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Carbohydrate Polymers 55 (2004) 47–55

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Equilibria of Cu(II) in alkaline suspensions of cellulose pulp

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Received 11 December 2002; revised 28 July 2003; accepted 29 July 2003

Abstract

Interaction of Cu(II) with cellulose pulp was studied by means of polarography, AAS, and ultraviolet–visible spectrophotometry. The experiments were carried out at room temperature and at selected initial cellulose pulp slurry pH values between 7.0 and 13.0.

The results obtained showed a trend of decreasing pH after chemical degradation of the pulp (2% w/w) as well as after further addition of a Cu(II) salt (0.5 mmol l^{-1}; pCu = 3.3). The pCu in solutions with initial pH values from 7.0 to 11.0 remained in the range 3.4–3.9, implying insignificant complexation of Cu(II). This is almost certainly caused by the relatively low solution pH (5.9–7.4) after pulp treatment and Cu(II) salt addition. When the pH of these solutions was raised to 12.0, the complexing ability of the dissolved cellulose degradation products rises, apparently, due to the deprotonation of hydroxyl groups, and pCu reached 13.0–13.5.

When the Cu(II) salt was added directly into cellulose pulp slurry at the onset of the alkaline treatment, some of the Cu(II) ions were bound (due to adsorption and/or chemical bonds formation) to the cellulose fibres. The extent of this interaction depended on the initial pH. The bound fraction of the Cu(II) ions represented about 50–70% of the initial Cu(II) amount at pH 7.0 and about 90–95% at pH 13.0. The pCu in filtered solutions with initial pH values in the range 7.0–11.0 remained in the range 3.9–6.1. When the pH of any of the solutions that had initial pH values between 7.0 and 11.0 was increased to 12.0, the complexing ability rised dramatically, and pCu reached 12.9–15.1.

Keywords: Copper(II); Cellulose pulp; Cellulose alkaline cleavage; Polarography; Complexation

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1. Introduction

Polysaccharides such as cellulose are cleaved during the alkali-catalysed hydrolytic reactions. A specific and broad review on cellulose degradation under alkaline conditions is published recently (Knill & Kennedy, 2003). In alkaline hydrolysis, the major loss of insoluble cellulose, in contrast to acidic degradation, is caused by endwise depolymerization reactions (peeling), leading to the formation of soluble carboxylic acid derivatives. The peeling reaction, which can take place even in mild alkali, is the most significant carbohydrate reaction in alkaline processes, especially in alkaline pulping (Hon & Shiraishi, 1986). Carboxylic & hydroxycarboxylic acids formed are strong ligands for the binding of heavy metal ions in alkaline media (Sillen & Martell, 1964).

Generally, interactions between heavy metal ions, their salts or other compounds and cellulose or it's derivatives can occur in four main ways: (1) intercalation into the cellulose matrix, (2) adsorption onto the cellulose fibres, (3) formation of the chemical bonds with the reactive groups of cellulose and (4) formation of complexes with dissolved cellulose degradation products.

The incorporation of metallic species into polymers is an active area of research. Intercalation of silver clusters (Kotelnikova et al., 1997), platinum and palladium aggregates (Kotelnikova et al., 1999) into cellulose has been studied by means of spectroscopic and microscopic methods. In addition, (Zr or Y)-oxalate-cellulose intercalation compounds were synthesed using structurally modified cellulose with a high sorption capacity (Gert, Torgashov, Shishonok & Kaputskii, 1993), and investigated using the X-ray structural analysis (Soloveva, Bashmakov, Novikov & Kaputskii, 1995).

It was found that the formation of a zinc–cellulose complex during the pretreatment of cellulose improves

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doi:10.1016/j.carbpol.2003.07.005

the yield of glucose in both the enzymatic and acid hydrolysis of cellulose (Cao, Xu, Chen, Gong & Chen, 1994; Cao, Xu & Chen, 1995). The spectral characteristics of aqueous zinc chloride solutions (67% w/w) containing cellulose were also investigated (Xu & Chen, 1999). The results suggest that zinc ion forms loose complexes with the C2 or C3 hydroxy-groups of glucopyranose. The absorption of light in the 200–220 nm range indicates the formation of these types of complexes. The presence of calcium ion also enhances the light absorption; however, calcium ion alone cannot form a complex with cellulose (Cao, Xu & Chen, 1995).

The high solubility of cellulose in amine-containing Cu(II) solutions is well known, but the exact role of Cu(II) in the cellulose-dissolution process and the nature of the Cu(II) coordination are ill-defined (Arthur, 1971). Analytical studies have suggest that the ratio of Cu(II) to cellulose glucopyranose units in the soluble complex is 1:2 (Gadd, 1982).

Several workers have studied interactions among Cu(II)–amine complexes and cellulose by adsorption of the amine complexes onto fibrous cellulose. These systems have been studied with ESR spectroscopy, and well-resolved spectra have been observed after treatment of the adsorbed complexes with sodium hydroxide. The spectra have been interpreted in terms of axially symmetric Cu(II) centers, bonded directly to the cellulose, with their major symmetry axes lying perpendicular to the cellulose fibres (Baugh, Hinojosa, Arthur & Mares, 1968; Hinojosa, Arthur & Mares, 1974; Mattar, 1989).

Electron spin resonance spectroscopy has been also used to study and characterise Cu(II)–cellulose complexes formed in solution. These have been compared with Cu(II) centers formed on adsorption by fibrous cellulose (Ajiboye & Brown, 1990). The free hydrated Cu(II) ion in aqueous solution exhibits characteristic ESR parameters associated with the hexahydrated ion. On adsorption of this species onto cellulose the parameters remain essentially unchanged, except for that the room-temperature spectrum is anisotropic, suggesting that the adsorbed Cu(II) species, while bonded in some way to the cellulose, retain most or all of their coordinated water molecules. Further treatment of this species with NaOH produces a new narrow-line ESR spectrum. Analysis of this spectrum indicates that each Cu(II) centre is coordinated to two glucose units, and the ESR parameters of the centre are characteristic of a Cu(II) ion in a square-planar or a tetragonally distorted octahedral configuration. According to the data given in (Baugh, Hinojosa Arthur & Mares, 1968), the major symmetry axis of this centre is perpendicular to the cellulose molecule, and the equatorial ligands are most likely OH-groups on two neighbouring cellulose molecules. On the basis of additional experimental data the authors of (Ajiboye & Brown, 1990) suggested that these OH-groups are deprotonated, and that each glucose unit of cellulose acts as bidentate ligand to the Cu(II) ion. There is only one suitable site on the glucose units for such bidentate coordination, and that is through deprotonated OH-groups on C-2 and C-3. These OH-groups, both of which are equatorial, are well-situated to form five membered chelates which are generally characterized by high stability (Schoenberg, 1971). The proposed structure leads to an extensive three-dimensional lattice of Cu(II) bridging cellulose molecules in the gel (Ajiboye & Brown, 1990).

The state of the copper(II) ions adsorbed by cellulose from aqueous solutions with different pH values has been studied by EPR, XPS and EDXA methods. It has been shown that the curve of copper(II) sorption has a S-like shape characteristic for weak acid sorbents. The authors found, that at pH 10 complexes connected by exchange interactions and diamagnetic clusters are formed (Druz, Andersone & Andersons, 2001).

Interaction of cellulose with heavy metal ions is utilized for practical purposes. Cellulose and modified cellulosic materials are used as sorbents of metal ions from aqueous solutions (Kabay et al., 1999). The technology of reduction of Cu(II) with cellulose in autoclave might have its potential as an alternative for electrowinning or can be used for small waste streams containing copper in relatively high concentrations (Hage, Reuter, Schuiling & Ramtahalsing, 1999).

Since copper(II) ions interfere with the catalytic decomposition of hydrogen peroxide during the bleaching of cellulose pulp, the knowledge on peculiarities of Cu(II) equilibria in cellulose pulp suspensions is very important. Preliminary investigations showed different behaviour of Cu(II) ions depending on pH in cellulose pulp. Therefore the aims of the work reported herein were evaluation of Cu(II) binding to the cellulose fibers and determination of the level of copper(II) ions complexation in alkaline treated cellulose pulp at different pH values. The main method used was polarography, since it is a sensitive general tool for the determination of the concentration of uncomplexed (‘free’) heavy metal ions.

2. Experimental

2.1. Materials

Analytical grade chemicals were used, and bone-dry bleached softwood pulp was obtained from a Finnish kraft pulp mill. 10 mol l^{-1} solution of NaOH was used for adjusting of pH. 5 mol l^{-1} solution of $NaNO_3$ was added to keep the ionic strength (I) of the polarographic experimental solutions constant and equal at 0.1 mol l^{-1}.

2.2. DC polarography

Polarographic curves were recorded by a *PU-1* polarograph (Belarus) using a dropping mercury electrode in a thermostated three-electrode cell at 20 ± 0.1 °C. The potential scanning rate was 100 mV/min. The characteristics of the dropping mercury capillary were as follows:

$m = 2.95$ mg/s, $t = 3.73$ s. The reference electrode was an Ag/AgCl electrode filled with a saturated KCl solution. The solutions were de-aerated by bubbling Ar through the solution.

The values of the actual half-wave potential $E_{1/2}$ were determined within ±1 mV from a plot of $\log(\bar{\imath}/\bar{\imath}_{\mathrm{lim}} - \bar{\imath})$ against E. The values of the transition coefficient α and the reversible half-wave potential $E^{\mathrm{r}}_{1/2}$ were calculated using the following method (Matsuda & Ayabe, 1959):

$$\alpha = 2.303\frac{RT}{nF}\left\{\frac{\Delta\log(\bar{\imath}/\bar{\imath}_{\mathrm{lim}} - \bar{\imath})}{\Delta(-E)}\right\}_{E\to-\infty}, \tag{1}$$

$$E^{\mathrm{r}}_{1/2} = E_{1/11} - 2.303\frac{RT}{nF} \times\left\{\log\left[10 - \exp\frac{\alpha nF}{RT}(E_{1/11} - E'_{1/2})\right]\right\}, \tag{2}$$

where $E'_{1/2}$ is the half-wave potential determined by extrapolation of the linear part of the graph $\log(\bar{\imath}/\bar{\imath}_{\mathrm{lim}} - \bar{\imath})$ against E at sufficiently negative potentials, and $E_{1/11}$ is the potential where the current exceeds the value equal to 1/11 of the limiting current value.

The values of the diffusion coefficient (D) were calculated using the Ilkovic equation (Heyrovsky & Kuta, 1966):

$$D^{1/2} = \frac{\bar{\imath}_{\mathrm{dif}}}{607ncm^{2/3}t^{1/6}}, \tag{3}$$

where $\bar{\imath}_{\mathrm{dif}}$ is the limiting diffusion current (μA), n is the number of electrons involved in electrochemical reaction, c is the total concentration of Cu(II) ions (mmol l^{-1}), m is the flow rate of Hg (mg s^{-1}), t is the time of the drop formation (s).

The corrections for decrease in $\bar{\imath}_{\mathrm{lim}}$ were made in calculation of $\Delta E^{\mathrm{r}}_{1/2}$ for the case of complex formation (Heyrovsky & Kuta, 1966):

$$\Delta E^{\mathrm{r}}_{1/2} = (E^{\mathrm{r}}_{1/2})\mathrm{compl} - (E^{\mathrm{r}}_{1/2})\mathrm{free} - 2.303\frac{RT}{nF} \log\sqrt{\frac{\bar{\imath}_{\mathrm{lim\ free}}}{\bar{\imath}_{\mathrm{lim\ compl}}}}, \tag{4}$$

Concentrations of free (uncomplexed) Cu^{2+} ions were calculated from $\Delta E^{\mathrm{r}}_{1/2}$:

$$\mathrm{pCu} = nF/2.303RT(-\Delta E^{\mathrm{r}}_{1/2}) - \log[\mathrm{Cu(II)}]_0, \tag{5}$$

where $[\mathrm{Cu(II)}]_0$ is the total Cu(II) concentration.

In the case of partial Cu(II) loss in the solution due to it binding to cellulose fibres, the total Cu(II) concentration ($[\mathrm{Cu(II)}]_0$) was found using AAS analyses of the filtered solutions (see below), and the value of $\bar{\imath}_{\mathrm{lim\ free}}$ was determined from the calibration graph.

2.3. Spectrophotometry

The UV–visible spectra were recorded with a Perkin Elmer Lambda 35 UV/VIS spectrometer at 20 °C in 1.0 cm path length quartz cells. The optical blank solution was pure water.

2.4. AAS analysis

Total copper(II) in the filtered solutions was determined by means of a Perkin Elmer 603 atomic absorption spectrophotometer (AAS) using standard procedures.

2.5. pH measurements

Measurements of the solutions pH were carried out by means of a Mettler Toledo MP 220 pH-meter using Mettler Toledo InLab 410 glass electrode.

2.6. Procedure

The pulp (as received) was torn into small pieces and soaked overnight at room temperature in triply distilled water prior to mixing and use for further experiments. pH of the suspension did not exceed 7.0, the mean value was 6.6–6.8.

The investigations were performed at room temperature in two different ways:

1. Separate samples of the pulp slurry (concentration of 2% w/w) were treated at selected initial pH values between 7.0 and 13.0 for 1, 24 and 72 h, then filtered (vacuum filtration through Buchner funnels). A Cu(II) salt (copper(II) nitrate) was then added to the filtrates to make the concentration 0.5 mmol l^{-1} (pCu = 3.3). This is Series I.
2. The slurry samples (concentration of 2% w/w) were treated at selected initial pH values between 7.0 and 13.0 in the presence of 0.5 mmol l^{-1} Cu(II) for 1, 24 and 72 h and then filtered (vacuum filtration through Buchner funnels). This is series II.

Further analyses were carried out by means of the dc polarogaphy and AAS.

3. Results and discussion

3.1. Series I

The results obtained in the first series (Tables 1 and 2) show a trend of decreasing pH as a consequence of pulp treatment for initial pH values between 8.0 and 13.0. This can be attributed to the chemical degradation of cellulose as well as the interaction of cellulose fibres with alkali. A mixture of carboxylic and hydroxycarboxylic acids is formed in the course of the depolymerization (Hon & Shiraishi, 1986; Lowendahl, Petersson & Samuelson, 1976; Petersson & Samuelson, 1976). It can be noted, that the duration of the alkaline treatment did not have a marked

Table 1
Characteristics of solutions formed after treatment of 2% cellulose pulp with alkali (1 h) and interaction of the filtrates with 0.5 mmol l^{-1} Cu(II)

Initial pulp pH	pH after filtration	pH after Cu(II) addition	i_{lim} (μA)	$\Delta E^{r}_{1/2}$ (mV)	pCu
7.00	7.20	5.76	2.4	−16	3.9
8.00	7.80	5.70	2.7	−12	3.7
9.00	7.93	5.86	2.9	−14	3.8
10.00	9.18	5.92	3.4	−13	3.8
11.00	10.85	6.30	2.7	−16	3.9
12.00	12.03	12.03	Precipitate	Precipitate	Precipitate
13.00	12.90	12.95	Precipitate	Precipitate	Precipitate

influence on the observed pH decrease in the solutions investigated (cf. Tables 1 and 2). However, at the initial pH 10–12 the effect of time was more important because of the combination of relatively fast reaction rate with limited charge of alkali.

Addition of Cu(II) to the filtrate obtained after the removal of cellulose fibers yielded a further decrease in solution pH (Tables 1 and 2). This latter decrease can be ascribed to Cu(II) complex formation with the degradation products of cellulose. If the complexation occurs with compounds containing carboxylic groups, displacement of the acid hydrogen ions with Cu(II) ions will lower the solution pH. This presumption is supported by the rather insignificant decrease in concentration of free Cu(II) ions (from pCu = 3.3 to pCu = 3.4–3.9), when the initial pulp pH was 7 and10 and the pH after Cu(II) addition did not exceed 7 (Tables 1 and 2). These results are in agreement with data about the stability of Cu(II) complexes with carboxylic acids, which show that the logarithms of the stability constants are quite low and equal to 2–5 (Martell & Smith, 1977; Perrin, 1979; Sillen & Martell, 1964; Sillen & Martell, 1971). It can be mentioned, that in the case of weak complex formation, the cause of the decrease in solution pH might be also the hydrolysis of Cu(II) ions.

The values of Cu(II) reduction limiting current in the filtered solutions of cellulose pulp treated at different initial pH values are quite similar in the pH range 5.70–6.57 (Tables 1 and 2), the mean value being 2.9 μA. The calculated mean value of diffusion the coefficient of Cu(II) complexes in these solutions is 3.4×10^{-6} cm^2 s^{-1}, less than that of uncomplexed Cu(II) obtained in 0.1 mol l^{-1} $NaNO_3$ (6.4×10^{-6} cm^2 s^{-1}). The mean of the diffusion coefficients of Cu(II) complexes determined in the solutions under investigation is comparable to values of diffusion coefficients of Cu(II) complexes with ligands of relatively low molecular mass, e.g. glycerol, tartaric acid, saccharose (Norkus, 2000).

The comparison of light absorption spectra of uncomplexed Cu(II) with that of Cu(II) obtained in the filtered solutions of cellulose pulp treated at different initial pH values shows either a decrease in absorbance or changes in both peak shape and absorbance. This confirms complex formation in the system under investigation (Fig. 1). Some differences in the spectra are observed as a function of initial pulp pH and/or solution pH after Cu(II) addition. There are small increases in light absorption maxima and shifts to shorter wavelengths, indicating minor differences in Cu(II) complexation as a function of pH (Fig. 1).

Table 2
Characteristics of solutions formed after treatment of 2% cellulose pulp with alkali and interaction of the filtrates with 0.5 mmol l^{-1} Cu(II)

Hydrolysis time (h)	Initial pulp pH	pH after filtration	pH after Cu(II) addition	After adjusting to pH = 12.00					
				i_{lim} (μA)	$\Delta E^{r}_{1/2}$ (mV)	pCu	i_{lim} (μA)	$\Delta E^{r}_{1/2}$ (mV)	pCu
24	7.00	7.46	5.86	3.0	−2	3.4	0.7	−295	13.5
	8.00	7.36	6.28	3.2	−12	3.7	0.5	−285	13.1
	9.00	7.56	6.45	3.3	−11	3.7	0.6	−286	13.2
	10.00	8.35	6.48	2.9	−9	3.6	0.7	−287	13.2
	11.00	10.20	7.43	Precipitate	Precipitate	Precipitate	Precipitate	Precipitate	Precipitate
	12.00	11.64	11.63	Precipitate	Precipitate	Precipitate	Precipitate	Precipitate	Precipitate
	13.00	12.74	12.72	0.5	−369	16.0	–	–	–
72	7.00	7.28	6.33	3.3	−10	3.7	0.8	−283	13.0
	8.00	7.50	6.40	2.8	−8	3.6	0.6	−283	13.0
	9.00	7.58	6.46	2.7	−11	3.7	0.6	−279	12.9
	10.00	8.39	6.57	2.6	−16	3.8	0.5	−286	13.2
	11.00	9.76	7.15	0.6	−42	4.8	0.3	−289	13.3
	12.00	11.53	11.20	Precipitate	Precipitate	Precipitate	Precipitate	Precipitate	Precipitate
	13.00	12.83	12.80	Precipitate	Precipitate	Precipitate	–	–	–

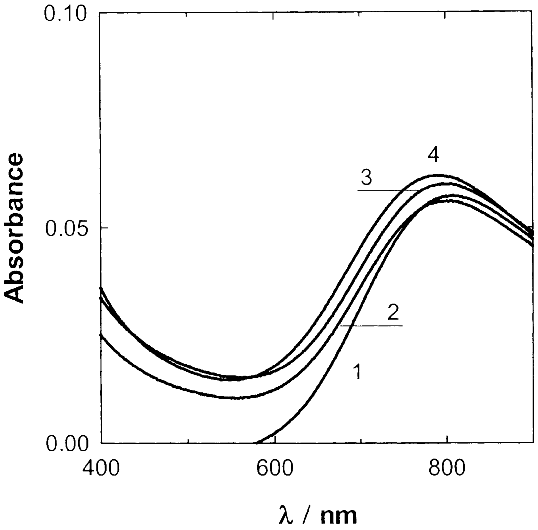

Fig. 1. Cu(II) spectra in the filtrates obtained after treatment of 2% cellulose pulp for 24 h. $[Cu(II)]_0 = 0.5$ mmol l^{-1}. Initial pulp pH/pH after treatment and filtration/pH after Cu(II) addition: 2-8.00/7.30/5.01, 3-9.00/7.48/5.07, 4-10.00/9.20/5.29. Curve 1 represents the spectrum of uncomplexed Cu(II).

Note that, when comparing results of the experiments in the first series obtained at different pulp pH values and treatment times, the levels of Cu(II) complexation in the pH range 7.0–10.0 (initial pulp pH) do not differ significantly. The concentrations of free copper(II) ions in these solutions are not dramatically lower than the initial concentration of added, uncomplexed Cu(II), showing that cellulose degradation products with weak complexing abilities are formed under the conditions investigated. At the longest treatment time (72 h) and the highest initial pH (11.0) for which no $Cu(OH)_2$ precipitate was formed (Table 2), the concentration of free copper(II) ions decreased about one order of magnitude compared to those at lower pH values. Apparently, different cellulose destruction compounds with higher complexing abilities are formed in the solution after treatment at higher initial pulp pH. This presumption is supported by UV–visible spectrophotometry which shows spectra with different positions and intensities obtained when initial pulp pH was 10.0 and 11.0 in comparison with that when the initial pulp pH was 8.0–9.0 and 12.0–13.0 (Fig. 2).

In aqueous solution, carbohydrate complexes are formed by the displacement of water molecules from the first coordination sphere of cations by the hydroxy-groups. Since the water molecules solvate cations much better than monohydroxy alcohols or diols, the latter cannot form stable complexes with cations in neutral aqueous solutions (Gyurcsik & Nagy, 2000). However, deprotonated carbohydrates and polyols represent rather strong and efficient metal binding agents (Burger & Nagy, 1990; Hegetschweiler, 1997; Hegetschweiler, 1999; Verchere, Chapelle, Xin & Crans, 1998). The same tendency is observed for hydroxycarboxylic acids with deprotonated OH-group, e.g. it was found that in alkaline medium L- and DL-tartaric acids form rather strong complexes with Cu(II), with log stability constants in the range of 18–22 (Norkus, Vaškelis, Žakaitė & Reklaitis, 1997).

In other words, hydroxy-groups can have strong complexing ability, but only in high pH solutions. Since compounds containing such groups can be formed during the degradation of cellulose pulp, we conducted further investigations of the complexing abilities of cellulose pulp degradation products at higher pH. After the cellulose was treated at a range of pH values, we adjusted each of the corresponding filtrates to pH 12.0 and then re-evaluated the Cu(II) complexation.

When the duration of the pulp treatment was 1 h and the filtrate pH was adjusted to 12.0 and Cu(II) was added,

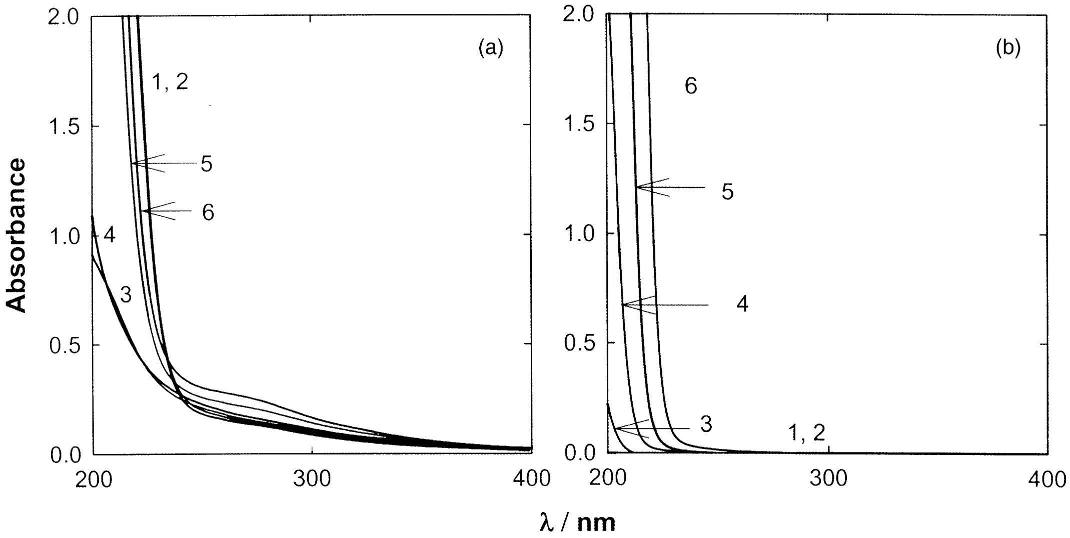

Fig. 2. UV-spectra of: (a) filtered alkaline solutions obtained after treatment of 2% cellulose pulp for 24 h. Initial pulp pH/pH after treatment and filtration: 1-8.00/7.30, 2-9.00/7.48, 3-10.00/9.20, 4-11.00/10.04, 5-12.00/11.96, 6-13.00/12.65; (b) sodium hydroxide solutions with pH: 1–8.00, 2–9.00, 3–10.00, 4–11.00, 5–12.00, 6–13.00.

a $Cu(OH)_2$ precipitate was formed in all cases, indicating low complexing ability in the solutions obtained. For longer treatment times, however, no precipitate was formed after Cu(II) addition regardless of the initial pH of the pulp slurries. In fact, the filtrate solutions become blue in colour, which is indicative of the presence of Cu(II) complexes (different from those formed at lower pH values, for which light absorbance is much lower). The half-wave potential for Cu(II) reduction shifts over 250 mV and reaches −280 to −295 mV. Thus, the complexing ability of the dissolved cellulose hydrolysis products rises drastically due to deprotonation at higher pH (Table 2). The UV-spectra for the non-pH adjusted filtrates also show changes when the filtrates are adjusted to pH 12 (Fig. 3). These differences can be attributed to the deprotonation of OH-groups at higher pH values.

Also note that the results obtained after adjusting the pH to 12.0 (Table 2) show Cu(II) complexation levels that are essentially independent of the initial pulp pH. The calculated pCu values in these solutions range from 13.0 to 13.5.

In addition, the mean value of Cu(II) reduction limiting current, equal to 0.6 μA (Table 2), is about 80% lower than that obtained prior to pH adjustment to 12.0. The calculated mean value of diffusion coefficient of Cu(II) complexes in the solutions after pH adjustment to 12.00 is $1.5 \times 10^{-7}\ cm^2\ s^{-1}$, i.e. more than 20 times lower than before pH adjustment. Such low Cu(II) diffusion coefficient values are characteristic of Cu(II) complexes with large size, e.g. macromolecular, ligands (Norkus, Vaičiūnienė, Vuorinen & Heikkilä, 2002). Estimation of the approximate diameter of Cu(II) complex species according to the data of graph given in (Norkus, 2000) yields about 10–20 nm. Apparently, the ligands that cause the relatively high Cu(II) complexation level at pH ≥ 12.0 could be, e.g. xylans dissolved from the pulp.

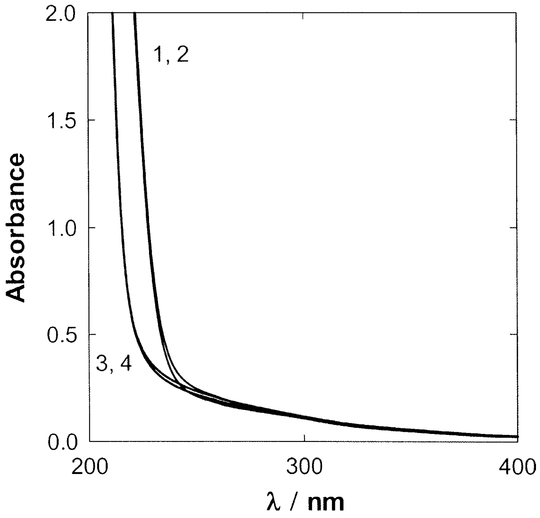

Fig. 3. UV-spectra of the filtrates obtained after treatment of 2% cellulose pulp for 24 h at initial pulp pH: 1–8.00, 2–9.00, 3 –10.00, 4–11.00, and adjusted up to pH 12.00.

3.2. Series II

When the Cu(II) salt was added directly into the cellulose slurry, part of Cu(II) (presumably, initially partially in form of $Cu(OH)_2$, especially at higher pH values) was bound by adsorption, intercalation and/or chemical bond formation to cellulose fibers. The extent and nature of these associations depended on initial pH.

This binding of Cu(II) reaches ca. 50–70% of the initial Cu(II) amount at pH 7.0 and ca. 90–95% at pH 13.0 (Table 3). Two general trends are observed-the residual amount of Cu(II) in the bulk solution decreases with increasing pH and with increasing duration of hydrolysis. The dependence on initial pulp pH is particularly clear for the experiment with a 1 h treatment time. The effect of the duration of cellulose pulp treatment on Cu(II) binding to cellulose fibers is largest at lower pH values (pH 7.0–10.0), presumably due to longer time needed to establish an equilibrium. The effect of treatment time on Cu(II) binding to cellulose fibers diminishes markedly at the highest pH investigated (pH 13.0). In this case the concentration of alkali solutions is rather high, and it is known that alkali can intercalate into the cellulose matrix and change its structure. Seemingly, alkali intercalation occurs fast enough and the altered cellulose matrix is favorable for binding of Cu(II). This process might include the formation of Cu(II) hydroxy-complexes, since these complexes are known to be formed with polyhydroxylic compounds, e.g. dextran (Norkus, Vaičiūnienė, Vuorinen & Heikkilä, 2002), saccharose and glycerol (Norkus, Vaškelis, Vaitkus & Reklaitis, 1995).

The calculated values of pCu in the solutions with initial pH values between 7.0 and 11.0 remain in the range 3.9–4.3, showing lower concentrations of free Cu(II) ions compared to those in Series I (cf. Tables 1–3). This is probably due to the binding of part of the initial Cu(II) into cellulose fibers. A sharp increase in pCu to 12.3–12.9 and to 16.4–17.2 was observed at pH 12.0 and 13.0, respectively.

When the pH of the solutions with initial pH values between 7.0 and 11.0 is adjusted to 12.0, the complexing ability of treated cellulose pulp rises and pCu reaches 12.9–15.1. A comparison of this data with that from Series I (pCu 13.0–13.5) shows that pCu is larger when the cellulose pulp is treated in presence of Cu(II) (cf. Tables 2 and 3). On the one hand, this decrease could be attributed to binding of most of the Cu(II) into the cellulose fibers (up to 96%). On the other hand, the calculations show that this increase in pCu does not only result from decreases in the total concentration of Cu(II) in the solution. It also results from different complexing properties of the solution containing the cellulose depolymerization (hydrolysis) products when cellulose pulp was treated in the presence of Cu(II). For example, when $0.5\ mmol\ l^{-1}$ of Cu(II) interacts with the filtered solution obtained after cellulose pulp treatment at initial pH 10.0 for 24 h, and the resulting solution is adjusted to pH 12.0, the pCu value determined is equal to 13.2 (Table 2). Under similar conditions, when the cellulose

Table 3
Characteristics of filtrates formed after treatment of 2% cellulose pulp with alkali in the presence of 0.5 mmol l^{-1} Cu(II)

Hydrolysis time (h)	Initial pulp pH	pH after filtration	Cu(II), mmol l^{-1} after filtration				After adjusting to pH = 12.00		
				i_{lim} μA	$\Delta E^{r}_{1/2}$ (mV)	pCu	i_{lim} μA	$\Delta E^{r}_{1/2}$ (mV)	pCu
1	7.00	5.25	0.25	2.2	−12	4.0	0.2	−273	13.0
	8.00	5.53	0.25	2.0	−12	4.0	0.3	−270	12.9
	9.00	5.65	0.20	1.6	−4	3.9	0.3	−279	13.4
	10.00	5.35	0.21	1.9	−10	4.0	0.3	−279	13.3
	11.00	6.25	0.16	0.8	−14	4.3	0.4	−275	13.3
	12.00	11.70	0.12	0.2	−244	12.3	0.3	−261	12.9
	13.00	13.02	0.06	0.2	−361	16.7	–	–	–
24	7.00	5.30	0.05	0.7	−1	4.4	0.2	−302	14.8
	8.00	5.10	0.10	1.4	−9	4.3	0.4	−287	13.9
	9.00	5.48	0.10	1.1	−8	4.3	0.4	−285	13.8
	10.00	5.94	0.02	0.4	−13	5.2	0.2	−301	15.1
	11.00	10.38	0.10	0.1	−137	8.8	0.2	−289	14.0
	12.00	11.80	0.03	0.1	−243	12.9	–	–	–
	13.00	12.73	0.02	0.1	−359	17.2	–	–	–
72	7.00	5.71	0.16	1.2	−6	4.0	0.2	−297	14.0
	8.00	5.95	0.06	0.6	−15	4.7	0.2	−293	14.4
	9.00	5.89	0.07	0.5	−15	4.7	0.3	−289	14.2
	10.00	6.35	0.05	0.3	−22	5.1	0.2	−292	14.4
	11.00	7.60	0.04	0.2	−51	6.1	0.1	−287	14.3
	12.00	11.39	0.04	0.1	−240	12.6	0.1	−285	14.2
	13.00	12.57	0.03	0.1	−343	16.4	–	–	–

pulp was treated in the presence of Cu(II), the total concentration of Cu(II) in the bulk solution diminishes to 0.02 mmol l^{-1}, and the pCu value increases, reaching 15.1 (Table 3). The decrease in total Cu(II) concentration from 0.5 to 0.02 mmol l^{-1} without additional complex formation should yield the increase in pCu value equal to 1.4 units. Actually, the observed increase is higher (1.9 pCu units) showing differences in complexing ability of the solutions obtained, seemingly due to different cellulose degradation products formed.

The UV–visible spectra of the solutions obtained after treatment of cellulose pulp in the presence of Cu(II) show formation of Cu(II) complexes that depend on the pH (Fig. 4). The spectra labeled 2 and 3, recorded at lower pH (Fig. 4) are similar to those from the first series (Fig. 1, spectra 2–4) showing, presumably, coordination of Cu(II) to compounds containing carboxylic groups. Comparison of the spectra obtained in the Series II with that of Series I shows minor decrease in Cu(II) complex absorption intensity (ca. 10%) when cellulose pulp was treated in presence of Cu(II). This decrease could be attributed to loss of copper(II) due to its binding to cellulose fibers. At higher pH values, however, the spectra change. For example, in the solutions with pH values between 11.33 and 12.35, the absorption intensities decrease (partly it can be connected with over mentioned Cu(II) loss due to interaction with cellulose fibers) and the maxima shift to shorter wavelengths (Fig. 4, spectra 4–6). Again, the changes observed, especially the shift to shorter wavelengths, might be attributable to Cu(II) complex formation with deprotonated OH-groups of hydroxycarboxylic acids or other compounds containing OH-groups (e.g. xylan or its degradation products).

On the one hand, this preliminary study has shown that polarography, alone or jointly with atomic absorption spectrometry, is a powerful tool for investigations of

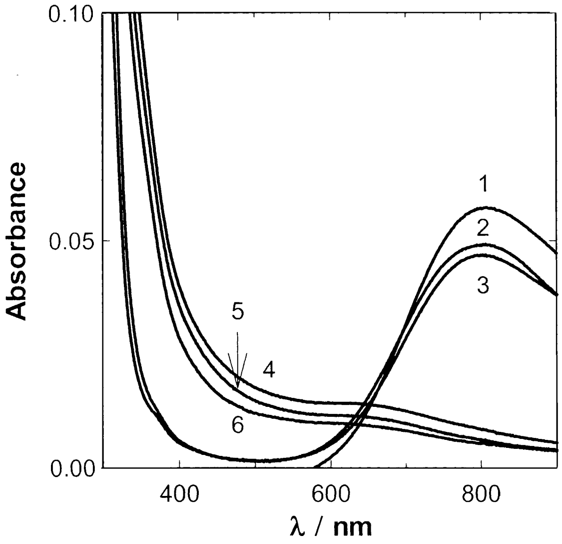

Fig. 4. Spectra of the filtrates obtained after treatment of 2% cellulose pulp in the presence of 0.5 mmol l^{-1} of Cu(II) for 24 h. Initial pulp pH/pH after treatment and filtration: 2-8.00/4.23, 3-10.00/4.81, 4-12.00/11.33, 5-the same as 4, but pH adjusted up to 12.00, 6-13.00/12.35. Curve 1 represents spectrum of uncomplexed 0.5 mmol l^{-1} of Cu(II).

the complexation of heavy metal ions in cellulose pulps or solutions of other macromolecular compounds. On the other hand, the polarographic method provides a very sensitive general tool for the determination of the concentration of uncomplexed (free) heavy metal ions. This will allow, for example, investigations involving the determination of levels of free Cu(II) ions, which interfere with the catalytic decomposition of hydrogen peroxide during the bleaching of cellulose pulp, in the presence of a variety of ligands.

4. Conclusions

1. Copper(II) forms weak complexes with the dissolved degradation products of cellulose pulp. The complex formation is accompanied by a decrease in solution pH, presumably due to the replacement of the acid hydrogen ions by Cu(II) ions in compounds containing carboxylic acid groups. The insignificant complexation of Cu(II) ions at pH 7–11 (pCu goes from 3.3 to 3.4–3.9) is related with the fairly low solution pH after pulp treatment and addition of Cu(II) (pH 5.9–7.4).
2. When the pH of the above-mentioned solutions was adjusted upward to 12.0, the complexing ability rose, apparently, due to the deprotonization of hydroxy-groups of the dissolved cellulose degradation products. The free Cu(II) levels fell drastically and pCu reached 13.0–13.5.
3. After addition of a Cu(II) salt directly to cellulose pulp, part of the Cu(II) is bound (due to adsorption and/or chemical bond formation) to the cellulose fibers. The binding of Cu(II) depends on the pH of the cellulose pulp and reaches 50–70% of the initial Cu(II) amount at pH 7.0 and 90–95% at pH 13.0.

Acknowledgements

E.N. thanks Helsinki University of Technology for short term visiting grant, which initiated this work, as well as for awarding of Visiting Professorship.

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