

EVALUATING SUITABLE CHELATING AGENTS FOR Q STAGE IN TCF BLEACHING OF WHEAT STRAW ALKALINE PULPS

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The aim of this study was to determine an appropriate chelating agent for Q stage in the TCF bleaching sequence of soda-oxygen, soda, soda-anthraquinone and alkaline-sulfite wheat straw pulps prior to P bleaching stage. In order to study the possible effect of chelating agents, three different chelating agents (EDTA, DTPA and DTMPA) were used. To evaluate the impact of transition metal ions on P stage, the residual Mn, Fe and Cu ion concentrations were determined with atomic absorption spectrometry. Ash and silica contents of pulps have been determined for each chelating agent, separately. FTIR-ATR spectroscopy was used to demonstrate the bleaching effect. The results showed that the most appropriate chelating agents varied depending on the type of pulp. The best chelating effect was achieved with DTMPA for soda-oxygen pulp, EDTA for both soda and alkaline-sulfite pulps, and DTPA for soda-anthraquinone pulp.

Keywords: TCF bleaching, chelating agent, phosphonates, wheat straw, alkaline pulp

INTRODUCTION

Increasing environmental concerns and the rising demand for high quality paper reveal the importance of raw materials and chemical resources. The use of non-wood plant species and agricultural residues as raw materials for papermaking industry has gained interest because of the shortage of wood resources and environmental concerns in general.¹ Non-wood plant species and agricultural waste constitute 8-10% of the total pulp and paper production worldwide.² Fast growth, lower cost, lower lignin content, easily accessible structure to the pulping liquor, lower consumption of chemicals and easy beating of pulp are some advantages of non-wood raw materials for paper pulping.^{3,4} Easy pulping and good bleaching properties⁵ are additional advantages of non-wood plants as raw materials.

Wheat straw is an agricultural residue that has gained importance as a promising raw material for the pulp and paper industry.⁶ The high strength, brightness and brightness stability of bleached

pulps are very important properties to produce long-lasting publication papers.

Bleached pulps have superior properties compared to unbleached pulps in terms of brightness, cleanliness and softness.⁷ The bleaching process is considered as a continuation of the pulping process through which it is attempted to achieve the desired brightness value while preserving the cellulose as much as possible. The industry's goal is to provide acceptable bleached pulp properties by performing the bleaching process, with reduced production costs. The chemical pulp bleaching process is a multistage sequential procedure, consisting of multiple bleaching steps performed to achieve high pulp brightness. Chemical bleaching of pulps includes delignification and removal of residual chromophores.⁸

The bleaching process in the pulp and paper industry has been commonly recognized as an important polluting system. The pulp industry has

made some changes in pulp bleaching processes to minimize environmental impacts. Totally chlorine-free (TCF) bleaching techniques have been developed as environmentally friendly pulp bleaching methods.

The purpose of bleaching is to remove lignin from the pulp in a highly selective manner, without any adverse effect on cellulose. Oxygen-based radicals, such as hydroxyl, superoxide, and superoxide anion are mainly responsible for the low selectivity in TCF bleaching sequences.^{9,10}

Most of the reactions that can easily change the oxidation state are induced by transition metal ions (particularly iron, copper or manganese) naturally occurring in pulp.^{11,12} These transition metal ions react with oxygen-based chemicals (ozone, hydrogen peroxide, oxygen, peracids),^{12,13} increase the consumption of bleaching agents¹⁴⁻¹⁶ and lead to the formation of radicals^{12,13} by causing the catalytic degradation of these chemicals during bleaching of cellulosic pulps.¹⁴⁻¹⁶ Transition metal ions reduce the viscosity of pulp and accelerate the darkening of the color of the final product.^{17,18}

Hydrogen peroxide (H_2O_2) is the most important and widely used as an environmentally friendly bleaching agent in chemical pulp bleaching due to higher bleaching efficiency and low cost.¹⁹⁻²² Hydrogen peroxide solutions are not stable and decompose with the effect of high temperature, transition metal compounds, alkalis and irradiation.²³ Most of the peroxide is consumed by decomposition with the effect of transition metals.^{24,25} If the metal ions are not controlled, this decomposition can greatly reduce the effectiveness of the bleaching process.

Perhydroxyl ions ($HOO\cdot$) formed by the effect of heterolytic cleavage under alkaline conditions are required for chromophore degradation.^{23,26} The perhydroxyl anion is a strong nucleophile and it is fundamental to achieve effective bleaching.²² In the case of homolytic cleavage of the bond between two atoms, each atom retains one of the bonding electrons and radicals are formed. The presence of metal ions accelerates the formation of radicals.^{23,27} The formed radical species adversely affect the efficiency of the bleaching process. The unselective radicals formed as a result of the catalytic degradation of hydrogen peroxide is the major drawback in the peroxide (P) bleaching stage of the bleaching sequence.²⁸ Especially hydroxyl radicals ($\cdot OH$), which have a high oxidation potential, can cleave hydrogen atoms from the cellulose chain,²⁶

and thus free electrons are formed in cellulose that can participate in reactions, such as further chromophore formation, oxidation and degradation.²³ These radicals are responsible for depolymerization of polysaccharides, cellulose degradation and thus, a decrease in pulp strength and quality.²⁸⁻³¹

The control of metal ions, the prevention of peroxide decomposition and the resulting cellulose degradation are possible with the use of chelating agents.²⁹ Chelating agents prevent the contact of hydrogen peroxide with transition metals, reducing the catalytic degradation of bleach.^{32,33} In this way, chelants optimize the bleaching process.

Aminopolycarboxylic acids, such as EDTA (ethylenediaminetetraacetic acid) and DTPA (diethylenediaminepentaacetic acid), are the most widely used chelating agents in the pulp and paper industry to remove metals from pulp by forming stable water-soluble chelates with transition metals.³³⁻³⁵ Phosphonic acids are the alternatives to EDTA or DTPA with very similar structures. DTMPA (diethylenetriamine penta methylene phosphonic acid) has a parallel structure to that of DTPA.⁹ The chelating agent is generally added to the pulp before the peroxide stage. The role of chelants is to form soluble complexes with metals in the pulp.³⁶ It is difficult to control the reactivity and behavior of transition metal ions in water.^{37,38} Chelating agents can reduce bleaching costs by improving pulp bleachability and controlling metal ions.³⁹

The objective of the present work was to determine the appropriate chelating agent for Q-stage of the totally chlorine-free (TCF) bleaching sequence of soda-oxygen (SO), soda (S), soda-anthraquinone (S-AQ) and alkaline sulfite (AS) wheat straw (*Triticum aestivum*) pulps prior to hydrogen peroxide bleaching stage (P). The same TCF bleaching sequence was used for each pulp and the main objective of this work was to determine the appropriate chelating agent (EDTA, DTPA and DTMPA) for the Q stage of each pulp to achieve a satisfactory brightness level. Comparisons were made among the Fe, Cu and Mn metal ion concentrations in the wheat straw pulps to determine which metal ions had a predominant role on peroxide decomposition and on bleaching performance. Ash and silica contents of pulps were also determined.

EXPERIMENTAL

Material

Wheat (*Triticum aestivum L.*) straw, taken from the Kastamonu region in Turkey, was used for pulping. The raw material was cleaned and cut to approximately 3-5 cm in length, and oven dry measurement was performed before the pulping experiments. The chemical composition (76.0% holocellulose, 47.7% α -cellulose, 20.1% lignin, 6.3% ash and 4.4% silica) and solubility (7.8% alcohol-benzene, 44.4% NaOH (1%), 10.0% hot water and 8.6% cold water) of wheat straw samples were determined according to TAPPI Test Methods and reported in a previous study of Ersoy Kalyoncu *et al.*⁴⁰ Fiber dimensions were measured as morphological characteristics. The fiber length was found as 1.34 mm, fiber width – 16.6 μm and fiber lumen width – 3.98 μm .⁴⁰

Pulping

Unbleached pulps were prepared from wheat straw using four different alkaline pulping processes, namely, soda-oxygen (SO), soda (S), soda-AQ (S-AQ) and alkaline-sulfite (AS) pulping. The wheat straw stalk charge (on oven dry basis) was 500 g per batch. A 15 L electrically heated, stainless steel rotating batch type rotary laboratory digester, equipped with digital temperature controller and a pressure control instrument, was used for pulping. The pulping parameters were adjusted so that the four different types of produced pulp could have a similar kappa number.

Cooking time was selected as 60 min for SO and AS, 120 min for S and S-AQ pulps. The ratio of stalk fiber to cooking liquor was fixed at 1/5 (d.w.). The cooking temperature was selected as 120 °C for SO pulp, 140 °C for S and S-AQ pulps and 170 °C for AS pulp. Since delignification in SO pulping has a synergistic effect of alkali and oxygen, the cooking temperature was kept lower than in conventional chemical pulping to minimize the carbohydrate reaction caused by alkali and oxygen at high temperature.⁴¹⁻⁴³ Total active alkali (calculated as Na_2O , based on oven dry weight of wheat straw stalk) ratio was 15.50% for SO, S and S-AQ pulps and 13.56% for AS pulp. $\text{Na}_2\text{SO}_3/\text{NaOH}$ ratio (for AS pulp) and oxygen pressure (for SO pulp) were selected as 4/1 and 7 kg/cm^3 , respectively.

Pulp bleaching procedure

AOPaQP as a totally chlorine-free (TCF) bleaching sequence was applied to unbleached SO, S, S-AQ and AS pulps. Table 1 displays the constant and detailed variable parameters for each stage of the bleaching sequence (A: acid hydrolyze stage, O: oxygen delignification, Pa: peracetic acid bleaching stage, Q: chelating pretreatment, P: hydrogen peroxide bleaching stage). Oxygen delignification was performed in a 15 L

electrically heated, stainless steel rotating digester, and temperature control was maintained in the range of 100 ± 0.2 °C with a digital processor system, also equipped with an instrument for control of pressure.

The other stages, such as acid washing (A), peracetic acid (Pa), chelating (Q) and peroxide (P) treatments, were carried out in sealed plastic bags placed into a heat controlled thermostatic water bath. The pulp was mixed by manual kneading.

Three different chelating agents (EDTA, DTPA and DTMPA) were used for each kind of pulps, separately to prevent the decomposition of H_2O_2 during P stage, caused by transition metal ions. The ratio of chemicals to pulp was calculated in mmol/g . 1 N H_2SO_4 solutions were used for adjusting the pH level of pulp to 5-6 during chelating. After each bleaching stage, the pulp samples were washed with deionized water.

Kappa number, viscosity and hexenuronic acid content of bleached and unbleached pulp samples were determined according to TAPPI T236 om-13 (2013), SCAN-CM 15:88 standards (1988) and TAPPI T282 pm-07 (Using Shimadzu UV-1208 model UV-VIS spectrophotometer), respectively.

Preparation of handsheets for characterization

Paper sheets (approximately 60 g/m^2) of each pulp sample were prepared on a Rapid Köthen Sheet Making Machine according to TAPPI T205 sp-12. The handsheets were conditioned at $23 \text{ °C} \pm 1 \text{ °C}$ and kept in a $50\% \pm 2\%$ relative humidity conditioned room overnight before testing. The ISO brightness of the paper handsheets were determined according to ISO/DIS 2470 (2016) standard using a Konica-Minolta CM-2600d model UV-spectrophotometer and ten different test paper sheets were used for each measurement. Fe, Mn and Cu metal contents of the pulp were determined both before and after Q stages of each pulp, according to TAPPI T266 om-02, using an ATI UNICAM AA-929 model atomic absorption spectrometer. FTIR-ATR spectra (Fourier-Transform Infrared Spectroscopy-Attenuated Total Reflectance Shimadzu IR Prestige-21, with a Pike Miracle ATR attachment) of each of the test papers were recorded to obtain some qualitative information about the functional groups and chemical characteristics of the pulps. Each spectrum was obtained within the range of $600\text{-}4000 \text{ cm}^{-1}$ with 16 cm^{-1} resolutions and 16 repetitions. The content of hexenuronic acid (HexA) was determined using the spectrophotometric method reported by Chai *et al.*,⁴⁴ adopted as TAPPI T 282 pm-07 test method using a Shimadzu UV-1208 model UV-VIS spectrophotometer. The ash content (TAPPI T211 om-12) and silica content (TAPPI T 244 cm-99) of handsheet paper samples produced from unbleached pulps, before and after Q stages of each pulp, for each chelating agent, were determined.

Table 1
Bleaching parameters of SO, S, S-AQ and AS wheat straw pulps

Symbol	Parameter	Chemical charge and process conditions			
			Time (min)	Temp. (°C)	Conc. (%)
A	pH (adj. with 1N H ₂ SO ₄)	4	70	100	3
		3			
O	NaOH (%)	1	60	100	12
		1.5			
	MgSO ₄ (%)	0.5			
Pa	Oxy. press. (kg/cm ²)	7	60	80	10
	Pa (as act. oxy. %)	0.4			
	NaOH (%)	0.7			
	MgSO ₄ (%)	1.3			
	CaSO ₄ (%)	0.2			
Q	DTPA (%)	0.2	60	70	10
	DTPA (mMol)	0.76			
	EDTA (mMol)	0.76			
P	DTMPA (mMol)	0.76	120	80	12
	H ₂ O ₂ (as act. oxy., %)	0.94			
		1.41			
	NaOH (%)	1.4			
		2.1			
	MgSO ₄	0.2			
DTPA	0.2				
Na ₂ Si ₂ O ₇	1				

Notes: MgSO₄ was added in O, Pa and P stages to protect the carbohydrates; Na₂Si₂O₇ was added in P stages as hydrogen peroxide stabilizer; DTPA was added in P stages to control the peroxide decomposition and cellulose degradation

Table 2
Properties of unbleached pulps used in this study

Property	SO	S	S-AQ	AS
Total yield (%)	53.53	45.38	45.85	51.96
Screened yield (%)	49.19	42.63	45.24	50.19
Shives (%)	4.34	2.75	0.61	1.77
Kappa number	20.40	17.18	11.19	12.43
Viscosity (cm ³ /g)	761	969	1204	1143
ISO brightness (%)	44.13	41.41	36.45	51.57

RESULTS AND DISCUSSION

All resulting pulps after pulping were analyzed. In pulp characterization, it was aimed to keep a high delignification rate and high pulp quality with the applied bleaching process, as well as to reduce the bleaching costs by reducing the consumption of bleaching chemicals. The unbleached pulp properties are shown in Table 2.

In the classification made according to the kappa numbers, SO and S pulps and S-AQ and AS pulps showed similarity to each other. Since the relatively low selectivity of oxygen delignification leads to significant degradation of

carbohydrates during pulping,⁴³ the viscosity value of SO pulp was lower than that of other pulps. Compared to other pulp types, the lowest screened pulp yield (42.60) and the high kappa number (17.8) were due to the high alkaline solubility of S pulp, which indicates reducing the delignification selectivity and thus the total pulp yield. The reason why S-AQ pulp is better than S pulp in terms of viscosity and kappa number is that AQ stabilizes carbohydrates by oxidation of the reducing end group and accelerates the rate of delignification by reductive cleavage of alkyl-aryl ether bonds in lignin.^{45,46} Also, S-AQ pulping

protected the hemicelluloses from deterioration during cooking,⁴⁶ thus, S-AQ pulp had the highest value in terms of viscosity compared to other pulps. Despite the high pulp yield, alkali sulfite pulp had excellent properties, such as high brightness (51.57) and high viscosity (1143).⁴⁷⁻⁴⁹

In this study, the three most important transition metals, iron (Fe^{2+}), copper (Cu^{2+}) and manganese (Mn^{2+}), were focused on.⁹ Control of metal ion concentration is crucial for the effectiveness of peroxide (P) stage. Although there have been many studies on chelating, the aim of this study was to determine the effect of different chelating agents on different pulp types. Table 3 shows the changes in Fe, Cu and Mn metal ion concentrations, determined by atomic absorption of SO, S, S-AQ and AS wheat straw pulps, before and after chelating (Q) stages depending on the chelating agents used. It was seen that the highest concentration of Mn and Fe ions was determined in the S-AQ pulp, and the highest concentration of Cu ions was determined in the S pulp. On the other hand, the AS pulp had the lowest Mn, Fe and Cu contents.

The transition metal contents of each pulp type have been reduced after Pa, the third stage of the bleaching sequence. After the Pa stage, the easiest removal was detected in the AS pulp for Fe and

Cu ions, and in the S pulp – for Mn ion. Mn ion was readily removed from all the types of pulps. Despite the weak acidic conditions, such as in the peracetic acid stage, a considerable amount of Mn ion can be removed from pulp. It can reach 91-99% of Mn removal after the Q stage for all pulps and chelating agents. The three chelating agents did not show the same effect for each of these different types of pulps, the most appropriate chelating agents varied depending on the type of pulp.

The best chelation effect of SO pulp was achieved with DTMPA. However, for S pulp, an effective removal of Fe and Cu ions was achieved with EDTA, while DTPA was efficient in removing Mn ions. This situation completely differed from S-AQ pulps. Here, effective Mn and Fe removal was achieved with chelation with DTPA, while EDTA was most suitable for Cu ion removal. In this instance, chelating with DTPA was effective in removing Mn ions, while EDTA was effective in Cu ion removal for both S and S-AQ pulps. In terms of AS pulp, the most appropriate chelating agent was EDTA for removal of Mn and Fe ions, whereas DTPA was suitable for Cu ion. Metal ions are attached to functional groups, such as carboxylic and phenolic in the pulp.⁵⁰

Table 3
Results obtained in determining the most appropriate chelating agents

Pulp specimens	Mn (mg.kg^{-1})	Fe (mg.kg^{-1})	Cu (mg.kg^{-1})
Soda-oxygen (SO) pulp	10.66	10.50	5.10
(SO)-AOPa	2.30	10.20	4.64
(SO)-AOPaQ1	0.54	9.92	0.55
(SO)-AOPaQ2	0.15	10.14	0.58
(SO)-AOPaQ3	0.15	7.82	0.41
Soda (S) pulp	19.05	34.43	8.59
(S)-AOPa	0.50	31.13	3.37
(S)-AOPaQ1	0.15	29.38	0.93
(S)-AOPaQ2	0.20	29.35	0.76
(S)-AOPaQ3	0.45	30.55	2.88
Soda-AQ (S-AQ) pulp	21.26	46.72	6.86
(S-AQ)-AOPa	0.51	26.00	2.22
(S-AQ)-AOPaQ1	0.14	17.07	0.53
(S-AQ)-AOPaQ2	0.21	22.08	0.43
(S-AQ)-AOPaQ3	0.26	24.08	1.08
Alkali-sulfite (AS) pulp	6.99	7.50	2.79
(AS)-AOPa	0.73	6.68	1.01
(AS)-AOPaQ1	0.35	6.63	0.29
(AS)-AOPaQ2	0.27	5.32	0.43
(AS)-AOPaQ3	0.56	6.36	0.98

Notes: Q1: DTPA chelation, Q2: EDTA chelation, Q3: DTMPA chelation

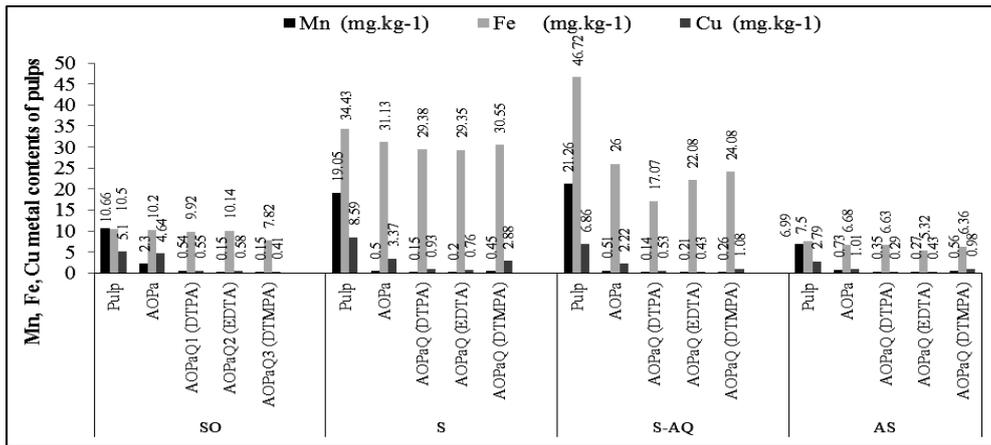


Figure 1: Varying Mn, Cu and Fe ion content of wheat straw SO, S, S-AQ, AS and AS-AQ pulps in different stages of the bleaching sequence

It has been stated in previous studies that the removability of different metal ions varies from one pulp to another.^{50,51} It has been found that iron is very difficult to remove from the pulp.⁵¹⁻⁵⁴ As seen in Figure 1, most of the Fe ions in all types of pulps were strongly fixed to the fiber. Chelation will not remove all transition metals that decompose hydrogen peroxide and, in particular, will not remove all iron.³⁶ One of the metal binder groups in pulps is phenolic groups in residual lignin.^{51,55} Iron ions can cause colorization of the pulp and the final paper product.^{51,56} This occurs as a result of the reaction of iron ions in the pulp with lignin and other components. Therefore, a chelating agent that can withdraw as much as possible Fe ion from the fibrous material is very important. In S, SO and AS pulps, Fe ions were highly resistant to chelating, compared to S-AQ pulp. In comparison with Fe ions, Mn and Cu ions reacted easily with all three chelating agents to create soluble complex structures that were easily moved away from the pulp. Norkus *et al.*⁵⁷ have shown that copper forms weak complexes with cellulose pulp. The most easily removable transition metal from all pulp types is Mn ion. Even weak acidic conditions, such as in the peracetic acid stage, allowed the removal of considerable amounts of Mn ion from the pulp. Thus, 91-99% of Mn removal can be reached after the Q stage for all the pulps and all the chelating agents.

As in previous studies, DTMPA is the compound of choice in bleaching bagasse and kenaf pulps (chemical pulp or mechanical pulp) successfully with peroxide.⁹ In this study, chelating with DTMPA was ineffective in

lowering the transition metal contents of all the kinds of pulps, except SO pulp. Thus, the most appropriate chelating agent for SO wheat straw pulp was determined as DTMPA.

Compared to wood, the ash and silica contents of wheat straw are very high. Ash contains metal ions, which can cause peroxide decomposition and increase the consumption of bleaching chemicals.⁵⁸ Annual plants have high silica content and strong alkaline cooking liquors dissolve them to a high extent.¹

The ash and silica contents of all unbleached and unchelated pulps were determined to observe whether or not they have any effect on chelating. Also, the changes in ash and silica contents of the chelated pulps, depending on the chelating agents used, are shown in Table 4.

Ash content is typically influenced by the presence of inorganic materials, including minerals and metals, which can include transition metal ions if they are present in the form of inorganic salts or compounds. As seen in Table 4, SO and AS clearly had higher ash contents, compared to S and S-AQ pulps, owing to alkaline pulping conditions. On the other hand, there were considerable decreases in silica content towards the last stages of the bleaching sequence for these pulps. However, the pulps produced under low alkaline conditions, such as SO and AS, had high silica content and showed resistance against its removal during the bleaching operation. When the metal, ash and silica content of unbleached, Pa bleached and chelated (Q) pulps were considered together, in terms of the best chelating effect of the three different chelating agents, EDTA was determined as the most suitable chelating agent

for S and AS pulps, whereas DTPA was the most suitable in the presence of AQ – in S-AQ pulp,

and DTMPA – for SO pulp.

Table 4
Ash and silica contents of SO, S, S-AQ and AS pulps before and after chelating

Pulp type	Sequences	Ash content (%)	Silica (x10 ³) (ppm)
SO	Unbleached	5.23	42.98
	AOPa	3.86	32.63
	AOPa-Q1	3.39	30.84
	AOPa-Q2	3.38	12.96
	AOPa-Q3	0.26	31.42
S	Unbleached	1.60	7.69
	AOPa	0.36	0.51
	AOPa-Q1	0.11	0.58
	AOPa-Q2	0.17	0.38
	AOPa-Q3	0.24	0.13
S-AQ	Unbleached	1.69	8.03
	AOPa	0.33	0.46
	AOPa-Q1	0.16	0.45
	AOPa-Q2	0.14	0.11
	AOPa-Q3	0.26	0.25
AS	Unbleached	6.41	54.97
	AOPa	4.50	41.20
	AOPa-Q1	4.22	39.99
	AOPa-Q2	4.20	40.55
	AOPa-Q3	4.28	40.58

Q1: DTPA Q2: EDTA Q3: DTMPA

Table 5
HexA content of unbleached and Pa bleached SO, S, S-AQ, AS and AS-AQ pulps

	Sample	Pulp type			
		SO	S	S-AQ	AS
HexA ($\mu\text{mol/g}$)	Unbleached pulp	3.61	8.97	12.41	2.74
	AOPa bleached pulp	0.53	3.14	1.73	2.20
	AOPaQP bleached pulp	2.31	2.24	2.84	2.60

Hexenuronic acid groups are formed from xylan-type hemicelluloses under alkaline conditions and consume permanganate in the pulp, causing the kappa number to increase.⁵⁹ In some studies, it was mentioned that transition metal ions bond very strongly with carboxyl groups. Most of the carboxyl groups are found in the hexenuronic acids formed during cooking.^{51,60-62}

As shown in Table 5, S and S-AQ pulps, produced under high alkaline conditions, had high hexenuronic acids (HexA) contents. Consequently, it was expected that unbleached S-AQ and S pulps could bound more metal ions. Figure 2a and 2b confirmed that S-AQ and S pulps have higher hexenuronic acids (HexA) content than the others. Also, the metal ion content of the pulps was lowered to a certain

extent by the Pa stage of the bleaching sequence. Compared with the S and S-AQ processes, SO and AS pulping give the highest retention of silica in the pulp.

Also, as noted in the FT-IR spectra, a prominent band with peaks between 3330 cm^{-1} and 3360 cm^{-1} for all pulps was attributed to the stretching vibrations of $-\text{OH}$ groups.⁶³ The peak height in this range for SO pulp increased after the QP stages. The peaks near 1734 cm^{-1} represent hemicelluloses⁶⁴ and the carbonyl band at 1735 cm^{-1} has been ascribed to hemicelluloses.⁶⁵ The 1740 cm^{-1} peak is assigned to the acetyl group in hemicelluloses or carbonyl in the carboxyl group.⁶⁶⁻⁶⁸

As can be seen from Figure 2a and 2b, the disappearance of the 1736 cm^{-1} peaks after the QP stages only for SO pulp, unlike other pulp types,

suggests a decrease in the hemicellulose content of SO pulp. Similarly, the disappearance of the 1229 cm⁻¹ peak is assigned to C-O-C stretching vibration in pyranose.⁶⁴ These changes show that the chemical bonds in the molecular structure of cellulose and hemicelluloses have changed. This is also evident from the viscosity value of the SO pulp after the QP stages (Table 6). Also, the 1734 cm⁻¹ peak is attributed to the p-coumeric acids of lignin and/or hemicelluloses.⁶⁹ The complete

disappearance of this peak from the spectra of the SO pulp after QP stages suggests that the removal of lignin was occurring, except in SO pulp.

The peaks in the ranges of 1635 cm⁻¹-1638 cm⁻¹ or 1641-1645 cm⁻¹ indicate the OH bending of adsorbed water or moisture.⁷⁰ The bands at 1372 cm⁻¹ and 1335 cm⁻¹ are typical of crystalline cellulose.⁷¹ A very weak peak formation at 1335 cm⁻¹ was observed in the S pulp after the Pa stage (Fig. 2a).

Table 6
Pulp properties after Pa and QP stages

Pulp type	Kappa number		Viscosity (cm ³ /g)		Delign. degree (%)		ISO Brightness (%)	
	Pa	QP	Pa	QP	Pa	QP	Pa	QP
SO	11.82	8.91	809	800	42.06	56.32	63.53	73.51
S	7.50	4.00	1123	1127	56.34	76.72	66.01	80.53
S-AQ	4.03	1.83	1168	1125	63.98	83.65	66.72	80.85
AS	5.08	4.35	1011	986	59.13	65.00	75.50	81.02

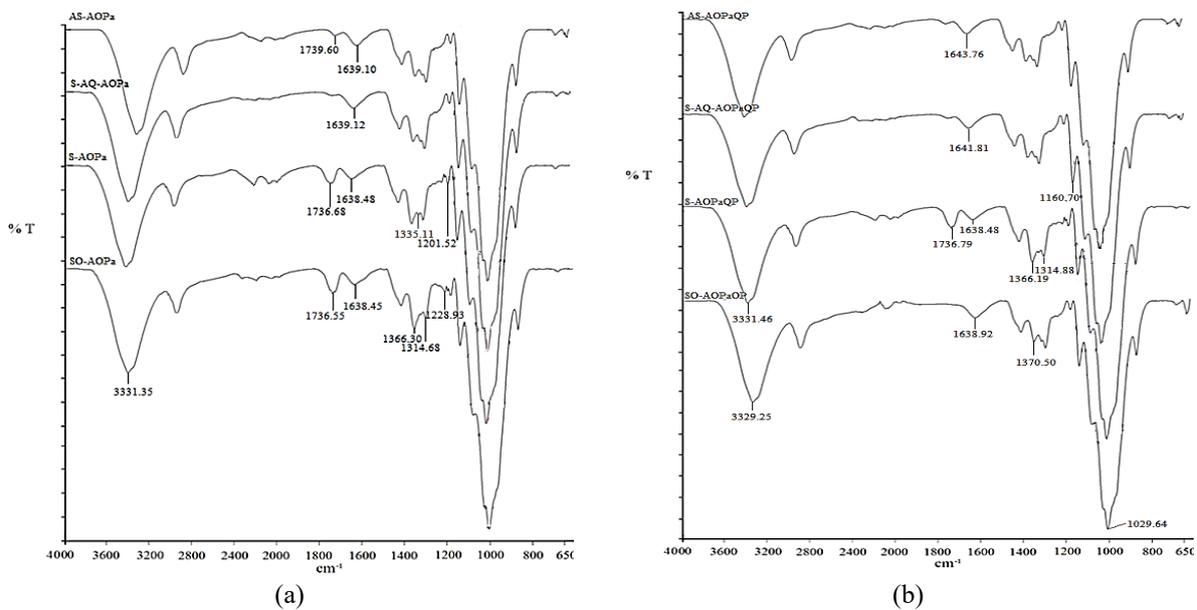


Figure 2: FTIR-ATR spectra of pulps (a) after Pa stage, and (b) after chelating with optimum Q and P stages

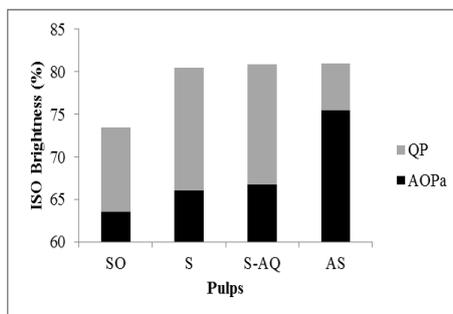


Figure 3: Brightness level of wheat straw alkaline pulps before and after QP stages

This weak peak formation was also observed in S and SO pulps after the QP stages (Fig. 2b). The band at 1372 cm⁻¹ lost its intensity and

became weaker due to a higher amount of amorphous cellulose.^{71,72} The intensity of the peak at 1365 cm⁻¹ decreased for AS pulp, after the QP

stages. The 1335-1316 cm^{-1} doublet is related to the contents of crystallized and amorphous cellulose,^{73,74} and can be used to monitor the degradation. In some cases, both bands occur during the degradation of the amorphous phases.⁷⁵ After the QP stages, a slight increase was observed in the height of the peaks at 1316 cm^{-1} for AS and S-AQ pulps, while a slight decrease was observed for the S pulp. The properties of each type of pulp are given in Table 6. Also, the brightness increase of the pulps after the QP stage is presented in Figure 3. As seen in Table 6, the kappa number of SO pulp is higher than those of other pulps. This situation points out that the lignin structure of SO pulp seems different from others. Also, the brightness and viscosity of SO pulp had the lowest values among all the pulps.

CONCLUSION

In this study, the transition metal ion concentrations of soda (S), soda-oxygen (SO), soda-AQ (S-AQ) and alkaline-sulfite (AS) pulps obtained under alkaline conditions were determined, with a focus on preventing the decomposition of TCF bleaching agents, especially peroxide decomposition. The performance of the chelating stage, applied before the peroxide stage, with different chelating agents, was determined by the removal of Mn, Cu and Fe metal ions.

The results of the study highlighted the following findings:

1. It was determined that Mn ion was the easiest to remove metal ion from the four different wheat straw pulps produced under alkaline conditions, with results varying between 98-99% for S and S-AQ, and 95-99% for SO pulp;
2. In terms of Mn ion removal, the best results were achieved with DTPA from S and S-AQ, whereas EDTA was more suitable for S and AS pulps;
3. The best performance in removal of Cu ions was achieved with EDTA for S and S-AQ pulps, with DTMPA for SO and DTPA for AS pulps;
4. It was determined that Fe is the hardest to remove metal ion from all the types of pulps; the success in Fe removal with the chelating stage (Q) was very limited;
5. Removal of Fe ions from AQ added pulp (S-AQ) with Q stage is higher than from other kinds of pulps and the best results were obtained by DTPA and EDTA. The

removal of Fe ions from S-AQ pulp with DTPA with EDTA reached 63%;

6. Even after Q stage, there is a significant amount of Fe ions in the composition of S and SO pulps. The most important reason of this may reside in the behavior of SO pulp towards bleaching reagents;
7. The high ash and silica contents of SO and AS pulps enabled the pulps to resist the delignification reactions during the TCF bleaching process;
8. The highest amount of HexA has been obtained in S and S-AQ pulps, produced in a high pH region. Although in S-AQ pulp, HexA can be removed with acidic bleaching stages and chelating, S pulp gave the highest amount of 3.14 $\mu\text{mol/g}$ even after the AOPa stages.

As a result, there were predominant effects of the pulp type and metal ion contents of the pulps on the TCF bleaching performance. Higher ash content of wheat straw alkaline pulps, availability of transition metal ions on the pulps, difficulty in the splitting off especially Fe ion from the pulp with acidic bleaching stages and chelating were the important handicaps of the study.

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