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Removal of transition metals from alkaline suspensions of cellulose pulp using *CDTA* as chelating agent

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Abstract

Removal of transition metals (Fe, Mn, and Cu) from oxygen delignified alkaline cellulose pulp slurry was carried out using *CDTA* (*trans*-cyclohexane-1,2-diaminetetraacetic acid) as chelating agent. After simple treatment in alkaline solutions the initial natural concentrations of the metals above-mentioned can by reduced by ca. 50% for Fe and Mn and by ca. 70% for Cu, whereas the lowering of concentration of Ca varies in the range from 30% to 60%, depending on solution pH and concentration of chelating agent.

Keywords: Cellulose pulp; Transition metal ions; Removal; Chelating agents; *CDTA*

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1. Introduction

Transition metals, mainly Mn, Fe and Cu, interfere with the catalytic decomposition of oxygen-based chemicals during the ECF or TCF bleaching processes of cellulose pulp and cause an increase of consumption of these agents (Evans & Upton, 1985; Colodette & Dence, 1989) as well as lower some characteristics of pulp and final product (Rämö, Sillanpää, Klasila, & Piepponen, 2001), therefore pulp and paper industry uses different chelating agents to remove mentioned metals from the production processes of pulps. In the recent decade several new chelating agents have been proposed, e.g., *EGTA* (ethylenedioxydiethylenediaminetetraacetic acid) and *HEDTA* (hydroxyethylethylenediaminetri-acetic acid) (Ager & Marshall, 2001), *EDDS* (*N*,*N*′-ethylenediaminedisuccinic acid) (Jones & Williams, 2002; Orama, Hyvönen, Säärinen, & Aksela, 2002), *IDS* (iminodisuccinic acid) (Jones & Williams, 2002; Hyvönen, Orama, Säärinen, & Aksela, 2002), *BCA6* (*N*-bis[2(1,2-dicarboxyethoxy)ethyl]aspartic acid) (Räsänen, van Heiningen, Koukkari, Pajarre, & Aksela, 2004; Metsärinne, Peltonen, Aksela, & Tuhkanen, 2004; Metsärinne et al., 2005), *BCA3* (*N*-bis[(carboxymethoxy)ethyl]glycine) (Metsärinne et al., 2004; Metsärinne et al., 2005), *TCA6* (*N*-tris[(1,2-dicarboxyethoxy) ethyl]amine) (Hyvönen et al., 2005) and *BCA5* (*N*-bis[2(1,2-dicarboxyethoxy)ethyl]glycine) (Metsärinne et al., 2005).

However *EDTA* (ethylenediaminetetraacetic acid) and/or *DTPA* (diethylenetriaminepentaacetic acid) remain mainly used chelating agents for lowering of content of transition metals in industrial pulp bleaching procedures (Lapierre, Bouchard, Berry, & Vanlierop, 1995; Volkel, Weigl, & Ruf, 1995; Bredl & Friberg, 1998; Rämö, Sillanpää, Orama, Vickackaite, & Niinistö, 2000; Räsänen and Karkkainen, 2003). In addition, it can be mentioned that alkali earth metals are favourable elements since they stabilize hydrogen peroxide (Lapierre et al., 1995; Bredl & Friberg, 1998).

When analysing the published data on stability of complexes of transition metal ions of interest with *EDTA* and

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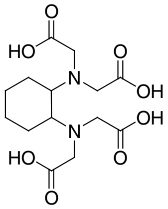
Table 1
Logarithms of stability constants of 1:1 metal ion complexes with polyaminopolycarboxylic ligands

Ligand	Metal ion						
	Mn(II)	Mn(III)	Fe(II)	Fe(III)	Cu(II)	Ca(II)	Mg(II)
EDTA (ethylenediaminetetraacetic acid)	13.87	25.3	14.32	25.0	18.8	10.69	8.79
DTPA (diethylenetriaminepentaacetic acid)	15.60	31.1	16.5	28.0	21.55	10.83	9.30
CDTA (*trans*-cyclohexane-1,2-diaminetetra-acetic acid)	17.48	28.9	19.0	30.1	22.0	13.20	11.02



Scheme 1. Schematic picture of *CDTA*.

DTPA (Martell & Smith, 1977), it is seen that *DTPA* forms more stable complexes with metal ions comparing with *EDTA* (Table 1). Some trends are observed – the difference is negligible for alkali earth metals (Ca and Mg), does not exceed 3 logarithm units for divalent transition metal ions and is the highest for trivalent transition ions reaching up to 5.8 logarithm unit. In the same Table 1 there are summarized data on the stability of the complexes of the same metal ions with *CDTA* (Scheme 1), showing higher chelating ability of *CDTA* comparing with that of *EDTA* and *DTPA*.

Therefore the aim of the work reported herein was to investigate the possibility and peculiarities of using *CDTA* for removal of transition metals from alkaline cellulose pulp slurries.

2. Experimental

2.1. Materials

Analytical grade chemicals were used, and oxygen delignified and washed pulp (dry pulp content 32.5%) was obtained from a Finnish kraft pulp mill.

2.2. AAS analysis

The concentrations of Mn, Fe, Cu, Ca and Na in cellulose pulp were determined by means of a Perkin-Elmer 603 atomic absorption spectrophotometer (AAS) using standard procedures.

2.3. pH measurements

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

2.4. Procedure

The procedure for removal of transition metals from cellulose pulp was carried out at room temperature in the following sequence:

(a) 18.5 g of wet pulp (dry matter content 32.5% w/w) was added to 181.5 ml of distilled water (final concentration of dry pulp in slurry – 3% w/w) and mixed with a mechanical mixer (730 rpm) for 1 hour;
(b) solution of *CDTA* and sodium hydroxide were added to reach the target concentration and pH, and the slurry was mixed for 15 min (mechanical mixing);
(c) the slurry was kept for 45 min while mixing the slurry with a glass stick after every 15 min;
(d) the slurry was filtered using a Buchner funnel;
(e) the filter cake was washed with a *CDTA* solution (the same pH and concentration) in the Buchner funnel (four times);
(f) the filter cake was washed with distilled water in the Buchner funnel (five times);
(g) the cake was dewatered using the Buchner funnel;
(h) the pulp was dried overnight at 105 °C;
(i) the pulp was analysed for Cu, Fe, Mn, Ca and Na by AAS.

3. Results and discussion

The cellulose pulp contained the following amounts of metals of interest: Mn, 10.7 $\mu g\ g^{-1}$; Fe, 51.2 $\mu g\ g^{-1}$; Cu, 7.7 $\mu g\ g^{-1}$; Ca, 1.08 $mg\ g^{-1}$; Na, 1.54 $mg\ g^{-1}$. The blank experiment, i.e. standard treatment without *CDTA* and washing only with distilled water (Sample 0 in Table 2) gave the following results: Mn, 10.4 $\mu g\ g^{-1}$; Fe, 49.6 $\mu g\ g^{-1}$; Cu, 5.8 $\mu g\ g^{-1}$; Ca, 1.05 $mg\ g^{-1}$; Na, 1.54 $mg\ g^{-1}$ (Table 3). Since determination errors for Mn, Fe, Cu, Ca and Na were $\pm 0.3\ \mu g\ g^{-1}$, $\pm 0.2\ \mu g\ g^{-1}$, $\pm 0.8\ \mu g\ g^{-1}$, $\pm 0.02\ mg\ g^{-1}$ and $\pm 0.01\ mg\ g^{-1}$, respectively, it is seen that Mn, Fe, Ca and Na remained in the cellulose pulp practically quantitatively or in limits of errors, whereas Cu was washed out noticeably. Since generally it is agreed that interactions between heavy metal ions, their salts or other compounds and cellulose 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

Table 2
Conditions of cellulose pulp treatment

No. of sample	Additives	Washing I (with alkaline *CDTA* solution)	Washing II (with distilled water) (ml)
0	No	No	9 × 50
1	0.4 ml *CDTA* (30 g/l) + 0.1 M NaOH up to pH = 10	4 × 50 ml (0.06 g/l *CDTA*, pH = 10)	5 × 50
2	2.0 ml CDTA (30 g/l) + 0.1 M NaOH up to pH = 10	4 × 50 ml (0.3 g/l *CDTA*, pH = 10)	5 × 50
3	0.4 ml CDTA (30 g/l) + 0.1 M NaOH up to pH = 11	4 × 50 ml (0.06 g/l *CDTA*, pH = 11)	5 × 50
4	2.0 ml CDTA (30 g/l) + 0.1 M NaOH up to pH = 11	4 × 50 ml (0.3 g/l *CDTA*, pH = 11)	5 × 50
5	0.4 ml CDTA (30 g/l) + 0.1 M NaOH up to pH = 12	4 × 50 ml (0.06 g/l *CDTA*, pH = 12)	5 × 50
6	2.0 ml CDTA (30 g/l) + 0.1 M NaOH up to pH = 12	4 × 50 ml (0.3 g/l *CDTA*, pH = 12)	5 × 50
7	0.4 ml CDTA (30 g/l) + 1.0 M NaOH up to pH = 13	4 × 50 ml (0.06 g/l *CDTA*, pH = 13)	5 × 50
8	2.0 ml CDTA (30 g/l) + 1.0 M NaOH up to pH = 13	4 × 50 ml (0.3 g/l *CDTA*, pH = 13)	5 × 50
9	0.4 ml CDTA (30 g/l) + 10.0 M NaOH up to pH = 13.8	4 × 50 ml (0.06 g/l *CDTA*, pH = 13.8)	5 × 50
10	2.0 ml CDTA (30 g/l) + 10.0 M NaOH up to pH = 13.8	4 × 50 ml (0.3 g/l *CDTA*, pH = 13.8)	5 × 50

Cellulose pulp slurry: 18.5 g of pulp (dry pulp content 32.5% w/w) + 181.5 ml of distilled water (final concentration of dry pulp in slurry – 3% w/w).

Table 3
Results on removal of metals from cellulose pulp slurry using *CDTA* as chelating agent[a] (Content of metals in untreated cellulose pulp: Mn, 10.7 μg g^{-1}; Fe, 51.2 μg g^{-1}; Cu, 7.7 μg g^{-1}; Ca, 1.08 mg g^{-1}; Na, 1.54 mg g^{-1})[a]

No of sample	Mn, μg g^{-1}	Fe, μg g^{-1}	Cu, μg g^{-1}	Ca, mg g^{-1}	Na, mg g^{-1}
0	10.4	49.6	5.8	1.05	1.54
1	5.9	37.0	3.4	0.71	1.27
2	5.5	30.3	2.8	0.57	1.30
3	7.4	33.7	3.4	0.80	0.80
4	5.8	28.6	2.9	0.44	0.70
5	7.5	32.9	3.1	0.84	1.20
6	6.2	26.6	2.6	0.39	1.18
7	7.9	47.1	3.1	0.71	1.80
8	7.7	38.8	2.4	0.47	1.85
9	7.7	48.6	3.7	0.63	2.07
10	7.5	43.9	3.0	0.36	1.96

[a] Average value of three experiments.

with dissolved cellulose degradation products (Norkus, Vaičiūnienė, Vuorinen, & Macalady, 2004), it can be supposed that all Mn, Fe, Ca, Na and most of Cu were strongly bonded with cellulose in the samples investigated (presumably due to formation of the chemical bonds), while part of Cu was weakly bonded with cellulose (presumably adsorbed on cellulose fibres in form of washable compounds).

The treatment of cellulose with *CDTA* according the procedures given in Table 2 reduced the content of metals in cellulose, except Na at the highest pH investigated (Table 3).

The pH dependence of the residual content of Mn in treated cellulose pulp showed rather good removal degree at pH = 10 (ca. 50% of initial Mn content). Increase pH up to 12 led to similar results at higher chelating agent concentration (Table 3, samples 4 and 6). Further increase in pH did not improve Mn removal, and the amount of residual Mn was raised by ca. 20%.

In the case of Fe a trend of increasing removal degree was observed when pH was raised from 10 to 12. This increase can be attributed to strengthening of the chelating ability of *CDTA* with pH rise due to formation of Fe(III) hydroxycomplex. The formation of mixed Fe(III)-*CDTA*-OH$^-$ complex has been documented. The equilibrium constant (logK_e) of the reaction

$$\mathrm{Fe}Y^- + \mathrm{OH}^- \rightleftarrows \mathrm{Fe}Y(\mathrm{OH})^{2-}, \tag{1}$$

(where Y^{4-} is fourfold deprotonized anion of *CDTA*) was found to be 9.7 (Martell & Smith, 1977). This value shows a considerable shift of the equilibrium towards formation of the mixed complex in alkaline solutions. Under optimum operating conditions (pH = 12) ca. 50% of Fe can be removed (Table 3). Unexpected results were obtained at higher pH values where the amount of residual Fe rises dramatically. Such result can be accounted for decomposition of the Fe(III) hydroxycomplex with *CDTA* at higher pH and precipitation of Fe(OH)$_3$ which was left in cellulose pulp, since is known that Fe(III) forms very insoluble Fe(OH)$_3$ with solubility product value equal to $10^{-38.6}$ (Inczedy, 1976).

The best result on removal of transition metals was obtained for Cu – ca. 65–70% of initial Cu could be removed from pulp at pH = 12–13. According to Table 3 the complexing ability of *CDTA* remained practically constant at pH = 10–11, which is in a good agreement with the experimental data showing that in the pH region mentioned no changes in Cu(II) complexation with *CDTA* occur and CuY^{2-} complex prevails in alkaline solution up to pH = 11 (Norkus & Pauliukaitė, 2000). Further increase in pH (pH = 12–13) led to diminishing of residual Cu amount in cellulose pulp (Table 3). This rise of chelating ability of *CDTA* can be explained by formation of a mixed hydroxycomplex, like in the case of Fe(III) (see above). It was shown recently that the mixed hydroxycomplex is formed at mentioned pH values, equilibrium constant (logK_e) of the reaction

$$\mathrm{Cu}Y^{2-} + \mathrm{OH}^- \rightleftarrows \mathrm{Cu}Y(\mathrm{OH})^{3-} \tag{2}$$

being 1.5 (Norkus & Pauliukaitė, 2000). At the highest pH investigated (pH = 13.8) the removal degree of Cu decreased in the same way as described for Fe (Table 3). On the one hand this decrease in strongly alkaline milieu can be accounted for the decomposition of CuY(OH)$^{3-}$ complex and its transformation to the tetrahydroxycuprate complex Cu(OH)$_4{}^{2-}$ (Norkus & Vaškelis, 1994; Norkus & Pauliukaitė, 2000), on the other hand the decrease in the chelating ability of *CDTA* in strongly alkaline solutions can be explained by decrease in activity coefficient of *CDTA* anion Y^{4-}, since such kind decrease in activity coefficients of anions of polyaminopolycarboxylic acids (including *CDTA*) is known (Norkus, Vaškelis, & Žakaitė, 1996; Norkus & Pauliukaitė, 2000).

Different trends are observed when comparing residual content of earth alkali and alkali metals in cellulose pulp after treatment with *CDTA* (Table 3). The amount of Ca was reduced due complex formation with *CDTA* (Table 1) and the Ca content remained almost constant irrespective of cellulose pulp slurry pH, being lower when higher concentration of the chelating agent was employed. The mean values of residual Ca varied in the range from 40 to 70% (comparing with the initial content), depending on the *CDTA* concentration (Table 3). In the case of Na, two opposite processes can be indicated – lowering of the initial content at lower pH limits (pH = 10–12) and increase in Na content overfulfilling initial amount. The first one of the processes can be attributed to formation of Na(I) complex with *CDTA*, because formation of such 1:1 complex with stability constant logarithm being 2.7 is documented (Sillen & Martell, 1971). The explanation of the rise in Na content after treatment in strongly alkaline solutions is fairly simple – the concentration of sodium hydroxide, accordingly Na(I), in such solutions is rather high (0.1–1 mol l^{-1}) and additional amounts of Na(I) are bounded to cellulose pulp.

Thus, *CDTA* could be potentially used as a chelating agent for removal of Cu and Fe from cellulose pulps before or after an oxygen delignification stage in which pH is 10–12. Under these conditions *CDTA*'s ability to bind Mn is, however, much lower than that of *EDTA* and *DTPA* under slightly acidic conditions where they are commonly applied.

4. Conclusions

1. *CDTA* (*trans*-cyclohexane-1,2-diaminetetraacetic acid) can be used as chelating agent for removal of transition metals (Fe, Mn, and Cu) ions from cellulose pulp.
2. The removal degree of transition metals above-mentioned depends on conditions of treatment – pH and concentration of *CDTA* in alkaline slurry of cellulose pulp.
3. After simple treatment in alkaline solutions the initial natural concentrations of transition metals can by reduced by ca. 50% for Fe and Mn and by ca. 70% for Cu.

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