

INTERACTION OF CELLULOSE WITH ALKALI METAL IONS AND COMPLEXED HEAVY METALS

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The interaction between cellulosic textile materials and metal ions can follow different ways such as swelling, ion-exchange and metal complexation. Uptake of alkali metal hydroxides (LiOH, NaOH, KOH, TMAH) can lead to splitting of lyocell fibres into different numbers of microfibrils. The split number indicates the different local situation of alkali inside the fiber. Up to 5 M alkali concentration, split number is determined by the cation accessibility into the fiber. Above 5 M, no split was observed due to the homogeneous distribution of alkali inside fiber.

The uptake of Ca²⁺ ions follows an ion exchange mechanism which is limited by

the carboxyl content of cellulosic material.

Heavy metal complexes can be formed in the polysaccharide matrix by ligand exchange reactions. The amount of metal complexed with cellulosic material depends on co-ligand used and pH of the complex solution. Thus the amount of metal complexed with cellulose is not limited by carboxyl group content of the cellulosic material and high concentrations of metal ions can be deposited in the insoluble cellulose material.

Keywords: *lyocell, alkali treatment, swelling*

Introduction

The absorption of metal ions into cellulose fibres is of interest for many applications. While the absorption of heavy metals such as copper or manganese is of interest in the processing of cellulose fibres e.g. bleach operations, incorporation of metal ions also is of interest for dietary fibres, production of nanomaterials or for coloured fibres with high level of fastness. Dependent on the type of metal ion present, binding of ions occurs via ion-exchange e.g. in case of calcium ions or via ligand exchange e.g. in the case of heavy metals. The type of metal cation to be inserted and selection of appropriate conditions for metal insertion determine the chemical mechanism occurring and the binding capacity of the cellulose. The

incorporation of metal ions via ligand exchange reaction permits to insert metal ions up to very high level e.g. copper content above 5000 mg/kg of cellulose fibre can be obtained. (Urbano and Goi 2002, Kotelnikova et al. 2007, Vainio et al. 2007, Kongdee and Bechtold 2004a, Kongdee and Bechtold 2004b, Kongdee and Bechtold 2009, Fitz-Binder and Bechtold 2009).

The methods indicate new strategies for preparation of high metal content fibres which will be useful both for improved understanding of behaviour of polysaccharide (PS) material and for production of new PS based materials.

There are three mechanisms for metal ions to bind to cellulose:

a) Sorption is the action of both absorption and adsorption taking place simultaneously. Hydrated alkali ions present in aqueous systems swell the cellulose by penetration into it and also an exchange of hydrated shell with OH groups of cellulose can occur.

b) Electrostatic interaction between metal ions and cellulose occurs in the absence of ligand in the solution. Carboxylic groups of cellulose exchange cations, i.e. hydrogen leaves carboxylic group and metal ions attaches instead.

c) Metal ion and co-ligand (ex. ethylene-diamine, ammonia, tartaric acid, etc) form complexes in solution. In the presence of cellulose which acts as ligand, competition for the metal ion occurs between ligand and co-ligand. When the stability of metal ion and co-ligand complex is sufficient weak, cellulose complexes with the metal ion are formed and the the co-ligand is released. As examples cellulose solutions FeTNa, Cuen, Cuam, etc. can be given.

In the current study, cellulose-metal ion interaction was investigated with regard to swelling, ion-exchange mechanism (electrostatic interaction) and metal complexation. Effect of various alkali metal hydroxides (LiOH, NaOH, KOH, TMAH) on lyocell fibers was investigated by alkali retention value and splitting tendency. The uptake of earth alkali metal, Ca^{2+} , into woven lyocell fabric was studied at pH 5 and pH 9. The uptake of Ca^{2+} ions into the material was visualized by dyeing alizarin which complexes with Ca^{2+} . The incorporation of heavy metal ion, Cu^{2+} , into cotton yarns was achieved in the presence of different co-ligands e.g. D-gluconate and glycine.

Experimental

Materials

Lyocell staple fibers without spin finishing, with 1.3 dtex titer and 38 mm length were provided from Lenzing AG.

Scoured and bleached cotton yarn (Nm 65 m/g) supplied by Getzner Textil AG (Austria). Woven fabric (135.6 g/m^2 , yarn count 50 m/g, warp 36 y/cm, fill 29y/cm, desized) was made from 100 % lyocell fiber (1.3 dtex Tencel[®] Lenzing AG, Austria).

Iron (III) chloride-6 Hydrate, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, (>99%); NH_3 solution (approx. 25 % w/w); glycine (GLY) from Riedel-de Haen AG; Tartaric acid, $\text{C}_4\text{H}_6\text{O}_6$, (>99.5%) from Merck; research grade Sorbitol ($\text{C}_6\text{H}_{14}\text{O}_6$) from Serva-Feinbiochemica GmbH & Co; methylene blue (microscope quality) from Merck; $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ from Carl Roth GmbH (Karlsruhe, Germany); sodium D-gluconate (DGL) from Merck (Darmstadt, Germany) were used. From Fluka (Buchs, Switzerland) analytical grade sodium hydroxide, NaOH, (>98 %), microscopy quality of alizarin (1,2-dihydroxy-9,10-anthra-quinone), HCl (25% w/w), analytical grade NaOAc (sodium acetate), analytical grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were used.

Under technical conditions for sequestering experiments of Ca^{2+} containing woven lyocell fabrics, from BASF (Ludwigshafen, Germany) Trilon[®] TA liqu. (aqueous solution of nitrilo-triacetic-acid sodium salt) as complexing agent and Kieralon B[®] hochkonz. as surfactant were used.

Methods

Fiber diameter

The lyocell fibers were swollen in alkali solutions for about 1 min and the diameter of fibers were measured by Reichert projection microscope with a magnification of 500 \times . Ten fibers were counted and mean value was taken for each type of alkali.

Alkali retention value (ARV)

The lyocell fiber samples, 0.5 g in weight, were put into alkali solutions for 2 h at room temperature. The fibers were then centrifuged at 4000 \times g for 10 min and weighed (w_w). The fibers were washed with

hot water at 50°C and cold water, then they were neutralized with the 0.01 M acetate buffer (pH 5) solution, rinsed with hot and cold water again. The fibers were dried in an oven at 105°C for 4h and the weight was measured (w_d). ARV was calculated by $ARV = [(w_w - w_d) / w_d] \times d_{alk}$, where d_{alk} is the density of alkaline solution. The measurement was repeated four times for each sample to obtain mean value.

Splitting test (Öztürk et al. 2006a)

Crockmeter is used in order to apply defined shear force onto the fiber so that swollen lyocell fiber can be splitted into its microfibrils. Crockmeter was modified by putting a 0.5 kg weight on the rubbing arm so that total downward force on fiber was 13.9 N with a downward pressure of 34.8 kPa. The arm of tester was turned in clockwise direction between 0-90 for 10 times in 10 s so that rubbing arm moves in a straight line on the microscope slide. The photos of the fibers were taken at 500× magnification by Reichert optical microscope and the number of splitted fibers were counted. To evaluate the degree of splitted fibers, numbers were used. The number 0 means no splitting was observed. One means the fiber is unique but some line/cracks on fiber were observed. Two and more numbers represent how many splits were counted from the photos of fibers. Three fibers were tested for each type of alkali so that average was calculated.

Impregnation and extraction of Ca²⁺

A mass of 2 g woven lyocell fabric was extracted with 50 ml 5 % HCl at 40°C for 1 h to remove Ca²⁺. The samples were rinsed with water, neutralized in a solution of 1 g/l NaOAc and line dried.

Samples of 2 g mass were impregnated in 80 ml buffered CaCl₂·2H₂O solution for 1 h at 40°C. The Ca²⁺ concentration in the solutions ranged from 1 to 8 mM. The Ca²⁺ 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 NH₃ solution). After impregnation the samples were washed 3 times with water.

Determination of Ca²⁺

Removal of Ca²⁺ from the impregnated fabric (woven lyocell) was performed in 5 % HCl solution. A mass of 1 g fabric was treated with 25 ml 5 % HCl at 40°C for 1 h to dissolve Ca²⁺. The filtered solutions were diluted with 5 % HCl and analysed by atom emission spectroscopy (AES). At least two repetitions were made for the determination of the Ca²⁺ content in the woven fabric. The Ca²⁺ content were determined in raw fabric and in fabrics after Ca²⁺ removal with 5 % HCl.

Ca²⁺ was determined by AES using a Hitachi Polarized Zeeman Absorption Spectrometer in the emission mode (wavelength 422.7 nm, Air-C₂H₂ flame). For calibration a 100 mg/l Ca²⁺ stock solution of CaCl₂·2H₂O was diluted with 5 % HCl to obtain standard solutions in the range of 0.1-1 mg/l Ca²⁺.

Color strength (K/S) (Fitz-Binder and Bechtold 2009)

About 0.5 g of Ca²⁺ impregnated woven lyocell fabric 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 room temperature. The samples were then rinsed three times in a solution of 4.7 mM Na₂CO₃. Exhaustion of alizarin was monitored by photometry of the dyebath, color depth of dyed samples was characterized K/S values.

K/S of the dyed fabrics was determined according to Kubelka-Munk function (Kubelka 1948, Kubelka 1954). The K/S values were calculated from the reflectance determined at the absorption maximum at 545 nm (one beam spectrophotometer Specord 50, Analytik Jena, Germany, diffuse reflectance sphere 8°/d).

Preparation of Cu²⁺-DGL complex solutions (Kongdee and Bechtold 2009)

0.01 M stock solutions of Cu²⁺ salt and 0.02 M DGL solution were prepared and mixed with 0.1 M GLY to buffer pH. Kongdee and Bechtold 2009 shows the composition of the complex solutions.

A precise weight about 0.5 g of cotton yarn was subjected to 100 ml of Cu²⁺-DGL complex solution for 24 h at 60°C. The samples were then washed in distilled water and dried at room temperature. Two repetitions of each experiment were done and average values of heavy metal content are given.

Analysis of Cu²⁺ content in cotton yarns (Kongdee and Bechtold 2009)

The Cu²⁺-DGL treated samples were extracted with 25 ml of 6 M HCl at 85°C for 60 min. The extraction of Cu²⁺-DGL/GLY treated samples were performed at 90°C for 30 min. The volume of the extract was made up to 50 ml with distilled water. Heavy metal content of the properly diluted solution from Cu²⁺-DGL solutions was determined using inductively coupled plasma-mass spectrometer (ICP-MS) (Agilent 7500 Series). AAS (Hitachi Polarised Zeeman AAS spectrophotometer Z-8230, Inula, Vienna, Austria) was used for Cu²⁺ content analysis from Cu²⁺-DGL/GLY solutions.

Preparation of FeTNa solution (Vu-Manh et al. submitted)

FeTNa solutions were prepared with a mole ratio between FeCl₃.6H₂O: Tartaric acid as 1:3.275. The concentration of Fe ion varied from 0.15 M to 0.55 M. Additionally 0.4, 0.8, 1.25, 2.5, and 5 M free NaOH were used.

All solutions were prepared by following 'direct procedure' without isolation of an intermediate (Bayer 1964; Valtasaari 1957). To exclude light a weighed amount of tartaric acid was introduced into a dark bottle which contains magnetic stirring bar. Tartaric acid was dissolved in slightly more than the minimum amount of water.

Ferric (III) chloride was quantitatively added to the solution with a few milliliters of water. After brief agitation, the dark bottle was introduced into a cooling bath to decrease the temperature of the mixture to about 0°C. NaOH solution was introduced dropwise to the mixture. The addition rate of NaOH was adjusted to prevent the temperature of the mixture from exceeding about 15°C.

Results and Discussion

Swelling of lyocell fibers in alkali metal hydroxides (Öztürk et al. 2006a, Öztürk et al. 2006b)

Figure 1 represents the optical microscope pictures of splitting of one lyocell fiber into different split numbers after swelling in different concentrations of NaOH.

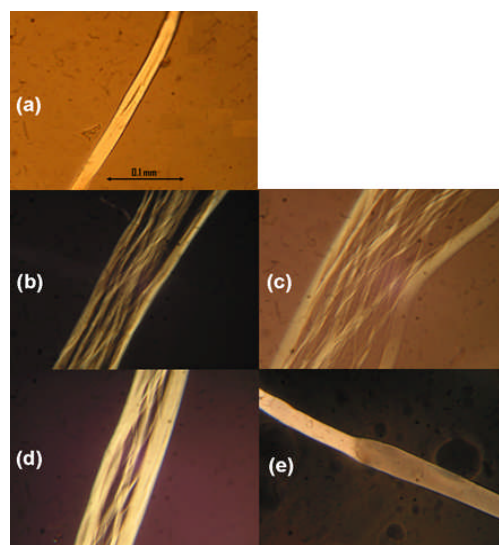


Figure 1. Lyocell fiber swollen and splitted in (a) 0.5 M NaOH, split number is 1 (b) 2 M NaOH, split number is 6 (c) 2.5 M NaOH, split number is 15 (d) 3 M NaOH, split number is 3 (e) 8 M NaOH, no splitting (Öztürk et al. 2006a).

Figure 2 shows the relation between split number and alkali concentration of lyocell fiber after swelling in LiOH, NaOH, KOH and TMAH. Up to 5 M different split numbers were observed depending on alkali type. This shows that at the same concentration the penetration of various alkali types into lyocell fiber is different. Above 5 M irrelevant to alkali type, no

split was observed. Above 5 M, homogeneous distribution of alkali occurs resulting in decrease in swelling stress and also no split.

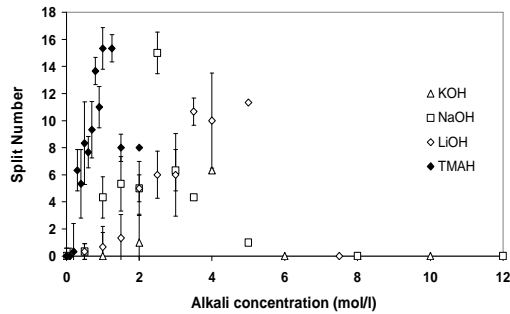


Figure 2. Split number of lyocell fiber as a function of concentration in different alkali solutions (Öztürk et al. 2006b).

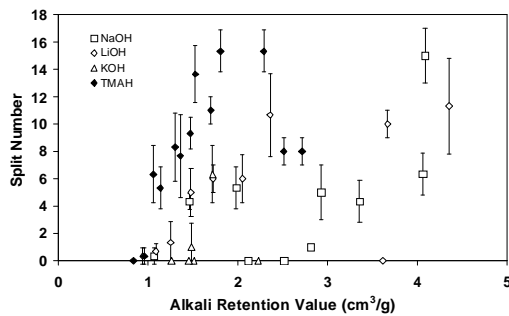


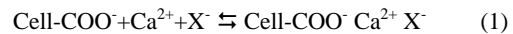
Figure 3. Split number of lyocell fiber as a function of alkali retention value (ARV) (Öztürk et al. 2006b).

Figure 3 shows the relation between split number and alkali retention value (ARV) of lyocell fiber. Different split numbers were found for LiOH, NaOH, KOH and TMAH at the same ARV. For example, around 1.5 cm³/g ARV the split number of lyocell was as following: TMAH>LiOH>NaOH>KOH. Same ARV of fiber in different alkali types indicates the same swelling degree but the different split numbers shows the difference in distribution of alkali inside the fiber. ARV is a bulk property indicating average swelling whereas splitting indicates the local situation of alkali due to swelling stress inside fiber. Thus up to 5 M alkali concentration, the splitting is influenced by cation modulated accessibility of alkali.

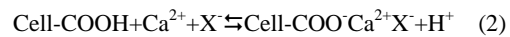
Electrostatic interaction (Ion exchange mechanism) between a metal ion and cellulosic material (Fitz-Binder and Bechtold 2009)

Figure 4 shows the relation between Ca²⁺ amount in treatment solution and Ca²⁺ amount found in woven lyocell fabric after its extraction. As the Ca²⁺ concentration in the treatment solution increased, the amount of Ca²⁺ found in lyocell fabric also increased. The Ca²⁺ amount found in woven lyocell fabric is limited by the carboxyl group content of the material which is around 20 mmol/kg.

The basic mechanism for Ca²⁺ sorption on a cellulosic material is ion exchange mechanism. The Ca²⁺ amount found in woven lyocell fabric at pH 9 was found to be higher compared to that found at pH 5. This is due to the higher amount of negatively charged carboxyl groups found at higher pH. The ion exchange mechanism at pH 9 follows equation (1).



At lower pH, partial protonation of cellulose occurs so that degree of carboxyl group dissociation reduces. At pH 5, both equation (1) and equation (2) occur.



Alizarin marks Ca²⁺ by complex formation (Fitz-Binder and Bechtold 2009). Ca²⁺ and Mg²⁺ ions, which arise partly from the hard water and sometimes also from soil and fabrics, should be removed during laundry. Otherwise they tend to form precipitates on the cellulosic material during laundry.

Figure 5 shows a practical example for the removal of Ca²⁺ using ingredients of a detergent separately. Since the woven lyocell fabric contained a rather high amount of Ca²⁺, it showed the highest color strength due to the complexation between Ca²⁺ and alizarin. After washing the fabric in deionised, only a slight decrease in Ca²⁺ content of the fabric was observed. Little decrease was also

observed after washing lyocell fabric with surfactant or alkali. A significant decrease in Ca²⁺ amount of fabric was observed when complexing agent was used.

During household laundry usually complexing agent is present in the wash bath. Hard water is used for rinsing, thus Ca²⁺ amount in the fabric increases again during the rinse operation.

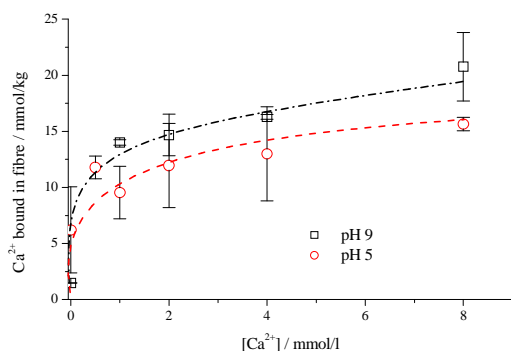


Figure 4. Ca²⁺ binding in woven lyocell fabric as function of Ca²⁺ concentration in impregnation solution (Fitz-Binder and Bechtold 2009).

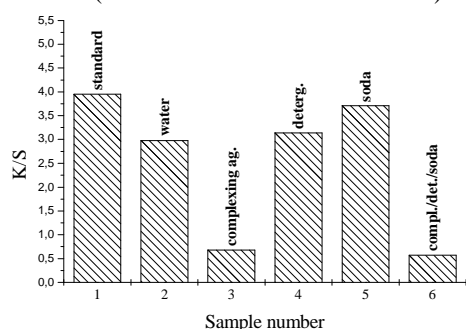
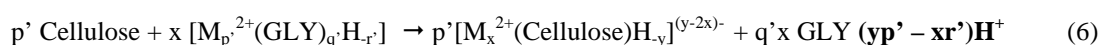
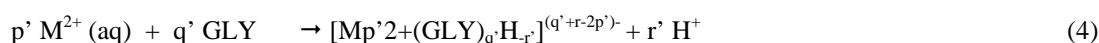
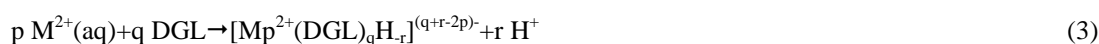


Figure 5. K/S values (545 nm) of the alizarin dyed woven lyocell fabric. Sample 1: desized woven lyocell fabric, 2: water treated, 3: complexing agent treated, 4: surfactant treated, 5: NaOH treated, 6: complexing agent/surfactant/NaOH treated (Fitz-Binder and Bechtold 2009).

Cation uptake via ion exchange mechanism is of importance for a wide range of applications such as:

- processing of pulp and cellulose fibers in paper and textile industry



- use of cellulose substrates as carriers for food enrichment with minerals and medical applications
- sorption of heavy metals from water on polysaccharide materials
- textile dyeing operations (dyestuff precipitates with hardness)
- household laundry
- formation of metal anchors as fixed complexing sites on the polysaccharide substrate
- mordant dyeing with natural dyes (e.g. alizarine complexes with Ca²⁺)

Metal complexation

In a first step complexes of metal ion (Fe³⁺, Cu²⁺, etc) and co-ligand (ammonia, ethylenediamine, tartaric acid, etc) are formed in the solution. When cellulose (ligand) is introduced into the treatment bath, a competition between insoluble polysaccharide ligand and soluble co-ligand occurs. When the metal ion is able to form a complex with the polysaccharide matrix and the stability of metal ion/co-ligand complex is sufficient weak, a metal exchange between ligand and co-ligand occurs. Equations 3 to 6 show the reaction model for metal complexation of cellulose where DGL is D-gluconate, GLY is L-glycine. Equations 3 and 4 show complex formation between metal ion and co-ligand (DGL or GLY). Equations 5 and 6 show the metal exchange reaction, which is dependent on pH (bold marked). In order to have a complex formed between metal ion and ligand (cellulose), stability of complex (metal ion/co-ligand) in the solution and pH (bold marked in equation 5 and 6) are important parameters.

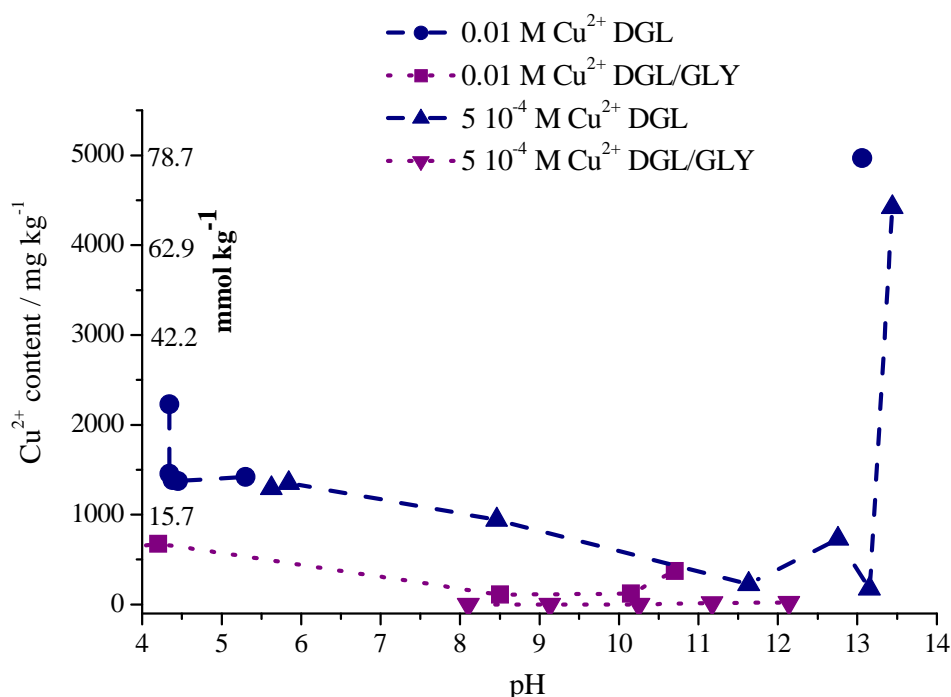


Figure 6. Complexation of Cu^{2+} ions as function of pH (Kongdee and Bechtold 2009).

The insertion of heavy metal ions into insoluble polysaccharide matrices can be controlled by selection of:

- metal ion e.g. Fe^{2+} , Co^{3+} , Zn^{2+} , Cu^{2+} , etc.
- oxidation number of metal ion e.g. Fe^{2+} , Fe^{3+}
- polysaccharide matrix e.g. cellulose, chitosan, amylose, etc.
- co-ligand (ammonia, ethylenediamine, tartaric acid, etc) in solution
- experimental conditions e.g. pH, temperature, time, etc.

Complexation of Cu^{2+} on cotton yarns as function of pH (Kongdee and Bechtold 2009)

Figure 6 shows Cu^{2+} the amount found in cotton yarns after treatment with Cu^{2+} complexes having either DGL or DGL/GLY as co-ligands. Higher amount of Cu^{2+} was found in cotton when DGL was used as co-ligand which shows the complex stability of Cu^{2+} -DGL is lower than Cu^{2+} -DGL/GLY. The lower complex stability of Cu^{2+} -DGL compared to Cu^{2+} -

DGL/GLY results in easier exchange of ligand (cellulose) and co-ligand (DGL).

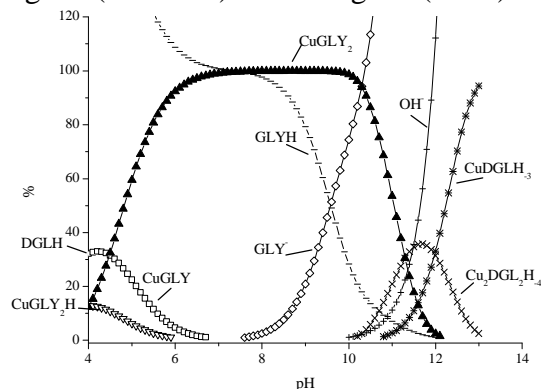


Figure 7. Calculated species distribution of the Cu^{2+} -DGL/GLY system as function of pH (Cu^{2+} concentration as denominator for 100 %) (Kongdee and Bechtold 2009).

Figure 7 shows calculated species distribution of Cu^{2+} -DGL/GLY system as function of pH. SPE program was used to calculate species distribution while using formation constants of complexes from literature. The presence of CuGLY_2 increased up to pH 6, above which it leveled off up to pH 10, and got lower up to pH 12. Above pH 11, the presence of CuDGLH_3 increased with increase in pH.

The high Cu^{2+} amount found in cotton yarns at around pH 13 (Figure 6) can be attributed to the presence of Cu-DGL complex in the solution found by species distribution (Figure 7).

Swelling and dissolution studies on lyocell fibers by using FeTNa (ferric tartaric acid complex in the presence of alkaline aqueous solution) (Vu-Manh et al. submitted)

FeTNa is a common cellulose solvent and has many advantages such as

- it is non-toxic,
- cellulose degradation by air oxygen is very low,
- numerous variability in concentration of Fe and free NaOH is possible in order to get different phases of cellulosic material e.g. swelling, dissolution, disintegration, etc.

The optimum combining mole ratio of iron to tartrate in the FeTNa solution was found to be 1 to 4.5. The 1:3 ratio is found to be the most stable one and has a green color which is used as solvent for wood pulp and other cellulosic materials (Heinze and Wagenknecht 1998). The ligand deficiency at 1:3 ratio is filled by the glycol pair of hydroxyl groups on carbon atoms two and three on the glucopyranoside repeating unit of cellulose to fulfill 1:4.5 ratio which is the optimum one (Bayer 1964).

Figure 8 shows changes in the morphology of lyocell fibers depending on Fe and free NaOH concentration. At lower NaOH concentrations (0.4 M), limited swelling was observed which is comparable to swelling in pure water. At higher free NaOH concentrations (0.8 and 1.25 M), disintegration of fibers was observed. Around 2.5 M free NaOH, dissolution of fibers was found. At 5 M free NaOH, uneven-uniform swelling occurred when Fe concentration was 0.4-0.5 M. Excess increase in fiber diameter so that fiber diameter could not be measured by microscope (blooming) was observed at 5

M free NaOH and when Fe concentration was up to 0.45 M.

Figure 9 shows morphology of lyocell fiber during FeTNa treatments.

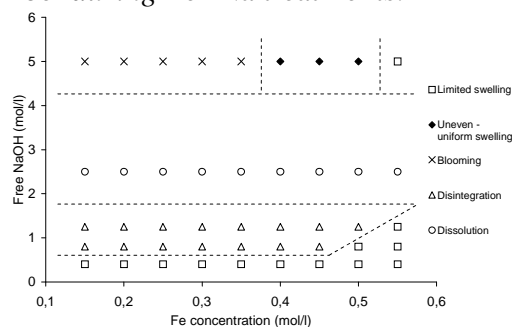


Figure 8. Swelling-dissolution diagram of lyocell fibers for 10 min swelling in FeTNa solutions with varying Fe and free NaOH concentration (Vu-Manh et al. submitted).

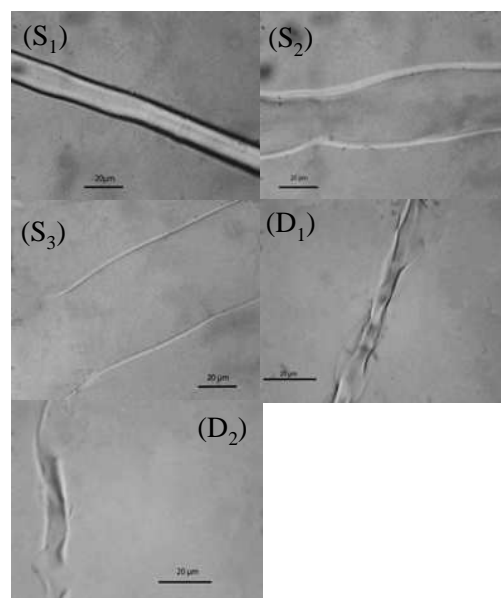


Figure 9. Morphology of lyocell fiber during FeTNa treatments: S_1 symbolizes uniform swelling at a low degree comparable to that of in pure water; S_2 denotes uneven swelling proceeding into S_3 , i.e. uniform swelling at a high degree; D_1 and D_2 are time dependent disintegration of a fiber into rod-like fragments (Vu-Manh et al. submitted).

Conclusions

A huge number of new products and applications for metal-polysaccharide interaction is available. This can be achieved by

- modification of cellulosic materials in order to modify porosity,

accessibility, sorption properties of the cellulosic material

- incorporation of metal ions at well defined conditions e.g. single metal ion insertion without precipitation, pigment coloration, catalytic properties, dietary fibers and food applications, fibers with antimicrobial activity (Ag^+ , Cu^{2+} , etc), fibers containing anchors for binding of organic substances e.g. alizarine
- dissolution of cellulose by metal-ligand complexes in order to form fibers, films or amorphous precipitates.

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