



# Politechnika Łódzka

Katedra Inżynierii Mechanicznej, Informatyki Technicznej  
i Chemii Materiałów Polimerowych  
Wydział Technologii Materiałowych i Wzornictwa Tekstyliów

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*Badania zmian ładunku na powierzchni włókna celulozowego  
w procesach obróbki wstępnej i jego wpływu na wybrane następcze  
procesy technologiczne*

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**Łódź 2023**

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***Pracownikom Katedry Inżynierii Mechanicznej,***  
***Informatyki Technicznej i Chemii Materiałów Polimerowych***

*za przyjazną atmosferę,*

***Koleżankom i Kolegom***

*ze środowiska kolorystyki i barwnikarstwa*  
*za cenne dyskusje i doping w realizacji badań.*

***Szczególne podziękowania***

***składam Mojej Żonie Danucie i Rodzinie***  
***za wyrozumiałość i cierpliwość.***

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## Streszczenie

Niniejsza praca opisuje badania zmian ładunku na powierzchni włókien celulozowych w procesach obróbki wstępnej oraz ich wpływ na wybrane późniejsze procesy technologiczne. Większość operacji technologicznych w chemicznej obróbce włókien celulozowych prowadzi się z użyciem środków chemicznych o charakterze anionowym, co powoduje naturalne oddziaływania odpychające między tymi substancjami a włóknem, którego powierzchnia w środowisku wodnym przyjmuje ładunek ujemny. Badania wykazały, że na każdym z etapów obróbki włókna celulozowego (bawełnianego) następuje w mniejszym lub większym stopniu zmiana wielkości ujemnego ładunku na jego powierzchni. Wartość tego ładunku zależy od rodzaju, ilości i dostępności grup funkcyjnych obecnych w celulozie, zanieczyszczeń naturalnych i innych substancji wprowadzonych na powierzchnię włókna. Efektem tego jest zmiana potencjału  $\xi$  (dzeta), ładunku powierzchniowego, oraz gęstości elektronowej na powierzchni włókna, a przede wszystkim zmiana oddziaływań między włóknem a związkami chemicznymi stosowanymi do jego obróbki chemicznej.

Badania nad tymi zjawiskami prowadzono na etapach wstępnej obróbki alkalicznej i enzymatycznej, modyfikacji włókna poprzez kationizację różnymi modyfikatorami oraz w procesach barwienia barwnikami reaktywnymi. Wyniki badań potwierdziły hipotezę o konieczności uwzględnienia wartości ładunku i gęstości elektronowej oraz ich wpływie na przebieg reakcji, zwłaszcza w odniesieniu do kationizowanej bawełny.

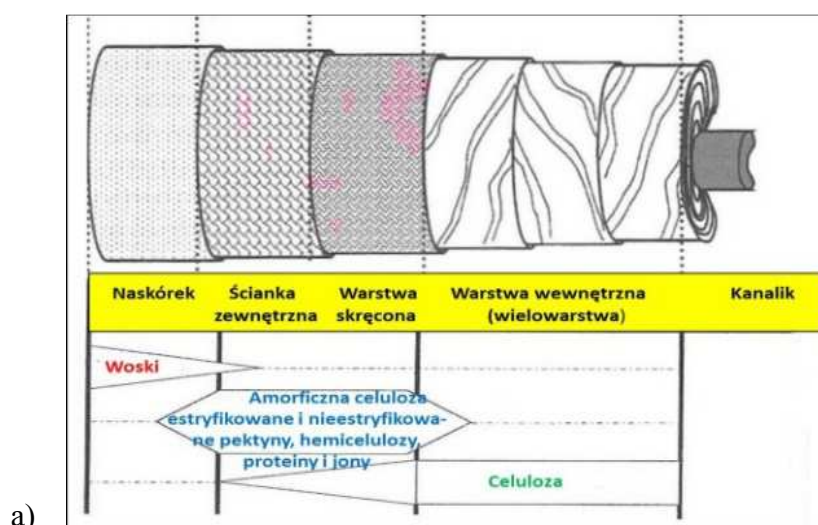
Badania barwienia kationizowanej celulozy barwnikami reaktywnymi wykazały, że proces ten można przeprowadzić w ekologicznych warunkach: bez dodatku elektrolitów i alkaliów, i w temperaturze pokojowej. Wykazano, że w tych warunkach barwnik reaktywny tworzy wiązanie kowalencyjne między grupą hydroksylową obecną w łańcuchu modyfikującym w pozycji sąsiadującej z czwartorzędową grupą kationizowanej celulozy zamiast z grupą hydroksylową w łańcuchu celulozy.

Na podstawie przeprowadzonych pomiarów wielkości ładunku na powierzchni włókna, barwienia barwnikami kwasowymi i reaktywnymi, ekstrakcji, chromatografii TLC, spektroskopii FTIR i w świetle odbitym, analizy gęstości elektronowych oraz oceny odporności wybarwień na światło potwierdzono sposób wiązania barwnika reaktywnego z kationizowaną celulozą.

# 1. Wstęp

## 1.1. Włókna celulozowe

Najważniejszym przedstawicielem naturalnych włókien celulozowych są włókna bawełniane. Stanowią one ponad 40% całkowitego zużycia surowców włókienniczych w przemyśle tekstylnym. Głównym składnikiem tych włókien jest celuloza. Naturalne surowe włókna bawełniane są z natury hydrofobowe dla ochrony podczas wegetacji, są szorstkie w dotyku i mają żółtawo-brązowy odcień. W zależności od gatunku, regionu pochodzenia, stopnia dojrzałości i warunków uprawy [1] zawierają od 4 do 12% składników niecelulozowych, takich jak hemicelulozy, białka, substancje pektynowe, woski, kwasy organiczne, proteiny, substancje barwiące oraz związki mineralne. Włókno celulozowe bawełniane zbudowane jest z kilku warstw [2]. Składniki niecelulozowe znajdują się głównie w najbardziej zewnętrznej warstwie struktury o grubości około 0,1-0,2 μm.



b)

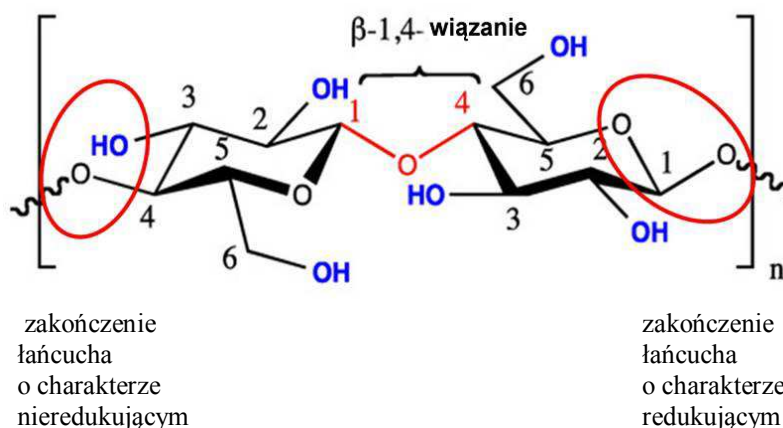
Składnik	Zawartość [%]	
	Całe włókno	Warstwa zewnętrzna
Celuloza	94	54
Woski	0,6 – 1,3	14
Substancje pektynowe	0,9 – 1,2	9
Proteiny (substancje zawierające azot)	0,6-1,3	8
Związki mineralne	1,2	3
Kwasy organiczne	0,8	-
Inne	1,4	12

Rys.1. Struktura warstw włókna celulozowego (a) oraz typowy skład włókna i warstwy zewnętrznej (b) [2]

Makrocząsteczki polimeru celulozy tworzą obszary amorficzne (nieuporządkowane) i krystaliczne (uporządkowane) [3]. Duża wytrzymałość włókna jest związana z wysokim stopniem polimeryzacji i krystaliczności.

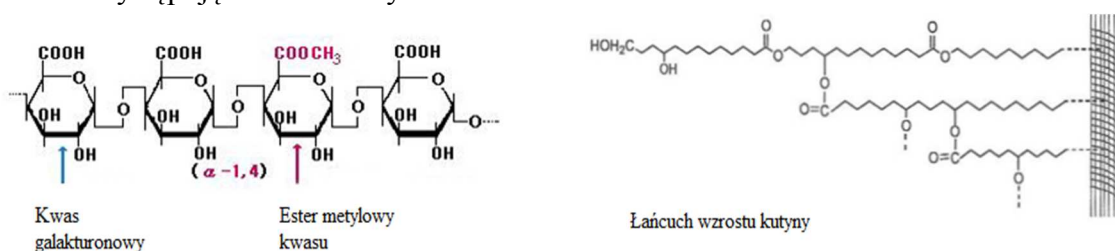
### 1.1.1. Grupy funkcyjne w celulozie

Makrocząsteczka celulozy zawiera trzy różne rodzaje jednostek anhydroglukozy: zakończenie łańcucha o charakterze redukującym z wolną grupą hemiacetalową (aldehydową) na węglu C-1, zakończenie łańcucha o charakterze nieredukującym z wolną grupą hydroksylową na węglu C-4 oraz wewnętrzne pierścienie połączone poprzez atomy węgla C-1 i C-4, z których każdy zawiera dwie wolne grupy hydroksylowe na drugorzędowych atomach węgla C-2 i C-3 oraz wolną grupę hydroksylową na pierwszorzędnym węglu C-6 [4].



Rys. 2. Budowa makrocząsteczki celulozy [4]

Ze względu na długość łańcuchów celulozy w reakcjach chemicznych dominuje wpływ grup hydroksylowych jednostek wewnętrznych. Wolne grupy hydroksylowe znajdujące się w każdej wewnętrznej jednostce glukozy stanowią blisko 31,5% jej masy. L. Fras i współautorzy [5], w swoich pracach analitycznych stwierdzili, że w celulozie istnieją dwa rodzaje grup kwasowych odpowiednio o stałych dysocjacji  $pK_a \approx 3,5$  i  $pK_a \approx 5,5-5,7$ . Pierwszy typ grup o wartości  $pK_a \approx 3,5$  odpowiada grupie karboksylowej silniejszego kwasu, typowej dla kwasów uronowych, powstałej z utleniania grupy hydroksylowej przy węglu C-6. Dla drugiej grupy nie ma jednoznacznych badań potwierdzających jakie grupy kwasowe odpowiadają dysocjacji dla  $pK_a \approx 5,5-5,7$ . Autorzy stwierdzili, że udział tych grup stanowi ok. 10% wszystkich grup kwasowych obecnych w naturalnym włóknie celulozowym po obróbce wstępnej. Sztuczne włókna celulozowe (wiskozowe, Lyocell) nie posiadają grup kwasowych o  $pK_a \approx 5,5-5,7$ . Potwierdza to, że za tą dysocjację odpowiedzialne są grupy kwasowe występujące w zanieczyszczeniach.



Rys. 3. Grupy odpowiadające za  $pK_a \approx 5,5 - 5,7$  [2]

Biorąc pod uwagę poznaną budowę chemiczną zanieczyszczeń bawełny, można z dużym prawdopodobieństwem stwierdzić, że pochodzą od składników o niższym stopniu polimeryzacji (ich prekursorami są także grupy estrowe bądź laktonowe) [2] oraz proste i rozgałęzione kwasy tłuszczowe pochodzące z hydrolizy wosków i tłuszczów jak kwas stearynowy [5] czy protein (kwas glutaminowy, asparginowy, prolina i hydroksyprolina) [6].

Oprócz grup kwasowych, przy pH powyżej 8 jonizowane są także niektóre grupy hydroksylowe celulozy, co powoduje wzrost ładunku ujemnego na powierzchni włókna. Stała dysocjacji elektrolitycznej dla celulozy obliczona przez Neale'a na podstawie eksperymentów w stężonych roztworach NaOH równa się  $1,84 \times 10^{-14}$  w 25 °C [7].

### 1.1.2. Reaktywność grup hydroksylowych celulozy

Potencjalnie w każdym pierścieniu anhydroglukozy znajdują się trzy grupy hydroksylowe zdolne do reakcji chemicznych. Z tego powodu produkty reakcji charakteryzują się tzw. stopniem podstawienia (DS), który w odniesieniu do całego łańcucha makrocząsteczki celulozy zawiera się w przedziale od 0 do 3. W większości przypadków reakcji o DS <3 powstają polimerowe produkty blokowe, w których przereagowały wszystkie dostępne grupy hydroksylowe znajdujące się w mniej uporządkowanych obszarach, a te w obszarach krystalicznych pozostają nieprzereagowane. Wyższy stopień podstawienia lub warunki reakcji, które naruszają obszar krystaliczny, prowadzą do zmniejszenia liczby wiązań wodorowych i obniżenia sił międzycząsteczkowych. W rezultacie pochodne celulozy są rozpuszczalne w popularnych rozpuszczalnikach organicznych i wykazują właściwości włóknotwórcze. Przeprowadzono szereg badań w celu określenia ilości dostępnych grup hydroksylowych na powierzchni włókna celulozowego [8-9] i ich preferencji reagowania z różnymi związkami chemicznymi [10]. Wykorzystując program Hyperchem v.8.06 (Hypercube, Inc. Gainesville, Florida, US) w układzie modelowym zawierającym trzy pierścienie glukopiranozowe obliczono dla grup hydroksylowych w środkowym pierścieniu glukopiranozowym gęstość elektronową. Obliczenia wskazują preferencję w reaktywności grup hydroksylowych do reakcji nukleofilowych w kolejności C-6 > C-3 > C-2 [11].

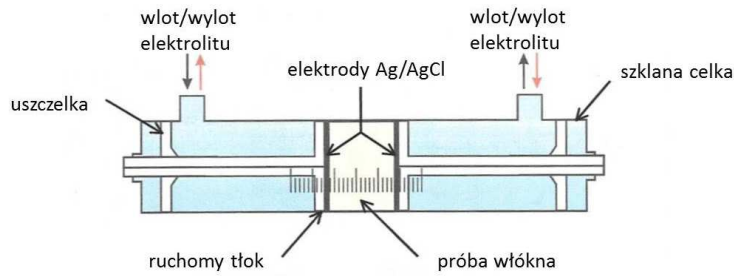
### 1.1.3. Elektrokinetyczne własności włókien celulozowych

Naturalne surowe włókna celulozowe w środowisku wodnym posiadają niewielki ładunek ujemny. Obecne w naskórku i warstwie zewnętrznej surowych włókien celulozowych woski, tłuszcze, pektyny, białka i hemicelulozy utrudniają dysocjację grup kwasowych i hydroksylowych, które są odpowiedzialne za tworzenie ładunku powierzchniowego na włóknie [2]. W środowisku wodnym, dochodzi do wzajemnego oddziaływania występujących we włóknach grup funkcyjnych i naładowanych elektrycznie cząstek barwników, elektrolitów czy środków pomocniczych wspomagających procesy technologiczne. W wyniku takiego oddziaływania, na granicy faz, powstaje podwójna warstwa elektryczna, tzw. warstwa Sterna. Potencjał generowany pomiędzy warstwą Sterna, a kąpielą nazywany jest potencjałem elektrokinetycznym i oznaczany symbolem  $\zeta$ . Jego wartość zmienia się w zależności od odległości między warstwami i zależy od wielu czynników, m.in. siły jonowej elektrolitów, wartości pH, temperatury, ruchu fazowego względem siebie.

W badaniach materiałów celulozowych najczęściej stosuje się dwie metody pomiarowe do oceny właściwości elektrokinetycznych:

#### 1.1.3.1. Pomiar potencjału $\zeta$ za pomocą urządzenia EKA (Electro Kinetic Analyzer) Anton Paar GmbH [12,13]

Badaną próbkę włókna umieszcza się w cylindrycznej celce, przez którą naprzemiennie tłoczy się elektrolit, zwykle 0,001 N KCl, a różnicę potencjałów powstającą podczas przepływu mierzy się za pomocą dwóch elektrod siatkowych Ag/AgCl umieszczonych po obu stronach badanego materiału.



Rys. 4. Schemat celi pomiarowej aparatu EKA Anton Paar (model klasyczny) [12]

Wartość potencjału  $\zeta$  oblicza się ze wzoru:

$$\zeta = \frac{dU}{dP} \times \frac{\eta}{\varepsilon \times \varepsilon_0} \times \kappa$$

gdzie:  $dU / dP$  - gradient zmiany napięcia w zależności od zmiany ciśnienia [mV / mbar]

$\eta$  - lepkość elektrolitu, [mPa × s],

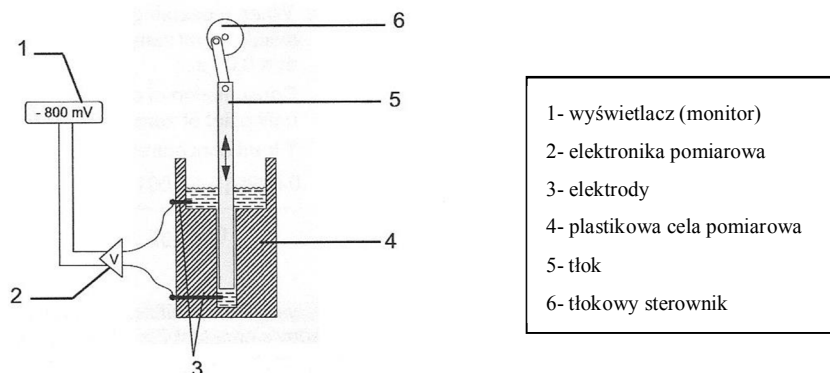
$\varepsilon$  - stała dielektryczna elektrolitu,

$\varepsilon_0$  - przenikalność elektryczna w próżni,

$\kappa$  - przewodnictwo elektrolitu.

#### 1.1.3.2. Pomiar ładunku powierzchniowego za pomocą urządzenia PCD pH 03 firmy Muetek GmbH [14-15]

Dla celulozy jako materiału porowatego możemy mówić o całkowitym ładunku powierzchniowym i wewnętrznym. Zhang Hongjie i in. [16] wykazali, że stosując poli-DADMAC (kationowy polielektrolit) o masie cząsteczkowej 7,5-15 kDa uzyskuje się wyższy poziom oznaczenia. Wynika to z jego większej penetracji do włókna. Przy masie cząsteczkowej poli-DADMAC większej niż 100 kDa można określić jedynie ładunek na powierzchni zewnętrznej. Zasada pomiaru na urządzeniu Muetek polega na tym, że kiedy badaną próbkę umieści się w celi pomiarowej, cząsteczki elektrolitu adsorbują się na plastikowej powierzchni tłoka i na ścianie celi za pomocą sił van der Waalsa, a ich przeciwjony pozostają w roztworze w ich sąsiedztwie. Uruchomienie ruchu posuwisto-zwrotnego tłoka powoduje oddzielenie przeciwjonów od zaadsorbowanych cząsteczek co skutkuje powstaniem potencjału który jest rejestrowany przez złote elektrody umieszczone w górnej i dolnej części celki pomiarowej.



Rys. 5. Schemat urządzenia Muetek (na przykładzie PCD-03 pH) [14]



Próbki włókien nie mogą być umieszczane bezpośrednio w celi pomiarowej. W takim przypadku możliwe jest zastosowanie tego urządzenia w miareczkowaniu odwrotnym – tzw. „back titration”. W tym celu próbkę włókien miesza się mieszadłem magnetycznym z nadmiarem odpowiedniego polielektrolitu anionowego lub kationowego (oznaczanie dodatniego lub ujemnego ładunku), następnie filtruje (dekantuje) i miareczkuje elektrolitem o przeciwnym ładunku, aż do uzyskania potencjału zerowego. Wielkość ładunku na powierzchni badanej próbki oblicza się ze wzoru:

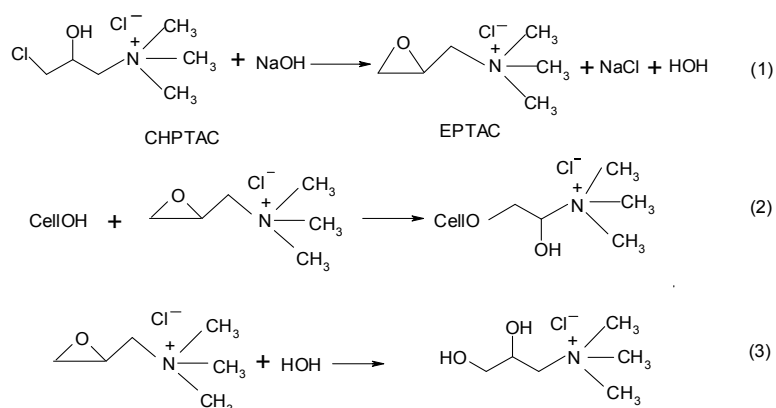
$$Q_{dz} = \frac{(V_0 - V_1) c V_c}{m V_a} \text{ [eq/g]}$$

gdzie:  $V_0$  – ml polielektrolitu PES-Na do zmiareczkowania 10 ml roztworu polielektrolitu poli-DADMAC zastosowanego do obróbki próbki materiału (ślepa próba),  
 $V_1$  – ml polielektrolitu PES-Na na zmiareczkowanie 10 ml filtratu po obróbce próbki,  
 $c$  – stężenie/koncentracja polielektrolitu poli-DADMAC  
 $V_c$  – ml polielektrolitu poli-DADMAC użyta do obróbki próbki  
 $V_a$  – ml pobrana do miareczkowania  
 $m$  – masa próbki do badań [mg]

## 1.2. Modyfikacja celulozy na drodze kationizacji

Modyfikacja włókien celulozowych poprzez kationizację czwartorzędowymi solami amoniowymi zmienia powierzchniowy ładunek elektryczny z ujemnego na kationowy [17]. W przemyśle włókienniczym prowadzone są próby wykorzystania tej metody do zwiększenia sorpcji związków chemicznych, takich jak barwniki, fluorescencyjne środki wybielające i inne tekstylne środki pomocnicze. Schlack [18] jako pierwszy doniósł o zdolności aminowanych pochodnych epoksydowych do modyfikacji celulozy i jako pierwszy zauważył zwiększone powinowactwo modyfikowanej celulozy do barwników kwasowych. Inni badacze analizowali proces modyfikacji polimerów z grupami hydroksylowymi, w tym celulozy, epoksydietyloamino-3-propanem metodą czwartorzędowania jodkiem etylu. Zmodyfikowane w ten sposób polimery znajdują zastosowanie jako wymiennicze jonowe [19].

Na przestrzeni ostatnich 20 lat najczęściej badanym modyfikatorem kationowym do celulozy był chlorek 3-chloro-2-hydroksypropylotrimetyloamoniowy (CHPTAC) [20,21]. Opublikowano wiele badań w zakresie poprawy powinowactwa barwników anionowych do tkanin bawełnianych poprzez wprowadzenie dodatnio naładowanych miejsc na bawełnie [22, 23]. Grupy hydroksylowe obecne w jednostkach glukozy są głównymi miejscami modyfikacji chemicznej [24].



Rys. 6. Kationizacja celulozy (reakcje 1 i 2) i reakcja uboczna hydrolizy EPTAC (reakcja 3) [20]

Podstawową wadą tego modyfikatora jest brak substancywności do włókna celulozowego, co przyczynia się do niskiej wydajności procesu. Utworzona reaktywna forma epoksydowa EPTAC (rys 6. – reakcja 3) w środowisku alkalicznym łatwo ulega hydrolizie z wodą, co utrudnia stosowanie tego produktu w aplikacji metodą wyczerpywania z kąpieli. Z tego powodu wielu naukowców zwraca uwagę na kationowe modyfikatory celulozy o liniowej lub rozgałęzionej strukturze polimerowej oraz o średniej substancywności. Różne typy polimerów: poliepichlorohydrynodimetyloamina, żywice poliepichlorohydrynowe, polimery typu poliamid epichlorohydryny, czwartorzędowe związki amoniowe poli(4-winylopirydyny), poli(chlorek winyloaminy), polimery dendrytyczne, kationowe kopolimery diblokowe, chitozan i jego pochodne zostały przedstawione w pracach przeglądowych [24-28] Również kationowe nanosferyczne poli(St-BA-VBT) [26], skrobia i pochodne skrobi [29] zostały opisane w literaturze. Modyfikatory wiążące się chemicznie lub fizykochemicznie z celulozą nie powinny niekorzystnie wpływać na właściwości celulozy.

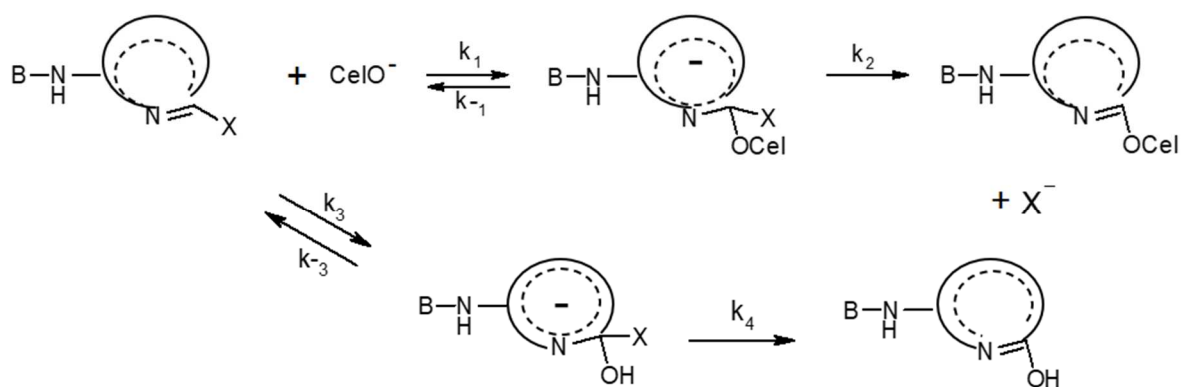
### 1.3. Barwienie włókien celulozowych barwnikami reaktywnymi

Barwniki reaktywne, ze względu na wysoką odporność na pranie i gamę jaskrawych kolorów, są od kilkudziesięciu lat jedną z najpopularniejszych grup barwników stosowanych do barwienia wyrobów celulozowych [30]. Reaktywne barwienie bawełny jest uważane za duże źródło zanieczyszczenia środowiska elektrolitem oraz barwnikami reaktywnymi, które w procesie barwienia nie związały się z włóknem celulozowym. Roczne zużycie elektrolitów tylko w Europie wynosi ok. 200 000-250 000 ton. Do ścieków w Europie trafia także ok. 20-50% barwników reaktywnych [31]. Szacuje się, że co roku na świecie do ścieków trafia ponad 70 000 ton barwników reaktywnych z całkowitej konsumpcji na poziomie 400 000 ton [41].

Pierwszą interakcją między włóknami a barwnikami podczas procesu barwienia jest wyczerpanie barwnika na włókno. W kąpielach wodnych na powierzchni włókien celulozowych generuje się ładunek ujemny. Grupy sulfonowe w barwnikach reaktywnych dysocjują także do jonu ujemnego ( $-\text{SO}_3^-$ ). W ten sposób ujemnie naładowane barwniki i ujemnie naładowane włókno ulegają jonowemu odpychaniu, co powoduje utrudnienie w ich wyczerpaniu na włókno. Aby przezwyciężyć ten problem i wspomóc proces wyczerpywania barwnika do kąpieli barwiących dodaje się duże ilości elektrolitów (najczęściej chlorek sodu lub siarczan disodu).

Po wyczerpaniu barwnika do kąpieli dozuje się porcjami alkalia aby zainicjować wiązanie barwnika za pośrednictwem wiązań kowalencyjnych z grupami hydroksylowymi celulozy. Na tym etapie procesu temperatura barwienia jest dostosowywana odpowiednio do stosowanej grupy barwników.

Reaktywne wiązanie barwników zawierających w cząsteczce atom chloru lub fluoru (triazynowe, pirymidynowe, chinoksalinowe) przebiega według mechanizmu nukleofilowego podstawienia (substytucji) aromatycznego typu  $\text{S}_{\text{N}}2$  anionem celulozanowym w celu utworzenia pseudoestrowego wiązania kowalencyjnego przedstawionego na poniższym schemacie:



**Rys. 7.** Schemat reakcji barwników reaktywnych z celulozą wg. mechanizmu nukleofilowego aromatycznego podstawienia (X- chlor lub fluor; B- reszta barwnika reaktywnego) [32]

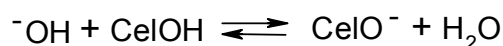
Barwniki zawierające jako układ reaktywny ugrupowanie winylosulfonyłowe lub ugrupowanie 2-siarczanoetylosulfonyłowe będące prekursorem ugrupowania winylosulfonyłowego reagują z włóknem celulozowym według mechanizmu reakcji nukleofilowego przyłączenia (addycji) do wiązania nienasyconego:



**Rys. 8.** Schemat reakcji barwników reaktywnych winylosulfonyłowych z celulozą (B- reszta barwnika reaktywnego) [33]

Tworzenie wiązań kowalencyjnych między barwnikiem a włóknem może nastąpić tylko wtedy, gdy barwnik jest w bezpośrednim kontakcie z fazą celulozową. Szybkość reakcji wiązania się z włóknem rośnie wraz ze stężeniem zjonizowanych grup hydroksylowych celulozy, czemu sprzyja dodatek alkaliów do kąpeli. Jednocześnie przebiega konkurencyjna reakcja hydrolizy układu reaktywnego, zależna również od stężenia jonów hydroksylowych w środowisku reakcji.

Stężenie barwnika we włóknie jest wyższe niż w kąpeli. Anion  $\text{CelO}^-$  wykazuje silniejszy charakter nukleofilowy niż jon hydroksylowy  $\text{HO}^-$ . Ponadto na włóknie ustala się stan równowagowy:



co powoduje, że szybkość reakcji z celulozą jest kilkakrotnie większa niż szybkość reakcji hydrolizy barwnika znajdującego się na włóknie.

Jedną z metod rozwiązania problemów stosowania ogromnych ilości elektrolitów w procesie barwienia i ich zrzutu do ścieków jest modyfikacja barwników reaktywnych poprzez wprowadzenie do ich struktury chemicznej grup kationowych [34]. Jednakże, tą drogą nie udało uzyskać się dotychczas satysfakcjonujących wyników. Alternatywną metodą może być kationowa modyfikacja bawełny, po której, głównie dzięki wprowadzeniu na

powierzchnię włókna pełnych ładunków dodatnich, może być barwiona nie tylko barwnikami reaktywnymi, ale także innymi grupami anionowych barwników, np. bezpośrednimi, kwasowymi czy rozpuszczalnymi barwnikami siarkowymi [35].

Mechanizm reakcji chemicznego wiązania wszystkich grup barwników reaktywnych z niekationizowaną celulozą jest powszechnie znany [36-38], to jednak w przypadku barwienia kationizowanych włókien celulozowych tymi samymi barwnikami sposób i miejsce wiązania barwników nie jest jednoznacznie określony.

Chociaż, w ostatnich dziesięcioleciach opublikowano blisko tysiąc publikacji [39] dotyczących kationizacji włókien bawełny i warunków wykorzystania takiej modyfikacji do barwienia, drukowania i innych zastosowań użytkowych, to istnieje tylko kilka spektakularnych doniesień na temat mechanizmu reakcji wiązania barwników reaktywnych z kationizowaną celulozą [25,28,40], które jednak nie zawierają dowodów na ich prawdopodobieństwo. Żadne z nich nie jest nawet zbieżne z hipotezą zawartą w niniejszej pracy i nie donosi o analizie tworzonych wiązań w powiązaniu z jednym z ważniejszych parametrów użytkowych wyrobów, a mianowicie odpornością na światło dla uzyskanych wybarwień. W pracy przedstawiono dowody na proponowany przebieg reakcji barwników reaktywnych z kationizowanym (z zastosowaniem wyselekcjonowanych modyfikatorów) włóknem w oparciu o znane metody analityczne wsparte obliczeniami gęstości elektronowych na elektroujemnych atomach tlenu i azotu, kationowych centrach zdolnych do reakcji jonowych oraz ładunku na powierzchni włókna.

## 2. Cel badań

Celem pracy było badanie zmian ładunku powierzchniowego celulozy na różnych etapach obróbki wstępnej, kationizacji i późniejszego barwienia barwnikami reaktywnymi. Zastosowano szereg metod badawczych, aby potwierdzić hipotezę o możliwości tworzenia wiązania kowalencyjnego między ugrupowaniem reaktywnym barwnika reaktywnego i grupą hydroksylową w łańcuchu modyfikatora zamiast z grupą hydroksylową pierścienia glukopiranozy:

1. Wykorzystano metodę pomiaru ładunku na powierzchni włókna za pomocą urządzenia PCD pH 03 firmy Muetek GmbH
2. Zastosowano modyfikatory o określonej budowie chemicznej do kationizacji celulozy
3. Zastosowano barwniki reaktywne o różnych układach reaktywnych do barwienia celulozy modyfikowanej i niemodyfikowanej
4. Zastosowano dimetyloformamid do ekstrakcji barwników niezwiązanych kowalencyjnie z celulożą modyfikowaną i niemodyfikowaną
5. Wykorzystano mechanikę molekularną MM+ (opcja z analizą ładunku) a następnie półempiryczną metodę obliczeń kwantowo-chemicznych PM3 do analizy gęstości elektronowej na atomach tlenu i azotu do ustalania mechanizmów reakcji
6. Zastosowano metodę Kjeldahla do analizy zawartości azotu
7. Wykorzystano analizy FTIR i chromatografii TLC w analizie budowy chemicznej oraz spektrofotometr Datacolor 850 do pomiaru zmian intensywności barwy

### 3. Publikacje włączone do rozprawy doktorskiej

5. Stanisław Pruś, Piotr Kulpiński, Edyta Matyjas-Zgondek, Joanna Rutowicz & Krzysztof Wojciechowski (2023) The Light Fastness of the Reactive Dyes on Cationized Cellulose, *Journal of Natural Fibers*, 20:2, 2215995, DOI: 10.1080/15440478.2023.2215995
4. Stanisław Pruś, Piotr Kulpiński, Edyta Matyjas-Zgondek, Krzysztof Wojciechowski, (2022). Mechanism of bonding reactive dyes with copolymer (chloromethyl)oxirane-1H Imidazole cationised cellulose. *Materials* (2022), 15, 4664. <https://doi.org/10.3390/ma15134664>
3. Stanisław Pruś, Piotr Kulpiński, Edyta Matyjas-Zgondek, Krzysztof Wojciechowski (2022). Eco-friendly dyeing of cationised cotton with reactive dyes: mechanism of bonding reactive dyes with CHPTAC cationised cellulose. *Cellulose*, 29(7), pp. 4167–4182 doi.org/10.1007/s10570-022-04521-w
2. Stanisław Pruś, Piotr Kulpiński, Edyta Matyjas-Zgondek (2021). Comparison of the effects of the cationisation of raw, bio- and alkali scoured cotton knitted fabric with different surface charge density. *AUTEX Research Journal*, vol 21, No 2, DOI 10.2478/aut-2020-0049
1. Stanisław Pruś, Piotr Kulpiński, Edyta Matyjas-Zgondek (2019). Changes in the specific charge amount on the surface of cotton fibres during the alkali pre-treatment process. *Fibres & Textiles in Eastern Europe* 27, 4(136): 30-37. DOI: 10.5604/01.3001.0013.1817

**Tabela 1.** Zestawienie danych bibliograficznych zawartych w rozprawie.

Numer publikacji	Impact Factor	Punktacja MNISW 2022/2023	Punktacja podzielona przez liczbę współautorów	Liczba cytowań (Scopus)
1	0,75	70	23,33	5
2	1,375	140	46,67	2
3	5,93	100	25	8
4	3,748	140	35	0
5	3,507	140	28	0
			$\Sigma = 158$	

#### 3.1. Uczestnictwo w konferencjach i seminariach

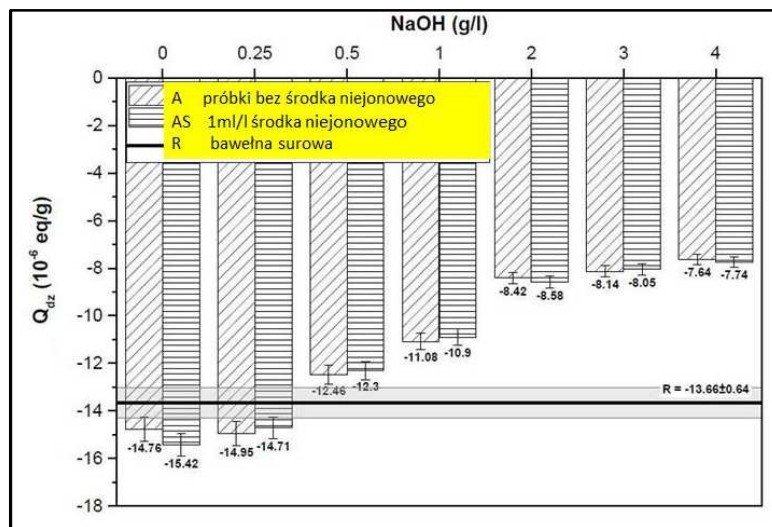
8. Stanisław Pruś, Piotr Kulpiński, Edyta Matyjas-Zgondek, Krzysztof Wojciechowski, Joanna Rutowicz (2023). Odporność na światło barwników reaktywnych na kationizowanej celulozie. XXXVI Seminarium Polskich Kolorystów, Zakopane, 24-26.05.2023 str. 91-100, ISBN 978-83-944176-3-5
7. Stanisław Pruś, Piotr Kulpiński, Edyta Matyjas-Zgondek, Krzysztof Wojciechowski, (2023). Mechanizmy reakcji w barwieniu barwnikami reaktywnymi kationizowanej celulozy. XXXVI Seminarium Polskich Kolorystów, Zakopane, 24-26.05.2023 str. 37-54, ISBN 978-83-944176-3-5
6. Stanisław Pruś, Piotr Kulpiński, Edyta Matyjas-Zgondek, Krzysztof Wojciechowski (2022), Mechanism of binding reactive dyes with copolymer(chloromethyl)oxirane-

- 1H Imidazole cationised cellulose (Texamin ECE New). Czech Republic, Hradec Kralove, 10-11.11.2022, Sprawodaj STCHK 4/2022 pp. 40, ISSN 1214-8091
5. Stanisław Pruś (2017), Wpływ ładunku powierzchni włókna bawełny na efekt kationizacji. XXXIII Seminarium Polskich Kolorystów, Bydgoszcz 20-22.09.2017 str. 181-194, ISBN 978-83-927176-9-0
  4. Stanisław Pruś, Edyta Matyjas-Zgondek (2016), New aspects in cationisation of cotton. XXIV International Congress IFATCC, Czech Republic, Pardubice, June 13-16, Book of Abstracts, ISBN 978-80-906086-8-9, pp.405
  3. Stanisław Pruś (2015) ,Bielenie chemiczne włókien celulozowych. XXXI Seminarium Polskich Kolorystów, Ustroń-Jaszowiec 23-25.09.2015, str. 129-135, ISBN 978-83-927176-7-6
  2. Stanisław Pruś (2014), Druk kationizowanej bawełny. XXX Seminarium Polskich Kolorystów, Zakopane 24-26.09.2014, str. 121-146, ISBN 978-83-927176-6-9
  1. Stanisław Pruś, Bogumił Gajdzicki (2013), Zrównoważone działania w uprawie i chemicznej obróbce bawełny. XXIX Seminarium Polskich Kolorystów, Piechowice 25-27.09.2013, str. S 93-130, ISBN 978-83-927176-5-2,

## 4. Streszczenie artykułów wchodzących w skład rozprawy doktorskiej

### 4.1. Zmiany wielkości ładunku właściwego na powierzchni włókien bawełny w czasie alkalicznej obróbki wstępnej

Naturalne włókna bawełniane zawierają znaczne ilości zanieczyszczeń, które muszą zostać usunięte na etapie obróbki wstępnej. W procesie tym, oprócz zanieczyszczeń pochodzących z uprawy, z zewnętrznej warstwy włókna usuwane są również zanieczyszczenia niecelulozowe, do których należą substancje tłuszczowe, woski, pektyny i białka. Ich usunięcie jest niezbędne do uzyskania surowca włókienniczego do dalszej obróbki, charakteryzującego się jednorodnością i dobrą zwilżalnością.



**Rys. 9.** Zmiany wielkości ładunku właściwego na powierzchni surowych dzianin bawełnianych po obróbce alkalicznej z lub bez obecności niejonowych środków powierzchniowo czynnych (temperatura obróbki wstępnej 100 °C).

**Tabela 2.** Zmiany zwilżalności surowych dzianin bawełnianych po obróbce alkaliczną z dodatkiem i bez dodatku niejonowego środka powierzchniowo czynnego

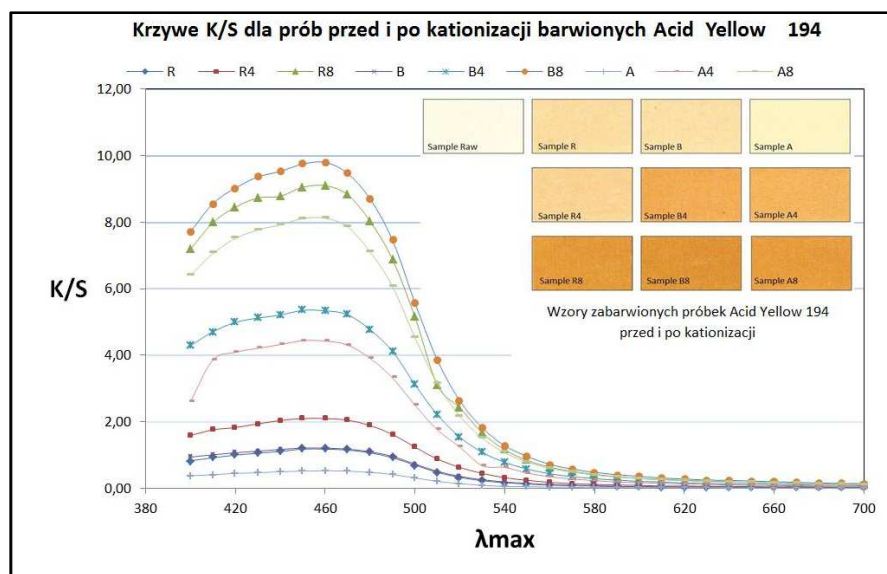
Sample	A0	A0,25	A0,5	A1	A2	A3	A4
Wettability [s]	No wettability	No wettability	No wettability	300	135	20 (penetration) <sup>o</sup>	20 (penetration) <sup>o</sup>
Sample	AS0	AS0,25	AS0,5	AS1	AS2	AS3	AS4
Wettability [s]	300 (penetration) <sup>o</sup>	180	10	6	2	1	1

W konwencjonalnym procesie alkalicznej obróbki wstępnej w podwyższonej temperaturze zanieczyszczenia niecelulozowe ulegają emulgowaniu i hydrolizie do form rozpuszczalnych w wodzie i są usuwane z włókna w postaci soli sodowych. W zależności od zastosowanego stężenia wodorotlenku sodu, temperatury i czasu stopień oczyszczenia włókna jest różny. W wyniku obróbki wstępnej zmniejsza się masa włókna, zwiększa się stopień bieli, a włókno uzyskuje odpowiednią zwilżalność wymaganą w kolejnych procesach technologicznych. Konsekwencją alkalicznej obróbki wstępnej jest również znaczne zmniejszenie ładunku ujemnego na powierzchni włókna. Wykonane badania potwierdziły oczekiwane zmiany ładunków na powierzchni, a także zwilżalności, ubytku masy i zmian stopnia bieli.



#### 4.2. Porównanie efektów kationizacji dzianin z bawełny surowej, po obróbce enzymatycznej i alkalicznej i mających różną gęstość ładunku powierzchniowego

Kationizując surową bawełnę, po obróbce enzymatycznej lub alkalicznej w tych samych warunkach recepturowych chlorkiem 3-chloro-2-hydroksypropylotrimetylo-amoniowym (CHPTAC), uzyskano różne efekty końcowe tego procesu. Analiza bawełny surowej, poddanej obróbce enzymatycznej i alkalicznej wykazała, że miały one różne wartości ujemnego ładunku powierzchniowego przed i po procesie kationizacji. Wyższy stopień kationizacji włókien celulozowych CHPTAC uzyskano dla materiałów bawełnianych o wyższych wartościach ładunku ujemnego na powierzchni. Do analizy wielkości ładunków powierzchniowych próbek bawełny niemodyfikowanej i modyfikowanej wykorzystano urządzenie Muetek PCD 03 pH oraz metodę miareczkowania odwrotnego („back-titration”) z zastosowaniem kationowych i anionowych polielektrolitów. Po procesie kationizacji oceniono również ubytek masy, zmianę stopnia bieli, zwilżalności próbek i zawartości azotu w próbkach. Zawartość azotu oznaczona metodą Kjeldhala (oznaczenie azotu następuje w próbce po mineralizacji) okazała się nieprzydatna do obliczenia stopnia kationizacji (bawełny surowej i poddanej obróbce enzymatycznej). W procesie kationizacji w środowisku alkalicznym obok wprowadzania azotu w postaci grupy czwartorzędowej następuje jednocześnie usuwanie zanieczyszczeń naturalnych z włókna zawierających atom azotu. Stopień kationizacji próbek można ocenić w sposób pośredni za pomocą porównania wartości K/S próbek barwionych Acid Yellow 194 (barwnik kwasowy metalokompleksowy). Próbki o większym stopniu kationizacji charakteryzowały się wyższymi wartościami K/S. W procesie barwienia utworzyło się wiązanie jonowe między grupą czwartorzędową (dodatnią) kationizowanych próbek bawełny i ujemną grupą sulfonową barwnika kwasowego.

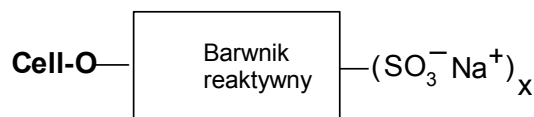


- Próbka R – dzianina surowa bawełniana (single jersey) bez obróbki wstępnej
- Próbka R4 – próbka R kationizowana przy 4% owf z CHPTAC
- Próbka R8 – próbka R kationizowana przy 8% owf z CHPTAC
- Próbka B – próbka R po obróbce enzymatycznej pektynazą alkaliczną
- Próbka B4 – próbka B kationizowana przy 4% owf z CHPTAC
- Próbka B8 – próbka B kationizowana przy 8% owf z CHPTAC
- Próbka A – próbka R po obróbce alkalicznej z wodorotlenkiem sodu
- Próbka A4 – próbka A kationizowana przy 4% owf z CHPTAC
- Próbka A8 – próbka A kationizowana przy 8% owf z CHPTAC

Rys. 10. Krzywe K/S dla wybarwień Acid Yellow 94 na próbkach przed i po kationizacji

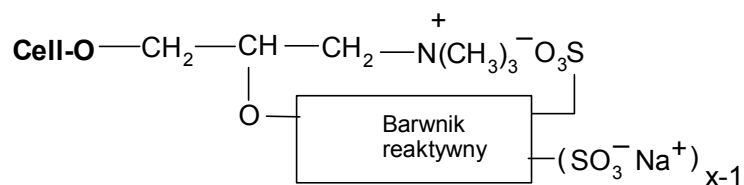
#### 4.3. Ekologiczne barwienie kationizowanej bawełny barwnikami reaktywnymi – mechanizm wiązania barwników reaktywnych z celulozą kationizowaną CHPTAC

Barwniki reaktywne stanowią podstawową klasę barwników do barwienia włókien celulozowych. Podczas procesu barwienia metodami konwencjonalnymi tworzą trwałe wiązania chemiczne w mechanizmie reakcji addycji lub podstawienia z grupą hydroksylową należącą do pierścienia glukopiranozy.



Rys. 11. Schemat wiązania barwnika reaktywnego z celulożą niemodyfikowaną

Ze względu na ujemne ładunki powstające na powierzchni celulozy w procesie barwienia kąpielowego konieczne jest stosowanie dużej ilości elektrolitów i środków alkalicznych. Ta ogromna ilość soli powoduje wzrost zasolenia wody w środowisku. Kationizacja celulozy może stanowić rozwiązanie problemu użycia dużych ilości soli w procesie barwienia metodami kąpielowymi. Wprowadzenie do celulozy na drodze eteryfikacji grup czwartorzędowych o ładunku dodatnim mogłoby być szansą na wyeliminowanie problemów środowiskowych. Bazy publikacji przedstawiają blisko tysiąc prac badawczych dotyczących modyfikacji celulozy na drodze kationizacji. Nie ma jednak prac dotyczących tego, w jaki sposób barwniki reaktywne reagują z kationizowaną celulożą w procesie barwienia pod nieobecność soli i alkaliów. Przeprowadzone badania są pierwszymi, które wyjaśniają, że w ekologicznych warunkach (w kąpeli wodnej o temperaturze pokojowej, bez dodatku soli i alkaliów) barwniki reaktywne tworzą wiązanie chemiczne z grupą hydroksylową należącą do modyfikatora (CHPTAC) używanego do kationizacji celulozy.



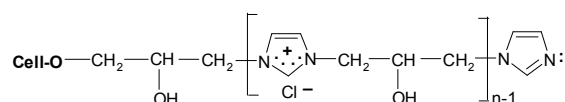
Rys. 12. Proponowany schemat wiązania barwników reaktywnych z celulożą kationizowaną CHPTAC

Czwartorzędowa grupa modyfikatora, która wykazuje ładunek dodatni, w pierwszym etapie procesu barwienia tworzy silne wiązanie jonowe z grupą sulfonową barwnika. W kolejnym etapie grupa reaktywna barwnika reaguje z nukleofilem utworzonym w pozycji sąsiadującej (pozycja  $\beta$ ) do tej grupy czwartorzędowej. Odkrycie to całkowicie zmienia punkt widzenia na mechanizm reakcji barwienia i może mieć decydujący wpływ na parametry użytkowe uzyskiwanych wybarwień.

Tworzenie wiązania kowalencyjnego w tym miejscu (pozycja  $\beta$ ) potwierdzono dla wybranych barwników należących do różnych klas barwników reaktywnych przez ekstrakcję niezwiązanego kowalencyjnie barwnika w DMF, hydrolizę kwasowo-zasadową utworzonego wiązania kowalencyjnego, oraz analizę gęstości elektronowej.

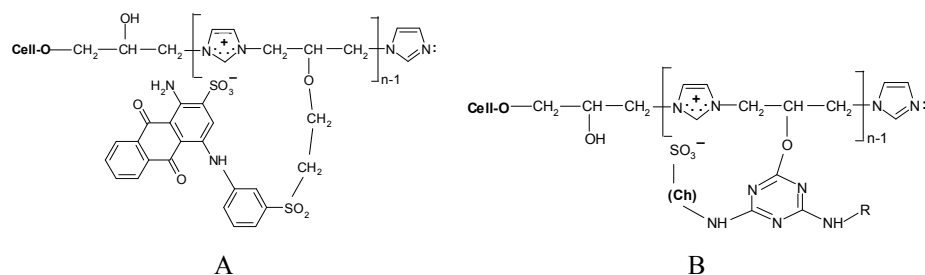
#### 4.4 Mechanizm wiązania barwników reaktywnych z celulozą kationizowaną kopolimerem (chlorometylo)oksiran-1H-imidazolu

Kopolimer (chlorometylo)oksirano-1H-imidazolu {[IME]<sup>+</sup>Cl<sup>-</sup>} jest poliheterocyklicznym liniowym związkem kationowym o dużym potencjale komercyjnym ze względu na umiarkowaną substancyjność i zadowalające wiązanie z celulozą w procesie kationizacji. W badaniach ustalono wzór budowy dla produktu handlowego o nazwie Texamin ECE New. Reakcja kationizacji z celulozą przebiega z wytworzeniem układu epoksydowego w modyfikatorze i następczą eteryfikację, podobnie jak z CHPTAC.



Rys. 13. Proponowany wzór chemiczny celulozy kationizowanej z [IME]<sup>+</sup>Cl<sup>-</sup> (stopień polimeryzacji n = 5)

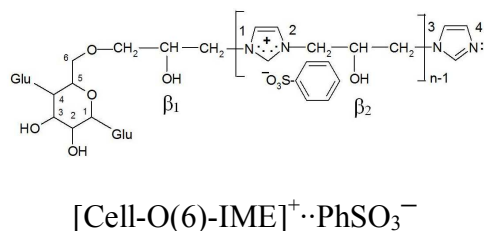
Barwniki reaktywne podczas procesu barwienia w warunkach przyjaznych dla środowiska (w kąpeli wodnej o temperaturze pokojowej, bez dodatku soli i alkaliów) tworzą trwałe wiązanie chemiczne w mechanizmie reakcji addycji lub substytucji z grupą hydroksylową w pozycji β2 (rys. 15) sąsiadującej z czwartorzędową grupą należącą do łańcucha modyfikatora.



gdzie: Ch – chromofor barwnika reaktywnego: RR 24:1, RB 160, RR 221 i RR 274,  
R - różne podstawniki chemiczne w budowie chemicznej nad barwnikami,  
Ch i R mogą zawierać inne grupy sulfonowe

Rys. 14. Proponowane wzory chemiczne kationizowanej celulozy z wiązaniami kowalencyjnymi:  
RB19 (A) wg. mechanizmu addycji i RR 24:1, RB160, RR 221 i RR 274 wg mechanizmu substytucji  
Sn2 (B)

Czwartorzędowa grupa modyfikatora wykazująca ładunek dodatni w pierwszym etapie procesu barwienia tworzy silne wiązanie jonowe z grupą sulfonową barwnika, a w kolejnym etapie grupa reaktywna barwnika reaguje z utworzonym nukleofilem. Tworzenie wiązania kowalencyjnego w tym miejscu (pozycja β2) zostało potwierdzone dla wybranych barwników należących do różnych klas barwników reaktywnych poprzez hydrolizę kwasowo-zasadową wiązania, ekstrakcję DMF oraz analizę gęstości elektronowej.



Rys. 15. Struktura chemiczna celulozy kationizowanej parami jonowymi z kwasem benzenosulfonowym przyjęta do analizy elektronowej gęstości

**Tabela 3.** Zestawienie gęstości elektronowej dla analizowanych atomów tlenu [Cell-O(6)-IME]<sup>+</sup>··PhSO<sub>3</sub><sup>-</sup>

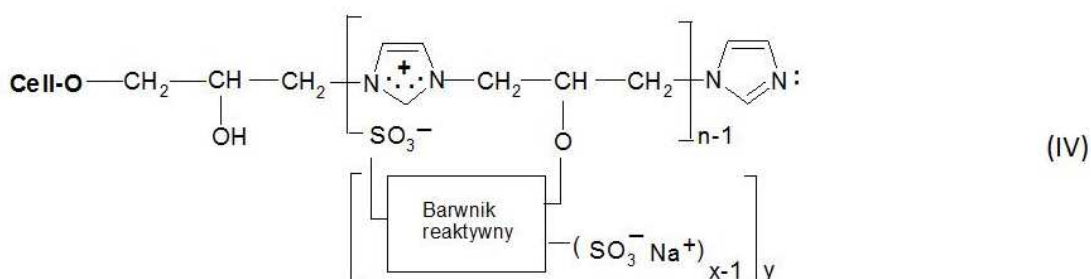
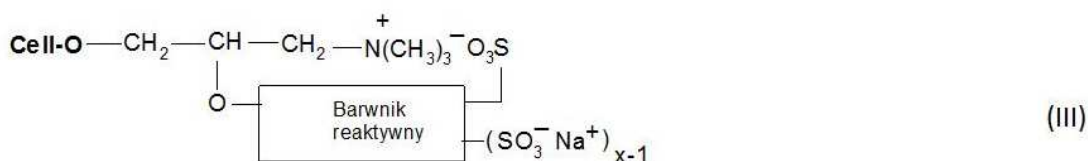
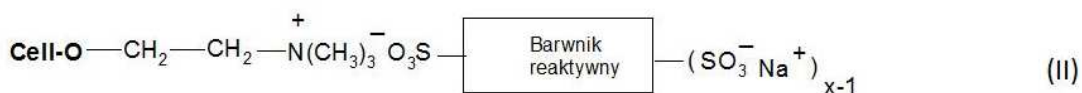
Związek modelowy	Gęstość elektronowa na atomach tlenu i azotu					
	O(2)	O(3)	O(β <sub>1</sub> )	O(β <sub>2</sub> )	N(1)	N(2)
[Cell-O(6)-IME] <sup>+</sup> Cl <sup>-</sup>	-0,286	-0,315	-0,319	-0,311	0,445	0,407
[Cell-O(6)-IME] <sup>+</sup> ··PhSO <sub>3</sub> <sup>-</sup>	-0,292	-0,311	-0,311	-0,318	0,410	0,368

Tabela 3 pokazuje, że utworzenie wiązania jonowego pomiędzy grupą sulfonową kwasu benzenosulfonowego i grupą czwartorzędową modyfikatora w kationizowanej celulozie powoduje wzrost gęstości elektronowej na atomie tlenu w pozycji β<sub>2</sub> (z wartości -0,311 do -0,318). Pozwala to na przyjęcie założenia, że prawdopodobna jest również taka zmiana w reakcji pomiędzy grupą sulfonową barwnika reaktywnego i grupą czwartorzędową tego modyfikatora. W konsekwencji prowadzi to, do wytworzenia wiązania kowalencyjnego tej grupy hydroksylowej (najwyższy wskaźnik nukleofilowości) z grupą reaktywną barwnika reaktywnego zgodnie z proponowanym w publikacji schematem [42].

#### 4.5. Odporność na światło barwników reaktywnych na kationizowanej celulozie

Odporność na światło barwionych tekstyliów jest jedną z najważniejszych cech gotowych wyrobów. Zjawisko płowienia barwników związane z fotodegradacją jest procesem złożonym. Na płowienie kolorowych tekstyliów wpływa wiele czynników, takich jak sposób związania barwnika z włóknem, budowa chemiczna barwnika i podłoża, jakość promieniowania oraz temperatura i wilgotność. Ważnymi czynnikami są również stężenie barwnika na włóknie i modyfikacja chemiczna włókna oraz współpłaszczyznowość cząsteczek barwnika i makrocząsteczki celulozy.

Poniżej przedstawiono sposób związania barwników reaktywnych z celulozą niemodyfikowaną i modyfikowaną z zastosowaniem trzech różnych modyfikatorów i poddanych badaniom odporności na światło:



gdzie:

barwnik reaktywny = RR 24:1, RR 221, RR 274, RB 19 i RB 160,

x - liczba grup sulfonowych w cząsteczce barwnika,

y - liczba cząsteczek barwnika reaktywnego związanych kowalencyjnie ( $y \leq n-1$ ),

n - stopień polimeryzacji.

**Rys. 16.** Wiązania chemiczne pomiędzy wybranymi barwnikami reaktywnymi z celulozą niekationizowaną (I) i kationizowaną: odpowiednio chlorek chlorocholiny (II), CHPTAC (III) i Texamin ECE New (IV).

Oczywiste jest, że trwała modyfikacja celulozy za pomocą różnych środków modyfikujących prowadzi do wytwarzania nowych pochodnych celulozy o zmienionych właściwościach w porównaniu z celulożą niemodyfikowaną. Dotyczy to zwłaszcza procesu kationizacji, w którym w zależności od zastosowanego modyfikatora nowa pochodna celulozy uzyskuje na swojej powierzchni częściowy lub całkowity ładunek dodatni.

**Tabela 4.** Obliczone gęstości elektronowe dla grup czwartorzędowych i sulfonowych


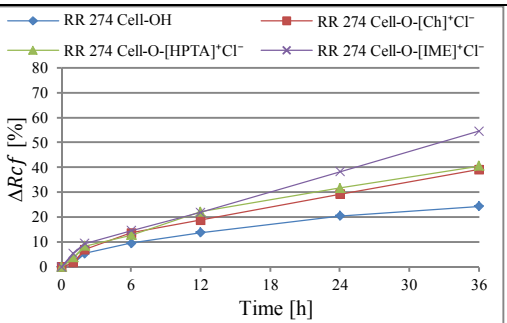




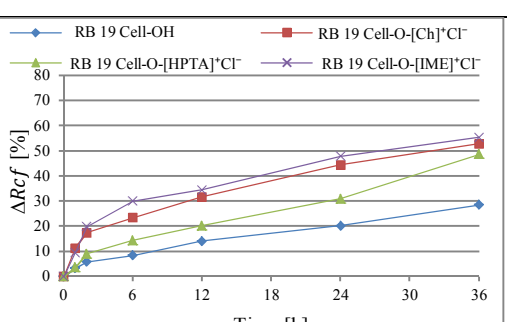




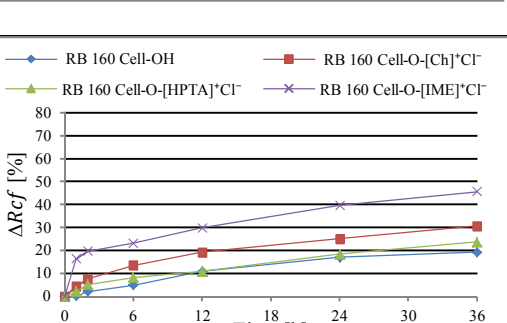



Związek modelowy	$-\text{SO}_3^-$	Grupa czwartorzędowa (gęstość elektronowa)	
Rys. 16. (I) celuloza niemodyfikowana	-0.497	brak	brak-
Rys. 16 (II) $-\text{[Ch]}^+$ -		$-\text{N}(\text{CH}_3)_3^+$	0.633
Rys. 16 (III) $-\text{[HPTA]}^+$ -		$-\text{N}(\text{CH}_3)_3^+$	0.638
Rys. 16 (IV) $-\text{[IME]}^+$ -		$-\text{N}(\text{CH}_3)_3^+$	$(0.852)_{n-1}$

Tabela 4., na przykładzie jednej grupy sulfonowej i jednej grupy czwartorzędowej, przedstawia obliczone zmiany gęstość elektronowej w obrębie cząsteczki barwnika reaktywnego związanego jonowo z kationizowaną celulozą. Zaobserwowano, że ubytek barwy podczas naświetlania zwiększa się wraz ze wzrostem dodatniej wartości gęstości elektronowej oraz odległości wiązania jonowego od głównego łańcucha modyfikowanej kationowo celulozy.

Wyniki badań odporności wybarwień na światło próbek barwionych w warunkach ekologicznych na celulozie kationizowanej wskazują obniżenie w stosunku do wybarwień na celulozie niemodyfikowanej, niezależnie od rodzaju zastosowanego modyfikatora i barwnika reaktywnego. Dane ekstrakcji DMF po naświetlaniu (Tabela 5) potwierdzają powyższe obserwacje.

**Tabela 5.** Wyniki badań dotyczących naświetlania kationizowanych próbek celulozy barwionych różnymi modyfikatorami w porównaniu z barwionymi próbkami niekationizowanymi

Barwione próby	Próby naświetlane 1, 2, 6, 12, 24 i 36 godz.	Odporność na światło po 36 godz. <sup>1)</sup>	$\Delta R_{cf}$ po 36 godz. [%]	Wykresy zmian kolorów w czasie naświetlania
RR 24:1 Cell-OH		4	41,90	
RR 24:1 Cell-O-[Ch]+Cl-		3-4	50,65	
RR 24:1 Cell-O-[HPTA]+Cl-		4	30,90	
RR 24:1 Cell-O-[IME]+Cl-		2-3	67,50	
RR 221 Cell-OH		4-5	29,85	
RR 221 Cell-O-[Ch]+Cl-		3	55,86	
RR 221 Cell-O-[HPTA]+Cl-		3-4	37,7	
RR 221 Cell-O-[IME]+Cl-		2-3	75,54	

<b>RR 274</b> Cell-OH		4-5	24,40	
<b>RR 274</b> Cell-O-[Ch] <sup>+</sup> Cl <sup>-</sup>		3-4	39,30	
<b>RR274</b> Cell-O-[HPTA] <sup>+</sup> Cl <sup>-</sup>		4	40,60	
<b>RR 274</b> Cell-O-[IME] <sup>+</sup> Cl <sup>-</sup>		3	54,67	
<b>RB 19</b> Cell-OH		3-4	28,60	
<b>RB 19</b> Cell-O- [Ch] <sup>+</sup> Cl <sup>-</sup>		3	52,81	
<b>RB 19</b> Cell-O-[ HPTA] <sup>+</sup> Cl <sup>-</sup>		3	48,64	
<b>RB 19</b> Cell-O-[IME] <sup>+</sup> Cl <sup>-</sup>		2-3	55,42	
<b>RB 160</b> Cell-OH		4	19,41	
<b>RB 160</b> Cell-O-[Ch] <sup>+</sup> Cl <sup>-</sup>		3-4	30,80	
<b>RB 160</b> Cell-O[HPTA] <sup>+</sup> Cl <sup>-</sup>		4	23,86	
<b>RB 160</b> Cell-O-[IME] <sup>+</sup> Cl <sup>-</sup>		3-4	45,74	

<sup>1)</sup> Odporność na światło po 36 godzinach naświetlania według niebieskiej skali

## 5. Podsumowanie i perspektywy

Podsumowując wyniki pracy można stwierdzić, że obecność ładunku na powierzchni włókna celulozowego jest znacznie ważniejsza niż dotychczas sądzono. Wykazano jak zmienia się jego wielkość na poszczególnych etapach obróbki wstępnej w powiązaniu z innymi parametrami jak: ubytek masy włókna, stopień zmiany bieli i zwilżalność. Potwierdzono hipotezę, że poprzez wprowadzenie dodatniego ładunku na powierzchnię włókna uzyskuje się nie tylko zwiększenie wyczerpania anionowych barwników reaktywnych lub kwasowych, a także, że celuloza kationizowana modyfikatorami o specyficznej budowie chemicznej (zawierające grupy hydroksylowe) wiąże kowalencyjnie barwniki reaktywne bez konieczności stosowania elektrolitów i alkaliów oraz w temperaturze pokojowej. Zaproponowano przebieg mechanizmu barwienia reaktywnego w tych warunkach.

Ustalono, że ładunki dodatnie wprowadzone w procesie kationizacji, w zależności od budowy i wielkości ładunku grupy kationowej, powodują zmiany gęstości elektronów w ich otoczeniu, wpływając jednocześnie na odporność barwionych materiałów na światło (w porównaniu do wybarwień na niekationizowanej celulozie zabarwionej tym samym barwnikiem). Wybarwienia kationizowanej celulozy, z uwagi na silną absorpcję na powierzchni włókna oraz utworzone silne wiązania jonowe, charakteryzują się (w porównaniu do wybarwień klasycznymi metodami barwienia) mniejszą równomiernością (tzw. chmurzastość wybarwień).

Wykonane badania uściślają mechanizmy wiązania się barwników reaktywnych z włóknem modyfikowanym i właściwości użytkowe uzyskanych wybarwień na światło, odpowiadają na nierozwiązane dotychczas zagadnienia.

Poznanie tych zjawisk pozwala na planowanie nowych prac badawczych z wykorzystaniem superekologicznych możliwości barwienia w celu wyeliminowania nierównomierności wybarwień i zjawiska tzw. wybarwień pierścieniowych. Poprzez zastosowanie odpowiednich środków pomocniczych i dobór barwników możliwe będzie wyeliminowanie tych wad, które aktualnie powodują, że pomimo tylu doświadczeń i badań barwienie kationizowanej celulozy nie zostało szeroko wprowadzone do skali przemysłowej.



## 6. Wnioski

Z przeprowadzonych badań można wyciągnąć następujące wnioski:

1. Rodzaj i wielkość ładunku powierzchniowego włókien i materiałów celulozowych jest ważnym parametrem oceny ich właściwości użytkowych.
2. Wielkość i rodzaj ładunku powierzchniowego jest ściśle związana z obecnością określonych grup funkcyjnych w strukturze włókna, zawartymi w nim zanieczyszczeniami oraz wprowadzonymi substancjami modyfikującymi lub funkcjonalizującymi.
3. Ładunek powierzchniowy, gęstość elektronowa włókna oraz substancje obecne we włóknie decydują o kierunku i szybkości reakcji chemicznych lub oddziaływań fizykochemicznych z innymi związkami.
4. Ładunki na powierzchni włókna, zwłaszcza w roztworach wodnych, decydują o procesach dysocjacji i absorpcji.
5. Znajomość wielkości ładunku powierzchniowego może być przydatna przy projektowaniu procesów technologicznych takich jak kationizacja, bielenie, barwienie, drukowanie i inne wykończenia funkcjonalne.
6. Wielkość ładunku oraz znajomość gęstości elektronowej na powierzchni włókna pozwalają przewidywać mechanizmy reakcji chemicznych, oceniać uzyskiwaną trwałość tworzonych produktów m.in. odporność wybarwień na działanie czynników mokrych, tarcie i światło.
7. Wykorzystanie wiedzy o ładunku może doprowadzić do znacznej eliminacji produktów służących do przesunięcia równowagi reakcji chemicznych, a tym samym zmniejszenia ilości zanieczyszczeń uwalnianych do środowiska.

## 7. Wykaz stosowanych skrótów

$[\text{Cel-O}(6)\text{-IME}]^+\cdot\text{Cl}^-$	- chlorek celulozy modyfikowanej Texamin ECE New
$[\text{Cel-O}(6)\text{-IME}]^+\cdot\text{PhSO}_3^-$	- benzenosulfonian celulozy modyfikowanej Texamin ECE New
$[\text{Ch}]^+$	- kation chlorku chlorocholiny
CHPTAC	- chlorek 3-chloro-2-hydroksypropylotrimetyloamoniowy
DMF	- dimetyloformamid
EPTAC	- chlorek 2-3-oksiranpropylotrimetyloamoniowy (epoksydowa forma CHPTAC)
$[\text{HPTA}]^+$	- kation CHPTAC
FTiR	- spektroskopia furierowska w podczerwieni
$[\text{IME}]^+\text{Cl}^-$	- kopolimer (chlorometylo)oksiran-1H-imidazolu (Texamin ECE New)
kDa	- jednostka masy atomowej (kilodalton)
PES-Na	- polielektrolit anionowy (sól sodowa kwasu polistyrenosulfonowego)
poli-DADMA	- polielektrolit kationowy (chlorek poli-diallilodimetyloamoniowy)
poli-(St-BA-VBT)	- chlorek polimeru styreno-butyloakrylo-winylobenzylotrimetyloamoniowego

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**ARTICLES INCLUDED IN THE PUBLICATION  
CYCLE OF THE DISSERTATION**

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# Changes in the Specific Charge Amount on the Surface of Cotton Fibres during the Alkali Pre-treatment Process

DOI: 10.5604/01.3001.0013.1817

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## Abstract

*The aim of the pre-treatment process is to prepare cotton fabrics for subsequent technological operations, which are, in the majority, carried out in aqueous solutions. The pre-treatment processes modify, to some extent, the properties of cotton, resulting in a significant change in their zeta potential, the amount of specific surface charge or free energy surface. This study makes an assessment of the effect of the alkali pre-treatment process on changes in the amount of negative specific charges on cotton knitted surfaces, known as cationic demand. A "back-titration" method with the use of a Muetek PCD device was adopted for these experiments. It was found that the conventional process of alkali treatment of raw cotton knitted fabrics using sodium hydroxide in the presence of non-ionic surfactant reduced by nearly 50% the amount of negative specific surface charge. Also, changes in weight loss and improvements in the whiteness index, as well as the wettability of alkali pre-treated cotton knitwear, were observed.*

**Key words:** cotton, alkali pre-treatment, specific charge on cotton surface, cationic demand.

## Introduction

Cotton is one of the most important raw materials for textile production. Global cotton production was estimated at 22.4 million tons in 2016/2017 [1]. Natural raw cotton fibres are hydrophobic, coarse to the touch and have a yellowish/brownish appearance. The structure of cotton fibres consists of several layers. The outer layer of a cotton fibre is approximately 0.1-0.2  $\mu\text{m}$  thick [2] and has a very hydrophobic character, which corresponds to the fats, waxes, pectin and other non-cellulose substances present in it. The content of these substances may vary according to region, growing conditions, maturity etc. The hydrophobic nature of natural cotton fibres protects them during vegetation and facilitates their processing into yarn.

The removal of hydrophobic waxes and pectin, which form a protective barrier during cotton growth, is essential for achieving uniform cotton wettability before further processing [3]. Besides natural colour substances that can be removed by bleaching using oxidants, most of the remaining impurities are removed during the alkali pre-treatment step [4]. Conventional cotton pre-treatment processes are carried out at 90-100  $^{\circ}\text{C}$  in alkaline conditions using sodium hydroxide. According to literature [5], when a water solution with sodium hydroxide is brought into contact with cotton fabric, some of the alkali is absorbed, since the hydroxyl groups of cellulose have a weak acidic character. At pH 13-14, cellulose absorbs

about 10 g of sodium hydroxide per 1 kg of cellulose. It is estimated that in order to carry pectin into water, soluble salts of pectic and meta-pectic acids need about 5 g of sodium hydroxide per 1 kg of cotton. The neutralisation of amino acids obtained by the hydrolysis of proteins requires approximately 5 g of sodium hydroxide per 1 kg of cotton. In summary, approximately 30-40 g of sodium hydroxide per 1 kg of cotton is needed for the saponification of the waxes and maintenance of sufficient alkalinity. The literature indicates [5] that the fatty esters of glycerol and fatty acids account for about 37-47% of the total amount of waxes in raw cotton. These have low melting points and are hydrolysed into soaps and glycerol (saponification reactions). In this form, they can be easily removed from cotton in aqueous sodium hydroxide solutions. Following the hydrolysis of the waxes, fatty alcohols with a high melting point are removed from the material due to the emulsifying action of surfactants, usually non-ionic.

Raza et. al. [3] observed that when cotton is treated at boiling temperature with alkali, a pronounced weight loss in the treated fabric occurs upon increasing the NaOH concentration. This loss in weight might be due to pectin degradation, as well as the removal of oil, grease and so on. Chowdhury [6] found the concentration of sodium hydroxide at 3 g/l in a boiling bath as suitable.

A lower concentration of NaOH gives poor results, while a higher concentration

risks fibre damage and reducing of the strength of the textile product. A sample treated with the scouring-bleaching process was evaluated with respect to weight loss, and with the immersion and wicking test. It was found that the concentration of NaOH increases relative to the weight loss of the knit fabric and while the immersion time decreases.

Another parameter to determine the efficiency of the scouring process is the measurement of ROG (Residual Oil and Grease) [3] in the treated fabric. A gradual improvement in scouring efficiency up to 30 g of NaOH/l was observed. Above this concentration, the ROG value remained almost constant. As dirt, dust and lint play a role in rendering colour, these impurities were also removed during the scouring process; hence the resultant fabrics were characterised by improved whiteness.

A significant influence on the sorption properties of cotton fibres is exercised by the amount of available groups (hydroxyl and carboxyl), which are more accessible in the amorphous regions. Any change in the number of functional groups produces different phenomena of interaction between the solid (textile material) and liquid phases (mostly water or water solutions of different types of chemicals), which are applied in technological processes. Negative charges on the surface of cellulosic fibres cause the repulsion of molecules with the same negative charges when they are applied to the surface and to the interior of the fibre. Since most

of the chemicals applied in cotton finishing processes (pre-treatment, bleaching, dyeing, printing and functional finishing) are anionic, these processes must be carried out in such a way as to overcome the barrier of mutual repulsion of ions. Elevated temperature, overpressure and the addition to finishing baths of several chemical compounds, such as electrolytes (NaCl, Na<sub>2</sub>SO<sub>4</sub>) as well as alkali (Na<sub>2</sub>CO<sub>3</sub> or NaOH), reduce the impact of ion repulsion and enable the effective application of technological processes. Another way to reduce these unfavourable phenomena is the chemical or physico-chemical modification of the surface of cotton fibres. The charge properties of cellulosic materials can be determined by several methods, among the most common of which are conductometric titration, potentiometric titration, polyelectrolyte adsorption and zeta potential measurements [7, 8]. The electrokinetic properties of cotton can be characterised by the zeta potential and a specific amount of charge [9-11]. Electrokinetic potential is mainly measured by a method involving streaming potential/current using an electrokinetic analyser. A number of works [12-15] have shown that the surface properties of cellulose materials can be successfully characterised by electrokinetic methods. In most cases, the zeta potential, which is calculated from the electrokinetic effect of the streaming potential, is recorded at a different pH of the aqueous solution or with time. Measuring the streaming potential can also be applied to the monitoring of the swelling process of cotton fabrics. The swelling process actually represents the process of water adsorption and can be described by pseudo first-order kinetics. The solid surface zeta potential is a suitable parameter for the surface characterisation of raw cellulose materials. The different chemical composition of non-cellulosic impurities and the complex structure of cotton fibres, however, make it difficult to interpret zeta potential results. The electrokinetic investigation of natural fibres is challenging because of their strong hydrophilicity [16]. It is possible, however, to use electrokinetic measurements to characterise the swelling capacity of such fibres. The results reflect the changes in the chemical properties of the fibre surface and are in good agreement with solvatochromism experiments. In any case, cellulose-based fibres need an intensive surface treatment, which may be monitored and controlled by electrokinetic investigations.

Streaming potential measurements clearly show [17] that among other morphological changes, the differences in surface properties determine the adsorption properties of solid materials. The method can be used to describe the interaction mechanism between textile fibres and components of the liquid phase.

As an alternative to the streaming potential, the "back-titration" method can be a useful indicator for estimation of the specific amount of surface charge of cellulose-based materials [9]. Practically all of the colloidal solutes and solids in aqueous systems produce electrical charges, which leads to the creation of counter-ions. The potential of zero mV, indicated as PZC (Point Zero Charge), indicates that all current charges in the sample are neutralised. The principle of measurement on a Muetek PCD (Particle Charge Detector) [18, 19] is based on the fact that when a sample is placed in the sample cell, the dissolved molecules will adsorb onto the plastic surface of the piston and on the wall of the cell using van der Waals forces. Activation of the reciprocating motion of the piston causes the separation of counter-ions from the adsorbed molecules and elicits the potential between the permanently installed gold electrodes. The values are shown on the display of the device. In the case of long fibres and large molecules, the sample cannot be placed directly in the measuring cell because the time required for reaching equilibrium with the titrant is too long. In this case, it is possible to use this device in reverse titration, a process known as "back titration".

According to the research of Zhang et. al. [20], cellulose fibre charge is a significant parameter for porous cellulose fibres as it strongly affects their swelling ability as well as the properties of cellulose-based materials. Surface charge is mentioned often in papermaking wet-end chemistry, whereas the inner or total charge receive less attention. Zhang et. al. stated that higher fibre charge (surface and inner charge) was detected by lower MW poly-DADMAC (7.5-15 kDa) due to its efficient penetration into the fibre cell walls and neutralisation with inner charges. Lower fibre charge (surface charge) was determined using higher MW poly-DADMAC (higher than 100 kDa).

There are some works carried out by various authors focused on the study of the phenomenon of electrokinetic po-

tential and specific charge on the surface of cotton fibres [21-23] occurring during mercerisation, cationisation processes, dyeing and printing. None of these works, however, contain detailed research on changes in the value of the negative charge on the cotton fibres surface occurring in one of the most important pre-treatment processes, which is the conventional alkali treatment process. Tests were carried out taking into account the effect of the temperature, concentration of the sodium hydroxide used, treatment time and the presence of a nonionic surfactant.

Although finishing processes have been used for several years, they are still only partially understood, especially in terms of their influence on fibre absorption ability, hydrophilicity and the accessibility of active groups for the final finishing as dyes or surfactants. It is extremely important to be able to determine the quantity of accessible reactive groups in order to judge cotton interaction ability, ion exchange capacity and the progress made by technological processes. Weight loss, wettability and, on occasion, the whiteness index are used for monitoring the efficiency of pre-treatment results. Nevertheless, these parameters do not provide any precise information about the interaction ability of the negatively charged surface of cotton fabrics with chemical compounds in water conditions. In this paper, the influence of process conditions on changes in weight loss, the whiteness index and wettability and their correlation with the value of surface charge is discussed.

## ■ Experimental design

### Materials

Raw cotton knitted "single jersey" fabric with a surface weight of 145 g/m<sup>2</sup> was obtained from "MIRWAL" textile company, Poland. Tanaterge Advance – surfactant (non-ionic) was obtained from NewTanatex, Poland. Polyelectrolyte standard solutions, ready for use, PES-Na (MW 21.800 g/mol) and poly-DADMAC (MW 107.000 g/mol) were purchased from BTG Instruments AB Sweden. Other reagents were used as LR.

### Apparatus

Ugolini Redkrome – model RED P laboratory dyeing machine (Ugolini Spa, Italy), heated by infrared ray radiators, equipped with 150/400 ml cups for the pre-treatment of cotton knitted fabric.

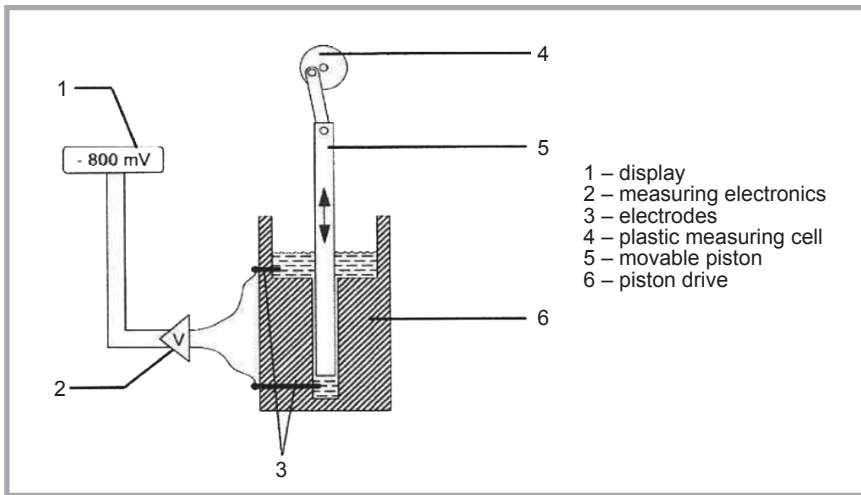


Figure 1. Schematic of test setup Muetek PCD 03 pH.

Muetek PCD 03 pH Particle Charge Detector (BTG Muetek GmbH, Germany) for the measurement of potential and determination of the value of the specific charge on the surface of cotton knit samples analysed by the “back titration” method.

Datacolor 850 type dual beam d/8° spectrophotometer (Datacolor AG, Switzerland), illumination source – pulsed xenon filtered to approximate D65 for determination of the whiteness index of cotton knitted fabric samples.

### Pre-treatment process

The treatment process for all samples of cotton knitted fabrics (10 g) was started at room temperature at a 1:15 liquor ratio in a Ugolini Redkrome laboratory dyeing machine with heating rates of 4 °C/min to the temperature and time required. **Table 1** presents procedures for the pretreatment process with varying NaOH concentration with or without a non-ionic surfactant.

In order to obtain more reliable results, all experiments were repeated three times

Table 1. Procedures for treating cotton fabric samples. Note: 0\* – time 0 min. for the sample AS3/100/0 means that the process started from the room temperature with a rate of 4 °C/min to 100 °C and when the temperature reached 100 °C the sample was immediately cooled to 70 °C and rinsed as the rest of the samples.

	Sample	NaOH, g/l	Non-ionic surfactant, ml/l	Time, min	Temperature, °C
Raw cotton	R	–	–	–	–
Alkali treatment without a non-ionic surfactant	A0	0.00	0	60	100
	A0.25	0.25			
	A0.5	0.50			
	A1	1.00			
	A2	2.00			
	A3	3.00			
Alkali treatment with a non-ionic surfactant	AS0	0.00	1	60	100
	AS0.25	0.25			
	AS0.5	0.50			
	AS1	1.00			
	AS2	2.00			
	AS3	3.00			
Alkali treatment with a non-ionic surfactant for different times and temperatures	AS3/100/0	3.00	1	0*	100
	AS3/100/20			20	100
	AS3/100/40			40	100
	AS3/100/60			60	100
	AS3/90/60			60	90
	AS3/80/60			60	80

and the data obtained were averaged. For all tests, the process was terminated by cooling the cup contents at a temperature of 70 °C with a rate of 4 °C/min. The next samples were rinsed three times with 300 ml of distilled water at a temperature of 70 °C, followed by cold distilled water to obtain a neutral pH. The samples were dried in ambient temperature.

### Measurement of the specific charge amount of the cotton knitted fabric surface

Specimens of 0.25 g of tested cotton knitted fabric, cut into ca. 0.5 × 0.5 cm pieces, were placed in a 400 ml conical flask, adding 50 ml of 0.0001 N poly-DADMAC cationic polyelectrolyte, and stirred with a magnetic stirrer for 1 hour at room temperature. As a next step, the fabric pieces were removed and the solution was filtered in order to remove all fibres released to the liquid during stirring. An amount equal to 10 ml of filtrate was placed in a measuring cell of the Muetek PCD 03 pH apparatus (**Figure 1**) and the piston vibration motion was activated. After stabilisation of the potential, the filtrate was titrated with 0.0001 N PES-Na anionic polyelectrolyte to a stable 0 mV potential.

The value of the specific charge was calculated according to the formula:

$$Q_{dz} = \frac{(V_0 - V_1) c V_c}{m V_a}, \text{ eq/g} \quad (1)$$

where:

$V_0$  – ml of polyelectrolyte PES-Na for titration of 10 ml polyelectrolyte poly-DADMAC used for cotton knit processing (blind test),

$V_1$  – ml of polyelectrolyte PES-Na for titration of 10 ml of filtrate after treatment,

$c$  – polyelectrolyte concentration of poly-DADMAC,

$V_c$  – amount of polyelectrolyte poly-DADMAC used for treatment,

$V_a$  – ml of filtrate used for titration,

$m$  – test sample weight.

### Measurement of the whiteness index

In order to estimate the influence of the treatment on the colour of the samples, whiteness index measurements were made. According to EN 105 – J02, the standard whiteness of white textile materials is calculated from the following formula:

$$WI = Y10 + 800(0.3138 - x10) + 1700(0.3310 - y10) \quad (2)$$



White fabric is that for which WI is in the range  $40 < WI < 5Y - 280$ . The authors decided to use the word 'whiteness index' for measuring changes in the whiteness of the pretreatment samples due to the following reasons:

- there is not any specific word or formula for calculating the whiteness index for whiteness obtained after pretreatment processes before bleaching,
- there are a lot of other authors using such words for calculating changes in whiteness during and after the pretreatment process with a formula according to EN 105-J02 [24-27].

Measurements were taken at three different points of the surface of the samples tested.

### Weight loss measurement

The weight loss of each sample was calculated based on the formula:

$$\Delta W = \frac{m_0 - m_1}{m_0} \times 100\% \quad (3)$$

where:

$\Delta W$  – weight loss in, %,

$m_0$  – weight of the sample before treatment, g,

$m_1$  – weight of the sample after treatment, g.

### Measurement of the degree of wettability

For evaluation of the degree of wettability of the cotton knitted samples, the authors decided to use the modified Tegewa Drop Test [28]. Instead of Patent Blue (anionic dye), we used Methylene Blue (cationic dye) as 0.2% water solution. The time between the contact a drop of 30  $\mu$ l of the solution, carefully deposited on the fabric surface, and its disappearance into the fabric matrix was reported as the fabric wetting time. Images were taken by a Canon SX 410 IS digital camera.

## Results and discussion

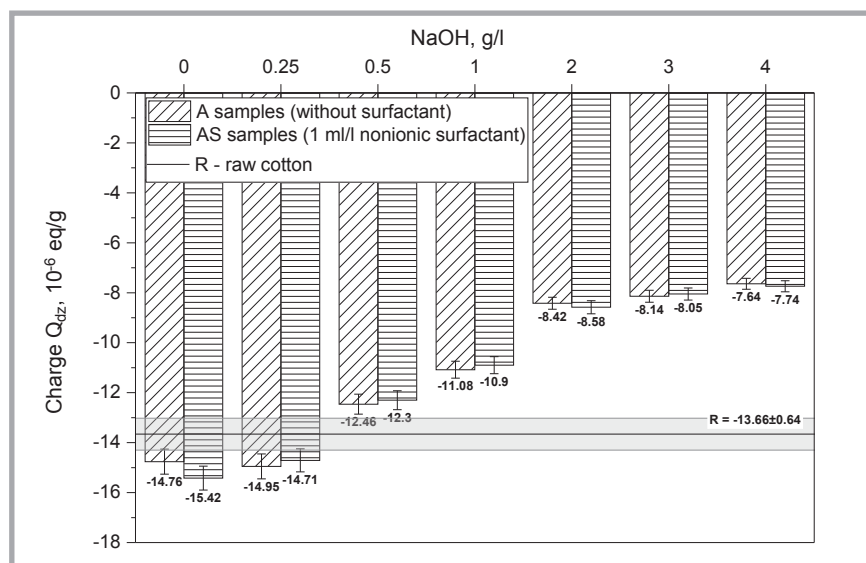
All measurement data in our study are presented in **Table 2**.

### Specific charge amount on the surface of raw cotton knitted fabrics after alkali treatment

The measurement data presented in **Table 1** and **Figure 2** show that the alkali treatment of raw cotton knitted fabrics changed the specific charge amount on their surface. Generally it is seen that

**Table 2.** Averaged data of all experiments for weight loss ( $\Delta W$ ), whiteness index (WI), wettability (WET) and specific charge amount ( $Q_{dz}$ ) on cotton knitted fabric surfaces. **Note:** <sup>1)</sup> No wettability means that after 600 s the drop of water solution of Methylene Blue deposited on the cotton knitted fabric surface was still a drop, <sup>2)</sup> 20 s (penetration) means that after 20 s some parts of the drop of water solution of Methylene Blue deposited on the cotton knitted fabric surface were absorbed and the rest crossed to the other side of the material and dropped.

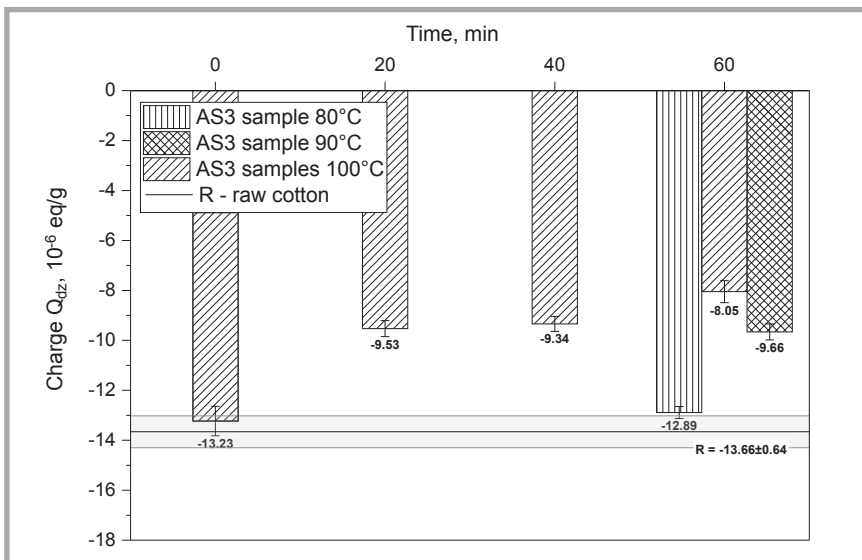
Sample	$Q_{dz}$ , $10^{-6}$ eq/g	$\Delta W$ , %	WI	WET, s
R	-13.66	–	5.47	No wettability <sup>1)</sup>
A0	-14.76	1.93	18.61	No wettability <sup>1)</sup>
A0,25	-14.95	2.04	20.7	No wettability <sup>1)</sup>
A0,5	-12.46	2.3	22.02	No wettability <sup>1)</sup>
A1	-11.08	3.3	24.14	300
A2	-8.42	3.73	28.82	135
A3	-8.14	4.32	32.19	20 (penetration) <sup>2)</sup>
A4	-7.64	4.61	36.34	20 (penetration) <sup>2)</sup>
AS0	-15.42	2.43	20.08	300 (penetration) <sup>2)</sup>
AS0,25	-14.706	2.58	22.16	180
AS0,5	-12.3	3.2	22.82	10
AS1	-10.9	4.0	26.11	6
AS2	-8.58	4.75	34.92	2
AS3	-8.05	4.85	42.88	1
AS4	-7.74	4.87	44.61	1
AS3/100/0	-13.226	2.89	19.86	3
AS3/100/20	-9.53	3.64	29.72	1
AS3/100/40	-9.34	3.98	33.60	1
AS3/100/60	-8.05	4.85	42.88	1
AS3/90/60	-9.66	3.57	30.96	1
AS3/80/60	-12.89	2.01	18.83	42



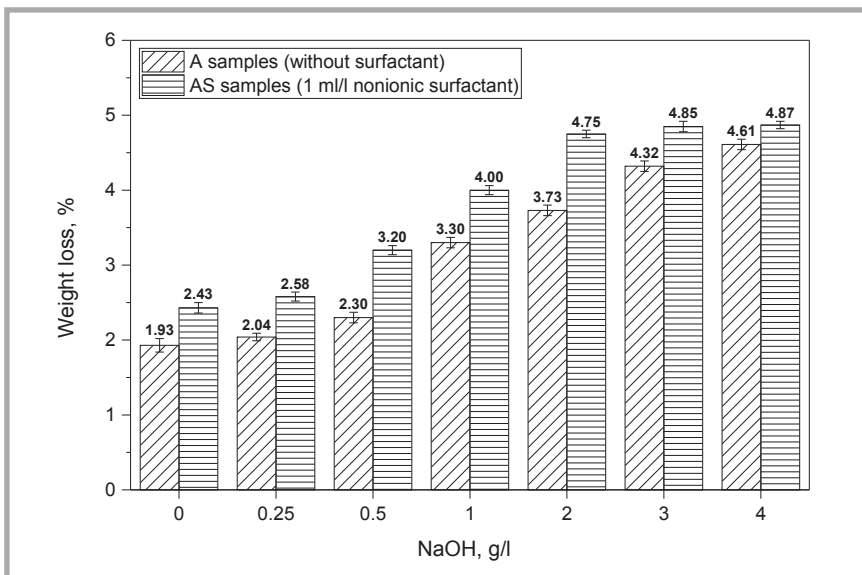
**Figure 2.** Changes in the specific charge amount on the surface of raw cotton knitted fabrics after alkaline treatment with and without the presence of non-ionic surfactant (pre-treatment temperature 100 °C).

there is no significant influence of using a non-ionic surfactant in the alkali pretreatment of cotton knitted samples on increasing the specific charge amount on the cotton surface. It was only observed that upon treating raw cotton knitted fabrics in a boiling bath containing 1 g/l of a non-ionic surfactant at neutral pH, a higher value of negative charge was obtained than that present in raw cotton. This confirmed the fact that during

treatment, emulsified fats and other ingredients that are soluble in water were removed, resulting in a more open raw cotton surface with better availability of acidic groups. Increasing concentrations of sodium hydroxide above 2 g/l leads to a decrease in the value of negative charge to 50% compared to raw cotton fabric. This is connected with the alkaline hydrolysis (saponification) of fats, pectin and waxes. Hydrolysis products such as



**Figure 3.** Changes in the specific charge amount on the surface of raw cotton knitted fabric after alkali treatment for different times and temperatures.



**Figure 4.** Changes in weight loss of raw cotton knitted fabric after alkali treatment with and without the presence of non-ionic surfactant (pre-treatment temperature 100 °C).

glycerine and sodium salts of fatty acids, pectinic and meta-pectinic acids are soluble in water and can be removed from raw cotton surfaces.

The results of the treatment of raw cotton knitted fabric with 3 g/l of sodium hydroxide in the presence of non-ionic surfactant at temperatures of 80, 90 and 100 °C during 60 min. (**Figure 3**) showed that the treatment temperature had a significant influence on changes in the specific charge amount of the cotton surface. The treatment of raw knitted cotton fabric in a bath using the same recipe at 100 °C for 0, 20, 40 and 60 min. (**Figure 3**) showed that the specific charge amount on the cotton surface

at the beginning of the process (time 0 min/100 °C) was on a par with that for raw cotton, while as the treatment time increased the specific charge decreased. This is connected with the alkaline hydrolysis of fats, pectin and waxes and their removal from the cotton surface. Based on the results, it can be stated that the temperature had a bigger influence than time on changing the specific charge amount on the cotton surface.

#### Weight loss of raw cotton knitted fabric after alkali treatment

The weight loss observed on the samples after alkaline treatment with sodium hydroxide, with and without the addition of non-ionic surfactant, is shown in

**Figure 4.** It is seen that the application of a non-ionic surfactant causes larger weight loss. The non-ionic surfactant at high temperature was emulsified unsaponifiable waxes. Their content in mature dry raw cotton fibres is 52-62% of the total quantity of waxes [5]. Their main components are high molecular alcohols  $C_{23}$  to  $C_{34}$  (n-tricontanol, 1-octacosanol and coloured gossypol) with a melting point in the range between 83-214 °C, saturated and unsaturated hydrocarbons  $C_{27}$  to  $C_{32}$  (heptacontane, triacontane, untriacontane, dotriacontane), as well as some phytosterols and sterols  $C_{20}H_{50}$  ( $\beta$ - and  $\gamma$ -sitosterols) with a melting point above 140 °C. The chemical analysis of the surface of raw cotton fibres in [29] confirms the presence of these compounds/materials even after the scouring and bleaching processes. The addition of non-ionic surfactant to alkali baths enhances the cotton pre-treatment process (no increase in the samples' weight loss was observed following pre-treatment in a bath with a concentration of NaOH above 2 g/l) in comparison with alkali pre-treatment in a bath without surfactant; while a significant increase in the samples' weight loss was observed when increasing the NaOH concentration up to 4 g/l.

The treatment of raw cotton knitted fabric with 3 g/l of sodium hydroxide in the presence of a non-ionic surfactant at temperatures of 80, 90 and 100 °C for 60 min and at 100 °C for 0, 20, 40 and 60 min. (**Figure 5**) showed a larger influence of temperature than time on the samples' weight loss. It can be argued that weight loss in a treatment time equal to 20 min. at 100 °C was equivalent to that in treatment for 60 min at 90 °C with the same concentration of alkali and presence of a non-ionic surfactant.

#### Whiteness index of raw cotton knitted fabric after alkali treatment

Changes in the whiteness index of cotton knitted fabric after alkali treatment with different NaOH concentrations with and without the presence of a non-ionic surfactant are shown in **Figure 6**. Based on those data, it can be stated that the whiteness index of all samples increased together with sodium hydroxide in the bath from 0 to 4 g/l. All experiments showed a positive influence of the presence of a non-ionic surfactant. The increase in the whiteness index is connected with the partial removal of substances causing the colouration of raw cotton fabrics. There is no information in the literature on this

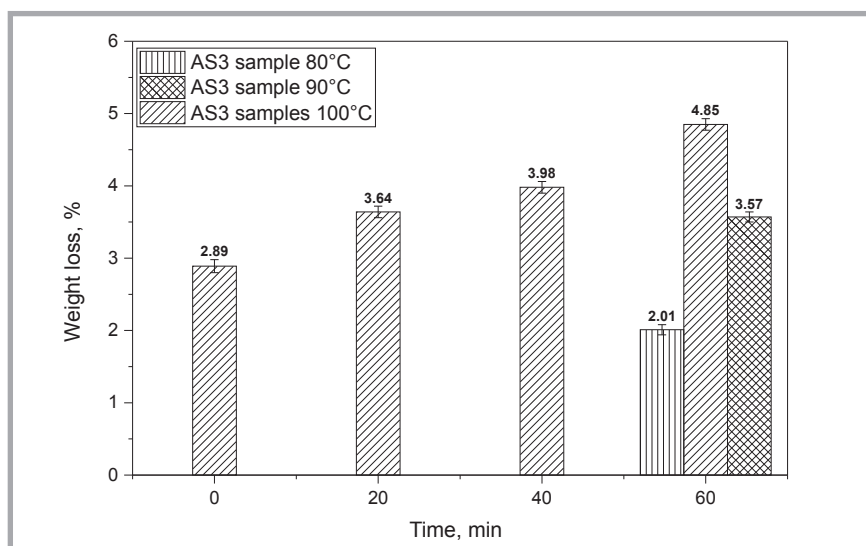
subject, but it can be surmised that the alkaline hydrolysis of proteins on raw cotton surfaces creates amino acids, which in the presence of a non-ionic surfactant can be emulsified and removed more easily. It is known that compounds containing nitrogen cause yellowing on cotton fibres.

The results of data measured for the whiteness index after the treatment of raw cotton knitted fabric with 3 g/l of sodium hydroxide in the presence of a non-ionic surfactant at temperatures of 80, 90 and 100 °C for 60 min. and at 100 °C for 0, 20, 40 and 60 min. (**Figure 7**) show a larger influence of the temperature than the time, similar to the weight loss (**Figure 6**). It can be argued that the whiteness index for a treatment time of 20 min. at 100 °C was only a little lower than after treatment of 60 min. at 90 °C with the same concentration of alkali and presence of a non-ionic surfactant.

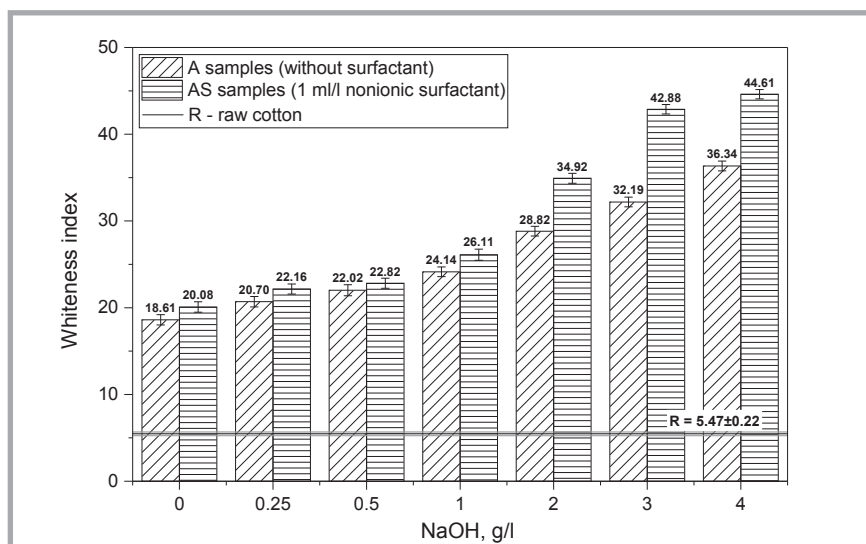
### Wettability of raw cotton knitted fabrics after alkali treatment

Wettability is the most important parameter for textile materials during finishing operations. This factor plays a dominant role, particularly in “dry-on-wet” impregnation processes, where the material has to absorb a defined liquid quantity over a short contact period. An integral part of wettability is the uniformity of absorption in all directions of the material. For evaluation of changes in the wettability of pretreated samples of cotton knitted fabric modified with Methylene Blue (MB), the Tegewa Drop Test was used. MB is often used for qualitative determination of chemical damage to cellulosic fibres (where MB formed an ionic bond with the carboxylic group of hydro- or oxycellulose) mainly during the bleaching process. In our work we used this test for qualitative evaluation of anionic groups present on the cotton surface in the alkali pretreatment process. Results of the modified MB Tegewa Drop Test are shown in **Table 3**.

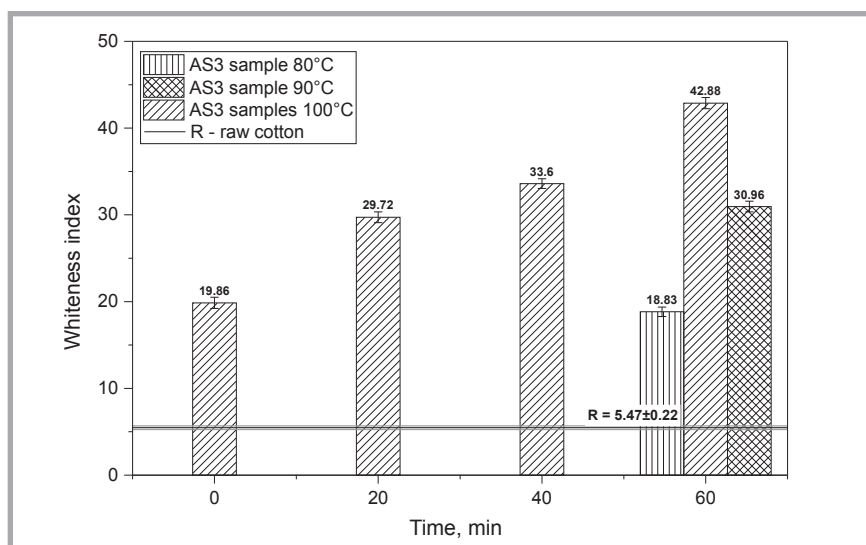
The front of the water spot and the absorbency time determined the wettability of samples (as in absorbency test method – AATCC 79-2000), whereas the spreading view of the dye indicated the quality of purification of the cotton surface after the pretreatment process. The spot on well pretreated fabric is characterised by a round or oval shape. When the spot has an irregular, serrated edge it can be stated that fatty impurities are unevenly



**Figure 5.** Changes in weight loss of raw cotton knitted fabrics after alkali treatment for different times and temperatures.

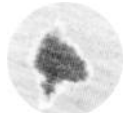

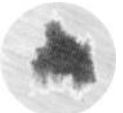




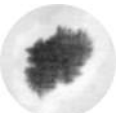





**Figure 6.** Changes in the whiteness index of raw cotton knitted fabric after alkali treatment with and without a non-ionic surfactant (pre-treatment temperature 100 °C).









**Figure 7.** Changes in the whiteness index of raw cotton knitted fabric after alkali treatment for different times and temperatures.

**Table 3.** Changes in wettability of raw cotton knitted fabrics after alkali treatment with and without a non-ionic surfactant.

Sample	A0	A0,25	A0,5	A1	A2	A3	A4
Wettability, s	No wettability	No wettability	No wettability	 300	 135	 20 (penetration)*	 20 (penetration)*
Sample	AS0	AS0,25	AS0,5	AS1	AS2	AS3	AS4
Wettability, s	 300 (penetration)*	 180	 10	 6	 2	 1	 1

**Table 4.** Changes in wettability of raw cotton knitted fabrics after alkali treatment in different times and temperatures.

Sample	AS3 100/0	AS3 100/20	AS3100/40	AS3 100/60	AS3 90/60	AS3 80/60
Wettability, s	 3	 1	 1	 1	 1	 42

distributed on the fabric surface (Tege-wa Drop Test interpreting). As is seen from **Table 3**, the influence of the presence of a non-ionic surfactant on the improvement of wettability during the alkaline treatment of raw cotton knitted fabrics for all concentrations of NaOH is evidently positive. The results from **Table 3** for samples after alkali treatments with a non-ionic surfactant are also in good correlation with other parameters measured, like the value of the negative charge on the cotton surface, weight loss and the whiteness index. From an industrial point of view, the optimum wettability time of fabrics is between 1 and 2 seconds. The data measured showed that these expectations were fulfilled only by the samples which underwent alkaline treatments with NaOH above 2 g/l in the presence of a non-ionic surfactant (AS2, AS3 and AS4 samples). While the rest of the samples were acceptable for specific amounts of charge, weight loss and the whiteness index; but their wettability was not acceptable. It was seen that for trials A1–A4 the absence of a non-ionic surfactant resulted in the insufficient emulsification of unsaponifiable hydrocarbons and waxes.

The alkaline treatment of raw cotton knitted fabrics (AS3/100/20, AS3100/40,

AS3/100/60 and AS3/90/60 samples) in a boiling bath containing 3 g/l of NaOH in the presence of a non-ionic surfactant showed acceptable results of the wetting time (**Table 4**, wetting time – 1 second). The best results were obtained for the AS3/100/60 sample, which apart from a 1-second wettability time, had the best uniform levelness, as evidenced in the picture of the absorbed Methylene Blue solution drop.

## Conclusions

Determination of the specific charge amount on the surface of cotton knitted fabrics, calculated as the cationic demand, was achieved through the “back titration” method using Muetek PCD 03 pH apparatus. A basic assumption of this method is that there is a 1:1 stoichiometric relationship between the number of anionic groups on the fibre surface and that of cationic groups and cationic polyelectrolyte.

The amount of cationic polyelectrolyte adsorbed on the fibres was determined by titrating the excess (non-adsorbed) polyelectrolyte with anionic polyelectrolyte. The research has shown that the conventional process of alkali treatment of raw cotton knitted fabrics reduces by nearly 50% the amount of the specific charge

from the surface. In all alkali treatment experiments, a high positive effect of the presence of non-ionic surfactant was observed on weight loss, the whiteness index and especially on the degree of wettability. We did not observe a significant influence of using a non-ionic surfactant in the alkali pretreatment of cotton knitted samples which led to an increase in negative charge on their surface. A higher value of negative charge was only found for samples treated in boiling water without sodium hydroxide and with a non-ionic surfactant. This increase was due to the partial removal of waxes with low melting points and fats from the outer layer of the fibre, as well as that of the preparations applied before the knitting process. Removing these impurities exposes more acid groups on cotton knitted fabrics, giving a more negative charge. Generally, the application of non-ionic surfactant, thanks to its good parameters regarding wettability, causes the emulsification of unsaponifiable saturated and unsaturated hydrocarbons, as well as high molecular weight fatty alcohols formed from the hydrolysis of waxes. Alkaline treatment at different temperatures and times showed the higher influence of temperature than time on the amount of charge, weight loss, the whiteness index and wettability. The aim of alkali pre-treatment is preparing textile ma-

terials of good and uniform wettability for the subsequent finishing processes. Knowledge about the amount of negative charge can be helpful on an industrial scale for the design and analysis of new finishing processes (bleaching, dyeing and printing) and many other applications specifically related to cationic compounds, for example cationic softeners and different anti-bacterial, insecticidal, fungicidal and other functional cationic preparations.



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Received 05.09.2018 Received 06.03.2019

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# COMPARISON OF THE EFFECTS OF THE CATIONIZATION OF RAW, BIO- AND ALKALI-SCOURED COTTON KNITTED FABRIC WITH DIFFERENT SURFACE CHARGE DENSITY

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## Abstract:

*Modification of cotton with 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) has been studied extensively and can be operated by means of exhaustion, cold pad-batch, and continuous and pad-steam methods. Most of the research addresses the cationization of cotton fabric after bleaching or mercerization, or during the mercerization process. In our studies, we performed a comparison of the cationization effects on raw, enzymatic, and alkali-scoured cotton knitted fabrics applying CHPTAC according to the exhaustion method. The charge density of the cotton surface was measured using a Muetek Particle Charge Detector and a "back titration" method with polyelectrolytes. These results were compared with the nitrogen content in the samples, K/S measurements of tested samples after dyeing with anionic dye (Acid Yellow 194), and other physicochemical parameters such as weight loss, whiteness, and wettability.*

## Keywords:

*Cotton charge measurement, cationization of cotton, Kjeldahl method, K/S value*

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## 1. Introduction

In many industries, cationic polysaccharides are replacing the traditional application of cationic polyacrylamides for use as colloid flocculants, due to their lower toxicity and fewer legal restrictions [1]. The cationic functionalization of cellulose is of considerable industrial importance and has been used in the paper industry, cosmetics, textiles, in flotation and drilling fluids [2]. Cationization is the modification of cotton cellulose using quaternary ammonium compounds. In the textile industry, it is an alternative method for achieving better adsorption of chemical compounds and substances, such as dyestuffs, fluorescent whitening agents, and other textile auxiliaries. The cationization of cotton cellulose changes surface electrical charge (electrokinetic potential) by significantly increasing its adsorption properties [3]. Schlack [4] was the first to report the ability of aminated epoxy derivatives to modify cellulose and the first to notice the increased affinity of the modified cellulose toward acid dyes. Champetier and Merle [5] have studied the modification of hydroxylated polymers, including cellulose, by epoxy diethylamine-3-propane followed by an ethyl iodide quaternization to yield ion exchangers. They have also reported the properties of the modified polymers to acid dyes. For many years, different chemical compounds have been studied to achieve the best results of cellulose cationization [6]. In research over the past 20 years, the most frequently studied cationic reagent was 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) [6, 7], which has been used in the industry for a long time, and in the cationization of starch among others.

Natural cotton contains approximately 4–12% of non-cellulosic components, such as hemicellulose, proteins, pectic matter, ash, colorants, waxes, and organic acids, depending on the type, origin, maturity, weathering, and agricultural conditions of raw cotton [8]. The non-cellulosic constituents are mainly located in the outermost layer of the structure, the cuticle, except for the protein residues of the protoplasm and some mineral matter believed to be within the lumen. Although proteins account for the largest portion of the constituents of the cuticle, there is no specific information available on the distribution of nitrogen-containing substances in the cuticle and primary wall [9]. Most of these impurities must be removed by wet preparation procedures involving elevated temperature and long treatment duration before subsequent coloring and finishing operations [8]. For this, in common practice, cotton-based fabrics are subjected to three consecutive steps, namely desizing, scouring, and bleaching [10].

One important step is scouring, in which the complete or partial non-cellulosic components found in cotton are removed alongside impurities, such as machinery and size lubricants [11]. Nowadays, in the textile industry, there are two ways of pretreating cotton, namely, the conventional pretreatment process in alkaline conditions using sodium hydroxide or the implementation of a new, effective alternative to chemical scouring, using enzyme combinations. Conventional cotton pretreatment processes are carried out at 95–100°C in alkaline conditions and are mainly based on the reaction between cotton impurities and sodium hydroxide. During the alkali scouring process, the intra- and intermolecular hydrogen bridges of the cellulose are partly cleaved and the polar hydroxyl groups of



the polysaccharides are solvated [12]. Alkaline pectinase was found to have the optimal bio-scouring process conditions: pH, 8.5; temperature, 55°C; and incubation time, 90 min. Under these conditions, the amount of pectin removed from the greige cotton fabrics was equivalent to that removed by the scouring and bleaching procedures [13].

Hauser et al. have performed a series of practical works in the field of cotton cationization at the University of North Carolina, USA [14]. Grancaric et al. [13] stated that the fixation of CHPTAC on cellulosic fabrics varies greatly depending on the choice of method, the CHPTAC concentration used, and the amount of alkali, time, temperature, and other parameters. The exhaust method is the least efficient, with typically well under 10% fixation of used CHPTAC. The pad-batch and pad-steam methods are more effective, with fixation levels at about 25%. The pad-dry-steam method gives about 50% fixation and the optimized pad-dry-cure yields around 85%. Before increasing the currying temperature, a key in the pad-dry-cure and pad-dry-steam applications is to remove the water maximally. The modified cotton retains all the beneficial properties of mercerized cotton with a change in surface charge that ensures further quality improvement [13].

Cationization during mercerization with epihalohydrin resulted in novel cotton cellulose. As such, it adds a new dimension to cotton pretreatment and finishing [3]. Published papers describe the dyeing or printing of cationized cotton materials after alkaline or enzymatic pretreatment, bleaching, mercerizing, or directly during the mercerization process [15–20]. The cationization of cotton should be carried out after pretreatment processes such as scouring and bleaching because cationized cotton is more attractive to oxidizing agents, thus contributing to the higher formation of oxycellulose [21].

Numerous studies have aimed to improve the affinity of anionic dyes toward cotton fabric by introducing positively charged sites on cotton [14, 22]. This enables the formation of an electrostatic attraction between the sites and the negatively charged dye molecules, thus eliminating the need for electrolytes in the cotton dyeing process and increasing the dye exhaustion and color yield of the fabric. The use of cationized cotton achieved superior dyeing results without the addition of salt over a short dyeing period. The hydroxyl groups present in glucose units are the main sites of reactive dye fixation and chemical modification [1].

Since 2012, as reported by the Höhenstein Institute of America, ColorZen® cotton coloring has been widely advertised as a new innovative solution [23–30], yielding enormous savings. It was first produced by a specially established LLC ColorZen company in New York. According to corporate information, the company has production facilities located in China, where the technological process of ColorZen® is applied to all raw cotton bales. The cationization of raw cotton fibers (bales) is designed to eliminate unevenness in dyeing since the spinning fibers can be thoroughly mixed. By determining the nitrogen content, it is also possible to define the maximum amount of dye bonding by the fibers to achieve optimum durability. This innovative technology has been certified by the Oeko-Tex organization as

Standard 100, indicating the absence of harmful substances. ColorZen® cotton can be dyed in all available dye systems without additional baskets resulting in fastness properties comparable to those obtained by conventional dyeing. For reactive dyes, ColorZen® technology can reduce dye usage (up to 50%) due to much higher (97%) exhaustion. Moreover, the water can be used in a closed circuit.

In a previous study [31] using the Muetek PCD (Particle Charge Detector) and the "back-titration" method, the authors found that after consecutive stages of pretreatment, the size of the negative charge on the surface of cotton fibers decreased in relation to the size of the charge on raw cotton. In the case of alkaline treatment, the negative charge volume decreased alongside an increase in the amount of NaOH used, the time, and the temperature of the process. This resulted in the removal of pollutants containing negative charge groups from the surface of the cotton. In the case of enzymatic treatment with alkaline pectinase, the final negative charge was much higher, due to the removal of fewer impurities from the surface of the fibers.

This article aims to study the influence of surface charge in raw, enzymatic, and alkali scoured cotton on the effects of cationization mainly through the estimation of nitrogen content and the properties of cotton dyeing.

## 2. Experimental section

### 2.1. Materials and methods

Raw cotton knitted "single jersey" fabric with a surface weight of 145 g/m<sup>2</sup> was obtained from "MIRWAL" Textile Company, Poland. Tanazym EVO (alkaline pectinase) and Tanaterge Advance (nonionic surfactant) were obtained from Tanatex Poland.

3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) as 60% aqueous solution was purchased from Sigma Aldrich. Ready-for-use polyelectrolyte standard solutions, PES-Na (MW 21.800 g/mol) and poly-DADMAC (MW 107.000 g/mol), were purchased from BTG Instruments AB Sweden. C.I. Acid Yellow 194 (Gryfalan Yellow RL commercial quality) was obtained from Boruta-Zachem, Poland. Other reagents were used without further purification.

All scouring (enzymatic and alkaline) and cationization processes were performed using a Redkrome laboratory dyeing machine, model RED P, product of Ugolini, Italy.

### 2.2. Enzymatic scouring

The scouring process for samples of cotton knitted fabrics (20 g) was started at room temperature in a bath containing 1.5 g/l Tanaterge Advance and 0.5 g/l Na<sub>2</sub>CO<sub>3</sub> at a 1:15 liquor ratio. As soon as the bath temperature reached 50°C (heating rate 2°C/min), 1% owf Tanazym EVO was added. Next, the bath was heated to 60°C (rate 2°C/min), and at this temperature, the scouring process was conducted for 30 min.

In the next step, 1% owf ethylenediamine-tetraacetic acid disodium salt (EDTA·2Na) was added to the bath, and the bath temperature was raised to 85°C (rate 2°C/min) for 10 min. After the scouring, the samples were rinsed three times with 300 ml of distilled water at a temperature of 60°C, followed by cold distilled water to obtain a neutral pH. The samples were dried at ambient temperature.

**2.3. Alkaline scouring**

The alkaline scouring process for samples of cotton knitted fabrics (20 g) was started at room temperature in a bath containing 1.5 g/l Tanaterge Advance and 3 g/l NaOH (4% owf) at 1:15 liquor ratio. Then, the bath was heated at a rate of 4°C/min to 100°C temperature and kept for 60 min. For all tests, the process was terminated by cooling the cup contents to 70°C at a rate of 4°C/min. Next, the samples were rinsed three times with 300 ml of distilled water at a temperature of 70°C, followed by cold distilled water to obtain a neutral pH. The samples were dried at ambient temperature.

**2.4. Cationization treatment**

Cationization was carried out by the exhaustion method for cotton knitted fabric samples (20 g): raw cotton (R samples), after alkaline scouring (A samples), after enzymatic scouring (B samples), using 1:10 liquor ratio.

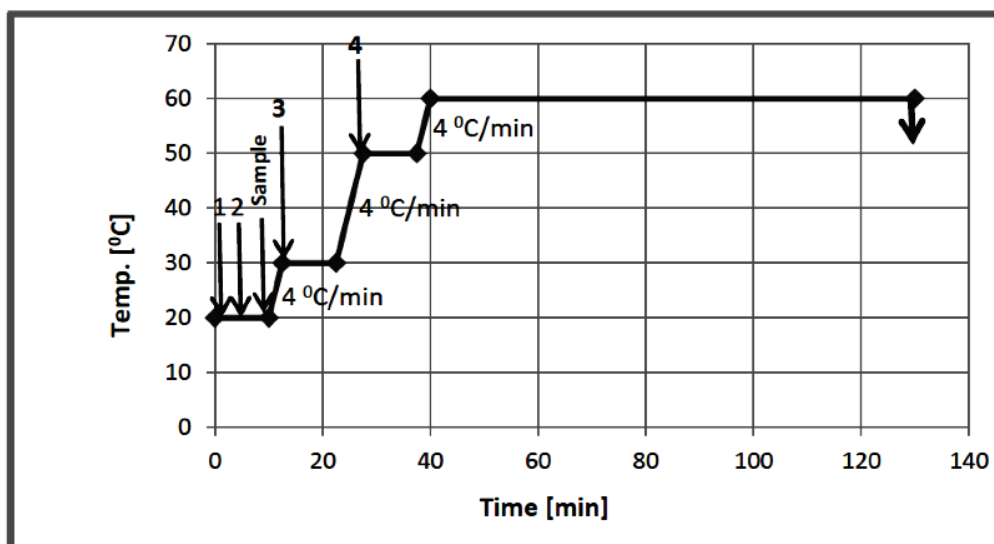
After cationization, the samples were rinsed three times with 300 ml of distilled water at a temperature of 60°C, followed by cold distilled water to obtain a neutral pH. They were then dried at ambient temperature. The temperature course of the cationization process is shown in Figure 1. NaOH was used as 50% liquid.

**2.5. Measurement of nitrogen contents**

In our study, the nitrogen content for the cotton knitted fabrics before and after modification was determined by the classical Kjeldahl method in the Institute of Technical Biochemistry, Faculty of Biotechnology and Food Sciences, Technical University of Lodz. Specimens of 1.5 g cotton knitted fabrics were mineralized in concentrated sulfuric acid with the addition of a selenium mixture in a Büchi K-424/435 apparatus. They were then alkalinized with a concentrated sodium hydroxide solution. The ammonia formed was saturated in a boric acid solution in the Büchi K-314 apparatus. The distillate was titrated with a hydrochloric acid solution against a Tashiro indicator using a Schott Geracle Titronic digital burette to change the color from green to violet.

**2.6. Measurement of the specific charge amount on the cotton knitted fabric surface**

Specimens of 0.25 g of the tested cotton knitted fabric, cut into approximately 0.5 x 0.5 cm pieces, were placed in a 400 ml conical flask, adding 50 ml of 0.0001N poly-DADMAC cationic polyelectrolyte, and stirred with a magnetic stirrer for 1 h at room temperature. As a next step, the fabric pieces were removed, and the solution was filtered to remove all fibers released in the liquid during stirring. An amount equal to 10 ml of filtrate was placed in a measuring cell of the Muetek PCD 03 pH apparatus, and the piston vibration motion was activated. After stabilization of the potential, the filtrate was titrated with 0.0001N PES-Na anionic polyelectrolyte to a stable 0 mV potential. The value of the specific charge was calculated according to the following formula:



1 – Tanaterge Advance	0.1 g/l	0.1 g/l
2 – CHPTAC	4% owf	8% owf
3 – NaOH	1.2% owf	2.4% owf
4 – NaOH	3.95% owf	3.95% owf

Figure 1. Cationisation process



$$Q_{\text{surf}} = \frac{(V_0 - V_1) c V_c}{m V_a} [\text{eq/g}]$$

where

$V_0$  – ml of polyelectrolyte PES-Na for titration of 10 ml polyelectrolyte poly-DADMAC used for cotton knit processing (blind test),

$V_1$  – ml of polyelectrolyte PES-Na for titration of 10 ml of filtrate after treatment,

$c$  – polyelectrolyte concentration of poly-DADMAC,

$V_c$  – ml of polyelectrolyte poly-DADMAC used for treatment,

$V_a$  – ml of filtrate used for titration,

$m$  – test sample weight [g].

### 2.7. Weight loss measurement

The weight loss of each sample was calculated based on the following equation:

$$\Delta W = \frac{m_0 - m_1}{m_0} \times 100\%$$

where

$m_0$  – weight of the raw sample [g], and

$m_1$  – weight of the sample after treatment [g].

### 2.8. Whiteness measurement

White fabric is that for which the Whiteness Index is in the range of  $40 < WI < (5Y - 280)$ . To assess the shade change of raw, pretreated, and cationized cotton knitted samples, the authors decided to use the word “whiteness” and equation given in the PN ISO 105-J02 standard:

$$WI_{10} = Y_{10} + 800(0.3138 - x_{10}) + 1700(0.3310 - y_{10})$$

where

$Y_{10}$  – tristimulus value,

$x_{10}$  and  $y_{10}$  – chromaticity coordinates of the specimen.

In fact, after these processes, there is no specific word and formula to evaluate changes in surface color obtained. Several authors use this word and formula to evaluate such changes in their publications [32–35].

### 2.9. Wettability measurement

For the evaluation of the wettability of cotton knitted samples, the authors decided to use the modified Tegewa Drop Test [36]. Instead of patent blue (anionic dye), methylene blue (cationic dye) was used as a 0.2% w/v water solution. The time lapsed between the contact of a drop of 30 ml of that solution, carefully deposited on the fabric’s surface, and its disappearance into the fabric matrix was reported as the fabric wetting time. Images were taken by a Canon SX 410 IS digital camera.

## 2.10. Dyeing process and K/S measurements

To show the influence of the cationization process on the affinity of the cellulose to anionic dyes, the cotton knitted fabric samples were dyed with Gryfalan Yellow RL (C.I. Acid Yellow 194,  $\lambda_{\text{max}} = 460 \text{ nm}$ ) in a bath containing a dye with conc. 2% owf, at pH 5 for 15 min at 95°C, with with liquor ratio 1:50. After dyeing, they were rinsed with hot (70°C) and tap water until a colorless bath was obtained and were then dried at ambient temperature.

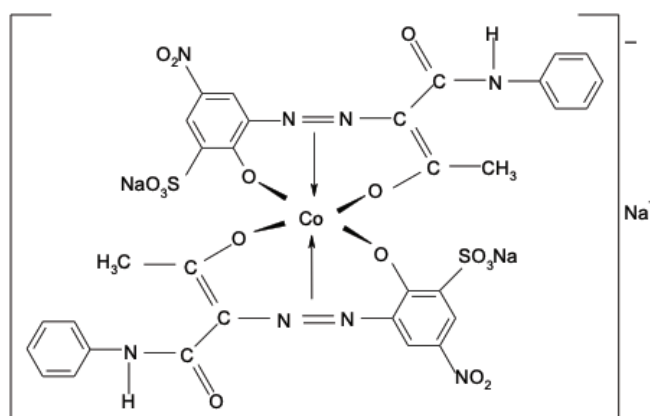


Figure 2. Chemical structure of C.I. Acid Yellow 194.

The concentration of dyes in the case of dyed knitted applications was determined based on the evaluation of colorimetric measurements (light reflected from a white or dyed sample) using a Datacolor 850 spectrophotometer. The results are presented in the form of the dependence K/S on the wavelength  $f(\lambda)$ . The ratio of light absorption coefficient K to the scattering factor S is a simple function of the reflection coefficient from this layer  $R_{\infty}$ . If the remission factor  $R_{\infty}$  is expressed as a percentage, then:

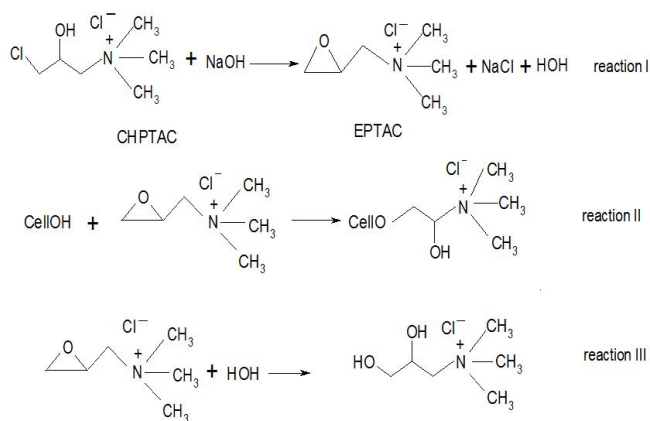
$$K/S = (100 - R_{\infty})^2 / 200 R_{\infty}$$

where K is the light absorption coefficient, S is the light scattering coefficient, and  $R_{\infty}$  is the remission factor.

## 3. Results and discussion

The cationization of cellulose with CHPTAC is a two-step reaction mechanism [15] (Figure 3). In the first fast step, the chlorohydrin form of CHPTAC is converted to 2,3-epoxypropyltrimethylammonium chloride (EPTAC) (as shown in reaction I), which subsequently reacts more slowly either with cellulose to form cationized cellulose (as shown in reaction II) or with water to form a hydrolyzed waste material (as shown in reaction III). A reaction could occur between EPTAC and water, which must be avoided as the formed diol is unable to react with cellulose, increasing the cost of the cationic modification [15, 22, 37].

During the cationization process, the degree of substitution is highly influenced by the quantity of base added and the liquor



**Figure 3.** Cationization of cellulose and hydrolysis of EPTAC.

ratio of the bath to the material. The alkali addition is necessary not only to generate EPTAC from CHPTAC but also to weaken the hydrogen bonds between molecules, making cellulose more accessible [38]. Therefore, it can be used as a pretreatment, because an excess of base favors polysaccharide hydrolysis and epoxide degradation toward the aforementioned diol. Besides the hydrolysis of the reactive epoxy system itself, three more directions are also indicated as adverse reactions:

- trimethylamine cleavage reaction (characteristic fishy odor appears) in an alkaline medium and at an elevated temperature from the product of cationization [39, 40],
- ether linkage hydrolysis reaction, similar to reactive vinylosulfon dye linkages with cellulose in a strongly alkaline environment [41], and
- probable, but not described in the literature, possibility of demethylation of a quaternary group in a strongly alkaline environment at the cationization process.

Since no characteristic odor was found, we believe that the first type of reaction did not occur.

The following is a list of sample abbreviations:

Sample R – raw cotton knitted fabric (single jersey) without pretreatment

Sample R4 – cationized sample R at 4% owf with CHPTAC

Sample R8 – cationized sample R at 8% owf with CHPTAC

Sample B – bio-scoured sample R with alkaline pectinase

Sample B4 – cationized sample B at 4% owf with CHPTAC

Sample B8 – cationized sample B at 8% owf with CHPTAC

Sample A – alkaline-scoured sample R with sodium hydroxide

Sample A4 – cationized sample A at 4% owf with CHPTAC

Sample A8 – cationized sample A at 8% owf with CHPTAC

The obtained results presented in Table 1 were analyzed considering the properties of raw, bio- and alkali- scoured cotton knitted fabrics and specific strongly alkaline conditions of their cationization process. To obtain more reliable results, all experiments were repeated three times, and the data were averaged.

### 3.1. Nitrogen content

Depending on their origin, growing conditions, and degree of maturity, raw cotton fibers that have been identified in their primary wall are 1.1–1.9% proteins, peptides, and free amino acids. These compounds are the major component of all non-cellulosic contaminants. The free amino acids that have been identified in raw cotton are glutamic acid, aspartic acid, valine, serine, threonine [42], proline, and hydroxyproline [43]. Using the standard conversion rate of 6.25 [42] to convert these constituents to nitrogen content, this ranges between 0.176 and 0.304%. Most of the amino acids, low-molecular peptides and proteins were removed with water during the washing process. High-molecular-weight proteins were removed during the alkaline pretreatment process. Depending on the kind of pretreatment, the nitrogen content of scoured fibers is about 0.035% [42]. After causticized treatment with 10, 20, and 30% NaOH, the amounts were decreased to 0.0180, 0.0171, and 0.0101%, respectively [44]. In cellulose obtained as a recycled newspaper, it is 0.063 and 0.075% [45], and for scoured and bleached cotton fabric with an additional 5 g/l solution of nonionic detergent (Hostapal CV Clariant) at 95°C over a 4 h treatment, it is 0.00% [44].

Figure 4 presents the nitrogen content in raw, bio- and alkaline scouring cotton knitted fabrics before and after cationization. According to the results shown in Figure 4, it can be stated that two parallel processes occur during cationization. Proteins containing natural nitrogen are partly removed from the fibers, and, at the same time, nitrogen in the quaternary form is added by the etherification of hydroxyl groups of cellulose. Kjeldahl analysis of nitrogen content in cotton knitted fabrics after cationization reveals the total quantity of nitrogen. Therefore, based on the results of nitrogen content, it is not possible to state in unambiguous terms that the total content of nitrogen found in the cotton after cationization is proportional to the degree of substitution of hydroxyl groups. It was also observed that, as the percentage of cationization increased (except raw cotton), the final content of nitrogen for the samples also increased. ΔN in Figure 4 presents the difference in nitrogen content value in the samples before and after the cationization process.

### 3.2. Specific charge amount on the cotton knitted fabric surface

After cationization, changes in negative charge value on the surface of cotton knitted fabrics were observed (Figure 5).

During the cotton cationization process in the presence of sodium hydroxide, two processes occur simultaneously,

**Table 1.** Averaged data of all experiments: for specific charge amount ( $Q_{surf}$ ) on the cotton knitted fabric surface, nitrogen content, K/S, weight loss ( $\Delta W$ ), whiteness (WI), and wettability (WET)

Sample	$Q_{surf}$ [ $10^{-6}$ eq/g]	N [%]	$\Delta N$ [%]	K/S	$\Delta K/S^4$ [%]	$\Delta W^{1)}$ [%]	WI	WET [s]
R	-12.96	0.182	0	1.19	0	0	-1.28	Non wettable <sup>2)</sup>
R4	-14.16	0.135	-0.047	2.11	92	2.2	18.02	Non wettable <sup>2)</sup>
R8	-13.2	0.1497	-0.032	9.10	791	2.3	28.12	600 <sup>3)</sup>
B	-13.74	0.122	0	1.21	0	3.38	24.4	5
B4	-10.52	0.1251	0.003	5.36	415	3.58	30.32	12 <sup>3)</sup>
B8	-10.47	0.147	0.025	9.80	859	3.78	28.97	18 <sup>3)</sup>
A	-7.86	0.049	0	0.53	0	5.4	41.2	2
A4	-6.71	0.0687	0.0197	4.43	390	5.75	48.86	4
A8	-7.11	0.118	0.069	8.12	759	5.77	42.86	10 <sup>3)</sup>

<sup>1)</sup>  $\Delta W$  was calculated for all samples as a percent weight loss against the weight of the raw sample (R).

<sup>2)</sup> Nonwetable means that after 600 s the drop of methylene blue water solution deposited on the cotton knitted fabric surface remained as a drop.

<sup>3)</sup> Penetration means that after a predefined period of time some parts of the drop of methylene blue water solution deposited on the cotton knitted fabric surface were absorbed, while the rest penetrated to the other side of the material and dropped.

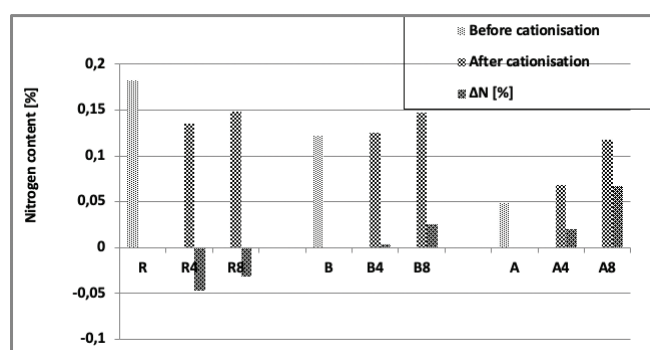
4)  $\Delta K/S$  – absolute increase K/S for dyed samples, against starting samples (R, B, A)

namely cationization of cellulose and alkaline hydrolysis of some natural cotton impurities. The hydrolysis products at alkaline conditions and elevated temperature form soluble sodium salts and are removed from the cotton surface. Because the cationization process is carried out at a lower temperature than in the pretreatment processes, it results in the incomplete hydrolysis of impurities and a lower degree of their removal. This is particularly evident for the R4 and R8 samples, obtained after the cationization of raw cotton, which contain mainly products of saponification fats, waxes, and pectins. The presence of impurities increases the negative charge value on their surface. It is most likely that due to the high concentration of sodium hydroxide and the high pH of the bath under the conditions of the cationization process for the A8 sample, the impurities in the deeper amorphous layers of cellulose are further reduced by their hydrolysis to produce products with the acidic group. This causes a slight increase in the negative charge in the fiber compared to the A4 sample, for which the same type of impurities can also be removed during the cationization process, but to a lesser extent.

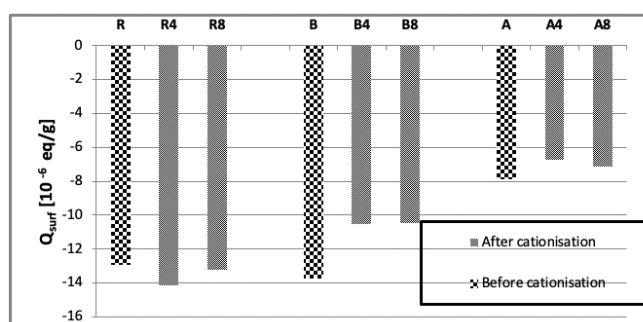
For samples B4 and B8 (enzymatic pretreated), the hydrolyzed impurities (i.e., the products of pectin deestrication and degradation) are removed from cotton as a soluble sodium salt in alkaline conditions during cationization. For these reasons, the negative charge on the cotton surface decreased. Such large variations, in the size of the negative charge on the cotton surface after cationization, are the result of differences in the pretreatment of the tested samples.

### 3.3. K/S values

The sorption properties of the cellulosic fibers are significantly influenced by the amount and availability of accessible groups. Thanks to this, it is possible to dye them physically or chemically. Most dyes used in cellulose fibers in the sorption step of the dyeing process are anionic, similar to cellulose. Due to the repulsion between the dye and the fiber, the substantivity of the dye to the fiber is reduced, and the final yield of the sorption is not satisfactory. Cationization modifies the cellulose eliminating such problems. The quaternary ammonium groups with positive charge chemically bonded with the cellulose chain



**Figure 4.** Nitrogen content in knitted cotton fabric samples.



**Figure 5.** Specific negative charge size on the surface of cotton knitted fabrics: raw, after enzymatic and alkali scouring, before and after cationization treatment.

are attractive to the negatively charged dyes. After modification by cationization, cotton fiber properties more or less are similar to protein fibers, and they can be dyed even with typical acid dyes.

C.I. Acid Yellow 194 (Figure 2) is a metal-complex 1:2 dye, which is generally recommended for dyeing polyamide and wool fibers in weak acid bath conditions. This compound, as a typical anionic dye, can also bind to cationized cotton fibers in a slightly weak acid bath. In this case, a strong ionic bond between the anionic sulfonic group of the dye and the quaternary ammonium group is formed. In the same manner, Acid Yellow 194 can also dye protein impurities in the cotton fibers, which are not fully removed during the pretreatment process. According to our experience, non-cationized bleached and mercerized cotton cannot be dyed with Acid Yellow 194 [unpublished works].

Table 1 and Figure 6 present the spectral curves K/S for the knitted cotton fabric samples dyed with C.I. Acid Yellow 194 as a result of the difference K/S before and K/S after dyeing according to the equation:

$$K/S = (K/S)_d - (K/S)_{bd}$$

where

$(K/S)_d$  - value for the sample after dyeing,  
 $(K/S)_{bd}$  - value for the sample before dyeing.

It is observed that for the non-cationized samples (reference samples) dyed with the anionic dye, color intensity was relatively low compared to the samples dyed after cationization. Their K/S value was in the following order due to the increased removal of natural nitrogen impurities: raw, bio-scoured, and alkali-scoured cotton. This may be connected with the binding of C.I. Acid Yellow 194 with only a few proteins (probably with different molecular weights) [42, 43] existing as remaining impurities in cellulosic materials after pretreatment. These proteins can bind via ionic bonds with a large anion molecule of the C.I. Acid Yellow 194. It seems that the intensity of dyeing (K/S value) depends on the content of protein impurities. As

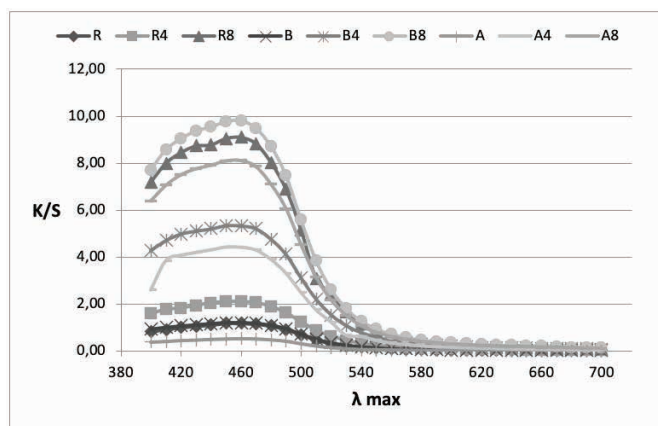


Figure 6. K/S graphs of dyed cotton knitted fabrics in spectral curves.

expected, all cationized samples have a much higher K/S value than the reference ones.

The measured K/S values do not correspond fully to the total nitrogen content in the samples after cationization. This means that the evaluation of the quantity of nitrogen in cationized cotton fabric samples does not correspond to the content of nitrogen introduced with the quaternary group. This is especially evident for raw cotton and not fully cleaned bio-scoured cotton fabric. Comparing  $\Delta K/S$  for R8, B8, A8, B4, and A4, it is observed that the cationization of cotton samples in the exhaustion process is similar between the available hydroxyl groups in cotton fibers and CHPTAC in the same conditions. The final results are not comparable only in the case of R4, probably due to the high amount of impurities consumed by sodium hydroxide during cationization.

According to the obtained results, a higher degree of cationization of cellulose fibers with CHPTAC was obtained for materials with higher negative charge values on the cotton surface. This was confirmed by dyeing with C.I. Acid Yellow 194 and measuring its K/S value. It seems that negative groups located on the cotton fiber surface in acid conditions do not disturb dyeing with anionic C.I. Acid Yellow 194, as the main dyeing mechanism, occurs via ionic bonds between the quaternary ammonium group of cotton and the anionic groups of the dye.

### 3.4. Weight loss

Figure 9 presents the summary results of weight loss for all cotton knitted fabrics during the pretreatment alkaline or bio-scouring process and alkaline cationization process compared to the weight of the raw cotton sample.

Cationization also leads to the additional removal of natural impurities. For raw cotton samples cationized on 4 and 8% owf with CHPTAC, maximal weight loss was observed. For the rest of the trials, weight loss is on a similar level. The lower weight loss for sample B4 seems to be the result of the higher consumption of sodium hydroxide for the creation of sodium salts and the soluble impurities contained in cotton after the bio-scouring process.

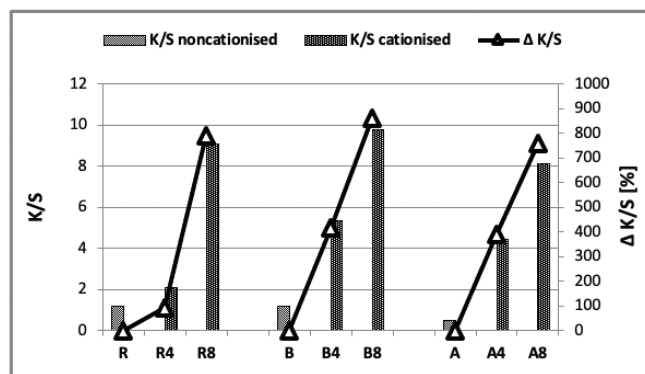


Figure 7. Change in K/S strength for dyed noncationized and cationized samples.

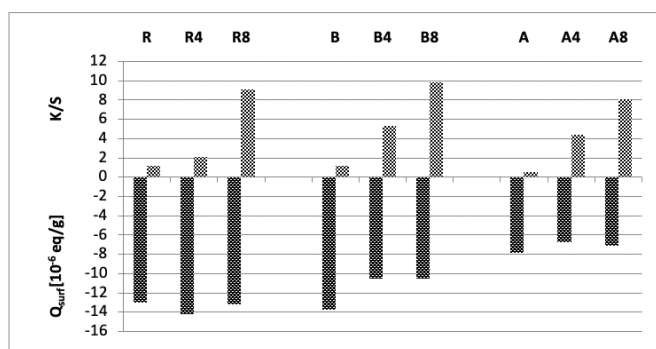


Figure 8. The relation between K/S strength and negative size charge on cotton knitted samples surface.

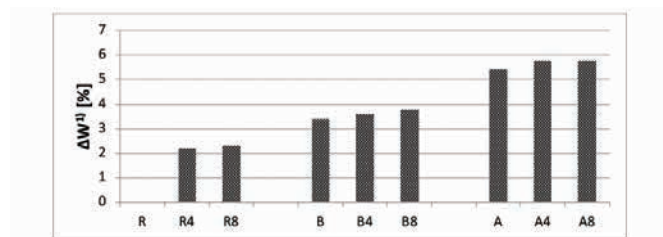
### 3.5. Whiteness

It was observed that after each individual treatment process (enzymatic scouring, alkali scouring, and cationization), the color of the cotton knitted fabric surface compared to the original samples was changed. The largest shade change occurred on the surface of the cationized raw cotton knitted samples, which was in line with expectations.

According to Figure 10, cationization of cotton knitted fabrics on 4% owf with CHPTAC leads to increasing whiteness due to the treatment of cellulose in alkaline conditions. Together with increasing cationization, a deterioration of whiteness effect on cotton was observed as a result of introducing more quaternary ammonium groups to the cellulose chain.

### 3.6. Wettability

The results presented in Table 2 show that the wettability of cationized bio- and alkali scoured cotton knitted samples decreased compared with the starter samples. During cationization, the available quantity of the hydroxyl groups, which are mainly responsible for wettability, was reduced by etherification. It is observed that cationized samples have decreased wettability. Improved wettability was observed only in the case of raw cotton knitted fabric due to the increased purification of the fibers in alkaline conditions during cationization.



ΔW<sup>(1)</sup> [%] – was calculated for all samples as a per cent weight loss against the weight of the raw sample (R)

Figure 9. Change in weight loss in cotton knitted samples after cationization.

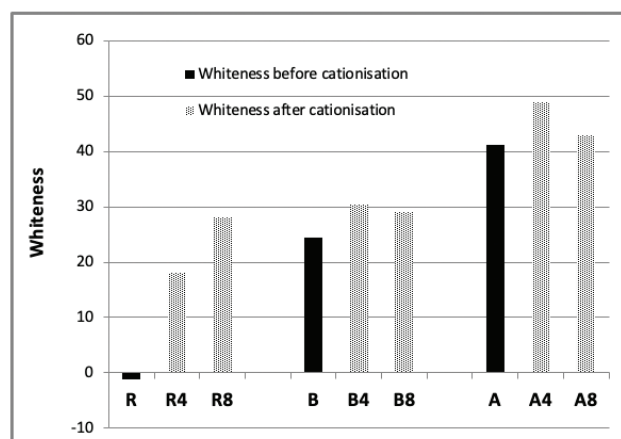


Figure 10. Change in whiteness in cotton knitted samples after cationization.

## 4. Conclusions

The obtained results of the tests confirmed the assumptions that cationization with CHPTAC/EPTAC under the same conditions for cotton knitted fabrics with different levels of pretreatment does not lead to obtaining materials with compatible parameters. At that stage, it was difficult to state that there was a specific relation between sodium hydroxide and CHPTAC and the impurities present in the cotton at each step of pretreatment. The bio- and alkali scouring processes created different negative surface charge values. CHPTAC, as a small molecule, is not substantive to cellulose, but the quaternary group can create ionic bonds with an anionic carboxyl group present in the cellulose and its impurities. These could probably be of help in increasing cationization. It was found that measuring the K/S value for dyed samples

Table 2. Changes in wettability of raw, bio- and alkali-scouring cotton knitted fabrics before and after cationization

Sample	R	R4	R8	B	B4	B8	A	A4	A8
Wettability [s]									
	Non wettable <sup>1)</sup>	Non wettable <sup>1)</sup>	600 Penetration <sup>2)</sup>	5	12 Penetration <sup>2)</sup>	18 Penetration <sup>2)</sup>	2	4	10 Penetration <sup>2)</sup>

<sup>1)</sup>Non-wettable means that after 600 s, the drop of methylene blue water solution on the cotton knitted fabric surface remained as a drop.

<sup>2)</sup>Penetration means that after a predefined period of time, some parts of the drop of methylene blue water solution deposited on the cotton knitted fabric surface were absorbed, while the rest permeated to the other side of the material and dropped.

of cotton with anionic dye was the optimal indicator for the evaluation of the degree of cationization, especially of  $\Delta K/S$  measured as the difference of K/S for samples dyed after and before cationization.

The total nitrogen content determined by Kjeldahl analysis in the cotton samples after cationization is the amount of the nitrogen introduced in the cationization reaction and the nitrogen contained in protein impurities that are not removed.

Additionally, we arrived at the following conclusions:

- after cationization, "whiteness" will deteriorate,
- cationization does not significantly affect the charge on the surface of the cotton knitted fabric. The negative charge reduction is related to additional treatment in alkaline conditions and is confirmed as an increase in fabric weight loss,
- after cationization, wettability decreases, and
- cationized cotton can be dyed effectively in a slightly weak acid bath with an anionic 1:2 metal-complex dye containing the sulfonic groups.

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# Eco-friendly dyeing of cationised cotton with reactive dyes: mechanism of bonding reactive dyes with CHPTAC cationised cellulose

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Received: 21 November 2021 / Accepted: 3 March 2022  
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**Abstract** The linkage between the dye and the cellulose is generally responsible for obtaining good washing and rubbing fastness properties of dyed materials. For reactive dyes this linkage is formed in reaction between reactive group of the dye with hydroxyl group of the cellulose. This reaction can go through nucleophilic substitution or an addition mechanism. Introducing the cationic groups to the chain of cellulose in the modification process completely changes the cotton surface charge from negative to partially or totally positive. Electrostatic interaction between the cation modifiers and sulfo group of anionic dye leads to the formation a strong ionic bond and rapid exhaustion the dye from the bath without addition of electrolytes. It was found and experimentally confirmed that when the cotton was cationised with 3-chloro-2-hydroxypropyltrimethylammonium chloride ( $[\text{CHPTA}]^+\text{Cl}^-$ ) reactive dye creates a covalent bond with hydroxyl group located in modification agent instead of with hydroxyl group in a glucopyranose ring. This reaction can be

done without salt and alkali and at room temperature. The analysis using particle optimisation with MM+ molecular mechanics and quantum-chemical calculations PM3 by the method of all valence orbitals confirmed the experimental results of high activity of the nucleophile being formed on the hydroxyl group in the chain of modifier.

**Keywords** Cationised cotton · CHPTAC · Molecular mechanics MM+ · Quantum-chemical calculations PM3 · Reactive dyes

## Abbreviations

Cell-OH	Cellulose
$[\text{ClCh}]^+\text{Cl}^-$	2-Chloroethyltrimethylammonium chloride
$[\text{Cell-O-Ch}]^+\text{Cl}^-$	Cellulose cationised with $[\text{ClCh}]^+\text{Cl}^-$
$[\text{Cell-O(2)-Ch}]^+\text{Cl}^-$	Cellulose cationised $[\text{ClCh}]^+\text{Cl}^-$ on hydroxyl group in position 2 glucopyranose ring
$[\text{Cell-O(3)-Ch}]^+\text{Cl}^-$	Cellulose cationised $[\text{ClCh}]^+\text{Cl}^-$ on hydroxyl group in position 3 glucopyranose ring
$[\text{Cell-O(6)-Ch}]^+\text{Cl}^-$	Cellulose cationised $[\text{ClCh}]^+\text{Cl}^-$ on hydroxyl group in position 6 glucopyranose ring

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[Cell-O(6)-Ch] <sup>+</sup> PhSO <sub>3</sub> <sup>-</sup>	Ionic pair [Cell-O(6)-Ch] <sup>+</sup> Cl <sup>-</sup> and benzenesulfonic acid	RR 274	Eriofast red 2B (reactive red 274)
[CHPTA] <sup>+</sup> Cl <sup>-</sup>	3-Chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC)	rpm VS	Round per minute Vinylsulfone type of reactive dyes
[Cell-O-HPTA] <sup>+</sup> Cl <sup>-</sup>	Cellulose cationised with [CHPTA] <sup>+</sup> Cl <sup>-</sup>		
[Cell-O(2)-HPTA] <sup>+</sup> Cl <sup>-</sup>	Cellulose cationised [CHPTA] <sup>+</sup> Cl <sup>-</sup> on hydroxyl group in position 2 glucopyranose ring		
[Cell-O(3)-HPTA] <sup>+</sup> Cl <sup>-</sup>	Cellulose cationised [CHPTA] <sup>+</sup> Cl <sup>-</sup> on hydroxyl group in position 3 glucopyranose ring		
[Cell-O(6)-HPTA] <sup>+</sup> Cl <sup>-</sup>	Cellulose cationised [CHPTA] <sup>+</sup> Cl <sup>-</sup> on hydroxyl group in position 6 glucopyranose ring		
[Cell-O(6)-HPTA] <sup>+</sup> PhSO <sub>3</sub> <sup>-</sup>	Ionic pair [Cell-O(6)-HPTA] <sup>+</sup> Cl <sup>-</sup> and benzenesulfonic acid		
DMF	<i>N,N</i> -Dimethylformamide		
DMSO	Dimethyl sulfoxide		
[EPTA] <sup>+</sup> Cl <sup>-</sup>	2,3-Epoxypropyltrimethylammonium chloride		
Glu	Glucopyranose ring		
Kayacelon React	Brand name of reactive dyes with nicotinic group		
LR	Liquor ratio		
MCT	Monochlorotriazine type of reactive dyes		
owf	On weight fibre		
PhSO <sub>3</sub> H	Benzenesulfonic acid		
PES-Na	Polystyrene sulfonic acid sodium salt		
poly-DADMAC	Polydiallyldimethylammonium chloride		
RB 19	Remazol brilliant blue R (reactive blue 19)		
RB 160	Kalpactive blue HE-BR (reactive blue 160)		
RR 24:1	Helaktyn red D-BN (reactive red 24:1)		
RR 221	Papizolon red HT-3BN (reactive red 221)		

## Introduction

With a total consumption of about 50% of all textile fibres, cotton is still a dominant one, mainly due to its unique properties, including hydrophilicity, biodegradability, and relatively inexpensive. After scouring and bleaching, cotton is almost pure cellulose (Acharya et al. 2014). Cellulose can be dyed with many classes of dyes, such as direct, sulphur, vat and reactive dyes. Among these colorant compounds, reactive dyes have become the most popular and most important group of dyes since began to be used in industry. They offer a wide range of colors and high resistance to washing fastness. Each year, the textile industry uses over 400,000 tonnes of the reactive dyes for dyeing and printing (Liu et al. 2019) and the greatest amounts of them are used for dyeing from the bath exhaustion method (Lewis 2014). The application of reactive dyes to cellulosic materials requires the use of very large amounts of salts such as NaCl and Na<sub>2</sub>SO<sub>4</sub>. It is estimated that every year only in Europe, 200,000–250,000 tonnes of these compounds are discharged into wastewater (Aktek and Malekul Millat 2017), causing an increase in the salinity of water in the environment. This amount is increased by the salts formed in the dyeing process from the added alkalis necessary for the covalent bonding of the dye with the fibre.

Much research has been done to eliminate the use of such large amounts of salt and alkali. Nippon Kayaku has developed a range of Kayacelon React dyes for neutral fixation based on a triazine ring in which chlorine atom was replaced by nicotinic acid, achieving the goal of non-alkaline fixation (Lewis et al. 2008). New solutions in reactive dyes were investigated by introducing cationic groups into the chemical structure of the dye (Lewis 2014; Zhang and Zhang 2015), increasing the sorption on the fibre. A number of new reactive dyes containing 2, 3 and even 4 reactive groups (the same or different) were developed. These solutions are still insufficient for end

users, due to the salt consumption and the washability of hydrolysed form of the dye.

Chemical modification of cellulose is generally performed in reaction with the functional hydroxyl groups present in the fibre (Wang and Lewis 2002; Montazer et al. 2007). However it leads to the reduction of the total number of free-hydroxyl groups mainly on the surface and in amorphous part of the fibres proportionally to the substitution degree by modifier agent. Cationisation of cellulose is most often associated with the introduction of tetraalkylammonium (quaternary) groups into its chemical structure. Such derivatives have a permanent positive charge with a high electron density regardless of pH (Heinze et al. 2018). Depending on the degree of cationisation, cellulose becomes a more or less cationic polymer capable of ionic reactions with anionic substances. Cellulose, after cationic modification, can be dyed with all kind of anionic dyes, for example with direct, reactive, acid and solubilized sulphur dyes (Atiq et al. 2019). Depend on the type of the applied dyes, different kind of linkage between cellulose and the dyes can be create. The energy of ionic bond energy of the sulfonate group with the cationic polymer is in the range of 550–1000 kJ/mol (Oakes et al. 2004). It is much higher than the energy of the hydrogen bond 21–30 kJ/mol, or the van der Waals intermolecular bond 2–5.5 kJ/mol (Stiepanow 1980). The kind of created linkage between cellulose and the dyes have great influence on the color fastness of dyeings.

In the past decades, nearly a thousand publications (Correia et al. 2020) involved with the cationisation of cotton fibres and conditions their utilising for dyeing, printing and other functional applications were published. There is a commonly known mechanism of reaction all groups of reactive dyes with cellulose (Łukoś and Ornaf 1966, Venkataraman 1972, Clark 2011 and Burkinshaw 2016). However there are only a few speculative reports about the reaction mechanism of reactive dyes with cationised cellulose (Lewis 2014, Aktek and Malekull Millat 2017, Arivithamani and Dev 2017, Niu et al. 2020). None of these reports present how covalent bond were formed, their fastness for hydrolysis and other technical parameters.

The basic aim of the experiments carried out was to establish in which way the reactive dyes react with cationised cellulose. For this purpose, two modifiers with similar chemical structures and with the same

cationic group capable to reaction with cellulose were selected. However only one modifier had possibility to introduce an additional hydroxyl group in the cationisation process. After cationisation this group was in close proximity to the cationic group but out of the glucopyranose ring of cellulose. Five reactive dyes with different reactive groups were chosen for the experimental studies. The most environmentally friendly conditions for dyeing cationised cellulose, i.e. room temperature and the bath without electrolytes and alkalis were used. It was assumed that Coulomb interactions between the positive ammonium group of modified cellulose and the negative sulfo groups of reactive dyes would cause chemical adsorption to form a very strong ionic bonds leading to complete exhaustion of the dyes from the bath. Chemical adsorption under these conditions eliminates the need to use electrolytes and elevated temperature. It was also assumed that during dyeing without alkali in room temperature no cellulose anions would be formed on the hydroxyl groups in the glucopyranose ring of cellulose. As a result, the bond between the reactive dye and the dissociated hydroxyl group in the modifier will be formed. After dyeing, a water rinsing instead of the alkali washing was applied.

To confirm creation of the covalent bond of the reactive dye with the hydroxyl group of the modifier, the methods of testing the resistance of the bond to acid and alkali hydrolysis, extraction chemically unbounded dye with DMF and electron density analysis were used.

## Experimental

### Materials

The cotton plain fabric after classical alkali scouring and bleaching with a surface weight of 180 g/m<sup>2</sup> (16 warps and 22 wefts) was used. Cationising agents: 3-chloro-2-hydroxypropyltrimethylammonium chloride and 2-chloroethyl-trimethylammonium chloride were purchased from Sigma Aldrich and ADAMA Poland, respectively. Reactive dyes: RR 24:1 from Boruta-Zachem Poland, RR 274 from Swiscolor Poland, RB 19 from Biliński Factory Poland, RB 160 from Kalpactive India and RR 221 from Kisco South Korea were purchased respectively. All dyes were applied without further purification. Ready for

use polyelectrolyte standard solutions, PES-Na (MW 21.800 g/mol) and poly-DADMAC (MW 107.000 g/mol) were purchased from BTG Instruments AB Sweden. Tanaterge Advance (non-ionic detergent) was purchased from Tanachem Poland. Other chemicals and solvents were used as laboratory grade purity. Chemical structures and data of cationising agents and dyes are shown in Tables 1 and 2.

## Methods

### Cationisation of cellulose

Ugolini Redkrome–model RED P (Italy) laboratory dyeing machine, heated by infrared ray radiators, equipped with 150/400 ml cups was used for cationising cotton fabric samples.

### Cationisation with $[ClCh]^+Cl^-$

Cotton fabric samples of 15 g were introduced into 400 ml Ugolini cups to 60 mL  $[ClCh]^+Cl^-$  66.5% (0.28 mol), and then 24 g of NaOH (0.6 mol) dissolved in 150 ml distilled water was added. Then the bath was heated to  $97.5 \pm 1$  °C.

(2 °C/min, rotation right/left 40 rpm), for five hours. Next, the bath was cooled to 50 °C and the cationised cotton material was washed with cold tap water, neutralised with 0.5% acetic acid, again rinsed to a neutral pH and dried at room temperature. Reaction of cellulose cationisation with  $[ClCh]^+Cl^-$  was shown on Fig. 1.

### Cationisation with $[CHPTA]^+Cl^-$

Cotton fabric samples of 15 g were introduced into 400 mL Ugolini cups contained 285 mL bath with 4.86 g NaOH (0.12 mol) and 1 g/l Tanaterge Advance, and then five min wetted. Next, 15 mL  $[CHPTA]^+Cl^-$  60% (0.055 mol) was added, and the bath was heated to 70 °C (2 °C/min with rotation right/left 40 rpm) and continued at that temperature for 90 min. After that, the bath was cooled to 50 °C and cationised samples were rinsed and washed with warm and cold tap water, neutralised with 0.5% acetic acid and again rinsed to reach a neutral pH. Cationised samples were dried at room temperature. Reaction of cellulose cationisation with  $[CHPTA]^+Cl^-$  was shown on Fig. 2.

### Nitrogen content

The Nitrogen content before and after modification the cotton samples by the classical Kjeldahl method in the Institute of Technical Biochemistry, Faculty of Biotechnology and Food Sciences, Technical University of Lodz (Poland) was determined (Pruś et al. 2019 and 2021). Specimens ca. 1.5 g cotton samples were mineralised in concentrated sulphuric acid with the addition of a selenium mixture in a Büchi K-424/435 apparatus. Then solution were alkalinised with a concentrated sodium hydroxide. The ammonia formed was saturated in a boric acid solution in the Büchi K-314 apparatus. The distillate was titrated with an hydrochloric acid solution against a Tashiro indicator using a Schott Geracle Titronic digital burette to change the colour from

**Table 1** Information data of the modification agents selected for experiments

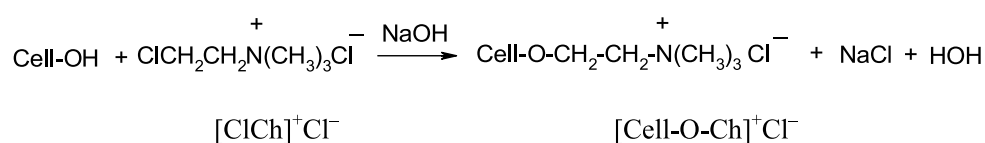
Modification agent	Chemical formula
$[ClCh]^+Cl^-$ 2-chloroethyltrimethylammonium chloride (chlorocholine chlorid) CAS: 999-81-5 Molecular weight: 158.07 g/mol	$Cl-CH_2-CH_2-N^+(CH_3)_3 Cl^-$
$[CHPTA]^+Cl^-$ 3-chloro-2-hydroxypropyl-trimethylammonium chloride (CHPTAC) CAS: 3327-22-8 Molecular weight 188.10 g/mol	$Cl-CH_2-CH(OH)-CH_2-N^+(CH_3)_3 Cl^-$

**Table 2** Information data of the reactive dyes selected for experiments

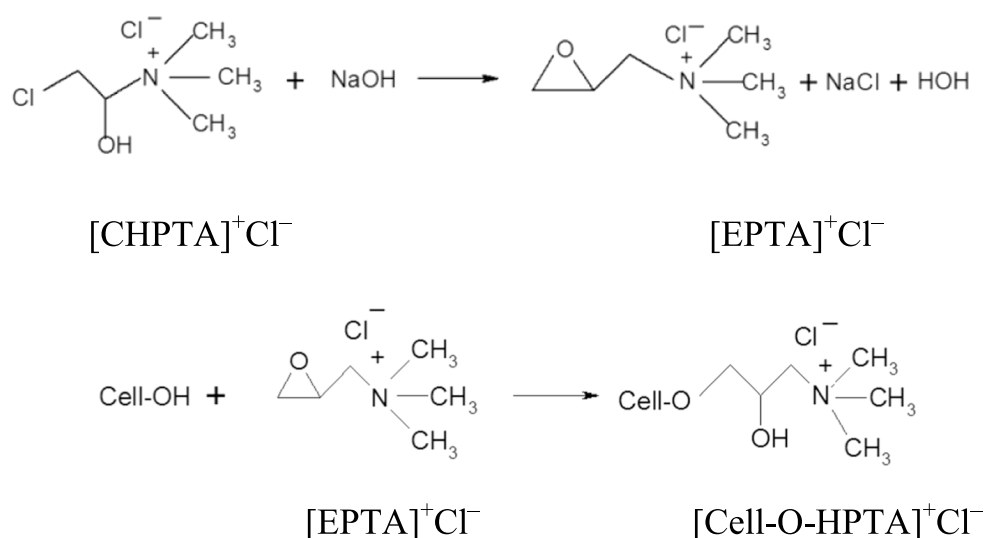
Dyestuff	Chemical data	Chemical formula	
RR 24:1	Helaktyn red D-BN Reactive red 24:1 C.I. 18,208:1 CAS: 72829-25-5	MCT Molecular formula $C_{27}H_{19}ClN_7O_{10}S_3 \cdot Na_3$ Molecular weight:802.10	
RB 160	Kalpactive blue HE-BR Reactive Blue 160 C.I. – CAS: 71872-76-9	bis-MCT formazan class Molecular formula $C_{38}H_{23}Cl_2N_{14}O_{18}S_5Cu \cdot Na_5$ Molecular weight: 1309.9	
RR 221	Papizolon red HT-3BN Reactive red 221 C.I. – CAS: 96726-27-1	bis-monocotinotriazine dyes Molecular formula $C_{57}H_{35}N_{16}O_{24}S_6 \cdot Na_6$ Molecular weight:1699.34	
RR 274	Eriofast red 2B <sup>a</sup> Reactive red 274 C.I. – CAS: –	MCT-VS (heterobifunctional) Molecular formula $C_{27}H_{20}N_8O_9S_3Cl \cdot Na_2$ Molecular weight:777.5	
RB 19	Remazol brilliant blue R Reactive blue 19 C.I. 61,200 CAS: 2580-78-1	VS Molecular formula $C_{22}H_{16}N_2O_{11}S_3 \cdot Na_2$ Molecular weight:626.5	

<sup>a</sup>Chemical formula known from (Kucharska et al. 2009)

**Fig. 1** Reaction of cellulose cationisation with  $[ClCh]^+Cl^-$



**Fig. 2** Two steps reaction of cellulose cationisation with  $[\text{CHPTA}]^+\text{Cl}^-$



green to violet. The Nitrogen content was calculated according to Eq. (1):

$$N = \frac{v \times c}{m} \quad (1)$$

where  $v$ —mL of hydrochloric acid used for titration distillate,  $c$ —concentration of hydrochloric acid 0.1 M [mol/L],  $m$ —weight of the sample for analysis [g].

#### Specific charge measurement

Muetek PCD 03 pH Particle Charge Detector (Muetek GmbH Germany) for measurement of the potential on the surface of cotton samples was used according to the previously developed recipe (Pruš et al. 2019 and 2021). The values of surface charges were calculated by Eq. (2):

$$Q_{surf}^+ = \frac{(v_0 - v_1)c_v c}{m v_a} \quad (2)$$

where  $v_0$ —mL of polyelectrolyte PES-Na for titration of 10 mL polyelectrolyte poly-DADMAC (blind test),  $v_1$ —mL of polyelectrolyte PES-Na for titration of 10 mL of filtrate after treatment,  $c$ —polyelectrolyte concentration of poly-DADMAC,  $v_c$ —mL of polyelectrolyte poly-DADMAC used for treatment,  $v_a$ —mL of filtrate used for titration,  $m$ —test sample weight [g].

#### Dyeing of cellulose

Ugolini Redkrome—model RED P (Italy) laboratory dyeing machine, heated by infrared ray radiators, equipped with 150/400 mL cups and simply 2- roll padder with 100% pick-up for dyeing in exhaustion method and cold pad batch (CPB) method were used respectively.

#### Conventional dyeing

For uncationised cotton samples, conventional methods of dyeing were used. Selected dyes were applied using methods and recipes recommended by their producers (Table 3).

All samples after conventional dyeing process were washed with 1 g/L  $\text{Na}_2\text{CO}_3$  and 1 g/L Tanaterge Advance at 90 °C for 15 min and next rinsed with warm and cold tap water for removing unfixed dye. Dyed samples were dried at room temperature.

#### Eco-friendly dyeing

Cationised cotton samples in eco-friendly dyeing conditions (LR = 1:20, temp.  $25 \pm 1$  °C, rotation right/left 40 rpm, distilled water, pH neutral, without salt and alkalis) were dyed for 30 min with 1% owf (RR 221 or RB 160) and 0.9% owf (RR 24:1 or RR 274 or RB 19) respectively. After eco-friendly dyeing samples were rinsed with cold distilled water to remove

**Table 3** Conventional dyeing data for selected reactive dyes

Dye	Method of dyeing	Dyeing conditions
RR 24:1	Cold pad batch	Cotton samples were twice padded/nipped with 100% pick-up in a bath containing 30 g/L dye, 40 g/L urea and 15 g/L NaOH solution, then wrapped in PE foil for 24 h and rinsed with cold and warm water
RB 19 RR 274	Exhaustion	Cotton samples were added to the bath (LR=1:20) with 2% owf dye. Then 80 g/L Na <sub>2</sub> SO <sub>4</sub> was added, the bath was heated to 50 °C and in two portions (with break 10 min) 1 g/L NaOH and 5 g/L Na <sub>2</sub> CO <sub>3</sub> was added. The bath was heated to 60 °C and kept 60 min. Next the bath was drop-up and dyed cotton samples were rinsed with cold and warm water
RB 160		Cotton samples were added to the bath (LR=1:20) with 2% owf dye. Then 60 g/L Na <sub>2</sub> SO <sub>4</sub> was added, the bath was heated to 70 °C and 20 g/L Na <sub>2</sub> CO <sub>3</sub> in two portion (with break 10 min) was added and kept by next 60 min at 75–80 °C. The bath was drop-up and dyed cotton samples were rinsed with cold and warm water
RR 221		Cotton samples were added to the bath (LR=1:20), with 2% owf dye, 70 g/L Na <sub>2</sub> SO <sub>4</sub> and 1 g/L buffer pH=7. The bath was heated to boiling and kept 60 min. Then the bath was cooled to 70 °C, next drop-up and dyed cotton samples were rinsed with cold and warm water

not fixed dye and dried at room temperature. For comparison, noncationised cotton samples were dyed under the same conditions and with the same amounts of dyes.

### Estimation of the type of bond between dye and cellulose

Hydrolysis of covalent bond between dye and cationised cellulose

In order to confirm the place of the covalent bond formed between the [Cell-O-HPTA]<sup>+</sup>Cl<sup>-</sup> and reactive dye in eco-friendly conditions the dyed material was hydrolysed under acid or alkali conditions. Two dyes were selected for these experiments: RR 24:1 (monochlorotriazine type) and RB 19 (vinylsulfone type) for acid and alkali hydrolysis respectively.

#### Acid hydrolysis

Four pieces of approx. 2 g of samples [Cell-O-HPTA]<sup>+</sup>Cl<sup>-</sup> dyed with 2% owf RR 24:1 were introduced into the bath (LR=1:30) containing 1 mL/L H<sub>2</sub>SO<sub>4</sub> 96% and 2 g/L Na<sub>2</sub>SO<sub>4</sub> at room temperature, then heated to boil, boiled for 6 h, then cooled to room temperature. The hydrolysis process was then repeated in a fresh bath for the same samples for next three hours. The samples after hydrolysis, were rinsed to neutral pH and dried at room temperature.

#### Alkali hydrolysis

Four pieces of approx. 2 g of samples [Cell-O-HPTA]<sup>+</sup>Cl<sup>-</sup> dyed with 2% owf RB 19 were introduced into the bath (LR=1:30) with 20 g/L Na<sub>2</sub>CO<sub>3</sub> at room temperature then heated to boil, boiled for 1.5 h, next cooled to room temperature. The hydrolysis process was then repeated in a fresh bath with the same samples for next 1.5 h. The samples after hydrolysis, were rinsed to neutral pH and dried at room temperature.

Two pieces the samples after acid or alkali hydrolysis were re-dyed respectively with the same dye and at the same eco-friendly dyeing conditions, rinsed in water and dried at room temperature.

#### Resistance of dyed cotton to DMF extraction

Cotton samples after dyeing, re-dyeing and hydrolysis treatment were extracted with DMF (LR=1:40) for 15 min at boiling temperature, then cooled down to 70 °C, rinsed in warm and cold distilled water and dried at room temperature.

Resistance of dyed cotton samples to DMF extraction was estimated based on the K/S measurement. The color strength of noncationised and cationised cotton samples before and after DMF extraction as well as before and after hydrolysis of the bonds was measured based on the evaluation of colorimetric measurements using a Daticolor 850

spectrophotometer (Datacolor, USA).  $K/S$  values were calculated in accordance with Eq. (3):

$$\frac{K}{S} = \frac{(1-R)^2}{2R} - \frac{(1-R_0)^2}{2R_0} \quad (3)$$

where  $K$ —light absorption coefficient,  $S$ —light scattering coefficient,  $R$ —decimal fraction of the reflectance of dyed fabric,  $R_0$ —decimal fraction of the reflectance undyed fabric.

Resistance to DMF extraction was calculated according to Eq. (4):

$$R_{DMF} = \frac{\left(\frac{K}{S}\right)_1}{\left(\frac{K}{S}\right)_0} 100(\%) \quad (4)$$

**Table 4** Summary of Nitrogen and  $Q_{surf}^+$  values for noncationised and cationised cotton samples

Cotton sample	Nitrogen		$Q_{surf}^+$	
	Content	$\Delta N$	Calculated	$\Delta Q_{surf}^+$
	( $10^{-6}$ eq/g)		( $10^{-6}$ eq/g)	
Cell-OH	25	–	+0.44	–
[Cell-O–Ch] <sup>+</sup> Cl <sup>–</sup>	30	5	+4.70	+4.26
[Cell-O–HPTA] <sup>+</sup> Cl <sup>–</sup>	136	111	+19.46	+19.02

Where  $\Delta N$ —difference of Nitrogen content between cationised and noncationised samples,  $\Delta Q_{surf}^+$ —difference of specific surface charge between cationised and noncationised samples

where:  $\left(\frac{K}{S}\right)_0$  - value measured for dyed samples before DMF extraction,  $\left(\frac{K}{S}\right)_1$  - value measured for dyed samples after DMF extraction.

**Table 5** Resistance to DMF extraction of dyed in different conditions noncationised and cationised cotton samples

Dye	$\lambda_{max}$ [nm]	$R_{DMF}$ [%]			
		Conventional dyeing method		Eco-friendly dyeing conditions	
		Cell-OH	Cell-OH	[Cell-O–Ch] <sup>+</sup> Cl <sup>–</sup>	[Cell-O–HPTA] <sup>+</sup> Cl <sup>–</sup>
RR 24:1	530	83.00	8.10	11.48	80.40
RB 160	630	95.15	21.11	19.61	90.53
RR 221	530	95.00	33.90	50.00	107.66
RR 274	530	101.30	8.80	12.45	141.87
RB 19	610	99.40	6.85	12.95	66.42

## Result and discussion

The research was aimed at confirming the hypothesis that reactive dyes in eco-friendly conditions can form a covalent bond with the hydroxyl group of the cationic modifier instead of the hydroxyl group of the glucopyranose ring. Two cationic modifiers and five reactive dyes with different reactive systems were examined. The concentration of dyes was used at such a level that it was possible to conduct a wide analysis of the test results. All obtained experimental data are presented in Tables 4, 5 and 6. The tables contain average data for four series of experiments. Percentage deviations were  $\pm 0.5\%$ ,  $\pm 1.5\%$  and  $\pm 2\%$  for the measurements of nitrogen content, the amount of charge on the fibre surface, and the measurements of color strength and resistance to DMF extraction, respectively.

### Cationisation of cellulose

The results of the cationisation cellulose experiments with selected modification agents in comparing to the starting material are presented in Table 4.

Cationisation cellulose with [ClCh]<sup>+</sup>Cl<sup>–</sup> create the product with a small degree of introduced quaternary groups, all of which were found on the cotton surface (Table 4). This is confirmed by the value of  $\Delta N$  ( $5 \times 10^{-6}$  eq/g) introduced by cationisation, which is almost consistent with the increase in the value of the positive surface charge ( $=4.26 \times 10^{-6}$  eq/g).

Cationisation cellulose with [CHPTA]<sup>+</sup>Cl<sup>–</sup> create the product with a much higher degree of introduced Nitrogen ( $\Delta N=111 \times 10^{-6}$  eq/g) in the form of

**Table 6** K/S data for samples dyed, extracted with DMF, after hydrolysis, re-dyed and re-dyed extracted in DMF (dyeing and re-dyeing in eco-friendly conditions)

Samples	K/S values	
	RR 24:1	RB 19
Dyed samples	27.26	25.46
Dyed samples after extraction in DMF	26.48	22.82
Dyed samples after acid hydrolysis:	15.25	–
Dyed samples after alkali hydrolysis	–	2.15
Re-dyed samples	28.08	22.27
Re-dyed samples after extraction in DMF	25.33	14.78

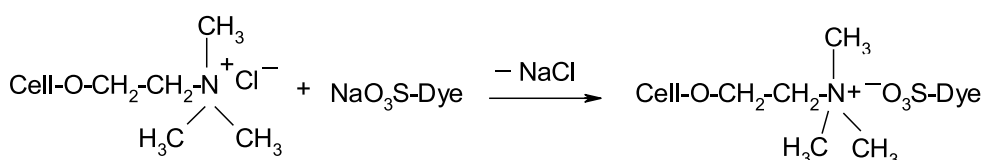
**Table 7** Electron density data for analysed oxygen atoms, as calculated by PM3 MO method

Compound	Electron density on an oxygen atoms			
	O(6)	O(2)	O(3)	O( $\beta$ )
Cell=(Glu) <sub>3</sub>	–0.341	–0.287	–0.291	–
[Cell-O(6)-Ch] <sup>+</sup> Cl <sup>–</sup>	–0.249	–0.300	–0.323	–
[Cell-O(2)-Ch] <sup>+</sup> Cl <sup>–</sup>	–0.320	–0.272	–0.354	–
[Cell-O(3)-Ch] <sup>+</sup> Cl <sup>–</sup>	–0.306	–0.299	–0.256	–
[Cell-O(6)-HPTA] <sup>+</sup> Cl <sup>–</sup>	–0.266	–0.281	–0.315	–0.319
[Cell-O(2)-HPTA] <sup>+</sup> Cl <sup>–</sup>	–0.340	–0.228	–0.296	–0.328
[Cell-O(3)-HPTA] <sup>+</sup> Cl <sup>–</sup>	–0.327	–0.284	–0.232	–0.333

quaternary groups, but only ca. 20% of this value was found in positive surface charge form ( $\Delta Q_{surf}^+ = 19.02 \times 10^{-6}$  eq/g). The rest of the introduced ammonium groups calculated by Nitrogen with the Kjeldahl method analysis were not available for

**Table 8** Electron density data for oxygen atoms and ammonium groups

Compound	Electron density on oxygen atoms and the ammonium group			
	O(2)	O(3)	O( $\beta$ )	N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>
[Cell-O(6)-Ch] <sup>+</sup> Cl <sup>–</sup>	–0.300	–0.323	–	0.633
[Cell-O(6)-Ch] <sup>+</sup> ⋯PhSO <sub>3</sub> <sup>–</sup>	–0.300	–0.324	–	0.683
[Cell-O(6)-HPTA] <sup>+</sup> Cl <sup>–</sup>	–0.281	–0.315	–0.319	0.638
[Cell-O(6)-HPTA] <sup>+</sup> ⋯PhSO <sub>3</sub> <sup>–</sup>	–0.290	–0.320	–0.309	0.718

**Fig. 3** The ionic bond between [Cell-O–Ch]<sup>+</sup>Cl<sup>–</sup> and reactive dyes (Dye = RR 24:1, RB 160, RR 221, RR 274, RB 19)

titrating with PES-Na anionic polyelectrolyte, which is typical for measuring the charge on the cotton surface.

The most important for dyeing are the positively charged ammonium groups on the surface of the fibre. They form strong ionic bonds with the sulfo groups of the anionic dyes. Although cationisation of cellulose with [ClCh]<sup>+</sup>Cl<sup>–</sup> was less effective than with [CHPTA]<sup>+</sup>Cl<sup>–</sup>, it was enough, however, to conduct comparative tests to determine the binding site of the reactive dye with cationised cellulose.

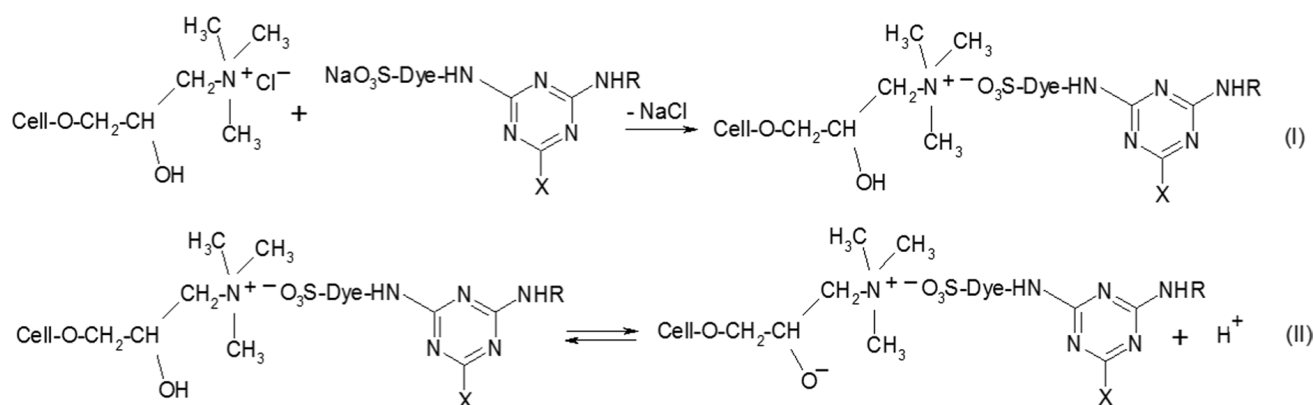
### Dyeing of cationised cellulose in an eco-friendly conditions

To confirm the hypothesis that reactive dyes under eco-friendly conditions can form a covalent bond with the hydroxyl group of the cationic modifier, comparative tests of dyeing non-cationised cellulose were performed in the same conditions and also in the conventional dyeing method. The reaction mechanisms have been proposed for selected reactive dyes with cationised cellulose (Figs. 3, 4, 5, 6 and 7).

#### [Cell-O–Ch]<sup>+</sup>Cl<sup>–</sup> dyeing

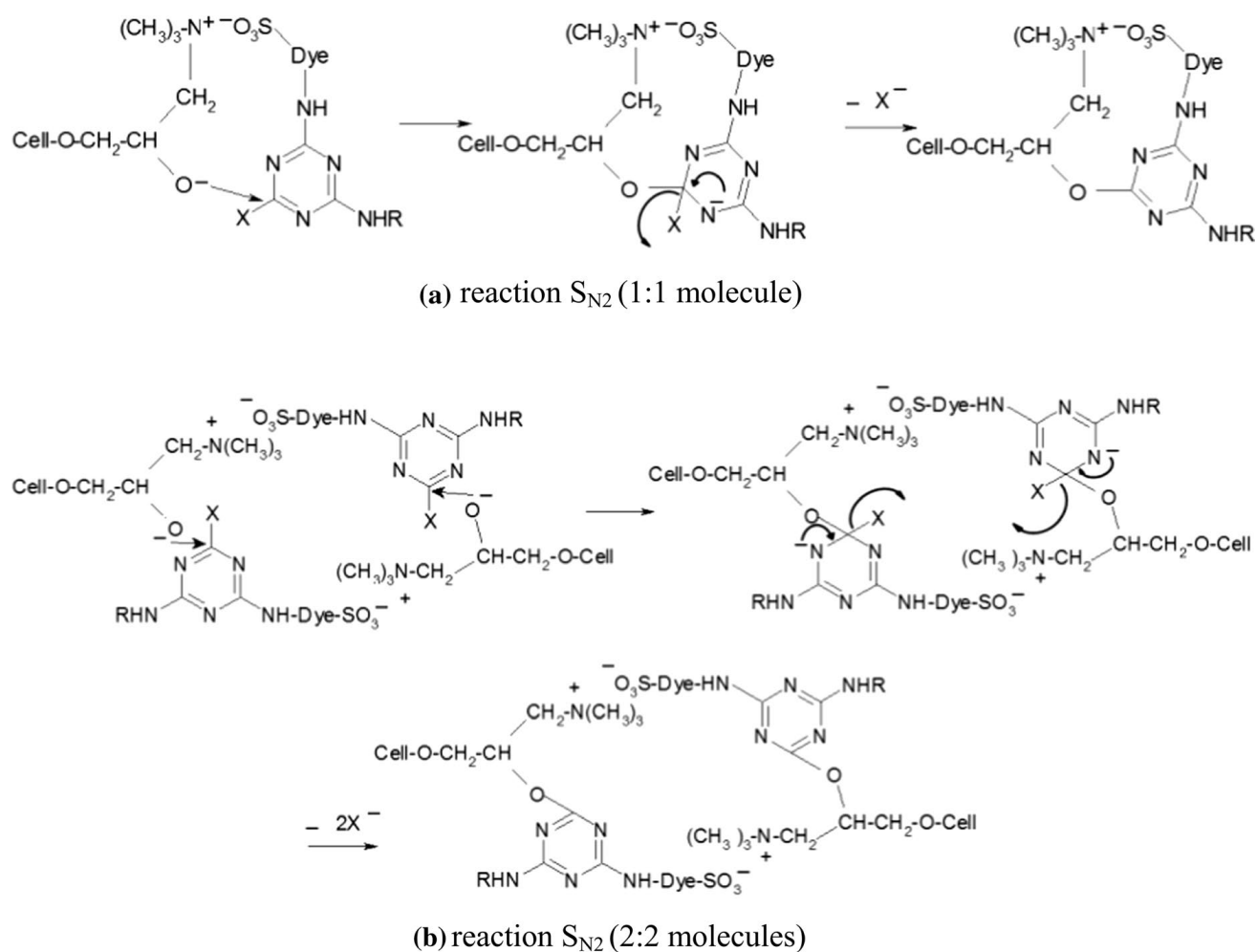
In the case of [Cell-O–Ch]<sup>+</sup>Cl<sup>–</sup> the amount of introduced dye mainly corresponds to the cationic group's presence. Formation of the linkage with reactive dyes and cellulose cationised with [ClCh]<sup>+</sup>Cl<sup>–</sup> was showed in Fig. 3.





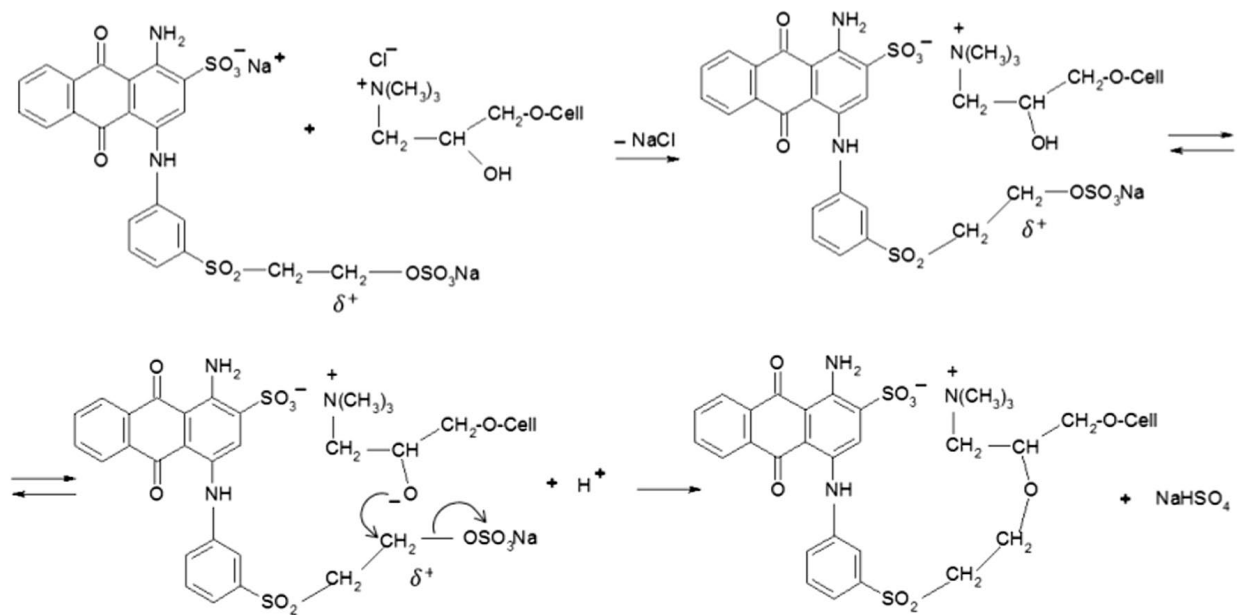
**Fig. 4** Proposed mechanism of the first step of dyeing [Cell-O-HPTA]<sup>+</sup>Cl<sup>-</sup> with triazine dyes: (I—ionic formation bonds on the fibre; II—dissociation of a hydroxyl group in ionic pair:

cationised cotton + reactive dye on the fibre) where R—different chemical substituents in the chemical structure of RR 24:1, RB 160, RR 221 and RR 274, X- halogen, nicotinic acid

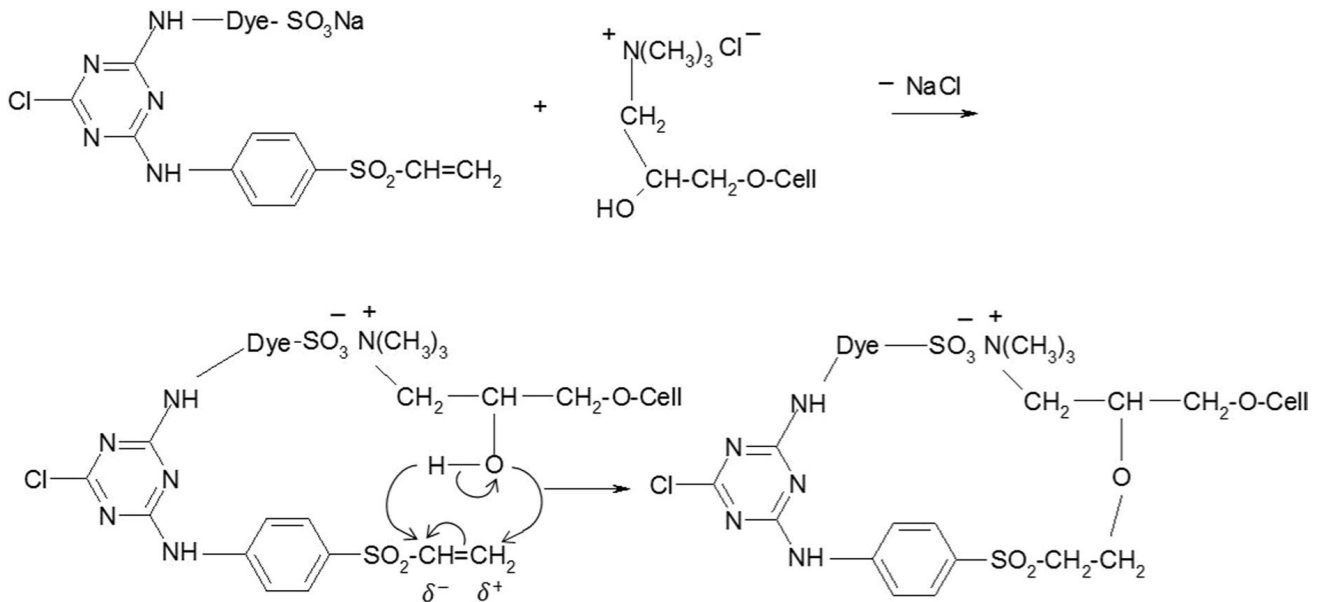


**Fig. 5** Proposed mechanism of second step of dyeing [Cell-O-HPTA]<sup>+</sup>Cl<sup>-</sup> with triazine dyes: **a** reaction substitution in one molecule and **b** between two molecules, where R- different

chemical substituents in the chemical structure of RR 24:1, RB 160, RR 221 and RR 274, X- halogen, nicotinic acid



**Fig. 6** Proposed mechanism of dyeing [Cell-O-HPTA]<sup>+</sup>Cl<sup>-</sup> with RB 19 (mono-VS reactive dye)



**Fig. 7** Proposed mechanism of dyeing [Cell-O-HPTA]<sup>+</sup>Cl<sup>-</sup> with RR 274

### [Cell-O-HPTA]<sup>+</sup>Cl<sup>-</sup> dyeing

[Cell-O-HPTA]<sup>+</sup>Cl<sup>-</sup> in eco-friendly dyeing conditions with reactive dyes firstly form strong ionic

bonds with positive quaternary ammonium group and next covalent bonds with the dissociated hydroxyl group being in adjacent β-position. The occurring possible reactions were showed in Figs. 4, 5, 6 and 7.

where R—different chemical substituents in the chemical structure of RR 24:1, RB 160, RR 221 and RR 274, X- halogen, nicotinic acid.

where R—different chemical substituents in the chemical structure of RR 24:1, RB 160, RR 221 and RR 274, X- halogen, nicotinic acid.

### Cell-OH dyeing

In the case of Cell-OH dyed at the same eco-friendly conditions. the amount of introduced dye to the fibre correspond to its substantivity and the durability to the formation of physicochemical bonds such as Van der Waals forces, hydrogen bridges, etc.

### Conventional dyeing of Cell-OH

Reactive dyes in the conventional dyeing process were bonded covalently on substitution or addition mechanism with hydroxyl groups belonging to the cellulose polymer in an alkaline medium. Only RR 221 (dinicotinic-triazine form reactive dye) was applied on cotton from the buffered bath at neutral pH with 1 g/L recommended buffer prepared from  $\text{Na}_2\text{HPO}_4$  and  $\text{KH}_2\text{PO}_4$ . The obtained DMF resistance values (Table 5) are generally in line expected for dyeing's after the final washing treatment. Some differences may be the result of the apparatus used and the application conditions.

### Estimation of the type of bond between dye and cellulose

Covalent bonds of cellulose with reactive dyes show the expected high resistance to DMF solvent (Venkataraman 1972). Non-covalently bound particles of reactive dyes with cellulose fibres (including hydrolysed forms of dyes) are easily removed by extraction with this solvent. The higher the resistance to DMF extraction, the smaller the K/S change in color.

### Resistance of dyed cellulose to DMF extraction

The  $R_{\text{DMF}}$  [%] parameter as resistance to DMF extraction was used to estimate the type/kind of reactive dye binding with dyed cellulose. Summary values of  $R_{\text{DMF}}$  [%] for noncationised and cationised

cotton samples dyed in different conditions presented Table 5.

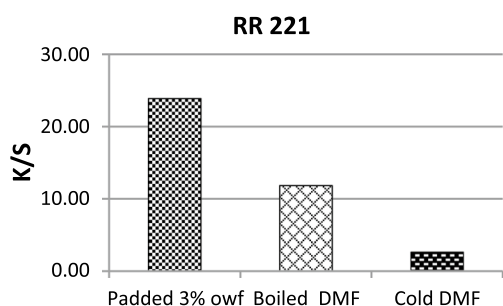
### *Cell-OH and [Cell-O–Ch]<sup>+</sup>Cl<sup>-</sup> dyeings*

It can be seen from Table 5 that Cell-OH and [Cell-O–Ch]<sup>+</sup>Cl<sup>-</sup> do not form the covalent bond with the dye in the dyeing process in environmentally friendly conditions. After DMF extraction only below 10% (RR 24:1, RB 19 and RR 274) and below 35% (RB 160 and RR 221) of the dyes remained on noncationised cotton samples. The resistances to DMF extraction of the dyeing's on cationised with [ClCh]<sup>+</sup>Cl<sup>-</sup> cellulose ranged from 11.48 to 50% and were slightly higher than on noncationised cellulose. These differences are due to the different chemical structures of the reactive dyes used and their substantivity to cellulose. Under ecological dyeing conditions, the hydroxyl groups in the glucopyranose chain do not dissociate to the extent that would allow the formation of an active nucleophile for a chemical reaction with reactive dye. The greater amount of RR 221 remaining on the cationised and noncationised cellulose after DMF extraction compared to other dyes was related probably with the chemical bonding of the absorbed dye to the cellulose hydroxyl groups during extraction. This assumption was confirmed in a special experiment. Noncationised cotton sample was padded in the bath contained 30 g/l RR 221 at 50 °C (this temperature was used for better solubility of the dye) then squeezed to ca. 100%, dried at room temperature and divided into three parts. One part was extracted in the boiling and the second in cold DMF, respectively, until the next portions of DMF were colorless. Then the samples were rinsed with cold tap water and dried at room temperature.

The measured K/S (Fig. 8) for all three parts confirmed the speculative explanation that the RR 221 dye (Kayacelon type dye), under boiling extraction conditions can form a chemical bond with the cellulose hydroxyl group.

### *[Cell-O–HPTA]<sup>+</sup>Cl<sup>-</sup> dyeings*

The bonding degree of reactive dyes applied in the eco-friendly conditions on [Cell-O–HPTA]<sup>+</sup>Cl<sup>-</sup> was similar to the bonding degree of the dyes with cellulose in the conventional method. This was confirmed by similar values of resistance to DMF extraction



**Fig. 8** K/S values for cotton samples dyed with RR 221 non-extracted and extracted (with boiled and cold DMF)

(Table 5). It confirmed that the reactive dyes are covalently bonded with the modified cellulose. The difference is only in the place of bonding. The hydroxyl group in the modifier chain of cationised cellulose can probably easily dissociate in water at neutral pH, forms a typical nucleophile anion ready for the substitution or addition reaction with a reactive part of the dye molecule. To confirm that the dissociated form of the hydroxyl group in the modifier chain is necessary for the chemical reaction between the reactive dye and  $[\text{Cell-O-HPTA}]^+\text{Cl}^-$  in eco-friendly conditions the dyeing in aprotic solvents was done. When aprotic solvents (DMF, DMSO) were used as a dyeing bath instead of water with the same dyes, the dyeing/fixation process was not observed. There was no dissociation of the hydroxyl groups in the aliphatic chain of the cationised cellulose, hence the reactive dyes do not bond covalently. When such solvent bath was diluted with water to 1:1, the dyeing process started immediately, and an increase in the color shade was observed. After 30 min of dyeing the final effect was comparable with samples dyed only in water bath and also with similar fastness for extraction with boiling DMF.

Table 5 presented some unexpected  $R_{\text{DMF}}$  [%] values for the samples of  $[\text{Cell-O-HPTA}]^+\text{Cl}^-$  dyed with dyes RB 19 and RR 274. It is likely that in the case of RB 19 in eco-friendly conditions, a strong ionic bond could be formed between an ammonium group of cationic cellulose and both anionic groups of the dye ( $\beta$ -sulfatoethylsulfonyl group or/and sulfo group). As a result of the ionic bond formation through  $\beta$ -sulfatoethylsulfonyl group, in eco-friendly condition, the dye probably cannot covalently bond with hydroxyl group of cationic cellulose modifier.

Additionally, such a linkage is not resistant to DMF extraction.

In the case of the RR 274, the situation is more complicated. RR 274 is a heterobifunctional dye which in eco-friendly conditions may react in different ways even with cross-linking. Dyeing of cationised cotton in these conditions favours aggregation of a dye molecules mainly on its surface and the resulting that dyeing's are therefore somewhat cloudy. Dye aggregates on surface of cationic cellulose fibres can be broken during DMF extraction leads to an increase of color strength and increase of degree of bonding up to 100%. Those phenomena require further research.

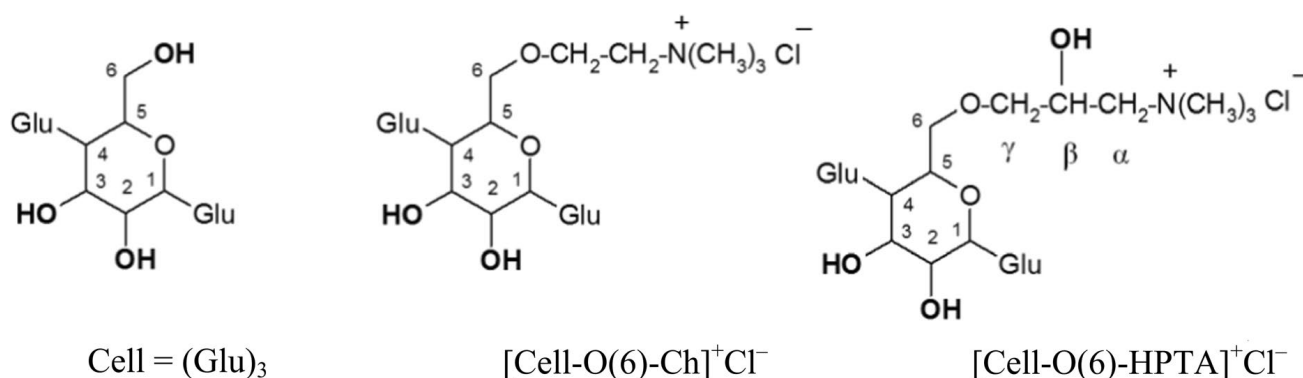
#### Hydrolysis of reactive bond reactive dye with cationised cellulose

The linkages formed between reactive dye molecules and those of the fibre should be stable under all or most of the conditions to which the dyeing is likely to be subjected during normal use (Beech 1970). Ether and pseudoester bonds formed between reactive dyes and cellulose are rather fast for acid and alkali hydrolysis. This fastness mainly depends on the chemical construction of the used dyes. Hydrolysis reactions of dye-fiber bonds on a cationised fabric have not been described so far. It was assumed that during such hydrolysis the dye-modifier bond would be broken without breaking the cellulose-(modifier+dye) bond. In such a case, it would be possible to re-dyeing the cationised cellulose under eco-friendly conditions with reactive dye in reaction with the restored hydroxyl group of the modifier.

The obtained results (Table 6) fully confirmed that dye molecules were bonded with a hydroxyl group belonging to the modification agent and that the hydrolysis reaction (bond cleavage) for ether/pseudoester bonds takes at the same place. It is clear that if the cleavage of the ether bond occurred between the modifying agent and the cellulose, the re-dye of the noncationised cotton under eco-friendly conditions would be impossible.

#### Density electron calculations

O(6), O(2) and O(3) are the reactive oxygen atoms in the cellulose molecule. The quantum-chemical PM3 MO method was used to calculate the electron



**Fig. 9** Chemical structure compound models for density electron analysis (ether bond formed with -OH group at C(6) carbon atom)

densities on these atoms, which will allow us to predict the direction of the cellulose etherification and modification reaction with the use of the quaternary ammonium salts of  $[\text{ClCh}]^+\text{Cl}^-$ ,  $[\text{CHPTA}]^+\text{Cl}^-$ , and also in the final the stage where the chemical bond with the reactive dye is formed. A fragment of the cellulose molecule  $\text{Cell}=(\text{Glu})_3$ , consisting of three glucopyranose molecules linked by glycoside bonds, was used as a model compound for the calculations.

The structures of the analysed molecules in the ground state was optimised with the use of molecular mechanics MM+(option with charge analysis) applying Hyperchem v.8.06 programme (Hypercube, Inc. Gainesville, Florida, US) and next with the semi-empirical method of quantum-chemical calculations PM3 (Stewart 1989), taking into account the length of all bonds, angles between them and torsion angles from following the eigenvector procedure (convergence criterion 0.02 kcal/mol).

The electron densities for all oxygen atoms were calculated, assuming that the etherification reaction could take place on each of the -OH groups of the glucopyranose ring.

The calculations showed that the most probable derivatives (Table 7) are ether bonds with the tested modifiers formed with the hydroxyl group on the C(6) carbon (Fig. 9). Such derivatives were accepted for further analysis.

As a result of the formation of these bonds, the electron densities on the remaining O(2) and O(3) oxygen atoms in the glucopyranose ring change, and these changes are so large that in some cases, their reactivity is even greater than in the unsubstituted  $\text{Cell}=(\text{Glu})_3$  molecule. The oxygen with the highest electron density as a nucleophile should react to form

a chemical bond in the  $\text{S}_{\text{N}}2$  reaction with a dye containing, e.g., cyanuric chloride as a reactive group. Then, in the case of  $[\text{Cell-O(6)-Ch}]^+\text{Cl}^-$  derivatives, the reaction should take place on the O(3) oxygen atom:

$$O(3)(-0.323) > O(2)(-0.300)$$

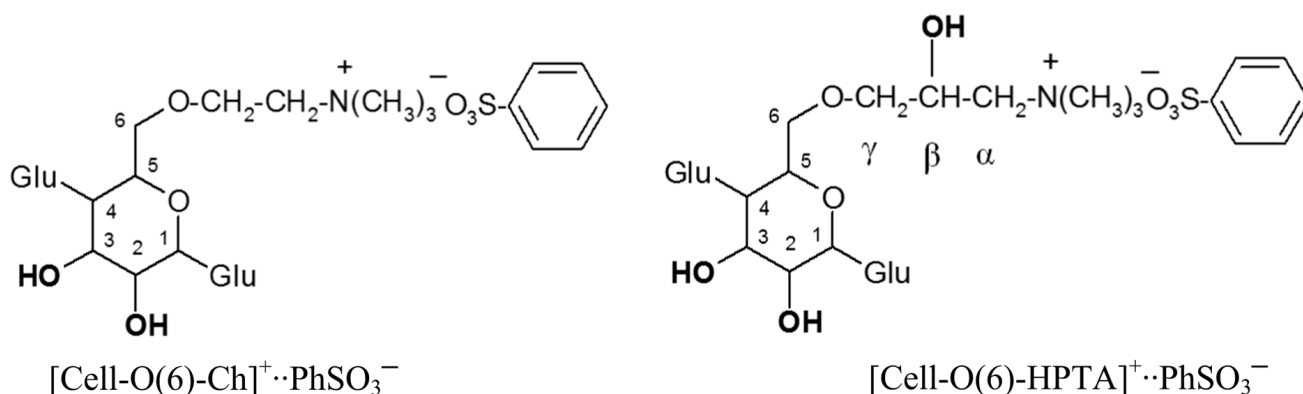
and for the  $[\text{Cell-O(6)-HPTA}]^+\text{Cl}^-$  derivatives on the oxygen atom O( $\beta$ ):

$$O(\beta)(-0.319) > O(3)(-0.315) > O(2)(-0.281).$$

However, it is known that oxygen atoms in hydroxyl groups in positions 2 and 3 in cellulose are very strongly involved in intermolecular hydrogen bonds (not included in quantum calculations), which significantly reduces their ability to perform chemical reactions, especially in neutral conditions. According to Nishiyama, Langan and Chanzy (2002) hydrogen bonds for cellulose I include two intramolecular bonding, namely, O(2)H $\cdots$ O(6) bonding and O(3)H $\cdots$ O(5) bonding and one intermolecular bonding, O(6)H $\cdots$ O(3).

A completely different situation was found in the hydroxyl group with the O( $\beta$ ) oxygen atom in the  $[\text{Cell-O(6)-HPTA}]^+\text{Cl}^-$  derivative, which does not participate in intramolecular hydrogen bonds and can easily undergo a dissociation reaction with the formation of a nucleophile and react with the reactive system of the dyes to form a strong covalent bond.

Additional calculations were performed using benzenesulfonic acid ( $\text{PhSO}_3\text{H}$ ) as an acid dye model containing a sulfo group capable of ion-pairing with a cellulose fragment, containing the introduced cationisation modifier. These derivatives (Fig. 10) showed further changes in the electron density at the oxygen



**Fig. 10** Chemical structure ionic pair cationised cellulose with benzenesulfonic acid for density electron analysis

atoms, but also marked changes on the quaternary group (Table 8).

The formation of an ionic bond between  $[\text{Cell-O(6)-Ch}]^+\text{Cl}^-$  and benzenesulfonic acid causes only changes in the value of the positive charge on the quaternary group without changes on the cellulose oxygen atoms in the glucopyranose ring.

(Table 8). In the case of a similar reaction of  $[\text{Cell-O(6)-HPTA}]^+\text{Cl}^-$  with benzenesulfonic acid, apart from a marked increase in the positive charge on the quaternary group, a significant change in the negative charge on the oxygen atoms is also observed. Lowering the electron density at the O( $\beta$ ) oxygen causes an increase in dissociation of that hydroxyl group.

The presented results of electron density calculations confirmed the results of experimental studies obtained in the process of dyeing  $[\text{Cell-O-HPTA}]^+\text{Cl}^-$  with reactive dyes in an aqueous bath, at ambient temperature without the addition of electrolytes and alkali. The dye is covalently bound to the hydroxyl group in the modifier. Cationic modification of cellulose with  $[\text{ClCh}]^+\text{Cl}^-$  allows it to be dyed with reactive dyes under the same conditions, only with the formation of ionic bonds as for acid dyes. As already mentioned in the experimental section, the extraction treatment with DMF allows distinguishing between these bonds.

## Conclusion

Existing reactive systems depend on two basic elements: an electron-deficient “reactive” carbon centre

in the dye and an electron-rich “nucleophile centre” in the fibre (Niu et al. 2020). Studying the processes of dyeing modified cellulose by cationisation with  $[\text{CHPTA}]^+\text{Cl}^-$ , it was found that in a water bath without the addition of electrolytes and alkali at room temperature, reactive dyes of various classes formed covalent bonds according to the substitution/addition mechanism with nucleophile hydroxyl group located in the modifier chain. These stable bonds of the reactive dyes were confirmed by extraction treatment in boiling DMF, acid/alkali hydrolysis of the formed ether/pseudoester linkage and effective re-dyeing under the same conditions as the basic process. The results of dyeing on noncationised and cationised cellulose with  $[\text{ClCh}]^+\text{Cl}^-$  (it does not contain hydroxyl groups in its structure) were compared. The analysis using particle optimisation with MM+molecular mechanics and quantum-chemical calculations by the method of all valence orbitals confirmed the experimental results of high activity of the nucleophile being formed on the hydroxyl group in the modifier chain.

**Funding** The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.

## Declarations

**Conflict of interest** The authors have no relevant financial or non-financial interests to disclose.

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## Article

# Mechanism of Bonding Reactive Dyes with Copolymer (chloromethyl)oxirane-1H-imidazole cationised Cellulose

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**Abstract:** Introducing the cellulose chain cationic groups in the modification process completely changes the charge on the cotton surface from negative to partially or totally positive. That allows the electrostatic attraction and simultaneous exhaustion and fixation of reactive dyes. This reaction can be carried out without salt and alkali at room temperature. Similarly, the reaction between reactive dye and an alone copolymer ([IME]<sup>+</sup>Cl<sup>-</sup>) with TLC chromatography was confirmed. The analysis with the use of particle optimisation with MM+ molecular mechanics and quantum-chemical calculations PM3 by the method of all valence orbitals confirmed the experimental results of the high activity of the nucleophile formed on the hydroxyl group in the chain of a modifier. It was found and experimentally confirmed that the reactive dyes during the dyeing process of the cotton cationised with copolymer (chloromethyl)oxirane-1H-imidazole ([IME]<sup>+</sup>Cl<sup>-</sup>) create covalent bonds due to a reaction with the hydroxyl group located in the modification agent instead of with the hydroxyl group in the glucopyranose ring. Although the dyeing takes place in very mild conditions, a high degree of setting is achieved, comparable to conventional methods.

**Keywords:** cationised cotton; reactive dyes; mechanism bonding; Texamin ECE New; molecular mechanics MM+; quantum-chemical calculations PM3



**Citation:** Prus, S.; Kulpiński, P.; Matyjas-Zgondek, E.; Wojciechowski, K. Mechanism of Bonding Reactive Dyes with Copolymer (chloromethyl)oxirane-1H-imidazole cationised Cellulose. *Materials* **2022**, *15*, 4664. <https://doi.org/10.3390/ma15134664>

Academic Editor: Fatimah Ali M. Al-Zahrani

Received: 21 May 2022

Accepted: 29 June 2022

Published: 2 July 2022

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## 1. Introduction

Modification of cellulose fibres by cationisation is one of the most frequently described methods that reduces the enormous amount of electrolytes and alkali emitted to the environment in the dyeing process with reactive dyes. In addition, 3-chloro-2-hydroxypropyltrimethylammonium chloride ([CHPTA]<sup>+</sup>Cl<sup>-</sup>) is the most commonly used cationic modifier due to its low cost and easy chemical reaction with cellulose. Its downside is a lack of substantivity in relation to fibres, which makes it impossible to use it in exhaustion methods. Currently, however, beyond this limitation, there are also other problems. The first is the unpleasant fishy smell that sometimes remains in the material after cationisation as a result of the cleavage of trimethylamine under strongly alkaline conditions [1]. The second is related to security categories. Currently, [CHPTA]<sup>+</sup>Cl<sup>-</sup> is classified by the EURL (European Union Risk Assessment) as a carcinogen category No. 3 [2]. Other problems concern levelness, penetration and ring dyeing [3]. Perhaps for these reasons, many scientists have turned their attention to cationic cellulose modifiers with a linear or branched polymer structure with medium substantivity to cellulose. Various types of polymers—polyepichlorohydrin dimethylamine, polyepichlorohydrin resin, polyamide epichlorohydrin type polymers, poly(4-vinylpyridine)quaternary ammonium compounds, poly(vinylamine chloride), dendritic polymers, cationic diblock copolymers, chitosan and its derivatives—were presented in reviews [4–8]. In addition, cationic Poly(St-BA-VBT)



nanospheres [6], starch and starch derivatives [9] were described in the literature. All of the above-mentioned cationic compounds may be used for cellulose cationisation.

There is still much expectation from the dyeing industry for cationised cellulose that allows obtaining dyeings with good durability in the most ecological conditions. A list of cationic cotton suppliers containing manufacturers from seven countries, mostly from the USA and China, has been published [10]. They offer cationised fibres, yarn, and knitted and woven materials. However, there is no information about cationic modifiers used for this production. One of the modifiers that could potentially solve or strongly reduce most of these problems is copolymer (chloromethyl)oxirane and 1H-imidazole ([IME]<sup>+</sup>Cl<sup>-</sup>) with the commercial name Texamin ECE New, introduced to the market by Inotex spol. s.r.o. (Dvůr Králové nad Labem, Czech Republic) [11]. It reacts with cellulose hydroxyl groups at the same chemistry as [CHPTA]<sup>+</sup>Cl<sup>-</sup>.

[IME]<sup>+</sup>Cl<sup>-</sup> is a polyheterocyclic cationic liquid copolymer compound. The producer recommends it as a cationising agent to improve cellulose fibres' dyeability with reactive dyes, resulting in an increasing dyestuff substantivity and lowering in environmental impact [12,13]. It is suitable for processes with reduced salt concentrations, enables one-bath applications for special dyeing effects, and, moreover, is suitable for bath and impregnation processing. [IME]<sup>+</sup>Cl<sup>-</sup> cationised cotton is also recommended for dyeing with natural dyes [14], forming composites [15], for membrane filtration processes [16] and for preparing innovative UV barrier materials [17]. [IME]<sup>+</sup>Cl<sup>-</sup> has a GreenScreen Certified™ silver certificate, which prohibits the use of any chemical of high concern listed on globally recognised chemical hazard lists as defined by the GreenScreen List Translator Actio [18]. [IME]<sup>+</sup>Cl<sup>-</sup> is exported by Inotex spol. s.r.o. to India, Netherlands, etc. [19,20].

Due to the fact that [IME]<sup>+</sup>Cl<sup>-</sup> has significant market potential, we decided to conduct some research on this product. This work aimed to establish the chemical structure of [IME]<sup>+</sup>Cl<sup>-</sup> (Texamin ECE New) as well as the reaction mechanism of bonding the reactive dyes with [IME]<sup>+</sup>Cl<sup>-</sup> cationised cotton. The most environmentally friendly conditions for the dyeing of cationised cellulose, i.e., room temperature and a bath without electrolytes and alkalis, were used. It was assumed that the reaction mechanism of dyeing in those conditions would be similar to that previously discovered when dyeing cationised cellulose with CHPTAC [21]. Five reactive dyes with different reactive groups were selected for the experimental studies. In order to confirm the formation of the covalent bond due to the reaction of the reactive dye with the hydroxyl group of the modifier, methods of extraction with dimethylformamide (DMF) and electron-density analysis were used. The thin layer chromatography method was also applied to analyse the formation of a chemical linkage between the reactive dye and the hydroxyl group belonging to the modifier.

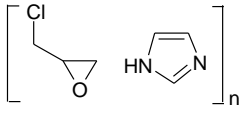
## 2. Materials and Methods

### 2.1. Materials

After alkali scouring and bleaching pre-treatment, the plain cotton fabric with a surface weight of 180 g/m<sup>2</sup> was used. Cationising agent [IME]<sup>+</sup>Cl<sup>-</sup> (Texamin ECE New) was purchased from Inotex Czech Republic. Reactive dyes: RR 24:1 from Boruta-Zachem Poland, RB 160 from Kalpactive India, RR 221 from Kisco South Korea, RR 274 from Swisscolor Poland and RB 19 from Biliński Factory Poland were purchased, respectively. Acid dye AB 62 was purchased from Yorkshire Group, Germany. All dyes were applied without further purification. Polyelectrolyte standard solutions: PES-Na (MW 21.800 g/mol) and poly-DADMAC (MW 107.000 g/mol), were purchased from BTG Instruments AB Sweden. Tanaterge Advance (non-ionic detergent) was purchased from Tanachem, Poland. Other chemicals and solvents were used at laboratory grade purity. Ugolini Redkrome-model RED P (Schio VI, Vicenza, Italy) laboratory dyeing machine, heated by infrared ray radiators and equipped with 150/400/5000 mL cups, was used for cationising and dyeing cotton fabric samples. Muetek PCD 03 pH Particle Charge Detector (Muetek GmbH, München, Germany) was used to measure potential and determine the value of the specific surface on the surface of cotton samples. Datacolor 850 spectrofotometer (Datacolor, Lawrenceville,

NJ, USA) was used for instrumental colour measurements. Chemical structures and data of modification agents and dyes are shown in Tables 1 and 2.

**Table 1.** Information data of the modification agent.

	Modification Agent	Chemical Formula
[IME] <sup>+</sup> Cl <sup>-</sup>	1H-imidazole, copolymer with (chloromethyl)oxirane (Texamin ECE New) CAS: 68797-57-9 Molecular weight of 1 mer of copolymer macromolecule [IME] <sup>+</sup> Cl <sup>-</sup> : 160.6	 adduct

**Table 2.** Information data of the dyes selected for experiments.

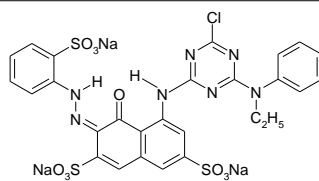
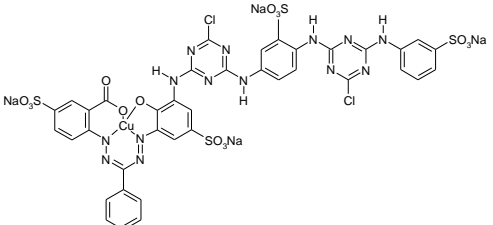
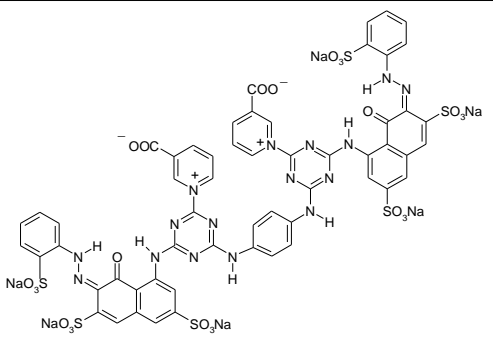
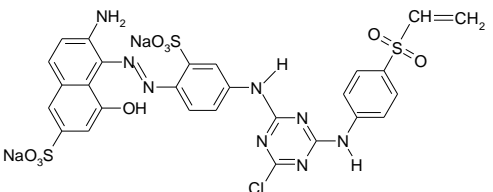
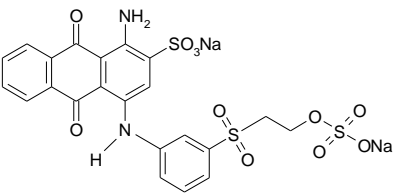
	Dyestuff	Chemical Data	Chemical Formula
RR 24:1	Helaktyl Red D-BN Reactive Red 24:1 C.I. 18208:1 CAS: 72829-25-5	MCT Molecular Formula C <sub>27</sub> H <sub>19</sub> ClN <sub>7</sub> O <sub>10</sub> S <sub>3</sub> .Na <sub>3</sub> Molecular weight: 802.10	
RB 160	Kalpactive Blue HE-BR Reactive Blue 160 C.I. - CAS: 71872-76-9	bis-MCT formazan class dyes Molecular Formula C <sub>38</sub> H <sub>23</sub> Cl <sub>2</sub> N <sub>14</sub> O <sub>18</sub> S <sub>5</sub> Cu.Na <sub>5</sub> Molecular Weight: 1309.9	
RR 221	Papizolon Red HT-3BN Reactive Red 221 C.I. - CAS: 96726-27-1	bis-monochromophore dyes Molecular Formula C <sub>57</sub> H <sub>35</sub> N <sub>16</sub> O <sub>24</sub> S <sub>6</sub> .Na <sub>6</sub> Molecular Weight: 1699.34	
RR 274	Eriofast Red 2B (1) Reactive Red 274 C.I. - CAS: -	MCT-VS (heterobifunctional) Molecular Formula C <sub>27</sub> H <sub>20</sub> N <sub>8</sub> O <sub>9</sub> S <sub>3</sub> Cl.Na <sub>2</sub> Molecular Weight: 777.5	
RB 19	Remazol Brilliant Blue R Reactive Blue 19 C.I. 61200 CAS: 2580-78-1	VS (vinylsulphone) Molecular Formula C <sub>22</sub> H <sub>16</sub> N <sub>2</sub> O <sub>11</sub> S <sub>3</sub> .Na <sub>2</sub> Molecular Weight 626.5	

Table 2. Cont.

Dyestuff	Chemical Data	Chemical Formula
AB 62 Acid Blue 62 C.I. 62045 CAS: 4368-56-3	Molecular Formula C <sub>20</sub> H <sub>20</sub> N <sub>2</sub> O <sub>5</sub> S.Na Molecular Weight 422.43	

<sup>(1)</sup> Chemical formula known from [22].

## 2.2. Characteristics of [IME]<sup>+</sup>Cl<sup>-</sup>

According to the safety data sheet [11], [IME]<sup>+</sup>Cl<sup>-</sup> is an adduct of 1H-imidazole and (chloromethyl)-oxirane. The copolymerisation of these products should lead to the copolymer having the following general chemical structure (Figure 1):

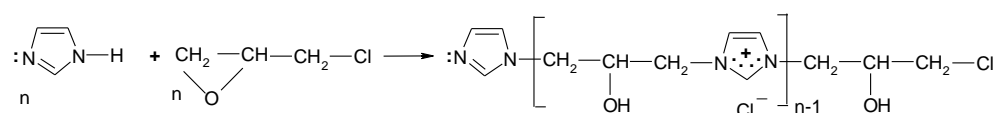


Figure 1. Proposed reaction of the synthesis [IME]<sup>+</sup>Cl<sup>-</sup>.

Commercial-grade quality [IME]<sup>+</sup>Cl<sup>-</sup> used for the cationisation of cellulose was analysed for its nitrogen content, cationicity and reactivity values, copolymerisation degree and macromolecular weight.

## 2.3. Cationisation of Cellulose with [IME]<sup>+</sup>Cl<sup>-</sup>

The cationisation of cellulose was carried out in accordance with the reaction scheme shown below (Figure 2):

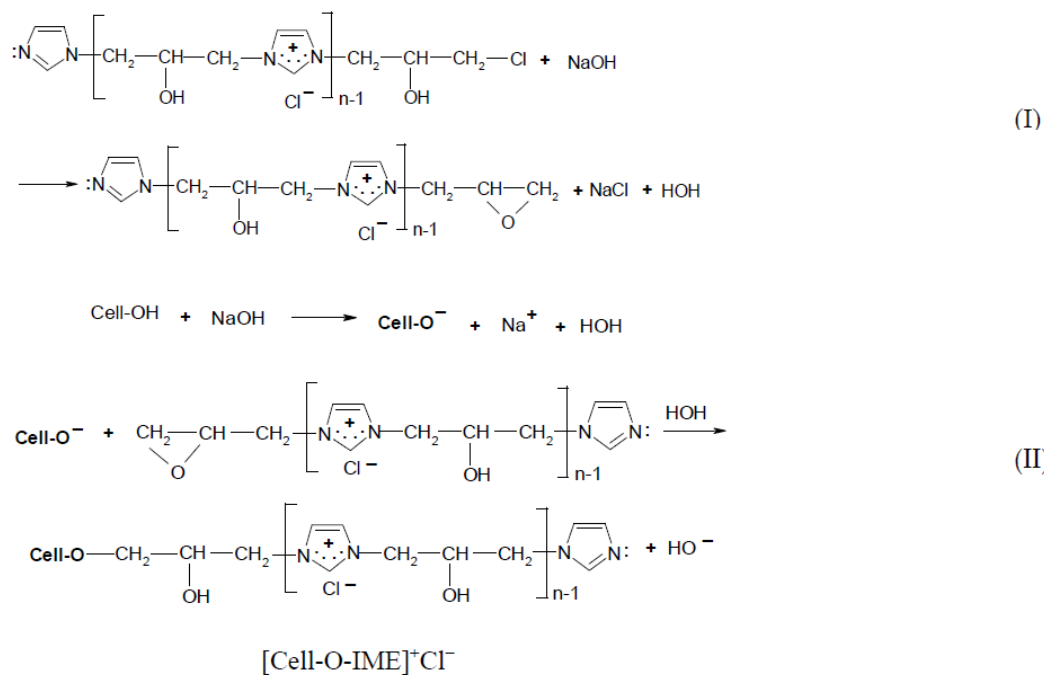


Figure 2. Two-step reaction of cellulose cationisation with [IME]<sup>+</sup>Cl<sup>-</sup> (I) step = epoxy-form of [IME]<sup>+</sup>Cl<sup>-</sup> and celulosan anion formation. (II) step = covalent bond formed of [IME]<sup>+</sup>Cl<sup>-</sup> with cellulose.

A total of 270 g of cotton material was introduced to Ugolini apparatus with 2650 mL bath containing 4% owf [IME]<sup>+</sup>Cl<sup>-</sup> and 1 g/L Tanaterge Advance and rotated right/left 40 for 15 min at room temperature. Next, 1.2% owf of NaOH dissolved in 50 mL distilled water was added to the apparatus and temperature was increased from 3 °C/min to 50 °C and heating was continued by 60 min. After that, the bath was dropped, and the cationised cotton was rinsed in warm and cold tap water to obtain pH neutrality. Next, the material was acidified with acetic acid 1 g/L to pH 6–7 and finally rinsed again with cold water to neutral pH, then dried at room temperature. The cationisation process is shown in Figure 3.

**Cationisation**

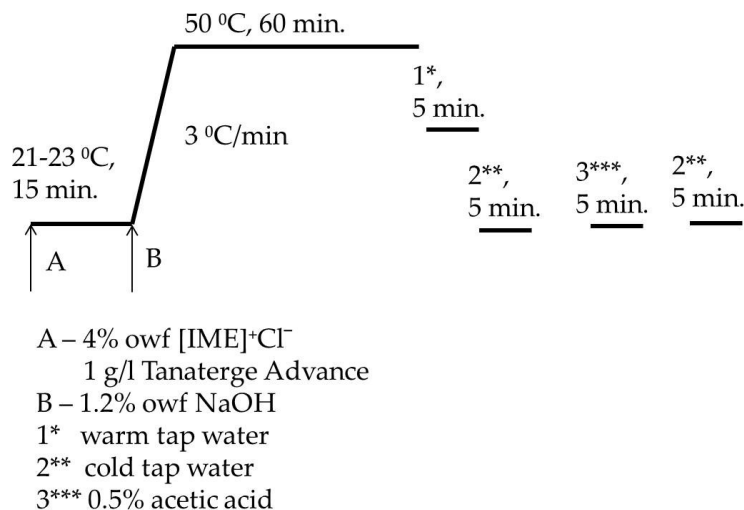


Figure 3. Diagram of cationisation process of cellulose with [IME]<sup>+</sup>Cl<sup>-</sup>.

2.4. Eco-Friendly Dyeing of [Cell-O-IME]<sup>+</sup>Cl<sup>-</sup>

[Cell-O-IME]<sup>+</sup>Cl<sup>-</sup> samples were dyed at the following conditions: LR 1:20, temp. 22 ± 1 °C, distilled water and pH neutral with 1% owf (RR 221 or RB 160) and 0.9% owf (RR 24:1, RR 274, or RB 19), respectively, time 30 min, rinsed with cold distilled water to remove not fixed dye and dried at room temperature. For comparing the same conditions, non-cationised cotton samples were dyed and rinsed after dyeing. The temperature course of the dyeing processes is shown in Figure 4.

**Eco-friendly dyeing**

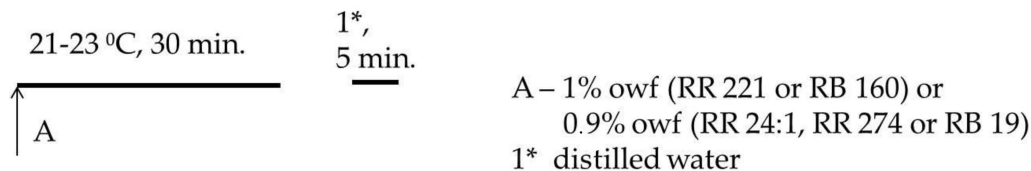


Figure 4. Diagram of dyeing process of cellulose cationised with [IME]<sup>+</sup>Cl<sup>-</sup>.

2.5. Characterisation Methods

2.5.1. Nitrogen Content

The values of N (eq/g) for the commercial [IME]<sup>+</sup>Cl<sup>-</sup> and the cotton samples before and after modification were determined by the classical Kjeldahl method described in detail elsewhere [23,24] and calculated according to Equation (1):

$$N = \frac{vc}{14m} \tag{1}$$

where:

$v$ —mL of hydrochloric acid used for titration;  
 $c$ —concentration of hydrochloric acid 0.1 M [mol/L];  
 $m$ —weight of the sample for analysis [g];  
 14—atomic mass for Nitrogen.

### 2.5.2. Specific Charge Measurement

The charge on the surface of cellulose fibres was measured according to the previously developed recipes [23,24]. The value of the specific charge was calculated according to Equation (2):

$$Q_{surf}^+ = \frac{(v_0 - v_1)cv_c}{mv_a} \tag{2}$$

where:

$v_0$ —mL of polyelectrolyte PES-Na for titration of 10 mL polyelectrolyte poly-DADMAC (blind test);  
 $v_1$ —mL of polyelectrolyte PES-Na for titration of 10 mL of filtrate after treatment;  
 $c$ —polyelectrolyte concentration of poly-DADMAC;  
 $v_c$ —mL of polyelectrolyte poly-DADMAC used for treatment;  
 $v_a$ —mL of filtrate used for titration;  
 $m$ —test sample weight [g].

### 2.5.3. Cationicity

To determine the  $[IME]^+Cl^-$  cationicity, 1 g of commercial product was dissolved with  $25 \times 10^3$  mL of distilled water. An amount equal to 10 mL of the  $[IME]^+Cl^-$  solution was placed in a measuring cell of the Muetek PCD 03 pH apparatus, and the piston vibration motion was activated. After stabilising the potential, the solution was titrated with 0.0001 N PES-Na anionic polyelectrolyte to a stable 0 mV potential. The cationicity value was calculated according to Equation (3):

$$Q_{[IME]^+Cl^-}^+ = \frac{v_1c \ 25 \times 10^3}{mv_a} \tag{3}$$

where:

$v_1$ —mL of polyelectrolyte PES-Na for titration of 10 mL of  $[IME]^+Cl^-$  solution;  
 $C$ —concentration of poly-DADMAC polyelectrolyte (eq/L);  
 $v_a$ —mL of the  $[IME]^+Cl^-$  solution used for titration;  
 $m$ —test sample weight [g].

### 2.5.4. Reactivity

Reactivity of  $[IME]^+Cl^-$  ( $R_{[IME]^+Cl^-}$ ) corresponds to the value of copolymer macromolecules that can react with the hydroxyl group of cellulose in the cationisation process. The amount of NaOH consumed corresponds to the amount of hydrogen chloride released in the epoxide formation according to the reaction (Figure 5):

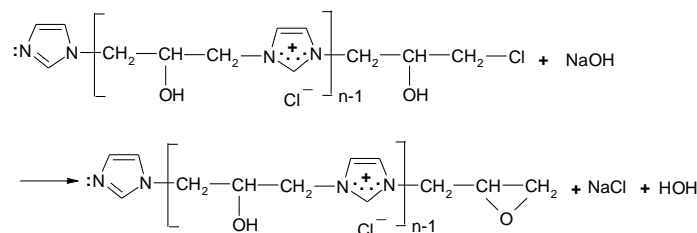


Figure 5. Scheme for creating a reactive form of  $[IME]^+Cl^-$ .

A total of 1 g of  $[IME]^+Cl^-$  commercial product and 40 mL 0.1 N NaOH were heated and stirred in a conical flask with a magnetic stirrer to 60 °C and, after 30 min, cooled to

room temperature, then moved to the 50 mL volumetric flask. Then, 10 mL of analysed solution was placed in the 250 mL conical flask, 50 mL of distilled water was added, and next titrated with 0.1 N HCl at phenolphthalein indicator.  $R_{[IME]^+Cl^-}$  was calculated using the following Equation (4):

$$R_{[IME]^+Cl^-} = \frac{(v_0 - v_1)0.1}{m_{[IME]^+Cl^-}} \quad (4)$$

where:

$v_0$ —mL of hydrochloric acid used for titration blind sample of 0.1 N NaOH;

$v_1$ —mL of hydrochloric acid used for titration analysed sample;

$m_{[IME]^+Cl^-}$ —test sample weight [g].

#### 2.5.5. Copolymerisation Degree and Macromolecular Weight of $[IME]^+Cl^-$

Copolymerisation degree and macromolecular weight of  $[IME]^+Cl^-$  were calculated according to Equations (5) and (6):

$$DP_{[IME]^+Cl^-} = \frac{0.5 N}{R_{[IME]^+Cl^-}} \quad (5)$$

$$M_{w[IME]^+Cl^-} = DP_{[IME]^+Cl^-} \times 160.6 \quad (6)$$

where:

$R_{[IME]^+Cl^-}$ —reactivity of  $[IME]^+Cl^-$ ;

$DP_{[IME]^+Cl^-}$ —copolymerisation degree of  $[IME]^+Cl^-$ ;

0.5 N—number of imidazole molecules in 1 g  $[IME]^+Cl^-$ ;

$M_{w[IME]^+Cl^-}$ —weight of 1 macromolecule  $[IME]^+Cl^-$ ;

160.6—molecular weight of 1 mer of copolymer macromolecule  $[IME]^+Cl^-$ .

#### 2.6. Characterisation of Reaction between Reactive Dye and Modification Agent

Very strong nucleophilicity and reactivity of hydroxyl groups in  $[IME]^+Cl^-$  copolymer chain was checked by direct reaction of modification agent with reactive dyes in water at room temperature. In these experiments, the 1% of water solution of  $[IME]^+Cl^-$  at room temperature was dropped to the 1% of water solution of reactive dyes. The same test was performed for acid dye AB 62. Precipitated solids were analysed with the TLC method. Pre-coated plastic sheets of Polygram® Sil/G/UV<sub>254</sub> (Macherey-Nagel + CO, Düren, Germany) were used for chromatography of reactive dyes. As eluent mixture n-propanol:ethylacetate:water = 6:1:3, respectively, was used.

#### 2.7. Resistancy for DMF Extraction of Dyed Cationised Cellulose

The resistance to DMF extraction was performed according to the procedure described elsewhere [21]. The colour strength of dyed non-cationised and cationised cotton samples before and after treatment with DMF were determined based on the evaluation of colourimetric measurements using a Datascolor 850 spectrophotometer. The values of resistance of the reactive dyes on dyed cotton samples for DMF extraction were calculated using the following Equation (7):

$$R_{DMF} = \frac{\left(\frac{K}{S}\right)_1}{\left(\frac{K}{S}\right)_0} 100 \quad (7)$$

where:

$\left(\frac{K}{S}\right)_0$ —value measured after dyeing; and  $\left(\frac{K}{S}\right)_1$ —value measured after extraction with DMF.

### 2.8. FT-IR Analysis

The chemical structure of  $[\text{IME}]^+\text{Cl}^-$  and cellulose before and after cationisation was analysed by FT-IR spectroscopy in the range  $500\text{--}4000\text{ cm}^{-1}$  in the Infrared Spectrometer NICOLET 380 (Thermo Fisher Scientific, Waltham, MA, USA). The sample of  $[\text{IME}]^+\text{Cl}^-$  for analysis was prepared by long-term drying at  $30\text{--}40\text{ }^\circ\text{C}$  under a vacuum to remove water. Before analysis, the samples of  $[\text{IME}]^+\text{Cl}^-$ , non-cationised and cationised cotton were powdered and mixed with KBr and next pressed into tablet form.

### 2.9. Density Electron Calculations

The structures of the analysed molecules in the ground state were optimised with the use of molecular mechanics MM+ (option with charge analysis) applying Hyperchem v.8.06 programme (Hypercube, Inc., Gainesville, FL, USA) and next analysed with the semi-empirical method of quantum-chemical calculations PM3 [25], taking into account the length of all bonds, angles between them and torsion angles from following the eigenvector procedure (convergence criterion  $0.02\text{ kcal/mol}$ ).

## 3. Results and Discussion

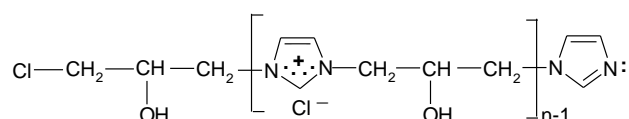
### 3.1. Characterisation of Copolymer $[\text{IME}]^+\text{Cl}^-$

The analysis of nitrogen content, cationicity and reactivity of  $[\text{IME}]^+\text{Cl}^-$  presented in Table 3 allows defining and confirming the most likely chemical structure, the average copolymerisation degree and its macromolecular weight.

**Table 3.** Summary of data for  $[\text{IME}]^+\text{Cl}^-$  copolymer.

Nitrogen Content	$Q_{[\text{IME}]^+\text{Cl}^-}^+$	$R_{[\text{IME}]^+\text{Cl}^-}$
$5.16 \times 10^{-3}$	$2.1 \times 10^{-3}$	$0.515 \times 10^{-3}$

The average copolymerisation degree and the macromolecule weight of the  $[\text{IME}]^+\text{Cl}^-$  copolymer were calculated according to Equations (5) and (6), and they were 5.01 and 804.6 g, respectively. Based on the obtained data, the structural formula of  $[\text{IME}]^+\text{Cl}^-$  can be drawn as shown in Figure 6:



**Figure 6.** Proposed chemical structure of  $[\text{IME}]^+\text{Cl}^-$  (where:  $n = 5$ ).

The FT-IR spectrum of  $[\text{IME}]^+\text{Cl}^-$  (Figure 7) showed a characteristic peak at  $3450\text{ cm}^{-1}$  for the  $\text{--OH}$  stretching vibration group. The peak at  $1631\text{ cm}^{-1}$  corresponds to the vibration bond present in the imidazole ring for  $\text{C}=\text{C}$ . The peaks at  $1558\text{ cm}^{-1}$  and  $754\text{ cm}^{-1}$  were assigned to the stretching vibration of the  $\text{C}=\text{N}$  group and the deformation vibration of the imidazole ring, respectively. The band at  $630\text{ cm}^{-1}$  was typical of the  $\text{C--Cl}$  stretching vibration in the  $\text{CH}_2\text{--Cl}$  group, and the peak at  $1265\text{ cm}^{-1}$  was also indicated by this group. The above analysis confirmed the proposed chemical structure of  $[\text{IME}]^+\text{Cl}^-$ .

$[\text{IME}]^+\text{Cl}^-$ , being a small length chain cationic copolymer, has medium substantivity to cellulose. The cationic charge in this compound is dislocated in each mer on the whole molecule of Imidazole and has a strong influence on the adjacent hydroxyl group for its acidity and dissociation rate.

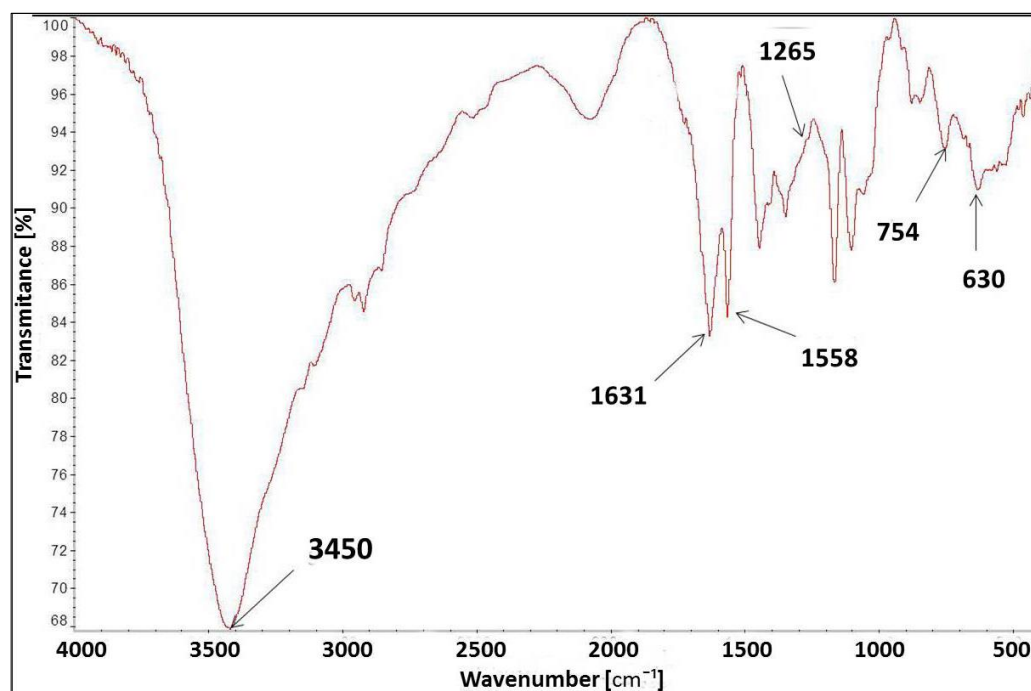


Figure 7. FT-IR spectrum for  $[\text{IME}]^+\text{Cl}^-$ .

### 3.2. Characterisation of $[\text{Cell-O-IME}]^+\text{Cl}^-$

Cationisation efficiency can be calculated using data from Tables 3 and 4. Cationisation of cellulose was performed with  $[\text{IME}]^+\text{Cl}^-$  4% owf, which corresponds to a value of  $206.4 \times 10^{-6}$  eq of nitrogen. After cationisation,  $101 \times 10^{-6}$  eq of nitrogen was found on the fibres, which corresponds to an approx. 50% yield.

Table 4. Calculated values of nitrogen content and specific surface charge for uncationised and cationised cotton samples.

Cotton Sample	Nitrogen		$Q_{surf}^+$	
	Calculated	$\Delta N$	Calculated	$\Delta Q_{surf}^+$
	[ $10^{-6}$ eq/g]		[ $10^{-6}$ eq/g]	
Cell-OH	25	-	+0.44	-
$[\text{Cell-O-IME}]^+\text{Cl}^-$	126	101	+14.2	+13.76

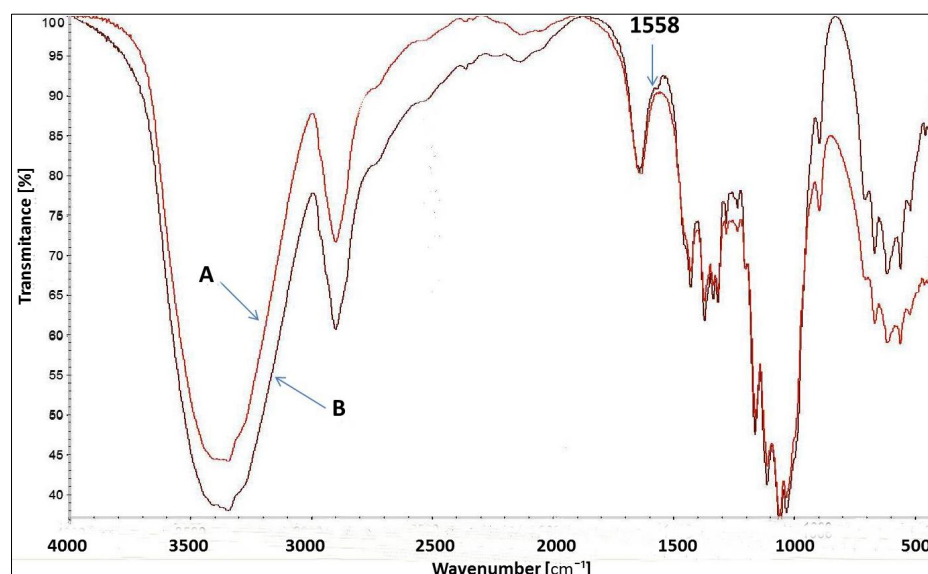
where:

$\Delta N$ —difference in nitrogen content between cationised and uncationised samples,

$\Delta Q_{surf}^+$ —difference in specific surface charge between cationised and uncationised samples.

Figure 8 presents the FT-IR spectrum for uncationised and cationised cellulose with  $[\text{IME}]^+\text{Cl}^-$ . Both spectra are very similar to each other. However, a slight change in the spectrum of cationised cellulose with wave number  $1558 \text{ cm}^{-1}$  corresponds to vibration stretching of the C=N bond present in the Imidazole ring belonging to the cationising agent. Such a small difference is due to the low content of the modifier in relation to the weight of cellulose fibres. In the cationisation process, a 4% owf modifier was used. Due to ca. 50% of its fixation, this value dropped to approx. 2%. Such amounts are difficult to identify in the FT-IR spectrum. However, measurements of the amount of nitrogen and the positive charges after cationisation confirmed this modification more clearly.





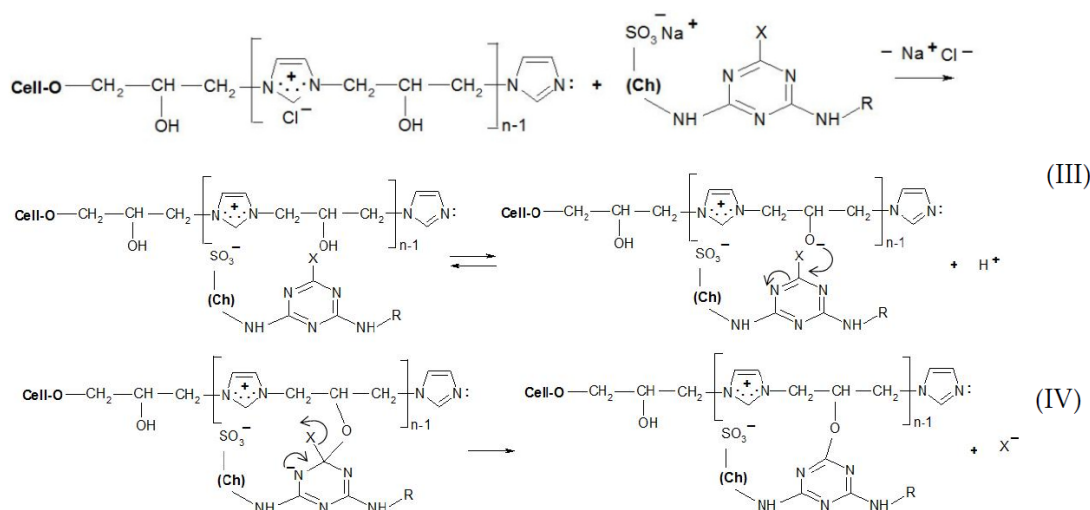
**Figure 8.** FT-IR spectrum of Cell-OH (A) and  $[\text{Cell-O-IME}]^+\text{Cl}^-$  (B) ( $1558\text{ cm}^{-1}$ —specific wavenumber. for  $\text{C} = \text{N}$  bond in imidazole ring).

### 3.3. Characterisation of $[\text{Cell-O-IME}]^+\text{Cl}^-$ Dyeing

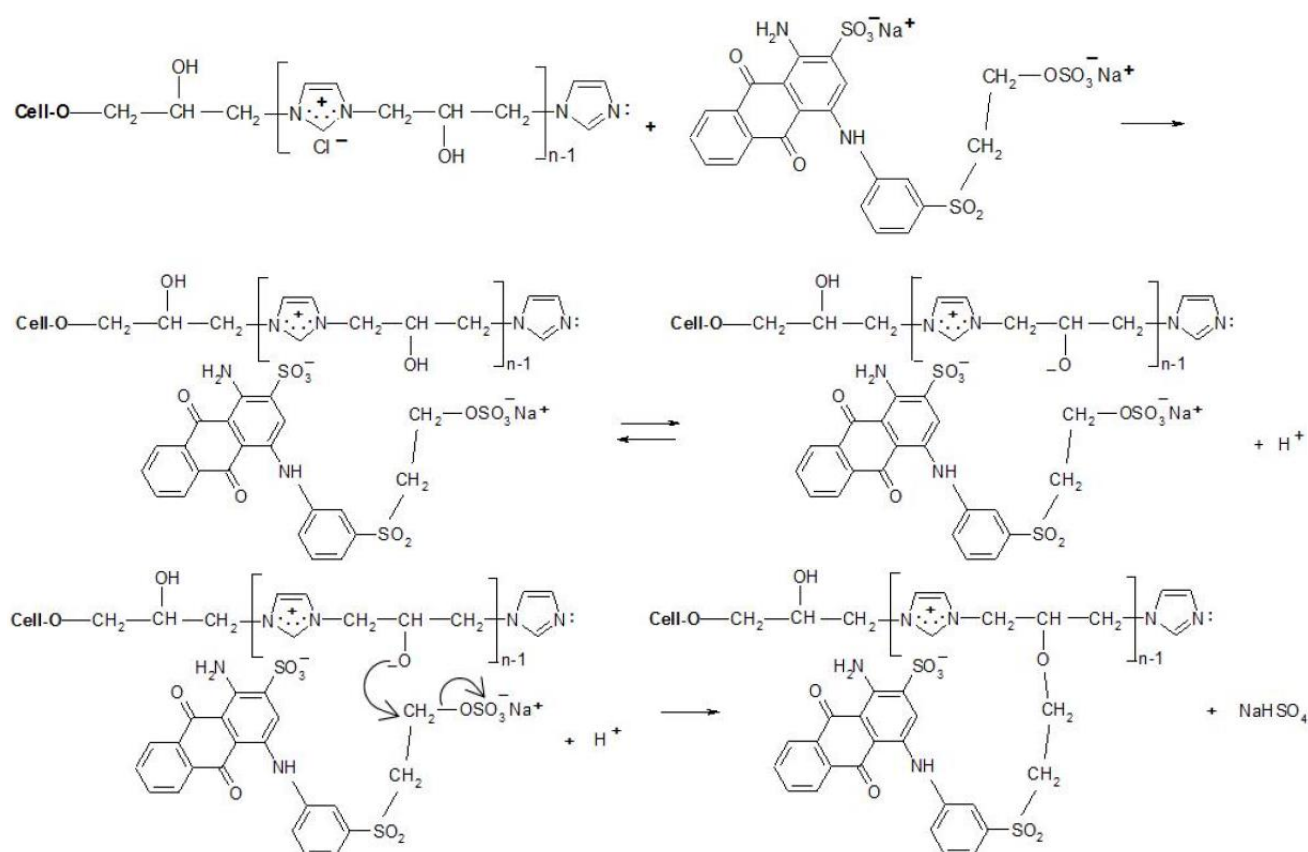
Thanks to the attractive positive charges on the fibre, the reactive dyes were absorbed quickly from the bath—formed ionic bonds (Figures 9 and 10), having two possible ways of the reaction with  $[\text{Cell-O-IME}]^+\text{Cl}^-$ :

- (1) Create a covalent bond with one of the hydroxyl groups in the chain of the copolymer by nucleophilic substitution or addition;
- (2) React (only for chlorotriazine reactive dyes) with a lone pair on the nitrogen atom of  $[\text{Cell-O-IME}]^+\text{Cl}^-$  to form the quaternary compounds [26]. Such compounds are very reactive and react quickly with the dissociated hydroxyl group in the modifier chain to form a covalent bond.

The reaction mechanisms for selected reactive dyes with cationised cellulose were proposed (Figures 9 and 10):



**Figure 9.** Proposed mechanism of the dyeing  $[\text{Cell-O-IME}]^+\text{Cl}^-$  with triazine dyes: (III) ionic formation bonds on the fibre and dissociation of a hydroxyl group in ionic pair: cationised cotton + reactive dye on the fibre, (IV) substitution reaction with formation of a covalent bond between reactive dye and nucleophile of the hydroxyl group where: Ch—chromophore of RR 24:1, RB 160, RR 221 and RR 274, R—different chemical substituents in the chemical structure above dyes X—nicotinic acid for RR 221, halogen for the other dyes.



**Figure 10.** Proposed mechanism of dyeing [Cell-O-IME]<sup>+</sup>Cl<sup>-</sup> with RB 19 (mono-VS reactive dye).

#### 3.4. Evaluation and Confirmation of the Type of Binding between the Reactive Dye and Cationised Cellulose

The research was aimed at confirming the hypothesis that reactive dyes in eco-friendly dyeing conditions can form a covalent bond due to a reaction with the hydroxyl group of the cationic modifier [IME]<sup>+</sup>Cl<sup>-</sup> instead of with the hydroxyl group of the glucopyranose ring. The results of colour fastness to extraction in boiling DMF confirmed the formation of a covalent bond. Strong nucleophilicity of the hydroxyl groups in the cationic modifier was confirmed by direct reaction with reactive dyes in a neutral aqueous medium. The analysis of electron densities on oxygen and nitrogen atoms in model compounds also confirms the hypothesis of the site of covalent-bond formation.

##### 3.4.1. Resistance of Dyed [Cell-O-IME]<sup>+</sup>Cl<sup>-</sup> for Extraction with DMF

All obtained experimental data presented in Table 5 show that the samples of cationised cotton dyed with reactive dyes in eco-friendly conditions are fast for extraction with boiling DMF in contrast to the samples of non-cationised cellulose. It confirmed covalent bonds between the reactive group of the dye and the hydroxyl group in the modifier chain. The  $R_{DMF}$  presented in Table 5 is also on the level of these values for conventional dyeing methods with dyes described in the research of [21]. Obtained results are comparable and even better than on cellulose cationised with CHPTAC and dyed in the same eco-friendly conditions.

The  $R_{DMF}$  value for RR 274 of higher than 100% is probably a result of the aggregation of the dye molecule on the surface of cationic cellulose fibres. Dye aggregates can be broken during DMF extraction leading to an increase in colour strength and an increase in the degree of bonding, up to 100%. It can be noted that this phenomenon is more intense for Cell-O-[HPTA]<sup>+</sup>Cl<sup>-</sup> (our earlier study [21]) than for [Cell-O-IME]<sup>+</sup>Cl<sup>-</sup>.

**Table 5.** Resistance data L a b and DMF extraction for dyed samples of [Cell-O-IME]<sup>+</sup>Cl<sup>-</sup> and Cell-OH.

Dye	Dyeing in Eco-Friendly Conditions												$R_{DMF}$ [%]	
	Cell-OH						Cell-O-[IME] <sup>+</sup> Cl <sup>-</sup>							
	After Dyeing			After DMF Extraction			After Dyeing			After DMF Extraction				
L	a	b	L	a	b	L	a	b	L	a	b			
RR 24:1	80.18	25.28	-2.40	92.39	2.71	1.82	46.40	64.93	13.46	43.11	61.22	7.81	8.10	92.47
RB 160	59.81	-5.30	-22.07	76.98	-3.83	-12.33	43.85	-3.77	-27.92	44.20	-3.03	-27.78	21.1	94.90
RR 221	64.26	43.92	-4.07	74.97	29.49	-3.27	45.86	57.29	3.53	46.25	57.35	3.18	33.9	96.37
RR 274	57.13	42.15	-6.10	82.06	15.90	-3.87	42.15	50.99	-1.09	40.63	52.62	-1.15	8.80	103.3
RB 19	60.30	-6.06	-14.98	86.24	-1.88	-2.97	31.13	-5.06	-20.03	31.41	-5.22	-21.17	6.85	98.30

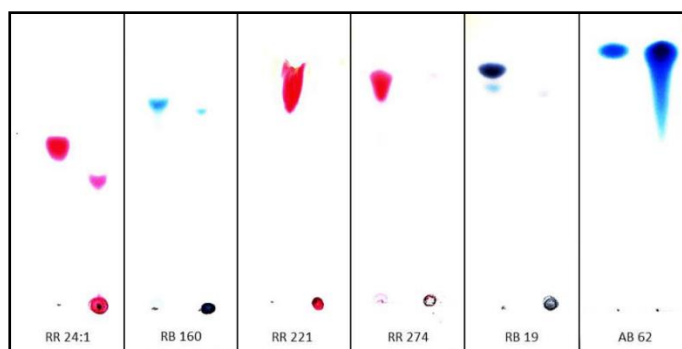
### 3.4.2. Reaction between Reactive Dyes and Modification Agent

When, to the 10 mL of 1% water solution of reactive dye, 1% water solution of [IME]<sup>+</sup>Cl<sup>-</sup> was added, insoluble solid precipitate immediately formed. Initially, a small quantity of insoluble solid with a bigger colourful halo on filter paper was observed. Next, portions of the 1% solution [IME]<sup>+</sup>Cl<sup>-</sup> formed a total colourless halo, and the filtrate was transparent. The precipitated solid was rinsed with water to obtain an entirely colourless bath and then filtered and dried at room temperature. The same reaction with 1% water solution of acid dye AB 62 was observed for comparison.

Dry reaction products of [IME]<sup>+</sup>Cl<sup>-</sup> copolymer with all selected reactive dyes were insoluble in DMF, DMSO, methoxypropanol, acetone, pyridine and 1% NaOH. However, the precipitated solid with AB 62 (acid dye) was fully dissolved with the used solvents. These experiments confirmed that coloured pigments were formed in a chemical reaction between reactive dyes and copolymer [IME]<sup>+</sup>Cl<sup>-</sup> (the covalent bonds were formed). TLC chromatography confirmed the above observation (Figure 11). The R<sub>f</sub> values for these products were 0 (remain at the start). The observed R<sub>f</sub> values for RR 24:1 and RB 160 may result from hydrolysed original dyes that cannot create a covalent bond with the modification agent.

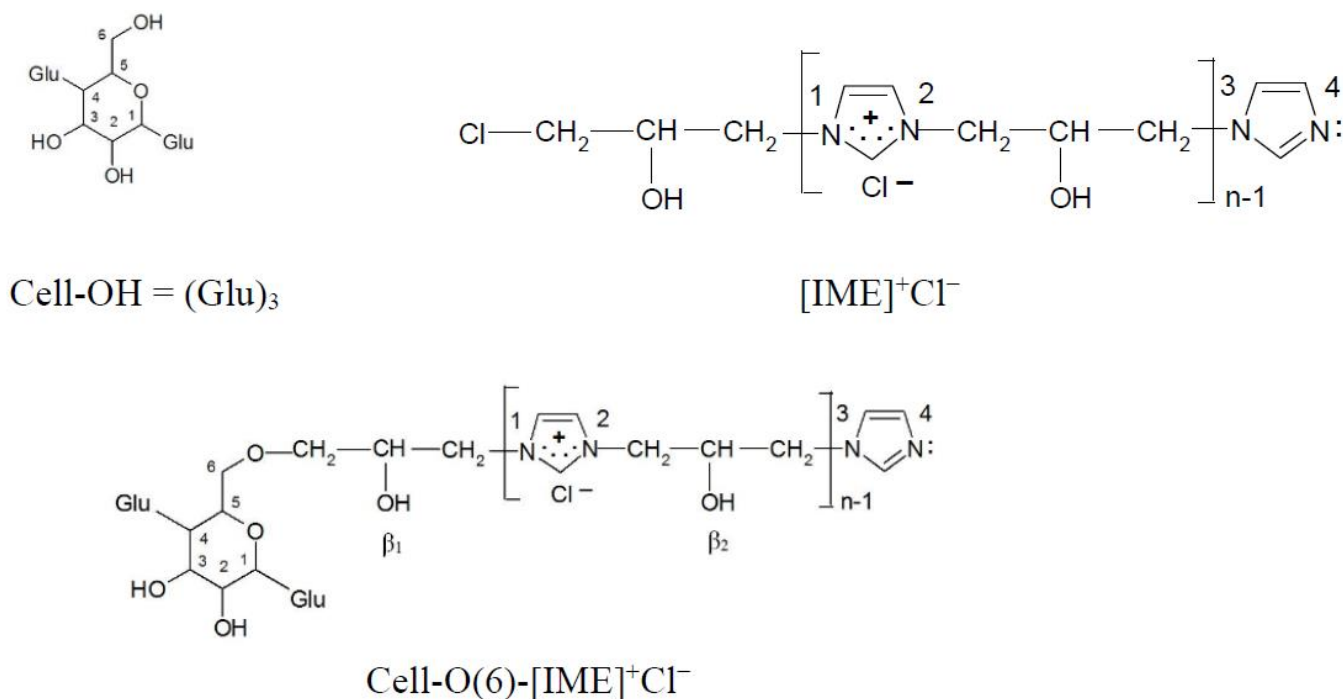
### 3.4.3. Density Electron Calculations

The dominant direction of epoxide cellulose etherification is attachment to the hydroxyl group located at carbon atom 6, as shown by the earliest calculations of the electron density on all hydroxyl groups in the glucopyranose ring [21]. Such a model (Figure 12) was also selected in this paper for further analysis and calculations.



Eluent: n-propanol:ethylacetate:water = 6:1:3.

**Figure 11.** TLC chromatography coloured compounds obtained in reactions between reactive dyes and acid dye with  $[\text{IME}]^+\text{Cl}^-$  (left side—analysed dye, right side—the reaction product of dye with  $[\text{IME}]^+\text{Cl}^-$ ).



**Figure 12.** Chemical structure compound models for electron density analysis (ether bond formed with -OH group at C(6) carbon atom).

The formation of  $[\text{Cell-O}(6)\text{-IME}]^+\text{Cl}^-$  causes changes in electron densities on the remaining O(2) and O(3) oxygen atoms in the glucopyranose ring (Table 6). The reaction of this product with the reactive dye could proceed according to the following order:

$$\text{O}(\beta_1) (-0.319) > \text{O}(3) (-0.315) > \text{O}(\beta_2) (-0.311) > \text{O}(2) (-0.286)$$

**Table 6.** Calculated electron-density data for analysed oxygen atoms.

Compound	Electron Density on An Oxygen Atoms				
	O(6)	O(2)	O(3)	O( $\beta_1$ )	O( $\beta_2$ )
$[\text{IME}]^+\text{Cl}^-$	—	—	—	−0.325	−0.315
Cell-OH = (Glu) <sub>3</sub>	−0.341	−0.287	−0.291	—	—
$[\text{Cell-O}(6)\text{-IME}]^+\text{Cl}^-$	−0.275	−0.286	−0.315	−0.319	−0.311

However, according to Nishiyama, Langan and Chanzy [27], the hydroxyl groups in positions 2 and 3 in cellulose are very strongly involved in intermolecular hydrogen bonds. The hydroxyl group with the O( $\beta_1$ ) and O( $\beta_2$ ) oxygen atom in the [Cell-O(6)-IME]<sup>+</sup>Cl<sup>-</sup> derivative does not participate in intramolecular hydrogen bonds. They can quickly form a nucleophile and react with the reactive system of the dyes to form a strong covalent bond.

Other calculations of the electron densities carried out on the nitrogen atoms in the modifier chain showed substantial differences, which depend on their location in the chain (Table 7).

**Table 7.** Electron densities on the selected atoms of [Cell-O(6)-IME]<sup>+</sup>Cl<sup>-</sup>.

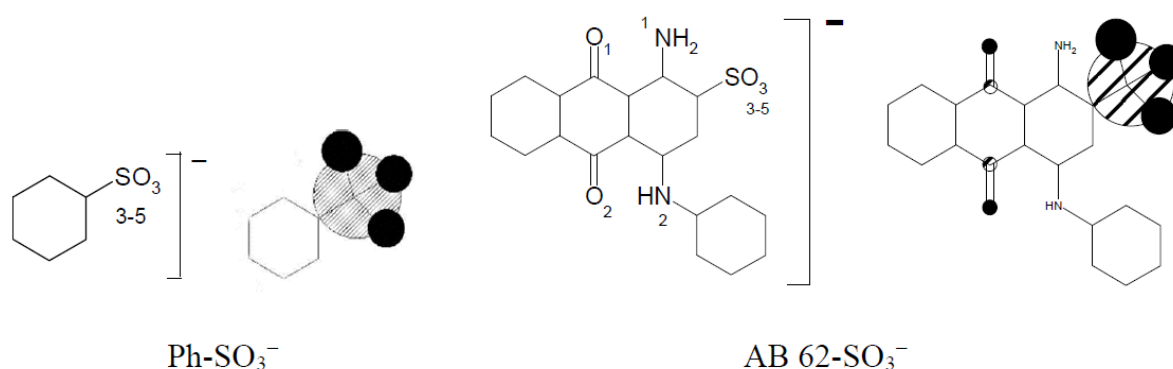
Atom	Electron Density
N(1)	0.445
N(2)	0.407
N(3)	0.236
N(4)	-0.085

Table 7 presents very high electron density differences in nitrogen atoms depending on their location in the cationic modifier chain. The positive charge is dislocated irregularly in the imidazole molecule between N(1) and N(2). Benzenesulfonic acid and acid dye AB 62 were selected to evaluate the strength of the ionic bond between the sulfo group of the reactive dye and the quaternary group in the modified cellulose.

The total sum of the electron density of all oxygen atoms sulfo groups in Ph-SO<sub>3</sub><sup>-</sup> and AB 62-SO<sub>3</sub><sup>-</sup> is nearly the same (Table 8) and is -2.820 and -2.812, respectively. It means that using benzenesulfonic acid to form a model compound could be accepted instead of much more complicated dyes with the sulfo group. The formation of an ionic bond between [Cell-O(6)-IME]<sup>+</sup>Cl<sup>-</sup> and benzenesulfonic acid (Figure 13) causes not only changes in the value of the positive charge on the quaternary group but also changes in the cellulose oxygen atoms in the modifier chain.

**Table 8.** The summary data of electron densities of oxygen atoms in the sulfo group of benzenesulfonic acid and AB 62.

Compound	O(3)	O(4)	O(5)
Ph-SO <sub>3</sub> <sup>-</sup>	-0.939	-0.939	-0.942
AB 62-SO <sub>3</sub> <sup>-</sup>	-0.956	-0.916	-0.940



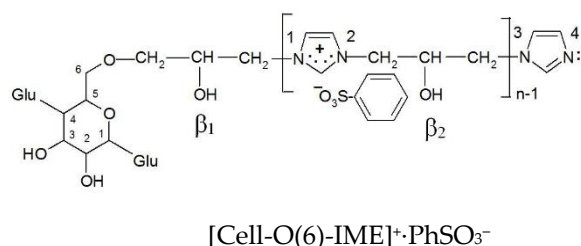
**Figure 13.** Example of graphical representation of the electron densities on oxygen atoms in sulfo group of benzenesulfonic acid and AB 62 calculated for their anionic forms.

Table 9 shows that the formation of an ionic bond between the sulfo group and the ammonium group of the modifier reduces the deficit in the cationic imidazole ring (sum of electron density nitrogen atoms from 0.852 in [Cell-O(6)-IME]<sup>+</sup>Cl<sup>-</sup> to 0.778 in Cell-O(6)-IME]<sup>+</sup>·PhSO<sub>3</sub><sup>-</sup>) (Figure 14) and increases the deficit on the adjacent O( $\beta_2$ ) oxygen

atom. The electron density on O( $\beta_2$ ) in  $[\text{Cell-O}(6)\text{-IME}]^+ \cdot \text{PhSO}_3^-$  is more negative, which makes this hydroxyl group the stronger nucleophile to react with reactive dyes and form covalent bonds in an aqueous bath without the addition of electrolytes and alkali at ambient temperature.

**Table 9.** The summary data electron density for analysed oxygen atoms of  $[\text{Cell-O}(6)\text{-IME}]^+ \cdot \text{PhSO}_3^-$ .

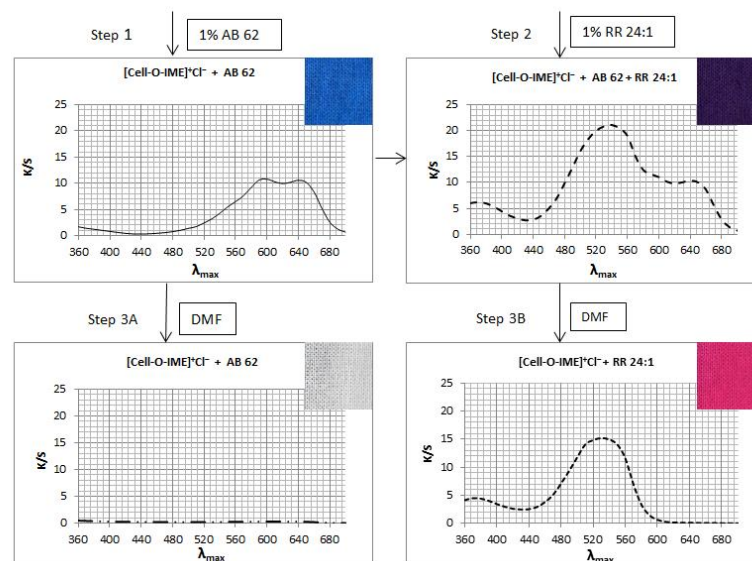
Compound	Electron Density on Oxygen and Nitrogen Atoms					
	O(2)	O(3)	O( $\beta_1$ )	O( $\beta_2$ )	N(1)	N(2)
$[\text{Cell-O}(6)\text{-IME}]^+ \text{Cl}^-$	−0.286	−0.315	−0.319	−0.311	0.445	0.407
$[\text{Cell-O}(6)\text{-IME}]^+ \cdot \text{PhSO}_3^-$	−0.292	−0.311	−0.311	−0.318	0.410	0.368



**Figure 14.** Chemical structure ionic pair cationised cellulose with benzenesulfonic acid for density electron analysis.

#### 3.4.4. Mixed Dyeing of $[\text{Cell-O-IME}]^+ \text{Cl}^-$ with Reactive and Acid Dyes

Two samples of  $[\text{Cell-O-IME}]^+ \text{Cl}^-$  each ca. 2 g were dyed (Figure 15 step 1) with 1% owf of AB 62 (acid dye) in eco-friendly conditions for 30 min. Then, one sample was removed, and 1% owf of RR 24:1 (reactive dye) was added to the same bath and dyeing was continued (Figure 15 step 2) for 30 min. The bath after dyeing was practically colourless. After dyeing, both samples were rinsed in cold water and dried at room temperature. One half of each of the dyed samples was extracted in boiling DMF (Figure 15 steps 3A and 3B) until the next aliquot was colourless. After extraction, the samples were rinsed in cold water and dried at room temperature. K/S values were measured for all four samples. The following diagram presents the running process:



**Figure 15.** The diagrams presented the running process of mixed dyeing of  $[\text{Cell-O-IME}]^+ \text{Cl}^-$  with RR 24:1 and AB 62 and the extraction results with DMF.

Mixed dyeing of  $[\text{Cell-O-IME}]^+ \text{Cl}^-$  with reactive and acid dyes showed that both dyes under ecological dyeing conditions were exhausted completely and formed ionic bonds

with strong ammonium centres. However, being resistant to the extraction treatment with DMF (step 3B), a covalent bond only between  $[\text{Cell-O-IME}]^+\text{Cl}^-$  and RR 24:1 was formed. This was another confirmation of the formation of covalent bonds between the reactive dyes and the hydroxyl/nucleophilic groups in the modifier chain.

#### 4. Conclusions

It was found that, during the dyeing of cationised cellulose with a copolymer of  $[\text{IME}]^+\text{Cl}^-$  in a water bath without the addition of electrolytes and alkali at room temperature, reactive dyes of various classes form a covalent bond according to the substitution/addition mechanism with the nucleophile hydroxyl group located in the modifier chain. These bonds were stable for extraction treatment in boiling DMF. TLC chromatography of the insoluble coloured compounds formed in water in the reaction between reactive dyes and the hydroxyl group of the modifier chain confirmed these linkages. Electron densities calculations on oxygen atoms confirmed the experimental results of the high activity of the nucleophile being formed on the hydroxyl group in the modifier chain.

**Author Contributions:** Conceptualization, S.P.; software, K.W.; supervision, P.K. and E.M.-Z.; methodology, S.P., P.K. and E.M.-Z., visualization, S.P. and E.M.-Z.; writing—original draft preparation, S.P.; writing—review and editing, S.P., P.K., E.M.-Z. and K.W. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding. The authors declare that no funds, grants, or other support were received during the preparation of this manuscript. The authors have no relevant financial or non-financial interests to disclose.

**Institutional Review Board Statement:** The study did not require ethical approval.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Conflicts of Interest:** The authors declared no potential conflict of interest with respect to the research, authorship and/or publication of this article.

#### Abbreviations

AB 62	Nylanthrene Brilliant Blue 2RFF (Acid Blue 62)
Cell-OH	cellulose
$[\text{CHPTA}]^+\text{Cl}^-$	3-chloro-2-hydroxymethyltrimethylammonium chloride (CHPTAC)
$[\text{Cell-O-IME}]^+\text{Cl}^-$	cellulose cationised with copolymer (chloromethyl)oxirane-1H-imidazole
DMF	N,N-dimethylformamide
DMSO	dimethyl sulfoxide
Glu	glucopyranose ring
$[\text{IME}]^+\text{Cl}^-$	copolymer (chloromethyl)oxirane-1H-imidazole
Kayacelon React	brand name monochlorotriazine type of reactive dyes with nicotinic group
LR	liquor ratio
MCT	monochlorotriazine type of reactive dyes
owf	on weight fibre
$\text{PhSO}_3\text{H}$	benzenesulfonic acid
PES-Na	polystyrene sulfonic acid sodium salt
poly-DADMAC	polydiallyldimethylammonium chloride
Poly(St-BA-VBT)	poly(styrene-butyl acrylate-vinylbenzyl trimethylammonium chloride)
RB 19	Remazol Brilliant Blue R (Reactive Blue 19)
RB 160	Kalpactive Blue HE-BR (Reactive Blue 160)
RR 24:1	Helaktyn Red D-BN (Reactive Red 24:1)
RR 221	Papizolon Red HT-3BN (Reactive Red 221)
RR 274	Eriofast Red 2B (Reactive Red 274)
TLC	thin layer chromatography
VS	vinylsulfone type of reactive dyes

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## The Light Fastness of the Reactive Dyes on Cationized Cellulose

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### ABSTRACT

Conventional dyeing of cellulose with reactive dyes requires the use of huge quantities of electrolytes and alkalis and the temperature between 60–90°C. Using the above conditions a stable covalent bond is formed between the reactive group of the dye and the hydroxyl group of cellulose. Cationization of cellulose allows to carry out reactive dyeing without electrolytes and alkalis even at room temperature. The dye, depending on the cationic modifier used, can form only ionic bond between sulfonic group of the dye and quaternary group of the modifier or also covalent bond between reactive group of the dye and hydroxyl group of the modifier. In this work we investigate how light fastness is affected by the type of bond with which the dye bound to the cationized cellulose. So far, such research has not been published. We found that the light fastness of the reactive dyeings on cationized cellulose was lower compared to non-cationized cellulose and depends on the kind of modifier used: chlorocholine chloride, 3-chloro-2-hydroxy-propyltrimethylammonium chloride and copolymer [(chloromethyl)oxirane +1 H-imidazole]. Density electron changes of ionic bonds between quaternary group of modified cellulose and sulfonic group of reactive dyes were analyzed in relation to the fading process.

### 摘要

用活性染料对纤维素进行常规染色需要使用大量的电解质和碱，温度在60-90摄氏度之间。使用上述条件，在染料的反应基团和纤维素的羟基之间形成稳定的共价键。即使在室温下，纤维素的阳离子化也可以在没有电解质和碱的情况下进行活性染色。根据所使用的阳离子改性剂，染料只能在染料的磺酸基和改性剂的四元基团之间形成离子键，也可以在染料的反应性基团和改性剂的羟基之间形成共价键。在这项工作中，我们研究了染料与阳离子纤维素结合的键类型如何影响耐光性。在这项工作中，我们研究了染料与阳离子纤维素结合的键类型如何影响耐光性。到目前为止，此类研究尚未发表。我们发现，与非阳离子纤维素相比，阳离子纤维素上的活性染料的耐光性较低，3-氯-2-羟基丙基三甲基氯化铵和共聚物[(氯甲基)环氧乙烷+1 H-咪唑]分析了改性纤维素季铵基和活性染料磺酸基之间离子键的密度电子变化与褪色过程的关系。

### KEYWORDS



light fastness; reactive dyes; covalent bond; cationized cellulose; eco-friendly dyeing; density electron analysis

### 关键词

耐光性; 活性染料; 共价键; 阳离子纤维素; 环保染色; 密度电子分析

## Introduction

The light fastness of dyed textiles is one of the most important features of finished products. Light fastness refers to the resistance of the dyed material to changes in its color during exposition to

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sunlight or artificial light and is in a special case of the broader concept of color fastness (Nelson 1995). The phenomenon by which dyes undergo fading is associated with photo degradation as a complex process (Latif et al. 2015). Many factors influence the fading of colored textiles such as the bond between the dye and the fiber, the chemical structure of the dye and substrate, radiation quality as well as temperature and humidity. The concentration of dye on the fiber and the chemical modification of the fiber are also important factors. Permanent bonding with the fiber ensures the coplanarity of the dye molecules. In the case of cellulose fibers, the large size, linear shape and the presence of electron donating groups in the dye molecules allow to create additional hydrogen bonds with cellulose (Tera et al. 2016). Oakes (2001) showed that 40% of fading is caused by UV rays, another 25% due to heat and 25% being caused by normal visible light. The remaining 10% of fading results from indoor artificial lighting, humidity, and poor dye anchorage. Both visible light and UV radiation cause fading, where visible light leads to photooxidation (Genc and Can-Dogan 2006), while UV radiation triggers the degradation process of molecules (Brenton, Morgan, and Beynon 1979). In both cases, this reaction requires energy in the form of light as well as oxygen in the form of singlet (Latif et al. 2015).

It was observed that reactive dye light fastness mainly depends on the chemical structure of chromophore (Thiagarajan and Nalankill 2010, 2014). The azo chromophore has lower light fastness, while metal complex and anthraquinone chromophore dyes has good light fastness. Sulfonic group in reactive dye does not have a noticeable impact on light fastness while the presence of –OH, –NH<sub>2</sub>, and –NHR groups in the azo dye molecule decrease light stability of the dyes.

Reactive dyes are becoming increasingly popular for dyeing cellulosic fibers because of their wide shade range, ease of application, and excellent wet fastness properties. Reactive dyes are mainly used in the long-liquor dyeing processes (exhaustion dyeing) (Lewis 2014). The first interaction between fibers and dyes during the dyeing process is dye exhaustion onto the fiber. However, in an aqueous bath, cellulosic fibers will develop a negative charge on their surface. Also, the sulfo group of the reactive dyes dissociate to a negative ion (–SO<sub>3</sub><sup>–</sup>) in water. Thus, the negatively charged dyes and negatively charged fiber undergo ion repulsion, causing the exhaustion to be more difficult. In order to overcome this problem, electrolytes (the most common one is sodium sulfate) are added to assist the exhaustion process. Following the exhaustion, fixation step is carried out by adding alkali. Covalent bond formation between the dye and the fiber can only occur when the dye has been absorbed into the cellulose phase.

Despite of the many advantages of this group of dyes, their application poses a high risk to the environment. Electrolytes environmental pollution is estimated at around 200,000–250,000 tons per year (Aktek and Malekul Millat 2017).

Introducing of the cationic groups to the chain of cellulose in the modification process completely changes the cotton surface's charge from negative to partially or totally positive. That allows the electrostatic attraction, simultaneous exhaustion, and fixation of reactive dyes on cellulose without presence of electrolytes and alkalis.

The most popular as modification agent for cellulose is still CHPTAC, which in cationization process react with hydroxyl group of cellulose on etherification way (Farrell 2012; Hashem et al. 2010). In the past decades, nearly a thousand publications (Correia et al. 2020) about the cationization of cotton fibers and dyeing, printing and finishing of cationized cotton were published.

Many of these works contain results of dyeing fastness to washing, rubbing and light in comparison to conventional methods. Giles (1957) showed, based on the statistical study, that the light fastness is often reduced by cationic surface-active agents or hydrogen-bonding compounds, e.g. phenols or urea, used as dyeing assistants or after treating agents. Also, the smaller particles of dye have tendency to fade more rapidly than larger ones, and therefore their fading rate determines the fastness grade of the dyed material, which is judged in the earlier stages of fading. Chattopadhyay (2001) showed that the poor light fastness on PAE/EDA treated cotton was attributed to the presence of dye mainly on the surface of the fiber. This phenomenon is commonly called as ring dyeing. Kannan et al. (2006) reported that the light fastness rating is slightly reduced for some dyes, about half to one point, as was presented by various researches previously. The presence of an aliphatic chain between the dye

and fiber may be disturbing the stable electronic configuration of dye that leads to the shifting of electrons disintegration of dye by the photons of light rays. Ghazal, El-Masry, and Mosaad (2011) reported that the better light fastness of Acid Blue 25 and Acid Yellow 36 on CHPTAC cationized fabrics results from higher concentration of the dyes on cationized samples (dark shade) compared to pale shade of uncationized samples. Ilango (2015) reported that the light fastness of dyeings with some reactive dyes on of the CHPTAC cationized fabric samples were improved when the dyeing process was performed comparably to conventional method in the absence salt only. Chatha et al. (2016) observed that all the dyed cotton fabric samples untreated and treated with different concentrations of chitosan have equally good light fastness properties. Aktek and Malekul Millat (2017) reported that cationization of cellulose with NMA-HTCC owning quaternary ammonium groups gave lower light fastness due to its molecular size compared to uncationised cellulose. The NMA-HTCC due to large molecule does not penetrate into the fiber structure and remains mainly on surface of cellulosic fibers. However, careful selection of reactive dyes can reduce above problem to some extent. Abedin et al. (2021) reported that the light fastness of the reactive dyes on CHPTAC cationised cotton were improved to 4 from 3 compared to conventional dyeing resulted from better dye fixation and the lack of dye degradation by the light photons. It can be noticed that cationized cotton was dyed with soda. Correia at coworkers (Correia et al. 2021) examined the light fastness of dyeings with Reactive Red 195 on cationized cellulose with two cationic agents i.e. CHPTAC and Polyquaternium2 (P42). The cationized samples were additionally treated with plasma before and after cationization process. Fabrics treated with CHPTAC have satisfactory level of light fastness (5/4–5) (both on fabric with and without plasma treatment) in comparison to conventional dyeings. In case of P42 the level of light fastness (2/1) was unsatisfactory.

It is obvious that the permanent modification of cellulose with the use of different modifying agents leads to the production of various new cellulose polymers with altered properties compared to unmodified cellulose. This is especially true of the cationization process in which, depending on the modifier used, the new cellulose polymer obtains a partial or complete positive charge on its surface.

It was shown in our previous researches (Pruš et al. 2022a, 2022b) that cellulose cationized with 3-chloro-2-hydroxy-propyltrimethylammonium chloride or copolymer [(chloro-methyl)oxirane +1 H-Imidazole] can be dyed with reactive dyes without electrolytes and alkalis at room temperature. Reactive dyes during the dyeing process in above conditions form covalent bonds with the hydroxyl group of the cationic modifier in adjacent position to the quaternary group instead of with the hydroxyl group of the glucopyranose ring. The mechanism of this reaction was proposed and confirmed by extraction with boiling DMF and by analysis electron density calculation. The dyes covalently bonded with the fiber were not extractable. The dyeing cellulose cationized with chlorocholine chloride (no hydroxyl group in modifier chain) showed that in the same conditions only electrostatic strong ionic pair was formed. The formation of an ionic bond between the sulfonic group of the dye and the quaternary group of the modifier is confirmed by its sensitivity to extraction in DMF.

The main aim of this study was to find the influence on light fastness of these bonds in comparison to the covalent bond formed between reactive dye and unmodified cellulose after dyeing in conventional process. Thus, unmodified and modified cellulose dyed with selected reactive dyes was used for examined their light fastness.

## Materials and methods

The unmodified and cationized cotton samples dyed with selected reactive dyes used for irradiation experiments in this work were prepared according to the our earlier research works receipies (Pruš et al. 2022a, 2022b). According to the above, a 100% bleached cotton fabric with a smooth wave and a declared basis weight of 180 g/m<sup>2</sup>, was modified with three different cationic modifiers (A, B and C - Figure 1). Dyeing process with selected reactive dyes (Figure 2) of unmodified cellulose samples was performed using conventional methods in accordance with the recipes recommended by the

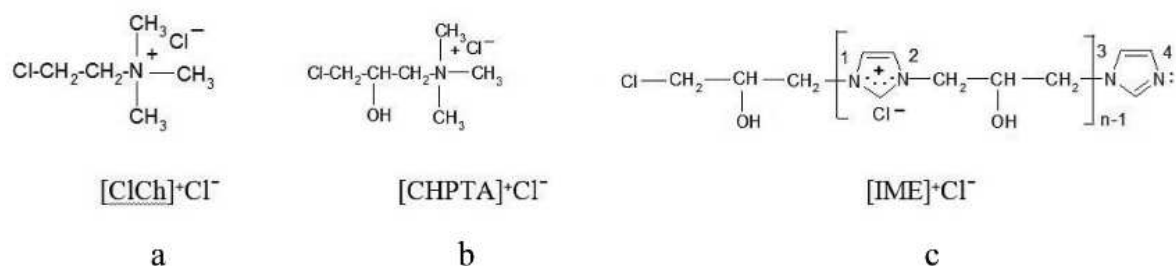


Figure 1. Structures of cationic modifiers.

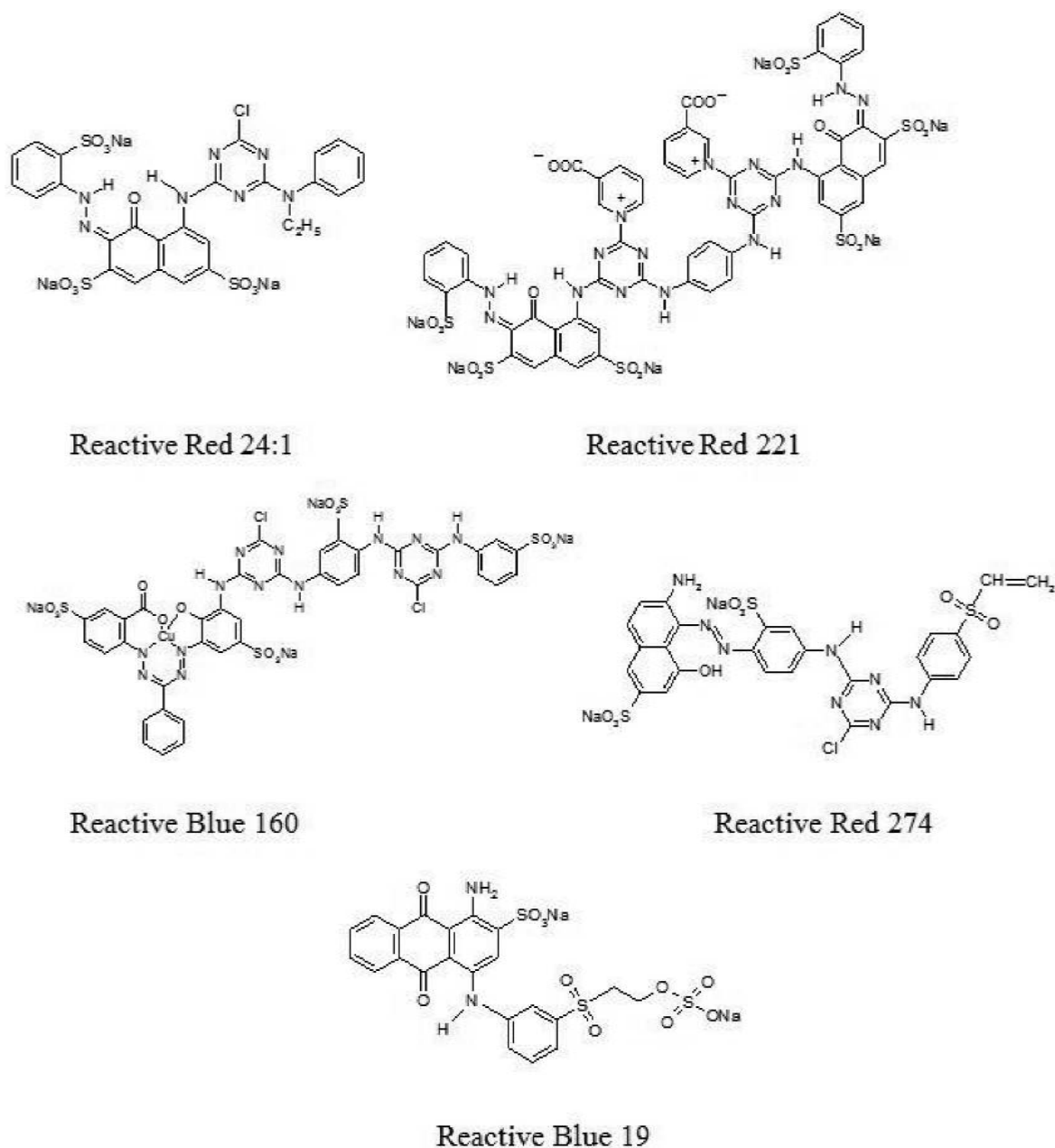


Figure 2. Chemical structures of reactive dyes.

manufacturers of these dyes (Pruš et al. 2022a). Cationized cellulose samples were dyed under ecological conditions (without electrolytes, alkalis and at room temperature), using 1% owf (RR 221 or RB 160) and 0.9% owf (RR 24:1 or RR 274 or RB 19) respectively to obtain a similar color strength. The samples prepared in this way were used for experimental tests to test the color fastness to light by irradiation under the same conditions.

The light fastness of dyed samples was studied after exposing to artificial light for 1, 2, 6, 12, 24 and 36 hours (according to the PN-EN ISO 105-B02: 2014–11 Method 2). The samples were irradiated in Q-SUN Xenon Test Chamber (Q-Lab Corporation, model XE-2). Change of color of covered part and exposed part of dyed sample was estimated by K/S on spectrophotometer Datacolor 400 (Datacolor, USA). Measurement was done using: measuring geometry d/8, measuring window 9 mm, DSLR disabled, no UV filter, D65 illuminant, and 10° observer.

Relative color change of the analyzed samples after exposition to light was calculated according to Equation 1:

$$\Delta R_{cf} = \frac{\left(\frac{K_0}{S_0}\right) - \left(\frac{K_1}{S_1}\right)}{\frac{K_0}{S_0}} \times 100\% \quad [1]$$

where:

$\Delta R_{cf}$  - relative color change after irradiation,

$\frac{K_0}{S_0}$  - color values for started sample,

$\frac{K_1}{S_1}$  - color values for samples after irradiation for 1, 2, 6, 12, 24 and 36 hours respectively.

## Results and discussion

The linkage of reactive dyes with unmodified and cationized cellulose samples according to our earlier works (Pruš et al. 2022a, 2022b) is shown in Figure 3: All analyzed samples lose some of their color strength and nuance of shade progressively to the time of exposition to irradiation. The changes after 1, 2, 6, 12, 24 and 36 hours irradiating measured as K/S at  $\lambda_{max}$  and expressed as  $\Delta R_{cf}$  were calculated accordingly to the Eq. [1] and presented in Table 1 as final results ( $\Delta R_{cf}$  after 36 hours irradiation) and as color changes (during the time of irradiation) respectively.

Taking under consideration that all dyed samples were irradiated in the same conditions it was possible to indicate the following general statements:

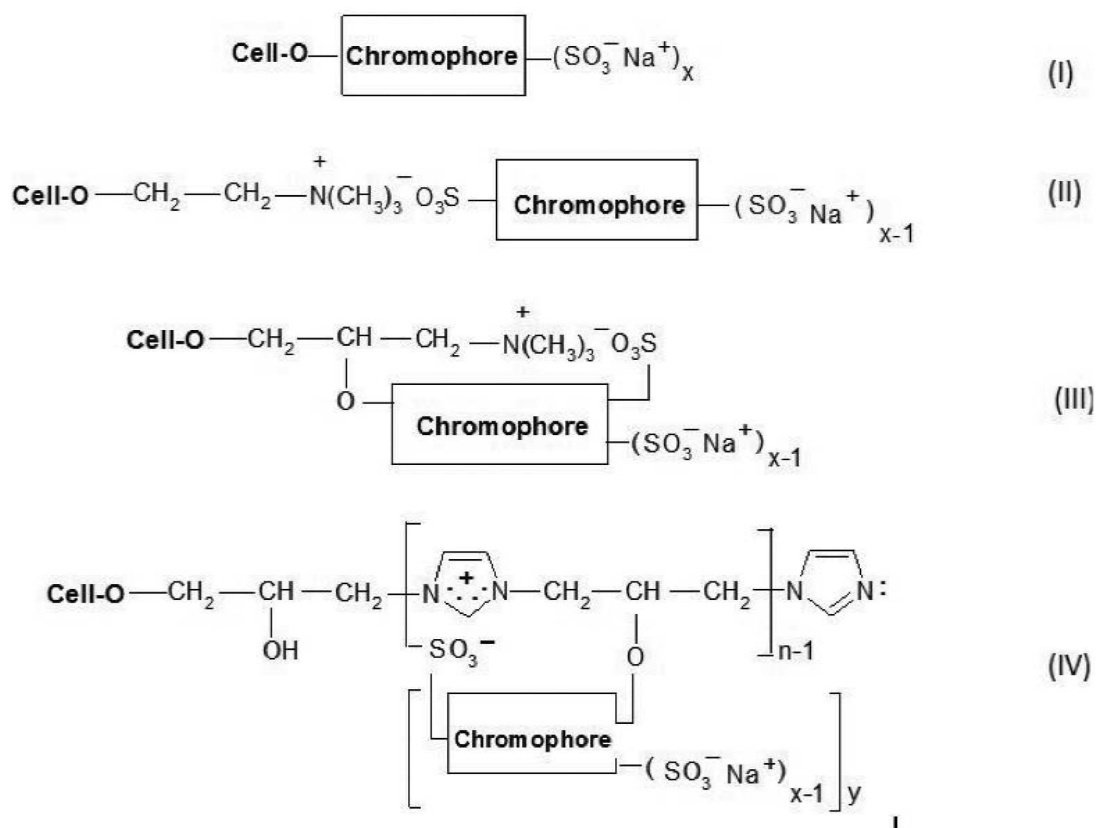
(1) Most of the reactive dyes used for dyeing unmodified cellulose in conventional method have better light fastness properties than on cationised ones. Apart of permanent covalent linkage between the dye and the hydroxyl group of the cellulose [Figure 3(I)] they have a possibility of creation a lot of hydrogen, van der Waals, dipoles and  $\pi$  bonds as well as intra- and intermolecular linkages. The light fastness of selected reactive dyes on unmodified cellulose according to the  $\Delta R_{cf}$  index after 36 hours irradiation can be ordered as follow:

RB 160 (19.41) > RR 274 (24.40) > RB 19 (28.60) > RR 221 (29.85) > RR 24:1 (41.90)

(2)  $\Delta R_{cf}$  index after 36 hours irradiation for dyes bonded with cationised cellulose only as ionic pair between the sulfonic group of the dye and quaternary group of the modifier (Figure 1A) indicate for all dyes lower values. Those types of bonds are typical for acid dyes and can be ordered as follow:

RB 160 (30.80) > RR 274 (39.30) > RR 24:1 (50.65) > RB 19 (52.81) > RR 221 (55.86)

(3)  $\Delta R_{cf}$  index after 36 hours irradiation for dyes bonded with cationised cellulose as ionic pair in the same way as the dyes in point 2. and covalent bonded according to the nucleophile substitution or addition mechanism like dyes with uncationised cellulose but with hydroxyl group belonging to the moderator chain instead to the hydroxyl group of glucopyranose ring.  $\Delta R_{cf}$  index for selected dyes can be ordered as follow:



where:

chromophore = reactive dyes: RR 24:1, RR 221, RR 274, RB 19 and RB 160,

x - number of sulfonic group in dye molecule,

y - number of molecules reactive dye bonded covalently ( $y \leq n-1$ ),

n - polymerisation degree.

**Figure 3.** Chemical bonds between selected reactive dyes with cellulose uncationised (I) and cationised with: chlorocholine chloride (II), CHPTAC (III) and Texamin ECE New (IV) respectively.

a) for cationised cellulose with  $[\text{CHPTA}]^+\text{Cl}^-$

RB 160 (23.86) > RR 24:1 (30.9) > RR 221 (37.7) > RR 274 (40.6) > RB 19 (48.64)

b) for cationised cellulose with  $[\text{IME}]^+\text{Cl}^-$

RB 160 (45.74) > RR 274 (54.67) > RB 19 (55.42) > RR 24:1 (67.50) > RR 221 (75.54)

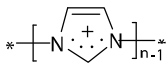
The results of the light fastness of samples dyed in ecological conditions on cationic modified cellulose indicate their decreasing relation to dyeings on unmodified cellulose, regardless of the type of modifier and reactive dye used. After 36 hours of irradiation the lowest loss of color was for dyeings on unmodified cellulose and the highest for dyeings of cotton samples cationised with  $[\text{IME}]^+\text{Cl}^-$ .

(4) Modification of cellulose fibers by cationisation creates many positive charge sites, mainly on their surface what allow to form of the ionic bonds with sulfonic group of reactive dye [Fig. 3 (II)]. At the second step covalent bond between reactive dye and hydroxyl group, belonging to the modifier chain of cationised cellulose was formed [Fig. 3 (III and IV)]. Cationization process leads to decreasing of amount of hydroxyl groups in cellulose capable to create bonds what reduced the ability to establish hydrogen bond between polymer and dye molecules. Lower amount of hydrogen linkages, causing weaker protection of the dye chromophore by cellulose macromolecules, results in a decrease in light fastness. Additionally, cationized cellulose, thanks to the introduction of quaternary groups containing

**Table 1.** Comparison of the light fastness for reactive dyes on cellulose unmodified in relation to cationised with selected modifiers  
 (1) Light fastness after 36 hours irradiation according to the blue scale).

Dyed sample	Irradiated samples 1, 2, 6, 12, 24 and 36 hrs	Light fastness after 36 hrs <sup>1)</sup>	$\Delta R_{cf}$ after 36 hrs [%]	Diagrams of color changes during the time of irradiation
RR 24:1 Cell-OH		4	41.90	
RR 24:1 Cell-O-[Ch] <sup>+</sup> Cl <sup>-</sup>		3-4	50.65	
RR 24:1 Cell-O-[HPTA] <sup>+</sup> Cl <sup>-</sup>		4	30.90	
RR 24:1 Cell-O-[IME] <sup>+</sup> Cl <sup>-</sup>		2-3	67.50	
RR 22:1 Cell-OH		4-5	29.85	
RR 22:1 Cell-O-[Ch] <sup>+</sup> Cl <sup>-</sup>		3	55.86	
RR 22:1 Cell-O-[HPTA] <sup>+</sup> Cl <sup>-</sup>		3-4	37.7	
RR 22:1 Cell-O-[IME] <sup>+</sup> Cl <sup>-</sup>		2-3	75.54	
RR 27:4 Cell-OH		4-5	24.40	
RR 27:4 Cell-O-[Ch] <sup>+</sup> Cl <sup>-</sup>		3-4	39.30	
RR 27:4 Cell-O-[HPTA] <sup>+</sup> Cl <sup>-</sup>		4	40.60	
RR 27:4 Cell-O-[IME] <sup>+</sup> Cl <sup>-</sup>		3	54.67	
RB 19 Cell-OH		3-4	28.60	
RB 19 Cell-O-[Ch] <sup>+</sup> Cl <sup>-</sup>		3	52.81	
RB 19 Cell-O-[HPTA] <sup>+</sup> Cl <sup>-</sup>		3	48.64	
RB 19 Cell-O-[IME] <sup>+</sup> Cl <sup>-</sup>		2-3	55.42	
RB 160 Cell-OH		4	19.41	
RB 160 Cell-O-[Ch] <sup>+</sup> Cl <sup>-</sup>		3-4	30.80	
RB 160 Cell-O-[HPTA] <sup>+</sup> Cl <sup>-</sup>		4	23.86	
RB 160 Cell-O-[IME] <sup>+</sup> Cl <sup>-</sup>		3-4	45.74	

**Table 2.** Electron densities data for quaternary groups and sulfonic group.

Compound	$-\text{SO}_3^-$	Quaternary group (electron density)	
Fig. 3 (I) untreated	-0,497	none	none-
Fig. 3 (II) $-\text{[Ch]}^+$		$-\overset{+}{\text{N}}(\text{CH}_3)_3$	0.633
Fig. 3 (III) $-\text{[HPPTA]}^+$		$-\overset{+}{\text{N}}(\text{CH}_3)_3$	0.638
Fig. 3 (IV) $-\text{[IME]}^-$			$(0.852)^{n-1}$

nitrogen atoms becomes like to proteinaceous fibers. The dyeings on this group of fibers tend to fade according to the photo-reduction mechanism (Oakes 2001) what need for excitation more high-energy states. Photoreductive processes also generally involve radicals but high-energy light (UV or near UV) is required to facilitate their formation via bond cleavage. On the other hand, the photo-oxidative route becomes progressively more important when the dye is subject to lower-energy visible excitation in the presence of oxygen, particularly with cellulosic substrates. Visible radiation quanta carry energy capable of breaking the weakest chemical bonds ( $\sim 160\text{-}300$  kJ/mol), while UV radiation energy also breaks permanent bonds.

(5) Presence of positive charges on cationized cellulose causes reduction of electron density on the surface of dyeings what decrease the barrier before UV light attack. Most of the active species responsible for degradation of chromophores of the dyes have total or partial negative charge. Table 2 presents electron densities for quaternary group of analyzed modifiers in cationised cellulose compared with sulfo group in reactive dye (Pruš et al. 2022a, 2022b). Results presented in Table 2 show that the most negative charge has the surface on unmodified cellulose. Modification cellulose with CHPTAC or chlorocholine chloride gives very similar changing in electron density per one quaternary group. The introduction of one quaternary group of  $[\text{IME}]^+\text{Cl}^-$  copolymer to cellulose gives the most positive values compared to  $[\text{ClCh}]^+\text{Cl}^-$  and  $[\text{CHPTA}]^+\text{Cl}^-$ . These values correspond to obtained results of light fastness after irradiation of unmodified and cationised samples cellulose materials.

## Conclusion

The research confirmed that cellulose modified by cationization with quaternary modifiers dyed with reactive dyes had lower light fastness parameters in comparison to unmodified ones. Probably this is one of the reasons, that this method of modification is not introduced to the industrial scale, although thanks to that modification is possible to eliminate a huge quantity of electrolytes and alkalis may be released from dyeing houses to environment. This research presents the problems with light fastness dyed cationised cotton samples related to chemical bonds formed during dyeing in ecological conditions (without electrolytes and alkalis in room temperature).

It seems also that, the greater impact for improving fading process is involved with decreasing of electron densities on the surface cationised cellulose materials. That hypothesis confirmed electron density analysis.

## Abbreviations

Cell-OH	cellulose
$[\text{ClCh}]^+\text{Cl}^-$	chlorocholine chloride
$[\text{CHPTA}]^+\text{Cl}^-$	3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC)
$[\text{Cell-O-IME}]^+\text{Cl}^-$	cellulose cationised with copolymer (chloromethyl)oxirane-1 H-Imidazole
DMF	dimethylformamide



Glu	glucopiranos ring
[IME] <sup>+</sup> Cl <sup>-</sup>	copolymer (chloromethyl)oxirane-1 H-Imidazole (Texamin ECE New)
NMA-HTCC	O-acrylamidomethyl-N-[2-hydroxy-3-trimethylammonium]propyl]chitosan chloride
owf	on weight fiber
PAE/EDA	polyamide epichlorhydrin/ethylenediamine polymer
PhSO <sub>3</sub> H	benzenesulfonic acid
Polyquaternium2 (P42)	poly[bis(2-chloroethyl)ether-alt-1,3-bis[3-dimethylamino]propyl]urea quaternized
RB 19	Reactive Blue 19
RB 160	Reactive Blue 160
RR 24:1	Reactive Red 24:1
RR 221	Reactive Red 221
RR 274	Reactive Red 274
$\Delta R_{cf}$	relative color change after irradiation

## Disclosure statement

No potential conflict of interest was reported by the authors.

## Funding

This research received no external funding.

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## Highlights

Reactive dyes when dyeing cationised cellulose strongly absorb the fibers which leads to elimination of the electrolytes normally used in conventional methods.

Our innovative work has also shown the possibility of eliminating alkalis from the dyeing process and obtaining permanent and efficient dyeing with these dyes even at ambient temperature. It was found that under these completely ecological conditions, covalent bonds are formed between the modified cellulose and the reactive dye, which are different than in the dyeing of unmodified cellulose. In this work, tests were performed to confirm the hypothesis that the dyeings obtained in ecological dyeing with reactive dyes on samples of cationised cellulose with three different modifiers may show significant differences in their light fastness.

Irradiation of the stained samples confirmed our hypothesis. The relative change in the color strength of the irradiated samples over time and after 36 hours showed a greater or lesser change. The tests were carried out in comparison to dyeings obtained according to the conventional method.

Further work taking into account the possibilities of other modifiers and dyes with full elimination of electrolytes and alkalis and dyeing in ambient temperature may lead not only to environmental protection, but also to better resistance indicators.

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**STATEMENTS OF THE CO-AUTHORS**



## Oświadczenie

Niniejszym potwierdzam swój procentowy udział w przygotowanie publikacji:

### Publikacja 1.

S. Prus (80%), P. Kulpiński (10%), E. Matyjas-Zgondek (10%). Changes in the specific charge amount on the surface of cotton fibres during the alkali pre-treatment process. From: *Fibres & Textiles in Eastern Europe* 27, 4(136): 30-37, DOI: 10.5604/01.3001.0013.1817.

Wkład doktoranta w przygotowanie publikacji obejmował:

- przygotowanie oraz redakcję manuskryptu,
- przegląd literaturowy,
- przygotowanie warstwy graficznej,
- analizę oraz zilustrowanie zebranych danych,
- opracowanie odpowiedzi do recenzentów i edytorów.

**Podpis doktoranta**

**Podpis promotora**



## Oświadczenie

Niniejszym potwierdzam swój procentowy udział w przygotowanie publikacji:

### Publikacja 2.

S. Prus (80%), P. Kulpiński (10%), E. Matyjas-Zgondek (10%). Comparison of the effects of the cationisation of raw, bio- and alkali scoured cotton knitted fabric with different surface charge density. AUTEX Research Journal, Vol. 21, No 2, April 2021, DOI 10.2478/aut-2020-0049.

Wkład doktoranta w przygotowanie publikacji obejmował:

- przeprowadzenie analiz i obliczeń ładunku powierzchniowego,
- przeprowadzenie pomiarów spektrofotometrycznych,
- przygotowanie oraz redakcję manuskryptu,
- przegląd literaturowy,
- przygotowanie warstwy graficznej,
- analizę oraz zilustrowanie zebranych danych,
- opracowanie odpowiedzi do recenzentów i edytorów.

Podpis doktoranta

Podpis promotora



## Oświadczenie

Niniejszym potwierdzam swój procentowy udział w przygotowanie publikacji:

### Publikacja 3.

S. Prus (65%), P. Kulpiński (10%), E. Matyjas-Zgondek (10%), K. Wojciechowski (15%).  
Eco-friendly dyeing of cationised cotton with reactive dyes: mechanism of bonding reactive dyes with CHPTAC cationised cellulose. *Cellulose*, 29(7), pp. 4167–4182,  
[doi.org/10.1007/s10570-022-04521-w](https://doi.org/10.1007/s10570-022-04521-w)

Wkład doktoranta w przygotowanie publikacji obejmował:

- przygotowanie koncepcji badań gęstości elektronowej,
- przeprowadzenie eksperymentów barwienia i ekstrakcji wybarwień
- przeprowadzenie pomiarów spektrofotometrycznych,
- przygotowanie oraz redakcję manuskryptu,
- przegląd literaturowy,
- przygotowanie warstwy graficznej,
- analizę oraz zilustrowanie zebranych danych,
- opracowanie odpowiedzi do recenzentów i edytorów.

Podpis doktoranta

Podpis promotora



## Oświadczenie

Niniejszym potwierdzam swój procentowy udział w przygotowanie publikacji:

### Publikacja 4.

S. Prus (70%), P. Kulpiński (10%), E. Matyjas-Zgondek (10%), K. Wojciechowski (10%).  
Mechanism of bonding reactive dyes with copolymer (chloromethyl)oxirane-1H-imidazole  
cationised cellulose. *Materials* 2022, 15 13, 4664. doi.org/10.3390/ma15134664

Wkład doktoranta w przygotowanie publikacji obejmował:

- przygotowanie koncepcji badań gęstości elektronowej,
- przeprowadzenie analizy konstytucyjnej zastosowanego do badan polimeru,
- przeprowadzenie pomiarów spektrofotometrycznych,
- przygotowanie oraz redakcję manuskryptu,
- przegląd literaturowy,
- przygotowanie warstwy graficznej,
- analizę oraz zilustrowanie zebranych danych,
- opracowanie odpowiedzi do recenzentów i edytorów.

Podpis doktoranta

Podpis promotora



## Oświadczenie

Niniejszym potwierdzam swój procentowy udział w przygotowanie publikacji:

### Publikacja 5.

S. Prus (55%), P. Kulpiński (10%), E. Matyjas-Zgondek (10%), J. Rutowicz (15%),  
K. Wojciechowski (10%). The Light Fastness of the Reactive Dyes on Cationized Cellulose,  
Journal of Natural Fibers, 20:2, 2215995, DOI: 10.1080/15440478.2023.2215995

Wkład doktoranta w przygotowanie publikacji obejmował:

- selekcja materiałów do badań odporności na światło
- przeprowadzenie analizy i dokonanie obliczeń,
- przygotowanie oraz redakcję manuskryptu,
- przegląd literaturowy,
- przygotowanie warstwy graficznej,
- opracowanie odpowiedzi do recenzentów i edytorów.

Podpis doktoranta

Podpis promotora