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Copper inclusion in cellulose using sodium D-gluconate complexes

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ABSTRACT

Copper containing cellulose material is of growing interest, e.g. offering alternative in the field of antimicrobials. Solutions of copper D-gluconate complexes (Cu^{2+}–DGL) were used to introduce copper ions into a swollen cellulosic matrix. A ligand exchange mechanism forms the chemical basis of the sorption process. Copper sorption in cellulose was studied in the range between pH 6 and 13. An estimate for the complex stabilities of the Cu-cellulose system could be derived from the calculated species distribution of the different Cu^{2+}–DGL complexes present. Spectrophotometry and cyclic voltammetry of Cu^{2+}–DGL complex solution were used to confirm the presence of different species participating in the ligand exchange reaction. The pH dependent uptake of Cu^{2+} ions in the cellulose matrix can be explained on the basis of the relative stabilities of Cu^{2+}–DGL complex vs. Cu^{2+}–cellulose complexes. In comparison to pH 10, higher copper content was observed at pH 6 and 13. Copper content was limited by carboxyl content of cellulosic materials, thus in analogy to the structure of Cu^{2+}–DGL complexes participation of the carboxyl group as complex forming site is proposed. At high Cu^{2+}-concentration and longer time of immersion in the copper complex solutions formation of solid deposits was observed on the surface of the treated fibres.

1. Introduction

The incorporation or deposition of metals and metal salts on cellulosic substrates and other polysaccharides is of continuously growing attention. A wide range of products and applications can be obtained by insertion of metal ions silver, copper, zinc, titanium in solid cellulose matrices. As a result functional products offering specialized properties such as antimicrobial, antifungal, UV protective, or self cleaning properties can be obtained (Bajpai, Gupta, & Bajpai, 2010; Becheri, Dürr, Lo Nostro, & Baglioni, 2008; Daoud, Xin, & Zhang, 2005; Grace, Bajpai, & Chand, 2009; Grace, Chand, & Bajpai, 2009; Kim, Kwon, & Ostler, 2009; Veronovski, Sfiligoj-Smole, & Viota, 2010; Zikeli & Endl, 2008).

The interaction of cellulose with highly concentrated solutions of metal ions Li^{+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Fe^{3+} also is used to dissolve cellulose e.g. LiCl/dimethylacetamide, cuoxam, nitren, cadoxen, alkaline iron-tartaric acid complexes (Cai & Zhang, 2005; Cai, Liu, & Zhang, 2006; Miyamoto, Inamoto, Matsui, Saito, & Okajima, 1995; Saalwächter et al., 2000; Smith, Bampton, & Alexander, 1963; Vu-Manh, Öztürk, & Bechtold, 2010a; Vu-Manh, Öztürk, & Bechtold, 2010b; Vu-Manh, Öztürk, & Bechtold, 2010c). In all these solvents the formation of stable metal-ion complexes is the fundamental condition to achieve cellulose dissolution.

Deposition of solid metal ion containing compounds often is achieved by formation of solid precipitates including nanoparticles, which adhere on the surface of the fibrous substrate. A common disadvantage of such processes involving two insoluble materials is poor reproducibility. Thus for a more controlled, stoichiometric formation of metal-ion containing materials two general chemical approaches are more favourable:

- Carboxylic groups present in cellulosic materials can serves as sites for ion exchange. In dissociated state carboxylate groups act as weak cation exchanger and metal ions can bind to these sites. In cellulose a high number of hydroxyl groups is available in short distance to the carboxylates, thus these groups will be involved into the complex formation and increased complex stability will be obtained. When the metal binding bases on ion exchange, the capacity will be limited by the carboxylic group number of the cellulose.
- Through the high number of hydroxyl groups available for complex formation the solid cellulose matrix also can serve as polymeric ligand for metal complex formation. The binding capacity then is limited only by the number of available sites offering the required number and geometric arrangement of hydroxyl groups and will follow a Freundlich isotherm

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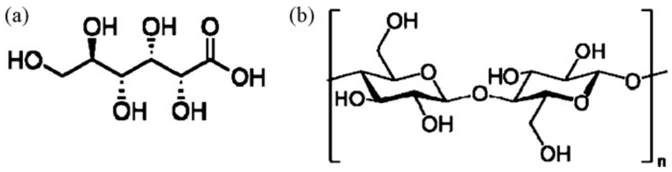

Fig. 1. Structure of (a) D-gluconic acid and (b) cellulose unit.

(Bagrovskaya, Nikiforova, & Kozlov, 2002; Öztürk, Vu-Manh, & Bechtold, 2009).

Cu^{2+} containing chemicals are widely used as disinfectants for water treatment and also for medical applications, where fungicide and antibacterial properties are of interest (Grace, Chand, et al., 2009). Compared to silver ions and many other heavy metals the lower toxicity favours the use of copper ions in applications, where ingestion by humans could be possible. As an example according to the Austrian legal regulations for waste water a limit of 0.5 mg/L Cu is maximum contaminant level, while for Ag concentrations have to be kept below 0.1 mg/L (Bundesminister für Land- und Forstwirtschaft, 1996).

Copper ligand complexes are formed during cellulose dissolution in $Cu(NH_3)_4(OH)_2$ and $Cu[C_2H_4(NH_2)_2]_2$ complexes (Miyamoto et al., 1995; Saalwächter et al., 2000). In these highly alkaline solutions, the solubility of cellulose is based on the formation of cellulose metal complexes, with involvement of the N-containing ligands. The presence of a strong ligand like ammonia or amines also is necessary to prevent precipitation of insoluble copper hydroxides. When diluted solutions are used for treatment of cellulose, fibre swelling and sorption of copper ions occurs without dissolution of the cellulose. This has been studied on different cellulosic materials (aspen wood fibres, sugar beet pulp, modified cellulose and regenerated cellulose) (Aksu & Işoğlu, 2005; Bao-Xiu, Peng, Tong, Chun-yun, & Jing, 2006; Chen et al., 2009; Gurgel, Junior, Gil, & Gil, 2008; Huang, Ou, Boving, Tyson, & Xing, 2009; Navarro, Tatsumi, Sumi, & Matsumura, 2001; Shen et al., 2009). Such ligand exchange reactions can be used to obtain cellulose material with high metal content (Kongdee & Bechtold, 2009).

The presence of a suited soluble ligand, which is able to complex Cu^{2+} in alkaline solution thus is required to achieve incorporation of Cu^{2+} in the swollen cellulose matrix. As a prerequisite the formation constant of the complex system has to be sufficiently high to prevent precipitation of hydroxides in alkaline solution but low enough to achieve ligand exchange reaction with the cellulose structure.

In this study gluconic acid was used as the ligand for copper complex formation. Gluconic acid and its salts were extensively used as a masking agent for metal ions in alkaline solutions. Metal gluconate complexes have been used in analytical, industrial, medical and agricultural applications (Sawyer, 1964). Complexation between gluconic acid and metal ions (Cd^{2+}, Fe^{3+}, $Al^{3+}$and Pb^{2+}) has been investigated over a wide range of pH (Lakatos, Kiss, Bertani, Venzo, & Di Marco, 2008; Pecsok & Juvet, 1956; Pecsok & Sandera, 1955, 1957). Copper–gluconate complexes have been characterized extensively by electrochemical methods, spectrophotometry, circular dichroism spectrum and electron paramagnetic resonance (EPR) (Blomqvist & Still, 1985; Gajda et al., 1998; Pecsok & Juvet, 1955). Insertion of metal ions (Fe^{3+}, Mn^{2+}, Co^{2+} and Zn^{2+}) in cellulose matrix using sodium D-gluconate (DGL) as co-ligand has been previously studied (Kongdee & Bechtold, 2004, 2009; Zhang, Okubayashi, & Bechtold, 2005).

As an alternative citrate and tartrate also could be used as ligand, but the structure of D-gluconate (Fig. 1) is more similar to the cellulose matrix, which favours its use for the study of ligand exchange reactions (Gajda et al., 1998).

Insertion of copper ions in cellulose fibres using Cu–DGL complex system was studied at different pH. Cu–DGL complex species present in solution were calculated with the program BEST, using formation constants, and also characterized experimentally by spectrophotometry and cyclic voltammetry. The uptake of the centre ion by the insoluble cellulose fibres was monitored by AAS analysis of the bound Cu. The state of the Cu-ions bound in the fibres can be described from analogy to the Cu^{2+}–DGL complexes in solution.

2. Materials and methods

2.1. Materials

Lyocell staple fibres (TENCEL®) without spin finishing were kindly supplied by Lenzing AG-Austria. As standard cellulose material filter paper no. 1 (Whatman®), diameter 110 mm (Whatman international Ltd, Maidstone, England) was used. $CuSO_4 \cdot 5H_2O$ (>99%, Fluka, München, Germany), sodium D-gluconate (>99%, Merck, Buchs, Germany), NaOH (99.5%, Carl Roth GmbH), HNO_3 (65%, Merck, Buchs, Germany), HCl (25%, Merck, Buchs, Germany), H_3BO_3 (99.5%, Carl Roth GmbH) and methylene blue dye ($C_{16}H_{18}N_3SCl$) (Merck, Buchs, Germany) were analytical grade reagents and used without further purification.

2.2. Preparation of Cu^{2+}–DGL complex solution

Stock solutions from $CuSO_4$ 50 mM and sodium D-gluconate (DGL) 100 mM and 150 mM were prepared and then were mixed together to achieve a molar ratio Cu:DGL of 1:2 and 1:3, respectively. The pH of the Cu^{2+}–DGL complex solutions then was adjusted using 0.1 M HNO_3, 0.1 M and 0.5 M NaOH. The values of pH were measured using a potentiometer equipped with a glass electrode (Electrode, Hamilton, MP225 Mettler and Flushtrode, Buchs, Switzerland).

UV–visible absorption spectra of Cu^{2+}–DGL complex solutions were measured using multi channel spectrophotometer (MCS 521 UV–VIS, path length 10 mm, Carl Zeiss, Jena, Germany).

2.3. Cyclic voltammetry

Cyclic voltammetry experiments were performed with an EG&G 264 A potentiostat equipped a 303 A HMDE (small drop size area 0.96×10^{-2} cm^2). The experiments were performed at room temperature. A platinum wire served as counter electrode in the three-electrode configuration. All potentials given were related to a (Ag/AgCl, 3 M KCl) reference electrode. The test solutions were aerated for 8 min with He/Ar (inert gas), to eliminate the interfering oxygen. The voltammograms were recorded on a Rikadenki X–Y recorder.

2.4. Copper sorption on cellulose

A 0.5 g of lyocell fibres, conditioned at 65 ± 2% RH and 20 ± 2 °C, were immersed into Cu^{2+}–DGL complex solutions at different pH (4, 6, 10 and 13) using material to liquid ratio of 1:200 g/mL. The samples were continuously agitated for 24 h at 30 °C or 60 °C. For each condition three repetitions were made. Blank samples in absence of sorbent were also processed to check the stability of Cu^{2+}–DGL complex. At the end of the immersion step, fibres were centrifuged at 2792 × g for 10 min for remove solution bound in capillaries (Multifuge 1L, D-37520 Osterode, Germany). The fibres then were weighed and solution retention value (SRV) of fibres was calculated according to Eq. (1) (Zhang et al., 2005). The treated cellulose samples were rinsed with deionised water using a mass to liquid ratio of 1:200 g/mL, agitated in the bath for 30 min with a laboratory shaker

(Heidolph Promax 2020, type 542-20020-00, Schwabach Germany) with 200 rotations per min at room temperature, then centrifuged at 2792 × g for 10 min and air dried at ambient temperature.

$$\mathrm{SRV} = \frac{W_1 - W_2}{W_2 \times d} \tag{1}$$

where W_1 and W_2 are wet mass (g) and mass after drying at room temperature (g), respectively, d is density of Cu^{2+}–DGL complex solution (g/cm^3).

The copper content in cellulose samples was determined by atomic absorption spectroscopy (AAS, Z-8230, Hitachi, Japan) using copper lamp (324.8 nm). A mass of 0.5 g Cu containing samples was extracted with HNO_3 (50 mL, 15%, w/w) at 80 °C for 2 h. The extracted solutions were centrifuged at 2792 × g for 10 min, and analysed by AAS. A 50 mg/L stock solution of $CuSO_4 \cdot 5H_2O$ was used to make calibration solutions in range of 0.1–5 mg/L Cu^{2+}. HNO_3 (5%, w/w) was used for dilution of stock solutions and samples to be within in the range of calibration. In addition Cu^{2+} content in the samples was calculated from the concentration differences in the Cu–DGL bath before and after the sorption experiment.

For microscopy a light microscope equipped with a digital camera was used (model CX41RF from Olympus, Tokyo, Japan).

2.5. Determination of moisture content

For determination of the moisture content a cellulose sample (1 g) was weighed accurately and dried for 4 h at 105 °C. The dried samples were allowed to cool down in a desiccator filled with powdered P_2O_5 and reweighed. The moisture content was calculated from Eq. (2):

$$\mathrm{MC} = \frac{W_c - W_d}{W_c} \times 100 \tag{2}$$

where MC is moisture content (%), W_c is conditioned mass (g) and W_d is mass after drying at 105 °C (g).

2.6. Determination of carboxyl group content

Carboxyl content of fibres was determined using the methylene blue dye sorption method (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998). A solution of aqueous methylene blue (300 mg/L, 25 mL) and borate buffer (30.92 g/L, 25 mL), pH = 8.5 were added to the 0.17 g of dried cellulose sample, shaken at room temperature for 20 h. Then a volume of 2.5 mL solution was transferred to volumetric flask (50 mL) and 0.1 M HCl (5 mL) was added. After filling to the flask to the required volume the absorbance was measured at 664.5 nm using a double beam spectrophotometer (10 mm path length, Hitachi U-2000, Japan).

2.7. Cu^{2+}–DGL complex species

The species distribution of Cu^{2+}–DGL complex solutions in the pH range 3–13 was calculated from formation constants of Cu^{2+}–DGL complexes using the software BEST (Martel & Motekaitis, 1992). The formation constants value of Cu^{2+}–DGL complexes were obtained from literature (Gajda et al., 1998).

3. Results and discussion

3.1. Complex formation

The Cu^{2+}–DGL complex was formed by mixing Cu^{2+} ions solution with DGL solution as dark blue solution. The complex solutions were not buffered, but in the experiments at 30 °C and pH 4, 6 and 13 the changes in pH during were less than 0.2 pH units (Table 1). Greater reductions of 0.5–0.8 pH units were observed in experiments at 60 °C and pH 10.

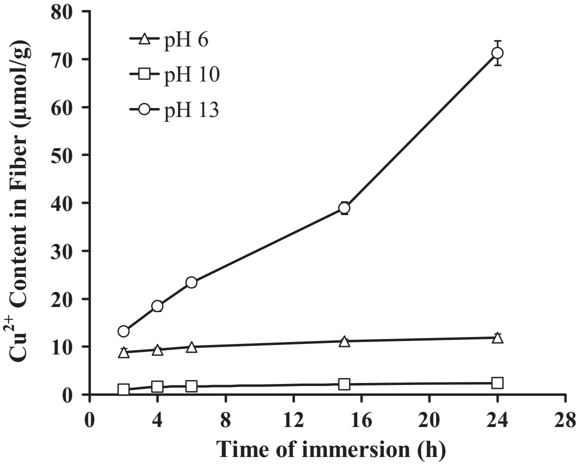

Fig. 2. Cu^{2+}-content in cellulose fibre as function of duration of sorption experiment, 10 mM Cu^{2+}-solution, molar ratio Cu^{2+}:DGL 1:3 at 30 °C: (△) pH 6, (□) pH 10, and (○) pH 13.

The stability of Cu^{2+}–DGL complex system was checked in sorption experiments by looking for precipitate formation as function of temperature and molar ratio of Cu^{2+} to DGL. In the range of Cu^{2+}:DGL 1:2 to 1:2.4 precipitate was observed. The precipitate formation is related to the insufficient molar excess of DGL. At higher DGL concentration (Cu^{2+}:DGL molar ratio 1:3) sufficient chemical stability for more than 6 h was achieved both at 30 °C and 60 °C. At pH 13 at a molar ratio of Cu^{2+}:DGL 1:3 deposition of a red precipitate was observed after 24 h sorption time.

Based on these results a molar ratio of 1:3 Cu^{2+}:DGL was chosen for Cu^{2+} sorption experiments on lyocell fibres. Experiments were performed at 30 °C and pH 6, 10 and 13 using 10 mM Cu^{2+} complex concentration. The Cu-content in the fibres was studied as function of the time of immersion in the range of 2–24 h (Fig. 2).

At pH 6 and 10, the copper content on cellulose fibre was only slightly affected with increasing duration of the experiment, which indicates time stable experimental conditions. No precipitate was observed on the treated fibres. At pH 13, the copper content in fibre continuously increased with contact time. A remarkable increase was also observed between 16 h and 24 h immersion time. Under these experimental conditions the precipitation of Cu-containing residues contributes to the copper content of the fibres. Light microscopy pictures of the treated fibres are shown in Fig. 3a–e.

While at pH 13 after 6 h immersion time no precipitate was detected, after 15 h a red precipitate was observed and increased amounts were found after 24 h. At higher alkalinity copper ions are known to catalyse the effects of reducing groups, present in cellulose and dissolved carbohydrates (Ródio, Pereira, Tavares, & Ferreira, 1999). Thus most probably the insoluble precipitate found on the fibres consists of insoluble Cu_2O, formed by reduction of Cu^{2+} to Cu^{1+}. Sorption experiments thus were limited to a maximum duration of 6 h to achieve equilibration, but to prevent formation of Cu-containing precipitates on the fibres.

3.2. Species distribution

Cellulose can act as a solid ligand which is able to bind Cu^{2+}-ions. The heterogeneous character and the complex structure of swollen cellulose make the application of formation constants questionable. DGL can be understood as a representative homogeneous model, which is in competition for the Cu^{2+}-ions in solution. Thus from an analogy in the behaviour of the dissolved Cu^{2+}–DGL system

Table 1
Change in pH of Cu^{2+}–DGL complex (concentrations) solutions at the beginning and the end of sorption experiment on CLY.

	1:2 Cu^{2+}:DGL				1:3 Cu^{2+}:DGL			
	30 °C		60 °C		30 °C		60 °C	
	pH begin	pH end	pH begin	pH end	pH begin	pH end	pH begin	pH end
pH 4	4.16	4.27	4.14	4.02	4.15	4.20	4.10	4.21
pH 6	6.14	5.98	5.93	5.40	6.05	6.02	5.96	5.81
pH 10	10.00	9.54	9.94	9.10	10.13	9.81	9.53	8.80
pH 13	12.78	12.65	12.82	12.63	13.05	13.03	12.84	12.79

information about the copper-binding behaviour of the insoluble cellulose matrix can be derived.

Using the formation constants given in Table 2 the composition and pH dependent distribution of main species was calculated for the pH range 3–13, for different copper concentrations and different molar ratio Cu^{2+}:DGL (Gajda et al., 1998). A representative example is shown in Fig. 4.

The following limitations in calculations of species distribution have to be taken in mind:

a) The impregnation was carried out at 30 °C, while the species distribution calculations are based on the formation constants for 25 °C.
b) The species distribution was calculated using formation constant for ionic strength of 0.1 M, while different ionic strength was used in these experiments.

Free Cu^{2+}, gluconate (DGL^-) and gluconic acid (DGLH) are observed only at low pH e.g. pH 3, while at pH 4 and above different

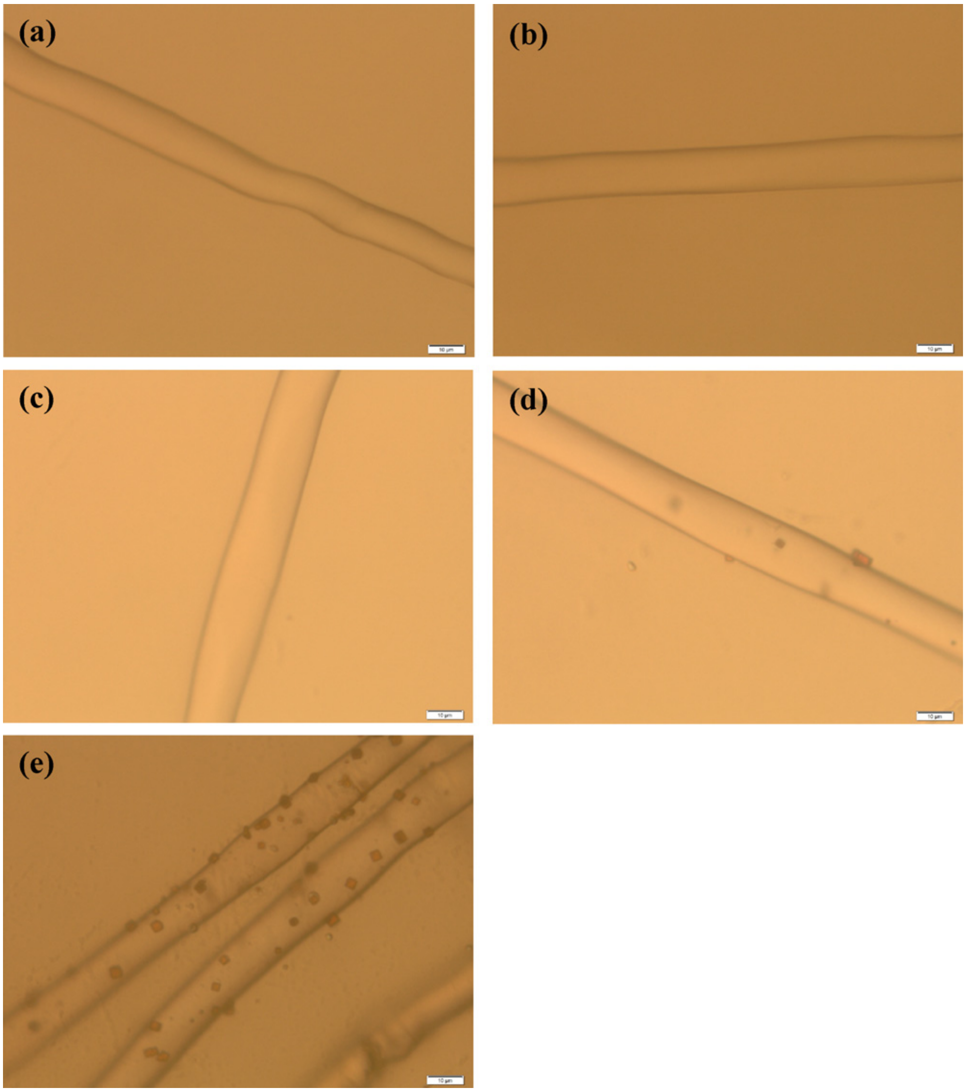

Fig. 3. Light microscope images of CLY fibres treated with 10 mM Cu^{2+} using 1:3 Cu^{2+}:DGL molar ratio at 30 °C: (a) pH 6 after 24 h, (b) pH 10 after 24 h, (c) pH 13 after 6 h, (d) pH 13 after 15 h, and (e) pH 13 after 24 h. Scale bar for all is 10 μm.

Table 2
Composition and formation constants β of Cu^{2+}–DGL complexes (q, p, and r stoichiometric factors in complex species) (Gajda et al., 1998).

Species	Stoichiometric factors					
	Cu (p)	DGL (q)	H (r)	Log β	Temp. (°C)	Ionic strength (M)
DGLH	0	1	1	3.50	25	0.1
$[CuDGL]^+$	1	1	0	2.51	25	0.1
$[CuDGL_2]$	1	2	0	4.59	25	0.1
$[CuDGL_2H_{-1}]^-$	1	2	−1	−0.60	25	0.1
$[CuDGL_2H_{-2}]^{2-}$	1	2	−2	−8.28	25	0.1
$[Cu_2DGL_2H_{-3}]^-$	2	2	−3	−7.25	25	0.1
$[Cu_2DGL_2H_{-4}]^{2-}$	2	2	−4	−15.46	25	0.1
$[CuDGLH_{-3}]^{2-}$	1	1	−3	−20.96	25	0.1

mononuclear or binuclear Cu^{2+}–DGL species are found. In pH range of 6–13 at molar ratio Cu^{2+}:DGL 1:3, around 60–65% of D-gluconate was found in the form of DGL^-. 50% of the D-gluconate is present in the form of DGL^- when a molar ratio Cu^{2+}:DGL of 1:2 is used.

Fig. 4 shows the calculated species distribution of Cu^{2+}–DGL complex as function of pH using Cu^{2+} concentration as denominator for 100%. From the results three main species can be recognized, each prevalent at a certain pH value. At pH 6 Cu^{2+} mainly is present as $[Cu_2DGL_2H_{-3}]^-$, while at pH 10 and 13, $[Cu_2DGL_2H_{-4}]^{2-}$ and $[CuDGLH_{-3}]^{2-}$ are formed, respectively.

The transfer of copper ions from Cu^{2+}–DGL complex solution to the insoluble cellulose matrix depends on the individual formation constant of the species in solution and the complexes formed in the cellulose at this pH. As an assumption participation of free DGL^- in mixed Cu^{2+}–DGL–cellulose complexes was neglected.

When the formation constant of the cellulose–Cu^{2+} complex is higher compared to the formation constant of the respective Cu^{2+}–DGL complex, ligand exchange reaction will occur and high copper concentrations will be found in the cellulose. At pH 6 and 13, where $[Cu_2DGL_2H_{-3}]^-$ and $[CuDGLH_{-3}]^{2-}$, respectively, were the major species, the high copper content in the cellulose fibres indicates, that the formation constant of the Cu^{2+}–cellulose complex is higher than the respective values given for $[Cu_2DGL_2H_{-3}]^-$ and $[CuDGLH_{-3}]^{2-}$ in Table 2.

Low copper concentration in cellulose is an indicator for a relatively high formation constant of the dissolved Cu^{2+}–DGL species present in solution. This behaviour is observed at pH 10, where $[Cu_2DGL_2H_{-4}]^{2-}$ is the major species in solution. The higher formation constant of $[Cu_2DGL_2H_{-4}]^{2-}$ prevents transfer of Cu^{2+} into the cellulose matrix at pH 10.

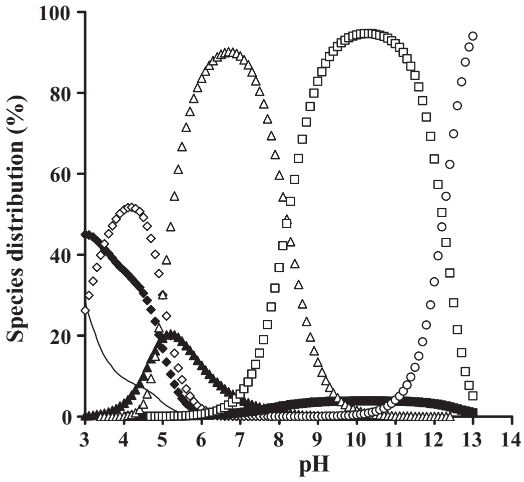

Fig. 4. Species distribution of 10 mM Cu^{2+}–DGL complex using molar ratio 1:3 Cu^{2+}:DGL; Cu^{2+} concentration as denominator for 100%: (black line) Cu^{2+}; (♦) $[CuDGL]^+$; (◊) $[CuDGL_2]$; (▲) $[CuDGL_2H_{-1}]^-$; (■) $[CuDGL_2H_{-2}]^{2-}$; (△) $[Cu_2DGL_2H_{-3}]^-$; (□) $[Cu_2DGL_2H_{-4}]^{2-}$; (○) $[CuDGLH_{-3}]^{2-}$.

The formation of the different species can also be followed by spectrophotometry of diluted Cu^{2+}–DGL solutions at pH 6, 10 and 13 (Fig. 5).

3.3. Cyclic voltammetry

The Cu^{2+}–DGL species are known to be electrochemically active (Pecsok & Juvet, 1955). Thus in this work cyclic voltammetry (CV) was used to demonstrate the presence of different species as function of pH.

Cyclic voltammetry experiments of Cu^{2+}–DGL complex solutions were performed at three different pH values, namely pH 6, 10 and 13. Scan rates from 5 to 100 mV s^{-1} were used. Cyclic voltammetry of DGL solutions with the same concentration and pH as in complex solutions was measured as blank. As expected DGL alone did not show significant electrochemical activity under the experimental conditions chosen (data not presented).

The cyclic voltammograms of Cu^{2+}–DGL complex solutions were recorded in the potential ranges +150 mV to −350 mV, +100 mV to −350 mV and −100 mV to −800 mV for pH 6, 10 and 13, respectively.

One cathodic reduction peak was observed in the voltammogram at pH 6 which can be attributed to the reduction of $[Cu_2DGL_2H_{-3}]^-$ (Fig. 6a).

At pH 10 one cathodic peak was observed in voltammogram which is attributed to $[Cu_2DGL_2H_{-4}]^{2-}$. The peak potential $(E_p)_d$ is independent of the scan rate and is different in shape to the signal at pH 6. $(E_p)_d$ values were measured −250 mV and −260 mV at scan rates 5 and 100 mV s^{-1}, respectively. The cathodic peak current $(I_p)_d$ increased from 0.95 μA to 3.55 μA with increasing scan rate from 5 mV s^{-1} to 100 mV s^{-1}. The height of the cathodic peak current $(I_p)_d$ is comparable to the values obtained at pH 6. Both species

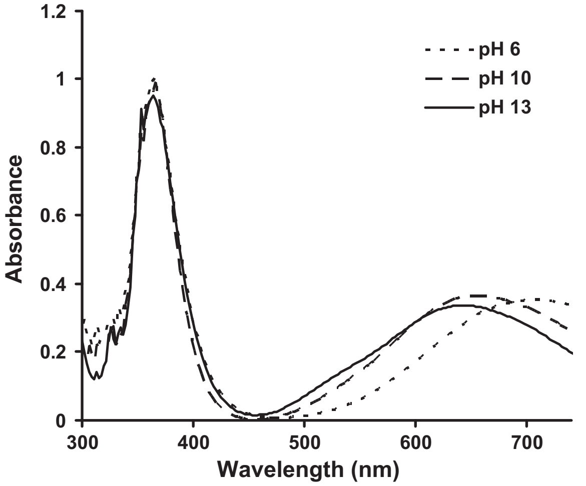

Fig. 5. Absorption spectra of a 10 mM Cu^{2+}/20 mM DGL solution at pH 6, 10 and 13.

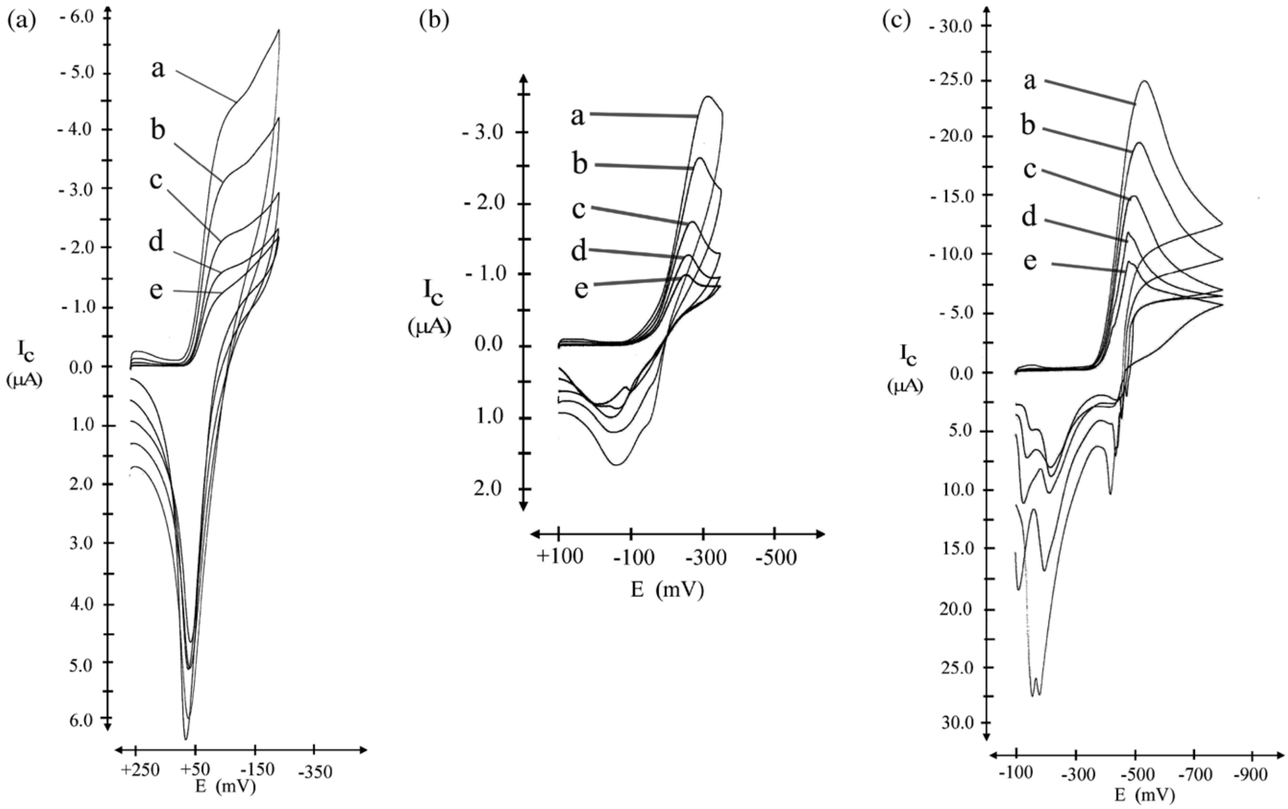

Fig. 6. Cyclic voltammograms of Cu^{2+}–DGL solutions contain 10 mM Cu^{+} and 30 mM DGL (1) pH 6, (2) pH 10, (3) pH 13, at different scan rates (a) 100 mV s^{-1}, (b) 50 mV s^{-1}, (c) 20 mV s^{-1}, (d) 10 mV s^{-1} and (e) 5 mV s^{-1}.

are binuclear complexes $[Cu_2DGL_2H_{-3}]^{-}$ and $[Cu_2DGL_2H_{-4}]^{2-}$ only differing in degree of deprotonation, thus we can expect similar current density.

At pH 13 one cathodic peak was observed with different shape compared to those at pH 6 and 10. Cathodic peak potential changed towards more negative values with scan rate. $(E_p)_d$ was determined with −480 mV at 5 mV s^{-1} scan rate and −535 mV at scan rate of 100 mV s^{-1}. $(I_p)_d$ rises from 9.5 μA at 5 mV s^{-1} to 24.5 μA at 100 mV s^{-1} and is significantly higher compared to values at pH 6 or pH 10. The prevalent species at pH 13 is $[CuDGLH_{-3}]^{2-}$ which is a mononuclear complex, which should exhibit higher diffusion constant and thus higher current density is expected. Several anodic peaks are observed in the reverse scan, indicating the formation of different species, which could include precipitated Cu–hydroxides.

Changes in the shape of the anodic peaks with scan rate indicate decomposition of the cathodically reduced complex within the timescale of the experiment. Instability of the reduced complex explains the formation of precipitates on the cellulose fibres during 24 h duration of experiment.

3.4. Sorption capacity

Sorption capacity of Cu^{2+} on lyocell fibres (CLY) was studied in the concentration range of 0.5–10 mM Cu^{2+} at 30 °C for 6 h at pH 6, 10, 13 (Fig. 7).

The copper content in CLY fibres reached high values at pH 13 and pH 6. Under these conditions the concentration of Cu^{2+} in CLY accumulated to 10 times the Cu^{2+}concentration of the solution. Cu^{2+}-sorption reached values of 15–20 μmol/g. The carboxyl content of CLY, determined by the methylene blue methode, was found with 18.5 μmol/g. Thus at pH 6 and pH 13 the sorption capacity of copper appears to be limited by the carboxyl group content of CLY. This indicates involvement of carboxylic groups in the complex formation. Much lower values were observed at pH 10, where formation constant of $[Cu_2DGL_2H_{-4}]^{2-}$ is higher compared to cellulose.

To confirm this hypothesis copper sorption on filter paper with very low carboxyl group content of 2.7 μmol/g was investigated (Fig. 7). Independent on pH low amount of Cu – in the range of 3.4–3.6 μmol Cu^{2+} per g paper was determined after 6 h. This supports the assumption of an involvement of carboxylic groups in the complexation of Cu^{2+}-ions.

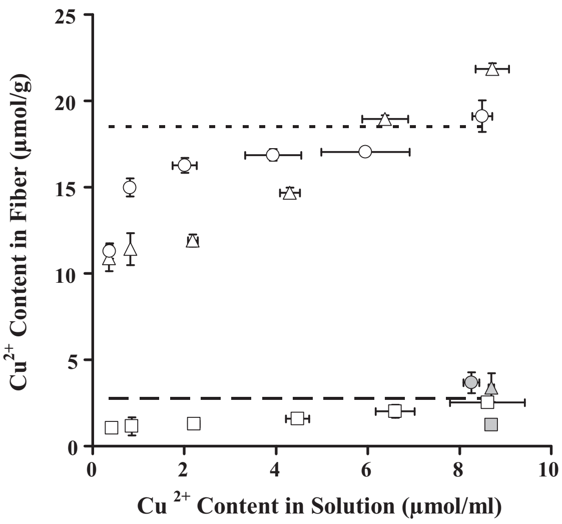

Fig. 7. Sorption capacity for copper on CLY fibres using Cu^{2+}–DGL complex 1:3 molar ratio at 30 °C for 6 h; (△) pH 6, (□) pH 10, (○) pH 13, filled symbols show values for filter paper at pH 6, pH 10, pH 13, horizontal dashed line represents fibre carboxyl content.

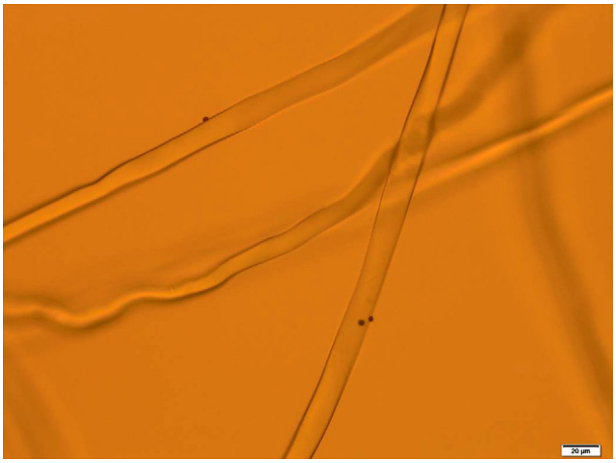

Fig. 8. Light microscope images of CLY fibres treated with 100 mM Cu^{2+} using molar ratio 1:3 Cu^{2+}:DGL at 30 °C for 6 h, pH 6. Scale bar is 10 μm.

Concentrated solutions of Cu^{2+}-complexes can cause swelling of cellulose fibres. To test fibre swelling in the Cu^{2+}–DGL solutions used, the solution retention value (SRV) was determined as a measure of the amount of solution retained in cellulose fibres. SRV can be considered as a measure for overall fibres swelling and access of solution into the cellulose fibres.

SRV of CLY fibres at different pH and Cu^{2+}-concentration range from 0.8 to 1.0 mL/g. Within the investigated conditions SRV was neither affected by pH nor by Cu^{2+}-concentration. Thus pH dependent cellulose fibre swelling will not be of distinct influence on the Cu^{2+} results found.

To study the formation of Cu-containing fibres in more detail, experiments at higher initial copper concentration were performed. The initial copper ion concentration was increased to 100 mM Cu^{2+} at a molar ratio Cu^{2+}:DGL of 1:3. The high concentration led to formation of an orange precipitate at pH 10 and at pH 13 a red precipitate was observed. Solutions at pH 6 exhibited higher stability and an orange precipitate was detected first after one week, thus sorption experiments were performed at pH 6 only. Although the sorption process was carried out from the clear supernatant solutions, precipitate was observed after the sorption experiment. Light microscopy pictures of the treated CLY are shown in Fig. 8.

4. Conclusions

Spontaneous sorption of Cu^{2+} ions occurs from dissolved DGL complexes into the swollen cellulose matrix. Due to the structural similarity between DGL and possible complex forming sites in the swollen cellulose, the Cu^{2+}–DGL system can be taken as model to describe the Cu^{2+}-binding in cellulose.

Using the program BEST and literature data of formation constants for the Cu^{2+}–DGL system, the species present under the chosen experimental conditions can be defined as $[Cu_2DGL_2H_{-3}]^-$ at pH 6, $[Cu_2DGL_2H_{-4}]^{2-}$ at pH 10 and $[CuDGLH_{-3}]^{2-}$ at pH 13. An experimental verification of the presence of different complexes was given by photometry and cyclic voltammetry.

Equilibrium of the ligand exchange reaction is pH dependent. At pH 6 and pH 13 formation of Cu^{2+}–cellulose complex is favoured and high Cu^{2+}-sorption into the fibre is observed. At pH 10 the formation constants of the dissolved Cu^{2+}-species is higher.

Experiments with filter paper proved that sorption capacity was limited by carboxyl group content. Based on the Cu^{2+}–DGL model thus the binding of Cu^{2+} in swollen cellulose will involve carboxylic groups, hydroxyl groups and hydroxide ions. As seen in the Cu^{2+}–DGL model a 1:1 stoichiometry Cu^{2+}:DGL is achieved independent on pH. Thus carboxylic group content will directly define the maximum content of Cu^{2+} in a cellulose substrate.

The high binding capacity of cellulose fibres for Cu^{2+}-ions at pH 6 and pH 13 from DGL complexes indicates a new route to form high copper content cellulose fibres, their maximum value being dependent on the respective carboxyl group content.

Investigations of chemical stability indicated that a molar ratio of Cu^{2+}:DGL of 1:3 is required to maintain stable conditions through the 6 h duration of the sorption experiment. Due to the reducing properties of the carbohydrates present at higher pH, e.g. pH 13, after 15 h immersion time precipitate was observed on the cellulose fibres. The formation of precipitate increased in particular at higher concentration of copper-complex (100 mM). This technique could be used to achieve well controlled deposition of insoluble Cu-containing solids on the surface of the cellulose fibres. The applicatory potential of these materials is under investigation in ongoing research.

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