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Study of the Performance of Nitrilotriacetic Acid and Ethylenediiminopropanedioic Acid as Alternative Biodegradable Chelating Agents for Pulp Bleaching

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ABSTRACT: The aim of this work was to study the ability of two biodegradable chelating agents, nitrilotriacetic acid (NTA) and ethylenediiminopropanedioic acid (EDDM) to complex metals, in the treatment of the pulp, prior to a totally chlorine free (TCF) bleaching process, and compare with the ethylenediaminetetraacetic acid (EDTA) performance. Firstly, speciation efficiency index (SEI) was calculated by computer simulations in order to evaluate the best pH conditions for metal chelating removal: pH range 6.5-7.0 for NTA and EDDM and pH range 5-5.5 for EDTA. After implementation of the bleaching Q-P1-Paa-P2 sequence, NTA and EDDM removed transition metals (Cu, Fe and Mn) from the pulp more selectively than EDTA. The treatment with either NTA or EDDM resulted in a final bleached pulp with residual lignin contents similar to the one obtained with EDTA. A higher peroxide consumption was recorded when EDDM was used, while equivalent peroxide consumptions were registered when NTA or EDTA were applied.

Key words: Biodegradable, Chelating agent, Ethylenediiminopropanedioic acid (EDDM), Nitrilotriacetic acid (NTA), TCF bleaching

INTRODUCTION

The ability of chelating agents, such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA), to form stable metal complexes has been widely used in a variety of industrial applications, including pulp bleaching processes (Takahashi *et al.*, 1997). Neither EDTA nor DTPA show biodegradation during the biological step of the wastewater treatment plant (Pitter and Sykora, 2001). Therefore, large quantities of EDTA and DTPA are released into natural water resources (Metsarinne *et al.*, 2007). The main problem of the presence of these chelating agents in the aquatic systems is the disturbance of natural speciation of metals as a consequence of their ability to remobilize heavy metal ions from the sediments (Fuerhacker *et al.*, 2003; Pirkanniemi *et al.*, 2003).

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In the totally chlorine free (TCF) pulp bleaching processes, oxygen based oxidants such as ozone, hydrogen peroxide, molecular oxygen and peracids are usually used (Ni and Liu, 2000). When, hydrogen peroxide is used as bleaching agent, manganese (Mn), iron (Fe) and copper (Cu) ions react with hydrogen peroxide forming radical species (Wuorimaa *et al.*, 2006), which increase the consumption of chemicals during the bleaching (Colodette *et al.*, 1988) and decrease the pulp viscosity, brightness and delignification. Unlike Cu, Fe and Mn, which are present in the pulp at low concentration levels, calcium (Ca) and magnesium (Mg) are usually present at high concentrations levels. Mg has a stabilizing effect in the hydrogen peroxide, retarding the decomposition reactions (Wuorimaa *et al.*, 2006) and promoting carbohydrates preservation (Povoas *et al.*, 2012). On the other hand, Ca does not cause any effect in the catalysis of hydrogen peroxide decomposition.

EDTA and DTPA are the most used chelating agents in pulp and paper industry for removing transition metals from the unbleached pulp. However, replacement of these chelating agents by others, with complexing forming properties comparable to the traditional ligands, but more environmental friendly, namely biodegradable and with low content of nitrogen, is of great interest (Hyvonen and Aksela, 2007). Ethylenediamine-N,N'-disuccinic acid (EDDS), especially the [S,S] isomer, and iminodisuccinic acid (IDS) are frequently mentioned for this application due to their fast biodegradability that meets OECD criteria (Chauveheid *et al.,* 1999; Jones and Williams, 2001, 2002; Renvall *et al.*, 1997; Seccombe and Dournel, 2007). However chelation ability of SS-EDDS for the target metals is not as good as EDTA and when it comes to IDS the results are significantly worse (Renvall *et al.*, 1997). Other studies have been held (De Almeida *et al.*, 2008; Hyvonen and Aksela, 2007; Jakara *et al.,* 1997) with the aim of finding an efficient, more environmentally-friendly and economically competitive alternative, because biodegradable chelating agents studied so far are usually not as good chelants as traditional ones. Dixon and Giles (2009) proposed a bleaching pre-treatment with a mixture of biodegradable and non-biodegradable chelating agents, thus combining biodegradability with chelating efficiency. Nitrilotriacetic acid (NTA) and ethylenediiminopropanedioic acid (EDDM) are classified as readily-biodegradable chelating agents (Aoki and Hara, 2002; Sykora *et al.,* 2001). NTA, which is commercially available as the free acid and as the sodium salt, contains only one nitrogen atom per molecule and has the ability to be biodegraded under aerobic and anaerobic conditions (Takahashi *et al.*, 1997), as well as, by a high variety of microorganisms (Egli, 2001). NTA has been used in a wide range of industrial and domestic fields (Schmidt and Brauch, 2004) and applied as an alternative to EDTA, particularly in detergents (Egli, 2001). EDDM is an ethylenediamine disubstituted derivative with two secondary nitrogen atoms in the molecule, which application in industry was not tested, probably due to the fact that it is not a commercial compound.

As far as we know, the performance of NTA and EDDM as chelating agents in the pulp bleaching process has never been studied. Since these compounds are readily-biodegradable, their potential ability to sequester transition metal ions from the pulp was evaluated. For this purpose, a preliminar theorethical study, based on the determination of the Speciation Efficiency Index (SEI), proposed by Jones and Williams (2001), was used to evaluate the best pH conditions for metal removal from the pulp metal, followed by chelation and subsequent bleaching process, tested in real pulp samples.

MATERIALS & METHODS

The unbleached pulp used in this work was an oxygen delignified *Eucalyptus globulus kraft pulp*, collected from a Portuguese pulp mill. Unbleached pulp was characterized by quantifying metals concentration (Ca, Cu, Fe, Mg and Mn) after acid digestion of pulp with aqua regia, by atomic absorption spectroscopy with flame atomization (AAS-FA) using a spectrophotometer AAnalyst 400, Perkin Elmer. Acid digestion of pulp with aqua regia was performed at 80ºC during 120 min, with a pulp consistence, based on dry pulp (DP), of 70 $DPkg/m^3$.

The Speciation Efficiency Index (SEI) consists in a value that measures the ability of a chelating agent to sequester transition metal ions, while leaving Mg ions and avoid being distracted by Ca ions (Jones and Williams, 2001). This parameter, calculated by computer simulations, allows comparing the chelating ability of different compounds and predicting their (un)suitability for being used in the pulp bleaching process. For calculating the SEI values for the pulp bleaching process, speciation for chelating-metal systems were performed using MINEQL+ Version 4.5 (Schecher and McAvoy, 2003), a computer program that generates chemical equilibrium concentrations of all species being considered in the model based on chemical reactions and stability constants. Computational simulations were performed in aqueous medium and pH between 5 and 12. Metals concentration, expressed in mol/dm^3, was calculated from the metals content in the pulp (after determination in real samples; for further details see section 2.1) and a defined solid-liquid ratio. SEI value was calculated according to equation (1) (Jones and Williams, 2001):

(1)

SEI = % total Mn, Cu, Fe complexed + (100 - % Mg complexed) + (100 - % chelating agent distracted by Ca)

Assays were realized with three different chelating agents: NTA, EDDM and EDTA (for comparative purposes). $Na_2EDTA.2H_2O$ (Titriplex® III p.a, Merck) and Na_3NTA (>98%, Alfa Aesar) were used to prepare the respective aqueous solutions and EDDM was synthesized following a literature procedure (Mashihar *et al.,* 1973).The pulp bleaching process consisted on a four stage sequence: Chelation (Q) – hydrogen peroxide (P_1) – peracetic acid (Paa) – hydrogen peroxide (P_2) (Hyvonen *et al.*, 2006), with washing and filtration between the stages. For each stage, the conditions used were:

- Q - Chelating agent concentration and pH were defined after SEI evaluation. Performed at 80ºC during 90 min, with a pulp consistence, based on dry pulp, of 70 DPkg/m^3
- P_1 – Hydrogen peroxide at 18.5 kg/DPton and sodium hydroxide at 5 kg/DPton. Performed at 80ºC during 120 min, with a pulp consistence of 70 DPkg/m^3.
- Paa - Peracetic acid at 12 kg/DPton and chelating agent, which concentration was half of the amount used on the Q stage. Performed at 80ºC during 120 min, with a pulp consistence of 70 DPkg/m^3.
- P_2 – Hydrogen peroxide at 28.5 kg/DPton and sodium hydroxide at 10 kg/DPton. Performed at 90ºC during 180 min, with a pulp consistence of 70 DPkg/m^3.

A fourth test, with only the Q stage, where no chelating agent was added (blank), was performed to study the water leaching effect on the metal ions removal.

Bleaching assays were performed in SCHOTT flasks at a shaking bath with temperature control (OLS200, Grant). Metals concentration in the filtrate was quantified by AAS-FA, after Q and Paa stages. Hydrogen peroxide consumption was quantified by iodometry. In unbleached pulp and after P_1 and P_2 stages, kappa number was determined according to TAPPI T236 *cm-85*.

RESULTS & DISCUSSION

For removing harmful metals from pulp, a suitable chelating agent should be biodegradable and able to sequester transition metal (Mn, Cu, Fe) ions, leave Mg uncomplexed and avoid being "distracted" through complexation with Ca ions. In order to evaluate the complexing properties of NTA and EDDM and predict their performance in the pulp bleaching process, SEI calculations were computed for these two compounds and compared to SEI performed for EDTA.

To perform the computer simulations, total metals concentration in unbleached pulp was quantified by AAS-FA after acid digestion of pulp with aqua regia (Table 1). The chelating agent concentration used was defined to be ten times higher than the sum of the transition metals (Mn, Fe and Cu) concentration. However, NTA forms metal complexes in a proportion of 2:1, so, its concentration should be two times higher. To avoid the use of an extremely high quantity of chemical compounds, a concentration of NTA approximately fifteen times higher than the sum of the transition metals concentration was tested. Computer simulations were performed using a concentration of 4.5×10^{-4} mol/dm^3 for EDTA and EDDM and a concentration of 7.0×10^{-4} mol/dm^3 for NTA. The stability constants used for EDTA, NTA and EDDM with Mn, Cu, Fe, Ca and Mg ions were compiled from NIST Database 46 (Martell and Smith, 2004). EDDM simulations were performed without including the equilibriums for Fe-EDDM complexes because the corresponding stability constants are not described in the literature.

Table 1. Total concentration of Mn, Cu, Fe, Mg and Ca ions in the unbleached pulp

	Metal concentration (kg/DPton)	Metal concentration[a] (mol/dm^3)
Mn	14.8 ± 0.9	1.9×10^{-5}
Cu	1.5 ± 0.5	1.6×10^{-6}
Fe	18 ± 2	2.2×10^{-5}
Mg	104 ± 7	3.0×10^{-4}
Ca	764 ± 59	1.3×10^{-3}

[a]Consistency=70 DPkg/m^3

For EDDM, EDTA and NTA, the calculated SEI values are presented in fig. 1. For all three chelating agents, figure evidences that SEI never reached the maximum value, which should be 300, in the pH range studied. The highest SEI values were recorded between pH 5 and 7 for the three chelating agents.

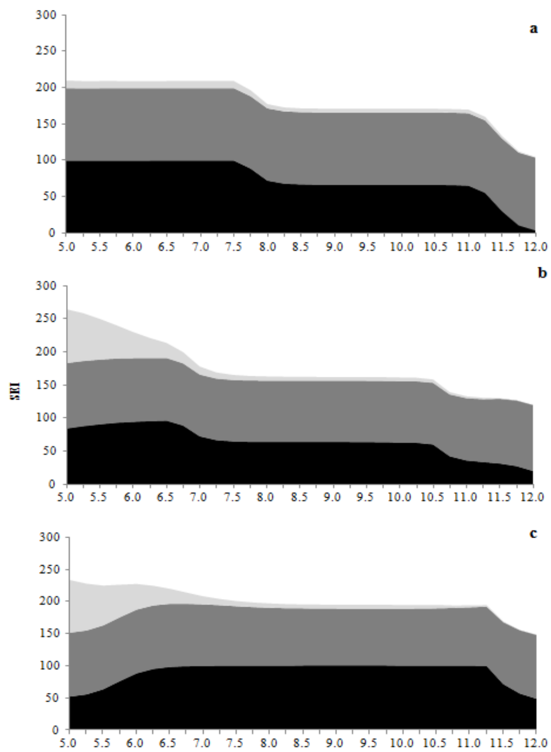

Fig. 1. Speciation Efficiency Index charts for EDTA (a), NTA (b) and EDDM (c), for pulp bleaching process as a function of pH: ■ % of transition metals (Fe, Mn and Cu) complexed; ■ % Free Mg; ■ 100 - % chelating agent lost to complex Ca

Despite the complexation with transition metals was almost total and the percentage of free Mg ions was higher than 99%, SEI for EDTA is clearly affected by the large complexation of EDTA with Ca, with a maximum value of 210 in the pH range between 5 and 7.5. For NTA and EDDM, SEI values were higher than for EDTA, between pH 5 and 6.5 and 5 and 7, respectively. This fact was due to the smaller complexation of NTA and EDDM with Ca. Both NTA and EDDM showed a weak complexation with Mg ions. These SEI values evidence that NTA and EDDM are selective to transition metals, which is fundamental to the success of the chelating agent (Povoas *et al.*, 2012).

The pH range to remove metals from the pulp by chelation must be chosen in order to obtain both high SEI values and maximum chelation of transition metals. Thus, a more specific analysis of the complexation between the chelating agents under study and the transition metal ions is needed. In which concerns Cu ions, the concentration of this metal ion in the unbleached pulp is very low; moreover, the three compounds form stable complexes with this metal ion until pH 10. So, it is expected that Cu ions are removed from the pulp and do not play a significant role in the formation of hydrogen peroxide radicals during bleaching (Wuorimaa *et al.*, 2006). For the other two metal ions, Fe (only for NTA) and Mn, the percentage of each metal ion complexed by NTA or EDDM in function of the pH is represented in fig. 2. The analysis predicts that NTA complexes totally with Fe, up to pH 6.5, but complete complexation with Mn is not achieved. Maximum complexation between Mn and NTA is predicted in the pH range 6.5 and 10. This means that the optimum pH value, at which NTA has a maximum performance with Fe and Mn ions, is 6.5. Due to the dificulty of performing bleaching experiments at an exact pH value, a pH range between 6.5 and 7.0 was defined to execut the Q stage experiments with NTA. Although pH 7 does not seem to be adequate to sequester Fe ions by NTA, priority must be given to complexation of Mn because it is known that Mn is the most critical metal ion for hydrogen peroxide decomposition (Lapierre *et al.*, 1995). In the case of EDDM, fig. 2 predicts that EDDM forms complexes with more than 95% of Mn ions at pH above 6.5. Thus, EDDM was used on the Q stage in the pH range between 6.5 and 7.0. The assays with EDTA were performed in the pH range between 5-5.5, where the highest SEI values were registered.

So, based on these theoretical simulations, both biodegradable chelating agents seem to be possible alternatives to EDTA in industrial pulp bleaching process under the evaluated conditions pointed out above.

TCF pulp bleaching process, via a Q-P1-Paa-P2 sequence, was applied in an oxygen delignified paper pulp *(Eucalyptus Globulus)*. Firstly, the Q stage of the pulp bleaching process was performed in order to test the efficiency of the chelating agents; then, the other three stages were executed. For the three compounds studied, results of metal removal from the pulp are shown in Table 2.

All compounds removed Mn ions efficiently, although the removal with EDTA was higher than with NTA or EDDM. Fe ions were not extensively removed from the pulp by all three compounds used. According to the NTA chemical simulations (Fig. 2), the pH range at which the experiments were performed was not the most suitable for complexing Fe. EDDM and EDTA also did not remove a significant amount of Fe, and other authors reported the difficulty of removing this metal from unbleached pulp even when EDTA was used (Kujala *et al.*, 2004; Loureiro *et al.*, 2011; Potucek and Milichovsky, 2000). On the other hand, the higher removal of Mn ions comparatively to Fe ions had already been reported (Loureiro *et al.*, 2011). Dick and Andrews (1965) explained this difference by the fact that Mn is loosely complexed with wood components when compared to Fe and Cu ions. No results were presented to Cu ions removal, because concentrations were below the detection limit of the method used.

Ca ions are a concern on the bleaching process due to the high concentration of this metal ion, usually present in the pulp, which can distract the chelating agent and thus requires a greater addition and increases the process costs (Jones and Williams, 2001). For NTA and EDDM assays, Ca percentage removals of 39 and 23%, respectively, were verified; these values corresponded to a percentage of distracted chelating agents of 72 and 66%, respectively, which is consistent with the corresponding SEI parameter. For EDTA assay, 43% of the Ca ions were removed.

Despite the speciation predictions (Fig .1), the three chelating agents showed high Mg removal (Table 2); assays with EDTA, NTA and EDDM registered removals of Mg of 41, 48 and 43%, respectively. When compared to the results obtained in the absence of a chelating agent it is evident that Mg ions were significantly removed from the pulp as a consequence of the water leaching effect (35 %) and not due to a chelating leaching. Since Mg removal occurred fundamentally due to water leaching, the application of NTA or EDDM in pulp bleaching seems to be feasible, regarding this parameter.

The efficient removal of Mn ions and the high concentration of Mg ions that remain in pulp after the

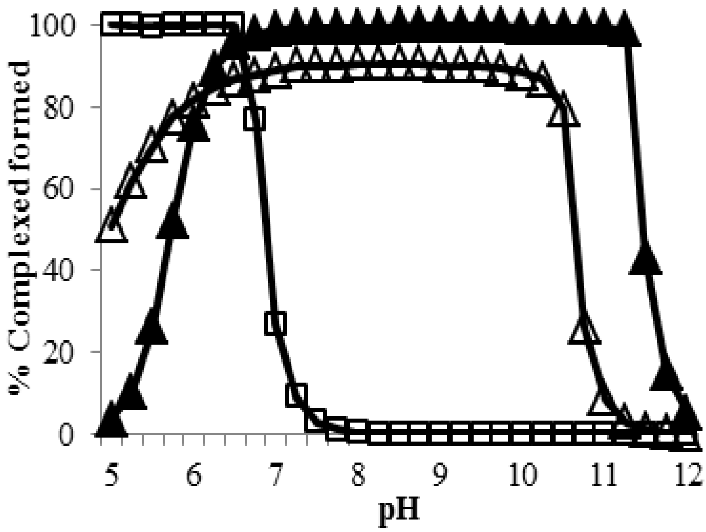

Fig. 2. Diagram of total percentage of Mn (△) and Fe (□) ions complexed with NTA (open symbols) and EDDM (filled symbols)

Table 2. Metal ions removal, expressed in percentage, after Q stage, for EDTA, NTA, EDDM and water assays

	Mn	Fe	Ca	Mg
EDTA (n = 4)	105 ± 3	13 ± 3	43 ± 1	41 ± 2
NTA (n = 11)	92 ± 3	19 ± 3	39 ± 3	47 ± 5
EDDM (n=10)	85 ± 4	16 ± 2	23 ± 1	43 ± 2
Water (n = 4)	34 ± 3	7 ± 1	23 ± 2	35 ± 2

Table 3. Hydrogen peroxide consumption and kappa number of pulp at P1 and P2 stages, for EDTA, NTA and EDDM assays

	P_1		P_2	
	H_2O_2 consumed (kg/DPton)	Kappa n.	H_2O_2 consumed (kg/DPton)	Kappa n.
EDTA	13 ± 2	5.2 ± 0.1	23 ± 1	2.8 ± 0.1
NTA	15.9 ± 0.8	4.9 ± 0.2	24.0 ± 0.8	3.8 ± 0.0
EDDM	16.3 ± 0.6	4.6 ± 0.1	27.5 ± 0.8	2.2 ± 0.1

Table 4. Total Mn, Ca and Mg ions removal, expressed in percentage, after Paa stage, for EDTA, NTA and EDDM assays

	Mn	Ca	Mg
EDTA	108	78	91
NTA	101	64	84
EDDM	98	60	84

Q stage, suggest that Mg ions concentration should be high enough to have a protector effect on the pulp bleaching. The stabilizer effect of Mg ions to hydrogen peroxide is explained by the deactivation of catalytic effect of Mn ions on the pulp due to the formation of Mg(II) –Mn(II)-OH (Liden and Ohman, 1997).

An overview of the results for Q stage showed that NTA and EDDM removed metals selectively. Despite the low removal of Fe ions from the pulp, both chelating agents removed Mn ions effectively, did not remove Mg ions, as desired, and were slightly distracted by Ca ions. Since Mn ions are the most harmful metal ion for hydrogen peroxide decomposition, the study of the next stages of bleaching was performed.

Before P_1 and P_2 stages, no Mg, in the salt form, was added because the amount of Mg ions on the pulp seemed to be high enough. Besides, the native Mg ions are more beneficial for pulp protection than added ones (Povoas *et al.*, 2012). After P_1 and P_2 stages, hydrogen peroxide consumption and kappa number of the bleached pulp were quantified (Table 3). Kappa number of the original unbleached pulp was also determined experimentally: 8.0 ± 0.1. Metals removal during Paa stage was also determined due to the chelating agent addition on this stage (Table 4).

After P_1 stage, similar hydrogen peroxide consumptions were attained for NTA or EDDM assays but slightly higher than the consumption for EDTA assay (Table 3). The amount of hydrogen peroxide consumed was higher than the values found in the literature for identical bleaching process where Mg salt was added (Hyvonen *et al.*, 2006). Possibly, the presence of some Mn ions when NTA and EDDM were used as chelating agents, compared to EDTA, together with the absence of addition of Mg salts for both cases, can justify the higher peroxide consumption during the experiments. Despite these results, the Kappa number in pulps resulting from NTA and EDDM experiments were lower than the one recorded for EDTA (Table 3) and those registered by Hyvonen *et al.*, (2006) for EDTA and DTPA (7.1 and 7.0, respectively); these results point out that the delignification process did not seem to be affected.

After P_1 stage, pulp was submitted to a new bleaching stage with peracetic acid together with the addition of a chelating agent. Removal of metals (Mn, Ca and Mg) was quantified and is shown in Table 4. Removal for Fe ion is not presented in the table because the reading values, after Paa, stage, were below the detection limit for the AAS-FA method. NTA and EDDM totally removed Mn ions from the pulp and had a similar removal effect for Mg and Ca. NTA and EDDM removed less Mg and Ca than EDTA. Even though the three chelating agents removed the totality of Mn ions from the pulp, NTA and EDDM were less distracted by Ca ions and left more Mg ions in the pulp than EDTA; these results indicate that, for this pulp bleaching process, NTA and EDDM were more selective to metals removal than EDTA. Despite NTA and EDDM removed less Mn ions in Q stage, the overall efficiency of both chelating agents was clear.

After P_2 stage (Table 3), the hydrogen peroxide consumption for NTA and EDTA assays presented minor differences between them and was lower than the consumption obtained for EDDM, which was almost total. The three assays had higher hydrogen peroxide consumption than the referred in the literature to an identical process (Hyvonen *et al.*, 2006), but, unlike the mentioned example, the present results were obtained with no addition of Mg salt. Despite the high consumption of hydrogen peroxide with EDDM, the bleached pulp registered the lowest kappa number among all assays whereas the one that resulted from the NTA set of experiments registered the highest value. These values are close to those found in the literature for a similar process (Hyvonen *et al.*, 2006) and indicate a successful removal of residual lignin (Colodette *et al.*, 2007).

CONCLUSION

In this study, the ability of two biodegradable chelating agents, NTA and EDDM, to complex metals, was evaluated for a specific TCF pulp bleaching process (Q-P_1-Paa-P_2) and compared with the EDTA performance. It was verified that NTA and EDDM were more selective on the metals removal than EDTA. The three chelating agents totally removed the Mn ions present in the unbleached pulp, but NTA and EDDM were less distracted by Ca ions and left more Mg ions in the pulp. The Q-P_1-Paa-P_2 pulp bleaching processes, where NTA and EDDM were used, showed identical metal ions removal and delignification efficiencies.
In conclusion, both proposed biodegradable chelating agents seem to be possible alternatives to be applied in the pulp bleaching process.

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