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ORIGINAL CONTRIBUTION

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The influence of classical and enzymatic treatment on the surface charge of cellulose fibres

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Abstract Natural cellulose fibres comprise several non-cellulose compounds and cationic trash which cause problems during different adsorption processes such as dying, printing, final fiber finishing and coating. Therefore the pre-treatment (classical NaOH or environmental friendly enzymatic treatment, demineralisation) is the most important step in cellulose textile prefinishing – cleaning. An appropriate way to describe the success of different processes in fiber pre-treatment which result in distinct surface charge is the determination of electrokinetic properties – zetapotential (ZP) of fibers and textile materials. The zetapotential was determined by streaming potential measurements as a function of the pH and the surfactant concentration in the liquid phase.

Cellulose fibers in an aqueous medium are negatively charged due to their characteristic carbonyl and hydroxyl groups. The degradation and removal of specific hydrophobic non-cellulose compounds which cover the primary wall of the cellulose polymer change the surface charge.

The ZP is mainly influenced by waxes, their removal decreases the negative ZP. This result is obtained by the classical chemical process as well as by an environmentally friendly enzymatic treatment.

Our results indicate that the progress of textile treatment and purification is reflected by the zetapotential of the fabrics. This method enables the estimation of the process'es progress and the interaction between components of the liquid phase and the fibre surface.

Key words Cellulose fibres – non cellulose substances – enzymes – surface charge – zetapotential

Introduction

The final quality of textile fibers, the interaction between fibres and specific compounds of the finishing or dyeing process strongly depend on the quality of the pre-treatment process. Due to the fact, that all these processes are performed in an aqueous environment, the surface charge of the fibres should express very clearly the modifications at different process steps.

The aim was to determine, if electrokinetic measurements are able to indicate the degradation of small amounts of non cellulose compounds, which are mainly located on the fibre surface.

The natural cotton fibre is the most popular cellulose fibre, it comprises several non cellulose compounds

Table 1 Avarage cotton composition

Content of:	% in the cross-section of the fibre	% in the primary wall
Cellulose	88 to 96	52
Pectins	0, 7 to 1, 2	12
Waxes	0, 3 to 1, 0	7
Proteins	1, 1 to 1, 9	12
Ashes	0, 7 to 1, 6	3
Other comp.	0, 5 to 1, 0	14

Table 2 Pretreatment operations of cotton fibres /6/

Processing stage	Purpose of processing	Kind of process
Alkaline treatment using caustic soda	– removal of non cellulose compounds – swelling of the cellulose – disintegration of seed husks – cleaning and prebrightening – removal of disturbing metals	extraction swelling
Acid treatment using different acid sequestering agents	– removal of alkaline earths and heavy metals – cleaning and prebrightening – improvement of wetting properties	demineralisation
Enzymatic treatment using specific enzymes (pectinase, lipase, cellulase..)	– removal of waxes, pectins, hemicellulose – improvement of wetting properties	depolymerisation degradation

which have to be removed during the textile treatment process.

It has to be distinguished between the whole fibre and the primary wall. The primary wall of the fibre contains almost all of the non-cellulose compounds and it is this section that creates problems – poor adsorbency, poor wettability and other undesirable textile properties. The pretreatment processes are applied to this part of the fibres.

The primary wall of the cotton fibre consists of approximately 50% cellulose and 50% of other compounds as hemicellulose, pectins, proteins, waxes and mineral salts /1/. The secondary wall makes up more than 90% of the mass of the matured fibre. In contrast to the primary wall, it consists of about 90% cellulose. The quantity of analytically defined components of the fibre is more or less dependent on the growth factors, the provenience and the degree of maturity.

Cellulose is a linear polymer of glucose units linked by β–1.4 glycoside bonds. The polymer chains are associated together to twisted rope-like structures by intermolecular hydrogen bonds and these ropes are associated to form fibres.

Closely associated with cellulose in plant walls are poorly-defined groups of low molar mass polysaccharides – the hemicellulose /2, 3/.

Pectins with their characteristic carboxyl groups are present in the form of insoluble calcium, magnesium and/or iron salts.

Cotton waxes represent problematical substances, since they are not water-soluble. These are pure hydrocarbons, fatty alcohols, fatty acids and different esters. They can only be removed with the help of a solvent (petrol–ether extraction) or by a saponification process (alkaline process).

The ashes are the alkali and earth metals potassium, calcium and magnesium. In most cases they are also present in cotton /4/.

Iron ions are problematical compounds due to their catalytic effect, causing damage during peroxide bleaching.

In addition to these components, cotton also contains about 0.5% of natural dyestuffs and pigments, which have to be removed by different oxidation processes. They are mainly associated to such compounds as hemicellulose, tannic acid or pectin and are not soluble in water /5/.

All non cellulose compounds have to be removed during the preparation of the fibres. To achieve the aim of the textile pretreatment, namely the cleaning of the raw fabrics by means of extraction, demineralisation and swelling processes, various operations are employed:

- alkaline treatment
- acid treatment
- enzymatic treatment

Table 2 lists some typical textile pretreatment processing stages of cotton, including purpose and kind of operation.

The previously described processes performed in an aqueous environment degrade non cellulose compounds, render active groups of the cellulose polymer surface accessible and cause swelling of polymer /7/.

Electreokinetic measurements are known to be a useful method for electrochemical characterization of polymer surfaces. Their contribution to surface characterization of cellulose polymers is especially important since the presence of electrical charges is an aspect which very often determines technological relevant interaction phenomena with the ingredients of the liquid phase as several kinds of ions, acid complex forming agents, specific enzymes, surfactants, dyes. An advantage estimating the electrokinetic charge related to the shear plane, which is somewhat different to the solids surface, is to get a more realistic impression of the electric charges interacting with the surroundings than it is possible by the use of surface-charge data. Variation of the solutions pH and electrolyte content enables the estimation of the acidic/basic and polar/nonpolar character of the solid surface from zetapotential data, since characteristic changes in the zetapotential values can usually be observed.

The pH dependence of the zetapotential at surfaces bearing charges, dominated by dissociation events, gives informations about the acidic or basic strength of the functional surface groups indicated by the position of isoelectric points and zetapotential plateau ranges. The specific ion adsorption, another event possibly determining the surface charge, is recognizable in the course of zetapotential with electrolyte concentration and depends on the surface properties of the polymer as well as on the type and kind of electrolyte and adsorption behaviour of the solvent.

Some results published /8/ show that the zetapotential is an appropriate parameter to study the interaction between fibres and dyes, nevertheless the influence of different purification processes and the progress of purification of natural cellulose polymers was never investigated.

The streaming potential measurement is a suitable technique to investigate the electrokinetic properties of compact solid materials. Therefore we used it to determine the zetapotential of different pre-treated or specifically purified cellulose fibres to obtain information about the adsorption ability of this natural textile polymer and its interaction with components of the liquid phase.

Material and methods

The material used for analysis was 100% pure cotton (BW).

Preparation methods

Removal of non cellulose compounds using textile pretreatment processes

– *Alkaline treatment*
(20 g/l NaOH; pH = 11.5; $t = 90$ min; T = 98 °C)

– *Demineralisation (acid treatment) – using sequestering agents (i.e. polyphosphonic acids) in acid environment*
(2 ml/l sequestering agent; pH = 2.7; $t = 30$ min; T = 98 °C)

– *Enzymatic treatment*
7.5 g cellulose material were treated in 153 ml 0.005 M citrate buffer at pH = 4.5 and T = 30 °C for 4 h. The following amounts of enzymes were applied:

– 1.2050 μl Schizophylum commune (S.c) filtrate (enzyme mixture containing xylanase, mannanase, cellulase) (3770 U/ml)
– 87 μl lipase (88.000 U/ml)
– 88 μl pectinase (90 U/ml)

Removal of individual non cellulose compounds applying specific methods

– *Petrol–ether extraction*
(Soxhlet extraction; min. 6 circles/hour)

– *HCl treatment*
(0.1 M HCl; 20 hours; 20 °C)

After each treatment the fibres were washed in destilled water until a conductivity less than 3 μs/m was reached.

Determination of the zetapotential

The streaming potential method was used, as it has been shown to be the most appropriate electrokinetic technique to study the zetapotential of fibres systems /9, 10/.

The streaming potential measurements were carried out using an Electrokinetic Analyser EKA manufactured by A. Paar K.G., Graz, Austria. The measurement is performed forcing an electrolyte solution through a fibre plug or along a sample surface which is placed in a measuring cell. The measuring cell containing the sample has to be the dominant hydrodynamic streaming resistance in the tubing system. Two measuring cells are available to investigate solids of different shapes (Fig. 1). By use of two silver/silver chloride electrodes and a pressure difference transducer connected to the input and output of the measuring chamber, the EKA registers the streaming potential data. The instrument's software permits calculation of the electrokinetic potential from the streaming potential data and, furthermore, measured solution parameters according to the Smoluchowski Eq. (1):

$$U = \frac{\xi \cdot \varepsilon \cdot \varepsilon_0 \cdot Q \cdot R \cdot \Delta p}{\eta \cdot L} \tag{1}$$

where U is the streaming potential, ξ is the zetapotential, η is the viscosity, Δp is the pressure difference, ε is the dielectricity constant, R is the resistance over the cell, L/Q is the length and cross section of the streaming channels.

The streaming potential values used for calculation were not obtained by single point measurements. The linearity of the streaming potential as a function of the pressure difference range of 25–350 mBar enables the use of the differential streaming potential, du/dp instead of the single point value to calculate the zetapotential with higher accuracy. The streaming potential of every sample was measured in 0.001 N KCl, the surface conductivity was not taken into account. The zetapotential was calculated according to the method of Fairbrother and Mastin /11/.

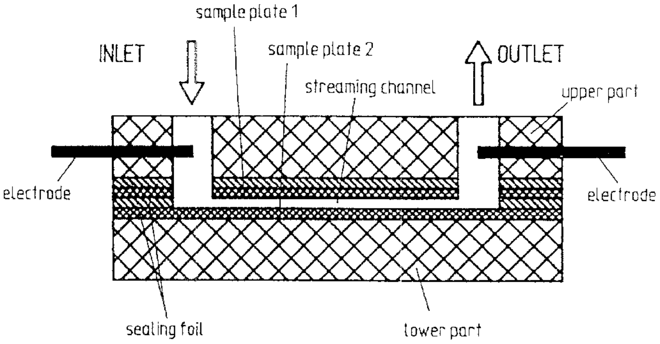


Fig. 1 Zetapotential measuring cell for fabrics, polmyer films and materials with flat surfaces

The here mentioned zetapotential values ZP_{max} are always these obtained at the constant part of the zetapotential – pH function in the alkaline region at pH = 9.

The ZP was investigated as a function of the pH (Figs. 2 and 4) and as a function of surfactant concentration (Figs. 3 and 5). The surfactant (N–Cetylpyridiniumchlorid N–CPC) concentration was increased step wise until the fibre was oppositely charged. The concentration at which the zetapotential = 0 mV is called the charge reversel concentration – CRC.

The ZP alteration reflects the adsorption of surfactant as shown in comparison with calorimetric data /11/. The concentrations at which the point of zero charge is obtained are used to compare the result.

The pK values were determined according to /12/:

$$pK = pH_{1/2\zeta_p} + 0.4343 \cdot \frac{F \cdot \zeta_p}{2RT} \qquad (2)$$

$pH_{1/2\zeta_p}$ pH value where ζ potential = $1/2\zeta$ of plateau, ζ_p = ZP of plateau, F = Faraday constant, R = gas constant, T = temperature.

Results and discussion

Classical textile treatment

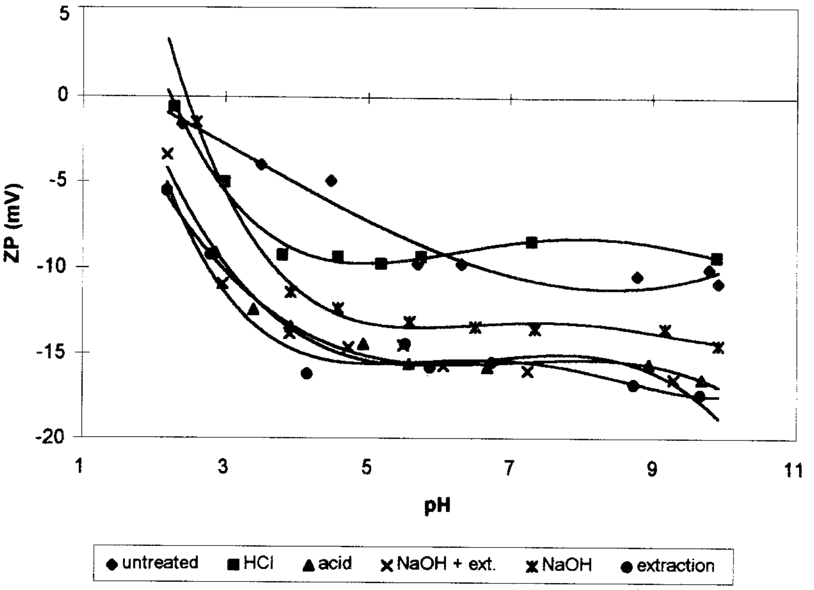
The non cellulose compounds were removed by classical textile processes or by methods removing specific compounds only the resulting ZP–pH functions are shown in Fig. 2:

Textile processes	*Methods Removing Specific compounds only*
• *Alkaline treatment* (NaOH) removing all non cellulose compounds except waxes	• *Petrol–ether extraction* removing waxes
• *Demineralisation* (acid) removing cationic trash	• *HCl treatment* supposed to remove all non cellulose compounds

The natural cellulose fibres are negatively charged (ZP = – 11 mV) due to the presence of carbonyl and hydroxyl groups. In the case of raw (untreated) material these groups are covered by non-cellulose compounds present in the primary wall of the natural fibre.

The textile finishing processes are applied in order to degrade, remove or complex these compounds and this causes an increase of the negative ZP depending on the

Fig. 2 ZP of different cleaned – purificated cotton fibres as a function of pH; elektrolyt solution 0.001 n KCl



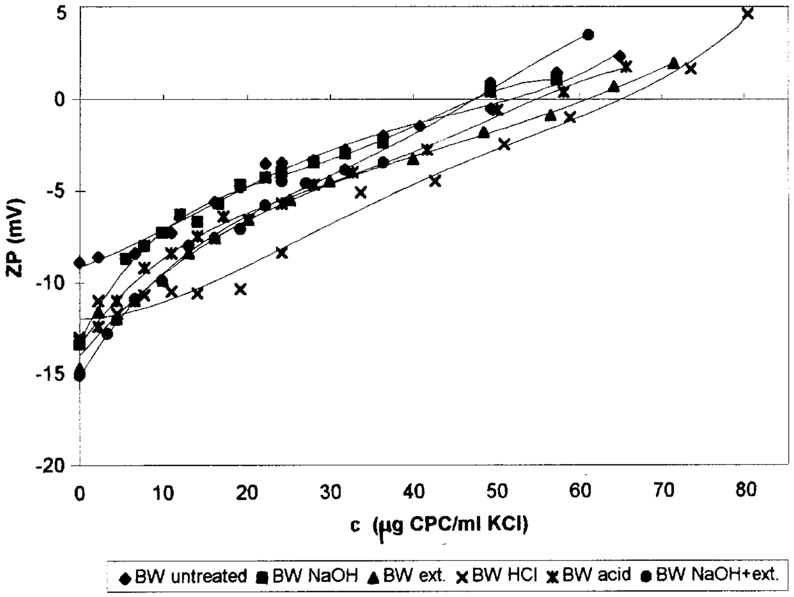


Fig. 3 ZP of different cleaned – pretreated cotton fibres as a function of surfactant concentration; pH = 8.7; 0.001 n KCl

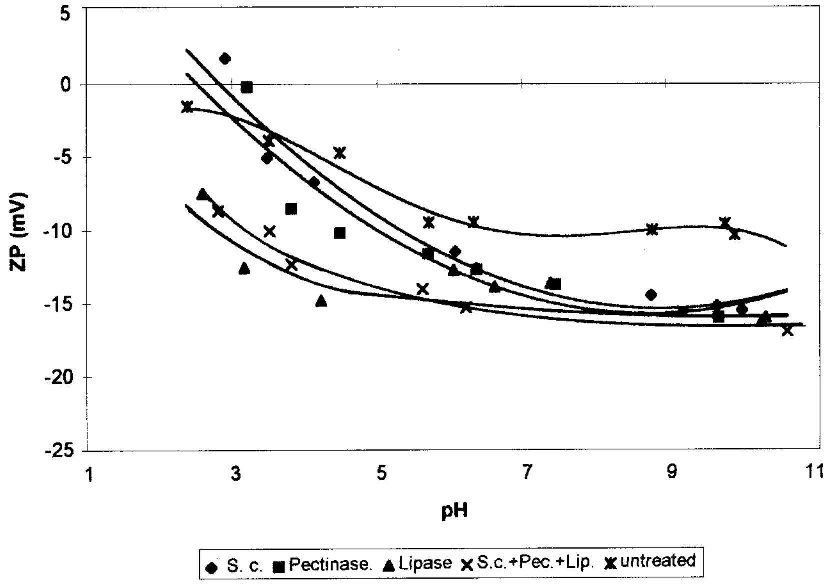


Fig. 4 ZP of different enzymatic cleaned cotton fibres as a function of pH elektrolyt solution: 0.001 n KCl

degree of purification. This is clearly represented by the above shown results (Fig. 2), the increase of the negative ZP can be explained by the improved accessibility of anionic groups.

The classical NaOH treatment degrades and removes practically all non-cellulose compounds except waxes which remain to about 50% on the fibre. This process results in an 40% increase of the negative surface charge expressed by an ZP of − 14.5 mV.

2% NaOH concentration used by pre-treatment, does not modify cellulose from cell. I to cell. II, but it causes swelling of surface layers. This increases the active surface, but the amount of dissociable groups is not changed. The swelling itself causes a reduction of the ZP, because of the shift of the shear plane into the liquid phase.

Petrol ether extraction is used to remove the waxes entirely. This treatment gives the highest ZP (− 17.4 mV) of all processes applied to cellulose fibres. If the NaOH treated fibres undergo an additional petrol ether treatment, the same ZP–pH function is obtained as in the case of the petrol ether treated samples. It can be concluded from these results, that the waxes are the one component mainly influencing the surface charge of cellulose fibres.

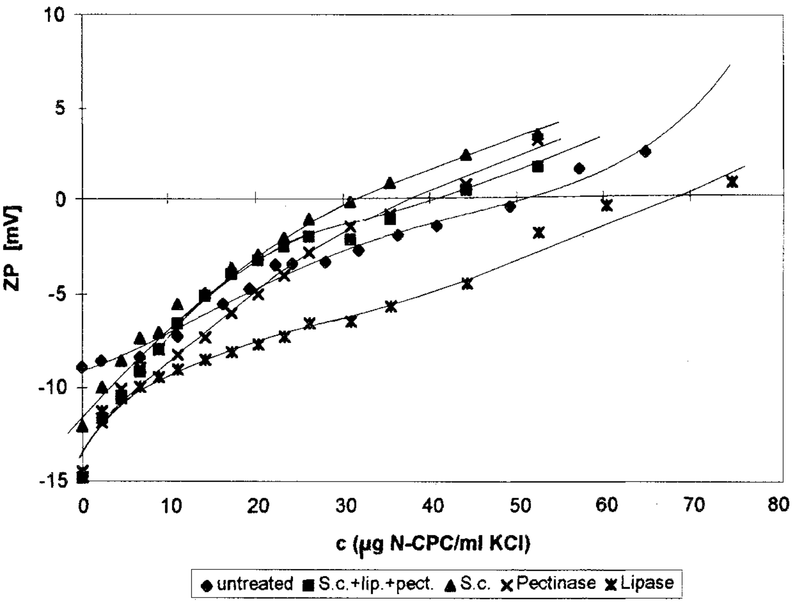


Fig. 5 ZP of different enzymatic cleaned cotton fibres as a function of surfactant concentration; pH = 8.7; 0.001 n KCl

A very similar result (− 16.5 mV) is obtained by acid treatment using complex forming agents (i.e. poly-phosphonic acid). All the cations on the surface of the fibres are complexed and dissolved by this treatment.

The non textile typical HCl treatment which should remove the non-cellulose compounds causes a completely different situation. The ZP–pH function is changed and the ZP plateau values (− 9.5 mV) are even lower than that of the raw material (− 11 mV). This observation can be explained by the formation of degraded cellulose rich in end-groups hydrocelluloses in acid medium (pH = 2.5). During the primary step of the hydrolyzation H_3O^+ cations and/or –CHO–groups are present and the dissociation equilibrium is shifted in such a way that the number of negative surface groups is decreased causing a reduction of the negative ZP.

These results indicate that the electrokinetic surface properties are dominated by the non- cellulose compounds, especially the waxes, even if their mass is less than 10% of that of the total fibre. The pH–ZP function is not changed qualitatively by the treatment, the ZP values of the plateau region are a function of the degree of removal of non cellulose compounds and can therefore be used to describe the progress of these process steps. The isoelectric points and pK values (Table 3) are shifted towards lower pH values during the cleaning process, due to the better accessibility of dissociable surface groups (IEP shifted from pH 2–3 to pH 1.5). The degradation of hydrophobic wax and fatty acids has greater influence on electrokinetic properties of materials than the enlargement of primary intramicellar places, caused by NaOH treatment.

The surfactant adsorption process shows a similar picture. The removal of waxes and cationic trash due to the extraction and acid (using complex forming agents) treatment causes an increase of charged groups and therefore a higher amount of N–CPC necessary to obtain charge reversal.

The NaOH treatment offers better accessibility due to fiber swelling and enlargement of the primary intra-micellar places and therefore faster adsorption of cationic surfactant.

The same phenomenon is shown by the materials which have been NaOH cleaned and afterwards treated by an extraction process, which cannot be observed by the pH–ZP function.

The non typical HCl cleaning process probably causes a chemical modification of cellulose (CHO-groups were formed), in this case the amount of N–CPC necessary to obtain the charge reversal is the highest one. Because of chemical modification of cellulose, pH–ZP and surfactant concentration–ZP functions of HCl cleaned material do not correlate. In this case different effects are observed, on the one hand the modification of the dissociable groups on the surface by the ZP–pH function (pK values are the smallest) and on the other hand the modification of adsorption sites.

Enzymatic pretreatment

Enzymatic prefinishing treatments of cellulose fibres are aspired alternatives to the classical textile processes because of their low environmental pollution. At the moment their function and chemical mechanism are not fully understand.

The individual non-cellulose components were removed using specific enzymes as pectinase, lipase to obtain the information about the influence of this components on the ZP. The degradation of waxes by lipase results in the similar ZPmax value of − 16.3 mV as the petrol ether

Table 3 Elektrokinetic properties of different purificated cellulose fibres

Sample	approx. ZP_{max} (mV)	approx. CRC (μg N-CPC/ ml KCl)	pK
untreated	– 10.8	51	4.59
NaOH	– 14.5	47	2.63
Extraction	– 17.4	61	2.95
Acid	– 16.5	53	3.05
HCl	– 9.5	65	3.08
NaOH + extraction	– 16.5	47	2.95
Lipase	– 16.3	61	3.14
Pectinase	– 16.5	44	3.85
S.c.	– 16.0	33	4.34
Lip. + Pect. + S.c.	– 20.4	44	3.68

extraction. This confirms the conclusion that the waxes are the one component mainly influencing the surface charge of cellulose fibres.

The application of an enzyme mixture (containing xylanase, cellulase, pectinase, lipase, S.c. filtrate) leads to the highest negative ZP indicating the total removal of the trash.

The ZP–pH functions represented by enzymatic cleaned materials are very similar to that obtained by the classical textile or specific treatment of cellulose fibres-the ZP values of the plateau region are a function of the degree of removal of non cellulose compounds.

The isoelectric points are, as by classical textile cleaning processes, shifted towards lower pH values (IEP shifted from pH 2–3 to pH 1.5).

Lipase degradation of hydrophobic fatty acids and waxes on cellulose fibers surface leads to a surfactant adsorption process similar to that obtained by material which has been petrol–ether extracted. The amount of N–CPC necessary to obtain the charge reversal is practically the same in both cases – approximately 61 μg N–CPC/ml KCl, which is an evidence of hydrophilization of cellulose, caused by an increase of active anionic groups.

The adsorption properties of cellulose material cleaned by specific enzymes (pectinase, S.c., pectinase + S.c + lipase) show the similarly fast adsorption characteristic of cationic surfactant as the NaOH treated material. An enlargement of the primary intramicellar places in cellulose polymer takes place during the process. This effect has greater influence on the surfactant adsorption ability than the degradation of a specific hydrophobic substance (wax, pectin) and the increased accessibility of active groups on cellulose polymer surface.

Conclusion

- The ZP_{max} increases due to increased accessibility of dissociable groups by removal of wax and cationic components by extraction, lipase and acid cleaning processes.
- The pK values reflect the chemical modification of the fibre surface – the formation of – CHO groups probably causes a shift towards increased acidity.
- NaOH, pectinase, and S.c. enzymatic pre-treatment – purification processes cause increase of the active surface, but the amount of dissociable groups is not changed. The swelling itself causes a reduction of the ZP, because of the shift of the shear plane into the liquid phase.
- The cleaning process shifts the IEP to the higher acidity indicating the dominance of dissociation process in the ZP–pH function.
- The enlargement of the primary intramicellar places in cellulose polymer obtained by NaOH treatment has greater influence on surfactant adsorption ability as degradation of specific hydrophobic substance (pectin wax)-improving the accessibility of active groups on cellulose polymer surface.
- The correlation between pH–ZP and surfactant conc.–ZP functions is not the same by chemical modified cellulose (HCl cleaning – causing formation of new groups). This is proven by the shift in pK values.
- The zetapotential is an appropriate tool to observe this kind of surface modification, the progress of the chemical cleaning process and the interaction of the fibres with components of the liquid phase.

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