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### A Model Compound Study: The Formation of Colored Metallic Extractive Complexes and Their Effect on the Brightness of Tmp Pulp

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A MODEL COMPOUND STUDY: THE FORMATION OF COLORED  
METALLIC EXTRACTIVE COMPLEXES AND THEIR EFFECT  
ON THE BRIGHTNESS OF TMP PULP

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ABSTRACT

Flavonoids, such as Quercetin, are the main polyphenol compounds found in extractives. When complexing with transition metal ions, these extractives may induce a significant discoloration to mechanical pulps. In this study, the effect of metallic extractive complexes was investigated using a model compound, Quercetin. It was confirmed that the complexes formed between some metal ions and Quercetin are strongly colored. However, most of the strong absorbance in visible light due to metallic Quercetin complexes, can be eliminated by the addition of diethylenetriaminepentaacetic acid (DTPA). The metal ions studied were Fe(III), Cu(II), Mn(II) and Al(III).

INTRODUCTION

The brightness of unbleached pulps in an Eastern Canadian mill has experienced a seasonal swing from a high of about 57% ISO in the winter period, to a low of about 52% ISO in the late summer period (August to November). This

seasonal swing in brightness has become known as the "summer sickness", resulting in a significant increase in bleaching costs and, at times, a complete inability to achieve a final brightness target for the speciality papers.

We hypothesized that the "summer sickness" may be related to the change in extractive content of the wood chips.

It is known<sup>1</sup> that the extractive content may range from 2 to 15% of wood. During the production of mechanical pulps, such as thermomechanical pulp (TMP), extractives may largely remain with pulp fibers<sup>2</sup>. An earlier work by Polcin and Rapson<sup>3</sup> showed that the presence of some extractives in groundwood pulps has a negative effect on the subsequent bleaching with either hydrogen peroxide or sodium thiosulfate. Also, these extractives decrease the brightness stability of the groundwood pulps during the heat-induced yellowing process. Consequently, Polcin and Rapson<sup>3</sup> found that the removal of extractives by extraction with organic solvents enhanced the performance of the subsequent bleaching stages, and that the brightness stability towards heat aging was improved for both bleached and unbleached groundwood pulps.

High levels of flavonoids and polyphenolic compounds were found among the various components in extractives. This is specially true for heartwood extractives<sup>4</sup>. It was reported<sup>4</sup> that in Douglas fir heartwood, flavonoids, of which Taxifolin and Quercetin are most abundantly present, represent 80 to 90% of the total phenols extracted. These extractive constituents, which in most cases are chromophoric compounds themselves, are largely responsible for the dark color and poor bleachability of Douglas fir heartwood pulp<sup>4</sup>.

Furthermore, the extractives may form complexes with transition metal ions, which would exhibit strong absorbance in the visible light region<sup>3</sup> and may be responsible for the lower brightness of the unbleached TMP during the summer months. This assumption is based on the fact that trees usually produce more extractives in the summer months (due to the fast growing season) than in the winter months. Because the decreased initial brightness of the mechanical pulps affects the

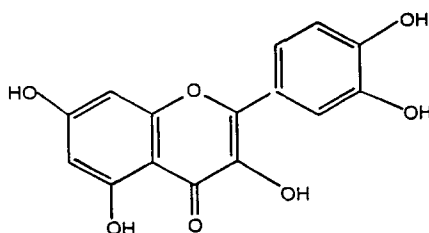
product quality negatively and increases the production cost in the bleach plant, finding a practical solution to recover the brightness loss during the summer months is of significant industrial merit.

Chelants, such as DTPA, have very high affinities with transition metal ions. Impregnation of Douglas fir chips with EDTA prior to lab scale thermomechanical pulping was an effective measure to increase the initial brightness of Douglas fir TMP pulp<sup>4</sup>.

In this project we will lend support to the assumption that the summer sickness is caused by the formation of more colored metallic extractive complexes. This was done by determining the absorbance in the visible light range of metallic extractive complexes at the model compound level. Quercetin was used as an extractive model compound. The metal ions studied were iron, copper, aluminum and magnesium. Also, the effect of adding DTPA to the system consisting of extractives and transition metal ions on the absorbance was investigated. The corresponding results obtained from a TMP pulp will be the subject of a future publication.

### EXPERIMENTAL

Quercetin, whose structure is shown below:



is practically insoluble in water, however, it does have a good solubility in ethanol<sup>5</sup>. DTPA is highly soluble in water but it precipitates out of solution in pure ethanol. Thus, a 1:1 ratio of ethanol to water solvent was used for the experiments.

Stock solution of DTPA was made in water, at concentrations of 10 mmol/L. Quercetin stock solution was made in 95% ethanol also at concentration of 10 mmol/L. NaOH and H<sub>2</sub>SO<sub>4</sub> solution were made in water at concentration of 30 mmol/L and 20 mmol/L respectively. All metal ion solutions were made separately at a concentration of 10 mmol/L in water. Suitable volumes of each component were than mixed in a vial. The pH adjustment was done with the NaOH or H<sub>2</sub>SO<sub>4</sub> solution after all the other components were mixed. The total volume of the mixture in each case was 30 mL. All the spectra were recorded 15 minutes after mixing the interested components to the solvent.

The cuvette used for the UV-visible spectra has a 1 cm width. The UV-visible spectra was recorded using a Milton Roy Spectronic 1001+ spectrophotometer interfaced with Quant software, which was run on an IBM PC.

### RESULTS AND DISCUSSION

We determined the absorbance increase in the visible light region due to the formation of metallic complexes with Quercetin. Figure 1 shows the spectra of Quercetin, Fe(III) and Quercetin + Fe(III) solutions. The concentrations were all at 60 μmol/L. It is obvious that Quercetin has a very low absorbance in the visible light range. However, the addition of Fe(III), which also has a low absorbance at that concentration, causes the absorbance to increase significantly. The increase in absorbance of the Fe(III)-Quercetin solution in the visible light range is due to the formation of colored metallic Quercetin complexes. It was found that other transition metal ions such as Fe(II) and Cu(II) can also form colored complexes with Quercetin. This is in agreement with the results by Polcin and Rapson<sup>3</sup> who reported that upon adding various metal ions to a solution containing D-catechin or pinobanksin, strongly colored complexes are formed with some metal ions (Fe(III) and Cu(II)). They have also found that Fe(III) is most effective. Based on these results, one may conclude that a considerable pulp brightness loss can occur for mechanical pulps due

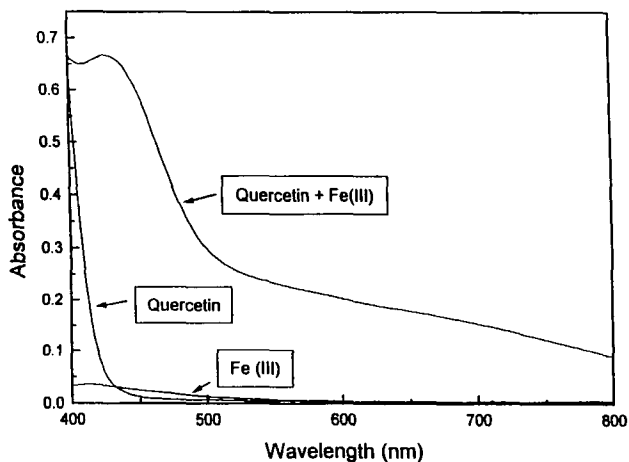


Figure 1. The spectra of Quercetin, Fe(III) and Quercetin-Fe(III) solutions (60  $\mu\text{mol/L}$  Quercetin, 60  $\mu\text{mol/L}$  Fe(III), pH 5)

to the formation of darkly colored complexes between some transition metal ions and phenolic extractives.

The extractive content in wood chips may change, depending on the harvest season. As a result, the brightness loss caused by the formation of colored metallic extractive complexes is expected to be a function of the extractive content. This can be simulated by studying the effect of the concentration of the metallic extractive complexes on the absorbance. The results obtained from the Quercetin-Fe(III) solutions at a 457 nm wavelength at which the brightness is measured, are shown in Figure 2. As expected, the higher the complex concentration, the higher the absorbance at 457 nm; the absorbance increases linearly with the concentration. These results imply that the higher concentration of extractives present in wood chips results in a stronger decrease in the pulp brightness due to the formation of more colored metallic extractive complexes.

Earlier results on metallic lignin complexes showed that, at different metal ion to lignin molar ratio, different structural complexes are formed, which

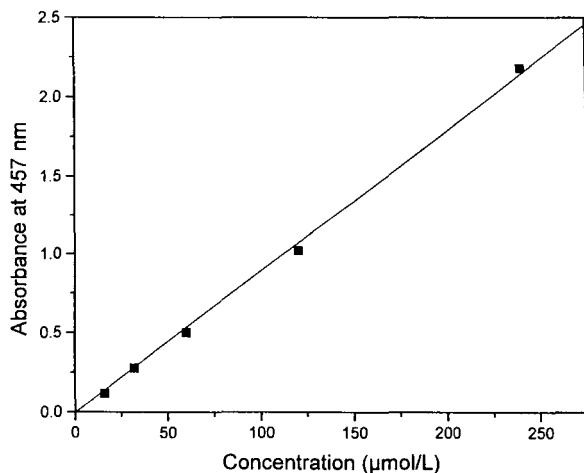


Figure 2. The absorbance at 457 nm versus the Fe(III)-Quercetin complex concentration ( $[\text{Quercetin}]/[\text{Fe(III)}] = 1$ , pH 5)

consequently changes the absorbance in the visible light range<sup>6</sup>. This may also be true for metallic extractive complexes. Therefore, we further studied the effect of metal ion to Quercetin molar ratio on the absorbance. The results from the Quercetin-Fe(III) solutions are shown in Figure 3, where the Quercetin concentration was kept constant at 400  $\mu\text{mol/L}$ . It is evident that the absorbance increases as the Fe(III)/Quercetin molar ratio increases. This is in agreement with the expectation that more metallic Quercetin complexes are formed at a higher Fe(III)/Quercetin molar ratio. However, Figure 3 shows that the relationship between the absorbance and Fe(III)/Quercetin molar ratio is not linear. This may suggest that at different ratios of Fe(III)/Quercetin, different structural complexes with a different ligand to metal ion molar ratio can be formed. The above hypothesis was supported by the results obtained from the transition metal complexes with polydent ligands<sup>7</sup>.

Chelants such as DTPA, may form much more stable complexes with Fe(III) than Quercetin, since the stability constants of metal ion-DTPA complexes are

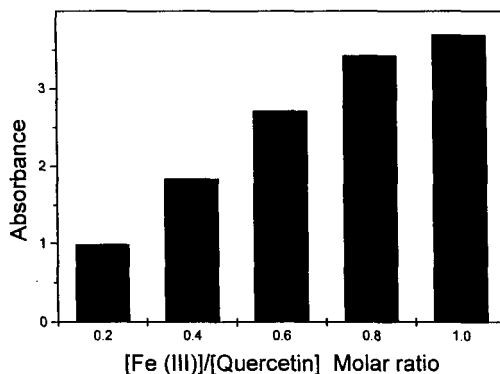


Figure 3. The absorbance at 457 nm versus the Fe(III)/Quercetin molar ratio (400  $\mu\text{mol/L}$  Quercetin, pH 5)

generally much higher than those of the corresponding metal ion with polyphenol compounds<sup>11</sup>. Our earlier results<sup>8</sup> have shown that spraying DTPA solution onto handsheets made from mechanical pulp can minimize the brightness loss caused by the formation of colored metallic complexes, which is explained by the fact that the colored metallic complexes are converted into the less colored metal ion-DTPA complexes. Furthermore, the DTPA spray largely eliminates the catalytic effect of harmful metal ions on the heat-induced and light-induced yellowing process, leading to a significant improvement in the thermo- and photo-stability of the brightness of mechanical pulps<sup>9</sup>. We investigated the potential to reduce the brightness loss caused by the formation of metallic extractive complexes with DTPA treatment. This was done by studying the effect of adding DTPA to the Fe(III)-Quercetin solution on its spectra in the visible light region. The results are demonstrated in Figure 4. It is evident that the Quercetin-Fe(III)-DTPA solution has much less absorbance than the Quercetin -Fe(III) solution. The reaction of DTPA with Fe(III) is very fast as supported by the experimental evidence that the color of the solution disappeared immediately upon addition of DTPA to a solution containing Fe(III) and Quercetin.



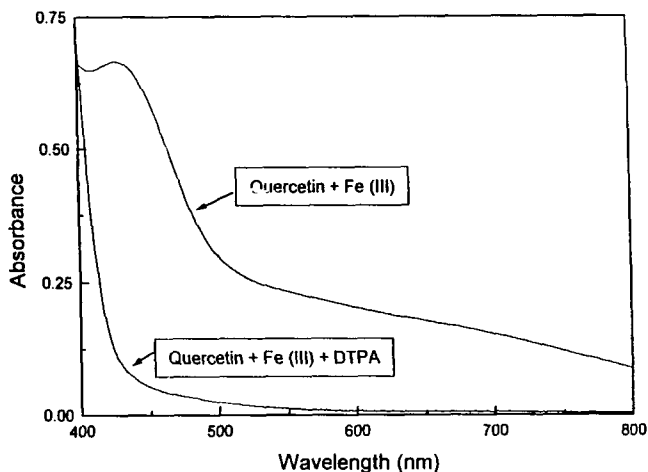


Figure 4. Effect of adding DTPA to the Fe(III)-Quercetin complex on the spectra (60  $\mu\text{mol/L}$  Quercetin, 60  $\mu\text{mol/L}$  DTPA, pH 5)

We have also studied the visible spectra of other metal ions to Quercetin complexes and the effect of DTPA addition. Figure 5 shows the comparison of absorbance at 457 nm with and without DTPA addition for Cu(II), Al(III), Mn(II) and Fe(III). It is evident that a more strongly colored compound is formed when Quercetin is in complexation with Cu(II), Fe(III), and Al(III). Mn(II) does not have any effect on the absorbance upon addition to the Quercetin solution. These results are consistent with those reported earlier with respect to the absorbance of metallic lignin complexes in the visible light region<sup>6</sup>. In comparison of the absorbance of the Quercetin-metal ion solutions with that of the Quercetin-metal ion-DTPA solutions, one can find that the decrease in absorbance by the addition of DTPA is about 95% for Fe(III), 99.7% for Cu(II) and 97% for Al(III). Again these results confirm that the DTPA addition is an effective approach to minimize the absorbance of the metallic Quercetin complexes in the visible light region. The presence of DTPA in the Mn(II)-Quercetin solution have practically no change in its absorbance. This is

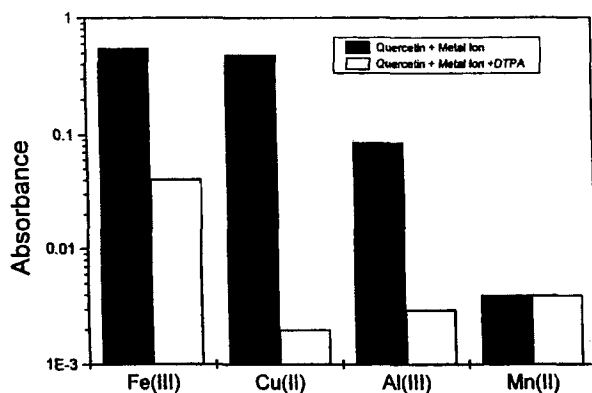


Figure 5. The absorbance at 457 nm of metal ion-Quercetin and metal ion-Quercetin-DTPA solutions (60  $\mu\text{mol/L}$  Quercetin, 60  $\mu\text{mol/L}$  metal ions, 60  $\mu\text{mol/L}$  DTPA, pH 5)

expected since Mn(II) does not have any effect on the absorbance upon addition to the Quercetin solution.

So far, we have demonstrated that the addition of DTPA to the colored metal ion-Quercetin solution effectively reduced the absorbance. A question arises as to what is the optimum DTPA charge? Therefore, we studied the effect of DTPA charge on the visible spectra of metallic Quercetin solution. The results obtained from Fe(III) are shown in Figure 6 where the absorbance at 457 nm is plotted against the DTPA/Fe(III) molar ratio. The absorbance (at 457 nm) decreases as the amount of DTPA increases. This is due to the decrease in the quantity of colored Fe(III)-Quercetin complexes since more Fe(III) is captured by DTPA and less is available for Quercetin as the DTPA charge increases. The experimental data also indicates that the visible spectra of the Fe(III)-Quercetin-DTPA system does not change significantly when the DTPA to Fe(III) molar ratio is further increased to higher than 1:1. This is consistent with the well known fact that the coordination stoichiometry of DTPA to transition metal ion is 1:1<sup>10</sup>.

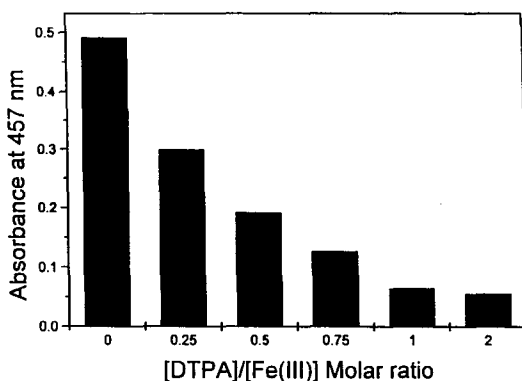


Figure 6. Effect of DTPA charge on the absorbance of the Fe(III)-Quercetin-DTPA solution (50  $\mu\text{mol/L}$  Quercetin, 50  $\mu\text{mol/L}$  Fe(III), pH 5)

### CONCLUSIONS

The decrease in the initial brightness of mechanical pulps caused by the formation of metallic extractive complexes was studied by using Quercetin as the extractive model compound. The absorbance in the visible light range of the Quercetin solution containing various metal ions was determined. The results showed that upon addition of metal ions such as Fe(III) and Cu(II) to the Quercetin solution the absorbance increases significantly, suggesting that highly colored complexes are being formed. The metallic Quercetin concentration is in a linear relationship to the absorbance of the system. However, when adding other metal ions, such as Mn(II), to a Quercetin solution there is a negligible absorbance in the visible light range.

It was found that DTPA can effectively eliminate the absorbance in the visible light range caused by the formation of metallic extractive complexes. This is explained by the fact that DTPA has a stronger affinity to transition metal ions than Quercetin, thus effectively destroying the metallic extractive complexes. The above process was proven to be very fast. An equimolar amount of DTPA with respect to

the harmful transition metal ion is sufficient to minimize the absorbance of the DTPA-metal ion-Quercetin solution.

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