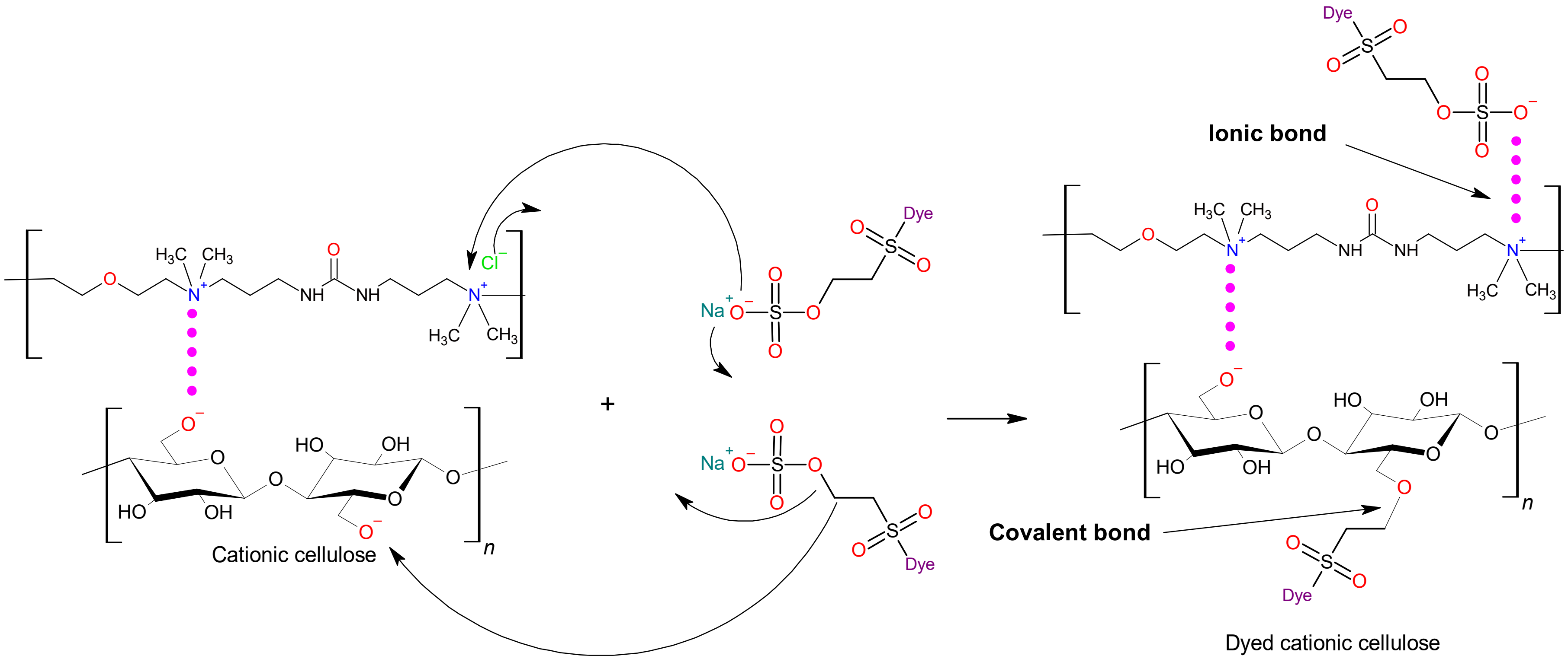
Scheme 10 – Fixation of Reactive Red 195 on cotton cationized with CHPTAC.



Scheme 11 – Fixation of Reactive Red 195 on cotton cationized with PDDACl.



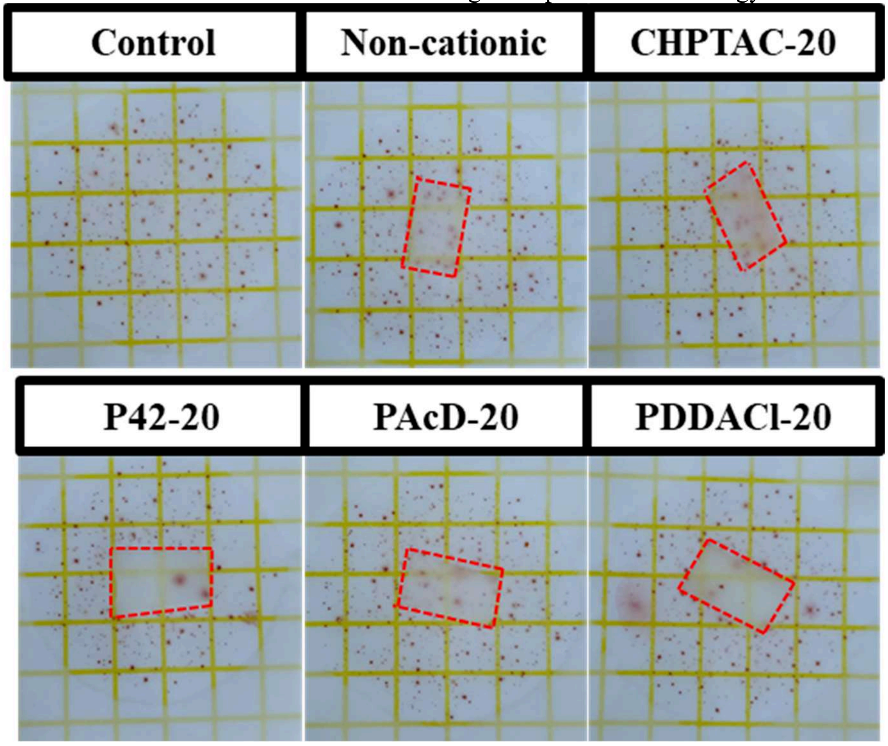
Scheme 12 – Fixation of Reactive Red 195 on cotton cationized with P42.



4.3.4 Bactericidal effect

The estimative of the bactericidal efficacy was evaluated according to Figure 27. The red dots are colonies of microorganisms. The control samples testified that the 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 activity than samples CHPTAC-20 and PAcD-20.

Figure 27 – Estimative of the bactericidal effect using a simplified methodology of the Petrifilm AC.



Source: the author.

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 following other published results. 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.

4.4 CONCLUSION

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 the 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, needs 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 enhanced 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 commercial cationic agent, with a low concentration: 20 % in H_2O against 65 % of CHPTAC. Besides, PDDACl and P42 presented bactericidal activities.

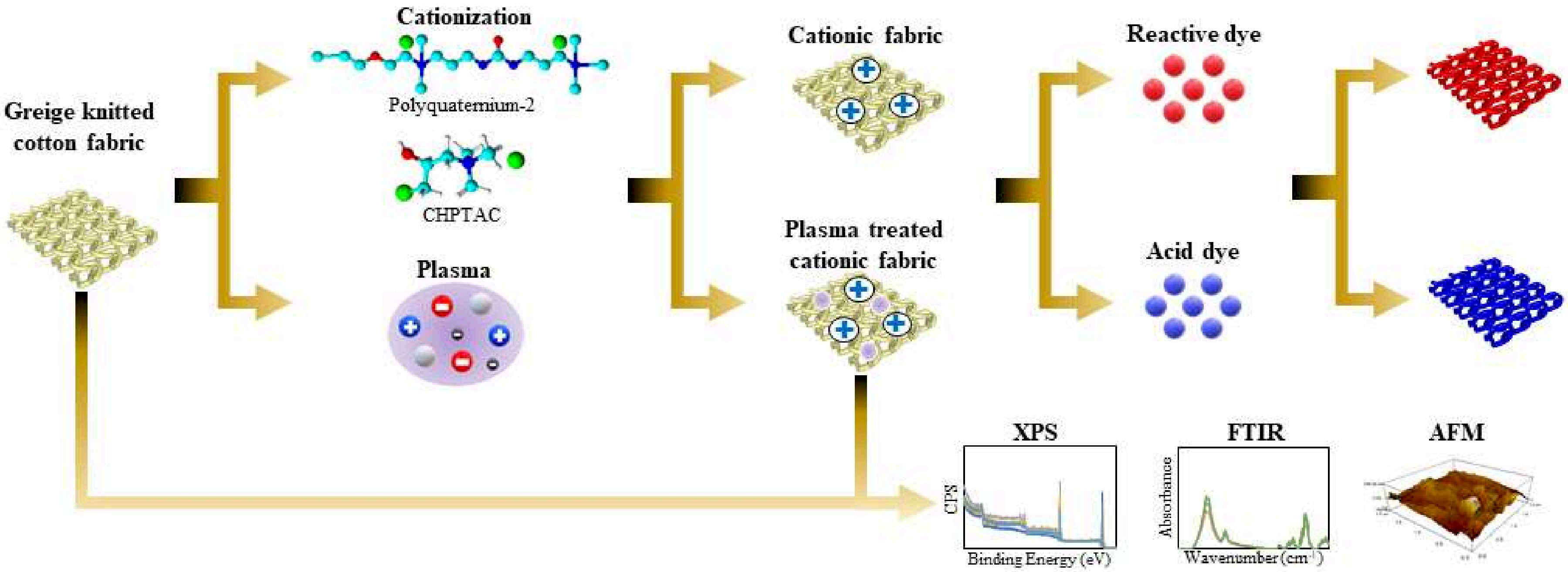
The pH is a fundamental control factor for the dyeing of cationic fabrics. The samples cationized with P42 and PDDACl benefited from the higher pH due to the cellulose ionization, which increases the interaction with the cationic group. However, the opposite occurred with the CHPTAC as the higher pH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

5 SURFACE FUNCTIONALIZATION OF GREIGE COTTON KNITTED FABRIC THROUGH PLASMA AND CATIONIZATION FOR DYEING WITH REACTIVE AND ACID DYES

Abstract: Dyeing cotton fabrics with anionic dyes produces high effluent loads and requires a considerable amount of water and energy due to the electrostatic repulsion with cellulose. Therefore, several approaches have been researched to increase the efficacy of cotton dyeing. One is the cationization, which adds cationic sites to the cellulose. Another is the treatment of the cotton surface with plasma. In this paper, the combination of both techniques was investigated. Two commercially available cationic agents were used: 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC) and poly[bis(2-chloroethyl) ether-alt-1,3-bis[3-(dimethylamino)propyl]urea] quaternized, a novel cationic agent also known as Polyquaternium-2 (P42). The plasma treatment was performed using a dielectric barrier discharge atmospheric plasma facility, helium was used as seed gas and 1.5 % of oxygen was injected. The cationic and plasma treated samples were dyed using Reactive Red 195 and Acid Blue 260 dyes. The effect of the treatments was evaluated by different characterization techniques such as X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM). The plasma treatment slightly increased the light fastness for some samples, but the cationization tends to prevail over the plasma treatment. The best results were attributed to the samples pretreated by CHPTAC, which presented the highest K/S and lowest unlevelness for samples dyed with reactive and acid dyes. Besides, the cationic agent P42 also presented good results, with colorimetric values similar to the conventional dyeing. Therefore, the cationic agent P42 offers a viable alternative to the use of the commercial cationic agent CHPTAC.

Keywords: Cationic agent. Polyquaternium-2. 3-chloro-2-hydroxypropyl trimethyl ammonium chloride. Plasma treatment. Acid dyeing. Reactive dyeing.

Graphical abstract:



5.1 INTRODUCTION

The plasma treatment is considered an environmentally friendly method for surface treatment as it reduces the use of chemicals in the textile processes (FENG et al., 2020). Surface treatment of textile fibers and fabrics has been performed with plasma since the 1960s (PALASKAR; KALE; DESHMUKH, 2020). Since then the technique has been gaining attention from many researchers (MORENT et al., 2008; ZILLE; OLIVEIRA; SOUTO, 2015). Moreover, plasma technology has recently attracted more attention from the industrial sector due to the development of large-scale equipment (MCCOUSTRA; MATHER, 2018).

Plasma can modify the surface of the fibers in different ways, including grafting, etching and polymerization (SUN et al., 2018). These alterations are restricted up to a few nanometers from the textile surface and result in no change to the bulk properties of the materials. Plasma treatment is responsible for roughening the surface, which causes changes in the coefficient of friction and yarn strength. Although, from a chemical point of view, the plasma treatment enhances the functionalization of the fiber and interaction with polymeric materials, such as cellulose (AHMED et al., 2020; NEGULESCU et al., 2000; PALASKAR; KALE; DESHMUKH, 2020).

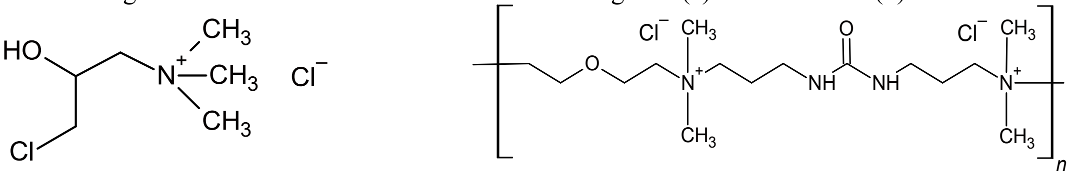
Cationization is another technique used for the surface treatment of textiles. It is a technology that uses a cationic reagent to raise the zeta potential of the cellulosic fabrics. Cellulose is anionic in nature. During the process, cationic groups interact with cellulose, which acquires a cationic behavior (AKTEK; MILLAT, 2017). This technique enhances the dyeing properties since most dyes are anionic (FAROUK; SHARAF; ABD EL-HADY, 2013). Cationization is commonly used to improve the dye uptake in reactive dyeing without the need for salts in the process. The cationization process is also used to enhance functional properties in the fabrics, such as antimicrobial activity (KIM et al., 2016; REHAN et al., 2017), ultraviolet protection (KAMAL ALEBEID; ZHAO, 2015), and hydrophobic properties (ABD EL-HADY; SHARAF; FAROUK, 2020).

Functionalization using a cationic agent with other types of treatment has been reported in the literature, such as ultrasonic treatment (KAMEL et al., 2009; ZHANG et al., 2015). Helmy et al. (2017) studied plasma-induced graft polymerization of diallyldimethylammonium chloride on cotton, to dye cotton with acid dye. Their approach led to enhanced acid dye uptake in cotton. Patiño et al. (2011) used reactive dye on cotton functionalized through corona plasma treatment and by cationization with CHPTAC. They reported increased hydrophilicity for cotton treated by plasma followed by cationization.

Existing literature mainly focuses on functionalizing ready for dyeing cotton fabrics that are already scoured and bleached.

A typical cationization process involves the reaction of 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC) to incorporate cationic charges into cotton (AKTEK; MILLAT, 2017). However, there are some limitations to the use of CHPTAC on an industrial scale due to concerns about the safety of the reagent (ROY CHOUDHURY, 2014). Therefore, many researchers focused on the application of novel and safer cationic agents (ARIVITHAMANI et al., 2014; GIACOMINI; DE SOUZA; DE BARROS, 2020; SAHITO et al., 2015). In this research, the cationization of cellulose was performed by using a novel cationic agent: Poly[bis(2-chloroethyl) ether-alt-1,3-bis[3-(dimethylamino)propyl]urea] quaternized (P42), also known as Polyquaternium-2. P42 is a commercially available hypotoxic cationic polymer and has been commonly used in the cosmetic industry (CHEN et al., 2016; KUMAR et al., 2016). CHPTAC was also used in this research since it has been widely used for the cationization of cotton fabric (ARIVITHAMANI; DEV, 2017). The chemical structure of the cationic agents is given in Figure 28.

Figure 28 – Chemical structure of the cationic agents: (a) CHPTAC and (b) P42.



(a) (b)

Source: the author.

Reactive and acid dyes were used for dyeing the cationic fabrics. Reactive dyes are mostly used for dyeing cotton because they are environmentally safe and have good fastness properties (CHATTOPADHYAY; CHAVAN; SHARMA, 2007). Acid dyes are anionic dyes, popular for dyeing fabrics with positive charges via ionic bonding. However, acid dyes have inferior substantivity to cellulosic fibers due to the absence of positive sites. Therefore, many researchers are making efforts for providing cationic groups to cellulosic fabrics (HELMY; HAUSER; EL-SHAFEI, 2017; PATIL; MAITI; ADIVAREKAR, 2019; REHAN et al., 2020). The possibility of using a new class of dyes would bring a new range of colors and brightness to cotton fabrics.

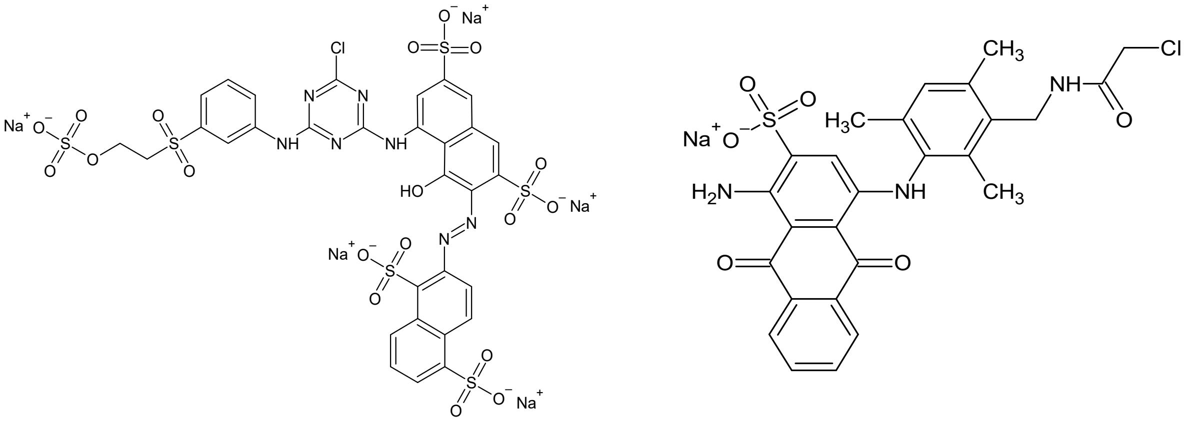
This research focuses on the pretreatment of greige cotton fabrics using plasma and two cationic agents, consequently promotes a sustainable approach for dyeing cotton fabrics at the greige stage as it eliminates conventional scouring and bleaching processes, which use a high amount of water and chemicals. It is estimated that about 32.5 L of water per kg of fabric are used in the scouring process, while bleaching requires about 13.8 L. It results in an average amount of 46.3 L of water necessary for conventional pretreatment of 1 kg of greige cotton fabric (GHALY et al., 2013). The plasma treatment is a dry process, therefore the approach performed in the present paper requires only 30 L of water for cationization. The proposed process results in saving 16.3 L of water per kg of pretreated fabric and consequently reduces the amount of effluent generated.

5.2 EXPERIMENTAL PROCEDURE

5.2.1 Materials

The greige cotton single jersey knitted fabric (160 gsm) was purchased from Pemgir Malhas (Brazil). Cotton was used because it is the most common cellulosic fiber in the world (GIACOMINI; DE SOUZA; DE BARROS, 2020). The commercial cationic agent CHPTAC solution (65 wt% in H_2O) was supplied from Werken Química (Brazil). The P42 solution (62 wt% in H_2O) was purchased from Sigma-Aldrich. The dyes C.I. Reactive Red 195 and C.I Acid Blue 260 (chemical structures shown in Figure 29) were supplied from Color Química (Brazil). Ecodyeing A 230, Ecodyeing IR 4, Stabplex EP 243 and RW 710 were respectively used as a non-ionic detergent, leveling agent, peroxide stabilizer and anionic detergent and were also supplied from Werken Química. Compressed helium gas was purchased from Arc3 Gases and compressed oxygen from Airgas. All other chemicals were general laboratory grade.

Figure 29 – Chemical structure of (a) Reactive Red 195 and (b) Acid Blue 260.



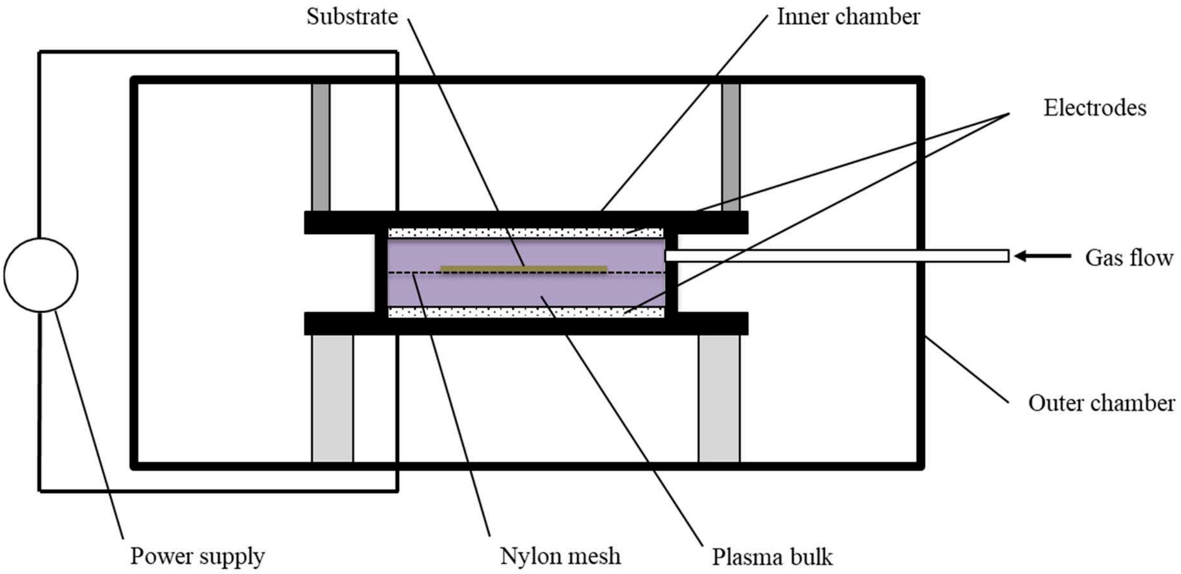
(a) (b)

Source: the author.

5.2.2 Plasma treatment

A laboratory-scale atmospheric pressure plasma generator was used for the surface treatment of cotton fabrics. The dielectric barrier discharge (DBD) atmospheric plasma facility was designed by the Wilson College of Textiles, North Carolina State University and includes an inner chamber and an outer chamber. A schematic drawing of the experimental facility is shown in Figure 30. The outer chamber is used for ventilation and filtering UV light generated from plasma discharge. The inner chamber contains two parallel copper electrodes, each embedded within a polycarbonate insulator, where plasma is generated. The inner chamber has an active exposure area of approximately 60 x 60 cm between the two copper electrodes with a 5 cm gap separation (MATTHEWS; MCCORD; BOURHAM, 2005). The fabrics were submitted for plasma treatment before cationization and dyeing. The sample was placed on a suspended nylon mesh for complete exposure to plasma on both sides of the surface. The parameters for plasma treatment were chosen based on previous publications (GAWISH et al., 2008; KRAMAR et al., 2018; SUN et al., 2018). Helium was used as seed gas at a flow rate of 20 $L.min^{-1}$ and 1.5 % oxygen was injected. For generating plasma, 8 power supplies are connected (Pyramid, model PS-52KX), which provides alternating current to direct current power conversion. The exposure time and power output were 135 s and 15V, respectively.

Figure 30 – Schematic drawing of the plasma treatment facility.



Source: the author.

5.2.3 Cationization, bleaching and dyeing

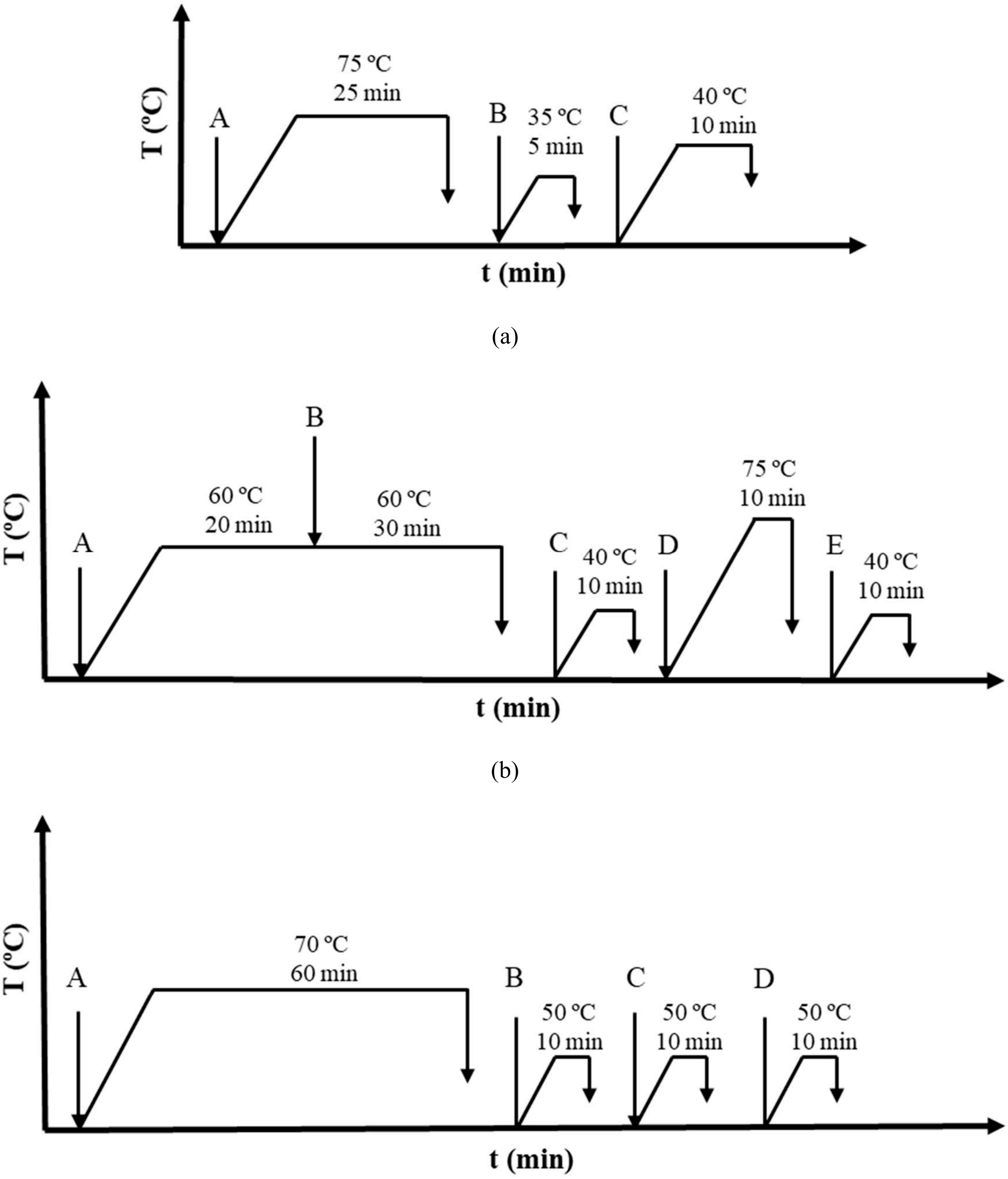
The fabrics were cationized, bleached and dyed by exhaustion method, using an Ahiba Nuance Infrared Laboratory Dyeing Machine (Datacolor International). The cationization and dyeing processes are summarized in Figure 31. Letters A, B, C and D represent dyeing and washing baths. The reagents used in each bath are shown in Table 22. The material-to-liquor ratio was 1:10 for all experiments and the bath agitation was maintained at 40 rpm throughout the process.

Cationic cellulose was prepared with a solution containing 2 g.L^{-1} of nonionic detergent, 20 g.L^{-1} of cationic agent and 10.5 mL.L^{-1} of 50 % NaOH. The solution was mixed with the fabric sample and inserted into the equipment, heated at a rate of 3 ºC.min^{-1} until 75 ºC and was maintained at that level for 25 min. After cationization, two washing baths were performed. The first bath was carried out with a solution of 0.5 g.L^{-1} of 85 % formic acid, at 35 °C for 5 min. Formic acid had the function to remove undesirable odors from the cationization process (FARRELL; ORMOND; GABLER, 2015). The second bath was done with deionized (DI) water, at 40 °C for 10 min.

The reactive dyeing was performed according to the recipe provided by the CHPTAC supplier. The reactive dyebath was done through a solution of 2 g.L^{-1} of leveling agent, 0.4 % owf (over weight of fiber) of Reactive Red 195 dye and 2.1 g.L^{-1} of sodium carbonate. 60 g.L^{-1} of NaCl was added to the bath for non-cationic samples. The dyebath and fabric were placed in

150 mL canisters for heating at 3 °C.min^{-1} until it reached 60 °C, maintaining at that temperature for 50 min. After dyeing, three washing baths were performed to remove the non-fixed dye. The first and third baths were done with DI water at 40 °C and 10 min. The second washing bath was carried out with 1.2 g.L^{-1} of 85 % formic acid solution and 1.0 g.L^{-1} of anionic detergent, maintained at 75 °C for 10 min.

Figure 31 – Scheme of the (a) cationization, (b) reactive and (c) acid dyeing processes.



(a)

(b)

(c)

Source: the author.

Acid dyeing was prepared using a dyebath solution composed solely with acid dye at 0.4 % owf, adjusted to pH 4.5 with a formic acid solution. Then, three consecutive washing processes were performed at 50 °C and 10 min with DI water, except for the second bath which was performed with a solution of 1.0 g.L^{-1} of anionic detergent.

Table 22 – Inputs used in the cationization, reactive and acid dyeing processes.

Bath	**Cationization**		**Reactive dyeing**		**Acid dyeing**	
	Input	**Dosage**	**Input**	**Dosage**	**Input**	**Dosage**
A	Cationic agent 50 % NaOH Nonionic detergent	20 g.L^{-1} 10.5 mL.L^{-1} 2 g.L^{-1}	Levelling agent Dye NaCl^{a} Na_2CO_3	2 g.L^{-1} 0.4 % owf 60 g.L^{-1} 2.11 g.L^{-1}	Dye	0.4 % owf
B	Formic Acid	0.5 g .L^{-1}	DI water	-	DI water	-
C	DI water	-	Formic acid Anionic detergent	1.2 g.L^{-1} 1.0 g.L^{-1}	Anionic detergent	1.0 g.L^{-1}
D	-	-	DI water	-	DI water	-

Source: the author.

Bleaching was performed in greige cotton for conventional dyeing comparison. The greige cotton was submitted to a solution containing 1 g.L^{-1} of nonionic detergent, 8 mL.L^{-1} of 50 % NaOH solution, 1 g.L^{-1} of peroxide stabilizer and 10 mL.L^{-1} of 35 % H_2O_2 solution. The bath was poured into the dyeing equipment and heated at a rate of 2 ºC.min^{-1} up to 95 ºC and was kept at this temperature for 45 min. The bleached fabric was washed using 1 g.L^{-1} of nonionic detergent solution at 60 ºC for 10 min.

5.2.4 Evaluation of dyed cotton fabric

The colorimetric properties of the fabrics were measured by X-rite reflectance spectrophotometer, model Color i7, using 25 mm aperture size, illuminant D65 and 10° standard observer. The CIELab color coordinates and color strength (K/S) values were determined for untreated, pretreated and dyed cotton fabrics. The whiteness was measured according to the Berger degree (PUEBLA, 2006). The fabric samples were folded twice to give a total of four layers and one measurement was taken at each layer. The collected data was an average of each layer. K/S was calculated according to the Kubelka-Munk equation, Eq. 10:

$$K/S = \frac{(1-R)^2}{2R} \qquad \text{Eq. 10}$$

Where R is the reflectance, K is the absorption coefficient, and S is the scattering coefficient. The effective K/S value was calculated by the summation of the K/S values at 10 nm intervals from the wavelength of 360–700 nm (FU et al., 2013).

The relative unlevelness indices (RUI) were obtained by using the reflectance values over the spectrum range of 390–700 nm at intervals of 10 nm (CHONG; LI; YEUNG, 1992; TANG et al., 2017). Eight randomly selected spots on the dyed fabric were considered. RUI is calculated according to Eq. 11 and Eq. 12:

$$S_\lambda = \frac{\sqrt{\sum_{i=1}^{n}(R_i - \bar{R})^2}}{n-1} \qquad \text{Eq. 11}$$

$$RUI = \sum_{\lambda=390}^{700} \left(\frac{S_\lambda}{\bar{R}}\right) V_\lambda \qquad \text{Eq. 12}$$

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 $\bar{R}$ are the reflectance values of the ith measurement and the mean, respectively. V_λ is the photopic relative luminous efficiency function, which is related to the human sensitivity of colors. V_λ data are available in the work of Guild (1932). The visual appearance of levelness followed the suggested interpretation of the RUI values listed in Table 23.

The statistical significance of the color properties was assessed by One-way ANOVA with a confidence level of 95 %. Tukey procedure was used for comparing pairs of means. The analysis was performed using the statistical software BioEstat 5.3 (AYRES et al., 2007).

The fastness properties were tested according to AATCC standard methods (AMERICAN ASSOCIATION OF TEXTILE CHEMISTS AND COLORISTS, 2010). The rubbing fastness was tested according to AATCC Test Method 8-2007, using a manual horizontal crockmeter. The washing fastness was tested according to AATCC Test Method 61-2009 (method 2A). The fabric samples were washed with an ATLAS LEF Launder-Ometer.

The light fastness was tested according to AATCC Test Method 16-2004 (option 3). The samples were exposed for 20 and 40 hours to simulated indoor lighting by using a xenon lamp in an Atlas Ci3000+ Weather-O-meter. Fading and staining due to rubbing, washing and light were measured with the spectrophotometer and rated according to the gray scale.

Table 23 – Interpretation of RUI values.

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

Source: Chong, Li and Yeung (1992).

5.2.5 Characterization

The surface chemistry of the fabrics was investigated using a Fourier Transform Infrared spectrometer with built-in diamond ATR crystal (FTIR, Nicolet iS50, Thermo Fisher Scientific). The FTIR spectra were obtained with 4 cm^{-1} of resolution and 64 scans per sample. The surface chemical composition of the samples was also analyzed with an X-ray photoelectron spectrometer using a PHOIBOS 150 hemispherical analyzer (XPS, SPECS FlexMod XPS). The measurements were performed at a base pressure in the range of 10^{-10} mbar with Mg kα excitation source (1254 eV). The takeoff angle was at normal to the surface. The X-Ray incidence angle was ~30° from the surface and ~60 from the source to the analyzer. The energy calibration was established by referencing to adventitious Carbon (C1s line at 285.0 eV). Data reduction was accomplished using CasaXPS. Curve fitting was achieved for three chemical states and constraints were used for peak position and full width half maximum (FAIRLEY, 2009).

The effect of the plasma treatment on the morphology of the samples was studied using an atomic force microscope operating in tapping mode (AFM, Asylum Research MFP-3D, Oxford instrument). The surface roughness of the samples was evaluated by the root mean square (RMS) values of the distribution of heights in the topographical images, according to Eq. 13:

$$RMS = \sqrt{\frac{1}{n}\sum_{i=1}^{n} {y_i}^2} \qquad \text{Eq. 13}$$

Where n is the number of samples along the assessment length and y_i is the height measured from the mean line (GADELMAWLA et al., 2002).

5.3 RESULTS AND DISCUSSION

5.3.1 Color properties for pretreated and dyed fabrics

The CIELab color space coordinates and color strength were measured for all samples. The whiteness degree and RUI were measured only for undyed and dyed samples, respectively. The data is shown in Table 24. The fabrics were categorized according to the number of plasma treatments and the chemical treatment adopted. The plasma treatment was performed once (before cationization) or twice (before cationization and before dyeing). The bleached sample was considered as a control since it is used traditionally for the dyeing of cotton fabrics. Photographs of dyed samples are available in the supplementary material (APPENDIX D: Supplementary material for manuscript 4).

The greige cotton has a natural yellowish coloration due to the proteins and the flavones pigments of the cotton flowers (YIN et al., 2015). The cationization reduced 19 % and 23 % of the yellow color (b* coordinate) of the substrate when treated with P42 and CHPTAC, respectively. The presence of sodium hydroxide in the cationization process was responsible for the solubilization of waxes in the bath. However, it can be seen from the b* coordinate analysis of the substrates that bleaching was the best process for the removal of the natural pigments. The whiteness degree and L* coordinate increased for all pretreated fabrics, especially for the bleached substrate, which had the lowest b* coordinate (4.7±0.1). The yellowish impurities can be easily removed with the bleaching process. Hydrogen peroxide is the most widely used method for bleaching (ALTAY et al., 2019). Other impurities, such as waxes and ashes, also affect the color.

The plasma treatment had little influence on the color of the substrate. For fabrics cationized with P42, the whiteness degree was statistically equivalent for samples treated with or without plasma. However, the degree of whiteness changed significantly when the plasma was applied after cationization with CHPTAC. Without plasma treatment, the whiteness degree for sample cationized with CHPTAC was 22.1±.0.5 and after the first plasma treatment was 21.1±0.8, these values are statistically equal. Then the whiteness degree increased to 23±1 after the second plasma treatment, which was statistically different from the sample without plasma. The reason is probably related to the better accessibility of the plasma in the cellulose fiber after the removal of waxes during cationization.

The reactive dyeing in the fabric cationized with P42 presented the same color strength as the control sample (K/S was 29.9±0.6 for control and 30±1 for cationic fabric). The best result was achieved for the sample cationized with CHPTAC, with a gain of around 10 % in relation to the a* coordinate. The plasma treatment did not significantly change the color properties of reactive dyed fabrics cationized with CHPTAC, but it slightly decreased the a* coordinate when P42 was the cationic agent, from 44.8±0.7 to 43.0±0.8 after applying the plasma two times. The effect of cationization prevailed over plasma. A similar observation was obtained by Patiño et al. (2011).

For a detailed comparison, the greige cotton fabric treated solely by plasma (e.g., without the cationization step) was dyed with Reactive Red 195. The result was an uneven dyeing. Due to the low quality of the dyeing and the high presence of stains, the color properties of this sample were not measured, except for the RUI value, which was 1.28. This is considered as conspicuous unlevelness according to Table 23. In comparison, the RUI values of the plasma treated cationic samples were 0.22 and 0.26 (e.g., good levelness) for CHPTAC and P42 pretreatments, respectively.

The cationization step was necessary for the complete removal of the waxes, which gives the cotton sufficient hydrophilicity for dyeing. Cotton is composed of 90-96 % cellulose, 4-10 % correspond to impurities in the fiber. These impurities correspond to waxes, resins, hemicellulose and proteins (KOLÁŘOVÁ et al., 2013; MA et al., 2017; SUN; QIU, 2012). They are mainly found at the outermost layers of the cotton, in the cuticle layer and the primary wall. The surface layers protect the fibers against the environment during growth, but also are responsible for poor hydrophilicity (ZHU; LIU; GAO, 2017). All of these impurities could not be removed by plasma treatment but were removed in the cationization process.

The cationization increased substantially the color strength when dyed with Acid Blue 260 dye. The K/S value of the control samples was 3.2±0.1, after the cationization process this value increased to 24.1-28, depending on the treatment (an increment about 8-9 times). This substantial increase is attributed to the cationic character of the fabrics after the cationization process (HELMY; HAUSER; EL-SHAFEI, 2017). However, the K/S for fabrics cationized with P42 decreased significantly after two plasma treatments (from 28±2 to 24.1±0.9). A similar situation was observed for reactive dyeing: the reduction of the a* coordinate from 44.8±0.7 to 43.0±0.8. Plasma treatment is usually known for increasing hydrophilicity in cotton, but many considerations may explain the decrease of the dye uptake. Similar results were obtained by other researchers (AKBARPOUR et al., 2013; GORJANC et al., 2018; WONG et al., 2000).

The gas selection for plasma treatment influences the dye uptake in cotton dyeing. Gorjanc et al. (2018) pretreated cotton with oxygen plasma and ammonia. They observed a reduction in color strength in samples treated with oxygen. The opposite effect was noticed in the samples treated by NH_3 plasma. The loss of efficiency could be related to the incorporation of superficial groups of anionic character in cotton after plasma treatment with oxygen. Wong et al. (2000) considered that plasma treatment changes the size and shape of the fiber, which affects the color reflection of the material. According to Akbarpour et al. (2013), the more the sample is exposed to the plasma, the more will be the effect of destructive conditions.

The cationic agent has a great influence on the dyeing. However, the treatment with plasma had little influence on the color properties of dyed fabrics. The greatest effect is related to the uniformity of the dyeing. The RUI values increased for the sample cationized with CHPTAC when applied with plasma treatment before dyeing. The highest values were 0.49 and 0.54 for reactive and acid dye, respectively. This is probably due to the increased reactivity of the plasma-treated fabric. The higher the reactivity on the cotton surface is, the lower the diffusion of the dye into the fiber, which may have caused uneven dyeing (WANG; LEWIS, 2002).

Table 24 – CIELab coordinates (L*, a* and b*), color strength (K/S), whiteness degree and relative unlevelness index (RUI) for dyed and undyed fabrics.

(to be continued)

Substrate						
Chemical treatment	**Plasma**^{z}	**L***	**a***	**b***	**K/S**	**Whiteness**
None (greige cotton)	-	87.82±0.05^{f}	2.58±0.03^{a}	15.4±0.1^{a}	4.82±0.02^{a}	4.3±0.2^{g}
Bleaching (control)	-	95.88±0.07^{a}	0.05±0.02^{g}	4.7±0.1^{e}	0.55±0.02^{f}	66.1±0.8^{a}
Cationization/P42	-	89.6±0.2^{d}	1.73±0.02^{c}	12.41±0.05^{b}	3.36±0.05^{c}	18.9±0.1^{e,f}
Cationization/CHPTAC	-	90.01±0.08^{c}	1.53±0.04^{e}	11.8±0.1^{d}	3.09±0.07^{d}	22.1±.0.5^{b,c}
Cationization/P42	1	89.10±0.05^{e}	2.02±0.03^{b}	12.36±0.08^{b,c}	3.56±0.05^{b}	18.1±0.3^{f}
Cationization/CHPTAC	1	89.96±0.09^{c}	1.63±0.03^{d}	12.0±0.2^{c,d}	3.1±0.1^{d}	21.1±0.8^{c,d}
Cationization/P42	2	89.5±0.2^{d}	1.61±0.03^{d}	12.2±0.2^{b,c}	3.41±0.08^{c}	19.8±0.7^{d,f}
Cationization/CHPTAC	2	90.49±0.04^{b}	1.43±0.03^{f}	11.7±0.2^{d}	2.90±0.07^{e}	23±1^{b}

Dyed with reactive dye						
Chemical treatment	**Plasma**^{z}	**L***	**a***	**b***	**K/S**	**RUI**
Bleaching (control)	-	61.0±0.2^{a,b}	49.8±0.2^{b}	-6.16±0.06^{c}	29.9±0.6^{b}	0.10
Cationization/P42	-	60.2±0.5^{b}	44.8±0.7^{c}	-5.45±0.06^{b}	30±1^{b}	0.24
Cationization/CHPTAC	-	54.5±0.4^{c}	54.5±0.5^{a}	-4.6±0.2^{a}	54±2^{a}	0.26
Cationization/P42	1	60.8±0.6^{a,b}	44±1^{c,d}	-5.3±0.2^{b}	29±1^{b}	0.26
Cationization/CHPTAC	1	54.2±0.4^{c}	54.6±0.6^{a}	-4.6±0.2^{a}	55±2^{a}	0.22
Cationization/P42	2	61.4±0.5^{a}	43.0±0.8^{d}	-5.18±0.06^{b}	28±2^{b}	0.25
Cationization/CHPTAC	2	54.4±0.7^{c}	54.8±0.6^{a}	-4.4±0.3^{a}	55±3^{a}	0.49

Table 24 – CIELab coordinates (L*, a* and b*), color strength (K/S), whiteness degree and relative unlevelness index (RUI) for dyed and undyed fabrics.

(conclusion)

Dyed with acid dye

Chemical treatment	Plasma^{z}	L*	a*	b*	K/S	RUI
Bleaching (control)	-	83.7 ± 0.2^{a}	-4.7 ± 0.1^{a}	-11.9 ± 0.7^{a}	3.2 ± 0.1^{c}	0.07
Cationization/P42	-	60.2 ± 0.9^{b}	-4.78 ± 0.06^{a}	-28 ± 1^{b}	28 ± 2^{a}	0.46
Cationization/CHPTAC	-	60.5 ± 0.2^{b}	-5.4 ± 0.2^{d}	-27.9 ± 0.2^{b}	27.8 ± 0.3^{a}	0.17
Cationization/P42	1	61.0 ± 0.6^{b}	$-5.0\pm0.1^{a,b}$	-26.9 ± 0.5^{b}	$26\pm1^{a,b}$	0.47
Cationization/CHPTAC	1	60.5 ± 0.2^{b}	$-5.37\pm0.08^{c,d}$	-27.4 ± 0.2^{b}	27.7 ± 0.4^{a}	0.14
Cationization/P42	2	61.0 ± 0.8^{b}	-4.82 ± 0.06^{a}	-26.9 ± 0.9^{b}	24.1 ± 0.9^{b}	0.51
Cationization/CHPTAC	2	61 ± 1^{b}	$-5.1\pm0.2^{b,c}$	-28 ± 1^{b}	27 ± 3^{a}	0.54

Source: the author.

Note: ^{z}No plasma treatment (-), 1 plasma treatment (before cationization) or 2 plasma treatments (before cationization and dyeing). $^{a-f}$Data that share the same letters, in the same column, are considered statistically equals.

5.3.2 Colorfastness properties

Table 25 shows the washing, rubbing and light fastness of the fabrics dyed with Reactive Red 195 and Acid Blue 260. When dyed with reactive dye the fabrics treated with CHPTAC presented the same washing fastness as the control sample. Fabrics treated with CHPTAC also presented high rubbing and light fastness for reactive dye. However, the fabrics treated with P42 had exhibited low washing and light fastness for the Reactive Red 195, below the level achieved by the control sample.

The dyeing with Acid Blue 260 presented enhanced fastness when the samples were treated with cationic agents. The high staining level for washing fastness of the control sample is attributed to the lower color strength of the dyed fabric. It is observed an increase of 0.5 to 1 degree in the color change of the washing fastness for the cationic samples, except for the one treated with plasma before cationization with P42. Nevertheless, this slight increase is not enough to enable the acid dye to be used on a large scale by the textile industry. Besides, there is a considerable decrease in wet rubbing fastness for treatments carried out with the P42 cationic agent. In this case, the water acted as a lubricant and stained the adjacent fabric (NAIKWADE et al., 2017).

The plasma treatment had a strong influence on the wet rubbing fastness of dyed fabrics with reactive dye. A decrease of 1.5 and 0.5 in the fastness levels was observed for fabrics cationized with P42 and CHPTAC, respectively. This result is probably related to the diffusion of the dye into the fiber. Since plasma and cationization are both surface treatments the dye tends to interact on the external surface, instead of diffuse to the interior of fiber. This effect is known as ring dyeing (MAHAPATRA, 2016). Both fixed and unfixed dye might be on the cotton surface.

The plasma effect was also observed to a lesser extent in the washing fastness properties. A slight reduction of washing fastness for plasma treated fabrics was also reported by other authors (AKBARPOUR et al., 2013; FENG et al., 2020). Some research observed a physical degradation of the fabric after plasma treatment, such as microcracks pitting and splitting of the fiber (FENG et al., 2020; SHEPHERD; FREY, 2018). These degraded fibers were probably removed from the fabric during the washing and rubbing fastness tests. On the other hand, fiber degradation has little influence on the light fastness since no mechanical effort is made during the test. In fact, samples dyed with reactive dye and cationized with P42 obtained better light fastness with the application of plasma.

Table 25 – Colorfastness of the dyed cotton fabrics.

Dyed with reactive dye

Chemical treatment	Plasma	Washing fastness		Rubbing fastness		Light fastness	
		Color change	Staining on CO[a]	Dry	Wet	20 h	40 h
Bleaching (control)	-	3.5	5	5	5	4.5	4.5
Cationization/P42	-	2	4.5	5	5	1.5	1
Cationization/CHPTAC	-	3.5	5	5	5	5	4.5
Cationization/P42	1	1.5	4.5	5	3.5	2	1
Cationization/CHPTAC	1	3.5	4.5	5	4.5	5	5
Cationization/P42	2	1.5	4.5	5	3.5	2	1
Cationization/CHPTAC	2	3.5	5	5	4.5	4.5	4.5

Dyed with acid dye

Chemical treatment	Plasma	Washing fastness		Rubbing fastness		Light fastness	
		Color change	Staining on PA[b]	Dry	Wet	20 h	40 h
Bleaching (control)	-	1	4	5	5	2	1.5
Cationization/P42	-	1.5	2.5	4.5	2.5	3	2.5
Cationization/CHPTAC	-	2	2.5	5	4	4.5	4
Cationization/P42	1	1	2	4.5	2.5	2.5	2.5
Cationization/CHPTAC	1	2	2	4	4	4.5	4
Cationization/P42	2	1.5	2.5	4.5	2	3	2.5
Cationization/CHPTAC	2	2	2.5	5	4	4.5	4.5

Source: the author.

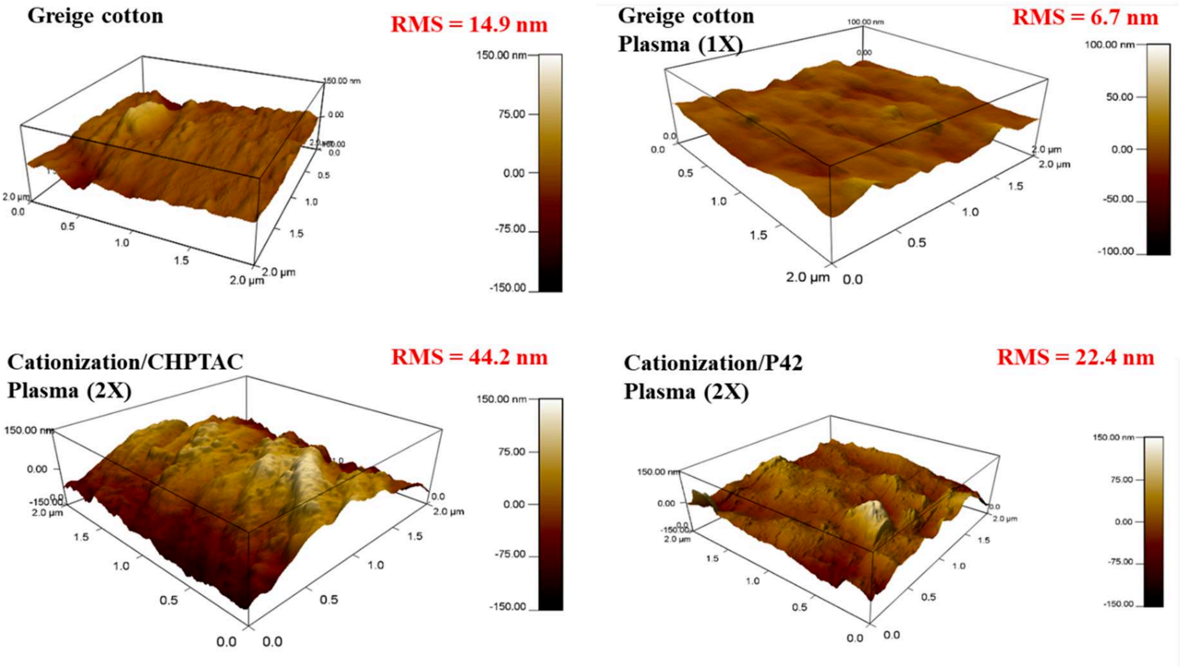
Note: [a]CO – cotton, [b]PA – polyamide.

5.3.3 AFM analysis

The AFM technique was used to analyze the effect of the plasma treatment on surface morphology and measure the surface roughness. Figure 32 shows the AFM images and the root mean square (RMS) roughness of the cotton fiber before and after plasma treatments. The RMS roughness measured for greige cotton was 14.9 nm. Then the RMS roughness decreased to 6.7 nm after the plasma treatment. The decrease is probably due to a partial etching of the fiber.

The waxes present on the surface of the fabric might act as a barrier that prevents the contact between plasma and cellulose. Therefore, probably only a portion of the waxes was removed after 135 s of plasma treatment. It also explains the conspicuous unlevelness obtained after the dyeing of plasma-treated greige cotton. The dye could not diffuse into the fiber because of the remaining waxes on the surface of the fabric after the plasma treatment.

Figure 32 – AFM images and RMS roughness of greige cotton and plasma treated cotton fabrics.



Source: the author.

The surface etching by atmospheric plasma partially destroyed the hydrophobic layer and the hydrophilicity is dependent on the power and time of the plasma treatment (CARNEIRO et al., 2001; KARAHAN; ÖZDOĞAN, 2008). Shepherd and Frey (2018) treated scoured and greige cotton yarns with long plasma exposure times (15-90 min). Scoured cotton had severe physical damage, even at the lowest exposure time (15 min), while greige yarns had less degradation. The authors attributed the better resistance of the greige cotton yarn to the greater amount of waxes and other components present at the surface.

The fabrics treated before and after plasma treatment presented higher RMS roughness. The waxes and other impurities of the cotton surface were removed after the cationization process, then allowing better corrosion of the fiber due to the second plasma treatment. The highest RMS roughness occurred for the sample treated with CHPTAC and two plasma treatment. This is probably related to the size of the cationic molecule. The pore diffusion of the P42 cationic agent into the cellulose fiber is limited due to the polymer structure, thus the interaction is partially restricted to the external surface of the fiber. Therefore, the P42 cationic agent has more tendency to be deposited in the external surface of the fiber, which hinders the contact between plasma and cellulose.

5.3.4 FTIR and XPS analysis

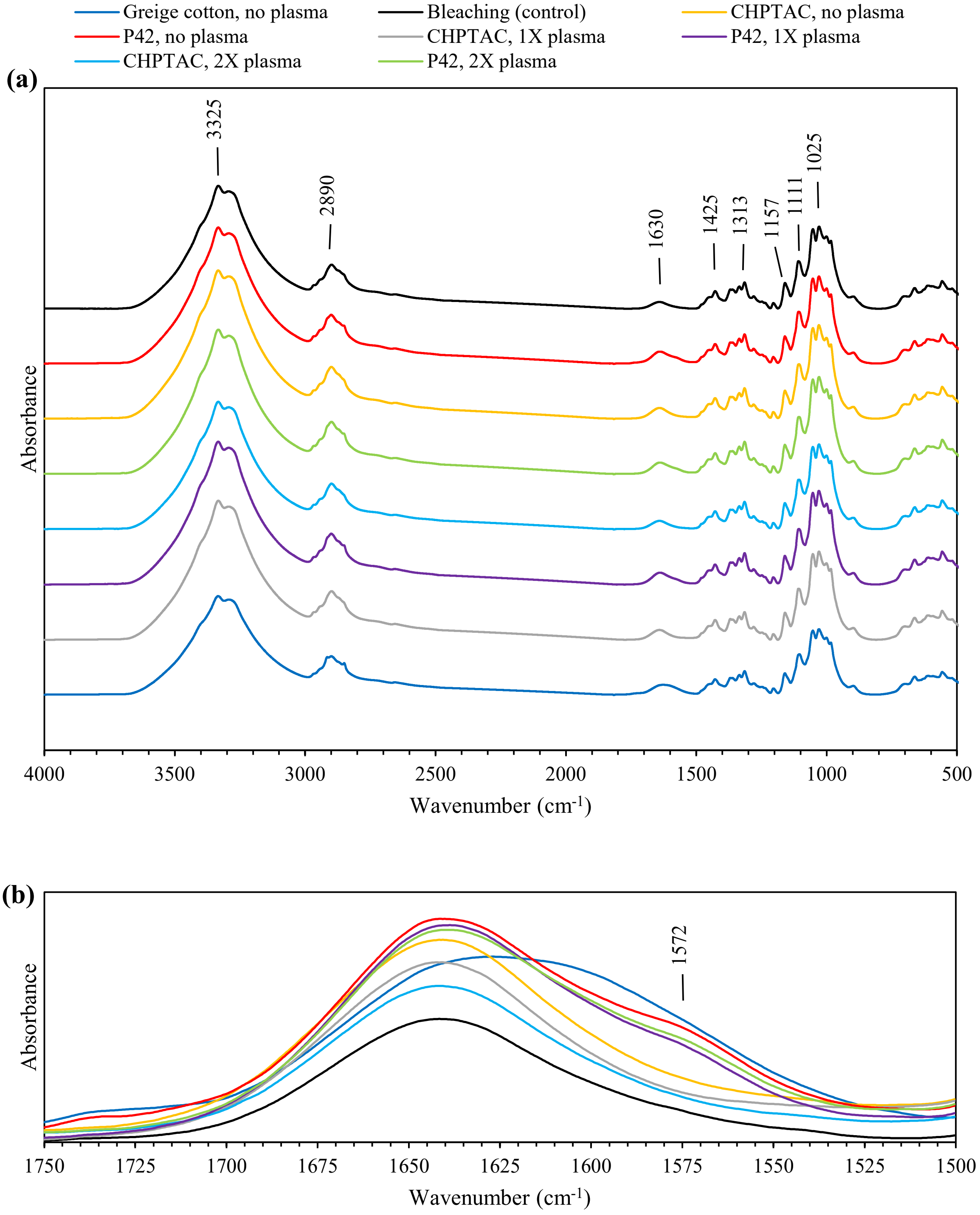
FTIR is a simple technique useful to characterize the functional groups on the surface of the fabric. FTIR spectroscopy of greige cotton and treated fabrics are given in Figure 33. Apart from the intensity of the peaks, the spectra of the fabrics presented similar characteristics. The peaks in the region 3500–3100 cm^{-1} are related to the –OH stretching. The peaks in region 3000–2800 cm^{-1} correspond to asymmetrical and symmetrical vibrations of CH_2 (methylene) groups of the alkyl chains. The peak around 1425 cm^{-1} corresponds to –CH and C–OH bending vibrations. The broad absorption peak in the region 1400–1300 cm^{-1} is related to –CH or –CH_2 bending vibrations. The peaks at around 1157 cm^{-1}, 1111 cm^{-1} and the broad peak in the region 1030–1000 cm^{-1} are assigned to C–O–C stretching vibrations. (CHUNG; LEE; CHOE, 2004; MA et al., 2016; MOLINA et al., 2020)

A smaller peak between around 1630 cm^{-1} is usually related to the O-H bending vibrations of adsorbed water (CHUNG; LEE; CHOE, 2004) but can be also assigned to N-H asymmetric deformation (ABDELILEH et al., 2019). An enlarged graph in this wavenumber region is given in Figure 33 (b) for detailed investigation. It can be observed that there is a small protuberance around 1572 cm^{-1} for all samples treated with the cationic agent P42. This may be attributed to the presence of secondary amide groups (SUN et al., 2018), which indicates that the P42 cationic agent was successfully deposited onto the textile surface.

In the spectra is shown absorption peaks characteristic of the cellulose structure. This is probably due to the low concentration of cationic agents used in the treatment. The concentration was not high enough, therefore the peaks were overlapped with the cotton. An exception occurs for the peak around 1572 cm^{-1}, for samples cationized with P42. Secondary amide groups are present in the P42 molecule but not in the cellulose.

Holländer et al. (1999) estimated that the plasma treatment acts mostly at the first 50 nm of the material surface, while the FTIR analysis is typically between 600 nm and 1000 nm (MOLINA et al., 2020). Therefore, the FTIR technique is not suitable to analyze the interaction between the plasma and the uppermost layer of the cotton fabric. A good method to analyze the changes in the surface of the cotton fabrics treated by plasma is the XPS technique, which is restricted to the first 10 nm of the surface (COOLS; MORENT; DE GEYTER, 2015). The atomic composition of the samples, measured by XPS, is given in Table 26.

Figure 33 – Infrared absorption bands of untreated and treated cotton fabrics (a) with wavenumber from 4000 to 500 cm^{-1} and (b) enlarged region for detailed analysis (1750 – 1500 cm^{-1}).



Source: the author.

Table 26 – Atomic percent and elemental compositions from high-resolution XPS of C1s peaks of the untreated and treated fabrics.

Chemical treatment	**Plasma**	**Atomic percent (%)**			**Possible functional groups (%)**		
		C	**O**	**N**	**C-C**	**C-O**	**O-C-O**
None (greige cotton)	-	92.2	7.3	0.5	90	6	4
Bleaching (control)	-	76.5	23.1	0.4	69	24	7
Cationization/ P42	-	71.3	27.5	1.2	57	36	7
Cationization/ CHPTAC	-	66.5	33.0	0.5	52	38	10
Cationization/ P42	1	74.7	24.1	1.2	67	26	7
Cationization /CHPTAC	1	72.5	27.0	0.5	65	28	7
Cationization/ P42	2	70.5	28.0	1.5	57	33	10
Cationization/ CHPTAC	2	68.3	31.1	0.6	55	36	9

Source: the author.

The untreated greige cotton fabric contains the highest concentration of carbon (92.2 %) and the lowest concentration of oxygen (7.3 %). This is due to the high content of waxes in the greige cotton fabric. After the conventional bleaching process, the carbon content drops to 76.5 %, while the oxygen rises to 23.1 %. The nitrogen content in the greige cotton is 0.5 %. It is related to impurities, thus it is expected that cotton fabrics have a low concentration of nitrogen. The nitrogen content decreases to 0.4 % after the bleaching process due to the removal of impurities. The amount of nitrogen in the non-cationic fabrics was similar to other literature cited in this paper. Generally, the nitrogen concentration of untreated fabric samples varies from 0 to 0.5 % (ARIVITHAMANI; GIRI DEV, 2017a; CAI et al., 2018; LIU; YAO, 2011).

The cationic treatment is responsible for the incorporation of nitrogen functional groups into the cellulose fiber. This effect was detected by XPS analysis only for samples treated with cationic agent P42. The XPS technique detected a higher amount of nitrogen for cationic fabrics treated with P42 because the molecules of the cationic agent are mainly at the external surface of the fiber. The CHPTAC molecules have better penetration to the cellulose pores, at a fiber depth greater than the range of the XPS analysis.

Since quaternary ammonium groups are incorporated in the fiber, the amount of nitrogen in the cotton samples is usually measured as an indirect method to monitor the efficiency of the cationization (HASHEM, 2006; MA et al., 2017). However, other factors interfere with the interaction between the anionic dye and the cationic fiber. An increase in the physical presence of surrounding ligands results in lower dye-fiber interaction. So, the effect of the cationic nitrogen may be dominated by the steric hindrance (MAITI et al., 2018).

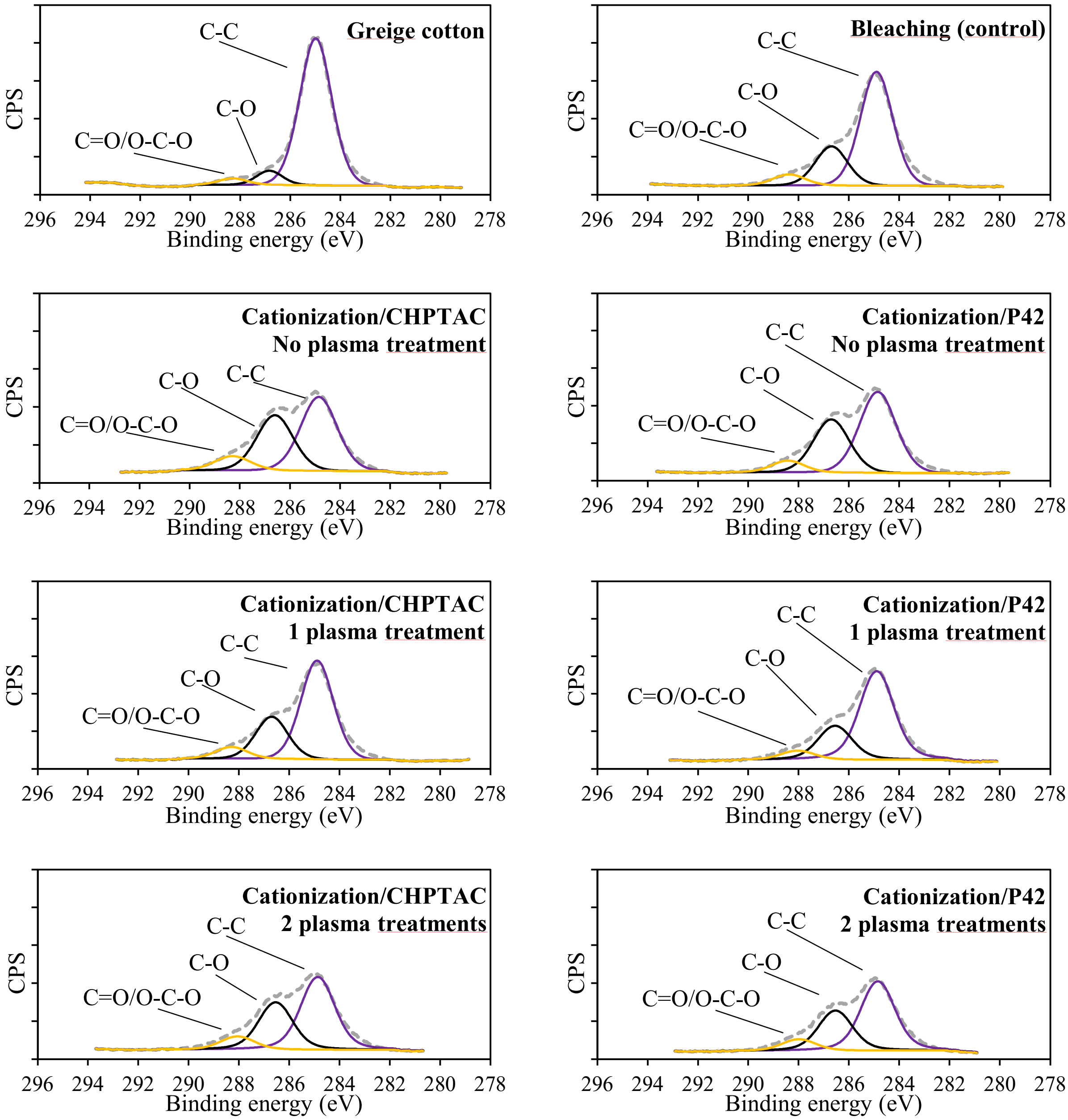
The plasma treatment of the greige cotton increased the concentration of oxygen. The plasma is composed of 1.5 % oxygen, which interacts with cellulose and provides new functional groups for the cotton surface. The cationization after the plasma treatment increased the carbon concentration probably due to the incorporation of the cationic agent into the fabrics. After the second plasma treatment, the carbon concentration decreases again due to a new interaction with oxygen from plasma.

For more detailed information, C1s high-resolution scans were performed for the fabrics and the results are also indicated in Table 26. As shown in Figure 34, the deconvoluted C1s spectrum presents three peaks: at 285.0, 286.5 and 288.2 eV, which can be respectively attributed to C-C, C-O and O-C-O/C=O bonds (CAI et al., 2018; MOLINA et al., 2020; VANDENCASTEELE; RENIERS, 2010).

The greige cotton has the highest C-C content due to some non-cellulosic components such as waxes. The plasma treatment was responsible for increasing the concentration of C-O and O-C-O/C=O functional group. The bleaching process removed the waxes, which decreased the C-C concentration. The cationization also removed the waxes from greige cotton, however, the C-C concentration rises again if the fabric was previously treated by plasma. This is also related to the incorporation of the cationic agent into the fabrics.

The incorporation of oxygenated functional groups by plasma increased the acidity of the cotton surface (KRAMAR et al., 2018), which tends to lower the pH of the dyebath (OLIVEIRA et al., 2012). This may be related to the loss of efficiency in the process when the samples were treated with plasma before dyeing with Reactive Red 195 (Table 24). The reactive dye is usually applied in an alkaline medium to enhance interaction with the fiber (PAL, 2017).

Figure 34 – XPS high-resolution C1s spectra of untreated and treated cotton fabrics.



Source: the author.

5.4 CONCLUSIONS

The dyeing of plasma treated cationic greige cotton has shown promise since it decreases the consumption of water and the generation of effluent as conventional scouring and bleaching are eliminated. Besides, the findings related to the P42 might enable its use as a cationic agent for the textile sector, as a substitute for the well-known CHPTAC.

In this research, the cationization was successfully applied with plasma assistance. The novel cationic agent P42, better known as Polyquaternium-2, successfully incorporated new ammonium groups to the cellulose surface. The dyeing of cotton fabrics cationized with P42 presented higher color strength comparable to conventional dyeing, without feeding salt to the process. CHPTAC is still the best cationic agent, considering the best color strength and RUI values. However, P42 might be used as an alternative due to the safety concerns related to the use of CHPTAC.

The pretreatments increased the interaction between cotton and Acid Blue 260 dye, especially the cationization. The incorporation of cationic groups into cotton fabric increased substantially the color strength of the dyed samples. However, considering industrial-scale applicability, further improvements are necessary due to the limited fastness properties of the dyed fabrics.

The cationization effect prevailed over plasma. Plasma treatment changed the chemical cotton surface but had little influence on the color properties of the dyed fabrics. The biggest influence of the plasma was related to the improvement in light fastness, probably due to the increased reactivity. With the conditions proposed in this research, the plasma treatment itself is not enough for providing enough hydrophilicity for the dyeing of greige cotton fabrics. In contrast, the plasma treatment followed by cationization can remove completely the waxes present in the greige cotton fabrics, which is essential for an even dyeing.

6 GENERAL CONCLUSIONS AND SUGGESTIONS FOR FUTURE RESEARCH

The cotton dyed with reactive dyes improved after the cationization process. Different benefits occurred according to the dye used. Using the Red Colorsupra PF-3B dye, the color properties of the cationic and conventional dyeing were similar, but the amount of effluent generated reduced substantially for the cationic fabrics. A single washing bath was enough for the CHPTAC cationic cotton sample. The dyeing with Reactive Red 195 dye also requires only a single washing bath when the fabric was cationized with CHPTAC. Besides, the K/S of the cationic fabrics treated with CHPTAC and dyed with Reactive Red 195 dye were 28-50 % higher than the conventional dyeing.

The cationization improved substantially the dye-fiber interaction when used P42 CHPTAC and PDDACl. But the acid dyeing of cotton fabrics still needs to be optimized. Most of the dye has been lost during washing. The introduction of plasma technology was not enough to overcome this issue.

Regarding the plasma treatment, it has little influence on the properties of the dyed fabrics as the cationization effect is more evident. The reason is probably related to the presence of waxes over the cotton surface even after the plasma treatment. A higher period of plasma treatment may increase the etching of the cotton surface, which tends to raise the hydrophilicity.

Among the new cationic agents researched, PDDACl and P42 have great potential. The cationic agent PDDAC1 presented a high affinity for Reactive Red 195 dye, higher than the commercial agent CHPTAC. P42 presented good K/S values and is a novel cationic agent. Besides, P42 and PDDACl presented bactericidal activity. PAcD may still provide better results from experiments with a higher amount of cationic agent or low dyeing pH.

Some suggestions for future research are proposed to improve the knowledge of the process of cationization of fabrics. The suggestions are based on the state of the art and the research carried out in this thesis and are listed below:

i. Evaluation of the influence on the degree of polymerization in the cationization process when used cationic agents PDDACl and P42. According to Figure 2, the penetration of the cationic agent into the pores of the fiber depends on the particle size.

ii. Evaluation of the properties of cationization with PDDACl and plasma treatment. According to the literature review, there is a great potential for using PDDACl as a cationic agent.

iii. Correlation between the hydrophilicity of the greige cotton knitted fabric and the plasma treatment time.
iv. Quantification of the bactericidal activity of cationic fabrics using a standardized procedure.
v. Dyeing with reactive dye in acid pH to promote the protonation of the nitrogen.
vi. Dyeing of cationic fabrics cationized with PAcD at 20 $g.L^{-1}$ with acid dye and pH less than 3.4. Below this value, the fabric cationized with PAcD behaves positively charged.
vii. Cationization of cotton with PAcD at concentrations above 40 $g.L^{-1}$.
viii. Improvement of uniform dyeing with different concentrations and types of leveling agents.

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APPENDIX A: First page of the review paper

Figure A.1 – First page of the review paper (manuscript 1), published by the Cellulose Journal. DOI: https://doi.org/10.1007/s10570-020-03361-w.

Cellulose (2020) 27:8527–8550
https://doi.org/10.1007/s10570-020-03361-w

REVIEW PAPER

Cationization of cotton fiber: an integrated view of cationic agents, processes variables, properties, market and future prospects

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Received: 15 May 2020 / Accepted: 20 July 2020 / Published online: 10 August 2020

Abstract Anionic dyes are often used for conventional cotton dyeing. This process, however, has a moderate affinity and it is estimated that less than 70% of the dye interacts with the cotton fiber. Cationization of cellulose is a chemical treatment that modifies the cellulose molecule, making it strongly cationic. This pretreatment increases the affinity between cotton and anionic dyes. Therefore, cationic dyeing reduces water, time, energy and chemical consumption. In this scenario, there is a growing demand to develop new cleaner products, as well as to elucidate the reaction mechanism aiming to create a clean and low-cost process for cotton cationization. In the last decades, more than 800 documents were published, and this number continues to rise. Among the cationic agents, 3-chloro-2-hydroxypropyl trimethylammonium chloride is the most researched and has achieved niche markets. However, poly-diallyldimethylammonium chloride combines effectiveness with a cleaner process. These characteristics make this cationic agent promising for future research. This review reports the state of the art on the techniques used for cationization, with a brief description of the market available for cationic cotton and a critical evaluation of the future perspectives for cationization.

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Source: The author.

APPENDIX B: Supplementary material for manuscript 2

Figure B.1 – Certificate of conformity of the IEC reference detergent for washing fastness according to ISO 105 C06.

Testfabrics, Inc.

Your source for Quality Test Materials

CERTIFICATE OF CONFORMITY

Product Code: *EMPA 602*
Description: *IEC reference detergent type A*, no phosphates, EN/IEC Publication 60456, in packages of 1kg each*
Product Lot Number: *298-948*

Product Certification

It is to certify that above mentioned product has been evaluated according to the standards and conform to the specifications for manufacturing and performance outlined in:

ISO 6330 Textiles -- Domestic washing and drying procedures for textile testing

Other Domestic, International and Corporate Test Methods where specified.

Our Assurance

Test Materials supplied by Testfabrics, Inc. are tested by Testfabrics in house lab as well as approved ISO Certified Labs. Each production Lot is tested under strict performance testing to ensure that products fit the specifications.

Trackable Lot Numbers

Testfabrics products are marked with identifiable lot numbers. This lot number is the key identification of the product, if you have any questions please advise us the lot number.

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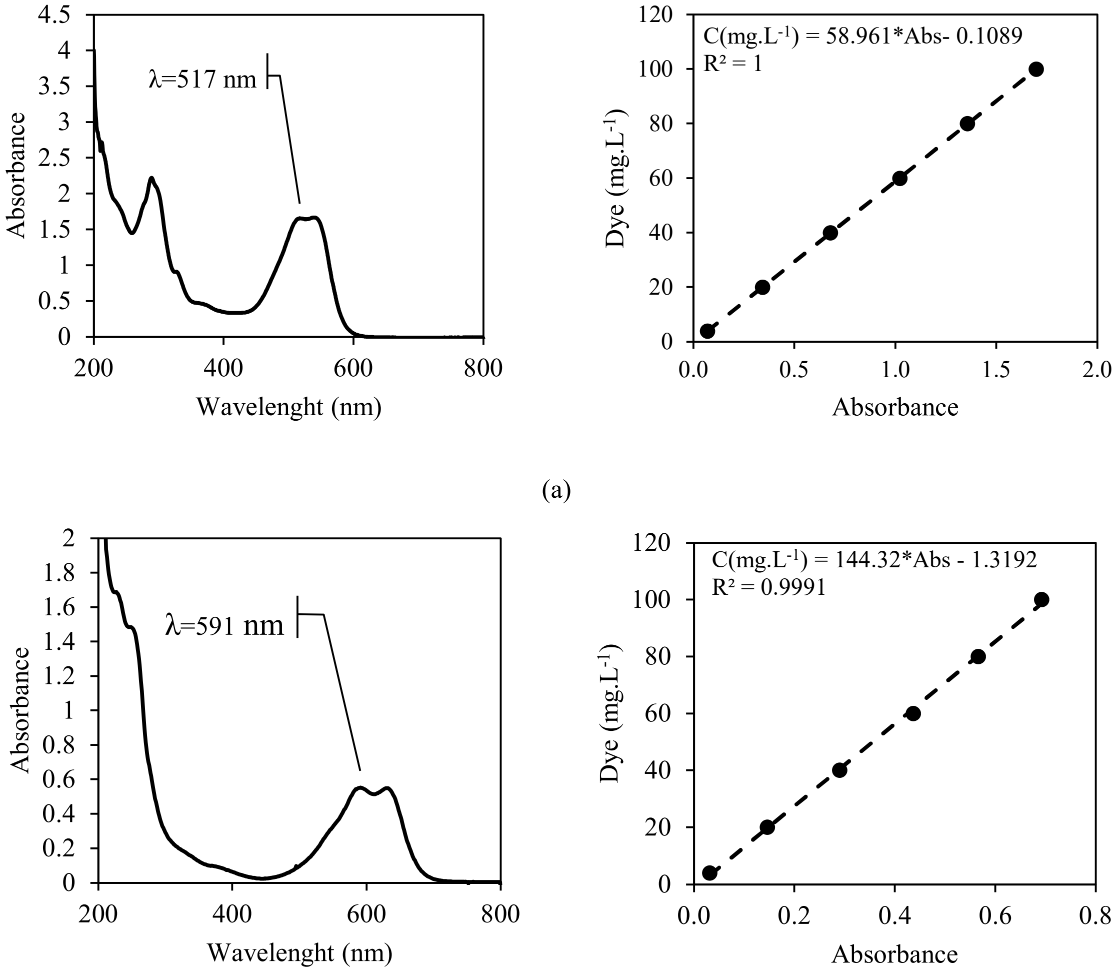
Source: Testfabrics (2019).

Figure B.2 – Wavelength scan and calibration curve of (a) Reactive Red Colorsupra PF-3B dye and (b) Acid Blue 260.

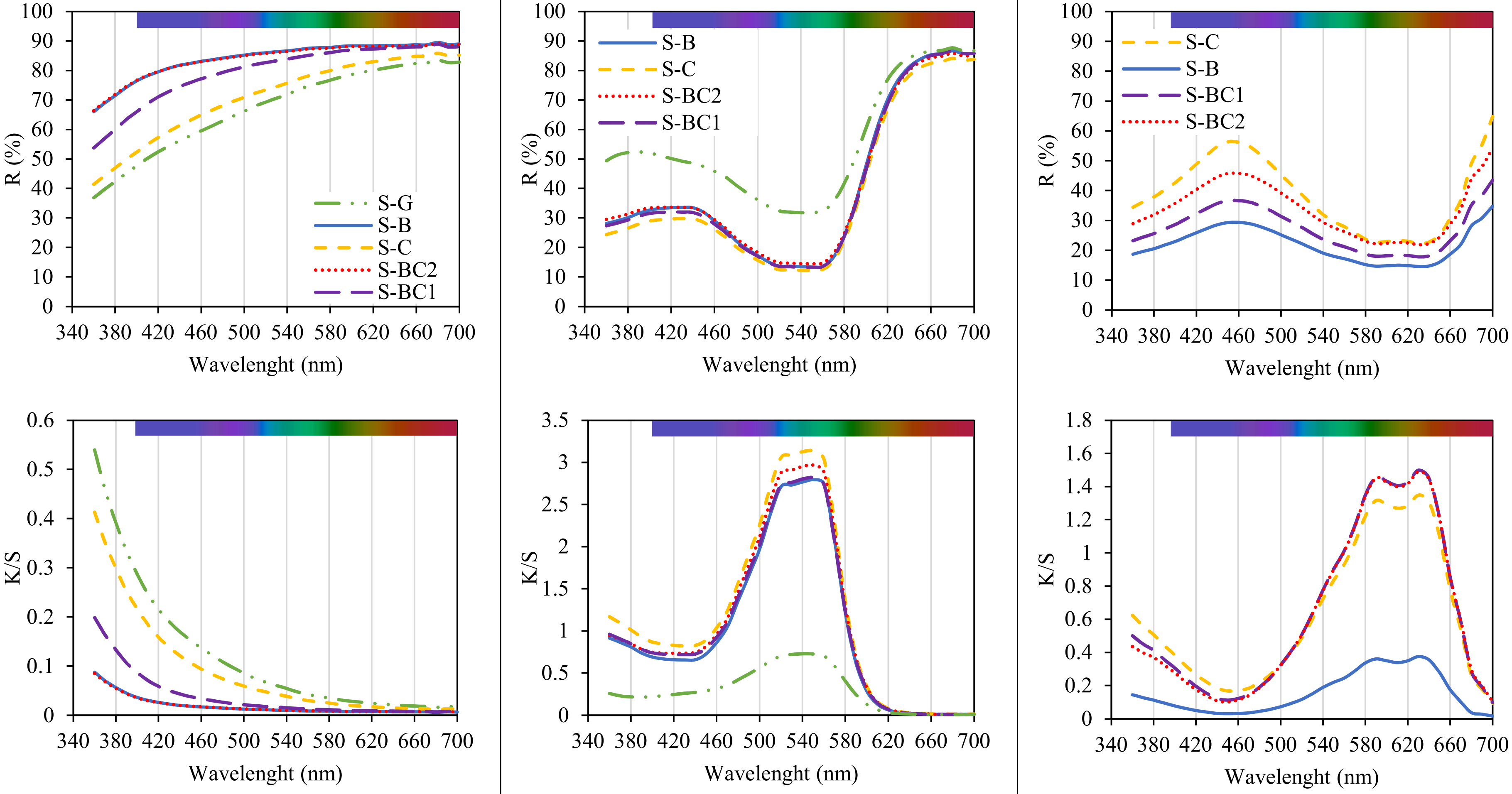


(a)

(b)

Source: the author.

Figure B.3 – Reflectance and K/S spectrum for (a) undyed fabric samples and dyed with (b) Red Colorsupra PF-3B and (c)Acid Blue 260.



(a)

(b)

(c)

Source: the author.

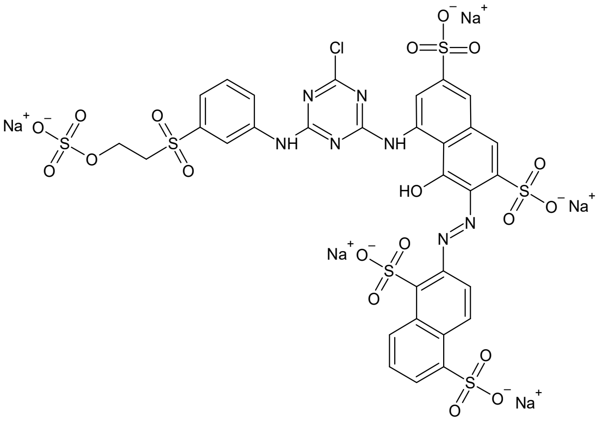
APPENDIX C: Supplementary material for manuscript 3

Table C.1 – List of chemical products used in this paper.

Material	**Specification**	**Source**
Ecodyeing A 230	Non-ionic detergent.	Werken Química, Indaial, Brazil
Stabplex EP 243	Peroxide stabilizer	Werken Química, Indaial, Brazil
Ecodyeing IR 4	Leveling agent	Werken Química, Indaial, Brazil
Formic acid	85 % solution	Werken Química, Indaial, Brazil
Buffer CS 85	Alkalizing agent	Werken Química, Indaial, Brazil
Ecodyeing RW 710	Anionic detergent	Werken Química, Indaial, Brazil
H_2O_2	35 % solution	Neon Comercial Ltda, Suzano, Brazil
NaOH	P.A.	Neon Comercial Ltda, Suzano, Brazil
NaCl	P.A. ACS	Alphatec, São José Dos Pinhais, Brazil
IEC detergent	Reference detergent for fastness analysis	Testfabrics Inc., West Pittston, USA

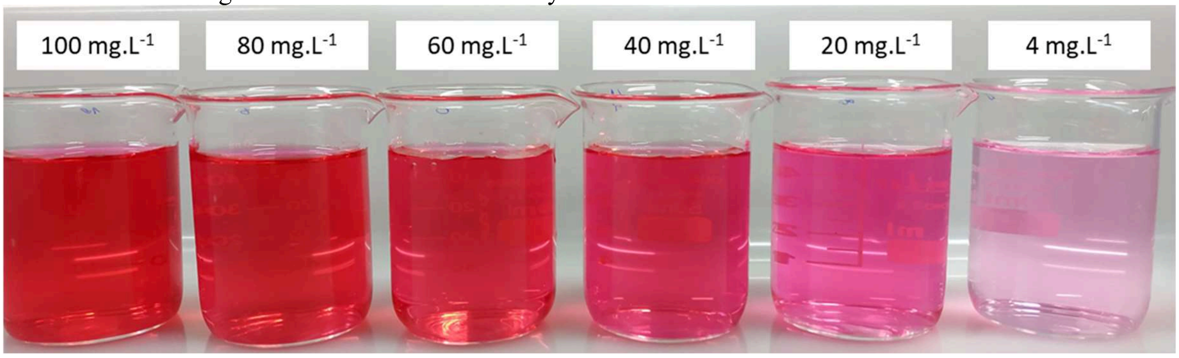
Source: the author.

Table C.2 – Additional information of the dye.

Dye	Red Colorsupra AC-5BL
Manufacturer	Color Química, Blumenau, Brazil
Color Index	Reactive Red 195
Molecular formula	$C_{31}H_{19}ClN_7Na_5O_{19}S_6$
Molecular Weight (g.mol^{-1})	991.82
CAS Registry Number	93050-79-4
Chemical structure	

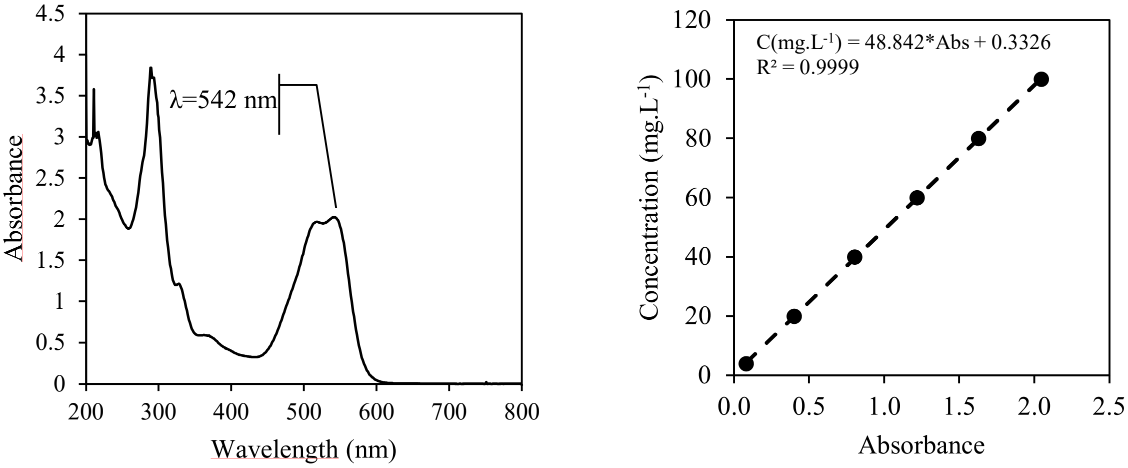
Source: the author.

Figure C.1 – Reactive Red 195 dye concentrations used for calibration curve.



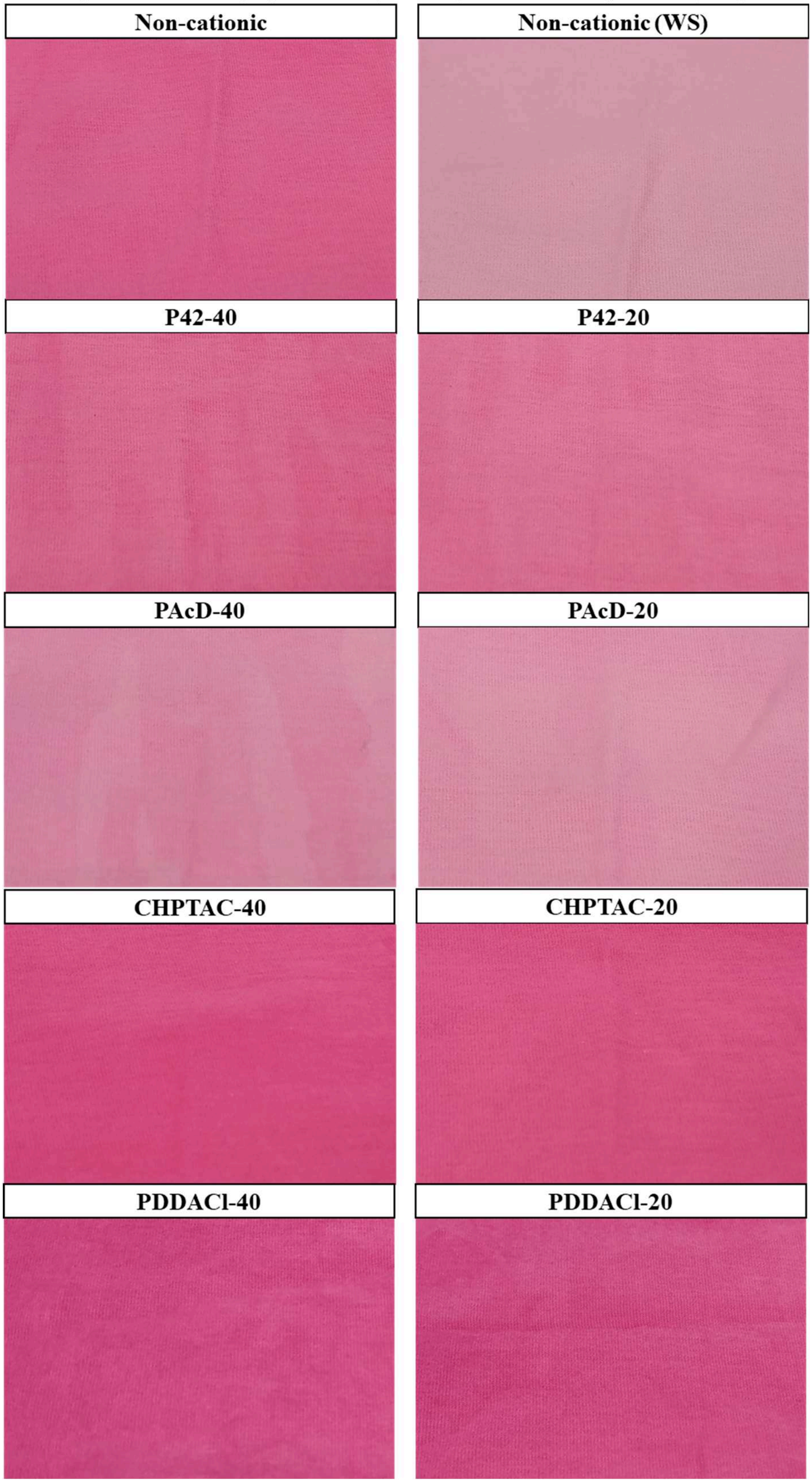
Source: the author.

Figure C.2 – Wavelength scan and calibration curve for Reactive Red 195.



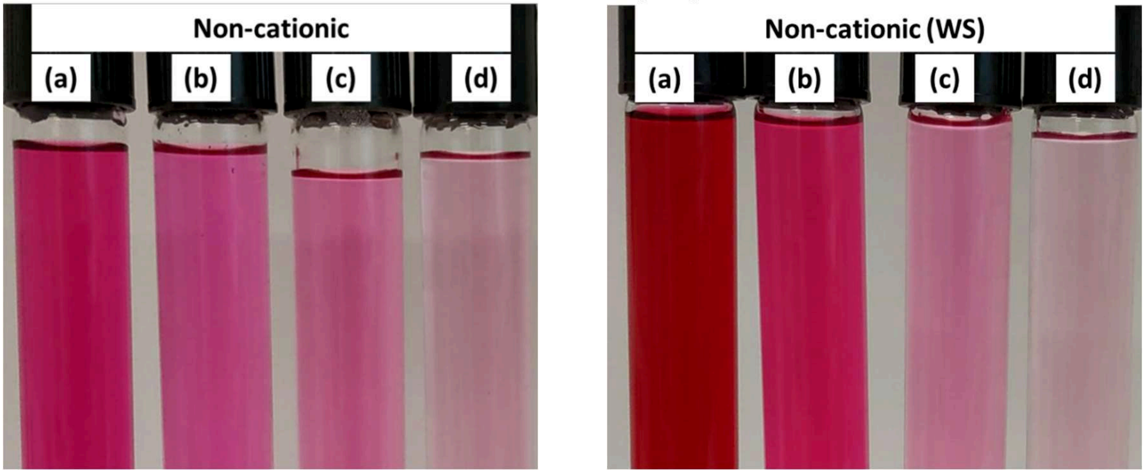
Source: the author.

Figure C.3 – Photographs of all dyed samples in non-competitive dyeing.



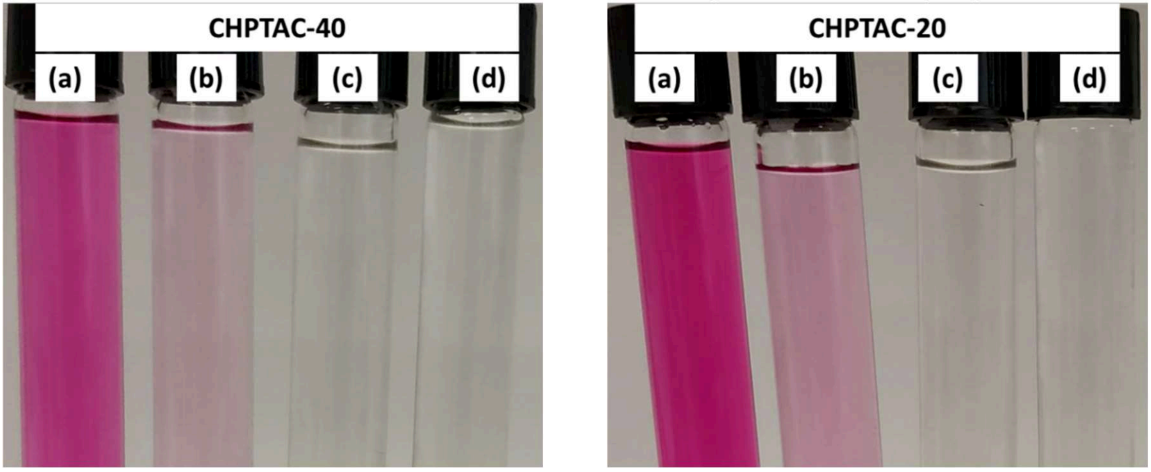
Source: The author.

Figure C.4 – Exhaustion (a), first (b), second (c) and third (d) washing bath for conventional dyeing and non-cationic salt-free dyeing.



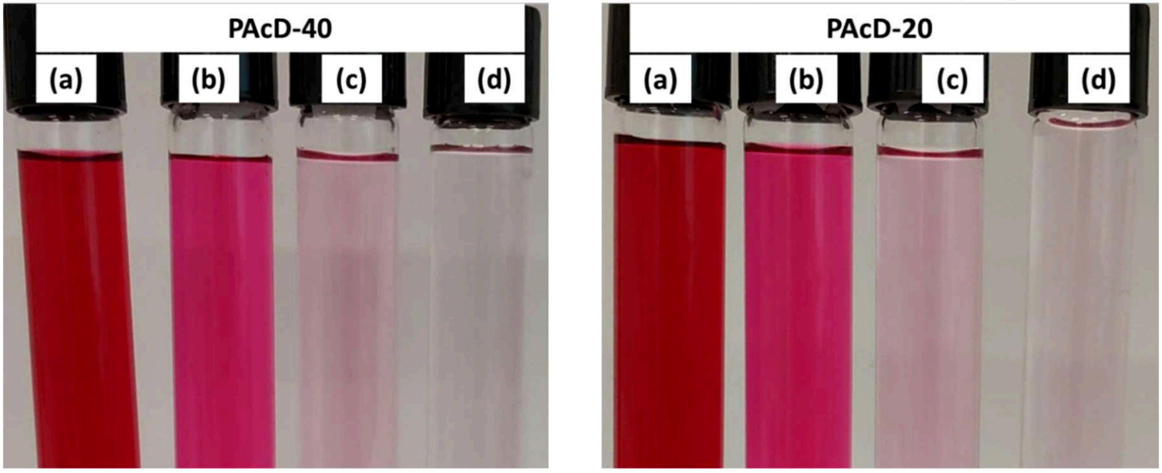
Source: the author.

Figure C.5 – Exhaustion (a), first (b), second (c) and third (d) washing bath for cationic dyeing with CHPTAC.



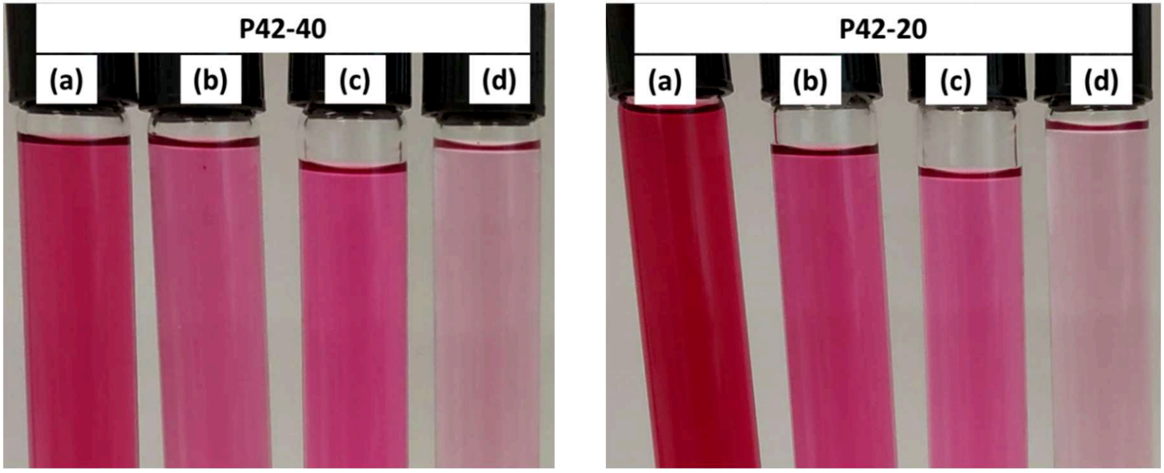
Source: the author.

Figure C.6 – Exhaustion (a), first (b), second (c) and third (d) washing bath for cationic dyeing with PAcD.



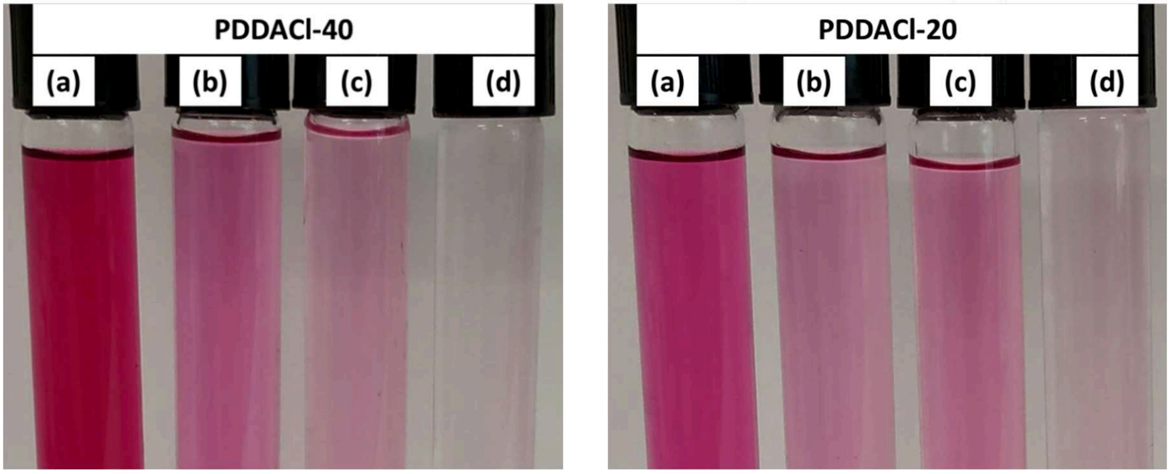
Source: the author.

Figure C.7 – Exhaustion (a), first (b), second (c) and third (d) washing bath for cationic dyeing with P42.



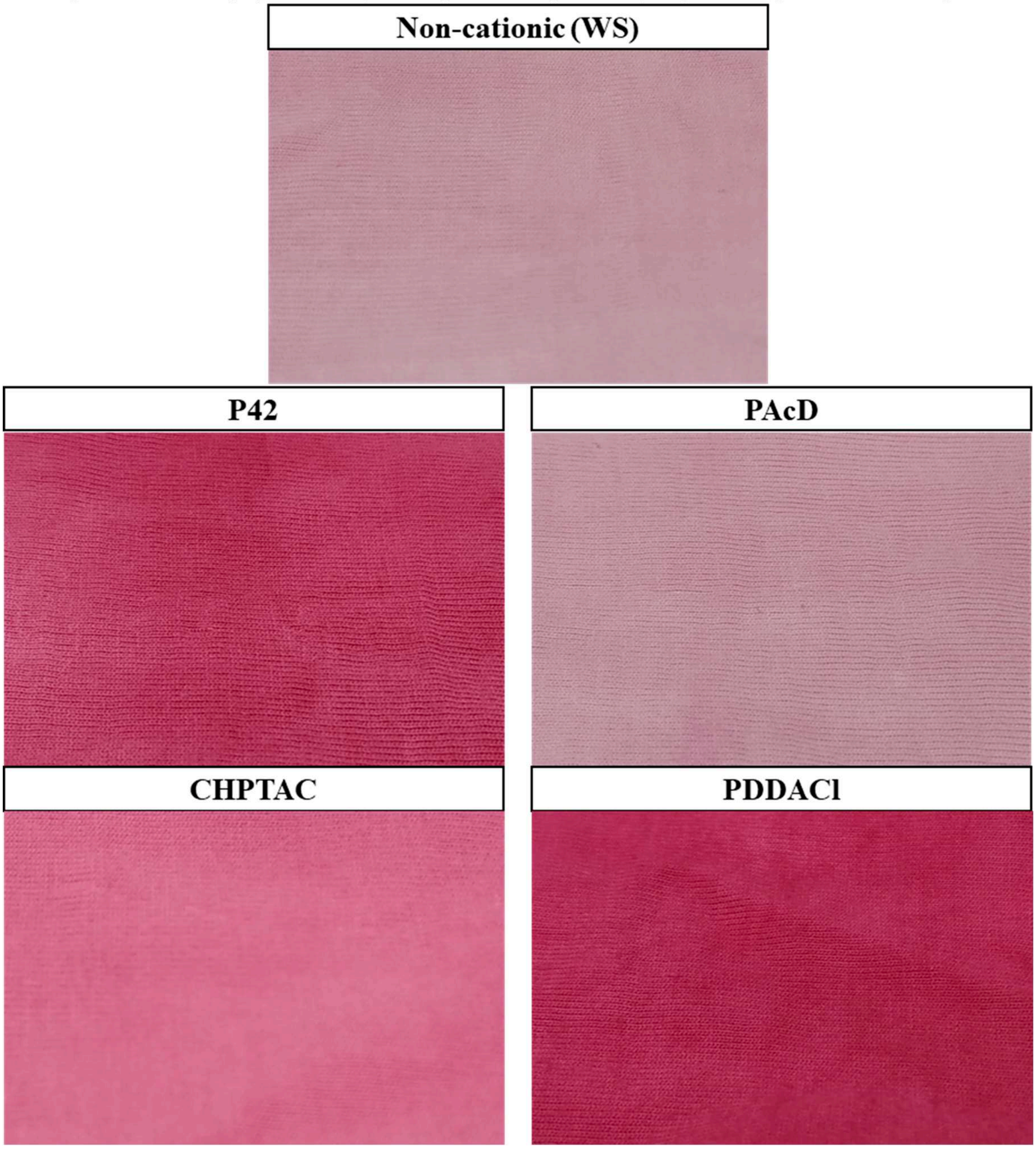
Source: the author.

Figure C.8 – Exhaustion (a), first (b), second (c) and third (d) washing bath for cationic dyeing with PDDACl.



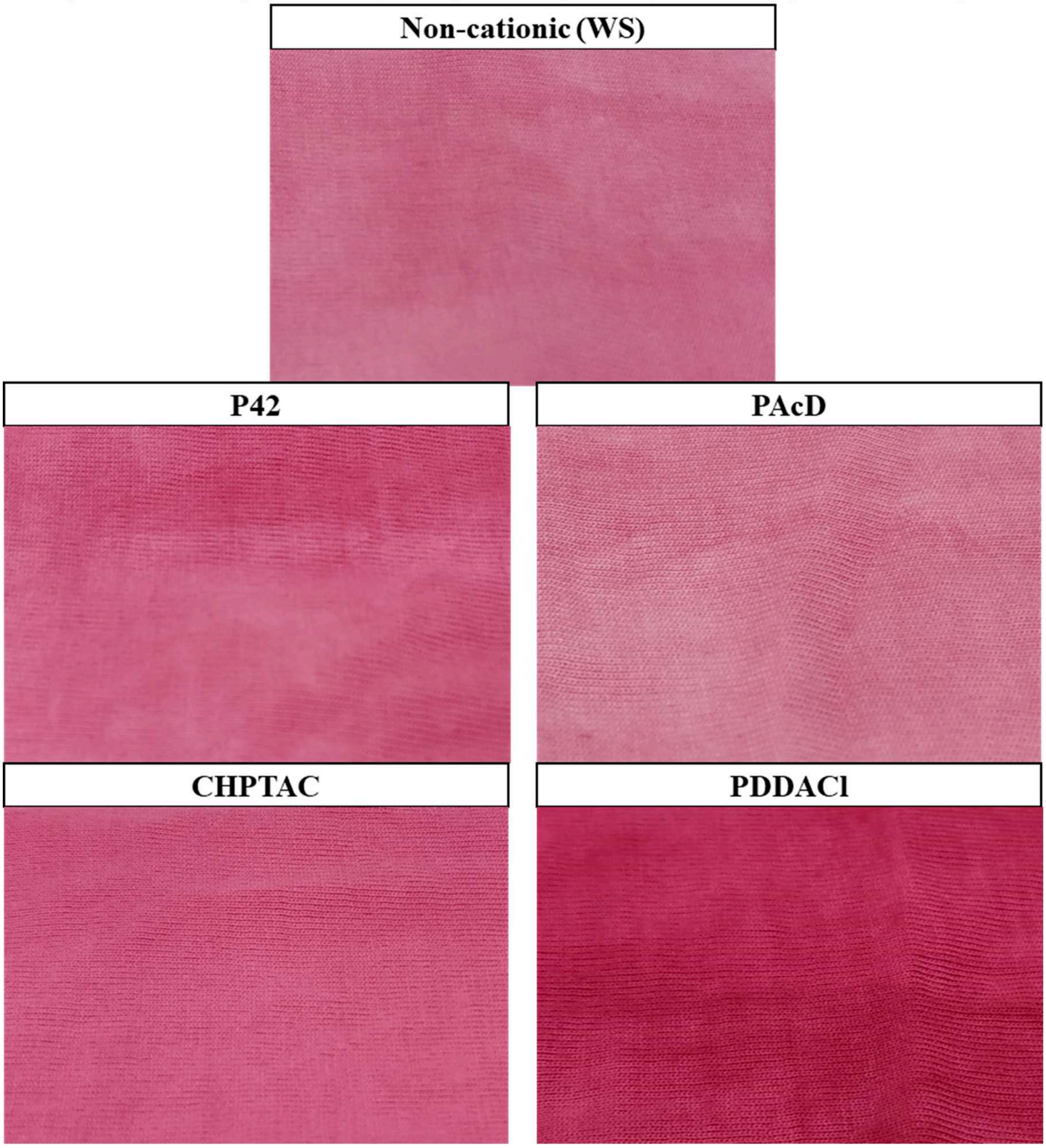
Source: the author.

Figure C.9 – Photographs of all dyed samples in competitive dyeing with 20 $g.L^{-1}$ of cationic agent.



Source: The author

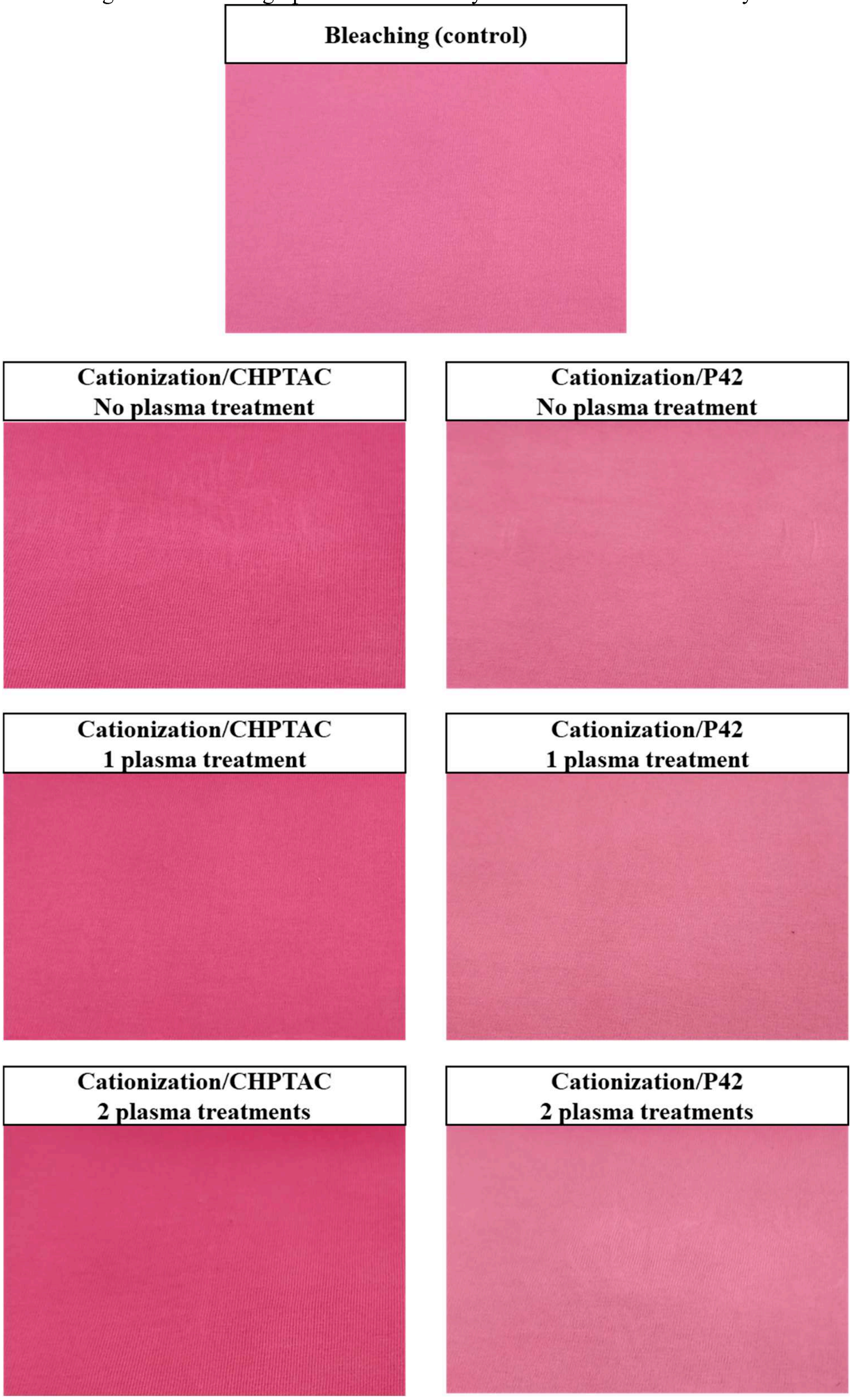
Figure C.10 – Photographs of all dyed samples in competitive dyeing with 40 $g.L^{-1}$ of cationic agent.



Source: The author.

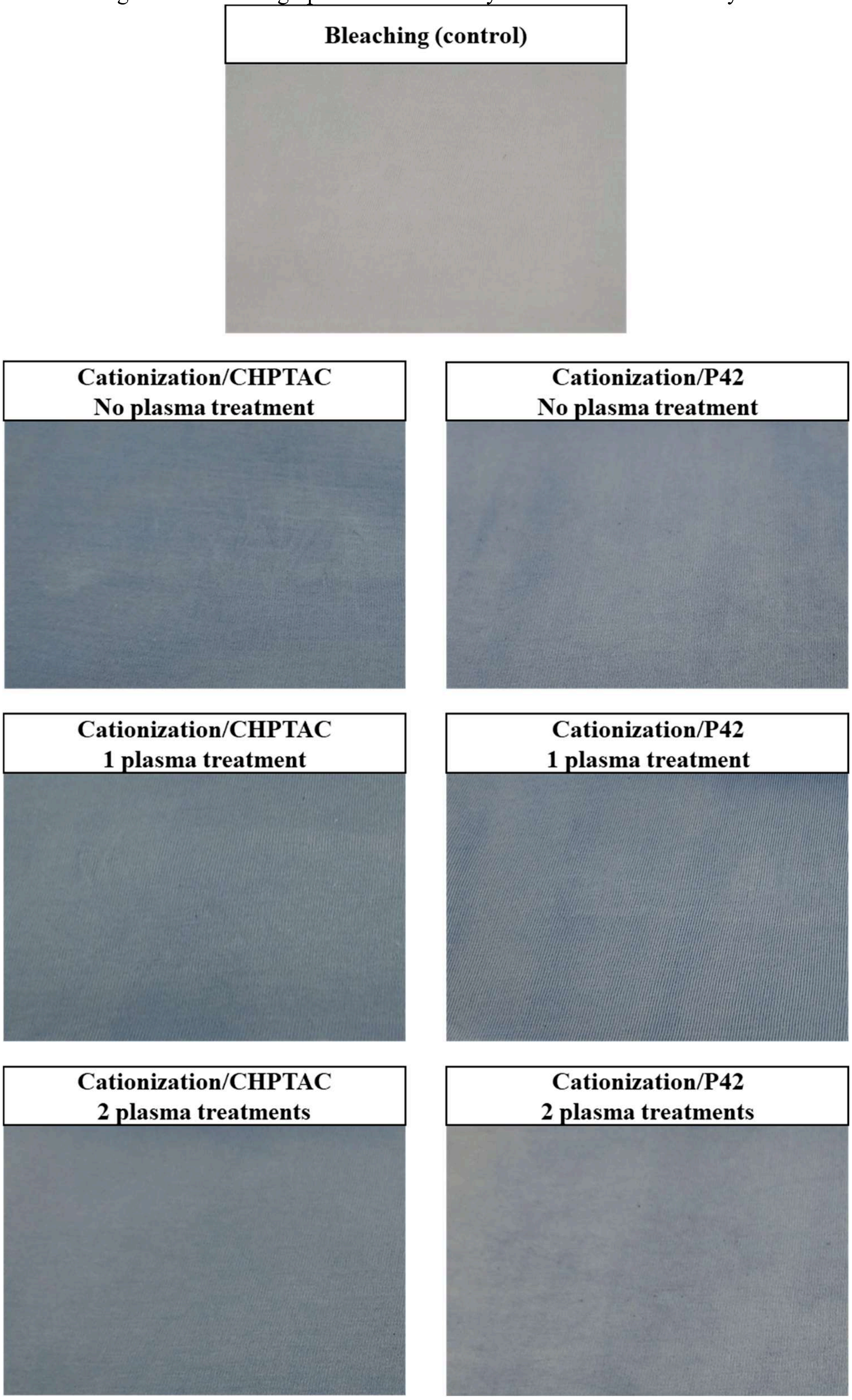
APPENDIX D: Supplementary material for manuscript 4

Figure D.1 – Photographs of the fabrics dyed with Reactive Red 195 dye.



Source: The author.

Figure D.2 – Photographs of the fabrics dyed with Acid Blue 260 dye.



Bleaching (control)

Cationization/CHPTAC
No plasma treatment

Cationization/P42
No plasma treatment

Cationization/CHPTAC
1 plasma treatment

Cationization/P42
1 plasma treatment

Cationization/CHPTAC
2 plasma treatments

Cationization/P42
2 plasma treatments

Source: The author.

APPENDIX E: Images of some equipment that were used for the research

In Figure E.1 and Figure E.2 is shown the equipment available in Textile Beneficiation Laboratory. In Figure E.3 is shown the reflectance spectrophotometer for color measurement of the fabrics, available at Textile Care Laboratory. These laboratories are located at Federal University at Santa Catarina (Blumenau, Santa Catarina, Brazil). In Figure E.4 is shown the electrokinetic analyzer, for zeta potential measurement, this equipment is available at the Analysis Center of the Department of Chemical Engineering and Food Engineering (Federal University at Santa Catarina, Florianópolis, Brazil). Figure E.5-Figure E.8 show some of the equipment available at NCSU that were used for the research.

Figure E.1 – Dyer machine, model TC 2200, brand Texcontrol (Brazil).

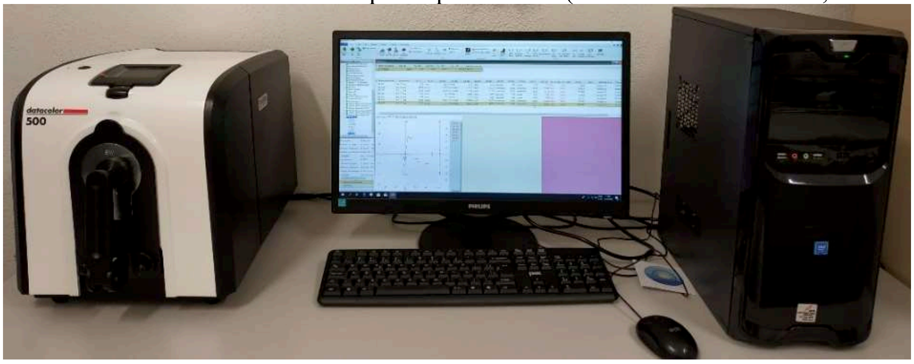
Source: the author.

Figure E.2 – (a) UV-M51 transmittance spectrophotometer from BEL Engineering (Italy). (b) Rubbing Fastness Tester, Model CA-11, Brand Kimak (Brazil).

(a) (b)

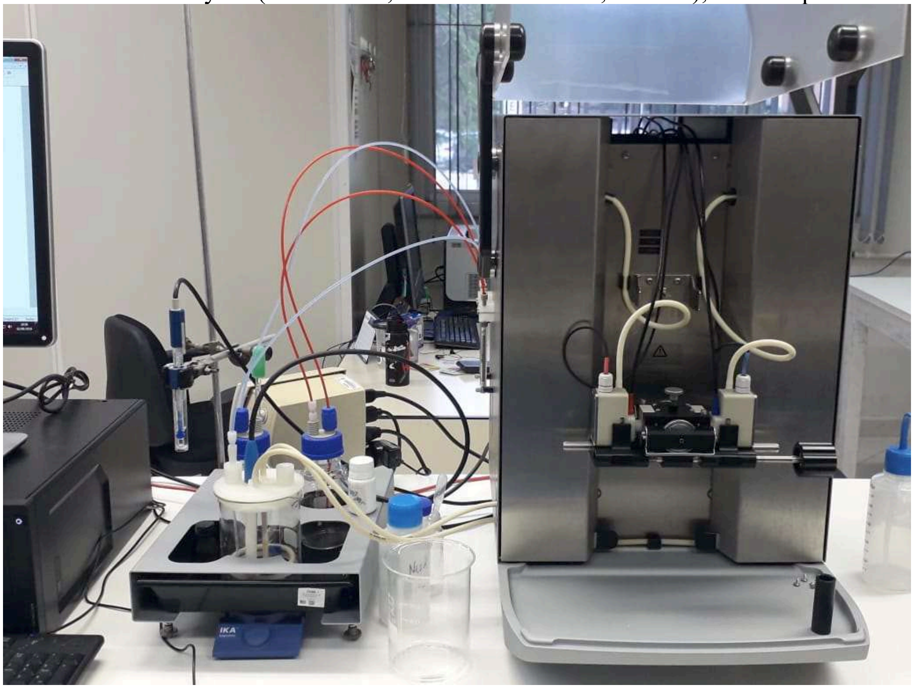
Source: the author.

Figure E.3 – Datacolor 500 reflectance spectrophotometer (Datacolor International, Switzerland).



Source: the author.

Figure E.4 – Electrokinetic analyzer (SurPASS 2, Anton Paar GmbH, Austria), for zeta potential measurement.



Source: the author.

Figure E.5 – Ahiba Nuance Infrared Laboratory Dyeing Machine (Datacolor International, USA).

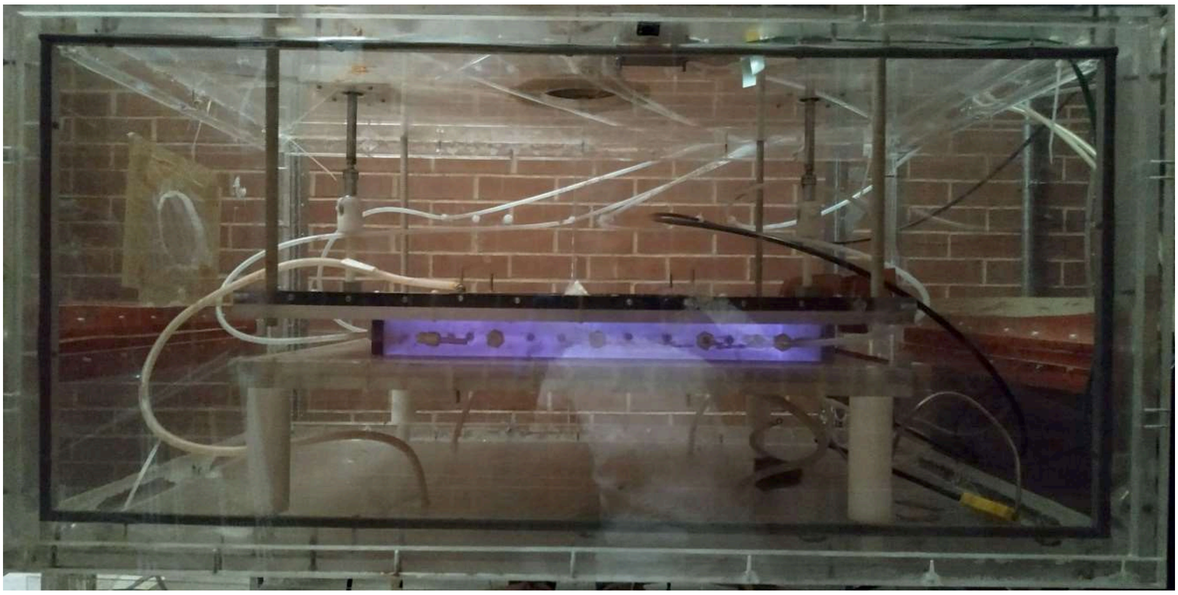
Source: the author.

Figure E.6 – Reflectance spectrophotometer, model Color i7 (X-rite, USA).

Source: the author.

Figure E.7 – DBD atmospheric plasma facility designed by College of Textiles, North Carolina State University. (a) Outer and inner chamber, (b) detail of inner chamber and plasma bulk.

(a)



(b)

Source: the author.

Figure E.8 – (a) Power supplies and function generator, (b) gas cylinders for generating plasma.

(a) (b)

Source: the author.