

ON THE IMPORTANCE OF HYDROQUINONE/*p*-QUINONE REDOX SYSTEM IN THE PHOTOYELLOWING OF MECHANICAL PULPS

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ABSTRACT

In the area of photoyellowing of mechanical pulps, recently obtained experimental evidence has shown that hydroquinone/*p*-quinone redox couple is present in lignin-rich mechanical pulps. It was also noted that compared to a control pulp the concentration of *p*-quinones was significantly higher in a photoyellowed pulp. Under ambient conditions, upon exposure to light, the existent pulp hydroquinones were converted to *p*-quinones. To further investigate the importance of hydroquinone/*p*-quinone redox couple in photoyellowing, studies of methylhydroquinone and methyl-*p*-quinone were carried out. Based on presently reported as well as previously published research, it is shown that the hydroquinone/*p*-quinone redox system can successfully explain most of the observations related to photoyellowing. Consequently, the hydroquinone/*p*-quinone redox couple plays a highly significant role in pulp photoyellowing.

INTRODUCTION

Recent FT-Raman studies of untreated, bleached (single and multiple stages), and photoyellowed thermomechanical pulps (TMPs) provided information that unequivocally established that *p*-quinones structures were present in photoyellowed¹ and untreated² samples. In the case of bleached TMPs, *p*-quinone concentration depended upon the extent of bleaching (higher brightness pulps showed lower amounts²). Moreover, when the pulp-handsheet brightness data were plotted against the decline of the *p*-quinone Raman band intensity a good linear correlation was obtained². Another method, ¹³C NMR spectroscopy, has recently provided further evidence in support of *p*-quinones. It was reported that such structures were present in softwood MWLs³. Therefore, detection of *p*-quinones by two independent non-destructive techniques proves beyond any doubt that these structures are integral part of native lignin's molecular structure.

In other investigations¹, oxygen quenching of laser-induced fluorescence (LIF) was used to show that

hydroquinone structural were present in significant concentration in woods, mechanical pulps, and MWLs.

Based, in part, on these findings a photoyellowing mechanism was proposed¹. This mechanism in conjunction with the studies of the methylhydroquinone/methyl-*p*-quinone (MHQ/M-*p*-Q) redox couple successfully accounted for several aspects of the photoyellowing behavior of mechanical pulps¹.

In this report, results of further experiments that were performed using the model system and mechanical pulps are described. These as well as previously reported results are used to evaluate the importance of the role of hydroquinone/*p*-quinone redox system in photoyellowing.

EXPERIMENTAL

Experimental aspects of the work described in this abstract are provided in reference 1 and in references cited therein.

RESULTS AND DISCUSSION

UV-vis. reflectance spectra

UV-Vis. has been extensively used in the study of the photoyellowing phenomenon. However, because of the presence of many chromophores in pulps and their overlapping spectral profiles, obtaining reliable information has not been easy.

To determine if such spectra could be better interpreted using MHQ/M-*p*-Q lignin redox model system, diffuse reflectance difference (ΔR) spectra of bleached-kraft-pulp-adsorbed MHQ and M-*p*-Q (at several concentrations) were obtained (Fig. 1 and 2).

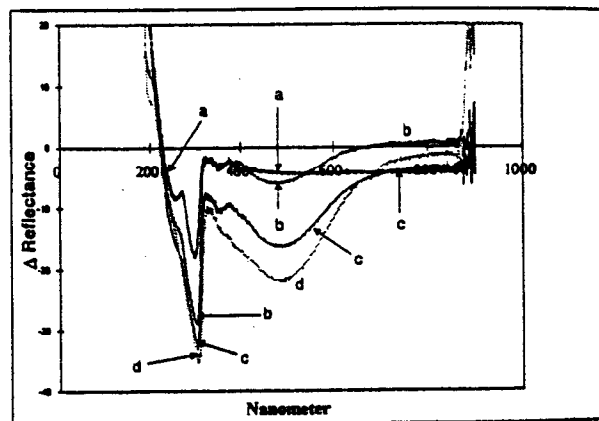


Fig. 1: Reflectance difference spectra (AR) of methylhydroquinone (MHQ) on bleached kraft pulp; (a) 0.60 %, (b) 0.69 %, (c) 1.10 %, and (d) 1.88 %

For MHQ, absorption bands were detected at 254, 295, 352 (very weak), and 485 nm. On the other hand, M-*p*-Q spectra showed band maxima at 254, 346, 443,

and 500 nm. The various sample concentrations for which spectra were obtained are given in Fig. 1 and 2. As can be noted from the spectra, there are spectral regions where the contributions of these models overlap.

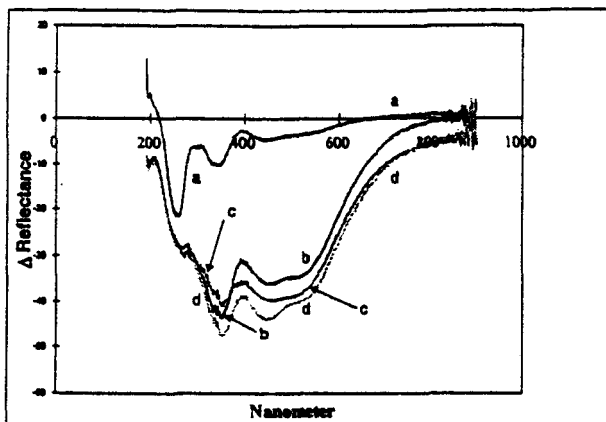


Fig. 2: AR of methyl-*p*-quinone (M-*p*-Q) on bleached kraft pulp; (a) 0.50 %, (b) 0.68 %, (c) 0.80 %, and (d) 1.04 %

In the case of MHQ, the longer wavelength absorption at 485 nm could be due to the interactions between MHQ and metal ions (present in kraft pulp) because UV-Vis. spectrum of 1 % MHQ solution (in methanol) did not absorb significantly beyond 360 nm⁴. However, the solution had a band at about 295 nm. On the contrary, the spectrum of 1 % M-*p*-Q solution (in methanol) showed absorption well in to the red.

If both the hydroquinone and *p*-quinone units are present in mechanical pulps, as suggested by our findings, their contributions are expected to resemble AR spectral curves shown in Fig.3. These curves were generated mathematically by combining ΔR spectra for MHQ and M-*p*-Q.

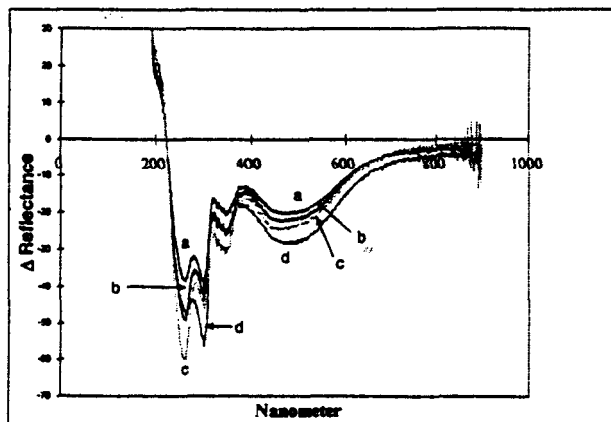


Fig. 3: Combinations of ΔR Spectra of MHQ and M-*p*-Q; (a) $\Delta R_{MHQ} + \Delta R_{M-p-Q}$, (b) $\Delta R_{MHQ} + 1.5 * \Delta R_{M-p-Q}$, (c) $\Delta R_{MHQ} + 2 * \Delta R_{M-p-Q}$, and (d) $1.5 * \Delta R_{MHQ} - \Delta R_{M-p-Q}$

ΔR spectra of untreated, bleached, and hydrogenated TMPs are shown in Fig. 4. Reflectance changes upon photoyellowing of borohydride bleached and diimide hydrogenated pulps are shown, respectively, in Fig. 5a and 5b.

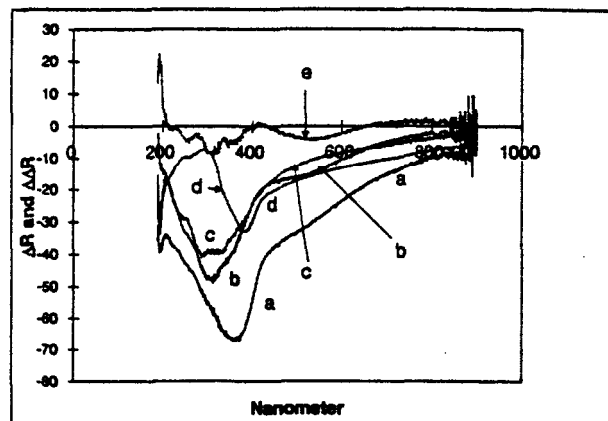


Fig. 4: ΔR and $\Delta \Delta R$ of non-photoyellowed TMPs; (a) unbleached, (b) borohydride bleached, (c) diimide reduced, (d) is (a-b), and (e) is (b-c)

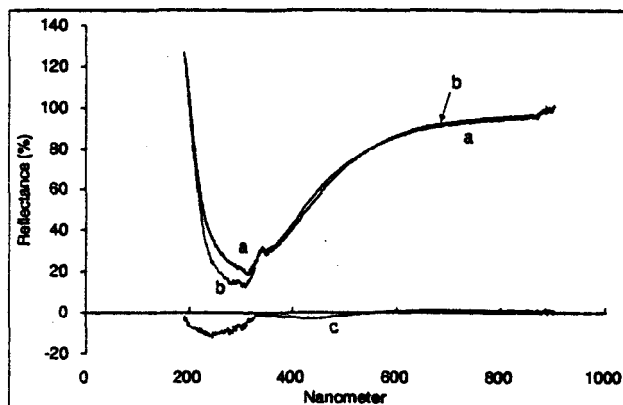


Fig. 5: Diffuse reflectance spectra (with reference to a fully bleached kraft pulp sheet) of 24 h photoyellowed TMPs; (a) borohydride bleached, (b) diimide reduced, and (c) is (b-a)

When spectra in Fig. 1-3 are compared to those shown in Fig. 4, it is clear that contributions of MHQ and M-*p*-Q can be used to explain ΔR curves for borohydride bleached (Fig. 4b) and diimide hydrogenated (Fig. 4c) pulps. For unbleached TMP, it is well known that contribution of the coniferadehyde

groups dominates ΔR curve (Fig 4a) and in its presence, contributions of hydroquinone and *p*-quinone groups play a secondary role. $\Delta\Delta R$ curve (Fig. 4e), obtained when borohydride bleached TMP was hydrogenated, can be interpreted in terms of *p*-quinones being modified by diimide.

Similarly, upon photoyellowing the observed reduced reflectance in Fig 5, having distinguishable features at 295 and 348 nm, can also be interpreted in terms of oxidation of hydroquinones to *p*-quinones. The major variation between what is detected in Fig 5 and what is expected on the basis of Fig. 3 is the fact that in the former case ΔR spectra are not discrete. This is possibly due to the simplicity of the models (compared to real lignin hydroquinones/*p*-quinones structures in pulps). Another possibility is that the ΔR spectra of photoyellowed TMPs (Fig 5) have contributions from photoproducts other than *p*-quinones.

IR spectra of photoexposed MHQ and M-*p*-Q

It is well known that in the IR spectra of photoyellowed mechanical pulps a band at about 1727 cm^{-1} is present¹. To determine if a similar carbonyl peak is present in the IR spectra of photoexposed MHQ and M-*p*-Q, the models were adsorbed on bleached kraft pulp (4 % by weight), photoexposed, and analyzed by IR. The DRIFT spectra of photoexposed and control samples are shown in Fig. 6. This Figure also shows spectra of photoexposed kraft pulp.

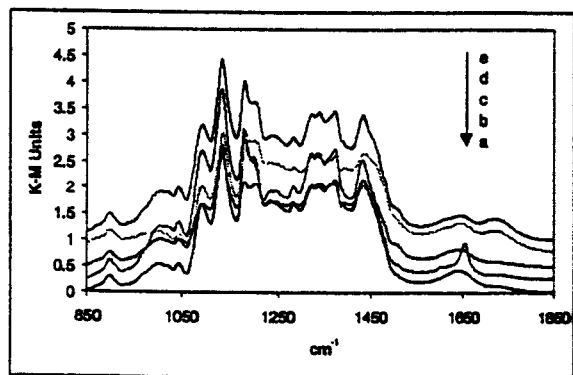


Fig. 6: IR absorbance of photoexposed and control MHQ and M-*p*-Q; (a) bleached kraft pulp, (b) M-*p*-Q, (c) MHQ, (d) photoexposed M-*p*-Q, and (e) photoexposed MHQ

From the IR spectra, it was noted that upon photoexposure both the MHQ and M-*p*-Q showed a peak at 1722 cm^{-1} (Fig. 6d and 6e) which was not present in the spectra of controls (Fig. 6b and 6c). Or for that matter, in the IR spectrum of light exposed kraft pulp (Fig. 6a). Another point that is worth noting is the fact that when 3-methoxy catechol was adsorbed

on kraft pulp (4 % by weight) and photoexposed, the carbonyl contribution appeared (not shown) to be similar to the contribution in photoexposed kraft pulp (Fig. 6a). This indicated that no significant contribution due to photoexposed 3-methoxy catechol was present in the carbonyl stretch region. The formation of a carbonyl peak in both MHQ and M-*p*-Q could be explained by the mechanism in reference 1.

Emission spectra of MHQ and TMP

Emission spectroscopy has been used to study mechanical pulps⁵⁻⁷. How pulp emission spectra are affected upon photoexposure has also been investigated. When mechanical pulps are exposed to light emission at shorter wavelength declined and band maximum at longer wavelength became more intense. The emission behavior of TMP pulp is shown in Fig. 7 and is typical of mechanical pulps.

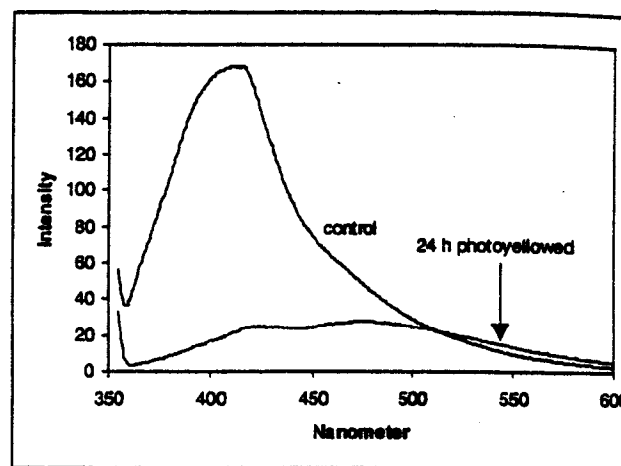


Fig. 7: Emission spectra (excited at 320 nm) of control and 24 h photoyellowed TMPs

The emission behavior of MHQ and its modification with time was studied by adsorbing MHQ on cellulose paper and obtaining spectra at various time intervals. The spectra are shown in Fig. 8. It can be seen that upon continued excitation at 320 nm the emission declined at 428 nm and increased at 462 nm. Qualitatively, this behavior is similar to the emission behavior of TMP when it was photoyellowed (Fig. 7).

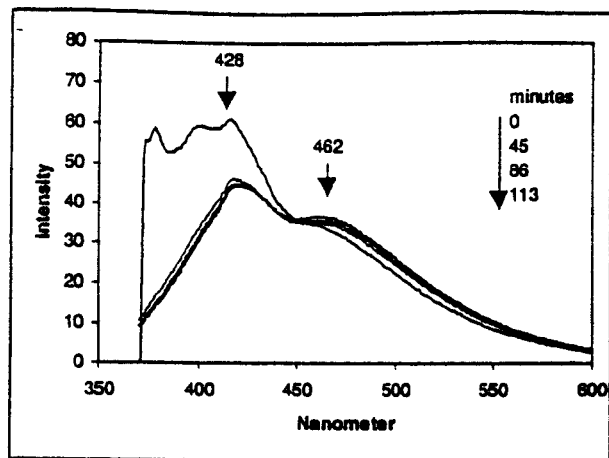


Fig. 8: Emission spectra (excited at 320 nm) of MHQ at various times; shown time intervals apply to the left side of the emission curves

Photoyellowing of methylated pulps

As reported previously¹, photoyellowing behavior of methylated mechanical pulps could be explained by the hydroquinone/*p*-quinone mechanism. Under pulp methylating conditions, it was found that hydroquinones were not methylated completely and the remaining hydroquinones were responsible for the photoyellowing of methylated pulps. Supporting evidence was obtained by the studies of the models and the fact that the LIF of the methylated pulp showed sensitivity to molecular oxygen.

Photoyellowing of acetylated pulp

When TMP pulp was acetylated it became resistant to photoyellowing (Table 1). This behavior of acetylated TMP was previously explained by the fact that acetylation resulted in complete derivatization of hydroquinones in a pulp¹. The LIF of an acetylated pulp was not sensitive to molecular oxygen and this was taken as evidence of hydroquinones being not present in the pulp.

Table 1 Brightness of TMPs - Before and after photoyellowing

TMP	Initial Brightness	After 14 Days Photoyellowing
Unbleached	51.4	32
Acetylated	64.2	61.8

Photoyellowing inhibitors

In reference 1, it was reported that well-known pulp-photoyellowing inhibitors polyethylene glycol, ascorbic acid, and 1-thioglycerol were effective against the photoyellowing of MHQ. This provided further support to the hypothesis that photoyellowing is primarily caused by hydroquinones.

Sunlight Vs. accelerated photoyellowing

Mechanical pulp based papers were photoyellowed to similar brightness using Rayonet photoreactor (λ_{max} 350 nm) and sunlight. Afterwards, they were analyzed with IR spectroscopy. Although IR spectra of both the papers showed the 1727 cm^{-1} carbonyl band, the peak height (relative to the 2900 cm^{-1} band) in the spectrum of the sunlight-yellowed paper was about 33 % higher compared to the peak height for the paper that was yellowed in the Rayonet reactor⁴. This implied that the spectrum of the light source played a role in the formation of the carbonyl group. This was explained by using the mechanism in reference 1 wherein it was proposed that conversion of *p*-quinones to hydroquinone is accompanied by formation of carbonyl groups. Because *p*-quinone to hydroquinone reaction is more efficiently driven by visible light (as is evident by the fact that the chromophores in a pulp can be recycled by different wavelengths of light), more carbonyl groups were produced upon sunlight yellowing (more visible light).

CONCLUSION

Using recently discovered evidence that *p*-quinones and hydroquinones groups are present in mechanical pulps, a number of observations (associated with the photoyellowing behavior of mechanical pulps) were satisfactorily explained such interpretations provided further support to the photoyellowing mechanism that was previously proposed¹.

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