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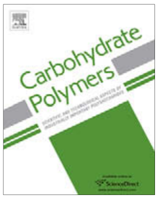

Sorption of alkaline earth metal ions Ca^{2+} and Mg^{2+} on lyocell fibres

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ABSTRACT

Ca^{2+} and Mg^{2+} content of cellulose fibres is of relevance for a wide range of applications e.g. textile processing, pulp/paper, food. Sorption of Ca^{2+} and Mg^{2+} ions were found on lyocell type regenerated cellulose fibres. Higher affinity was found for Ca^{2+} ions compared to Mg^{2+} ions. At pH 9, fibre saturation was observed at a calcium binding capacity of 18–20 mmol/kg. A carboxylic group content of 18 mmol COOH per kg fibre material was determined based on the Methylene Blue absorption. This indicates a 1:1 molar stoichiometry between the carboxylic groups present in the fibres and the bound Ca^{2+} ions. Thus it is proposed that the salt in fibre shows the general composition (Cell-O^- Ca^{2+} X^-), X^- being an anion bound in the salt to achieve charge neutrality.

The sorption of Ca^{2+} also can be demonstrated by complex formation with 1,2-dihydroxy-9,10-anthraquinone (alizarin) which forms a red-violet Ca^{2+}-complex. Colour fixation thus can be used as an indicator for the Ca^{2+}-ions bound in the fibre.

1. Introduction

The sorption of alkaline earth metal ions on cellulosic substrates is of relevance for a wide range of applications, representative examples are:

- processing of pulp and cellulose fibres in paper and textile industry (BASF, 1976a, 1976b; Eriksson & Gren, 1996; Farrar & Neale, 1952; Karhu, Snickars, Harju, & Ivaska, 2002; Lindgren, Persson, & Ohman, 2001);
- cellulose substrates as carriers for food enrichment with minerals and medical applications (Jacopian et al., 1974; Luccia & Kunkel, 2002);
- sorption of heavy metals from water (Burba & Willmer, 1983);
- mordant dyeing with natural dyes e.g. 1,2-dihydroxy-9,10-anthraquinone, the major component extracted from madder, forms complexes with Ca^{2+} adsorbed in the cellulose material (Bilgic, Karaderi, & Bapli, 2007; Derksen, 2001; Schweppe, 1992).

Two basic mechanisms can be discussed for the sorption of metal ions from aqueous solutions (Burba & Willmer 1983; Farrah & Pickering, 1978; Lieser & Gleitsmann, 1983):

- carboxylic groups present in the cellulose substrate can dissociate and act as anionic groups in a weak-acid cation exchanger. In this case the number of carboxylic groups will be of relevance for ion uptake such as Ca^{2+}, Mg^{2+}, Na^+. Kinetics and sorption equilibria of the binding of Ca^{2+} and Na^+ ions in kraft pulps have been reported in the literature (Duong, Nguyen, & Hoang, 2004, 2005, 2006). In case of unbleached kraft pulps Ca^{2+} sorption follows Langmuir isotherm, at higher pH the dissociation of phenolic groups also has to be considered. Jacopian et al. analysed the binding of Ca^{2+}, Fe^{2+} and Fe^{3+} on cellulose powders and demonstrated the relevance of the ratio $[M^{2+}]$ to $[H^+]$ and the amount of carboxylic groups present in the material. In their experimental conditions a full saturation of the carboxylic groups was not obtained (Heinze & Wagenknecht, 1998; Jacopian, Philipp, Mehnert, Schulze, & Dautzenberg, 1975).
- the amorphous part of the insoluble cellulose substrate swells in aqueous media and can act as an insoluble carbohydrate-type ligand which complexes metal ion such as $Fe^{2+/3+}$, $Co^{2+/3+}$, Cu^{2+} from their corresponding hydrate complexes. In this case binding capacity can far exceed the carboxylic group number in the cellulose (Kongdee & Bechtold 2004a, 2004b).

In textile chemical processing of cellulose fibres, the main treatment steps are performed in aqueous systems usually with soft water. However in selected processes, e.g. enzymatic desizing of woven fabric, alkaline earth metal ions are present, which could adsorb in the cellulose fibre and induce problems in later processing steps such as in dyeing. In household laundry, tap water is used during rinse and undesirable uptake of hardness can occur during

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the rinse, thereby changing softness and handle of the washed goods.

Lyocell type fibres are an emerging class of regenerated cellulose fibres with enormous future potential. The fibre formation process is based on NMMO/water as cellulose solvent which yields fibres with high tensile strength and high wet modulus. Depending on the type of lyocell fibre and analytical method used, typical values for the carboxylic group content of the fibres range from 20 to 28 mmol/kg (Kongdee & Bechtold 2004a; Manian et al., 2008). Thus Ca^{2+}-binding properties could be expected for lyocell fibres.

In the scientific study presented in this paper, woven and knitted fabric made form 100% lyocell fibres were used as representative examples to investigate the properties of lyocell type fibres for Ca^{2+} and Mg^{2+} complexation. The sorption of Ca^{2+}, Mg^{2+} from solutions of different metal concentration has been studied at pH 5 and pH 9. Besides analytical determination of the Ca^{2+}, and Mg^{2+} in samples, dyeings were performed using 1,2-dihydroxy-9,10-anthaquinone as a marker dye for Ca^{2+}/Mg^{2+} ions. To relate the Ca-binding capacity to the carboxylic group content of the fibres the Methylene Blue sorption method was to analyse carboxylic group content of the material (Philipp, Rehder, & Lang, 1965).

2. Experimental

2.1. Materials and chemicals

Woven fabric A (135.6 g/m^2, yarn count 50 m/g, warp 36 y/cm, fill 29 y/cm, desized), woven fabric B (137.5 g/m^2, warp 32 y/cm, fill 27 y/cm, desized) and knitted fabric (111.0 g/m^2, yarn count 68 m/g) were all made from 100% lyocell fibres (1.3 dtex fibres, Tencel® Lenzing AG, Lenzing, Austria).

Acetic acid, Titriplex III (Ethylenediamine-tetra-acetic-acid disodium salt, 99.0% purity), H_3BO_3 (96% pro analysi), Na_2CO_3 (99.0% purity) and Methylene Blue.2–3 H_2O (microscopy quality) were supplied by Merck. $CaCl_2.2H_2O$, NaOH (Carl Roth Gmbh, Karlsruhe, Germany), HCl (25% w/w), NH_4Cl, NH_3 solution (approx 25% w/w), Ethanol (99.8%, Riedel-de-Haen, Seelze, Germany) and NaOAc, $MgCl_2.6H_20$ (Fluka, Buchs, Switzerland) were analytical grade quality.

Alizarin (1,2-dihydroxy-9,10-anthraquinone) of microscopy quality (Fluka, Buchs, Switzerland) was used.

For sequestration experiments of Ca^{2+} containing fabrics under technical conditions, the following commercial auxiliaries were used: Trilon® TA liqu. (aqueous solution of nitrilo-tri-acetic-acid sodium salt, complexing agent), Kieralon B hochkonz. (surfactant) both BASF, Ludwigshafen, Germany.

2.2. Impregnation and extraction of Ca^{2+}, Mg^{2+}

A mass of 2 g fabric was extracted with 50 ml 5% HCl at 40° for 1 h to remove Ca^{2+}. The samples were rinsed with water, neutralised in a solution of 1 g/L NaOAc and line dried.

Samples of 2 g mass were impregnated in 80 ml buffered $CaCl_2.2H_2O$ solution for 1 h at 40 °C. The Ca^{2+} concentration in the solutions ranged from 1 to 8 mM. The Ca^{2+} uptake was studied at pH 5 and pH 9. A mixture of acetic acid and ammonia was used as buffer (the pH of a solution of 9 mM acetic acid was adjusted 5 or 9 by addition of 1 M NH_3 solution). After impregnation the samples were washed 3 times with water.

The sorption of Mg^{2+}-ions on lyocell fibres was studied on woven fabric samples which were pre-treated earlier with 5% HCl to remove any present Ca^{2+}/Mg^{2+}. 1 g of HCl pre-treated sample was impregnated with 20 ml of 1, 5 or 10 mM $MgCl_2$ solution for 1 h at 50–60 °C. For impregnation at pH 9 the required amount of $MgCl_2$ was dissolved in a solution of 0.25 g/L acetic acid and NH_3 was added to adjust pH to 9. In another set of experiments, no pH buffer was used and pH was measured at the beginning and at the end of the experiment. In absence of buffer the pH decreased during the experiment from initial values of pH 5.5 (1 mM $MgCl_2$) and pH 4.5 (10 mM $MgCl_2$) to values of 3.7–3.8 for all investigated solutions. After the impregnation step, the concentration of Mg^{2+} in the exhausted bath was determined.

2.3. Determination of Ca^{2+} and Mg^{2+}

Removal of Ca^{2+} from the impregnated fabric was performed in 5% HCl solution. A mass of 1 g fabric was treated with 25 ml 5% HCl at 40° for 1 h to dissolve Ca^{2+}. The filtered solutions were diluted with 5% HCl and analysed by AES. At least two repetitions were made for the determination of the Ca^{2+}-content in the woven and knitted fabric. The Ca^{2+} content were determined in raw fabric and in fabrics after Ca^{2+} removal with 5% HCl.

Ca^{2+} was determined by atom emission spectroscopy using a Hitachi Polarized Zeeman Atomic Absorption Spectrometer in the emission mode (wavelength 422.7 nm, Air–C_2H_2 flame). For calibration a 100 mg/L Ca^{2+} stock solution of $CaCl_2.2H_2O$ was diluted with 5% HCl to obtain standard solutions in the range of 0.1–1 mg/L Ca^{2+}.

The direct analysis of Mg^{2+} in the HCl extracts of the impregnated fabric failed. The high NaCl content formed in the neutralised solution hindered development of a sharp endpoint. Mg^{2+} sorption thus was monitored by analysis of the Mg^{2+} sorption from the impregnation baths.

Magnesium concentration in solution was determined by complexometric titration of an exact volume of impregnation bath in presence of NH_3/NH_4Cl buffer (54 g NH_4Cl and 350 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 and Erichrome Black T as indicator. Titration was performed at 50–60 °C with a titroprocessor (Mettler DL25 equipped with a phototrode DP660).

2.4. Dyeing of samples and colour measurement

About 0.5 g of M^{2+}-impregnated sample was dyed at liquor ratio of 1:100 in a solution of 0.05 g/L alizarin in 0.1 M NaOH for 1 h at RT. The samples were then 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).

K/S values of the dyed fabric were determined according the Kubelka–Munk function. The K/S values were calculated from the reflectance determined at the absorption maximum at 545–560 nm (one-beam spectrophotometer Specord 50, Analytik Jena, Germany, diffuse reflectance sphere 8°/d).

2.5. Simulation of Ca^{2+} removal from fabrics under technical conditions

Removal of Ca^{2+} from fabrics under technical conditions was simulated in laboratory experiments using solutions containing soda, Trilon TA and Kieralon B according Table 1 at 40 °C for 1 h at liquor ratio 1:100. For comparison a sample was treated in water only. Then the samples were rinsed in deionised water. Samples then were dyed in an alkaline alizarin solution containing

Table 1
Composition of solutions used for the pre-washing experiments.

No		Complexing agent Trilon TA (g/l)	Detergent Kieralon B (g/l)	Alkali Na_2CO_3 (g/l)
1	Untreated			
2	Water	–	–	–
3		0.5	–	–
4		–	0.5	–
5		–	–	2.0
6		0.5	0.5	2.0

0.21 mM alizarin in 0.1 M NaOH for 24 h at room temperature, liquor ratio 1:100.

2.6. Determination of carboxyl group content

The carboxyl group content of the following samples was determined: woven fabric A, knitted fabric, woven and knitted fabric after 5% HCl pre-treatment, and woven and knitted fabric after 20 min pre-wash with ethanol at RT followed by three times 5 min rinsing with water.

A solution of 0.30 g Methylene Blue was dissolved in 1 l water. 30.9 g boric acid was dissolved in 750 ml water, adjusted to pH 8.5 by addition of 4 M NaOH and filled to 1 L. Before analysis the samples were cut into small pieces and stored in the normal climate (20 °C, 65% r.h.). To determine the moisture content of the material a weighted part of the sample was dried for 4 h at 105 °C and then cooled down in the desiccator and weighted in dry state. For determination of the carboxylic group content an exact weight of about 0.25 g was treated in a 100 ml glass vessel with 25 ml Methylene Blue solution and 25 ml buffer solution pH 8.5. 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, 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 by means of a double beam spectrophotometer (Hitachi U-2000 Spectrophotometer, 10 mm cuvette, borate buffer was used as reference). The carboxyl group content then was calculated as mmol/kg cellulose material (Philipp et al. 1965).

3. Results and discussion

3.1. Calcium content in fabric

The test materials were analysed for their calcium content before any further treatment. Ca^{2+} was extracted with 5% HCl and analysed by AES spectrometry. The data of the analysis are shown in Table 2.

Table 2
Calcium content in woven and knitted fabric, individual values, mean and standard deviation.

Material	Results (mmol/kg)	Ca^{2+} content, mean ± std. dev.	
		mmol/kg	mg/kg
Woven A	18.0		
Woven A	18.3		
Woven A	19.2		
Woven A	20.5		
Woven A	17.6		
Woven A	16.2		
Woven A	16.6	18.0 ± 1.5	721 ± 60
Woven B	18.2		
Woven B	15.3	16.8 ± 2.1	670 ± 83
Knitted	4.3		
Knitted	3.8		
Knitted	4.6	4.2 ± 0.4	162 ± 15

The results clearly indicate a much higher Ca^{2+} content of 18.0 ± 1.5 mmol/kg in the woven fabric A (fabric B 16.8 ± 2.1 mmol/kg) compared to 4.2 ± 0.4 mmol/kg found in the knitted fabric. Woven fabrics and knitted material were produced from the same type of fibre, thus the unexpectedly high Ca^{2+} content in the woven fabric cannot be attributed to differences resulting form fibre production. The only processing step during the wet processing of the woven fabric which could cause the high Ca^{2+} content is the desizing step. In enzymatic desizing of starch sizes, amylases are applied in presence of Mg^{2+} and Ca^{2+} salts which act as activators for the amylase. As rather low concentrations of alkaline earth metal ions are present in enzymatic desizing processes, the concentrations of Ca^{2+} observed in our experiments indicate a remarkable affinity of Ca^{2+} ions to absorb in the regenerated cellulose fibre.

3.2. Affinity of Ca^{2+} and Mg^{2+} to lyocell fibres

To study this property in more detail, woven fabric samples were extracted with hydrochloric acid to remove the Ca^{2+}/Mg^{2+} and then treated with Ca^{2+} solutions at defined pH. The Ca^{2+} concentration in the solutions ranged from 0.5 to 8 mM. The Ca^{2+} uptake was studied at pH 5 and pH 9. For comparison the Ca^{2+} content of a sample was analysed after extraction with HCl.

Experimental data and results are given in Table 3 (see Fig. 1).

The results indicate increasing Ca^{2+}-binding in CLY fibres with higher Ca^{2+}-concentration in solution. The binding capacity is limited and saturation can be assumed to be almost complete after treatment in 8 mM Ca^{2+}-solution. At concentration of 8 mM Ca^{2+}, a total amount equivalent to 320 mmol Ca^{2+} was available for sorption per kg fibre material – but sorption values observed were 22.8 ± 3.0 mmol Ca^{2+} per kg fabric at pH 9 and 17.4 ± 1.6 mmol/kg at pH 5, *i.e.* less than 10% of the moles of Ca^{2+} present in the impregnation solution was absorbed in the fibre.

After the impregnation step, one part of samples was analysed for their Ca^{2+} content and another part was used for dyeing with alizarin. As expected the colour depth of the alizarin dyeings increased with Ca^{2+}-content in the fibres.

Samples which had been pre-washed in 5% HCl showed up almost colorless, as no Ca^{2+}-ions were available in the fabric to form a complex with alizarin. The uptake of alizarin from the solution can be monitored both by measurement of the exhaustion from the dyebath and by colour measurement of the dyed samples.

Fig. 2 shows the exhaustion of alizarin measured at the end of the dyeing experiments as function of Ca^{2+}-concentration and pH of impregnation solution.

Table 3
Sorption of Ca^{2+} on lyocell fibres as function of solutions pH and Ca^{2+} concentration.

pH	Ca^{2+} conc. (mmol/l)	Ca^{2+}-content	
		mmol/kg	mg/kg
–	0	1.3	52
9	1	14.0	560
9	2	14.7	587
9	4	16.3	652
9	8	20.8	831
–	0	6.2	248
5	0.5	11.6	466
5	1	9.8	392
5	2	12.8	512
5	4	16.1	646
5	8	15.7	627

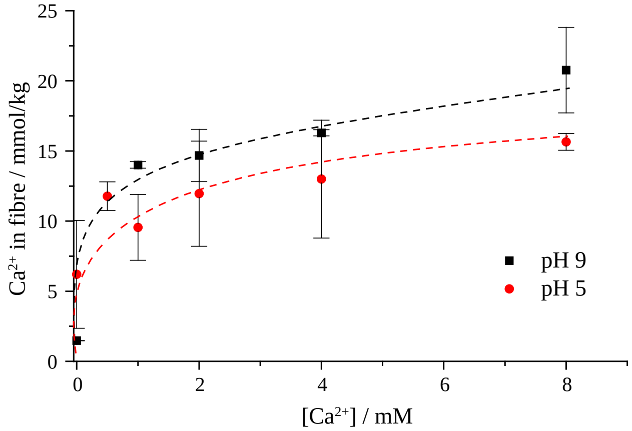

Fig. 1. Ca^{2+}-binding in CLY fibres as function of Ca^{2+} concentration in impregnation solution (■ pH 9; ● pH 5).

In Figs. 3 and 4 the L^*-value and K/S values of the dyed samples are presented. L^*-values decrease with increasing concentration of Ca^{2+} in the impregnation bath and in the fibre. K/S values increase, because there is an increase in fixation of alizarin by complex formation with increase in calcium concentration of solution. K/S values are directly related to the amount of dyestuff fixed on the sample and thus correspond to the Ca^{2+} concentration. L^*-values indicate the lightness of the dyeings, which is not in directly proportional to the amount of dyestuff on the fibres.

When comparing results of the dyeing experiments with the Ca^{2+} analysis it has to be considered that the Ca^{2+}-analysis shows the amount of absorbed ions, while the dyeing steps contain further treatment steps in alkaline baths which also can influence the Ca^{2+}-content in the fibre and furthermore the dyestuff will form complexes only with accessible Ca^{2+} ions.

3.3. Sorption of Mg^{2+} on lyocell fibres

The sorption of Mg^{2+}-ions on lyocell fibres was studied on woven fabric samples, which had been pre-treated with 5% HCl to remove any present Ca^{2+}. Mg^{2+} content was measured by complexometric analysis of the impregnations baths before and after the sorption experiment.

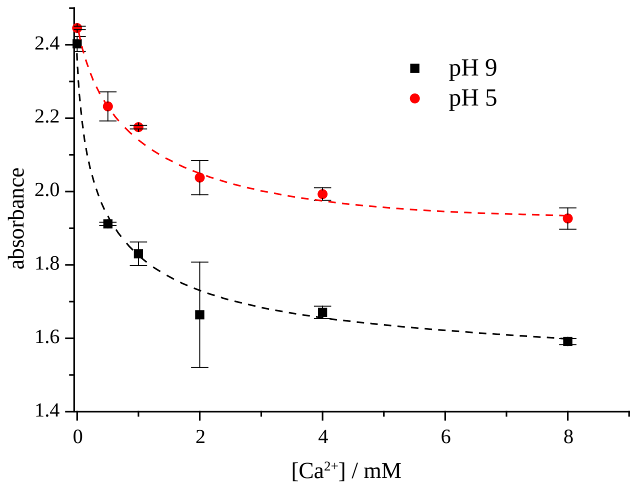

Fig. 2. Absorbance of the alizarin solution at 565 nm in dyeing experiments as function of Ca^{2+}-concentration in the impregnation solution (■ pH 9, ● pH 5).

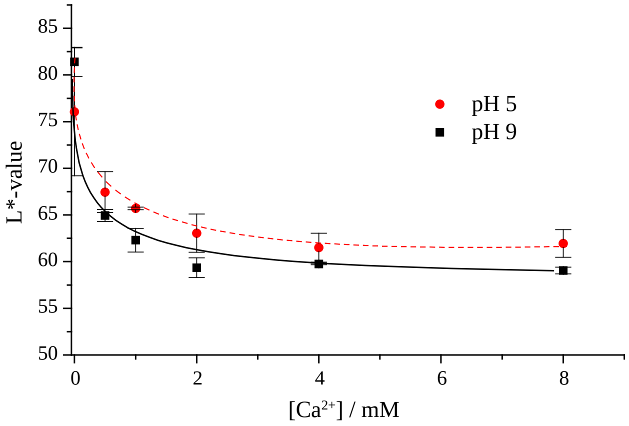

Fig. 3. L^*-value of alizarin dyed samples as function of Ca^{2+}-concentration in impregnation solution, solution pH: (■) pH 9 and (●) pH 5.

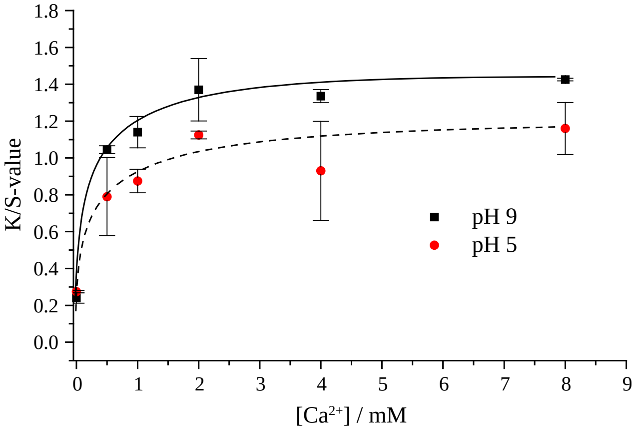

Fig. 4. K/S value of alizarin dyed samples as function of Ca^{2+}-concentration in impregnation solution, solution pH (■) pH 9 and (●) pH 5.

In one set of experiments, fabric samples were impregnated with 1, 5 or 10 mM $MgCl_2$ solution buffered to pH 9; while in another set of experiments no pH buffering was used. In the non-buffered solutions, initial pH values of 5.4 (1 and 5 mM $MgCl_2$) and 4.5 (10 mM $MgCl_2$) were observed which lowered to values of 3.7–3.8 at the end of the treatment. In Table 4, the results of double determination of Mg^{2+} content are given.

As can be seen in Table 4 lower sorption of Mg^{2+} into the cellulose fibres is observed compared to Ca^{2+}. At pH 9 Mg^{2+} content in the fibre ranges from 6.0 to 9.0 mmol/kg which lowers to 2.3–3.3 mmol/kg at pH values near pH 5.

The Mg^{2+} impregnated samples also were dyed with alkaline alizarin solution using the same procedure as the Ca^{2+} samples. The fixation of the alizarin was measured by photometry of the ex-

Table 4
Sorption of Mg^{2+} in lyocell fibres as function of solution pH and Mg^{2+} concentration.

Initial pH	Conc. Mg^{2+} (mM)	Mg^{2+} content	
		mmol/kg	mg/kg
9	1	8.5	207
9	5	6.0	146
9	10	9.0	219
5.4	1	2.3	56
5.4	5	2.3	56
4.5	10	3.3	80

hausted baths and the dyed samples were characterised by CIELab-values and *K*/*S* measurement (see (Figs. 5 and 6).

Lighter dyeings were observed for Mg^{2+} compared to Ca^{2+}, which can be explained by two reasons:

- the lower complex formation constant of Mg^{2+} with alizarin.
- high wash-off mobility of Mg^{2+} during the dyeing experiment which causes lower amounts of dyestuff fixed on the fibre.

3.4. Carboxyl group content

As given in the literature the carboxylic group content in cellulose pulp and powders is of relevance for the binding of ions including Ca^{2+}. (Jacopian et al., 1975; Lindgren et al., 2001). Hence, the carboxylic group content of the lyocell fibres was determined. To avoid possible disturbing influence of adsorbed Ca^{2+} (woven sample) or spin finish (knitted material) the carboxyl group content of samples after various pre-treatment procedures were also determined. Samples were either pre-treated in 5% HCl or pre-washed in Ethanol. The results of the carboxylic group determination are given in Table 5.

The carboxylic group content in the investigated samples ranged from 17 to 18 mmol COOH per kg of cellulose fibre. Much higher values were found for the knitted fabric and the EtOH pre-washed knitted fabric indicating the presence of a Methylene Blue absorbing substance on the material, which could for example be a preparation for the spinning process. This substance was removed by the hydrochloric acid treatment and lower values were found.

3.5. Removal of Ca^{2+} at technical conditions

The technical processing of cellulose textiles also includes treatments to remove Ca^{2+}/Mg^{2+}. For this purpose the material is treated at neutral to alkaline conditions with addition of strong Ca^{2+}/Mg^{2+} complexing agents e.g. nitrilo-triacetic acid, polycarboxylates, phosphonates. To study the binding strength of Ca^{2+} ions, samples were treated in various solutions (Table 1). Different composition of treatment solutions were tested, containing soda, surfactant and complexing agent. The removal of Ca^{2+} can be demonstrated by subsequent dyeing experiments with alizarin. As expected for woven fabric the untreated samples showed the darkest dyeing, while samples which were treated in solutions containing complexing agents showed strongest reduction in alizarin binding capability.

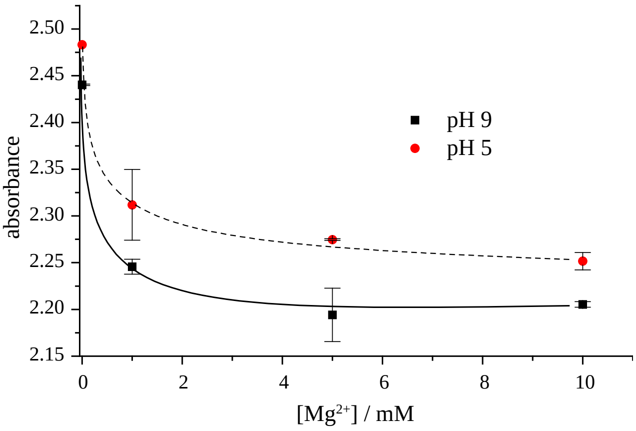

Fig. 5. Exhaustion (560–570 nm) of alizarin in dyeing experiments as function of concentration of Mg^{2+} in the impregnation solution (■) pH 9; (●) pH 5.

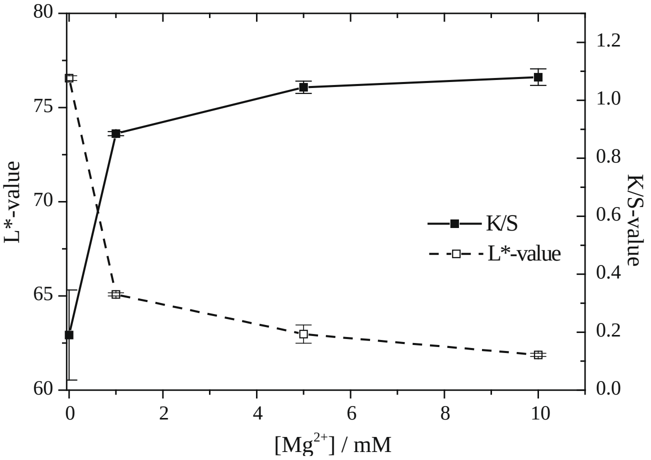

Fig. 6. (□) L^*-values and (■) *K*/*S* values of alizarin dyed samples as function of Mg^{2+}-concentration in impregnation solution (sorption experiment at pH 9).

The binding of alizarin mainly is due to the presence of calcium ions in samples; hence, removal of Ca^{2+}-ions will lower binding of alizarin and lower *K*/*S* values will be observed (Fig. 7).

Use of surfactant, soda (recipes 4 and 5) or water (sample 2) show limited removal of Ca^{2+} as *K*/*S* values remain at the level of the untreated sample (sample 1). Exchange of Ca^{2+} ions by Na^+ ions present in soda solution (sample 5) is of minor relevance.

Different results were observed with knitted fabric (see Fig. 8). As could be expected from the Ca^{2+} determination, much less Ca^{2+} is present in the knitted fabric. The *K*/*S* values of the dyeings are at the level of woven fabric, which has been treated with complexing agent. Lightest dyeings, as well as lowest *K*/*S* values, were observed for treatment in baths containing soda and complexing agent which offer best wash alkaline performance. As discussed in section on carboxylic group determination, the removal of an absorbing yarn preparation in alkaline baths might explain the found results for alizarine dyeing on knitted materials.

4. Conclusions

Lyocell type fibres exhibit significant tendency to absorb Ca^{2+}-ions from Ca^{2+}-salt containing solutions. Even at rather low Ca^{2+}-concentrations of 1–8 mM in solution, Ca^{2+} adsorption in fibre reaches values of 16–23 mmol Ca^{2+} per kg cellulose, which demonstrates a distinct affinity of Ca^{2+}-ions to the binding sites in the cellulose.

Sorption of Mg^{2+}-ions stabilizes at lower levels compared to Ca^{2+}. While at pH 9, 21 mmol Ca^{2+} were bound per 1 kg of fibres, only 9 mmol Mg^{2+} were adsorbed from a 10 mM Mg^{2+} solution. Both for Ca^{2+} and Mg^{2+}, sorption at pH 5 was lower compared to results at pH 9. For Ca^{2+}, 16 mmol/kg were adsorbed from a 8 mM solution of pH 5 and 3.3 mmol/kg of Mg^{2+} were adsorbed from a 10 mM Mg^{2+} solution.

For Ca^{2+}-ions the binding capacity stabilizes at the level of the carboxylic group content, which was determined in the range of 17–18 mmol/kg both for woven and knitted material.

The results indicate the stoichiometry of Ca-ion sorption. When an amount of 20 mmol Ca^{2+} is bound by the carboxylic groups available in the fibre, a carboxylic group number of 17–18 mmol COOH per 1 kg of material indicate the formation of a salt with a 1:1 stoichiometry $-COOH:Ca^{2+}$.

Thus a Ca^{2+}-ion will bind an anion X^- to achieve charge neutrality in the fibre (Scheme 1). The type of anion X^- bound in the fibre will be dependent on the concentration and properties of anions

Table 5
Moisture content and carboxylic group content of woven and knitted fabric (untreated, HCl or ethanol pre-treated; Methylene Blue method).

Sample no	Sample	Pre-treatment	Moisture content %	COOH content mmol/kg
1	Woven fabric A	–	6.35	17.1
2	Woven fabric A	5% HCL	7.65	18.1
3	Woven fabric A	EtOH	7.75	16.6
4	Knitted fabric	–	7.60	59.3
5	Knitted fabric	5% HCl	8.30	18.3
6	Knitted fabric	EtOH	7.15	59.8

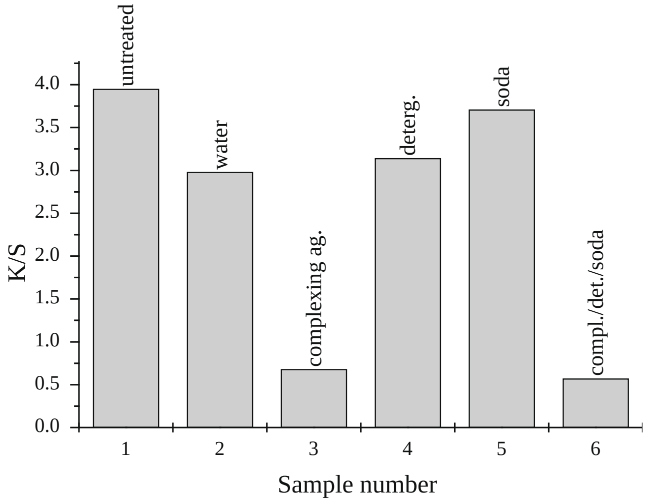

Fig. 7. *K*/*S* values (545 nm) of the alizarin dyeings on woven fabric, pre-treated according recipes numbers 1–6 (1 untreated sample, 2 water, 3 complexing agent, 4 detergent, 5 soda, 6 mixture of complexing agent, soda and detergent).

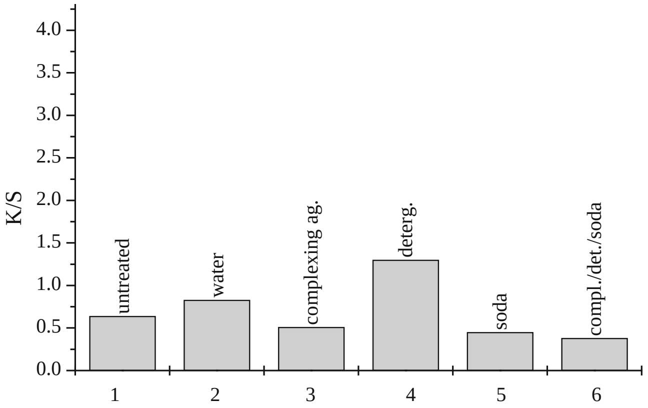

Fig. 8. *K*/*S* values (545 nm) of the alizarin dyeings on knitted fabric, pre-treated according recipes numbers 1–6 (1 untreated sample, 2 water, 3 complexing agent, 4 detergent, 5 soda, 6 mixture of complexing agent with soda and detergent).

$$\text{Cell-COOH} + Ca^{2+} + X^{-} \rightleftarrows \text{Cell-COO}^{-}\, Ca^{2+}\, X^{-} + H^{+}$$

Scheme 1.

present in solution. Experimental work to investigate the binding of these anions in more detail is in progress.

The finding is of high relevance for the processing of regenerated cellulose fibres in presence of Ca^{2+} containing solutions, Typical examples are enzymatic processing and rinse steps in household washings.

The complex formation of Ca^{2+} with alizarin can be used to indicate the amount of Ca^{2+} bound in the lyocell fibre. In case of textile dyes, complex formation with Ca^{2+} can lower fastness properties substantially. Assuming a molecular weight of 800 g/mol for a direct dye or reactive dye, 1% dyeing (10 g dye per 1000 g goods) will correspond to 12.5 mmol dyestuff per 1 kg of goods. An amount of 20 mmol/kg Ca^{2+} sorbed in the fibres would be more than sufficient to form a stoichiometric 1:1 Ca-dyestuff-complex.

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