Prebleaching of eucalypt kraft pulp with OP stages: Effect of an acid pretreatment or chelation step

TATIANA M. PÓVOAS, DINA A.G. ANGÉLICO, ANA P.V. EGAS, PEDRO E.G. LOUREIRO, LICÍNIO M. GANDO-FERREIRA, AND M. GRAÇA V.S. CARVALHO

ABSTRACT: We conducted a comparative evaluation of different treatments for the bleaching of eucalypt kraft pulps beginning with OP stages. The treatments tested were (1) an acid chelation stage with DTPA (OQP sequence); (2) a hot acid stage (AOP sequence); and (3) a chelant addition into the alkaline oxygen stage ((OQ)P and A(OQ)P sequences). The latter strategy was also studied for environmental reasons, as it contributes to the closure of the filtrate cycle. The OQP sequence leads to the highest brightness gain and pulp viscosity and the lowest peroxide consumption caused by an efficient metals control. Considering that the low biodegradability of the chelant is a problem, the A(OQ)P sequence is an interesting option because it leads to reduced peroxide consumption (excluding OQP) while still reaching high brightness values and similar brightness reversion to OQP prebleaching, with only a viscosity loss of 160 dm^3/kg. Therefore, a hot acid stage could be considered when a separate acid Q stage is absent in a prebleaching sequence of *Eucalyptus globulus* kraft pulps involving OP stages.

Application: Findings from this study can assist mill engineers in choosing the most suitable metal ions management in OP prebleaching of eucalypt kraft pulps.

In recent years, environmental regulations and social concerns have led to a decrease in chlorine-containing bleaching agents and, therefore, a rise in oxygen-based bleaching chemicals such as oxygen (O) and hydrogen peroxide (P). For this reason, chlorine dioxide (ClO_2) stages are being gradually replaced by O or P stages in light elemental chlorine-free (ECF) bleaching sequences or being eliminated as in totally chlorine-free bleaching sequences. Implementation of these alkaline stages reduces the effluent discharge, because the absence of chlorine compounds in the filtrates allows them to circulate into the recovery cycle and contributes to closing up the bleach plant [1]. The decrease of adsorbable organic halogens, BOD, and color of the discharged effluents is another benefit of installing an oxygen-based stage [2]. Energy gains are equally attractive because of the presence of organic compounds in the filtrates and the low oxygen manufacture requirements when compared to ClO_2 production [3]. Despite all the advantages of using oxygen as an oxidative bleaching agent, its application is restrained by its low selectivity that is the result of a combination of factors. These factors are the resistance to oxygen mass transfer from the gas phase to the fibers and the unselective reaction of radicals that are formed during the reaction with lignin. Moreover, the residual transition metal ions present in pulps catalyze the decomposition of oxygen and oxygen-based products in their radical forms. Because of the high reactivity of these radicals, many authors report significant cellulose depolymerization leading to pulp viscosity losses. Therefore, the effectiveness of an oxygen stage is limited to 50% of delignification. Beyond this level, severe cellulose degradation takes place, resulting in deterioration of pulp strength and reduction of yield [4,5].

In spite of not being a powerful delignifying agent, hydrogen peroxide (H_2O_2) is a good bleaching agent. However, it may also be decomposed under the alkaline conditions that are usually used in the P stage, particularly when transition metal ions are present [6]. The mechanisms of H_2O_2 decomposition induced by transition metal ions during pulp bleaching are well documented in the literature [7-9]. Because of this decomposition, aggressive radicals are formed that originate undesirable carbohydrate degradation, even though they also contribute to the pulp delignification. Consequently, a loss of the potential bleaching power of the H_2O_2 will occur, as will the formation of new chromophores groups [6].

Among various transition metal ions that have been reported, manganese (Mn), iron (Fe), and copper (Cu) are the most harmful species during the O and P stages. The most accessible way of improving the selectivity of these stages seems to be the removal or the catalytic inhibition of transition metal ions activity. These can be carried out by several known processes such as: 1) the application of a hot acid pretreatment (A stage), 2) a separate chelation stage in acidic media (Q stage), or 3) the addition of stabilizers and/or chelating agents directly into the O or P stages [4,5,7-15]. Compounds with a high affinity for transition metal ions, such as DTPA (diethylene triamine penta acetate); or organophosphonate-based stabilizers, such as DTPMPA (diethylene triamine penta methylene

phosphonic acetate); or only magnesium sulfate are some examples. The Mg ion is believed to promote the release of the Mn ion from the pulp by an ion-exchange mechanism [13], and a ratio of Mg/Mn greater than 30 has been claimed for pulp protection and best peroxide bleaching performance [16].

The use of organophosphonate compounds have shown improved results compared to aminocarboxylate compounds due to the greater chelating extent of Fe [11]. However, their application is not advisable for pulps produced from Portuguese eucalypt. In comparison with other woods, the Iberian *Eucalyptus globulus* has higher content of phosphorus (P), which leads to a recognized production of mill effluents with phosphorous charges greater than the standard emission limit values stated in European environmental legislation [17,18]. The emission limit values of phosphorous for each bleached kraft eucalypt pulp mill are established according to the phosphorus content of the wood used, which is the exception to the standard 0.01–0.03 kg P/ton a.d. pulp. Therefore, the use of organophosphonate stabilizers constitutes additional phosphorus mass input in the bleaching process and, consequently, a potential problem in the residual water treatment, which Portuguese mill management tends to avoid.

The main drawbacks of an acid chelation step are the impossibility of recycling the effluent to a mill's chemical recovery system and the nonbiodegradability of most chelating agents. It is also important to evaluate the economic feasibility of the application of this stage, which depends on its position in the bleaching sequence. The charged groups of fibers, such as glucuronic (GlcA) and hexenuronic acid (HexA), linked to xylan have high affinity for metal ions; therefore, chelants need to have even higher affinity for metals. An acid stage, on the other hand, reduces the chelating ability of the pulp for metal ions because the acid hydrolysis of HexA decreases the available binding sites of the unbleached pulp [16,19]. Another advantage of the acid pretreatment is that HexA removal lowers ClO_2 consumption in subsequent stages in ECF bleaching sequences [19]. However, the acid effluent cannot be recycled to the recovery line and the metal leaching is not selective. Moreover, the acidic A stage placed between the brown pulp washing and the oxygen predelignification will need more efficient washing to decrease the carryover, thus avoiding lignin precipitation phenomena on pulp. This precaution is similar to mill situations where a D_0 stage is used without an oxygen predelignification stage (as in some Portuguese pulp mills).

Our major purpose was to study a suitable strategy for controlling metal ions in prebleaching sequences with OP stages applied to kraft pulps produced from *E. globulus*.

EXPERIMENTAL

Kraft pulps

The unbleached kraft pulps used in this study were provided by a Portuguese pulp mill. Before laboratory usage, the pulps were thoroughly washed with warm deionized water (35ºC) for 30 min in an agitated tank and then centrifuged. This procedure was repeated three times. At the end, the pulps were stored in the freezer, at 4ºC, in plastic bags. By doing so, the effect of the amount and composition of the carryover, which is very process-specific and thus varies from mill to mill, could be eliminated. For instance, in a previous study, consumption of 14 kg sodium hydroxide (NaOH)/ton of industrial pulp was observed compared with 6 kg NaOH/ton of thoroughly washed pulp to attain the same kappa number after the oxygen predelignification stage.

Acid treatment (A stage)

Suitable operating conditions (temperature, pH, and reaction time) of an A stage are crucial for reducing cellulose and hemicelluloses depolymerization. Therefore, according to Primo and Carvalho [20], the pulps were brought to 10% consistency in plastic bags, and a solution of sulfuric acid (H_2SO_4) was used to adjust the pulp slurry to pH 3. The closed bags were put in a thermostatic bath held at 90ºC for 2 h. The bags were then transferred to an ice bath and after 2 min, the pulps were thoroughly washed with deionized warm water.

Acid chelation (Q stage)

The pulps were brought to 10% consistency in plastic bags with acidic aqueous solution (H_2SO_4) to get a final pulp slurry pH of 4.5–5. The chelating agent (DTPA) was also added at a charge of 0.2%. Chelation was performed in a water bath held at 70ºC for 60 min, as suggested by Cerqueira et al. [21]. The pulp was then washed with deionized warm water.

Oxygen delignification (O and (OQ) stages)

Oxygen delignification was carried out in a 1-L batch modified Parr reactor (Model number 4523, Parr Instrument Company; Moline, IL, USA), at 2.5% consistency. The alkaline charge was 1% (NaOH), and the initial pH of the slurry was about 11. The runs were performed at 95ºC for 60 min, with pressure of 8 bar and with agitation (1080 rpm). The temperature rise took about 20 min, after which the NaOH solution and the oxygen were introduced. The experiments with the chelant in alkaline medium ((OQ) stage) were performed with a 0.2% DTPA charge, and the chelant was introduced in the reactor during the alkali addition. After delignification, 1 L of cold water (4ºC) was added to the slurry to stop the reaction, and then the pulp was thoroughly washed with deionized warm water.

Hydrogen peroxide bleaching (P stage)

The bleaching experiments with H_2O_2 were also carried out in sealed plastic bags, at 10% consistency in alkaline media (0.7% NaOH). The H_2O_2 charge used was 1.0% of the dry pulp mass. A thermostatic bath was used to bring the pulp to the reaction temperature (90ºC). After 2 h of reaction, the bags were put into an ice bath for 2 min. A sample of the filtrate was collected into a dark glass bottle to determine the H_2O_2 consumption by iodometry. Cold water (4ºC) was added to the slurry, and then the pulp was thoroughly washed with deionized warm water.

Analytical methods

Routine analytical methods were used to evaluate the bleaching processes stage by stage. Pulps were characterized for kappa number (ISO 302 "Pulps — determination of kappa number"); intrinsic viscosity (ISO 5351 "Pulps — determination of limiting viscosity number in cupri-ethylenediamine [CED] solution"); brightness and brightness stability (ISO 2470 "Paper, board and pulps — measurement of diffuse blue reflectance factor [ISO brightness]" and TAPPI T 260 "Test to evaluate the aging properties of bleached chemical pulps") using Data Color Elrepho (Model SE-070, Lorentzen & Wettre USA; Roswell, GA, USA); metal ions content (TAPPI T 266 om "Determination of sodium, calcium, copper, iron, and manganese in pulp and paper by atomic absorption spectroscopy"); and hexenuronic acid content. The latter was quantified by ultraviolet absorption of the solution resulting from their hydrolysis with a mercuric chloride–sodium acetate mixture as described elsewhere [22]. This method is similar to TAPPI T 282 pm-07 "Hexenuronic acid content of chemical pulp." The contribution of HexA to the pulp kappa number was estimated using the empirical equation developed by Pedroso and Carvalho [22] for kraft *E. globulus* pulps (Eq. [1]):

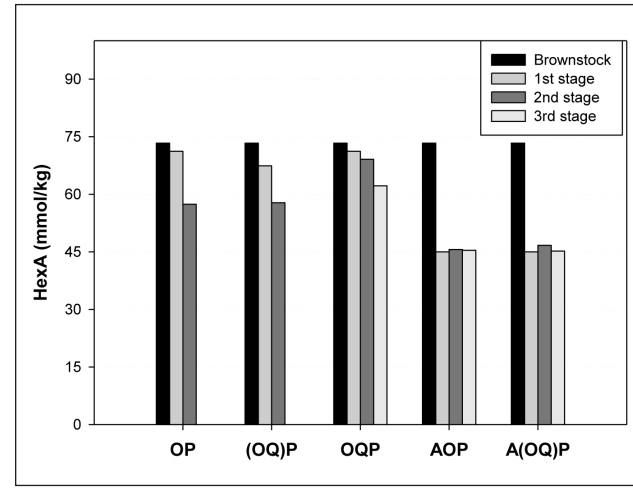
$$KN \approx \text{Lignin KN} + \text{HexA KN} = 5.3\ TL + 0.09\ C_{HexA} \quad (1)$$

where KN is kappa number, TL is the total lignin content (% o.d. pulp), and C_{HexA} is the HexA content (mmol/kg o.d. pulp). This equation was used even though some points deviated slightly from the specified range of $7.5 \le KN \le 69$, $1.2 \le TL \le 12$, and $18 \le C_{HexA} \le 61$. The experimental error associated with HexA and kappa number measurements was 5 mmol/kg o.d. pulp and 0.25 kappa number units, respectively. Brightness reversion was expressed in terms of the ISO brightness difference between initial and postaging values, in %. **Table I** presents the washed kraft pulp characterization.

Property	Initial Pulp	Pulp after A Stage
Kappa number	13.5	10.3
Intrinsic viscosity (dm^3/kg)	1,295	1,202
HexA content (mmol/kg)	73.3	45
HexA KN[a]	6.6	4.1
Lignin KN[b]	6.9	6.2
ISO brightness (%)	42.5	43.5
Brightness reversion (%)	0.6	0.8
Ca (ppm)	2,349	397
Mg (ppm)	98	24
Fe (ppm)	6.7	4.5
Mn (ppm)	20	4.9
Cu (ppm)	2.2	1.8
Mg/Mn	4.9	4.8

[a] HexA KN = 0.09 C_{HexA} ([16]).
[b] Lignin KN = KN - HexA KN (Eq. [1]).

I. Summary of the pulp properties before and after the acid treatment.



1. Hexenuronic acid (HexA) content in pulps after each stage of the prebleaching sequences studied.

RESULTS AND DISCUSSION

Metal ions and hexenuronic acid removal

An acid treatment and/or a chelation step were employed to remove unwanted transition metals in oxygen delignification and peroxide bleaching of *E. globulus* pulp. Compared to softwoods, hardwoods such as *E. globulus* have higher amounts of xylan and the corresponding branches of GlcA groups [23]. These groups, easily ionizable, are responsible for the fiber's charge where metal ions are often attached to [13,16,23-25]. Hexenuronic acid, formed from the partial degradation of GlcA during alkaline cooking, increases the attraction of pulps for metals [16]. Therefore, the removal of transition metal ions by chelating agents becomes more difficult and selective chelants like amino-carboxylates (such as DTPA) are needed to overcome the binding ability of those pulps for metals. Moreover, HexA contributes to the pulp kappa number [22,26] and is claimed to decrease the stability of pulp brightness [26]. The HexA content was determined in pulps after each stage of the prebleaching sequences studied. **Figure 1** presents the results.

Although it is known that oxygen and hydrogen peroxide do not react with HexA [23], a 3%–19% decrease in their content was observed along O or P stages in the sequences not started by an A stage. The explanation might rely on the alkali solubilization and/or degradation of xylan, which can probably be enhanced by the attack of the aggressive radicals [27]. On the contrary, the acid treatment before the OP and (OQ)P sequences can degrade part of the HexA groups and/or cause xylan hydrolysis, thus allowing the solubilization of HexA linked to the degraded chains. Both processes led to the decrease of HexA content, about 38% (Fig. 1 and Table I), while HexA reduction was not observed along the following O and P stages. If used in further stages, ClO_2, ozone, or per-

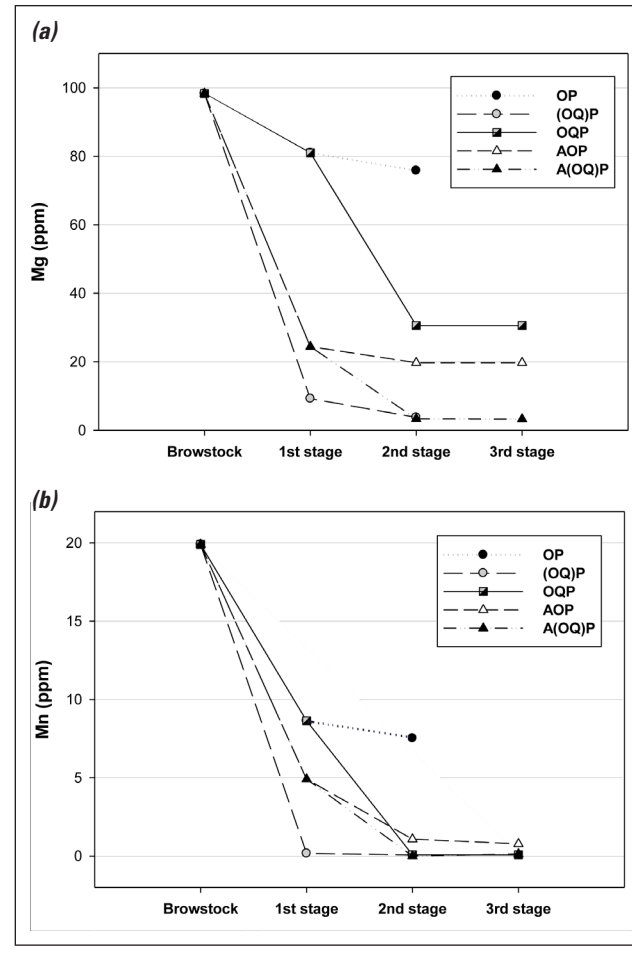
acids consumption would be lower as a consequence of the HexA content reduction in an A stage because these bleaching reagents do react with HexA [19].

The degradation of HexA groups by acid hydrolysis in the A stage led to a decrease in the available binding sites of the unbleached pulp, contributing, though unselectively, to the removal of metal ions. Therefore, transition and alkaline earth metal ions were both removed to a large extent, as shown in Table I. Indeed, the acid treatment removed 83% of calcium (Ca), 76% of Mg, 33% of Fe, 76% of Mn, and 18% of Cu. Table I also shows that approximately 50% of the initial pulp kappa number was due to the contribution of HexA (6.6/13.5). As a consequence of the acid treatment, the HexA content decreased ~39% and the variation in kappa number was mainly due to this reduction. Lignin removal corresponded to only 0.7 kappa number units.

Figure 2 shows a decrease in Mg and Mn content along O stages, even when no DTPA was used. This might be related to alkali degradation and/or solubilization of xylan, which diminished the pulp binding sites. Without chelant, Mn was more extensively removed than Mg (57% for Mn and 18% for Mg in OP sequence; 78% for Mn and 19% for Mg in AOP sequence) once that Mn was known to be more loosely bonded to pulp [7,11-12]. Pulps after A stages had lower viscosity (1200 dm^3/kg) than the original pulp, indicating higher carbohydrate degradation. This fact led to a stronger effect of the alkaline extraction occurring in the O stage, which was followed by a higher relative decrease of Mn content compared with that of Mg (Fig. 2).

A chelating agent is thought to be extremely efficient in binding transition metal ions through the formation of soluble complex ions [11–12]. The alkaline earth metals, mainly Mg, should stay on pulp while removing harmful transition metals to benefit carbohydrates preservation and to reduce H_2O_2 consumption [10,16]. The effect of the chelant DTPA on the Mg and Mn contents in the pulps studied can be seen in Fig. 2. The addition of chelant into oxygen, (OQ) stages, was able to remove 99% of Mn and 97% of Mg from the pulp in the (OQ)P sequence, whereas for A(OQ)P sequence, it was able to reduce 98% of Mn and 87% of Mg. As shown in Fig. 2, a chelation stage with DTPA in acid media, as in the OQP sequence, enabled greater removal of Mn compared with Mg: 99% of Mn and 62% of Mg. These results confirm the enhanced selectivity of the DTPA action in acid media [16]. Considering the results previously presented in O stages, it can be concluded that the additional decrease in Mn and Mg contents observed in the presence of DTPA (Q and (OQ) stages) should be attributed to the impact of the chelant itself.

During A stages, around 75% of both Mg and Mn content is removed, confirming the unselective removal of metal ions when this pretreatment is applied (Table I and Fig. 2). The A stage may be followed by careful replenishment of Mg to ensure an adequate level [16]; however, as noted by Yang et al. [28], the native Mg ions are more beneficial for carbohydrate protection than the ones added.



2. Metal content in pulps after each stage: (a) magnesium and (b) manganese.

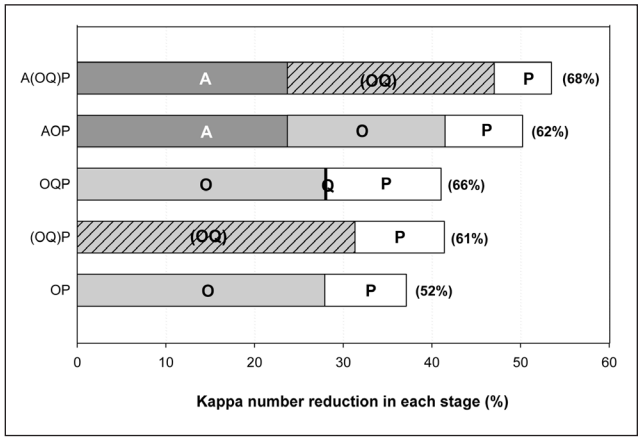
Effect of prebleaching sequences on delignification and selectivity

Table II presents the pulp properties obtained after the prebleaching sequences studied, as well as the lignin and HexA contributions to kappa number for the final pulps of each bleaching sequence. In addition, **Fig. 3** presents the kappa number variation for each stage (calculated as the change in kappa number relative to the initial kappa number), as well as the global delignification degree (based on the corrected kappa number, without the HexA contribution). As it is well known, the HexA contribution to the measured kappa number can be a very significant value in hardwoods. In fact, this contribution corresponded to 49% of the initial pulp used in this work and reached 70% after the OQP sequence. Consequently, the global kappa variation along the sequences studied did not exceed 53%. The highest values were found in the sequences that included an A stage, which was correlated with the fact that these sequences have three stages in which lignin and/or HexA is removed. However, on the basis of the corrected kappa number (without HexA contribution), higher delignification degree was found in A(OQ)P as well as in OQP sequences (68% and 66%, respectively). It was also observed

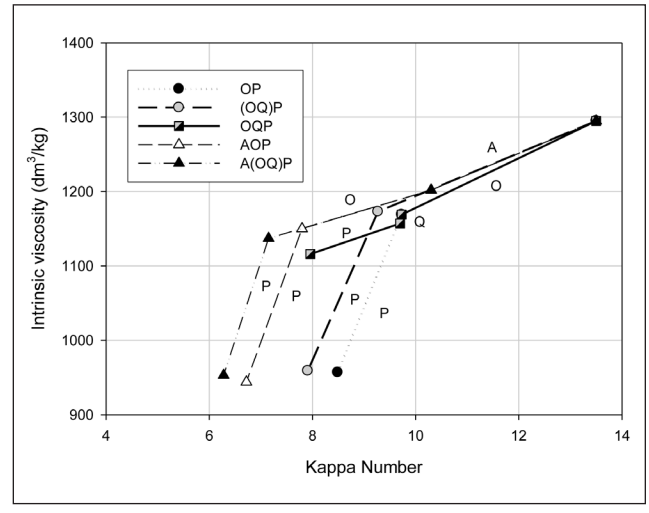
Sequence	Kappa Number (KN[a])	HexA[a] (mmol/kg)	HexA (KN[b])	Lignin (KN[c])	Intrinsic Viscosity (dm^3/kg)	H_2O_2 consumed (kg/ton o.d. pulp)	ISO Brightness (%)	Brightness Reversion (%)	Mg/Mn before P Stage
OP	8.5	57.4	5.2	3.3	957	9.8	64.9	2.0	9
(OQ)P	7.9	57.8	5.2	2.7	959	8.7	71.6	4.9	53
OQP	8.0	62.2	5.6	2.4	1116	3.0	73.4	3.7	81
AOP	6.7	45.4	4.1	2.6	944	9.7	67.5	1.7	18
A(OQ)P	6.3	45.2	4.1	2.2	953	8.2	71.7	3.5	24

[a] - as measured.
[b] HexA KN ≡ 0.09 C_{HexA} (Pedroso and Carvalho [22]).
[c] Lignin KN = KN - HexA KN (Eq. [1]).

II. Properties of the final pulp obtained after the prebleaching sequences studied.



3. Kappa number reduction for the studied stages. The global delignification degree of each sequence, based on the corrected kappa number (without HexA contribution), is represented in brackets on the right side of each bar.
Patterns: Q A O (OQ) P.



4. Selectivity (intrinsic viscosity versus kappa number) at each stage of the prebleaching sequences studied.

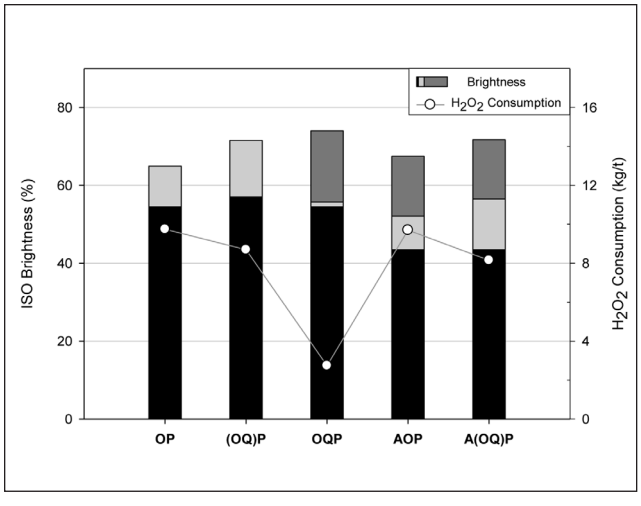
that the addition of DTPA to the oxygen stage (comparing (OQ)P and OP or A(OQ)P and AOP sequences) resulted in a higher degree of delignification obtained in this stage. This was probably a consequence of the chelating action of DTPA (even in alkaline medium) toward the transition metal ions that are responsible for oxygen consumption. Similarly, the removal of harmful metals in the Q stage previous to the P stage in the OQP sequence saved peroxide from being readily decomposed, enabling its efficient use in delignification and brightness gain. Table II confirms this; this sequence is characterized by the lowest reagent consumption, highest brightness, and highest viscosity. Consequently, a greater degree of delignification was obtained during P stage in comparison with the values observed in the same stage for the other sequences (Fig. 3).

Another factor that limits the performance of bleaching sequences is the overall selectivity of the process. **Figure 4** shows the selectivity of the various sequences studied, plotted as intrinsic viscosity versus kappa number. The results show that the selectivity was low during all P stages, except in OQP sequence. This behavior was consistent with the high H_2O_2 consumption verified in those P stages (Table II). The selectivity was low even in the (OQ)P sequence where relatively high values of Mg/Mn ratio were attained before the P stage compared to OP, AOP, and A(OQ)P sequences (Table II and Fig. 2). This was because Mg content was much lower when compared to the OQP sequence, except for OP where the high amount of Mn before the P stage was detrimental. On the other hand, the addition of chelant into the O stage ((OQ), in alkaline medium), improved its selectivity. It is also worth mentioning that after an acid treatment, the O stage had higher selectivity. This selectivity, calculated as the change in kappa number over the change in viscosity in the O stage, increased from 0.030 to 0.048 (O versus AO) and from 0.035 to 0.049 ((OQ) versus A(OQ)). The removal of metal ions decreased oxygen waste by decomposition, leaving a higher quantity of oxygen available for lignin oxidation and degradation.

Effect of prebleaching sequences on brightness, brightness reversion, and peroxide consumption

The use of a chelant in the O stage, even in alkali medium, improved the brightness gain in this stage as well as the brightness of the (OQ)P and A(OQ)P prebleached pulps while the peroxide consumption was only slightly reduced (**Fig. 5**). Nevertheless, OQP was the more efficient bleaching sequence studied because the corresponding pulps attained the highest brightness with the lowest peroxide consumption. It is worth mentioning that the values of Mg/Mn ratio obtained before the P stage of each sequence (Table II) did not confirm the claimed minimum value of 30 to ensure efficient peroxide bleaching performance [16]. In spite of having an Mg/Mn ratio of 53, the peroxide consumption in (OQ)P sequence was similar to the remaining sequences with Mg/Mn ratio values lower than 30. On the other hand, the chelant usage (as an independent acid stage or added into the alkaline O stage) increased brightness reversion, even though the HexA content in pulps at the end of the sequence was almost the same (OP versus OQP and (OQ)P and AOP versus A(OQ)P). From Table II, it can also be concluded that, besides removing HexA from the original pulp, the pretreatment with hot acid in the studied sequences slightly decreased brightness reversion (OP versus AOP and (OQ)P versus A(OQ)P). However, when comparing the values of HexA with those of brightness reversion, no correlation between these characteristics could be found.

In Portugal, there is a pulp mill that uses a sequence comprising OQ(PO) prebleaching followed by DP final bleaching. Other pulp mills use conventional ECF bleaching sequences without oxygen predelignification. As the focus of this study was on prebleaching with OP stages, the five studied alternatives were not completed regarding the whole bleaching sequence. However, the impact of different industrial prebleaching stages on final DP bleaching was studied previously, specifically $D_0(EOP)D_1P$ versus OQ(PO)DP sequences [29-30]. It was shown that bleaching history impacts the transition metals profile and residual chromophores, as well as pulp beatability and brightness reversion. Depending on the bleaching history, the final P stage had distinct performances toward the ISO brightness target of 90 ± 0.5%. For instance, chemical consumption, intrinsic viscosity, post-color number, and tensile index were, respectively, 11.3 kg H_2O_2/ton o.d. pulp, 850 dm³/kg, 0.44 and 73.4 N-m/g at 1000 revolutions for $D_0(EOP)D_1P$ pulp; for OQ(PO)DP pulp the corresponding values were 0.7 kg H_2O_2/ton o.d. pulp, 880 dm³/kg, and 0.48 and 54.5 N-m/g, respectively [29].



5. Brightness gain in each stage and peroxide consumption (kg/ton o.d. pulp).
Patterns: ***1st stage*** ***2nd stage*** ***3rd stage.***

CONCLUSIONS

An acid treatment and/or chelation with DTPA, before the P stages, decreased harmful Mn ions. In addition, a hot acid treatment reduced the HexA content, as expected, contributing to the decrease of pulp kappa number and its binding ability. The treatment also improved the selectivity of the following O stage, enhanced brightness and brightness stability, and slightly decreased H_2O_2 consumption. With chelation (OQP, (OQ)P and A(OQ)P) sequences), a more selective Mn removal was achieved, especially in the OQP sequence, where a separate acid Q stage was used. Consequently, the lowest H_2O_2 consumption was observed for this sequence.

The correct combination of acid treatment and chelation stage can be successfully used for metal management and influences the performance of OP prebleaching sequences. To select an adequate combination of treatment stages with efficient metal profiles and involving OP stages, delignification, chromophore elimination, chemicals consumption, viscosity loss, HexA removal, and brightness stability must be optimally balanced. Bearing in mind all these factors, the OQP sequence resulted in the highest brightness and pulp quality and the lowest peroxide consumption caused by an efficient metal ions control. However, if the low biodegradability of the chelant is a problem, A(OQ)P and AOP sequences are interesting options to evaluate. Excluding the OQP sequence, AOP had the lowest brightness reversion, while A(OQ)P had the lowest peroxide consumption while still attaining high brightness values. Therefore, an acid treatment is valuable when an acid Q stage is absent or if it cannot be used because of effluent management issues. **TJ**

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ABOUT THE AUTHORS

With this research, we intended to study alternatives to chlorine dioxide delignification by the use of oxygen and hydrogen peroxide delignification stages using *E. goblulus* kraft pulp. The work complements our previous studies on the optimization and bleaching kinetics of single chlorine dioxide, oxygen, and hydrogen peroxide delignification stages of *E. goblulus* kraft pulps. We focused on the more suitable metal ions management in the OP prebleaching.

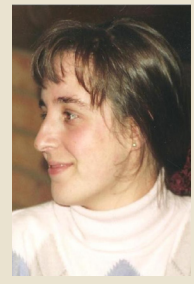
The most difficult aspect of this research was the control of transition metals and magnesium content, which needed several alternatives and bleaching experiments. The OQP prebleaching sequence led to the best results, including final pulp properties. Even considering an acid stage and simultaneously adding the same chelant into the O stage, the A(OQ)P sequence did not produce results as good as the OQP solution.

Mills that might be interested in changing prebleaching to a combination of oxygen and hydrogen peroxide bleaching stages may find this study helpful to them regarding criteria for choosing the most suitable metal ions management. The next step will be the use of bleaching alternatives to enhance the use of non-chlorine based reagents with good selectivity and bleachability output.

Póvoas is product manager at grupo PortucelSoporcel, Figueira da Foz, Portugal. Angélico is a consultant at VLM Consultores SA, Aveiro, Portugal. Egas is a doctoral candidate, Loureiro is a reseacher, and Gando-Ferreira and Carvalho are assistant professors at CIEPQPF, Department of Chemical Engineering, University of Coimbra, Coimbra, Portugal. Email Carvalho at mgc@eq.uc.pt.


Póvoas


Angélico


Egas


Loureiro


Gando-Ferreira


Carvalho

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