

XPS and contact angle study of cotton surface oxidation by catalytic bleaching

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Abstract

Surface chemistry and wetting properties of cotton fibres as affected by catalytic bleaching have been investigated. Two types of cotton fabric have been analysed: the regular and a model cotton fabric. In the regular – double scoured cotton fabric, cellulose was contaminated with both non-removable and removable impurities including different pigments. The model cotton fabric, previously freed of most removable impurities, was stained for the purpose of this study with one pigment only, i.e. morin, a component that is typically found in native cotton fibre. Bleaching effectiveness of the catalyst based bleaches has been compared to the non-catalyst based bleaching systems. Surface chemical changes of cotton have been identified by XPS. Contact angle and capillary constant of the cotton fabric have been measured applying the Washburn method. This approach has provided the tool to explore and to quantify the chemical and physical effects on cotton fibre after catalytic bleaching. The interrelationship between an increase in capillary constant and the removal of non-cellulosic impurities, characterised by the C1 component in C 1s XPS spectrum, has been elucidated.

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1. Introduction

Generally speaking, bleaching of cotton is an important process in the textile industry, being used to oxidise the impurities and colouring matter contained in fibres. Our previous research [1,2] has shown that short-time bleaching of cotton with hydrogen peroxide can be accomplished at temperatures as low as 30 °C by incorporating dinuclear tri- μ -oxo bridged manganese(IV) complex of the ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (MnTACN) [3] as the catalyst in the bleaching solution. To understand the role of the catalyst MnTACN in the bleaching process as well as the overall mechanism of the reaction of catalytic oxidation of colouring matter to colourless products, we have used a homogeneous model system based on morin (3,5,7,2',4'-pentahydroxyflavone) [4] – a pigment that is, together with gossypetin (3,5,7,8,3'4'-

hexahydroxyl flavone), typically found in native cotton fibre [5]. This study has pointed out the possibility of replacing H₂O₂ with O₂ as terminal oxidant in the catalytic bleaching system [6].

Nevertheless, the bleaching of cotton takes place in a heterogeneous system and phenomena other than interaction of active bleaching species with colouring matter present in fibres can also play an important role. Hence, the research has been taken one step further by investigating a heterogeneous system that included regular cotton fabric, as well as a model cotton fabric that has been prepared by staining with morin in order to mimic a raw cotton material. This approach provided the tool to explore and to quantify the chemical and physical effects on the cotton fibre surface caused by catalytic bleaching. Chemical surface changes on the cotton fibre are identified by X-ray Photoelectron Spectroscopy (XPS), whereas the water contact angle and the capillary constant are measured applying the Washburn method. The results obtained show an important interrelationship between the removal of non-cellulosic compounds and an increase in the capillary constant of the bleached cotton fabric.

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In order to get an integrated view, the results are compared to the bleaching effectiveness.

2. Surface chemistry of cotton

The chemical composition of cotton fibres varies with its variety and growth conditions [7,8]. Each cotton fibre is composed of concentric layers. The cuticle layer on the fibre itself is separable from the fibre and consists of wax and pectin materials. The primary wall, the most peripheral layer of the fibre, is composed of cellulosic crystalline fibrils. The secondary wall of the fibre consists of three distinct layers. All three layers of the secondary wall include closely packed parallel fibrils with spiral winding of 25–35° and represent the majority of cellulose within the fibre. The innermost part of cotton fibre – the lumen – is composed of the remains of the cell contents. Before boll opening, the lumen is filled with liquid containing the cell nucleus and protoplasm.

In general, cotton fibres are composed of mostly α -cellulose (88.0–96.5%). Non-cellulosic compounds in the fibres include protein (1.0–1.9%), wax (0.4–1.2%), pectin (0.4–1.2%), inorganics (0.7–1.6%), and other (0.6–8.0%) substances. Most of the non-cellulosics are located on the outer layer of fibres, except for protein, inorganic salts and colouring matter, which have been found in the fibre lumen. While these non-cellulosic compounds play an important role during cell growth and development, they are presenting an impermeable barrier to liquor penetration and are responsible for yellow/brown appearance of native cotton. Thus, they have to be removed thoroughly by scouring and bleaching, in order to enable efficient subsequent wet processing of textile material (i.e. dyeing and finishing).

The current development of new fibre surface modification methods as well as need to fundamentally understand change in surface fibre chemistry after conventional processes, such as scouring and bleaching and how it affects the properties of final textile products, has highlighted the interest for the application of the XPS technique. The use of XPS to study the chemistry of chemically modified cotton fibres was pioneered by Soignet et al. [9]. Since then, XPS has been used in many investigations of surface chemistry of cellulosic fibres [10–13], including the surface composition of paper and wood fibres [14–16]. Mitchell et al. [17] have recently published on surface chemical analysis of raw, scoured and hydrogen peroxide bleached cotton material. They have successfully analysed the surface chemical composition of raw unscoured cotton by XPS and ToF-SIMS (Time of Flight Secondary Ion Mass Spectrometry). The presence of non-cellulosic material at the fibre surface has been established and determined to be a complex mixture of fatty acids, alcohols, alkanes, esters and glycerides. The effect of bleaching and especially scouring was to reduce the surface concentration of these materials, but even after these treatments some non-cellulosic material residue was still detected at the fibre surface.

3. Wetting properties of cotton

For effective processing (dyeing and finishing) and maintenance (cleaning) of cotton assemblies involving aqueous media,

improved and uniform water wetting is essential, because it facilitates the transport of active reagents between and into the fibres. The purpose of scouring and bleaching is to confer these properties to cotton. Although it is commonly recognised that removal of non-cellulosic compounds improves water wetting and spreading on cotton, quantitative measurements of such a relationship have not been clearly established. Theoretical [18] and experimental [19,20] approaches for quantitative determinations of liquid wetting and retention in fibrous materials have been documented.

In the case of textile materials, the interactions with liquids are very complex. They involve several physical phenomena, such as wetting of fibre surfaces, spontaneous flow of a liquid into an assembly of fibres driven by capillary forces (wicking), adsorption on the fibre surface and possible diffusion of the liquid into the interior of the fibres [21,22]. In general, fibre assembly/liquid interactions depend on the wettability of fibres, their surface geometry, the capillary geometry of fabric, the amount and the nature of test liquid, and external forces (such as applied pressure).

Contact angles on single natural fibres can be measured either directly [23,24] or indirectly, using the modified Wilhelmy technique [22]. However, in the case of natural fibres the Wilhelmy method is hardly applicable, due to the wide variation in fibre perimeter and fibre shape [25]. Dimensional irregularities along the cotton fibre axis and in cross-sectional shapes complicate the measurements and thus affect the single-fibre contact angles. Greater variations in the measured contact angle might also be due to the inhomogeneous character of the fibre surfaces and therefore varying fibre surface wettability. Hsieh et al. [19,20] compared the measured contact angles on a variety of fabrics (natural and man-made textile fibres) with the wetting properties of single fibres. They found that contact angles derived from fabrics and single-fibre measurements were identical and that neither the existence nor the magnitude of liquid retention interfered with the contact angle determination from fabrics. However, the error range was broader for contact angles measured on single fibres.

4. Experimental

4.1. Bleaching procedure and sample preparation

Bleaching experiments with both regular (designated as the “as received”) and model cotton fabric were carried out in 300 ml wide neck Erlenmeyer flasks that were placed in a shaking water bath SW 21 (Julabo, Germany) controlled to $\pm 0.2^\circ\text{C}$ and with a shaking frequency of 150 rpm. Each flask was filled with buffer solution and once the target temperature achieved, a cotton fabric sample was introduced and required amounts of H_2O_2 (30 vol.%) and 1 mM stock solution of MnTACN added to make a final volume of 200 ml. In the experiments where H_2O_2 was replaced with O_2 , the bleaching solution was purged with air throughout the bleaching experiments. In each bleaching experiment 3 fabric strips with a total weight of 10 g were used. The conditions were as follows: liquor ratio, 20:1; [MnTACN], 10 μM ; [H_2O_2], 0.1 M; $\text{NaHCO}_3/\text{NaOH}$ buffer

Table 1
WI values for the “as received” fabric and model fabric before and after bleaching at 30 °C, pH 10.5 for 15 min

Sample label	Description	WI (Berger)
a	“as received” scoured once	46.00 ± 0.56
b	“as received” scoured twice	71.30 ± 0.66
c ^a	“b” treated in buffer solution	74.50 ± 0.33
d	“b” bleached with O ₂ /MnTACN	73.33 ± 0.42
e	“b” bleached with H ₂ O ₂	77.53 ± 0.46
f	“b” bleached with H ₂ O ₂ /MnTACN	80.93 ± 0.08
g ^b	“b” bleached with H ₂ O ₂ (at 70 °C, pH 11)	81.92 ± 0.29
h	“g” stained with morin (model fabric)	50.39 ± 1.10
i ^c	“h” treated in buffer solution	56.64 ± 0.31
j	“h” bleached with O ₂ /MnTACN	59.08 ± 0.37
k	“h” bleached with H ₂ O ₂	61.03 ± 0.21
l	“h” bleached with H ₂ O ₂ /MnTACN	79.70 ± 0.35

^a Blank for the “as received” fabric bleaching experiments.

^b Used for preparation of model fabric by staining it with morin.

^c Blank for the model fabric bleaching experiments.

pH 10.5, 30 °C, 150 rpm. After 15 min of the treatment the samples were removed, rinsed thoroughly twice in hot water and once in cold water, and dried at room temperature over night.

For bleaching experiments, we used both the “as received” and model cotton fabric. The “as received” cotton fabric (100% cotton woven plain fabric with a weight of unit area 105 g m⁻²) was previously desized and double scoured in industrial conditions (sample b, Table 1). Its whiteness index (WI) was 71 Berger units. The “as received” cotton fabric, desized and scoured once (sample a, Table 1), served as a reference only. Both fabrics were kindly supplied by Vlisco (Helmond, the Netherlands).

The main idea of producing the model cotton fabric was to take sufficiently white cotton fabric (which has most of the impurities removed) and to stain it in a controlled way with a pigment (morin) that mimics the natural cotton coloured impurities. Accordingly prepared model fabric mimics raw (unbleached) cotton fabric. The “as received” double scoured cotton fabric (sample b, Table 1) was used to produce the model fabric. To remove the coloured matter thoroughly, bleaching with H₂O₂ was carried out under the conditions that are characteristic for the conventional hydrogen peroxide bleaching process: liquor ratio, 20:1; [H₂O₂], 0.1 M; NaHCO₃/NaOH buffer pH 11, 70 °C. The bleached cotton fabric sample (sample g, Table 1) was subsequently stained with morin (sample h, Table 1). The staining procedure was as follows: liquor ratio, 20:1; [morin], 0.6 g/l; [NaCl], 2.5 g/l; NaHCO₃/NaOH buffer pH 11, 30 °C; 60 min; 130 rpm. After staining, the samples were rinsed twice in cold water for 60 min at a liquor ratio of 160:1.

4.2. Bleaching effectiveness

Bleaching effectiveness was evaluated by measuring the whiteness index with a spectrophotometer 968 (X-Rite, USA) set at 460 nm using D₆₅ illuminant and observer 10°. Four measurements of WI per piece of fabric were carried out. The XYZ scale was used to determine the WI applying the formula of

Berger [26] (Eq. (1)):

$$W_B = Y + 3.448Z - 3.904X \quad (1)$$

4.3. Surface chemical analysis

XPS analyses were performed to investigate the surface chemical changes of the cotton fibres using a PHI Quantera Scanning ESCA Microprobe spectrometer (Physical Electronics, USA). Two different spots were analysed per sample. The samples were irradiated with monochromatic Al K α X-rays (1486.6 eV) using a X-ray spot size with a diameter of 100 μ m and a power of 25 W. The standard take-off angle used for analysis was 45°, producing a maximum analysis depth in the range of 3–5 nm. Survey spectra were recorded with a pass energy of 224 eV (stepsize 0.8 eV), from which the surface chemical compositions were determined. In addition, high-resolution carbon (1s) spectra were recorded with a pass energy of 26 eV (stepsize 0.1 eV), from which the carbon chemical states were determined. All binding energies values were calculated relative to the carbon (C 1s) photoelectron at 285 eV applying a linear background subtraction method followed by C 1s curve deconvolution into three Gaussian's curves. Peak positions of these curves were fixed at 285.0 eV (C–C/C–H); 286.6 eV (C–O); and 288.1 eV (C=O/O–C–O) [27,28].

4.4. Wetting measurements

The wetting behaviour of cotton was characterised, according to the capillary-rise method, using a Processor Tensiometer K12 (software version K121, Krüss, Germany). The evaluation of the measured data was based on modifications of the Washburn equation for a single capillary (Eq. (2)) [29],

$$\cos \theta = \frac{2}{A^2 r} \frac{\eta}{\sigma \rho^2} \frac{m^2}{t} \quad (2)$$

which results from the combination of the expression for the Laplace pressure and the Hagen–Poiseuille equation for steady flow conditions [30–32], where σ , the liquid surface tension; θ , the solid/liquid contact angle; A , the cross-sectional area; r , the radius of the capillary; η , the liquid viscosity; ρ , the liquid density; m , the weight of the liquid that penetrates into the capillary, and t , the penetration time.

In the case of fibre assemblies, the geometry of the capillary system is unknown and, therefore, the factor $[2/A^2 r]$ is replaced by an unknown factor $1/c$, which leads to the modified Washburn equation (Eq. (3)):

$$\cos \theta = \frac{1}{c} \frac{\eta}{\sigma \rho^2} \frac{m^2}{t} \quad (3)$$

The factor $\eta/(\sigma \rho^2)$ reflects the properties of the test liquid, and m^2/t is to be measured. The constant c reflects the capillary geometry of the sample. Theoretically, the capillary constant for a porous solid is given by (Eq. (4)) [22]:

$$c = \frac{1}{2} \pi^2 r^5 n^2 \quad (4)$$

where r , the average capillary radius within the porous solid; n , the number of capillaries in the sample. From the Washburn data alone, r and n cannot be calculated independently, whereas the c factor can be determined quite reproducibly. The modified Washburn equation (Eq. (3)) can be applied by making the following assumptions: (1) the liquid flow is predominantly laminar in the “pore” spaces; (2) gravity is negligible; and (3) the pore structure of the porous solid or fibre assemblies is constant [33].

A detailed experimental procedure was given elsewhere [22]. In our experiment *n*-decane was used as a total wetting liquid ($\cos \theta = 1$) to determine capillary constant c [34]. Both capillary constant c and contact angle θ were determined as an average of five independent measurements performed always in the warp direction on the 2 cm \times 2 cm square fabric pieces cut from different (randomly chosen) locations on the sample. For each measurement the initial slope m^2/t of the function $m^2 = -t$ was determined using a second-order polynomial fit.

5. Results

5.1. Bleaching effectiveness

The results obtained for the WI are presented in Table 1. As it can be seen, the catalytic bleaching of the “as received” fabric (sample b) produces very high WI (~ 81) (sample f), whereas bleaching with H_2O_2 alone (sample e) does not reach the target value (above 80) for the WI under the same conditions. The target value has been established on wide experience that the provider of the cotton fabric has in industrial bleaching. The samples treated by O_2/MnTACN (sample d) and in buffer solution only (sample c) show a little change in WI.

For both the model fabric (sample h) and the “as received” double scoured fabric (sample b), the $\text{H}_2\text{O}_2/\text{MnTACN}$ bleaching system is more effective in terms of WI produced (WI ~ 81 , sample f; and WI ~ 80 , sample l) than the bleaching with H_2O_2 alone (WI ~ 78 , sample e; and WI ~ 61 , sample k).

5.2. Surface chemical analysis of cotton fibre

The only atoms analysable by XPS in pure cellulosic fibres are carbon and oxygen, since hydrogen cannot be detected due to the technique limitation. The chemical shifts of carbon (C 1s) in cotton fibres can usually be easily classified into four categories [17]: unoxidised carbon (C–C), carbon with one oxygen bond (C–O), carbon with two oxygen bonds (O–C–O or C=O) and carbon with three oxygen bonds (O=C–O). A detailed analysis of the oxygen (O 1s) peak is generally less useful. Thus, quantitative data on the surface chemical composition are mainly obtained from the O/C atomic ratio and the relative amount of each type of carbon (C 1s).

A low-resolution XPS scan is run to determine the percentages of the elements present at the cotton fibre surface before and after bleaching of both the “as received” cotton fabric and model cotton fabric (Fig. 1). As expected, the main elements detected are carbon and oxygen. Using area sensitivity factors, the oxygen-to-carbon (O/C) atomic ratio was calculated as an

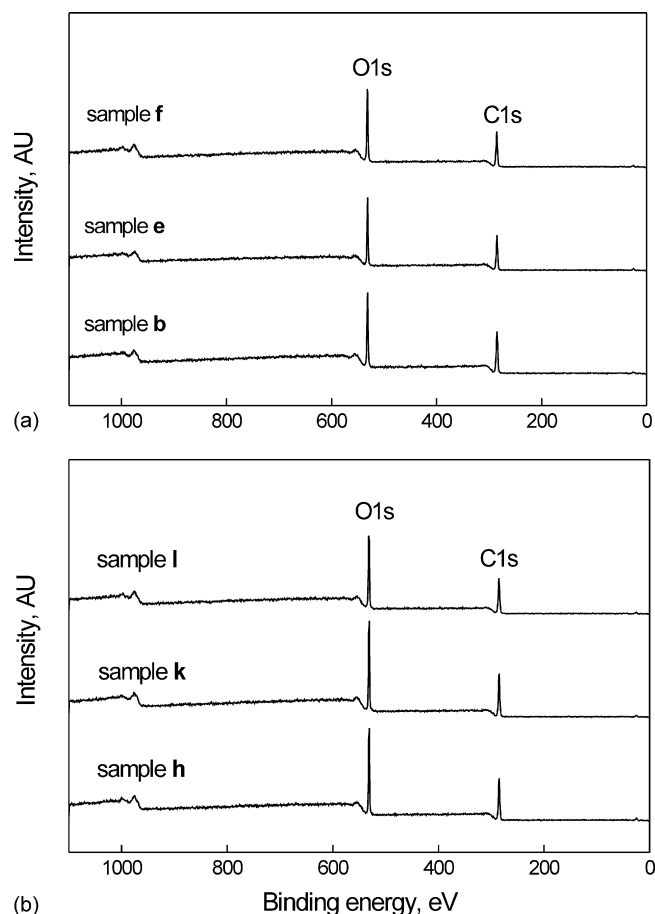


Fig. 1. Some XPS survey spectra of the “as received” (a) and model (b) cotton fabric before and after bleaching. Labelling scheme used in Table 1.

initial indication of surface oxidation. The O/C atomic ratio found for the “as received” fabric scoured once is 0.32 (sample a) and for the double scoured is 0.55 (sample b), while the value expected for pure cellulose is 0.83 (Table 2). The different bleaching treatments ($\text{H}_2\text{O}_2/\text{MnTACN}$; H_2O_2 or O_2/MnTACN) further increase the O/C atomic ratio where the highest value of 0.62 is obtained after the bleaching with the $\text{H}_2\text{O}_2/\text{MnTACN}$ catalytic system and H_2O_2 alone (samples f and e, respectively). It is interesting to note that the treatment in a buffer solution (sample c) also leads to a significant increase in the O/C atomic ratio (0.60).

When the “as received” fabric is replaced with the model fabric, the difference in the O/C atomic ratio after the bleaching with $\text{H}_2\text{O}_2/\text{MnTACN}$ (0.76, sample l) and H_2O_2 alone (0.69, sample k) becomes noticeable. It is important to realise that the “as received” double scoured cotton fabric (sample b) is used to produce the model fabric by staining it with morin (sample h) after it has been pre-treated with H_2O_2 at 70 °C (sample g). Knowing that, it is not surprising that sample g has the O/C atomic ratio of 0.63, which is similar to that of samples e and f. Nevertheless, the O/C of sample g is not significantly affected after staining it with morin (0.62). This cannot be explained by the similarity in stoichiometry of cellulose (O/C = 0.83) and morin (O/C = 0.47), but much lower proportion of morin when compared to that of cellulose at the cotton fibre surface.

Table 2
XPS analysis of the “as received” and model fabric before and after bleaching

Sample label ^a	O/C	Binding energy (eV)		
		285.0	286.6	288.1
		C–C or C–H aliphatic	C–OH or C–O– alcohol, ether	O–C–O or C=O double ether, carbonyl
		C1 (at.%)	C2 (at.%)	C3 (at.%)
a	0.32 ± 0.02	60 ± 2	32 ± 0	8 ± 2
b	0.55 ± 0.01	35 ± 2	52 ± 2	13 ± 1
c	0.60 ± 0.01	27 ± 1	58 ± 2	15 ± 1
d	0.60 ± 0.04	27 ± 2	60 ± 0	13 ± 1
e	0.62 ± 0.01	27 ± 1	59 ± 1	14 ± 0
f	0.62 ± 0.02	23 ± 3	59 ± 2	18 ± 1
g	0.63 ± 0.00	26 ± 2	58 ± 0	15 ± 2
h	0.62 ± 0.05	25 ± 2	59 ± 2	16 ± 1
i	0.67 ± 0.02	21 ± 1	64 ± 1	15 ± 1
j	0.69 ± 0.01	19 ± 1	66 ± 2	15 ± 1
k	0.69 ± 0.01	18 ± 0	66 ± 1	16 ± 1
l	0.76 ± 0.01	19 ± 2	69 ± 1	12 ± 3
Cellulose (theor.)	0.83			
Morin (theor.)	0.47			

^a Labelling scheme used in Table 1.

Similar to the “as received” cotton fabric, the treatment of the model fabric in a buffer solution (sample i) contributes approximately to the same increase in the O/C atomic ratio as in case of bleaching with H₂O₂ (sample k) and O₂/MnTACN (sample j). On the other hand, after bleaching of model fabric with the H₂O₂/MnTACN system, the O/C atomic ratio is remarkably increased (up to 0.76) which is the highest value obtained and hence the most comparable to the theoretical value for cellulose (0.83). The observed increase in the O/C atomic ratio cannot be assigned to the oxidation of morin at the fibre surface, as it has been seen that staining with morin (sample h) had no impact on the O/C atomic ratio of the original fabric (sample g). This indicates that more complex phenomena occur during bleaching, apart from oxidation of pigment present in cotton fibre.

The fact that the O/C atomic ratio obtained for all samples analysed (a–l) is much lower than in cellulose indicates that the surface of the unbleached cotton fibres and, to the less extent, of bleached cotton fibres, does not consist of pure cellulose. The low O/C atomic ratios obtained are due considerable amounts of carbon atoms without oxygen neighbours (C1 in Table 2) which should not be present in pure cellulose. It is well known that laminar layers of waxes, proteins and pectin, which originally more or less totally conceal the cellulose backbone, cover natural cotton fibres. Since waxes consist mainly of unoxidised type of carbon, C1 can be taken as a marker for the presence of such substances together with the O/C atomic ratio.

To obtain more detailed information, a high-resolution scan is conducted on the C 1s region for all samples listed in Table 2 in order to determine the types and amounts of carbon–oxygen bonds present (Figs. 2 and 3). The theoretical binding energies and corresponding bond types are shown in Table 2. Cellulose is made up of a chain of glucopyranose units, joined at the 1 and 4 positions through elimination of water. Therefore, it is expected

that pure cellulose exhibits a two-component C 1s XPS spectrum (C2 and C3 in Table 2), having the ratio of lower binding energy ($E_B = 286.6$ eV) to higher binding energy ($E_B = 288.1$ eV) components of 0.83:0.17 (or $\sim 5:1$). That is, the carbon bonded to two ether linkages appears at higher E_B while all other carbons, whether bonded to an ether or alcohol oxygen, appear at the lower E_B (C3 and C2, respectively).

In practice, however, additional peaks are found because of the presence of non-cellulosic impurities which, even though not considered to be covalently bound to the fibre, need to be removed in bleaching.

The C 1s XPS spectra and deconvolution peaks of the “as received” and model fabrics before and after bleaching with H₂O₂/MnTACN and H₂O₂ are presented in Figs. 2 and 3, respectively. The C 1s peak is deconvoluted into three subpeaks, C1, C2, and C3. The C1 peak does not include a carbon–oxygen bond, whereas C2 and C3 both include a carbon–oxygen bond. The experimentally determined ratios of the subpeaks for the “as received” cotton fabric scoured once (sample a) and twice (sample b) are C1:C2:C3 = 0.60:0.32:0.08 and C1:C2:C3 = 0.35:0.52:0.13, respectively (Fig. 2, Table 2), as compared to the abovementioned theoretical values of C1:C2:C3 = 0:0.83:0.17. This shows that the major chemical oxidation state at cotton fibre surface occurs at binding energy of 285.0 eV after the first scouring process, attributed to aliphatic C–C, C–H bonding only, indicating that it is of non-cellulosic origin.

In addition, the second scouring produces a significant effect on the C 1s XPS spectrum, where a reduction in the spectral contribution of the C1 component from approximately 60 to 35 at.% takes place. The C 1s XPS spectrum of the H₂O₂ and O₂/MnTACN bleached fabric (sample e and sample b), together with the blank (sample c), shows further, and to the same extent, decrease in component C1 (27 at.%) (Table 2). After the

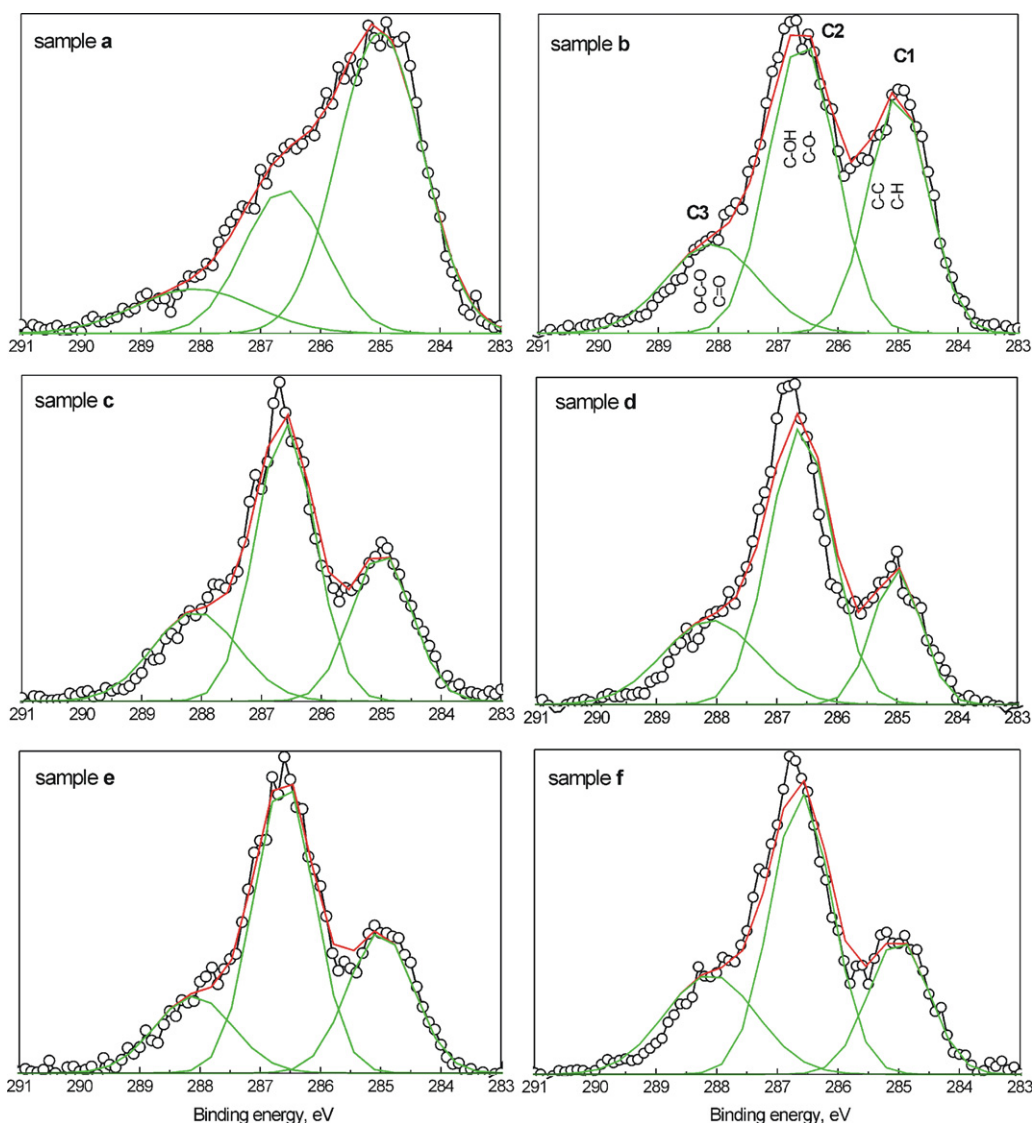


Fig. 2. XPS scan of C 1s region of the “as received” cotton fabric before and after bleaching. Labelling scheme used in Table 1.

$\text{H}_2\text{O}_2/\text{MnTACN}$ bleaching (sample f), the minimum percentage of this component is reached (23 at.%), showing that this system has the greatest effectiveness of removal of non-cellulosic compounds.

The lack of any further reduction in component C1 after bleaching of model fabric with $\text{H}_2\text{O}_2/\text{MnTACN}$ (19 at.%, sample l) as compared to that of model fabric bleached with H_2O_2 and O_2/MnTACN (18 and 19 at.%, samples k and j, respectively) (Table 2) suggests strong substantivity and inertness of the bound organic material. This is perhaps not entirely unexpected since even with “pure” cellulose materials there is always spectral intensity at 285 eV, typically contributing 10–20 at.% of the C 1s XPS spectral intensity [9–13,17] indicating either hydrocarbon contamination or polymer modification.

The magnitude of the C2 peak of the “as received” double scoured cotton fabric (52 at.%, sample b) is affected to approximately the same extent after bleaching with $\text{H}_2\text{O}_2/\text{MnTACN}$ (59 at.%, sample f) as after bleaching with O_2/MnTACN and H_2O_2 (samples d and e, respectively) (Table 2), whereas the

$\text{H}_2\text{O}_2/\text{MnTACN}$ bleaching of the model fabric (sample h) leads to a larger increase of spectral contribution of the C2 component (69 at.%, sample l) than after the O_2/MnTACN and H_2O_2 bleaching (both 66 at.%, samples j and k, respectively).

Finally, it is shown in Table 2 that the $\text{H}_2\text{O}_2/\text{MnTACN}$ bleaching of the “as received” fabric results in a greater increase of the spectral contribution of the C3 peak (from 13 to 18 at.%, sample b and sample f) compared to the O_2/MnTACN (sample d) and H_2O_2 bleaching (sample e) due to the formation of surface carbonyl species, which in addition to the O–C–O spectral component, contributed to the observed spectral increase at the C 1s binding energy of 288.1 eV. On the contrary, after the bleaching of the model fabric (sample g) with $\text{H}_2\text{O}_2/\text{MnTACN}$ (sample l), the contribution of the C3 component is reduced from 16 to 12 at.% suggesting that two concomitant processes could be postulated to interpret the effect of the $\text{H}_2\text{O}_2/\text{MnTACN}$ activity on the cellulose fibre surface: oxidative degradation and removal of low-molecular-weight carbonyl-rich products into the bleaching solution.

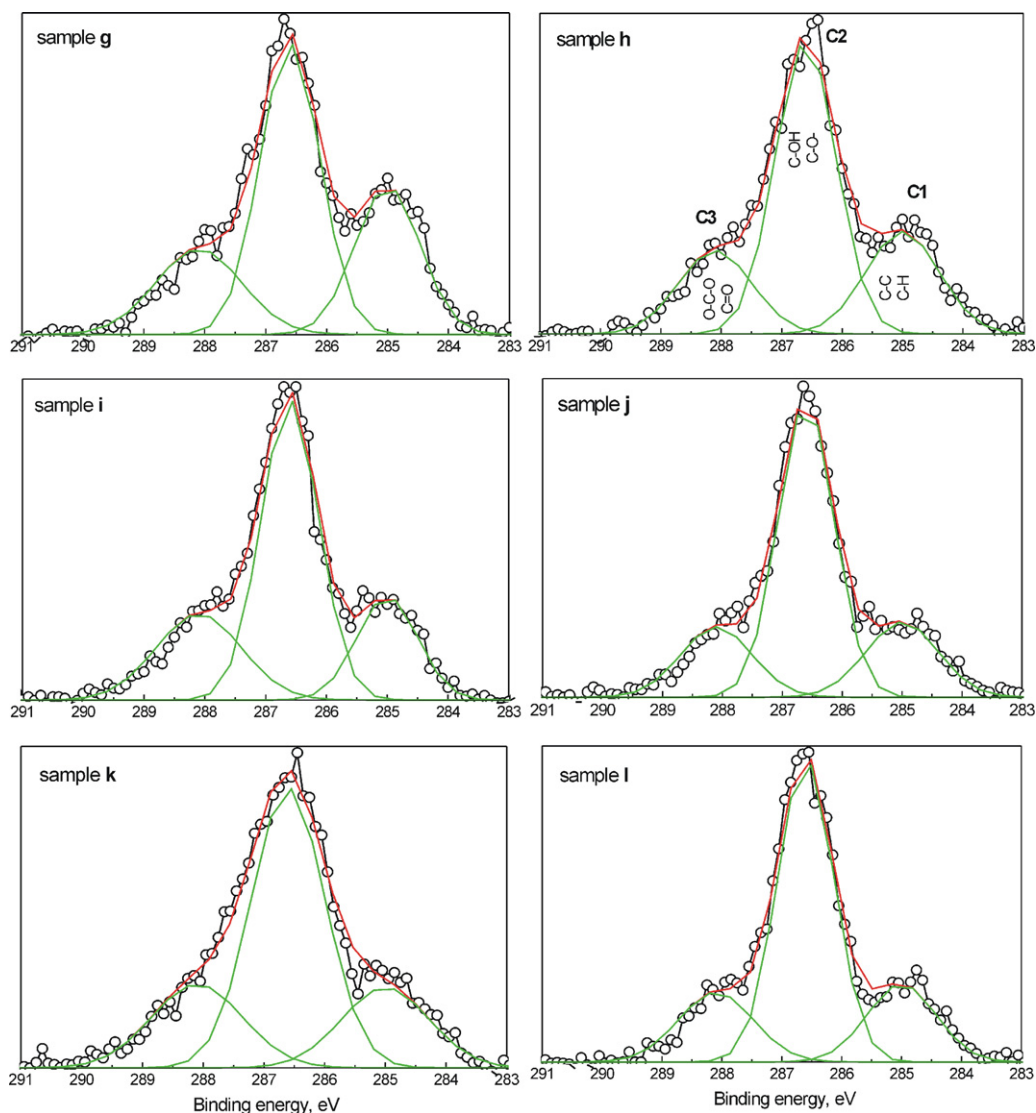


Fig. 3. XPS scan of C 1s region of the model cotton fabric before and after bleaching. Labelling scheme used in Table 1.

5.3. Contact angle and capillary constant

Water contact angles of the “as received” and model cotton fabric as a function of bleaching in the presence and absence of the catalyst MnTACN are determined. The same contact angle of *ca.* 50° is obtained for all bleached samples and the blanks listed in Table 1. This is probably not surprising when having in mind that the “as received” fabric is double scoured and therefore hydrophilic in nature. Similar results regarding the contact angle are obtained after bleaching of the model cotton fabric. The “as received” once scoured fabric (sample a) has, however, a contact angle above 90° . This can be related to the chemical composition of the fibre surface (Fig. 2, Table 2), where it is possible to see that C1 component is predominant in the C 1s XPS spectrum of this sample (60 at.%). This is direct evidence that the fibre surface is to a very high extent covered with non-cellulosic compounds. After the second scouring process, the proportion of C1 component decreases from 60 to 35 at.%, which certainly leads to a remarkable decrease in contact angle. In

this case, the bleaching (or the treatment in a buffer solution only) is not critical to the contact angle. It is likely that the majority of cotton fibre impurities that can strongly affect the contact angle are removed by repeated scouring rather than by the bleaching process. On the contrary, even small differences between the different bleaching treatments can be registered by plotting the capillary constant c (Fig. 4). The error bars in the plot represent the standard deviation of the measured wetting rate m^2/t averaged over at least five single measurements.

Capillary constant c for the “as received” sample b ($6.8 \times 10^{-7} \text{ cm}^5$) increases to $8.5 \times 10^{-7} \text{ cm}^5$ for the sample f bleached by $\text{H}_2\text{O}_2/\text{MnTACN}$. Interestingly, the treatment in a buffer solution (sample c) is of the same effect ($8.2 \times 10^{-7} \text{ cm}^5$) as bleaching with H_2O_2 (sample e) under the conditions applied. Bleaching of model fabric with $\text{H}_2\text{O}_2/\text{MnTACN}$ (sample l) causes a remarkable increase in the capillary constant (up to $10.2 \times 10^{-7} \text{ cm}^5$) when compared to that of the H_2O_2 bleached sample ($9.0 \times 10^{-7} \text{ cm}^5$, sample k). The increase in capillary constant c , i.e. the average capillary radius (Eq. (4)), is in

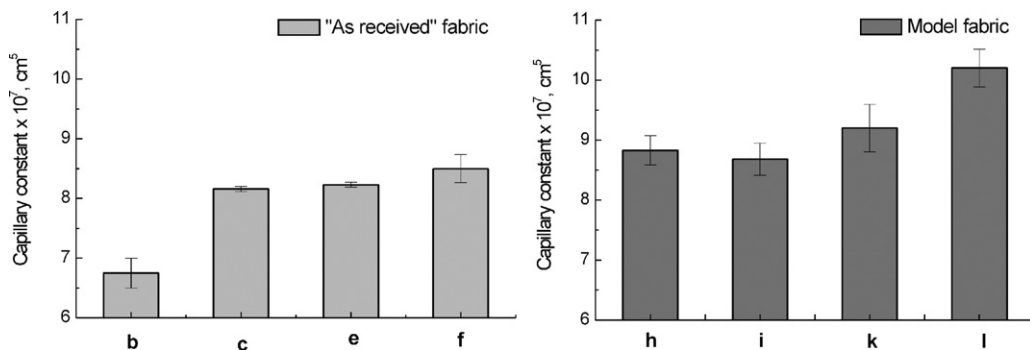


Fig. 4. Capillary constant as a function of bleaching in the presence and absence of the MnTACN catalyst. Labelling scheme used in Table 1.

agreement with the results published recently by Volkov et al. [35] and indicate that simultaneously with the chemical action, i.e. discolouration of cotton fibre pigments, an increase in pore size takes place due to the partial removal of the bleaching products.

5.4. Capillary constant versus removal of the bleaching products

It is evident from Eq. (4) that the capillary constant c is very sensitive to a change in average capillary radius within the porous solid ($c \sim r^5$). An increase in the capillary constant of cotton fabric after bleaching, i.e. an increase in the average capillary radius, can be explained by a lower concentration of component C1 (Fig. 5a) assigned to a removal of non-cellulosic compounds. A decrease in component C1 is followed by an increase in component C2 (Table 2) that also correlates with an increase in the capillary constant (Fig. 5a). Consequently, an increase in the O/C atomic ratio interrelates with an increase in the capillary constant (Fig. 5b). As it can be seen in Fig. 5, the capillary constant changes exponentially with the percentage of C1 and C2 components and the O/C atomic ratio.

It is interesting to note that although the proportion of component C1 slowly gets to 17–19 at.% (Fig. 5a), which is attributed to the presence of non-removable impurities [17], the capillary constant continues with a considerable increase from 9.0×10^{-7} to $10.2 \times 10^{-7} \text{ cm}^5$. This means that a further increase in capillary constant c , when only non-removable impurities are present at the cotton fibre surface, can be related to the removal of chain-shortened cellulose into the bleaching solution. It is well known that all cellulosic fibres can be damaged by oxidising bleaches [36,37]. Oxidation products are termed “oxycellulose”, whereby $-\text{OH}$ groups are converted to aldehyde, ketone, and carboxyl groups. Hydrolysis reactions sometimes occur during bleaching with the formation of chain-shortened “hydrocellulose” [38]. Hydrocellulose formation breaks glycosidic bonds and produces one reducing (aldehyde) and one non-reducing end group.

At the same time, this can be an explanation for the decrease in proportion of the C3 component at the fibre surface for the model fabric bleached with $\text{H}_2\text{O}_2/\text{MnTACN}$, whereas for the “as received” fabric proportion of the C3 component increases (Table 2). The different result concerning the change in C3 component obtained after the $\text{H}_2\text{O}_2/\text{MnTACN}$ bleaching of the “as received” and model fabric is in fact the consequence of

the different chemical composition at the cotton fibre surface, whereas the presence of C1 component plays an important role. In the presence of a significant amount of C1 component at the cotton fibre surface, non-cellulosic compounds represented by this component can be the target of catalytic action and therefore competitive with pigments and cellulose for the catalyst molecules. On the other hand, in the absence of the (removable) C1 impurities chain-breaking oxidative reactions are becoming predominant since more cellulose bonds are vulnerable on the “bare” surface.

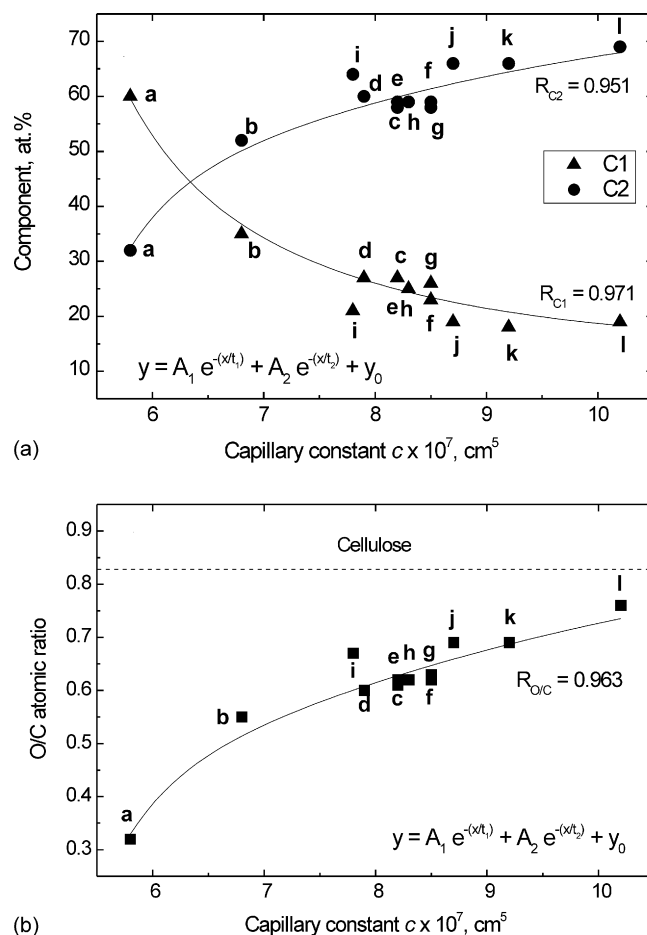


Fig. 5. Effect of removal of non-cellulosic compounds, represented by C1 and C2 component (a) and the O/C atomic ratio (b), on capillary constant. Labelling scheme used in Table 1.

6. Conclusions

The bleaching experiments in this study were done with two different cotton fabrics: the regular (designated as the “as received”) and model cotton fabric. The model fabric obtained by staining with cotton pigment morin and containing mainly non-removable non-cellulosic impurities provided the tool to differentiate between pigment discolouration and other phenomena that occur during catalytic bleaching by examining the chemical and physical effects on cotton fibre surface.

Apart from conferring the highest whiteness to both the “as received” and model fabric, the ability of the $\text{H}_2\text{O}_2/\text{MnTACN}$ catalytic bleaching system to remove non-cellulosic compounds was also remarkable compared to the non-catalytic H_2O_2 bleaching system in case of the “as received” fabric. The use of model fabric showed that further removal of these impurities is very difficult indeed.

The capillary constant of the cotton fabric changed after bleaching. The highest values were obtained using the $\text{H}_2\text{O}_2/\text{MnTACN}$ catalytic system in case of both the “as received” and model fabric. The increase in capillary constant (indirectly showing the increase in the average capillary radius), indicated that simultaneously with the chemical action, i.e. discolouration of cotton fibre pigments, an increase in pore size took place due to the partial removal of the bleaching products. Hence, the increase in capillary constant was interrelated with the removal of non-cellulosic (“wax-type”, characterised by the C1 component in C 1s XPS spectrum) bleaching products during bleaching and subsequent rinsing operations.

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