

Stanisław Pruś\*,  
Piotr Kulpiński,  
Edyta Matyjas-Zgondek

Lodz University of Technology,  
Department of Man-Made Fibres  
ul. Zeromskiego 116, 90-924 Lodz, Poland  
\* e-mail: rgbcolor@op.pl

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

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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.

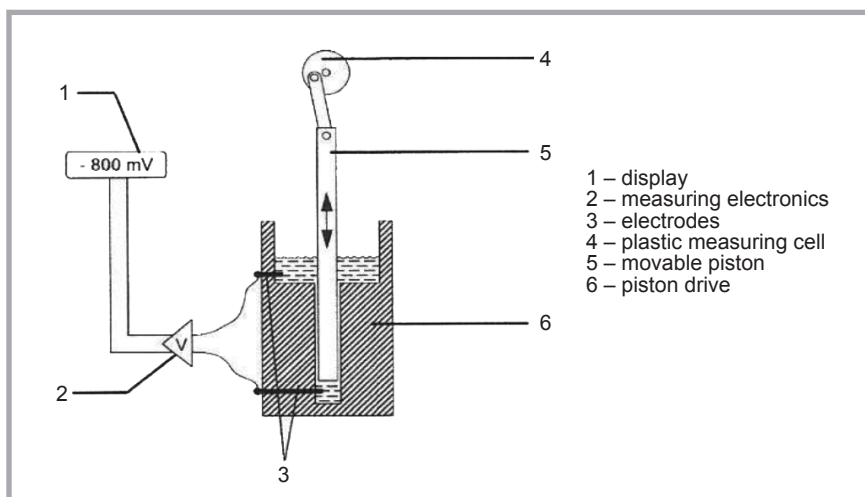


Figure 1. Schematic of test setup Muetek PCD 03 pH.

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

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:

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

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



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

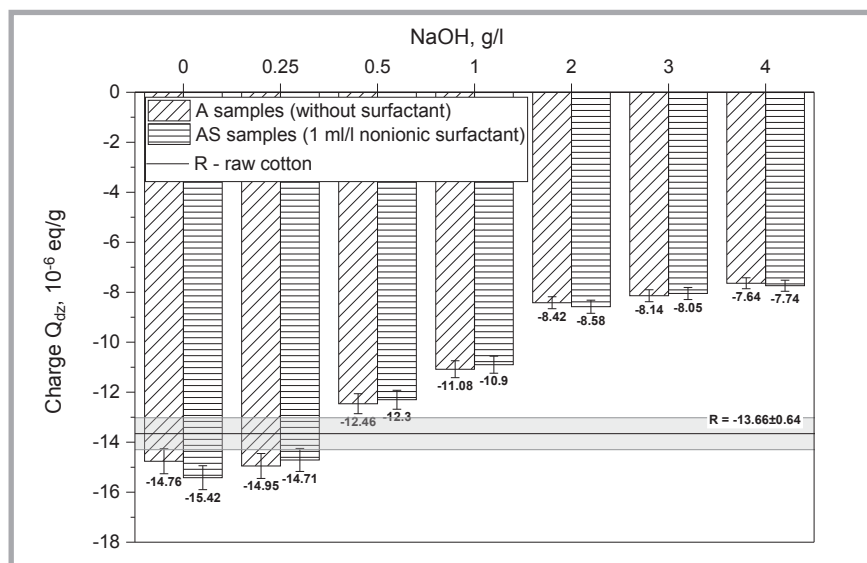
All measurement data in our study are presented in **Table 2**.

### 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.

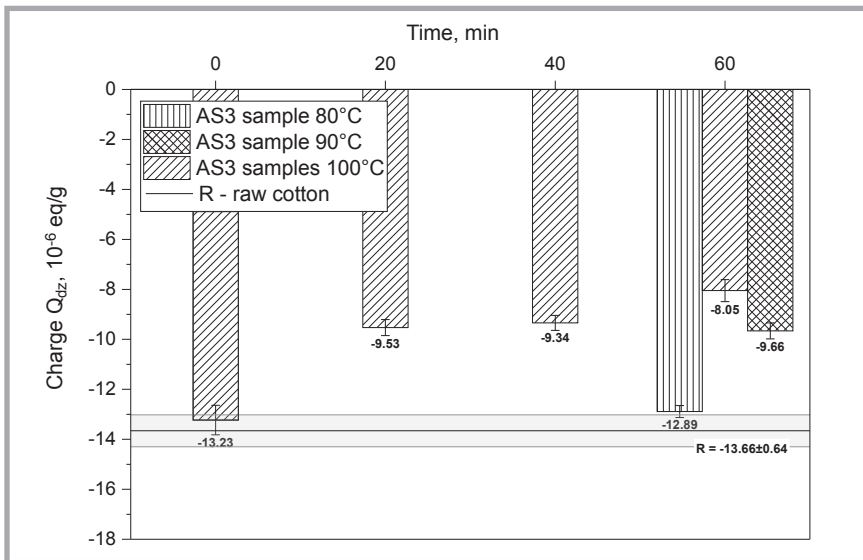
Sample	$Q_{dz}$ , $10^{-6}$ eq/g	$\Delta W$ , %	$WI$	$WET$ , s
R	-13.66	–	5.47	No wettability <sup>1)</sup>
A0	-14.76	1.93	18.61	No wettability <sup>1)</sup>
A0,25	-14.95	2.04	20.7	No wettability <sup>1)</sup>
A0,5	-12.46	2.3	22.02	No wettability <sup>1)</sup>
A1	-11.08	3.3	24.14	300
A2	-8.42	3.73	28.82	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



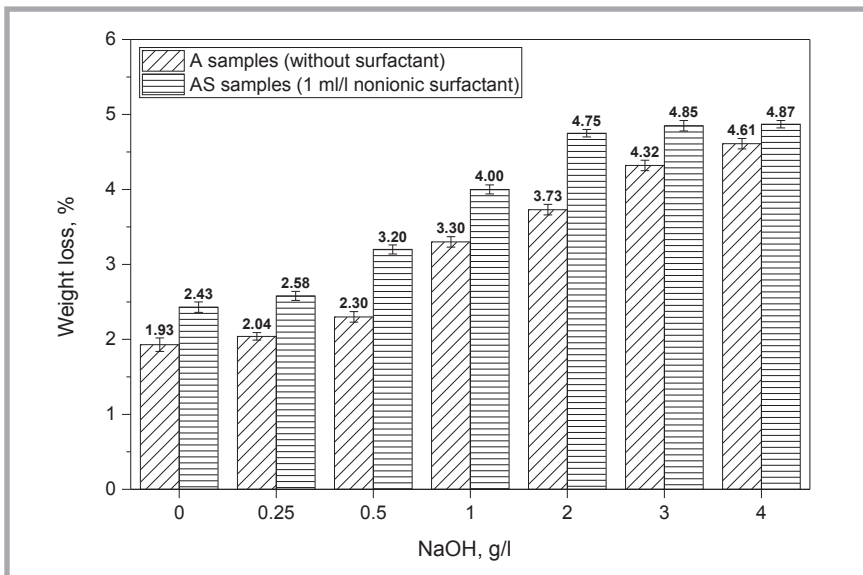
**Figure 2.** Changes in the specific charge amount on the surface of raw cotton knitted fabrics after alkaline treatment with and without the presence of non-ionic surfactant (pre-treatment temperature 100 °C).

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<sub>23</sub> to C<sub>34</sub> (n-tricontanol, 1-octacosanol and coloured gossypol) with a melting point in the range between 83-214 °C, saturated and unsaturated hydrocarbons C<sub>27</sub> to C<sub>32</sub> (heptacontane, triacontane, untriacontane, dotriacontane), as well as some phytosterols and sterols C<sub>20</sub>H<sub>50</sub> (β- and γ-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

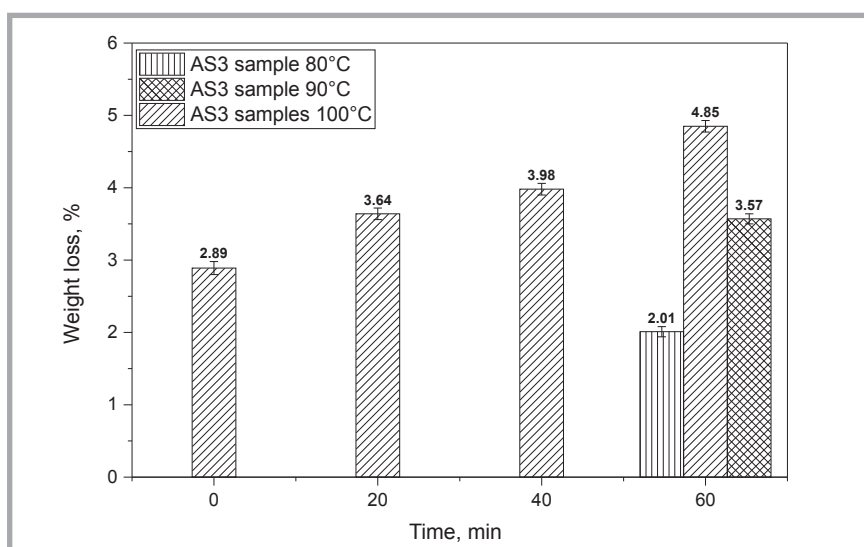
subject, but it can be surmised that the alkaline hydrolysis of proteins on raw cotton surfaces creates amino acids, which in the presence of a non-ionic surfactant can be emulsified and removed more easily. It is known that compounds containing nitrogen cause yellowing on cotton fibres.

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.

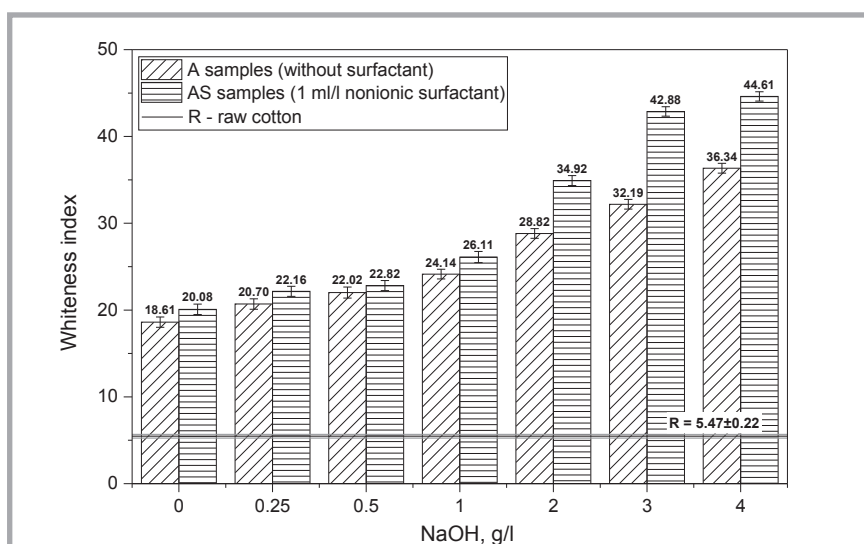
#### Wettability of raw cotton knitted fabrics after alkali treatment

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**.

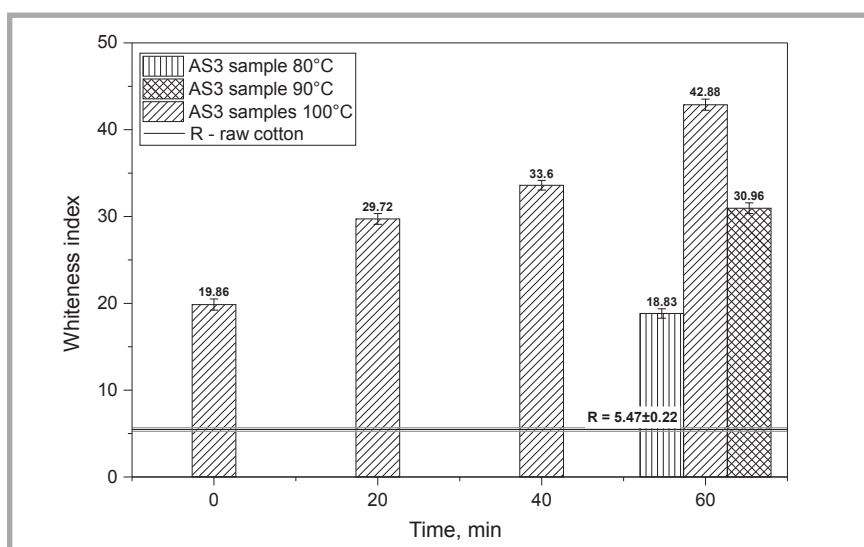
The front of the water spot and the absorbency time determined the wettability of samples (as in absorbency test method – AATCC 79-2000), whereas the spreading view of the dye indicated the quality of purification of the cotton surface after the pretreatment process. The spot on well pretreated fabric 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.

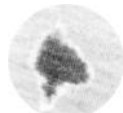

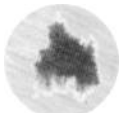










**Figure 6.** Changes in the whiteness index of raw cotton knitted fabric after alkali treatment with and without a non-ionic surfactant (pre-treatment temperature 100 °C).









**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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