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Ca^{2+} sorption on regenerated cellulose fibres

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ABSTRACT

High calcium content in cellulose materials can cause considerable problems in pulp processing, textile chemical treatment and consumer use, e.g. dyeing operations or household laundry. The Ca^{2+} binding capacity of cellulose also is of relevance in food and medical applications. Through their carboxyl group content regenerated cellulose fibres can act as weak anion exchangers, thus all types of regenerated cellulose fibres such as lyocell, viscose and modal fibres, show a distinct ability to bind Ca^{2+} ions. The binding capacity is limited by the carboxyl group content, which was determined with 15 mmol/kg for lyocell fibres and 20 mmol/kg for viscose fibres, using the Methylene Blue sorption method. The presence of bound Ca^{2+} also was demonstrated by complex formation with alizarin. The molar ratio between carboxylic group content and bound Ca^{2+} ions was one Ca^{2+} ion for a single carboxyl group. As a result of Ca^{2+} sorption a positive net charge of the cellulose results and another anion has to be bound as counter ion for reasons of charge neutralisation. Results of potentiometric titrations indicate HCO_3^- to be present as counter ion in the Ca^{2+} cellulose system. Thus under the experimental conditions studied, bound Ca^{2+} is proposed to be present in the form $-COO^-Ca^{2+}HCO_3^-$.

1. Introduction

A number of problems arise from the presence of Ca^{2+} ions bound in cellulose materials. Removal and control of build up of divalent cations including Ca^{2+} are of high relevance in strategies of low effluent mills (Rudie, Ball, & Patel, 2006). Scale formation and competition with transition metals for chelants are two other problems, which can arise from uncontrolled Ca^{2+} content in pulp and paper production (Duong, Hoang, & Nguyen, 2004). Complications appear during textile chemical processing, when fastness properties of dyeings are decreased or in household laundry, where stain removal is hindered (BASF, 1976a, 1976b). Metal binding is also of interest for food and technical applications, e.g. dietary fibres and waste water treatment (Burba & Willmer, 1983; Jacopian et al., 1974; Luccia & Kunkel, 2002). Increased adsorption of soluble polysaccharides, e.g. pectine and alginate on Ca^{2+} containing cellulose, is of interest in food applications (Paul, Manian, Široká, Duelli, & Bechtold, 2012). The ubiquitous presence of Ca^{2+} and the extensive utilisation of cellulose, both in technical products, e.g. pulp, paper and fibres, and as non-digestible fibrous parts structuring food may explain the growing scientific interest to investigate this system in more detail.

Oxidative steps are of high importance in the chemical processing of cellulose during regenerated cellulose manufacturing and paper production. As a result of these oxidation processes reducing ends of the cellulose chains were oxidised to carboxylic groups. Through the dissociation of these groups the polysaccharides exhibit properties of a weak anion exchanger (Karhu, Snickars, Harju, & Ivaska, 2002; Rudie et al., 2006).

This behaviour can be strengthened by further oxidation or chemical modification of the cellulose (Lindgren, Persson, & Ohman, 2001; Saito & Isogai, 2005). Ion exchange properties of highly oxidised celluloses have been studied in detail and a distinct capacity of oxidised celluloses to bind metal ions from aqueous solution has been reported (Eriksson & Gren, 1996; Heinze & Wagenknecht, 1998; Jacopian, Philipp, Mehnert, Schulze, & Dautzenberg, 1975).

Regenerated cellulose fibres for textile applications show carboxylic group contents in the magnitude of 20–40 mmol $-COOH$ groups per kg of fibre (Kongdee & Bechtold, 2004; Manian et al., 2008). These $-COOH$ groups can bind metal ions through an ion exchange mechanism. For pulp fibres the total charge of bound Na^+ and Ca^{2+} was found to exceed the number of $-COOH$ groups present in the cellulose (Duong, Nguyen, & Hoang, 2005, 2006). The ability of lyocell fibres to bind Ca^{2+} from diluted aqueous solutions already has been reported in the literature. Interestingly at the low carboxyl group content present in textile fibres, a 1:1 stoichiometry between $-COOH$ and Ca^{2+} was reported for lyocell fibres (Fitz-Binder & Bechtold, 2009). This can be explained with the distance between tow neighbouring $-COOH$ groups, which is too

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Table 1
Material characteristics of knitted fabric used for Ca^{2+} sorption experiments.

Symbol	Material	Fibre fineness (dtex)	Fabric mass/area (g/m^2)	Carboxylic group content (±std.dev.) (mmol/kg)
CLY	Lyocell	1.3	156	15.8 ± 1.4
A100	Lyocell crosslinked	1.4	110	15.2 ± 1.0
LF	Lyocell crosslinked	1.3	119	55.5 ± 1.8
CV	Viscose	1.3	118	20.3 ± 1.0
CMD	Modal	1.3	117	16.8 ± 1.2
µCMD	Micro-modal	1.0	122	17.1 ± 2.2

far for $(\text{—COOH})_2\text{Ca}$ salt formation. Thus in $\text{—COO}^-\text{Ca}^{2+}$ containing lyocell fibres a counter ion X^- has to be present to achieve charge neutrality.

As a result of this 1:1 stoichiometry, the presence of Ca^{2+} in regenerated cellulose fibres alters the sorption characteristics of cellulose fibres. For example increased sorption of the soluble anionic polysaccharides pectine, alginate and xanthan on Ca^{2+} containing regenerated cellulose fibres has been reported in the literature (Paul et al., 2012). Despite the fact that pure cellulose dose not bear charged groups, ionic interactions thus can play a distinct role in many polysaccharide reactions (Bechtold et al., 2012).

In this work the Ca^{2+} binding capacity of important regenerated cellulose fibres such as crosslinked lyocell fibres, viscose and modal type fibres has been studied in detail. Under model conditions Ca^{2+} binding capacity has been studied by complexometric analysis of the Ca^{2+} content and by staining experiments using alizarin as marker dye (Fitz-Binder & Bechtold, 2009; Schweppe, 1992). Lyocell fibres were used as representatives in a series of potentiometric analyses to identify the nature of the unknown counter anion bound in $\text{—COO}^-\text{Ca}^{2+}\text{X}^-$.

The binding of Ca^{2+} at carboxylic groups containing cellulose and the resulting incomplete charge neutralisation on the fibre surface can serve as model system to explain sorption and structuring effects induced by Ca^{2+} ions in many applications. Thus the given results deepen the understanding of the role of Ca^{2+} in chemical processing of pulp and regenerated cellulose fibres, in consumer use of textiles, e.g. household laundry and also in a wide range of food products.

2. Experimental

2.1. Materials and chemicals

Studies for Ca^{2+} binding capacity were performed with knitted fabric provided by Lenzing AG, Lenzing Austria (Table 1).

For the experiments to determine the counter-anion in Ca^{2+} containing material, woven fabric (100% lyocell fibres, Tencel®, 135.6 g/m^2, yarn count 50 m/g, warp 36 y/cm, fill 29 y/cm, desized) was used as provided by Lenzing AG, Lenzing, Austria.

Magnesium Titriplex (ethylenediamine-tetra-acetic-acid magnesium-dipotassium salt (p.a.), H_3BO_3 (96% pro analysis), Na_2CO_3 (99.0% purity) and Methylene Blue·2–3H_2O (microscopy quality), Eriochrom-black T were supplied by Merck. $CaCl_2 \cdot 2H_2O$, NaOH, Oxalic acid·2H_2O (99.5%), HCl (25%, w/w), NH_4Cl, NH_3 solution (approx. 25%, w/w), NaOAc and $NaHCO_3$, were of analytical grade quality. Alizarin (1,2-dihydroxy-9,10-anthraquinone) was of microscopy quality (Fluka, Buchs, Switzerland).

2.2. Ca^{2+} sorption experiments

A mass of 25 g knitted fabric was extracted with 1000 ml 0.5% HCl (liquor ratio 1:40, 1 g fabric for 40 ml liquid) at 40 °C for 1 h to remove Ca^{2+}, then neutralised with 1 g/l NaOAc, two times rinsed with deionised-water and line dried. This extract was used to measure Ca^{2+} content on the untreated fabric.

Such HCl pretreated fabric was impregnated in buffered $CaCl_2 \cdot 2H_2O$ solution for 1 h at 40 °C and pH 9 at a mass to volume ratio of 1:40. The Ca^{2+} concentration in the solutions ranged from 1 mM to 10 mM. A solution of 0.5 g/l ammonium chloride which had been adjusted to pH 9 by addition of 1 M NH_3 solution served as buffer. After the impregnation the samples were washed 3 times with water.

2.3. Dyeing of samples and colour measurement

0.5 g of Ca^{2+} impregnated sample (knitted) was dyed at liquor ratio of 1:100 in a solution of 0.05 g/l alizarin in 0.1 M NaOH for 24 h at RT. The samples then were rinsed three times in a solution of 4.7 mM Na_2CO_3. Exhaustion of alizarin was monitored by photometry of the dyebath. Colour depth of dyed samples was characterised by CIE-Lab-coordinates and K/S values.

CIE-Lab values of the dyeings were measured with a tristimulus colorimeter (Minolta Chroma-Meter CR 200, sample diameter 8 mm). Colours are given in CIE-Lab coordinates, L^* corresponding to the brightness (100 = white, 0 = black), a^* to the red–green coordinate (positive sign = red, negative sign = green) and b^* to the yellow–blue coordinate (positive sign = yellow, negative sign = blue).

2.4. Preparation of samples for anion analysis

To remove Ca^{2+} from the fabric a certain mass of sample was treated in 0.5% (w/w) HCl at 40 °C for 1 h at a mass to volume ratio of 1:40. Samples pretreated with HCl of 2 g mass were impregnated in 80 ml 10 mM buffered $CaCl_2 \cdot 2H_2O$ solution for 1 h at 40 °C. A mixture of ammonium chloride and ammonia was used as buffer. 0.5 g/l ammonium chloride solution was adjusted to pH 9 by addition of 1 M NH_3 solution. After the impregnation the samples were washed 3 times with water.

For comparison, the samples were treated in the same buffer solution, without the addition of Ca^{2+} salt.

To prepare a cellulose sample which contains the carboxylic groups in the acidic form, 0.5 g of material were cut into small pieces and treated with 25 ml 5% (w/w) HCl for 1 h at 40 °C. The samples were then collected in a glass filter and rinsed 3 times for 5 min with 50 ml deionised water each. To remove rinse baths completely the samples were filtered between each rinsing step and rinsed on the filter. Together with 50 ml deionised water the samples then were placed in the titration beaker, 5 ml 0.005 M HCl were added and potentiometric titration in presence of the solid samples was performed.

2.5. Extraction of Ca^{2+}/Cl^- from Ca^{2+} containing fabric

Removal of Ca^{2+} from the impregnated fabric was performed in 0.65% HNO_3 solution. A mass of 2 g fabric was treated with 80 ml HNO_3 (1:40) at 40 °C for 1 h to dissolve Ca^{2+}.

Calcium concentration in solution was determined by complexometric titration of an exact volume of impregnation bath in presence of NH_3/NH_4Cl buffer (0.5 g Mg-EDTA, 67.5 g NH_4Cl and

570 ml conc. NH_3 solution in 1 l distilled water), using a 0.005 M solution of ethylene-di-amine-tetra-acetic acid di-sodium salt as titrant. After the addition of few drops indicator (0.5 g Erichrome Black T in 100 ml Triethanolamine) titration was performed at 50–60 °C with a titroprocessor (Mettler DL25 equipped with a phototrode DP660). Two extracts were analysed by a total of four titrations.

Chloride analysis was performed by argentometric titration of HNO_3 extracts of the Ca^{2+} containing samples. Titration was performed with a titroprocessor (Mettler DL25 equipped with a Ag-electrode). Analysis of 50 ml extracts was performed with four repetitions. The sensitivity of the method allows the determination of chloride contents above 1 mmol/kg fabric.

2.6. Potentiometric titration of cellulose samples

For the titration experiments a sample of 0.5 g mass was cut into small pieces and placed into a glass flask. After addition of 50 ml deionised water an accurate volume of 5 ml of 0.005 M HCl was added and the samples were equilibrated in the solution for 1 h with agitation on a shaker. 50 ml of extract were analysed by titration with 0.005 M NaOH with a titroprocessor (Mettler Titrator DL25, Greifensee, Switzerland) equipped with a glass electrode. pH was recorded as function of added volume 0.005 M NaOH.

Analysis was performed in three repetitions, and the values given are mean values.

2.7. Potentiometric titrations of HCO_3^-

To 3 ml (5 ml) 0.005 M $NaHCO_3$ a volume of 40 ml deionised water and an accurate volume of 5 ml of 0.005 M HCl was added. The solutions were equilibrated for 1 h with agitation on a shaker. The solution then was analysed by titration with 0.005 M NaOH with a titroprocessor. For comparison a volume of 2 ml 0.005 M HCl in 40 ml deionised water was titrated without $NaHCO_3$.

2.8. Determination of carboxyl group content

The carboxyl group content was determined after acid pretreatment of the cellulose samples. The samples were first treated in 5% HCl for 60 min at 40 °C with a mass/volume ratio 1:25, then were neutralised and washed three times in 1 g/l NaOAc solution and dried at an ambient temperature.

As dye solution 0.30 g Methylene Blue was dissolved in 1 l. To prepare the buffer 30.9 g boric acid was dissolved in 750 ml water, pH was adjusted to 8.5 by addition of 4 M NaOH, then the solution was filled to 1 l. The samples were cut into small pieces and stored at 20 °C and 65% r.h. A weighted part of the sample was dried for 4 h at 105 °C, cooled down in a desiccator and weighted in dry state to determine the humidity content of the material. For the determination of the carboxylic group content to an exact weight of approx. 0.25 g sample, 25 ml Methylene Blue solution and 25 ml buffer solution pH 8.5 were added and the samples were shaken in the solution over night at RT. A blank value was determined by analysing a solution without addition of cellulose sample.

After equilibration time 2.5 ml of the solution was acidified with 5 ml 0.1 M HCl and filled to 50 ml with water. The absorbance of the solution at 664.5 nm then was measured with a double beam spectrophotometer (Hitachi U-2000 Spectrophotometer, 10 mm cuvette). Borate buffer served as reference. The carboxyl group content then was calculated as mmol/kg cellulose material (Philipp, Rehder, & Lang, 1965).

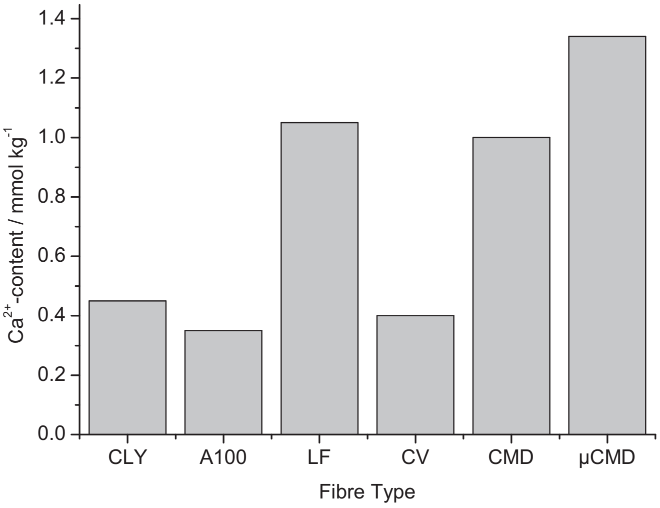

Fig. 1. Ca^{2+} content of samples determined from the HCl extract.

3. Results and discussion

3.1. Ca^{2+} sorption

In first experiments the Ca^{2+} content of the raw knitted samples was determined. During an enzymatic size removal woven fabric comes into contact with Ca^{2+} containing solutions. As regenerated cellulose fibres contain only low amounts of Ca^{2+} and no desizing is required for knitted materials, in knitted samples only a very low content of Ca^{2+} was found (Fig. 1).

When HCl-pretreated samples are brought into contact with a Ca^{2+} containing solutions, the carboxylic groups in the cellulose fibre can serve as weak an cation exchanger and Ca^{2+} ions can be bound to the material. To study the Ca^{2+} binding capacity of regenerated cellulose fibres, the HCl pretreated samples were treated in pH 9 buffered solutions containing 1, 2.5, 5 and 10 mM Ca^{2+}. The uptake of Ca^{2+} with increasing Ca^{2+} concentration is shown in Fig. 2. The Ca^{2+} content of the original samples was taken as zero. The build up of Ca^{2+} content in the cellulose fibre with increasing Ca^{2+} concentration is limited by the carboxylic group content in the fibres. For CLY, A100, CMD and µCMD saturation and maximum binding capacity is reached above a Ca^{2+} solution concentration of 5 mM. Then an amount of approximately 12 mmol/kg Ca^{2+} is bound in the fibre. Higher values of nearly 20 mmol/kg and 30 mmol/kg are observed for CV and LF respectively. In case of CV the higher binding capacity is explained with the comparatively lower degree of

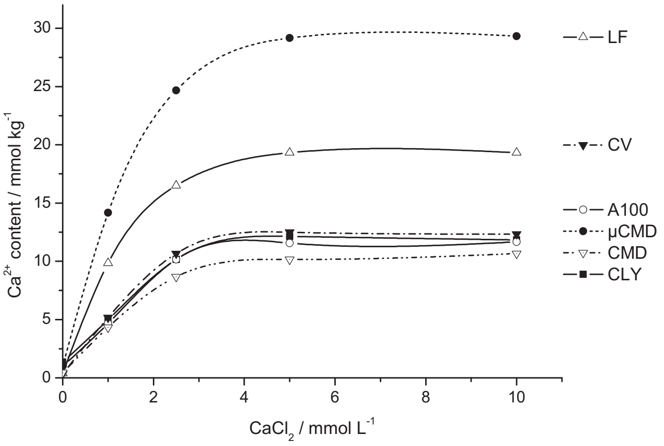

Fig. 2. Ca^{2+} sorption on cellulose fibres as function of solution concentration.

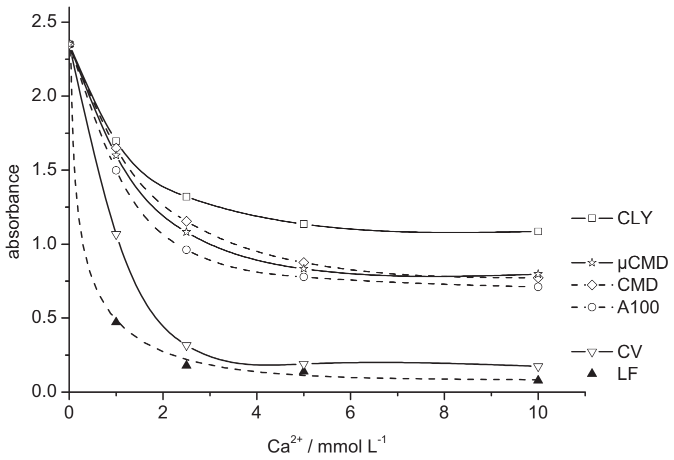

Fig. 3. Absorbance of residual alizarin solution after staining experiment as function of Ca^{2+} concentration used in Ca^{2+} sorption.

polymerisation and a higher carboxylic group content. For LF the unexpectedly high Ca^{2+} binding and the apparently high carboxylic group content most probably are due the presence of crosslinker (NHDT, 2,4-dichloro-6-hydroxy-s-triazine), which is supposed to contribute to both, the analytical determination of the carboxylic group content and the overall Ca^{2+} binding capacity.

While the Methylene Blue sorption method is widely used as a procedure to determine the carboxylic group content of cellulose it has to be considered that the sorption of the cationic dye will indicate only the carboxylic groups which are accessible to a molecule of this size. Titration methods with acid are expected to yield somewhat higher carboxylic group content as smaller ions with higher accessibility are involved. In comparison to Methylene Blue the accessibility of the hydrated Ca^{2+} ion is expected to be somewhat higher thus the maximum Ca^{2+} binding capacity derived form the Methylene Blue method will be slightly underestimating the maximum binding capacity for Ca^{2+}.

The presence of Ca^{2+} sorbed on the fibres also can be demonstrated by staining with alizarin solution. Due to the formation of a coloured Ca^{2+} alizarin complex, the colour of the samples changes with the amount of bound Ca^{2+} and in parallel the concentration of alizarin in the staining solution decreases. The sorption of dye on the samples thus can be measured both, by colour measurement of the dyed samples and by the decrease of dye concentration in the dyebath.

Fig. 3 shows the absorbance of the alizarin solution at the end of the dyeing experiment as a function of the Ca^{2+} concentration used for the Ca^{2+} impregnation experiment. Fig. 4 shows the L^*-coordinate of the alizarin stained samples.

As expected the samples with highest Ca^{2+} content, CV and LF, show highest exhaustion of alizarin due to the formation of the Ca^{2+} alizarin complex. In parallel the L^* value also decreases with increasing colour depth due to the formation of the Ca^{2+} alizarin complex. However this correlation is not strict, e.g. in case of the A100 dyeing the colour depth in terms of L^* is rather high and reaches the level of the CV and LF samples. These differences can be explained with different accessibility of the cellulose samples for the alizarin marker dye and with different distribution of sorbed Ca^{2+} respectively coloured Ca^{2+} alizarin complex in the solid cellulose matrix.

From the amount of Ca^{2+} bound in the cellulose structure a molar ratio between carboxylic groups and bound Ca^{2+} of one Ca^{2+} per single carboxylic group has been derived (Fitz-Binder & Bechtold, 2009).

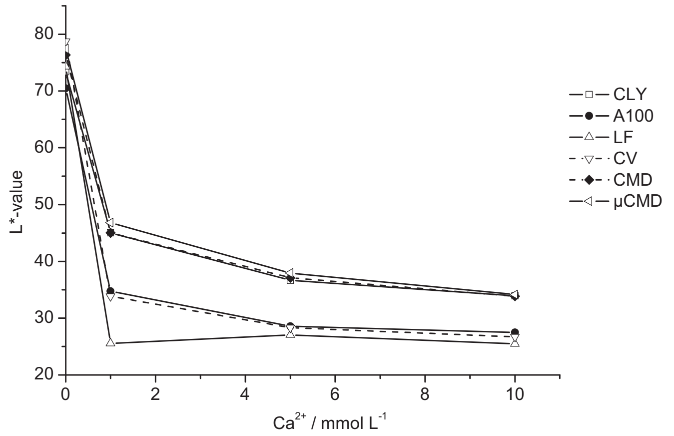

Fig. 4. L^*-values of alizarin stained samples as function of Ca^{2+} concentration used in Ca^{2+} sorption treatment.

The ion exchange reaction thus can be formulated according to Eq. (1). As a consequence an equivalent amount of an anion X^- has to be present as counter ion in the Ca^{2+} containing cellulose structure, to achieve charge neutrality. Ca^{2+} containing cellulose thus should be able to act similar to an anion exchanger.

$$\text{Cell-COOH} + Ca^{2+} + X^- \leftrightarrows \text{Cell-COO}^- Ca^{2+} X^- + H^+ \quad (1)$$

3.2. Anion analysis

As shown in this study for all regenerated cellulose fibres the maximum Ca^{2+} absorbed in the cellulose structure is limited by the respective carboxylic group number. Thus the charge of the bound Ca^{2+} is compensated by the carboxylic groups only by half and another counterion has to be bound for charge neutrality (Eq. (1)). The carboxylic group content of the HCl pretreated samples used for these experiments was determined by the Methylene Blue sorption method with 26.7 ± 3.4 mmol/kg.

For these experiments conditions during pretreatment and Ca^{2+} impregnation were designed in such a way, that the only Cl^- ions were anions present, and in a first experimental approach Cl^- was searched as possible counterion X^-. From the complexometric analysis of HNO_3 extracts of samples, which previously had been loaded with Ca^{2+} ion by impregnation in a 10 mM Ca^{2+} solution, a total Ca^{2+} content of 11.38 ± 0.20 mmol/kg fabric was determined. Argentometric determination of the chloride content in these samples indicated a low Cl^- content of approximately 0.7 mmol/kg. This value already is below the lower detection limit of the method, which is estimated with 1 mmol/kg. Compared to the Ca^{2+} content of 11.38 mol/kg, thus only neglectable amounts of chlorides were present in the analysed samples.

The only other anion present in the Ca^{2+} containing cellulose then could be the HCO_3^--ion, having its origin from CO_2 dissolved in the water. To identify carbonate as possible counter anion a series of potentiometric titrations with differently treated cellulose samples were performed (Fig. 5).

For all samples a mass of 0.5 g was treated with 50 ml distilled water and 5 ml 0.005 M HCl. Then from these solutions an aliquot volume of 50 ml was titrated with 0.005 M NaOH by potentiometric titration. The observed consumption of NaOH differs, depending on the pretreatment of the samples. The titration curves of representative examples are shown in Fig. 1, characteristic data are given in Table 2.

Titration of the calcium free sample in its acidic form: In these experiments the carboxylic groups in the samples were first transferred into their corresponding acid form. The samples were not removed from the solution during the titration, and thus carboxylic

Table 2
Sample characteristics, neutralisation capacity in mmol/kg (±std.dev.), and ion-species detected in the titration (positive sign: increased consumption of NaOH; negative sign: decreased consumption of NaOH).

Sample		Volume 0.005 M NaOH (ml)	Capacity (mmol/kg)	Groups determined
50 ml HCl	A	0	0	–
Acidic sample	B	+1.43 ± 0.087	+14.3 ± 0.87	$-COOH$
Neutralised (pH 9)	C	−1.08 ± 0.059	−10.8 ± 0.59	$-COO^-NH_4^-$
Ca^{2+} impregnated (10 mM)	D	−1.56 ± 0.085	−15.6 ± 0.85	$-COO^-Ca^{2+}$, HCO_3^-

groups in the cellulose also were neutralised. In addition to the HCl, also the carboxylic groups of the cellulose were determined by titration (Eqs. (2) and (3)). The additional consumption of NaOH corresponds to neutralisation of 14.3 ± 0.87 mmol/kg NaOH due to carboxylic groups present in acid form in the samples.

$$\mathrm{HCl} + \mathrm{NaOH} \leftrightarrows \mathrm{NaCl} + \mathrm{H_2O} \tag{2}$$

$$\text{Cell-COOH} + \mathrm{NaOH} \leftrightarrows \text{Cell-COO}^-\mathrm{Na}^+ + \mathrm{H_2O} \tag{3}$$

Treatment of the calcium free sample in neutralised form: after the hydrochloric acid treatment to remove any Ca^{2+} present in the fabric, these samples were neutralised in a NH_3/NH_4Cl buffer solution at pH 9, similar to the Ca^{2+} sorption experiment. The carboxylic groups in these samples thus were present as ammonium carboxylates. These samples were brought in contact with diluted HCl. After the removal of the solid sample the excess acid was determined by the neutralisation with NaOH. Part of the added HCl was consumed for protonation of the carboxylic groups (Eq. (4)). The reduced consumption of HCl due to transfer of $-COONH_4$ groups into COOH groups corresponds to 10.76 ± 0.59 mmol/kg $-COONH_4$ groups. This indicates that not all carboxylic groups in the cellulose were present in their ammonium salt form, most probably part already had been buffered to the COOH form in the rinse steps during the sample preparation.

$$\text{Cell-COONH}_4 + \mathrm{HCl} \leftrightarrows \text{Cell-COOH} + \mathrm{NH_4Cl} \tag{4}$$

Titration of the Ca^{2+} containing sample: following to the hydrochloric acid treatment to remove any Ca^{2+} present in the fabric, these samples had impregnated with 10 mM Ca^{2+} solution in a NH_3/NH_4Cl pH 9 buffer solution. From complexometric analysis a total Ca^{2+} content of 11.38 ± 0.20 mmol/kg fabric had been determined in the fibre. Such samples were brought in contact with diluted HCl. After removal of the solid sample an aliquot volume was analysed by titration with NaOH. In these experiments, part of the added HCl was consumed for protonation of the carboxylic groups and release of the Ca^{2+} ions. Furthermore possibly present hydrogen carbonate ions were released as counter ions of the bound Ca^{2+} and were transferred into carbonic acid (Eq. (5)). The consumption of HCl in this case is due to transfer of $-COOCaHCO_3$ groups into $-COOH$, and HCO_3^- into H_2CO_3 (Eq. (5)). From the acidity of carbonic acid we expected neutralisation to HCO_3^- during the titration with NaOH, thus no significant contribution should result from presence of HCO_3^- ions. An overall consumption of NaOH similar to the titration of the neutralised (pH 9) cellulose samples was expected. From the potentiometric titration a decrease in consumption of HCl corresponding to 15.58 ± 0.85 mmol/kg was determined, which is approximately 50% higher than the value determined for the neutralised sample in NH_4^+-form.

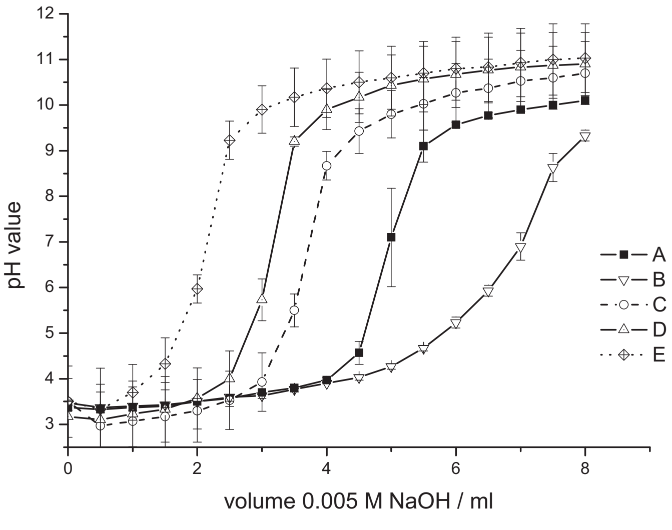

Fig. 5. Representative neutralisation curves obtained with different samples: (A) HCl solution; (B) Ca-free acid form of sample; (C) Ca-free neutralised sample; (D) Ca-impregnated samples; (E) original untreated fabric sample.

$$\text{Cell-COOCaHCO}_3 + 2\mathrm{HCl} \leftrightarrows \text{Cell-COOH} + \mathrm{CaCl_2} + \mathrm{H_2CO_3} \tag{5}$$

$$\mathrm{H_2CO_3} \leftrightarrows \mathrm{H_2O} + \mathrm{CO_2} \tag{6}$$

An explanation for this result was found from more thorough analysis of the behaviour of $NaHCO_3$ and H_2CO_3 under the experimental conditions applied during the potentiometric titrations. Due to rapid decomposition of H_2CO_3 to CO_2 and water (Eq. (6)) more than 80% of H_2CO_3 formed decomposes to CO_2 and degasses during the period of HCl treatment of the cellulose sample thus lower consumption of NaOH is found.

No difference in NaOH consumption between pH 9 neutralised samples and Ca^{2+} containing samples would be expected in case of chloride serves as counter ion X^-.

A titration curve of the original desized fabric sample which had not been pre-treated in HCl to remove calcium and carbonates also is shown in Fig. 5. The sample neutralises a rather high amount of the HCl, which can be explained in similar way by release of carbonates during the acid treatment. As for these samples technical details of chemical processing steps were not available, the systematic analysis had been undertaken with samples, which were treated with Ca^{2+} solutions under controlled laboratory conditions.

4. Conclusions

Regenerated cellulose fibres such as lyocell, viscose, modal fibres contain carboxylic groups in the range of 15–55 mmol/kg. These carboxylic groups can provide cation exchange properties and at pH 9 Ca^{2+} can be sorbed in the solid cellulose matrix. The maximum binding capacity is limited by the carboxylic group content and a molar ratio of 1:1 is observed for $-COOH{:}Ca^{2+}$. This behaviour can be explained with the distance between two neighbouring $-COOH$ groups, which prevents formation of $(-COOH)_2Ca$ salt. This salt possibly could be found in highly oxidised samples with high carboxylic group content.

The presence of Ca^{2+} can be proven by analytical results and staining experiments with alizarin.

Charge neutrality considerations indicate the presence of another anion to compensate for the positive charge of the Ca^{2+}.

Argentometric analysis did not indicate substantial amounts of chloride, but potentiometric titrations with NaOH indicate that HCO_3^- could serve as counter ion.

Thus when Ca^{2+} is sorbed from diluted solutions, e.g. hard water during rinse in household laundry, or calcium containing desizing solutions, on regenerated cellulose fibres, HCO_3^- will be bound in the cellulose structure for reasons of charge neutrality. Such cellulose materials will exhibit higher pH buffering capacity due to presence of HCO_3^- ions.

The presence of $-COO^-Ca^{2+}HCO_3^-$ groups in the cellulose also contributes to several problems known to occur during processing and consumer use. Through presence of mobile Ca^{2+} ions problems in following processing stages can arise, e.g. due to local precipitation and deposition of dyes during dyeing, leading to lower reduced fastness. Upon heating, e.g. technical drying processes, ironing, formation of solid $CaCO_3$ could occur, which then could serve as seed crystals for further deposition of $Ca(HCO_3)_2$ and $CaCO_3$ in following processes. The accumulation of high concentrations of Ca^{2+} containing deposits, found on textiles after several cycles of washing, also can be explained by the presented mechanism of Ca-hydrogen carbonate sorption.

Binding of negatively charged soil particles will be enhanced when $-COO^-Ca^{2+}$ is present in the fibre structure, which increases energy barrier for soil release during washing processes.

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References

BASF. (1976a). *BASF Ratgeber Cellulosefasern*, BASF AG, B 375 d, 8 77, Ludwigshafen a.M., Germany, p. 44.

BASF. (1976b). *BASF Ratgeber Cellulosefasern*, BASF AG, B 375 d, 8 77, Ludwigshafen a.M., Germany, p. 180, 280.

Bechtold, T., Manian, A., Oeztuerk, H., Paul, U., Široká, B., Široký, J., et al. (2012). Ion-interactions as drying force in polysaccharide assembly. *Carbohydrate Polymers*, http://dx.doi.org/10.1016/j.carbpol.2012.01.064

Burba, P., & Willmer, P. G. (1983). Cellulose: A biopolymeric sorbent for heavy metal traces in water. *Talanta*, *30*(5), 381–383.

Duong, T. D., Hoang, M., & Nguyen, K. L. (2004). Extension of Donnan theory to predict calcium ion exchange on phenolic hydroxyl sites of unbleached kraft fibres. *Journal of Colloid and Interface Science*, *276*, 6–12.

Duong, T. D., Nguyen, K. L., & Hoang, M. (2005). Sorption of Na^+ and Ca^{2+} ions from aqueous solution onto unbleached kraft fibres – Kinetics and equilibrium studies. *Journal of Colloid and Interface Science*, *287*, 438–443.

Duong, T. D., Nguyen, K. L., & Hoang, M. (2006). Competitive sorption of Na^+ and Ca^{2+} ions on unbleached kraft fibres – A kinetics and equilibrium study. *Journal of Colloid and Interface Science*, *301*, 446–451.

Eriksson, G., & Gren, U. (1996). Pulp washing: Sorption equilibria of metal ions on kraft pulps. *Nordic Pulp and Paper Research Journal*, *11*(3), 164–170.

Fitz-Binder, C., & Bechtold, T. (2009). Sorption of alkaline earth metal ions Ca^{2+}, and Mg^{2+}, on lyocell fibres. *Carbohydrate Polymers*, *76*, 123–128.

Heinze, U., & Wagenknecht, W. (1998). *Comprehensive cellulose chemistry* Weinheim, Germany: Wiley-VCH., pp. 71–99

Jacopian, V., Dautzenberg, H., Philipp, B., Schleicher, H., Schulze, J., Woggon, et al. (1974). *Enrichment of food with minerals*. Ger. (East) Patent DD 74-1781173 (29.04.1974).

Jacopian, V., Philipp, B., Mehnert, H., Schulze, J., & Dautzenberg, H. (1975). Untersuchungen zur Kationenbindung an hydrolytisch abgebauten Cellulosepulvern. *Faserforschung und Textiltechnik*, *26*(4), 153–158.

Karhu, J., Snickars, P. M., Harju, L. U., & Ivaska, A. U. (2002). Cation exchange of alkali and alkaline earth metal ions on hardwood kraft pulp. *Appita Journal*, *55*(5), 392–397.

Kongdee, A., & Bechtold, T. (2004). The complexation of Fe(III)ions in cellulose fibres – A fundamental property. *Carbohydrate Polymers*, *56*, 47–53.

Lindgren, J., Persson, P., & Ohman, L. O. (2001). Interactions of calcium(II), copper(II) and aluminium(III) ions with two chemically modified wood fibres. *Nordic Pulp and Paper Research Journal*, *16*(3), 225–234.

Luccia, B. H. D., & Kunkel, M. E. (2002). In vitro availability of calcium from sources of cellulose, methylcellulose, and psyllium. *Food Chemistry*, *77*(2), 139–146.

Manian, A. P., Abu-Rous, M., Lenninger, M., Roeder, T., Schuster, K., & Bechtold, C. T. (2008). The influence of alkali pretreatments in lyocell resin finishing – Fibre structure. *Carbohydrate Polymers*, *71*, 664–671.

Paul, U. C., Manian, A. P., Široká, B., Duelli, H., & Bechtold, T. (2012). Sorption of anionic polysaccharides by cellulose. *Carbohydrate Polymers*, *87*, 695–700.

Philipp, B., Rehder, W., & Lang, H. (1965). Determination of the carboxyl content of dissolving pulp. *Das Papier*, *19*, 1–10.

Rudie, A. W., Ball, A., & Patel, N. (2006). Ion exchange of H^+, Na^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, and Ba^{2+}, on wood pulp. *Journal of Wood Chemistry and Technology*, *26*, 259–272.

Saito, T., & Isogai, A. (2005). Ion-exchange behaviour of carboxylate groups in fibrous cellulose oxidized by the TEMPO-mediated system. *Carbohydrate Polymers*, *61*(2), 183–190.

Schweppe, H. (1992). *Handbuch der Naturfarbstoffe: Vorkommen, Verwendung, Nachweis*. Landsberg/Lech: Ecomed. ISBN 3-933203-46-5.