Reductive degradation of residual chromophores in kraft pulp with sodium dithionite

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ABSTRACT: The focus of this study is the chemistry of reductive bleaching of kraft pulps with sodium dithionite. A set of model compounds mimicking quinone structures, residual lignin structures with conjugated carbonyl/carboxyl groups and muconic acid, among others, was reduced with sodium dithionite and monitored by ultraviolet-visible (UV-vis) spectroscopy. Depending on the chromophore models, either reductive or sulfonation reactions are thought to be responsible for the degradation. No reductive degradation of hexeneuronic acid (HexA) residues was detected, but unsaturated structures of unknown origin were eliminated from the xylan. Additionally, the potential of the reductive stage with either sodium dithionite or sodium borohydride was tested using an industrial pine kraft pulp bleached by OOZEDD sequence. This pulp, with a 88.8% ISO brightness ceiling, exhibited a brightness increase to 90 ± 0.5% in the final reduction stage.

Application: From this study, mills might find reason to consider a dithionite stage in the bleaching of chemical pulps and will gain understanding about how it degrades kraft pulp chromophores.

Bleaching is one of the most expensive processes in pulp and paper production, mainly because of the difficulties in brightness development. In particular, a significant amount of bleaching chemicals is consumed in the final bleaching stages. Although the last stages are usually run under relatively harsh conditions to reach a target brightness, the amount of chromophores removed is minimal when compared with the initial bleaching stages [1,2]. On the other hand, brightness stability is a key property of high-grade bleached pulps. In the short-term, during final process/storage conditions, brightness can significantly decrease [3]. Accordingly, excessive brightness levels usually are reached at the pulp bleaching plant to overcome this short-term yellowing. Brightness reversion contributes to the bleaching costs; therefore, understanding and controlling it are of great importance in the production of bleached pulp.

The application of reducing agents in a final bleaching stage (Y) is an alternative to the excessive consumption of expensive bleaching reagents used to reach the targeted pulp brightness and brightness stability [4]. Although reductive bleaching using sodium dithionite ($Na_2S_2O_4$) is a well-established practice in the bleaching of mechanical pulp [5-9], its application to chemical pulps is modest and far less studied at the fundamental and technical levels. Previous studies on the brightening potential of sodium dithionite in chemical pulps bleaching focused on totally chlorine free (TCF) processes, either using kraft [9-13] or sulfite [9,14,15] pulps. The benefits of a final Y-stage include a boost in brightness gain [9-15] without negatively affecting pulp viscosity [12,14,15], hydrogen peroxide savings [13], and improved drying machine runnability [13], while preserving bleached pulp quality [10,12,13]. These studies included a dithionite final stage in OZPY, OZEPY, and ZO_{zw}PY bleaching of a black spruce kraft pulp [10], in OQ(PO)PY bleaching of eucalypt kraft pulp [13], and in (EPO)(EP)Y bleaching of a sulfite pulp [14,15], in addition to shorter sequences as OQY and OQPY and as intermediate stage in OYQP and OQYP bleaching of kraft pulp [12]. Nevertheless, sodium dithionite is seldom used in chemical pulp bleaching, which is reflected in a lack of basic knowledge on the reduction mechanisms implicated in kraft pulp chromophore reactions.

The main reducing specie responsible for dithionite bleaching is thought to be the sulfoxylate radical anion ($SO_2^{-\bullet}$), which is formed by homolytic splitting of the sulfur-sulfur bond of dithionite anion ($S_2O_4^{2-}$) (Eq. [1]). This anion radical reduces quinone chromophores to near colorless hydroquinone species [6,16]. It can further disproportionate to sulfur dioxide (SO_2) and the sulfoxylate anion (SO_2^{2-}) (Eq. [2]) [7]. Dithionite anion also can undergo hydrolysis to bisulfite anion (HSO_3^-) (Eq. [3]). Bisulfite anions are weak bleaching agents that can reduce some chromophore moieties by nucleophilic addition to unsaturated structures [6,7,17]. The formation of sulfur dioxide also generates bisulfite anions from SO_2 hydrolysis (Eq. [4]) [16].

$$S_2O_4^{2-} \leftrightarrow 2SO_2^{\bullet-} \quad (1)$$

$$2SO_2^{\bullet-} \rightarrow SO_2 + SO_2^{2-} \quad (2)$$

$$S_2O_4^{2-} + 2H_2O \rightarrow 2HSO_3^- + 2H^+ + 2e^- \quad (3)$$

$$SO_2 + H_2O \rightarrow HSO_3^- + H^+ \quad (4)$$

The side reactions in Eqs. (5-7) include dithionite decomposition induced by contaminants or in the presence of oxygen [5-7,17], including the anaerobic co-generation of thiosulfates ($S_2O_3^{2-}$), as in Eq. (7).

$$2S_2O_4^{2-} + O_2 \rightarrow 2S_2O_5^{2-} \quad (5)$$

$$S_2O_4^{2-} + H_2O + O_2 \rightarrow HSO_3^- + HSO_4^- \quad (6)$$

$$2S_2O_4^{2-} + H_2O \rightarrow S_2O_3^- + 2HSO_3^- \quad (7)$$

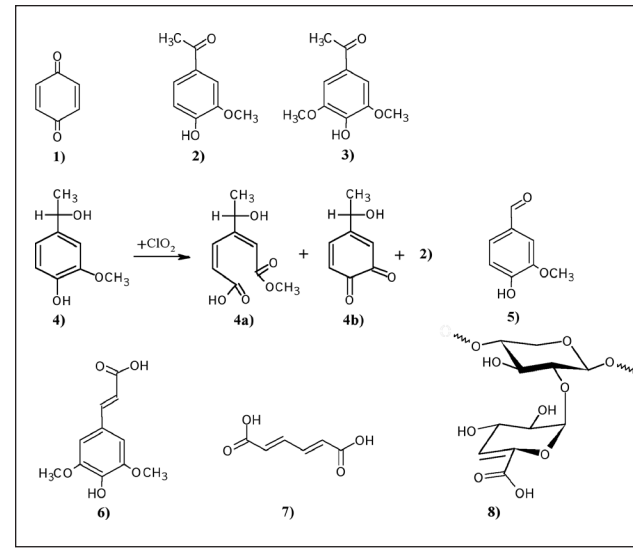
The degree of reductive bleaching is strictly dependent on the redox potential of the reducing agent [15,17]. In the context of mechanical pulp bleaching, dithionite is considered to react with conjugated carbonyl groups, including *o*- and *p*-quinone structures and coniferaldehyde side-chain units via reduction and sulfonation reactions [6,7,17,18].

One of the main objectives of this work was to study the reaction of particular chromophore groups found in kraft pulps partially bleached with sodium dithionite ($Na_2S_2O_4$). We used ultraviolet-visible (UV-vis) spectroscopy as a simple, informative, and convenient way to analyze the chemical modifications of a series of model compounds on treatment with dithionite. Therefore, instead of a lingering identification of all reaction products, the main purpose of this study was to determine whether dithionite can decrease the degree of conjugation of particular chromophore structures, either by reduction or sulfonation reactions, under typical bleaching conditions. In addition, the potential of sodium dithionite was evaluated as a final bleaching stage of OOZEDD bleached pine kraft pulps.

EXPERIMENTAL

Sodium dithionite reactions

The experiments conducted with sodium dithionite and the series of chromophore/chromogen model compounds (**Fig. 1**) were performed in closed Soverel screw-top tubes at pH 6.5 and 60ºC for 60 min, with the headspace previously purged with nitrogen. After the reaction, the tube content was analyzed qualitatively by UV-vis spectroscopy. The studied model compounds were high purity (pro analysis grade) reagents supplied by Sigma-Aldrich.



1. Model compounds mimicking the kraft pulp chromophores (models 1-7) and hexeneuronic acid (HexA) structure in xylan backbone (model 8).

The model compounds used included the following:

- Quinones – *p*-benzoquinone (model 1) and *o*-quinone derivative (model 4b)
- Aromatic compounds
  - with conjugated ketone group (acetovanillone [model 2] and acetosyringone [model 3])
  - aldehyde (vanillin [model 5])
  - ethylenic and carboxyl groups (sinapic acid [model 6])
- Muconic acid-type models – muconic acid derivative (model 4a) and *trans*, *trans*-muconic acid (model 7)

We also studied the reaction of dithionite with xylan enriched with hexeneuronic acid (HexA) structures (model 8). The HexA-enriched xylan was obtained by treating isolated birch xylan with 1 M NaOH solution at 150ºC for 30 min [19]. Compounds (model 4a) and (model 4b) were obtained from the reaction of 4-hydroxy-3-methoxy-α-methylbenzyl alcohol (apocynol, model 4) with chlorine dioxide [20].

Reductive final bleaching of pine kraft bleached pulp

Three industrial samples of OOZEDD bleached pine kraft pulp, with respective ISO brightness levels of 80.2%, 83.8%, and 88.8%, were washed in the laboratory with distilled water

Reagent	Charge (% o.d. pulp)	pH	Temperature (ºC)	Time (min)	Consistency (%)
$Na_2S_2O_4$	1.0-1.5	6.5-7.0	60 – 65	60-90	5 - 10
$NaBH_4$	1.5	9.5	65	60	5

I. Reaction conditions for the final Y ($Na_2S_2O_4$) and B ($NaBH_4$) stages applied to the OOZEDD bleached pine kraft pulp.

and then bleached with sodium dithionite (Y-stage). Sodium borohydride ($NaBH_4$) also was tested as a reducing bleaching agent (denoted as B-stage). **Table I** shows the operating conditions of the Y-stage for each reducing agent.

The pulp bleaching trials at 10% consistency were run in sealed polyethylene bags immersed in a thermostatic water bath. Trials at 5% consistency at atmospheric pressure were carried out in a reactor equipped with temperature and stirring controllers, and purged with nitrogen. After bleaching, the pulp samples were washed with distilled water and airdried in darkness.

Spectroscopic analysis

Brightness and brightness reversion

Handsheets for optical properties determination were prepared using the ISO 3688:1999 "Pulps – Preparation of laboratory sheets for the measurement of diffuse blue reflectance factor (ISO brightness)" procedure. ISO brightness and brightness reversion were measured in accordance with ISO 2470:1999 "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," respectively. Brightness measurements were conducted with an L&W Elrephro SE 070 spectrophotometer (Lorentzen & Wettre; Kista, Sweden). Brightness reversion was expressed in terms of percent units (absolute ISO brightness difference between initial and post-aging values) and of post color (PC) number.

UV-vis spectroscopy

Five mg of each chromophore model compound was dissolved in 1 mL of 2-methoxyethanol (except for model 7, which was dissolved in water) and then completed to 100 mL of aqueous solution. The spectrum of each chromophore solution was recorded on a JASCO V-560 spectrophotometer (JASCO; Tokyo, Japan) before and after reaction with 0.50 g/L sodium dithionite. The scanning speed was 200 nm/min and the bandwidth was 2 nm, and using the corresponding solutions without chromophores as blank references.

Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy

Xylans were dissolved in deuterium oxide (D_2O) and using sodium 3-(trimethylsilyl)-propionate-d_4 as the internal standard. The ^{1}H-NMR spectra were recorded at ambient temperature (about 25°C) on a Bruker AMX 300 spectrometer (Bruker; Wissemburg, France) operating at 300.13 MHz. A relaxation delay of 12 s and radio frequency (RF) angle of 90° were used, and 1000 scans were collected.

Attenuated total reflectance–Fourier transform infrared (ATR-FTIR) spectroscopy

The ATR-FTIR spectra of xylans at 4 cm^{-1} spectral resolution with 256 scans were recorded on a MATTSON 7300 Series FTIR spectrometer (Analytical Technology; Madison, WI, USA) equipped with an ATR-cell.

UV resonance Raman spectroscopy (UVRR)

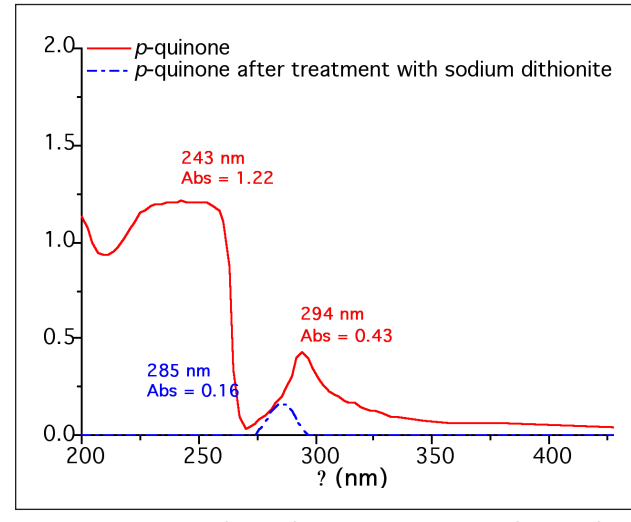
Xylan samples were pressed into 3 mm diameter pellets before spectral acquisition on a micro-Raman spectrometer at 325 nm (He–Cd UV laser, Kimmon IK series from Kimmon Koha; Tokyo, Japan) under backscattering configuration and using a 40 × near ultraviolet (NUV) objective and a neutral density filter (ND 0.6).

RESULTS AND DISCUSSION

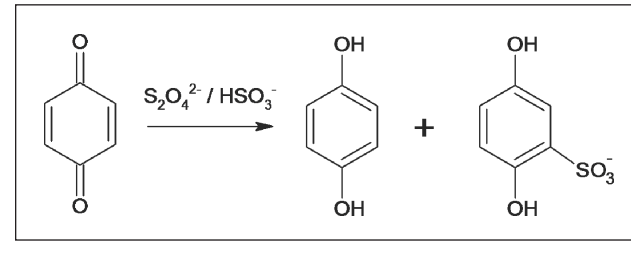
Sodium dithionite reaction with chromophore structures

Reaction with model of *p*-quinone type

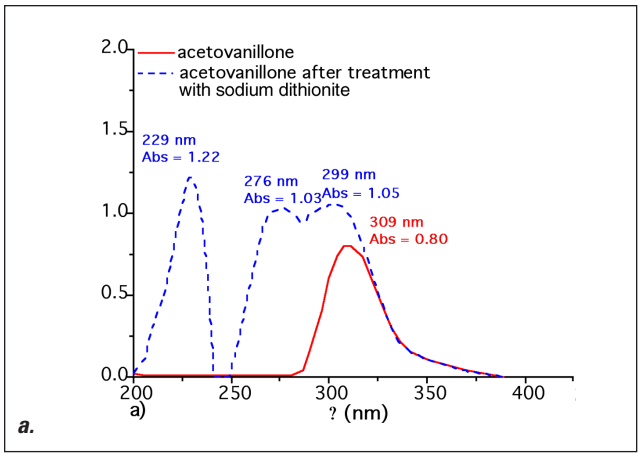
Qualitative monitoring of the reduction of model compound 1 by UV-vis spectroscopy revealed that quinones were readily reduced with dithionite, producing the corresponding hydroquinones leuco forms (**Figs. 2** and **3**). According to the data obtained by UV spectroscopy, the characteristic absorbance at about 240-250 nm of the initial model 1 is greatly reduced and a relatively small peak appeared at 285 nm being assigned to hydroquinone (Fig. 2) [21]. In previous studies, the formation of sulfonated hydroquinones was suggested in the reaction of *p*-quinone with sulfites [18, 22]. In the reduction with dithionite, co-generated sulfite/bisulfite anions also can affect the UV spectra of quinones [16]; therefore, the absorption of corresponding sulfonated hydroquinones could be expected

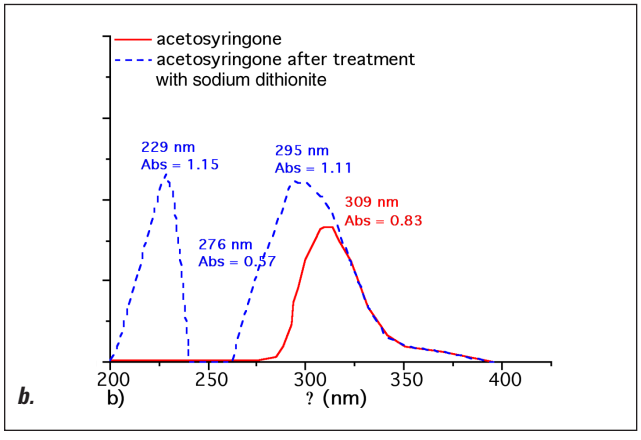


2. Ultraviolet-visible (UV-vis) spectra of p-quinone (model 1), before and after treatment with sodium dithionite.

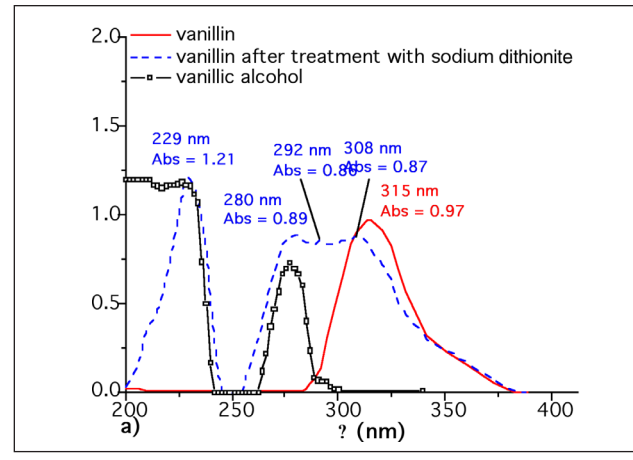


3. Reaction of dithionite/isulfite anion with p-quinone structure (reduction + sulfonation).

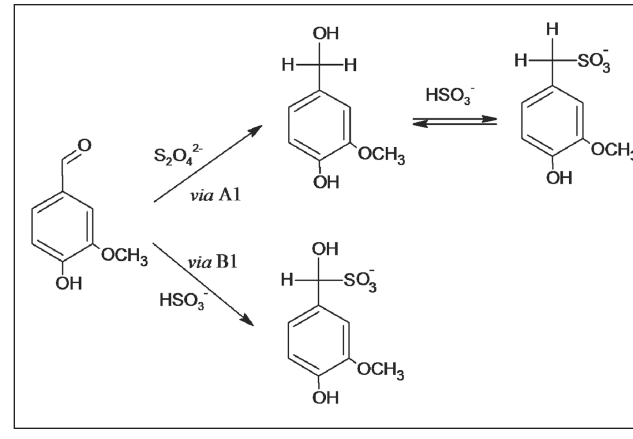




4. Ultraviolet-visible (UV-vis) spectra of a) acetovanillone (model 2) and b) acetosyringone (model 3), before and after treatment with sodium dithionite.



5. UV-vis spectra of vanillin (model 5), before and after treatment with sodium dithionite, and of vanillic alcohol.



6. Reaction pathways of dithionite (A1 pathway) or bisulfite (B1 pathway) anions with vanillin (model 5).

at about 300-305 nm [22]. However, the UV spectrum of reaction products did not reveal clearly the presence of sulfonation products on reduction of *p*-quinones with dithionite (Fig. 2).

The importance of the reduction of quinone structures by dithionite and sulfite species for the brightness development of pulps is well recognized [23]. Residual quinone structures are difficult to eliminate during ECF bleaching and contribute significantly to the pulp color and brightness reversion of chemical pulps [1,24]. In addition, past laboratory studies with model quinones have demonstrated that these compounds are notoriously difficult to study and characterize because of the ease with which they can be oxidized and self-condensation in aqueous media (acid, neutral, or alkaline) [25,26].

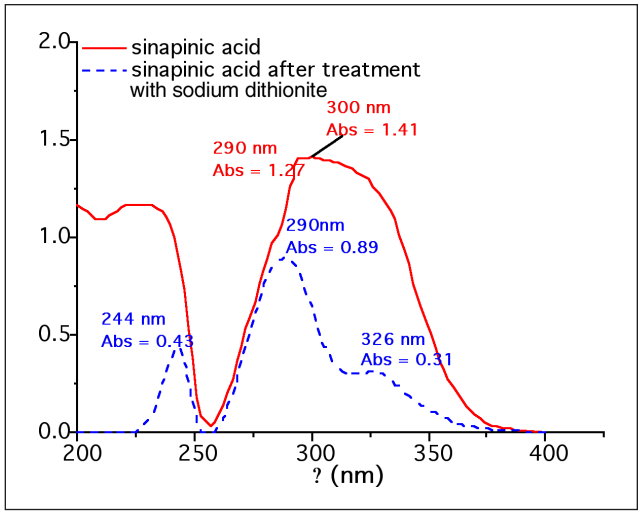
Reaction with aromatic models containing ketone and aldehyde groups

The reaction of dithionite with aromatic compounds containing conjugated ketone and aldehyde groups (models 2, 3, and 5) revealed a hypsochromic shift and new formed peaks in the deeper UV range (**Figs. 4** and **5**). The formation of the corresponding alcohol derivatives on reduction can be anticipated and agree with the UV spectra of analogous products. In fact, the spectra of vanillyl alcohol and reduced vanillin were comparable (Fig. 5), as were the spectra of reduced model 2 and model 4. Therefore, the new peak at about 280 nm was assigned to the benzyl alcohol derivatives. According to results of previous studies, the removal of the α-ketone, either by reduction or sulfonation, produces the same peak at about 275 nm [27].

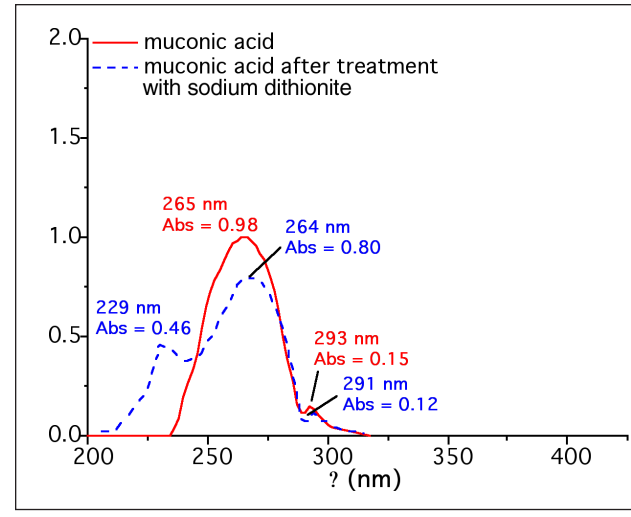
On the other hand, the new absorbance range at 290-300 nm, detected after treatment of models 2, 3, and 5 with dithionite, suggests the presence of sulfonated derivatives. **Figure 6** shows the eventual reaction pathways, which include the reduction of vanillin into vanillyl alcohol by dithionite (A1 route) followed by its possible sulfonation or the direct reaction of vanillin with bisulfite anion, thus producing a corresponding α-hydroxysulfonate derivative (B1 route).

Reaction with aromatic models containing conjugated carboxyl groups

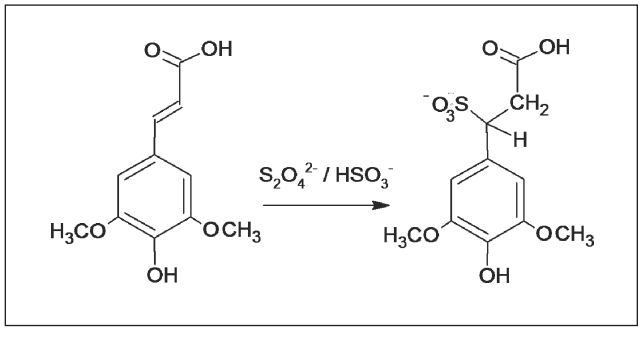
Above 290 nm, the aromatic model possessing a conjugated carboxyl group (sinapic acid, model 6) exhibited a great decrease in absorbance after dithionite treatment (**Fig. 7**). This



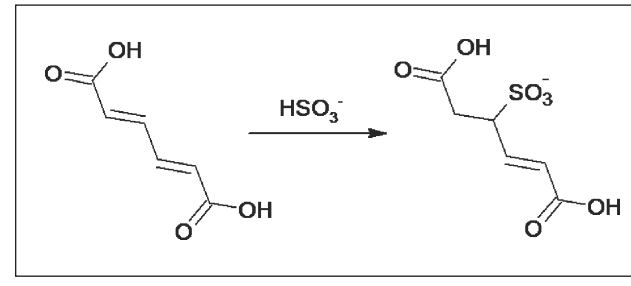
7. UV-vis spectra of sinapic acid (model 6), before and after treatment with sodium dithionite.



9. UV-vis spectra of trans, trans-muconic acid (model 7), before and after treatment with sodium dithionite.



8. Reaction of dithionite/bisulfite anions with sinapic acid (model 6).



10. Reaction of dithionite/bisulfite anions with trans, trans-muconic acid (model 7).

was caused by the ensuing sulfonation of the double bond, yielding a stable terminal CH_2COOH group (nonconjugated carboxyl group) absorbing at 244 nm without further degradation (**Fig. 8**). Although decreased, the absorbance above 300 nm indicates that the reaction with sinapic acid was incomplete. Similar sulfonation patterns by addition of bisulfite ions to double bond were reported for the reactions with coniferaldehyde/cinnamaldehyde-type models [18]. Sulfonation of chromophore structures represented by compound 6 (Fig. 1) will diminish the color of pulp by breaking down the π-π conjugation systems. Sulfonation of stilbene-like structures under conditions of the reductive treatment is highly likely, taking into consideration the reaction of bisulfite anions with the respective model compounds [18].

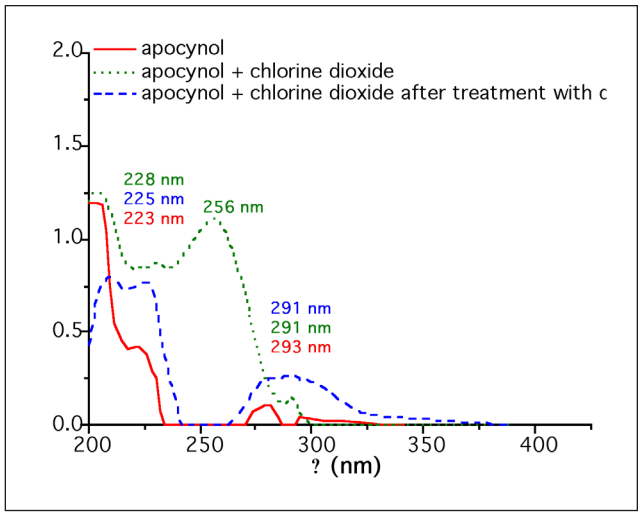
Reaction with muconic acid type structures

Muconic acid–type structures are extensively formed in pulp residual lignin during bleaching with different oxidizing reagents [20]. These chromophore/chromogen structures may eventually affect the pulp brightness and brightness reversion [2]. The reaction of model 7 (Fig. 1) with dithionite revealed a notable reduction in absorbance at 265 nm (n→π* transition in dienic structures) and at 293 nm (π →π∗ transition in polyconjugated carboxyls) (**Fig. 9**). Simultaneously, a new absorption peak at 229 nm is tentatively assigned to the nondienic α, β-unsaturated carboxylic structure (-CH=CH-COOH) [21]. These features allow us to propose at least a partial sulfonation of muconic acid type structure, as depicted in **Fig. 10**. The addition reaction of sulfites to 2,4-dienoic acids under conditions similar to those used in this study is well recognized [28]. Usually the molar ratio of added sulfite to dienoic acid is 1:1 and the reaction occurs rather slowly at moderate temperatures (<80°C). Hence, the addition of two sulfonic groups is less probable, if possible.

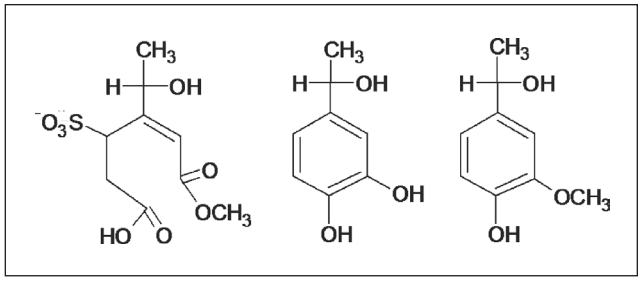
Overall, muconic acid–type structures may be partially sulfonated through reductive treatment with sodium dithionite. This fact will decrease the degree of conjugation in chromophore structures when muconic acid–type structures are part of them.

Reaction with apocynol oxidation products

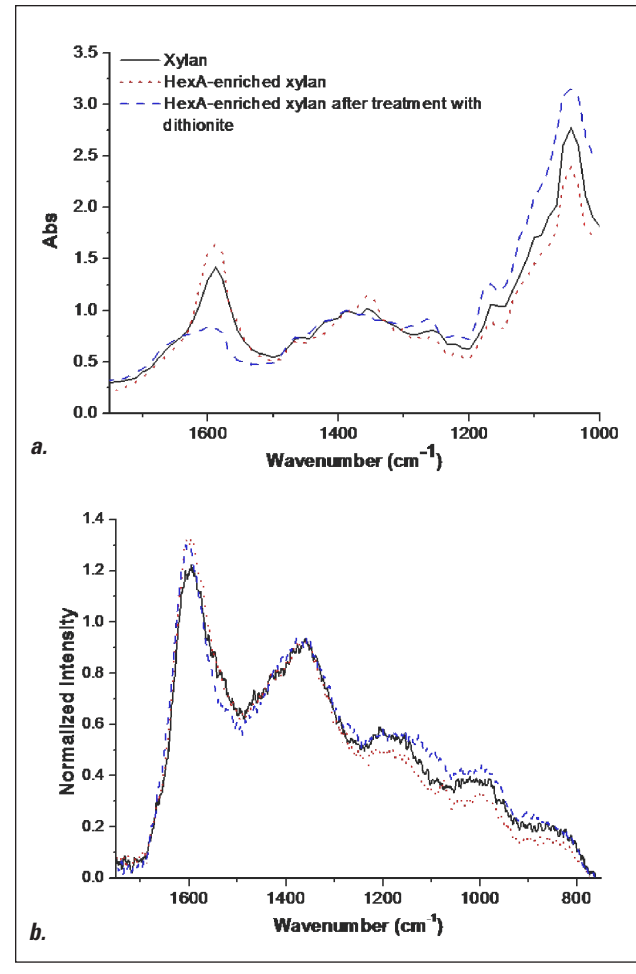
Oxidation of the phenolic model apocynol with equimolar amounts of chlorine dioxide under predetermined conditions (0°C) gives rise to quinones by demethylation, muconic acid derivatives by rupture of the aromatic ring (main product) or to acetovanillone by benzyl carbon oxidation [20,29]. Thus, the conversion of about 90% of starting apocynol (model 4) was reported to yield about 70% of muconic acid and less than 20% of *o*-quinone derivatives and trace amounts of acetovanil-



11. UV-vis spectra of apocynol (model 4) oxidation products with chlorine dioxide, before and after treatment with sodium dithionite.



12. Reaction products arisen after the reduction of apocynol (model 4) oxidation products with chlorine dioxide.



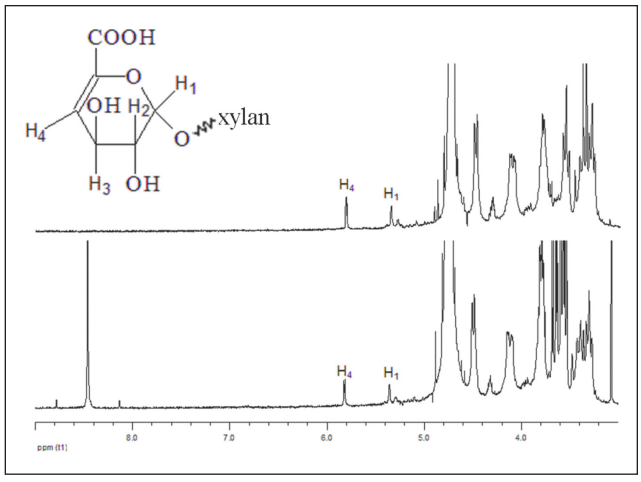
13. a) Attenuated total reflectance–Fourier transform infrared (ATR-FTIR) and b) ultraviolet resonance Raman spectroscopy (UVRR) (at 325 nm) of birch xylan and HexA-enriched birch xylan, before and after treatment with sodium dithionite.

lone [20]. Consequently, a rather complex reaction mixture can be expected, and an exact structural assignment is difficult based on UV-vis spectroscopy only. Nonetheless, based on the previous results of reaction products, the new absorbance detected at about 260-280 nm can be assigned to the presence of muconic acids, which possess very high molar absorbtivity in the range of 240-280 nm [30]; to acetovanillone at about 280-310 nm; and to *o*-quinone structures above 300 nm [31] (Fig. 1).

The treatment with dithionite helps to reduce the chromophores that arise in this apocynol-ClO_2 system. During the reaction with sodium dithionite, partially sulfonated muconic acid–type structures (increased absorption at 225-230 nm and decreased at 240-260 nm) and hydroquinones (absorption at 275-290 nm) can be anticipated (**Figs. 11** and **12**). This observation confirms the previous conclusions about the behavior of quinones and muconic acid in the reaction with sodium dithionite.

Reaction with HexA residues

The possibility of the reaction between HexA residues in xylan and sodium dithionite under the conditions of reductive bleaching has been examined. Birch xylan was alkali-treated to convert terminal 4-*O*-methyl glucuronic (MeGlcA) units to HexA residues [19]. The ATR-FTIR and UVRR at 325 nm spectra of xylans presented in **Fig. 13** did not clearly reveal the presence of HexA at about 1650 cm^{-1} because of the known limitations of the infrared and Raman techniques [2,32-34]. The lack of resonance of HexA structure in the UVRR at 325 nm spectra takes place because of the nonspecific excitation at 325 nm (a more suitable laser excitation would be at 244 nm [34]). In the ATR-FTIR, the intensity of the broad band at approximately 1500-1700 cm^{-1} hindered a selective assessment. The signal at 1600 cm^{-1} in Raman and ATR-FTIR spectra indicates the presence of aromatic units and structures with conjugated carbonyl groups, which are increased by the harsh alkaline treatment because of structural changes in the associated polysaccharide-aromatic substructures (xylan-lignin complex) [2]. This peak at 1600 cm^{-1} diminished in the UVRR at 325 nm spectra (approximately 1425-1600 cm^{-1}) after the xylan reduction with sodium dithionite (Fig. 13), which was assigned to the diminishing of chromophore/chromogen moieties in the sample [2]. However, such spectral features have nothing to do with HexA reactions, as confirmed by ^1H NMR



14. Proton nuclear magnetic resonance (^{1}H-NMR) spectra of the HexA-enriched birch xylan, before (lower spectrum) and after (upper spectrum) dithionite treatment.

spectra of xylan before and after the reductive treatment with sodium dithionite (**Fig. 14**). The characteristic proton resonances at 5.36 ppm and 5.82 ppm assigned to H_1 and H_4 in HexA, respectively, maintained intact after the reduction with dithionite. At the same time, some unknown, unsaturated structures arisen during xylan alkaline treatment to convert MeGlcA into HexA (high intensity signal at 8.43 ppm) were reduced and eliminated from xylan upon the reductive treatment (Fig. 14). Apparently, these unknown unsaturated structures were also partially responsible for the decrease in signal intensity at about 1600 cm^{-1} in UVRR at 325 nm and ATR-FTIR spectra during the reductive treatment (Fig. 13). Hence, although HexA maintains intact during reduction with dithionite, other unsaturated structures present in xylan may be effectively removed by the same reductive treatment.

Application of the final reductive stage

The potential of reductive bleaching with sodium dithionite was additionally assessed by applying a final reduction stage to the industrial OOZEDD bleached pine kraft pulps possessing different ISO brightness levels of 80.2%, 83.8%, and 88.8%. The last pulp had the highest brightness achievable under industrial conditions.

Table II shows the preliminary results on the performance of a reductive stage applied to each pulp with regard to the brightness gain and the brightness stability of the OOZEDDY bleached pulps. The Y-stage conditions were those previously optimized for the final reductive stage of hardwood sulfite/kraft pulps and proven under industrial trials [13-15]. Although improved brightness and brightness stability of the bleached pine kraft pulps was attained, those gains were still far from the required final ISO brightness of 90 ± 0.5% (Table II). However, some changes introduced in the conditions of the reductive treatment, especially dealing with a small increase of temperature and of the duration of treatment, allowed satisfactory results (**Table III**). Apparently, chromophores in softwood bleached kraft pulps are more difficult to reduce with dithionite than those in hardwood bleached pulps.

For comparative reasons, the OOZEDD bleached pine

Initial ISO Brightness (%)	Brightness Reversion		Final ISO Brightness (%)	Brightness Reversion	
	Δ (%)	Post Color Number		Δ (%)	Post Color Number
88.8	1.2	0.17	89.0 (0.2)	1.1	0.15
83.8	1.8	0.41	84.4 (0.6)	1.5	0.32
80.2	1.8	0.53	81.9 (1.7)	1.5	0.39
* - brightness gain in brackets.					

II. ISO brightness and brightness stability of the OOZEDD and OOZEDDY bleached pine kraft pulps. Y-stage conditions: 1.5% o.d. pulp $Na_2S_2O_4$; 60°C; 60 min; pH 6.5-7.0; 5% consistency.

$Na_2S_2O_4$ Charge (% odp)	Temperature (°C)	Time (min)	Consistency (%)	Final ISO Brightness* (%)	Brightness Reversion	
					Δ (%)	Post Color Number
1.5	60	60	5	89.0 (0.2)	1.1	0.15
1.0	65	60	5	89.0 (0.2)	1.0	0.14
1.0	65	90	5	89.6 (0.8)	1.6	0.21
1.5	65	60	10	89.2 (0.4)	1.3	0.18
*- brightness gain in brackets.						

III. ISO brightness and brightness stability of the OOZEDDY bleached pine kraft pulps using $Na_2S_2O_4$ in the final Y-stage. Initial ISO brightness of the OOZEDD pulp was 88.8%.

Initial ISO Brightness (%)	Final ISO Brightness*	Brightness Reversion	
		Δ (%)	Post Color Number
88.8	90.2 (1.4)	0.5	0.06
83.8	86.8 (3.0)	1.4	0.24
* - brightness gain in brackets.			

IV. ISO brightness and brightness stability of the OOZEDDB bleached pine kraft pulps. B-stage conditions: 1.5% o.d. pulp $NaBH_4$; 65°C; 60 min; pH 9.5; 5% consistency.

kraft pulp (ISO brightness of 88.8%) was treated in a final B-stage with sodium borohydride ($NaBH_4$) under the same conditions and the same reagent load as in the Y-stage with sodium dithionite (**Table IV**). Sodium borohydride possesses higher reduction potential (-1.9 V) than sodium dithionite (-0.53 V) and is less susceptible to disproportionation reactions and decomposition in the presence of oxygen [15]. This was apparently the main reason for the better brightening effect and brightness stability obtained for OOZEDDB bleached pine kraft pulp when using sodium borohydride instead of OOZEDDY sequence with a final dithionite stage (Tables III and IV). It is also unclear, however, if sulfonated chromophore structures could contribute to a higher brightness reversion of pulp treated in final Y-stage with dithionite. Nevertheless, both reducing reagents made it possible to reach a final ISO brightness of 90 ± 0.5% for the pine kraft pulp, which is difficult (if possible) to achieve under OOZEDD bleaching.

CONCLUSIONS

This study on the reductive degradation of model compounds in reaction with sodium dithionite led to several conclusions about the type of chromophore/chromogen structures that may be affected during a reductive bleaching stage. The structures of *p*- and *o*-quinone types are readily reduced under reductive treatment conditions. Residual lignin structures containing conjugated carbonyl groups also are reduced by sodium dithionite, though at a slower rate than the quinone structures. The structures possessing polyconjugated carboxyl groups (such as sinapic or muconic acid–type structures) suffer partial sulfonation in reaction with bisulfite anions resulting from disproportionation of sodium dithionite. This leads to relatively stable sulfonation products. Conversely, the carboxylic structures with one conjugated double bond did not react with sodium dithionite via the sulfonation pathway. No reactions of HexA residues derived from the 4-*O*-methylglucuronic acid in xylan were detected under conditions of the reductive bleaching stage, although some unknown, unsaturated structures in xylan were removed.

The use of a final reductive stage (1.0% o.d. pulp $Na_2S_2O_4$, 65ºC for 90 min) after OOZEDD bleaching of a pine kraft pulp made it possible to boost the ISO brightness level beyond the industrial maximum of 88.8% toward the targeted 90 ± 0.5% ISO brightness. However, the results obtained with sodium dithionite were inferior to those obtained with sodium borohydride under the same treatment conditions with respect to the brightness gain and the brightness stability. **TJ**

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The main motivation to conduct this research was to examine the potential of reductive bleaching of chemical pulps with sodium dithionite as an alternative to the prevailing oxidative bleaching chemicals that often exhibit low efficiency in the last stages of the bleaching process.

The majority of studies on reductive pulp bleaching with sodium dithionite have been carried out in the context of the bleaching process of mechanical pulps. Therefore, a basic understanding of the reductive degradation of residual chromophores in chemical kraft and sulfite pulps is still lacking.

The approach we used mainly relied on the use of UV-vis spectroscopy to cover several types of model compounds. Consequently, instead of a more time-consuming separation and identification of the reaction products, which would be restricted to few model compounds, our analysis was based on known reactions of similar model compounds with dithionite and bisulfite/sulfite ions, along with the proposition of reaction pathways linked to the degradation of the studied chromophores.

Although the reaction rates of dithionite with some model compounds probably are much faster than the reaction rates of bisulfite or sulfite, the role of bisulfite ions (from dithionite decomposition) cannot be ruled out in pulp bleaching. Therefore, the presence of sulfonation reactions with bisulfite anions can decrease the degree of conjugation of chromophore moieties, as was highlighted in the case of polyconjugated carboxyl groups (sinapic or muconic acid type structures).

From this study, mills might find reason to consider a dithionite stage in the bleaching of chemical pulps and will gain understanding about how it degrades kraft pulp chromophores.

The next step is to examine the synergistic use of dithionite bleaching with other bleaching alternatives applied to chemical pulps, along with a process-optimization study.

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