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# Evaluating chelating agents and their effects on cellulosic pulps during P-stage bleaching. Part 1: analytical method development

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**Abstract** During peroxide bleaching of pulp (“P-stage”), the heavy metal ions must be removed from the pulp and inactivated by chelation before the bleaching to prevent undesired degradation of cellulose by reactive oxygen species. Ethylenediaminetetraacetic acid (EDTA) is mostly used as a chelating agent; however, it may soon be banned because of environmental concerns. Therefore, there is a demand for new chelating agents to replace EDTA, and a comprehensive analytical method is necessary to investigate their chelating ability and the effects on the pulp. In this study, an

analytical sequence for evaluating chelating agents and oxidative damage to cellulose during chelation (Q-stage) and bleaching (P-stage) has been established and optimized. GPC provides the molar mass distribution and oxidative damage (as profiles of carbonyl groups relative to the molar mass distribution), and the metal content of the pulp was determined by ICP-OES. This method enables the analysis of the chelating potential of new chelating agents, with simultaneous determination of the impact on cellulose on a molecular level.

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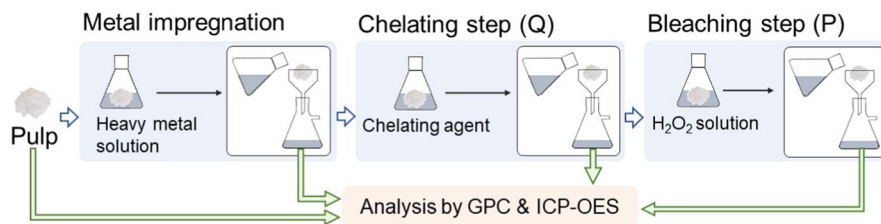
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## Graphical abstract



**Keywords** Bleaching · Cellulosic pulp · Chelating agents · GPC · ICP-OES · P-stage · Peroxide bleaching · Pulping process · Q-stage

## Introduction

Most of the chemical pulps used today for paper, fiber, or the production of cellulose derivatives need to undergo a bleaching sequence in order to reach the desired brightness level (Suess 2010). The latter highly depends on the final application and usually ranges between 85–90% ISO (ISO 2470–1, 2009). To reach this brightness, a combination of steps is necessary, which comprise the removal of residual lignin and eventually also the destruction of remaining chromophores.

After pulping, typically a few percent of lignin are contained in the still brownish-colored pulp. Bleaching is the process of selectively degrading and removing these chromophoric substances. How easily a pulp can be bleached highly depends on the origin of the raw material used for pulping and on the process. In general, sulfite pulps are easier bleachable than Kraft pulps. To obtain a largely lignin-free, bright pulp, a single chemical treatment is usually not sufficient. Hence bleaching is performed in a sequence of stages combining different chemical treatments to eventually reach the desired brightness. In general, two basic categories are used to describe a sequence, depending on whether the process contains chlorine-based chemicals or is totally chlorine-free (TCF) (Potucek and Milichovsky 2001). For chlorine-dependent chemistries, it is important whether elemental chlorine is part of the sequence or chlorine derivatives, mostly chlorine dioxide, are used. The latter variant is referred to as elemental chlorine-free (ECF) bleaching and is today the most common bleaching

type on a global scale (Suess 2010; Gellerstedt 2009; Loureiro et al. 2011; Axegard et al. 1996).

To describe an industrial bleaching sequence, commonly different abbreviations are used for the individual bleaching stages: chlorine  $\text{Cl}_2$  (C), chlorine dioxide  $\text{ClO}_2$  (D), alkaline extraction (E), hypochlorite  $\text{NaOCl}$  (H), oxygen  $\text{O}_2$  (O), hydrogen peroxide  $\text{H}_2\text{O}_2$  (P), chelation (Q), (xylanase) enzyme (X), or ozone  $\text{O}_3$  stage (Z) (Gellerstedt 2009).

The use of chlorine, chlorine dioxide and hypochlorite has the advantage of a very good selectivity towards lignin and chromophores (Gellerstedt 2009), which means that side reactions with carbohydrates (cellulose and hemicelluloses) are quite limited. From the perspective of bleaching and chromophore removal, those chemicals would be the oxidants of choice. Unfortunately, the chlorination of lignin fragments results in toxic and ecotoxic chlorinated phenols in the effluent streams, which have to be avoided. This problem had been especially significant when elemental chlorine was used. The ECF bleaching with chlorine dioxide as the major bleaching chemical also offers good selectivity and delignification properties, while keeping the formation of chlorinated degradation products at an acceptably low level. TCF sequences with oxygen, ozone, or hydrogen peroxide are evidently superior from the environmental perspective, but their selectivity is by far not as good as that of chlorine-based sequences. As a result, the carbohydrate fraction is oxidatively affected, and hence the quality of the cellulose may suffer, reflected for instance in impaired mechanical properties of the resulting paper or lower brightness stability.

Oxygen-based radicals (hydroxyl, superoxide, superoxide anion) are chiefly responsible for the low selectivity in TCF sequences (Suess 2010; Gellerstedt 2009). Most of these side reactions are induced by metal ions, especially transition metal ions, which

can readily change their oxidation state. These transition metal ions, most prominently iron, copper, or manganese, are naturally present in the pulp at a low ppm range as trace elements or bound in the active centers of natural enzymes contained in plant biomass (peroxidases, laccases) (Susilo et al. 2005). They react with oxygen-based bleaching species (ozone, hydrogen peroxide, oxygen, peracids) leading to the formation of radicals and other so-called “reactive oxygen species” (ROS) (Grönroos et al. 1998). Most detrimental are hydroxyl radicals due to their high reactivity (=low selectivity), the formation system being known as the *Fenton* process (Winterbourn 1995; Hobbs and Abbot 1994). The formed hydroxyl and hydroperoxyl radicals readily oxidize the hydroxy groups of cellulose to carbonyl structures, which are known to act as reactive “hot spots” for both chain cleavage and chromophore formation (Ahn et al. 2019; Korntner et al. 2015; Potthast et al. 2005). Independent of the position of the carbonyl at the glucopyranose ring, alkaline conditions cause immediate cellulose chain scission by  $\beta$ -alkoxy elimination (Golova and Nosova 1973; Knill and Kennedy 2003; Hosoya et al. 2018), already in relatively weak alkaline media (pH 8.5 and above). The resulting decrease in molecular weight and fiber length due to the cleavage of cellulose chains means a decrease in pulp strength, which severely impacts the quality of paper pulp. The introduced carbonyls in oxidatively damaged cellulose are also the starting points for the formation of cellulose-based key chromophores (Korntner et al. 2015), a process which is reflected both in decreased bleachability and decreased brightness stability (=increased brightness reversion) (Rosenau et al. 2004, 2007; Pouyet et al. 2013).

Consequently, these (transition) metal ions must be removed from the pulp—or at least their detrimental effect be neutralized—before the actual bleaching is performed to prevent the undesirable oxidation and degradation of cellulose. In the pulp and paper industries, chelating agents, such as EDTA (ethylenediaminetetraacetic acid) and DTPA (diethylenetriaminepentaacetic acid), are used for this purpose (Rämö et al. 2000; Lapierre et al. 1995, 2003; Suess 2010; Högberg et al. 2012; Brelid et al. 1997). They inactivate the transition metal ions by chelation (Q-stage) and extract them from the pulp (E-stage, washing stage). Mainly applied in the bleaching of Kraft pulps, EDTA / DTPA is typically used in the order of approx. 2 kg/t of pulp (Suess 2010; Gellerstedt 2009). EDTA

has been widely used in all kinds of detergents for household use, in cosmetic formulations, paints and drilling liquids in metallurgy and oil production, etc. However, EDTA is considered an environmental pollutant due to its persistence (Oviedo and Rodríguez 2003; European Committees, 2004). It is resistant to hydrolysis and is neither degraded by strong acids nor strong alkali. EDTA can be biodegradable under optimized conditions, but such conditions do not exist in municipal wastewater treatment plants, so EDTA is usually released into the environment. In the environment, there is no non-complexed EDTA, because there is typically an excess of metal ions in sewage and wastewaters. The EDTA-metal complexes are more stable and persistent than the host-free EDTA molecules. The complex formation between heavy metals and EDTA decreases the toxicity of metal ions, but at the same time increases their resilience and permanence in water and soil. This poses an increased risk to soil and aquatic organisms due to solubilization and leaching (European Chemicals Bureau 2004). For these reasons, there are discussions to ban EDTA and DTPA in the EU in the future, which is expected to occur from 2025 on. It is evident that there is a demand for environmentally friendly and (bio) degradable chelating agents as alternatives to EDTA and DTPA (do Nascimento et al., 2006; Pinte et al., 2015)—especially from the perspective of large users, such as the pulp and paper industry and detergent manufacturers, and even more if partial restrictions or a complete ban should become effective.

In order to develop alternative chelating agents and to test their efficiencies, an analytical method for the quantitative determination of the effect of chelation is needed. On the one hand, there are methods available for the sole quantitation of the metal contents of pulps (Eriksson and Grén, 1996; Jones and Williams 2002; Granholm et al. 2010), but this parameter does not say anything about possible oxidative damage to the pulp. On the other hand, the available methods to assess oxidative damage of cellulosic pulps by means of quantifying carbonyl group profiles (Potthast et al. 2003) and carboxy group profiles (Bohrn et al. 2006) relative to the molecular weight do not consider the presence of metal ions which might induce significant further damage later on. However, the impact at the molecular level with regard to molar mass reduction and oxidative damage during bleaching and eventually on bleached cellulose is usually not investigated

in parallel (Tamminen et al. 2007; Körlü and Bilgin 2008). Both the content of transition metal ions and the detailed knowledge of the molecular weight distribution (MWD) of the cellulosic pulp and its oxidative damage are of crucial importance when evaluating chelating agents and their effect during bleaching sequences, although these two aspects have been studied separately in most cases so far.

In this study, a laboratory-scale analytical procedure based on the combination of, first, gel permeation chromatography (GPC) with selective fluorescence-labeling of oxidized groups and, second, inductively coupled plasma optical emission spectrometry (ICP-OES) for investigating the efficiency of chelating agents during bleaching of celluloses has been established. The procedure allows simultaneous evaluation of the cellulose's oxidative damage, molecular weight changes and metal ion content. This provides a reliable analytical tool to support the future search for alternatives to EDTA and DTPA.

## Materials and methods

### Materials

Pulp: bleached Eucalyptus prehydrolysis Kraft pulp; kappa number: 0.37; brightness: 90.9%; ISO viscosity [cuen]: 530 mL/g; pentosan content: 1.73%; DCM extract: 0.13%; ash content: 0.05%.

Chemicals:  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (99–100.5%, Sigma-Aldrich),  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (analytical grade, Merck), HCl (ACS reagent, puriss. *p.a.*, Merck), hydrogen peroxide (50% w/w, pure),  $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$  (Merck),  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (98–101%, VWR); carbazole-9-carboxylic acid [2-(2-aminooxyethoxy)ethoxy]amide (CCOA) was synthesized according to published procedures (Röhring et al. 2002). *N,N*-Dimethylacetamide (DMAc) as GPC eluant was dried and purified as described (Chrapava et al. 2003).

### Pulp pre-treatment

The pulp was mixed in a kitchen blender with deionized (DI) water for homogenization and then filtered off. The weight of the wet pulp used in the following treatments was calculated based on the solid content of the pulp (odp = oven-dried pulp).

### Metal impregnation

Solutions of different concentrations of transition metal ions (between 2 and 100 ppm) in 0.1 M sodium acetate buffer (pH=4.5) were prepared with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ , respectively. The pulp (20 g odp) was shaken in the salt solution (200 mL) at RT. After three days, the pulp was filtered and washed with DI water until a neutral pH was reached and no metal ions were detectable in the concentrated washings.

### Chelating step (Q stage)

The procedure mimics the conditions of an industrial chelation (Q) stage. The metal-enriched pulps (2 g odp) were each immersed in either DI water (65 mL, blank) or aq. HCl solution (65 mL, pH=5.5) or aq. EDTA solution (65 mL, 4.9 mg of  $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ , 60 ppm, pH=5.5), and shaken at 80 °C. After 3 h, the mixture was cooled down in an ice-water bath and the pulp was filtered off, washed with DI water (160 mL) in a beaker, stirred for 10 s and then filtered off again. This washing process was repeated until a neutral pH was reached.

### Bleaching step (P stage)

The procedure mimics the conditions of an industrial peroxide bleaching (P) stage. The pulp (1 g odp) was shaken in aq.  $\text{H}_2\text{O}_2$  solution (10 mL, 2.2% in 0.1 M NaOH, pH=10.5–11.0) at 90 °C for 4 h. Then, the mixture was cooled down in an ice-water bath and the pulp was filtered off, washed with DI water (100 mL) in a beaker, stirred for 10 s and then filtered off again. This washing process was repeated until pH 7–8 of the washings, at least twice.

### Sample preparation for GPC analysis

Zinc acetate (3.66 g) was dissolved in DI water (1.0 L) and the pH of the solution was adjusted to 4.0 by glacial acetic acid. CCOA (1.25 mg per mL of the buffer solution) was added to the solution, which was then stirred for 30 min at RT. Meanwhile, an air-dried pulp sample (15–20 mg) was homogenized by mixing with a kitchen blender in DI water (250 mL) and collected by filtration. The CCOA solution (2.0 mL)

was added to the wet pulp, and the mixture was shaken at 40 °C for 7 days. The CCOA solution was filtered off, and the samples were extensively washed with DI water and subsequently ethanol. The samples were collected into clean vials, DMAc (3.0 mL) was added, and the mixture was left overnight on a shaker at room temperature for solvent exchange. DMAc was filtered off, DMAc/LiCl (1.0 mL, 9% w/v) was added, and the samples were shaken overnight at r.t. for dissolution. Before the GPC measurement, the sample solution (0.3 mL) was diluted with DMAc (0.9 mL) and filtered through a syringe filter (0.45 µm porosity).

### GPC analysis

The measurements of the molecular weight distributions and carbonyl contents were carried out according to literature following the CCOA-GPC protocol (Röhring et al. 2002; Potthast et al. 2003; Henniges et al. 2011). Briefly: DMAc/LiCl (0.9%, w/v), filtered through a 0.02 µm filter, was used as the eluent. The sample (100 µL) was injected automatically, chromatographed on four serial GPC columns, and monitored by MALLS, fluorescence, and RI detection. For measurements with UV detection ( $\lambda=290$  nm), the detector was installed between the MALLS and fluorescence detector. For details on the instrumental setup see Jusner et al. (2022).

### ICP-OES analysis

Dry samples (200 mg) were treated with 65% HNO<sub>3</sub> (3 mL, EMSURE® Reag. Ph Eur, ISO, Merck) overnight and 30% H<sub>2</sub>O<sub>2</sub> (0.76 mL) was added. The sample digestion was performed in MARSXpress Teflon vessels in a MARS 6 microwave system (CEM Corporation, Charlotte, NC, USA). Parameters: 1030–1800 W, the temperature was raised to 200 °C during 20–25 min and kept for 20 min. After digestion, ultrapure water (40 mL, 0.054 µS/cm) was added. The measurement was performed on an OPTIMA 8300 ICP-OES instrument (Perkin Elmer Inc., Waltham, MA, USA). The gas flows were 8.0 L/min, 0.2 L/min, and 0.60 L/min (plasma, auxiliary, and nebulizer, respectively). The RF power was 1450 W, and the plasma temperature was around 7000 K. The flow rate of the pump was 0.80 mL/min.

## Results and discussion

### Analytical parameter considerations

Complexation agents in pulp bleaching are used for one main reason: to hold transition-metal-induced side reactions at bay. These undesired (but hard-to-prevent) processes have two negative aspects, one is radical reactions that attack the cellulose and cause its oxidation and eventually chain degradation, and the second is the loss of the bleaching agent, hydrogen peroxide, by transition metal-induced decomposition (Wekesa and Ni 2003; Ni and Qiu 2003). In order to see whether complexation agents have the desired effect, it is insufficient to monitor only the transition metal ion content in the system. It might be that this content is very low during the actual P-stage, but the damage to the pulp can have occurred already before; it might also be that transition metal ions are present in higher amounts, but are well shielded in stable complexes so that they become more or less innocuous (Gellerstedt 2009; Granholm et al. 2009; Brelid and Friberg 1998). The transition metal content alone is not a reliable indicator of cellulose damage upon bleaching. Only monitoring transition metal ions blinds out the “cellulose side” and does not deliver the whole picture.

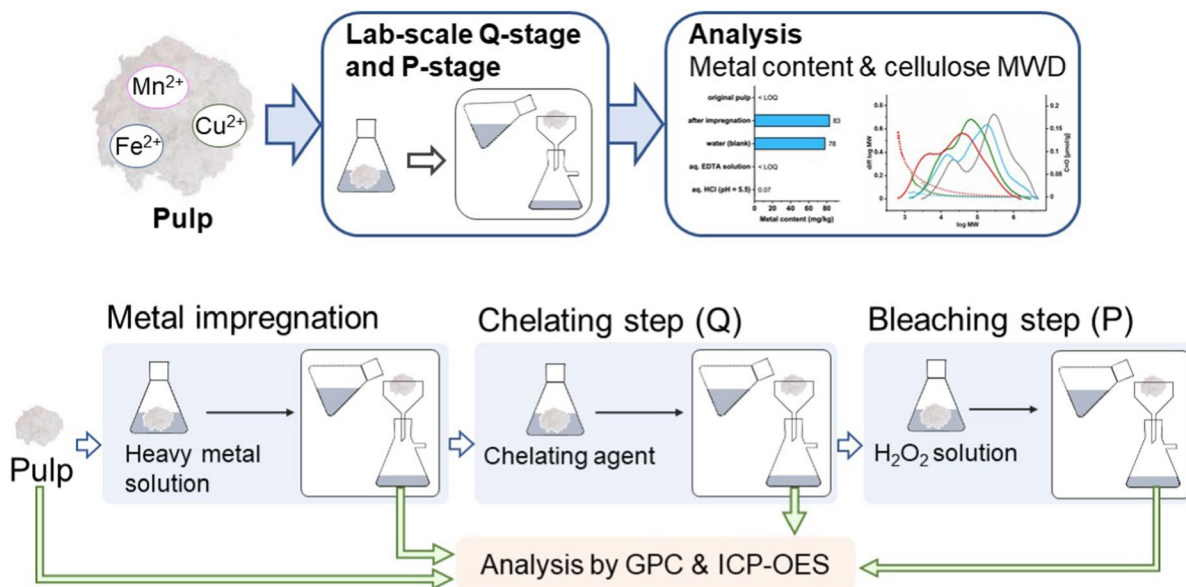
The same, however, is also true for the opposite case: only focusing on cellulose damage while disregarding the transition metal ion content. Monitoring only oxidative changes and molar mass distributions of the cellulose would not disclose whether they were caused hydrolytically or oxidatively, whether they were already present before the bleaching stage, or which metal ion might be responsible for the damage. Thus, monitoring the transition metal contents along the bleaching line is equally important. Only a combination of transition metal and cellulose analysis would provide information comprehensive enough to conclusively assess the efficiency of complexing agents. This evaluation must cover all important steps along the relevant bleaching stages, including also such seemingly trivial steps as the washing stages. The washing, chelation (Q-stage) and peroxide bleaching (P-stage) along a bleaching sequence are the critical stages where complexing agents would show their effect (Lapierre et al. 1995; Wuorima et al., 2006; Ni et al. 1999, Prasakis et al. 1996) and

these stages must be covered by an analytical method addressing the complexation topic.

Method development for the analytical procedure used a prebleached prehydrolysis Kraft pulp (see experimental) and was tested and confirmed with different pulps afterwards. A prebleached pulp was used to reduce the “protective” effect of the lignin on cellulose. From the cellulose’s perspective, lignin acts as a sacrificial substrate during bleaching, which reduces the reactions between reactive radical species and the polysaccharide. Using a largely lignin-free pulp in method development is a prerequisite to expose the cellulose to the full impact of possible side reactions, assuming that a complexing agent that eliminates these strong effects would easily cope with a much lower oxidative load. For the same reason, the concentrations of transition metal ions deliberately introduced into the pulp were also varied, including concentrations well above the usual levels in cellulosic pulps. Again, if the complexing agents being tested could handle these high concentrations, it is safe to assume that lower metal ion concentrations would also be neutralized and rendered innocuous. The focus of the development was to provide a method as robust and general as possible, a protocol that could handle different pulps, different conditions and metal ion concentrations, and different complexing agents.

Thus, it was necessary to consider also more extreme concentrations and conditions that would go beyond those in conventional pulp bleaching.

The optimized analytical procedure is schematically presented in Fig. 1 and described in detail in the experimental section. The pulp, containing different concentrations of transition metal ions, undergoes different treatments which mimic industrial chelation (Q) and peroxide (P) stages of a bleaching sequence, while samples of both effluents and pulp are taken and analyzed by ICP-OES for the metal content and by GPC for the molecular weight distribution and carbonyl group profiles, respectively (Fig. 1, upper row). In our study, we focused on the three transition metals most important in industrial pulp bleaching, namely iron ( $\text{Fe}^{2+}$ ), copper ( $\text{Cu}^{2+}$ ), and manganese ( $\text{Mn}^{2+}$ ) (Suess 2010; Susilo et al. 2005; Prasakis et al. 1996). There is a natural concentration of these trace elements in wood, coming from uptake with groundwater and from the natural transition metal ions content in enzymes, *e.g.*, Fe in peroxidases, Mn in manganese-peroxidases, Cu in laccases (Gellerstedt 2009; Brelid et al. 1998; Rabinovich et al. 2004). The content of metalloenzymes can vary and entail seasonal fluctuations in the metal contents in wood and pulp. Traces of all three transition metals can also be introduced through the contact of the pulp with pipes,



**Fig. 1** Scheme of the analytical testing procedure for chelation efficiency upon simulated Q and P bleaching stages (upper row). Treatment steps of the cellulosic pulp and points of sample withdrawal for analysis (lower row)

reactors and other construction materials during processing, especially caused by leaching from corrosion spots.

### Doping with transition metal ions

Metal ions were introduced into the pulp by means of soaking for extended time periods with aqueous transition metal solutions, typically containing between 2 and 100 ppm of the transition metal ions (see experimental part and Fig. 1). The used transition metal ions ( $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ) are well retained by the pulp due to their complexation with the hydroxy groups of cellulose, which are able to enter the coordination sphere of the central ions as ligands (Su et al. 2014; Loureiro et al. 2012; Susilo et al. 2005). This complex formation is on the one hand strong enough to protect the transition metal ions from being precipitated as hydroxide under the alkaline conditions of a P-stage but on the other hand sufficiently weak to yield to stronger complexing agents, such as EDTA / DTPA. Subsequent washing was done to remove adhering buffer solution. The washings were free of transition metal ions, proving that their concentration was far below the retention capacity of the pulp. The exact metal ion content in the pulp was determined by ICP-OES. GPC and carbonyl-labeling showed that the impregnation step had no influence on the molar mass distribution of the pulps and did not cause any oxidative damage (= introduction of carbonyl groups).

### Q-stage

The transition metal ion-doped pulp was then subjected to a chelation stage which mimics industrial conditions (see experimental section). As industrial bleaching, the simulated chelation (Q) stage used complexing agents to solubilize the transition metal ions which are covalently bound or adsorbed to the pulp and to mask them by forming chemical complexes. In this masked form, the ions are rendered innocent with regard to the induction of radical reactions and peroxide degradation, and they can simply be removed by draining and washing (Fig. 1). As this removal is not complete, there will always be a carryover of minor metal ion concentrations into the subsequent peroxide bleaching (P-stage) (Virtapohja and Alen, 1999). Here, the strength of the complexes formed in the Q-stage is of prime importance. They

should remain intact also under the conditions of peroxide bleaching to avoid the mentioned side reactions, and they should tolerate the change in pH from weakly acidic (pH~5) to alkaline (pH~11). These requirements are perfectly met by so-called chelating agents, such as EDTA and DTPA. The name comes from the Ancient Greek  $\chi\eta\lambda\acute{\eta}$  (crab claw) because the chelating ligands surround their central ions like crab scissors their prey. In most cases, chelating agents have multiple interaction sites, *i.e.*, electron lone pairs or anionic charges that are donated into the coordinative bond with the central ion, and shield their central ion very effectively, also sterically.

We used EDTA as the “gold standard” to compare to. It is one of the most effective complexing agents known and used so far during pulp bleaching. The concentration in the analytical procedure used generally resembled that of industrial application in pulp bleaching (approx. 2 kg/t of pulp), but was also varied in some experiments to test out the limits of the chelating agents. As a blank, distilled water was used, which should neither remove the metal ions in the Q-stage—as it has no chelating effect—nor protect the pulp and peroxide from the negative metal ion impact in the P-stage. When testing novel complexing agents or different conditions, the outcomes were expected to lie somewhere between the results for distilled water (no metal removal, no pulp protection) and EDTA (optimal metal removal, optimal pulp protection). We also used diluted hydrochloric acid with a pH similar to that of the chelating agent solution (pH~5–5.5) (Bouchard et al. 1995; Rämö and Sillanpää, 2001), which should have a metal ion-releasing effect in the Q-stage, but no complexing effect in the P-stage, so that the effects of the metal ions in these two stages could be clearly separated and demonstrated. The chelation step—due to its mild conditions, pH 5.5, 80 °C (see experimental section)—did not have any effect on cellulose integrity and did not cause any cellulose oxidation as seen by GPC analysis with carbonyl-selective fluorescence labeling (Fig. 1).

### P-stage

The chelation / extraction stage was followed by the actual bleaching step that used hydrogen peroxide as the oxidative agent (P-stage). Industrial conditions were also simulated here. This is the stage where effective complexation of transition metal ions



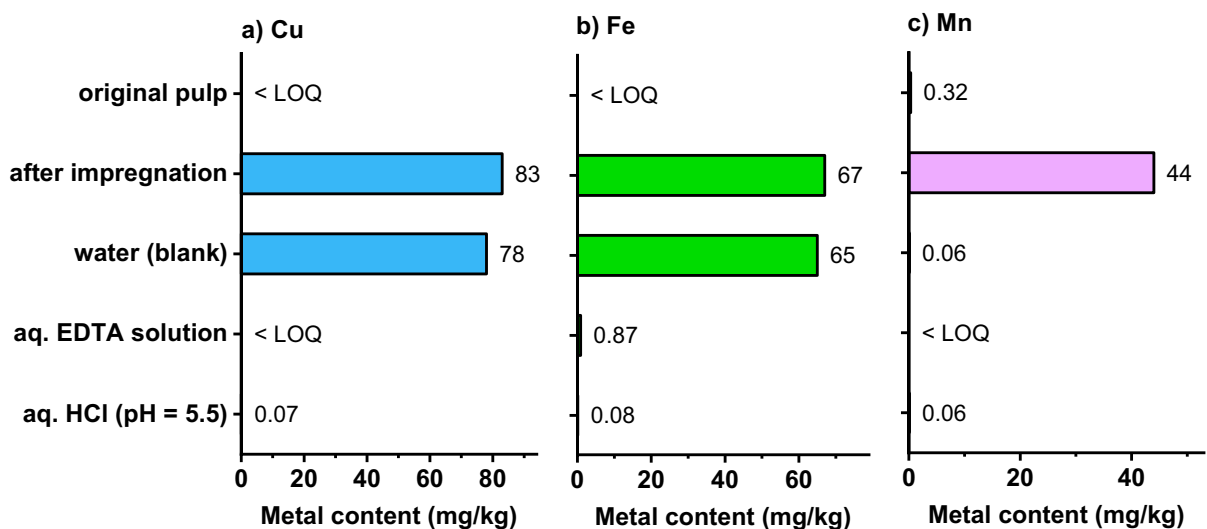
becomes decisive. Non-chelated transition metal ions stay redox-active, enter homolytic redox processes and generate oxygen-derived radicals that cause cellulose oxidation (Suess 2010; Gellerstedt 2009; Ni 2005; Potthast et al. 2005; Granholm et al. 2009; Loureiro et al. 2011). As a result, carbonyl structures in cellulose are introduced (Potthast et al. 2005). Together with minor amounts of carbonyl groups from previous oxidative damage, these structures cause immediate chain cleavage under the prevailing alkaline conditions, according to the  $\beta$ -alkoxy-elimination mechanism, independent of whether the oxidation had occurred at C-2, C-3, or C-6 (Hosoya et al. 2018). Mechanistically, the reactive (oxygen) radical species do not cleave the cellulose chains directly, but via the highly alkali-labile keto-intermediates. The products of the chain cleavage /  $\beta$ -elimination are  $\alpha,\beta$ -unsaturated ketones, which are prone to condensation reactions and, by follow-up process, chromophore generation and brightness reversion (Korntner et al. 2015; Rosenau et al. 2007).

Metal ion quantification and analysis of the celluloses' molar mass distribution and carbonyl profiles after the P-stage (Fig. 1) provided information about the extent of the transition metal carryover, *i.e.*, the quality of the preceding chelation / extraction step, and the quality of the chelation, *i.e.*, the ability of the metals to interact with hydrogen peroxide and damage the cellulose.

Along the analytical sequence, there are different points at which the quality of a chelating agent must be assessed. The transition metal ion concentration needs to be checked before and after the chelation stage to see the discharging effect of complexation and subsequent washing. The cellulose data (molar mass distribution and oxidation) before and after the P-stage are required to see whether the complexing agent is still active against remaining transition metal ion traces and is able to protect the cellulose from damage. As said introductorily, only by the combination of these two aspects, metal ion content and cellulose integrity along the sequence, the efficiency of chelators can be reliably assessed.

#### Transition metal ion content

The metal contents of the pulps were quantified by ICP-OES at different points along the analytical sequence: in the original pulp, in the pulp after metal impregnation, and after the chelation / washing stage which used the three conditions for comparison: EDTA, aqueous HCl (pH = 5.5) and distilled water (Fig. 2). In the process of method optimization, these points of aliquot withdrawal have been elaborated to be most informative. Indirect determination via the metal ion content in the washings is also possible (data not shown), but is less reliable due to adsorption to glassware and labware, especially in the case



**Fig. 2** Transition metal content (ppm) of the pulps before and after a chelating / washing step under different conditions

of low metal concentrations. For this reason, we generally used direct determination in the pulp, not the indirect measurement in the washings. It should not be concealed that in the early stages of this study we attempted metal ion quantification by UV spectrometry, which was hardly reproducible (different absorption characteristics because of the presence / absence of complexing agents, interference from competitive UV-active compounds, etc.). Thus, we resorted to ICP-OES which—although more time-consuming and laborious—provided consistent and highly reliable results throughout, independent of the different sample matrices and possible organic impurities.

### Metal ion management

Figure 2 shows the course of the transition metal ion contents over the Q- and P-stages by means of a representative example. The metal ion content in the deliberately enriched pulp was 44 ppm  $\text{Mn}^{2+}$ , 67 ppm  $\text{Fe}^{2+}$  and 83 ppm  $\text{Cu}^{2+}$ . In the original pulp matrix, a highly bleached Eucalyptus Kraft pulp, only  $\text{Mn}^{2+}$  was detectable while the contents of the other two transition metals were below the limits of quantification. As expected, a chelation stage with EDTA was very effective. It converted all transition metal ions nearly completely into their complexes, which then were efficiently washed out. Only traces of  $\text{Fe}^{2+}$  remained detectable afterwards, while  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  fell below the detection limit. Washing with dilute aqueous HCl (pH 5.5, the same as of the EDTA solution) had an almost equally good effect: the transition metal ion contents decreased below 0.1 ppm for all three species.

The removal of metal ions by aqueous HCl is less based on chelation, although some weak chloride complexes might occur, but rather on the high solubility of transition metal chlorides under acidic conditions, similar to an acidic washing stage (A stage), which makes use of a replacement of metal ions at acidic functionalities by protons. While in the Q-stage dilute HCl and EDTA seemed to be equally effective at metal ion removal, the P-stage showed severe differences (see below).

It can be speculated that the remaining low levels of transition metal ions, which apparently could not be removed by HCl washing but were removed by EDTA ( $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$ ), are due to some strongly complexing moieties in the pulp, such as glucuronic

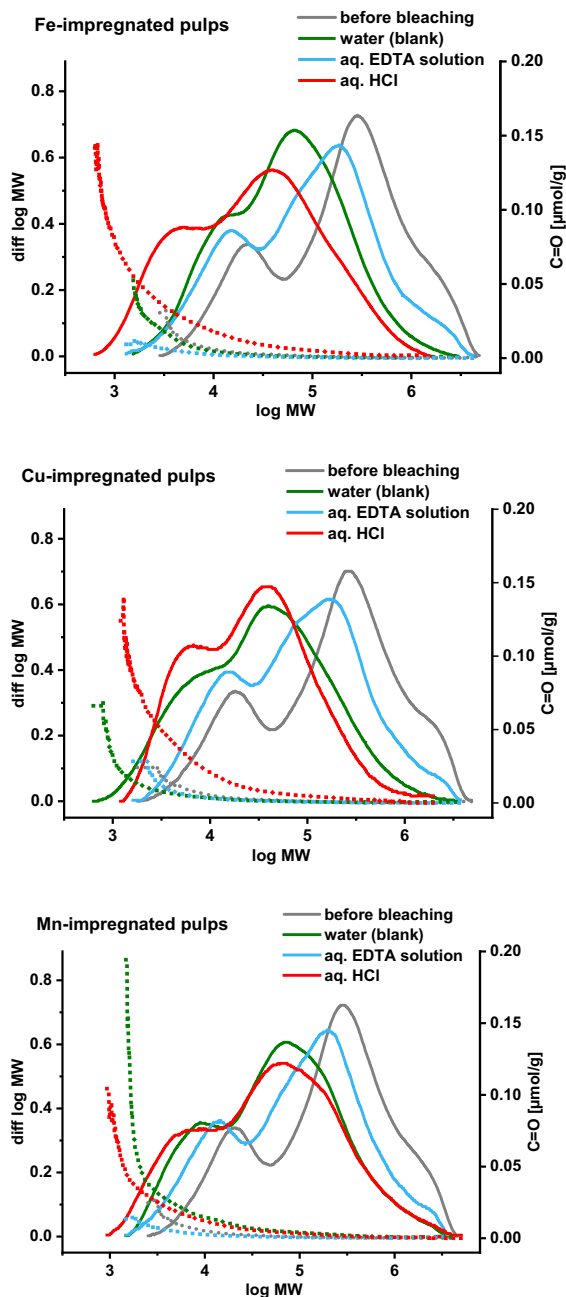
acid moieties. These are able to retain the metal ions when washed with water, but release the ions in the presence of EDTA, which forms even stronger complexes with them.

Exhaustive washing with neutral distilled water (instead of aqueous HCl or EDTA) showed only an insignificant loss of  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$ , but interestingly a nearly complete removal of  $\text{Mn}^{2+}$ . Although surprising at a first glance, this result can be easily explained through the complexation chemistry of these transition metals. While  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$  are able to form—albeit weak—complexes with alcoholic (cellulosic) hydroxy groups, and dynamically integrate them into their ligand shell, this is not the case with  $\text{Mn}^{2+}$  (Note: the ligand-field splitting, a measure of metal–ligand interactions, increases with increasing oxidation of the central ion.  $\text{Mn}^{2+}$  is the lowest possible oxidation state of Mn (vs.  $\text{Mn}^{3+}$ ,  $\text{Mn}^{4+}$  or  $\text{Mn}^{7+}$  in  $\text{MnO}_4^+$ ), and this parameter is low (Holleman et al. 2007)).

In summary, the metal ion analysis reflected the known effective chelation of EDTA, which allows Mn and Cu to be completely and Fe to be largely removed. Intensive washing with neutral water largely eliminates Mn but is otherwise completely inefficient. Washing with dilute HCl is quite effective in terms of metal ion removal, leaving only small traces. However, these traces can play a decisively negative role in the subsequent P-stages.

### Degradation and oxidation of cellulose

Figure 3 summarizes the molecular weight distributions and carbonyl group profiles of the pulp after the peroxide bleaching in comparison to the starting pulp. The corresponding molar mass and oxidation parameters are given in Table 1. Metal ion impregnation and chelation / washing step did not cause any changes (see above) – this state is shown by the corresponding “before bleaching” curves. The molar mass distribution shows the typical bimodal shape, with the low-molar mass peak mainly coming from the hemicelluloses, and a high-molar mass shoulder. After the peroxide bleaching, the pulp generally suffered degradation (chain cleavage and oxidation): all corresponding molar-mass profiles are shifted toward lower regions, and the carbonyl contents increased. However, there were very significant differences according



**Fig. 3** Molar mass distributions (solid lines, left y axis) and carbonyl group profiles (dotted lines, right y axis) of the pulps before and after peroxide bleaching (P-stage) depending on the conditions of a preceding chelation / washing stage

to whether the washing was done with distilled water, with diluted hydrochloric acid, or—as the “proper” chelation stage—with EDTA.

In the case of EDTA, the molar mass decrease was by far the lowest. It was slightly less pronounced for  $\text{Mn}^{2+}$  than for  $\text{Fe}^{2+}$  or  $\text{Cu}^{2+}$ , and it affected all molar mass regions (*cf.* Mn, Mw, Mz in Table 1). Most notably, there was no increase in carbonyl groups and thus no additional oxidative damage to the cellulose. Note that “new” carbonyl groups originate not only from oxidized hydroxy groups along the chain but also from new reducing ends (aldehyde groups present as hemiacetals) generated through chain cleavage (Ahn et al., 2018). Obviously, chain degradation in the P-stage was not fully prevented by the EDTA chelation step. However, the moderate degradation observed can also originate from  $\beta$ -alkoxy elimination reactions, induced by the prevailing alkaline conditions and starting from carbonyl groups already present in the pulps (see Table 1). Thus, chain degradation would be a consequence of oxidative pre-damage of the pulp rather than a direct effect of radical reactions in the P-stage. The largely constant carbonyl contents before and after the P-stage speak in favor of this assumption: while according to theory, the carbonyl content remains constant during  $\beta$ -elimination, it would increase due to “new” oxidation (Hosoya et al. 2018).

Replacing chelation by mere washing with either distilled water or dilute aqueous HCl gave rather disastrous results regarding cellulose integrity upon peroxide bleaching in the P-stage (*cf.* Figure 3 and Table 1). It should be noted that this general result is by no means new: after all, the implementation of chelation stages in bleaching sequences is industrial practice worldwide. However, the present work was concerned with the new aspect of capturing this effect analytically and measuring its extent reliably, in order to be able to quantify the positive influence of chelating agents. Both washing variants left traces of non-complexed transition metal ions in the pulp which—in combination with the peroxide in P-stage bleaching—caused extensive chain degradation according to *Fenton* chemistry, as expectable. The effect was even more pronounced for Fe and Cu (Table 1) but was in general rather severe, according to the molar weight distribution data obtained from the GPC measurements (Fig. 3). Important is the high increase of carbonyl groups under these conditions, which is corresponding to high oxidative damage. Their content is up to 10 times higher than in the starting pulp or the chelated pulp (Table 1). These

**Table 1** Summary of the molar mass data and carbonyl contents of the pulps before and after peroxide bleaching (P-stage) depending on the conditions of a preceding chelation / washing stage (cf. Figure 3)

Sample	Original pulp	Mn [kDa]	Mw [kDa]	Mz [kDa]	Đ [Mw/Mn]	C=O [μmol/g]
		65.59	425.7	1099	6.49	8.36
Cu	before bleaching	43.99	434.5	1322	9.878	9.67
	water (blank)	11.96	98.85	486.0	8.264	18.47
	aq. EDTA solution	28.29	223.2	898.7	7.892	9.45
	aq. HCl	11.99	68.31	357.1	5.695	107.53
Fe	before bleaching	54.85	456.3	1345	8.318	10.13
	water (blank)	22.36	121.2	455.6	5.419	16.16
	aq. EDTA solution	26.49	245.1	991.8	9.253	6.83
	aq. HCl	8.59	73.03	299.4	8.494	104.56
Mn	before bleaching	51.68	448.4	1316	8.676	8.62
	water (blank)	19.45	163.1	759.6	8.384	54.46
	aq. EDTA solution	27.08	254.5	955.3	9.395	7.65
	aq. HCl	13.99	165.5	914.3	11.83	53.21

carbonyl groups comprise newly formed reducing ends and carbonyl groups introduced along the cellulose chains.

When comparing washing with distilled water and with dilute HCl, it was very interesting to see that the oxidative damage and molar mass loss of cellulose did not correlate with the absolute content of transition metal ions. Otherwise, the values for water wash—with the large amounts of Fe and Cu remaining in the pulp (see Fig. 2)—should have been far above all others. However, cellulose damage and oxidation were more pronounced after HCl washing than after water washing. This is a clear indication that it is not the absolute transition metal content that is decisive, but the amount of free, redox-active transition metal species. While after water washing the metals remain weakly complexed by the cellulosic hydroxy groups—otherwise they would have been washed out—during HCl washing the metal ions have been liberated, and are now free to react with hydrogen peroxide and enter *Fenton* cycles. This is also supported by the fact that the trace chlorine content correlates linearly with the trace metal contents (ICP-OES, data not shown), which is indicative of highly reactive free chlorido complexes of the transition metals (in the case of HCl washing), while otherwise, in the case of water washing, less redox-active (partial) alkoxo/hydroxo complexes with the carbohydrates are present. In

addition, also the acidic HCl medium might depolymerize especially the hemicelluloses, as known from A stage (in which usually  $H_2SO_4$  is used), although this effect should be rather minor in the present case. As a result, cellulose gets better accessible and more susceptible to peroxide bleaching (Maréchal 1993; Pouyet et al. 2013).

It is known that  $Mn^{2+}$  cations primarily decompose hydrogen peroxide under P-stage conditions, but are not significantly involved in *Fenton* chemistry. Therefore, cellulose damage (molar mass loss and oxidation) in the case of  $Mn^{2+}$  is due to direct oxidation by hydrogen peroxide rather than *Fenton*-derived radicals (Colodette et al. 1988; Chirat and Lachenal 1994; Moreira et al. 2003).

The results displayed in Figs. 2 and 3 were very similar for other bleached or unbleached pulps. Also, EDTA and DTPA behaved similarly in all experiments with only negligibly small differences with regard to molar mass distributions and carbonyl profiles. When lower metal concentrations were used for pulp impregnation than the intentionally excessive concentrations employed above, the protective effect of the chelating agent was even greater and the difference with respect to the starting pulps, in terms of molecular weight distribution and carbonyl profiles, was even smaller. Transition metal ions other than Fe, Cu and Mn were not tested.

## Conclusions

An analytical approach has been developed to determine the effect of chelating agents during peroxide bleaching of cellulosic pulps. This method gives information on what happens during the chelation and bleaching steps, both in terms of metal content changes as well as cellulose degradation and oxidative damage to the pulp. ICP-OES provides the absolute metal contents of the pulps, and GPC delivers details about the cellulose, in terms of molar mass distribution and oxidation profiles. Neither of the two methods on its own is able to supply all the information necessary to assess the efficiency of a chelating agent, and only their combination is meaningful. Method optimization used also deliberately harsh conditions (high metal ion contents, extended peroxide impact) to make sure that also extreme cases can be covered.

The chelating agent (EDTA, DTPA) solution, in concentrations similar to industrial application, removed metal ions in the chelating step. Most importantly, the remaining transition metal ions stayed efficiently chelated also during the peroxide bleaching stage, and thus remained innocuous with regard to peroxide decomposition, induction of *Fenton* chemistry and cellulose damage. This preserves the pulp from degradation / oxidation during the bleaching step. The size of this protective effect relates to both the quality of a chelator and its concentration—it can be reliably quantitatively assessed by means of the molar mass distribution and carbonyl profile data. When the pulp was only washed with distilled water *in lieu* of an actual chelating step, metal ions remained in the pulp and caused severe degradation in the subsequent peroxide bleaching. Although washing with dilute aqueous HCl instead of water was more effective in removing the metal ions, it mobilized the transition metal ions so that their damaging effect on the pulp was even greater.

Alternative chelating agents for pulp bleaching will be required in the future because of environmental issues or possible regulatory obstacles with the EDTA / DTPA used so far. With the elaborated analytical protocol in hand, new chelator candidates can be tested and evaluated prior to industrial utilization, and later the subsequent large-scale application itself can be monitored. The second part of this work will

cover the testing of novel chelating agents for application in peroxide bleaching which are fully based on renewable resources, and the critical discussion of their efficiency and economic viability in comparison to EDTA / DTPA.

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**Code availability** Not applicable.

## Declarations

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