Spectroscopic evidence of silica-lignin complexes: implications for treatment of non-wood pulp wastewater

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Abstract This research examined the hypothesis that lignin compounds form aqueous complexes with silica increasing its solubility, thereby inhibiting its precipitation. An experimental program using four lignin model compounds was conducted to test the hypothesis. Laser Raman spectroscopy (LRS) was used to characterize, qualitatively, the interaction between lignin and aqueous silica, and to identify the possibility of silica-lignin complexation. Solubility studies were then performed by analyzing the solubility of silica in presence and absence of lignin within the relevant pH range to confirm the results of LRS, and to obtain a quantitative assessment of the relative solubility. The findings have established the formation of silica-ferulic, silica-vanillic, and silica-4-methoxycinnamic acid complexes, but no evidence was detected for the formation of silica-veratryl alcohol complex. In fact, the black liquor undoubtedly contains much more complex lignin materials than the simple model compounds used in this work. The more complex lignin compounds are likely to have an even greater tendency to form silica complexes, thus contributing to the initial hypothesis. This finding provides a fundamental understanding as to why previous efforts to precipitate silica by lowering the pH from 10–11 (for black liquor) to less than 9 did not achieve satisfactory silica separation, and why alternative strategies need to be investigated.

Keywords Complexation; industrial wastewater; laser Raman; lignin; silica; solubility

Introduction Caustic pulping, more commonly known as the Kraft process, is used for non-wood raw materials in order to dissolve the non-cellulose organic fraction, essentially lignin, and leave behind the fibrous residual as pulp for paper production. Rice straw, however, also contains a high percentage of silica that dissolves during caustic digestion (Wong, 1997). The wastewater deriving from vacuum filtration of the pulp solution is referred to as black liquor, owing to its dark color and complex makeup of high BOD, caustic, silica, and high TDS. Conventional handling of Kraft wastewater involves elevated temperature recovery of the caustic additives with the organic content serving as supplementary energy for the process that in turn reduces the BOD, allowing for safe discharge of the final effluent. The high silica concentration in the black liquor, however, prohibits chemical recovery and results in excessive scale and fouling on the boiler unit (Heinola et al., 1998; Assumpaco and Shou, 1998). Moreover, in this case the facility is left with a high BOD wastewater requiring further treatment before disposal. Therefore, a cost effective technology for desilication of black liquor is urgently needed (Fellegi et al., 1998).

At least seventeen developing countries in addition to Egypt are using rice straw in pulping and are facing the same problem. By virtue of its being the largest pulp and paper mill in the world using rice straw as the primary material, the Rakta facility in Alexandria, Egypt was chosen by the United Nations Environmental Program (UNEP-IE/PAC) as a pilot facility for the development of an environmentally sound protocol for rice straw paper production (Tohamy, 1994). Since the early 1980s, four attempts have been made to solve the...
problem. Three of these have focused on desilication of black liquor by lowering the pH using recovered flue gas, and precipitating the silica as amorphous SiO$_2$ followed by solid/liquid separation using a centrifuge and/or more traditional settling. The latter also employed seeding with sand to enhance crystal formation, but provided no laboratory data to substantiate the pilot approach. All three efforts have been abandoned due to the failure to provide adequate separation of silica (Tohamy, 1994). The fourth effort is currently ongoing and utilizes a fluidized bed reformulator. While this essentially reduces the liquor to ash, the energy consumption is high, silica is predictably deposited in the evaporators, and there is no conceived scheme for recovering the useful inorganic chemicals from the ash due to the presence of silica. Recent environmental enforcement in Egypt has required Rakta mill to eliminate all but a small pilot production on its rice straw utilization facility until a suitable solution to the black liquor disposal problem can be found. The previous attempts to solve the problem involved implementing existing processes and equipment, with little attention given to understanding the chemistry of the system and the interaction of various solution phase elements, in particular lignin, with aqueous silica and the impact of this interaction on silica separation via precipitation. Therefore, this research aims at developing a fundamental understanding of the chemistry of the system as a step in the ultimate objective, which is to develop a cost effective strategy for managing the high silica wastewater stream with accompanying high dissolved organic materials. The hypothesis here is that lignin forms aqueous complexes with silica, thereby increasing its solubility under the solution conditions of interest and inhibiting its removal by conventional precipitation.

Due to the heterogeneous polymeric character of lignin, and the uncertainties in its chemical structure, lignin model compounds were used to represent lignin in laboratory experiments (Harvey et al., 1993; Conrad and Huck, 1996; Ford, 1997). Veratryl alcohol, ferulic acid, vanillic acid, and 4-methoxycinnamic acid were the lignin model compounds (LMCs) examined in this study.

Materials and methods
The experimental plan was divided into two main parts; Laser Raman experiments and solubility experiments. Laser Raman spectroscopy (LRS) was used to characterize, qualitatively, the interaction between lignin and aqueous silica, and to identify the possibility of formation of silica-lignin complexes. In case of complex formation, chemical reactions describing such complexes should be proposed based on the Laser Raman spectrograms. The second set of experiments focused on analyzing the solubility of silica in presence and absence of lignin at various pH values to verify the results of the LRS, and to obtain a quantitative assessment of the relative solubility.

Materials
Four lignin model compounds were used in the study to represent lignin, while silica gel and silicic acid were used to account for the silica phase. Several buffers were used to buffer sample pH at known values. These materials are described as follows, with important properties summarized in Tables 1 and 2 for LMCs and buffers, respectively.

Veratryl alcohol (3,4-Dimethoxy benzyl alcohol) has been used as a LMC in other research involving lignin (Harvey et al., 1993; Ford, 1997). It has a relative density of 1.173 and is soluble in ethanol and methanol. Fluka brand in a viscous oil state was used with an assay of 97%.

Ferulic Acid (trans-4-Hydroxy-3-methoxycinnamic acid) was used previously to represent lignin in investigating chloro-lignin interactions in the chlorination of pulp (Conrad and...
Huck, 1996). It is soluble in ethanol, ethyl acetate, and hot water. Aldrich brand in powder form with 99% assay was used throughout the experimental work.

*Vanillic Acid (4-Hydroxy-3-methoxybenzoic acid)* is a LMC that resembles ferulic acid but of simpler atomic structure. It is soluble in water and very soluble in ethanol. Aldrich product in powder form with 97% assay was obtained for this study.

*4-Methoxycinnamic acid* is the complement to ferulic and vanillic acids in that it does not contain the 3-methoxy group. It is soluble in AcOH and moderately soluble in ethanol. A powdered form Fluka brand (98% assay) was used in these investigations.

Seven pH buffers were obtained from Metrepak for buffering laboratory working solutions in the pH range of interest for silica solubility, namely 7–12. These are summarized in Table 2.

*Silica Gel* was the source of silica in the solubility experiments. Its chemical formula is SiO$_2$·xH$_2$O. Mallinckrodt product was used in the experiments with surface area of 300 m$^2$/g, pore volume of 1.15 cm$^3$/g, and average pore diameter of 150 Å. It also contains 600 ppm of sodium as Na$_2$O, 100 ppm of iron as Fe$_2$O$_3$, 100 ppm of carbon, and less than 5 ppm of heavy metals. The particle size is between 35–60 mesh (250–500) µm.

*Silicic Acid* was used in Laser Raman spectroscopy investigations to represent the silica phase. The formula is SiO$_2$ (aq). It was used in previous studies to determine the interactions between silica and simple organic acids such as oxalic acid (Marley *et al*., 1989). Fluka brand was used with 99% assay.

### Table 1: Properties of LMCs used in this study

<table>
<thead>
<tr>
<th>LMC</th>
<th>Molecular formula</th>
<th>Molecular weight (g)</th>
<th>Boiling or melting point (°C)</th>
<th>$pK_a$ (25°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Veratryl alcohol</td>
<td>C$<em>9$H$</em>{12}$O$_3$</td>
<td>168.2</td>
<td>135–137</td>
<td>10.78 ± 0.34</td>
<td>Measured by potentiometric titration</td>
</tr>
<tr>
<td>Ferulic acid</td>
<td>C$<em>{10}$H$</em>{10}$O$_4$</td>
<td>194.2</td>
<td>168–169</td>
<td>4.57 ± 0.12</td>
<td>Measured by potentiometric titration</td>
</tr>
<tr>
<td>Vanillic acid</td>
<td>C$_8$H$_8$O$_4$</td>
<td>168.2</td>
<td>210–213</td>
<td>4.52</td>
<td>Heilborn and Bunbury, 1953</td>
</tr>
<tr>
<td>4-Methoxycinnamic acid</td>
<td>C$<em>{10}$H$</em>{12}$O$_3$</td>
<td>178.2</td>
<td>173.5</td>
<td>4.67</td>
<td>Heilborn and Bunbury, 1953</td>
</tr>
</tbody>
</table>

### Table 2: Properties of pH buffers used in this study

<table>
<thead>
<tr>
<th>Buffer pH</th>
<th>Accuracy</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.4</td>
<td>±0.05</td>
<td>Sodium phosphate dibasic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Potassium phosphate monobasic</td>
</tr>
<tr>
<td>8.0</td>
<td>±0.02</td>
<td>Sodium phosphate dibasic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Potassium phosphate monobasic</td>
</tr>
<tr>
<td>8.4</td>
<td>±0.02</td>
<td>Sodium bicarbonate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Potassium phosphate monobasic</td>
</tr>
<tr>
<td>9.0</td>
<td>±0.02</td>
<td>Sodium bicarbonate</td>
</tr>
<tr>
<td>10.0</td>
<td>±0.02</td>
<td>Sodium carbonate</td>
</tr>
<tr>
<td>11.0</td>
<td>±0.05</td>
<td>Sodium phosphate tribasic</td>
</tr>
<tr>
<td>12.0</td>
<td>±0.10</td>
<td>Sodium phosphate tribasic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sodium bicarbonate</td>
</tr>
</tbody>
</table>
Sodium nitrate (NaNO₃) (from Surechem) was used to account for the ionic background in the solubility experiments.

Water was distilled using Barnstead Fistreem III distiller that provides high grade pyrogen free distilled water, then was de-ionized in a Barnstead Nanopure UV de-ionized system that yields Type I reagent grade water equal to or exceeding standards established by ASTM with a capability of achieving TOC values of less than 3 ppb. It will be referred to as water in the study.

**Laser Raman experiments**

Laser Raman spectroscopy is useful for identifying structural changes associated with the formation of aqueous complexes, and has even been employed previously for interactions between silica and organic acids (Marley et al., 1989). Therefore, it was used in this study to investigate the possibility of silica-LMC complexation.

FT-Raman analysis was performed using a Bruker-IFS 66/S spectrometer of type RFS 100/S. It provides high resolution to 0.1 cm⁻¹. It is equipped with a liquid nitrogen cooled Ge diode detector of high sensitivity. The laser source used was Nd:YAG laser with a laser power of 1,500 mW. Each sample was scanned 20 times to assure good spectrum quality and statistically approved results.

Initially, 0.1 molar solutions of the target LMCs were prepared and stored in polyethylene (Nalgene) 125 mL bottles. In addition, a 0.1 molar solution of silicic acid was prepared, and then a basic solution of silicic acid was made by adding NaOH to the silicic acid until the pH reached ~12. The prepared solutions were then mixed and the pH adjusted to the desired value by the addition of the organic acid solution to the basic solution of silicic acid. Finally, Raman spectra of the solutions were obtained using standard quartz cuvettes and the Laser Raman apparatus described previously.

**Solubility experiments**

The relative solubility of silica in presence and absence of veratryl alcohol, ferulic acid, and vanillic acid was studied over a pH range between 7 and 12. The impact of 4-methoxycinnamic acid was tested at pH of 9.5 only because it is not soluble except in highly basic solutions like ammonium hydroxide, rendering pH adjustment a difficult task even with the use of pH buffers.

pH buffers were prepared by dissolving pre-measured packets in 100 mL of water and stored in polyethylene (Nalgene) 125 mL bottles. Four grams of silica gel were then added to each bottle to assure that silica is present in excess of the solubility capacity (Iler, 1979; Baes and Mesmer, 1976). In case it is required to adjust the ionic background to one molar, 8.5 grams of NaNO₃ were added in each bottle. A stock solution of 0.1 molar LMC dissolved in ethanol was prepared for both ferulic acid and veratryl alcohol. Stock solutions of 0.1 molar 4-methoxycinnamic acid dissolved in ammonium hydroxide and 0.1 molar vanillic acid dissolved in water were also prepared. An equivalent volume of the respective stock solution was added in each bottle to obtain the desired molar concentration of the background. The pH meter was then calibrated using two buffers that bound the examined pH range; normally buffers of pH 7 and 12 were used. The pH of the solution in each bottle was measured using a Schott pH meter with temperature probe of accuracy ±0.01 pH units, and the temperature was monitored as well. In case the buffers did not position the pH to the required value, the solutions were adjusted using either sodium hydroxide or hydrochloric acid according to the case. The bottles were then mounted on a Cole Parmer shaker and agitated at 150 rpm at room temperature. The pH was monitored every couple of days and adjusted to the desired pH value until steady state was reached (normally two to three
weeks). A small volume from the supernatant of each bottle was taken and diluted with water, then filtered using Hach # 30 filters (3.4 µm pore size). Finally, the samples were analyzed for dissolved silica using a Hach direct reading spectrophotometer (DR-2000 model) method, which is based on Standard Method 4500-Si (D): Molybdosilicate method (Standard Methods, 1992).

Results and analysis
Laser Raman spectrograms
In order to identify the possibility of silica-LMC complex formation for a given case, individual spectrograms are obtained for the relevant solvent, silicic acid, the LMC, and a mixture of silicic acid and the LMC. The spectrograms were then investigated for any irregularities that might have occurred due to a silica-LMC complex formation.

Vanillic acid. The $pK_a$ of vanillic acid is 4.52 (Heilbron and Bunbury, 1953). Since the pH of the black liquor is always more than two units above this $pK_a$ value, vanillic acid would be expected to be in the ionized form and, therefore, spectrograms adjusted to pH values in the range of interest (7–11) are expected to give similar results. The spectrogram of vanillic acid and a mixture of vanillic and silicic acids adjusted to pH 9 only is shown here (Figure 1). Due to the presence of water as a solvent, the spectrogram is a bit noisy. Therefore, it was not possible to analyze every band in the spectrogram, and it was also difficult to isolate the prominent bands for each constituent, but a comparison between the two spectrograms with and without vanillic acid was made to find the differences.

Analyzing the spectrograms shown in Figure 1, the peak at 805 cm$^{-1}$ (vanillic acid only) was shifted to 785 cm$^{-1}$ in the mixture, and a new band is produced at 1,240 cm$^{-1}$. The new observed band at 1,240 is expected to be due to the formation of a new bond, namely Si-O-C asymmetric stretching. The C-C stretch, which was at 805 cm$^{-1}$, was shifted to 785 cm$^{-1}$ because of the heavier silica atom bonding to the oxygen. Results of samples adjusted to pH 11 exhibited similar Raman spectrograms. The above description suggests that a silica-vanillic complex is formed in which vanillic acid in the ionized form combines with silicic acid. In the process, a water molecule is produced from the deprotonation of the organic acid and the removal of an OH$^-$ from the silicic acid molecule that bonds to the benzoic acid group, with the overall reaction illustrated in Figure 2.

Ferulic acid. The $pK_a$ value of ferulic acid was measured by potentiometric titration to be $4.57 \pm 0.12$, or close to that of vanillic acid. Similarly, ferulic acid will ionize in solutions
for the pH range of interest for black liquor. Spectrograms of ethanol (the solvent), silicic acid, ferulic acid, and a mixture of silicic and ferulic acids were analyzed to identify the possibility of silica-ferulic complex formation.

For pH 7 solution, the ferulic acid (only) case was found to be distinguished by only one medium strong band at 1,159 cm$^{-1}$ due to C-O stretching. Examining the mixture spectrogram showed that the spectrum band at 1,159 disappeared, and a new weak band appeared at 1,070. The disappearance of the C-O stretching band at 1,159 is expected to be due to the formation of a new bond, C-O-Si(OH)$_3$ instead of C-O. This change in symmetry of bonding corresponds to the C-O bond becoming Raman inactive. The new band is believed to be due to the asymmetric Si-O-C stretching at wave number of 1,070 cm$^{-1}$. Therefore, a silica-ferulic complex is postulated according to the pattern observed for vanillic acid and depicted in Figure 3.

4-methoxycinnamic acid. The spectrograms of 4-methoxycinnamic acid and a mixture of 4-methoxycinnamic acid and silica are shown on Figure 4. A peak at 971 cm$^{-1}$ is shifted to 980 cm$^{-1}$, and a new peak arises at 1,002 cm$^{-1}$.

The new peak is expected to appear due to the formation of a new Si-O-C asymmetric stretching bond. The strong C-H out of plane bending that was at 971 cm$^{-1}$ was shifted to 980 cm$^{-1}$. This shift is expected to be due to the heavier silica atom bonding to the oxygen of the ionized form of the organic acid. The previous discussion suggests that a
4-methoxycinnamic-silica complex is formed that has a chemical reaction as described by Figure 5.

**Veratryl alcohol.** Laser Raman spectroscopic scans were taken on ethanol (the solvent), silicic acid, veratryl alcohol, and two mixtures of silicic acid and veratryl alcohol. One of these was adjusted to pH 10 and the other adjusted to pH 12 to capture the two species of the veratryl alcohol (pK$_a$ = 10.78 ± 0.34 as determined by potentiometric titration). Both Figures (6 and 7) show that only the magnitude of the peak changes for the mixture spectrogram when compared to the organic alcohol spectrogram, and this is due merely to the variation in veratryl alcohol concentration in the compared samples. No change in prominent bands and no new bands appear. This indicates that no silica-veratryl alcohol complexes are formed.

**Solubility studies**
Solubility studies revealed that when 0.001 M ferulic acid was added to the silica samples, the solubility increases by about 15–20 mg/L as SiO$_2$. This increase is nearly constant over the pH range of the experiment. Although 15–20 mg/L seems a small value, this accounts for about 20% of the total soluble silica from pH 6–9. That means at pH 8.5–9 which is the desired range for desilication in the pulping industry, 20% of the silica expected to precipitate due to the presence of only 10$^{-3}$ M of the organic acid (Ferulic acid in this case). Issues about the experimental significance of this small value can be defended by the fact that random errors cannot be unidirectional but it should fluctuate between plus and minus values. In our case, an increase of about 15–20 mg/L was noticed for all data points. Furthermore, a yellow color was developed in the samples containing ferulic acid during the experimental work, while no color development was observed for control samples in absence of the acid or with ferulic acid without silica. This colorimetric evidence confirms the complex formation. Therefore, based on both the spectrograms and the solubility study,
there is satisfactory evidence that silica forms a complex with ferulic acid, thus increasing its solubility.

Results of the solubility experiment in presence of vanillic acid are presented in Figure 8. Figure 8 indicates that in the presence of 0.001 M vanillic acid, the solubility of silica increases by about 20 mg/L as SiO₂, or similar to the case of ferulic acid. Also like the ferulic acid solution, this increase is relatively constant up to pH 8.5–9. Based on both the spectrograms and the solubility study, there is plausible evidence to suggest that silica forms a complex with vanillic acid that increases its solubility in aqueous solution.

By contrast, results for the solubility experiments in presence of veratryl alcohol showed that this LMC has no impact on the solubility of silica as seen in Figure 9. This outcome is in direct agreement with the Laser Raman experiment. Therefore, it can be stated that no silica-veratryl alcohol complex is formed in the pH range from 7 to 11 under the stated experimental conditions.

As described in Methods, various means of solubilizing 4-methoxycinnamic acid samples at different pH values were tried but were unsuccessful due to the relative insolubility of the acid. One set of samples was examined at pH 9.1 in ammonium hydroxide solvent.
An average silica solubility of 125 mg/L as SiO$_2$ was achieved for silica samples in absence of 4-methoxycinnamic acid and an average value of 143 mg/L as SiO$_2$ was measured in presence of the organic acid at pH 9.1. The increase in solubility due to the presence of the LMC provides additional evidence of complex formation of the organic acid with silica.

Discussion

The findings have established the formation of silica-ferulic acid, silica-vanillic acid, and silica-4-methoxycinnamic acid complexes, but no evidence was detected for the formation of silica-veratryl alcohol complex. It could be inferred from these findings that silica-lignin complex formation is a general reaction provided that lignin is found in ionized form at the pH range from 7–11. The proposed general reaction for Silica-Lignin complex formation can be described as follows:

$$\text{H}^+ + \text{LMC}^- + \text{Si(OH)}_4^- \rightleftharpoons \text{Silica-Lignin Complex} + \text{H}_2\text{O}$$

in which the ionized form of the lignin reacts with silicic acid to form the complex and a water molecule from the proton and hydroxyl released from the LMC and silicic acid, respectively. It would appear that these organic acids could readily act as nucleophilic reagents to attack silicic acid in solution leading to the complex formation. A new Si-O-C product band in the lignin-silica mixture spectrogram should be observed. This leads to the formation of a new dissolved silica species increasing solubility. Additional solubility data and speciation modeling are required to confirm the actual form of the silica-lignin complex.

In fact, the lignin composition of black liquor is probably much more complex than the model compounds used in this work (e.g. multi-ring aromatic polymers, or long chain methoxy phenyl propanes). For instance, dehydrogenation of coniferyl alcohol alone forms more than 30 types of lignins (Freudenberg, 1965). While these compounds are difficult to study by methods used here, they may have an even greater tendency to form silica complexes than the ones studied, adding to the original hypothesis that silica-lignin complexation is leading to enhanced silica solubility and inhibiting its precipitation.

Conclusions

- Previous attempts to solve the black liquor problem at the Rakta facility by silica
separation via pH adjustment were unsatisfactory due (likely) to the formation of silica-lignin complexes that increase silica solubility in the pH range of interest. This increase in solubility means that the silica left for precipitation decreases proportionally leading to inefficient silica/liquid separation.

- Laser Raman spectroscopy and solubility experiments revealed the formation of silica-ferulic acid complex, silica-vanillic acid complex, and silica-4-methoxycinnamic acid complex, but no impact of veratryl alcohol was observed on the solubility of silica.
- It could be inferred from these findings that silica-lignin complex formation is a general reaction provided that the lignin is found in ionized form.
- Delignification prior to desilication of the black liquor requires further investigations to determine a cost-effective scheme for treating wastewaters deriving from pulping of high silica agricultural residues such as rice straw.

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