Deciphering the Interaction Between Wood Components and Preservative Chemicals:

A QCM-D STUDY

Orysia Meouch[1], Thu V. Vuong[1], Mojgan Nejad[2], and Emma R. Master[1]

[1] University of Toronto, 184 College St, Toronto, Ontario, Canada, M5S 3E4
[2] Michigan State University, 480 Wilson Rd, East Lansing, Michigan, USA 48824

Summary

The durability of preservative-treated wood is highly dependent on the interaction of wood components (cellulose, hemicellulose, lignin, and extractives) with preservative chemicals. Wood preservatives are generally comprised of metal ions, commonly copper, chromium, and arsenic, along with iron as a colorant. The goal of this work is to establish methods to quantify interactions between preservative chemicals and main wood components, to thereby aid efforts to develop formulations that extend the weathering performance of preservative-treated wood. This initial study focused on using quartz crystal microbalance with dissipation (QCM-D) to investigate the interaction of individual standard metal solutions (chromium, copper, arsenic, and iron) with well-characterized lignin (organosolv softwood) and hemicellulose (beechwood xylan) wood components. Wood components (lignin and xylan) were spin-coated onto SiO_2 sensors, the coated sensor was then exposed to an individual metal ion solution, and changes in the resonance frequency were related to changes in mass due to surface modifications using the Kelvin-Voigt viscoelastic model. The reversibility of interactions was assessed by washing the sensors with water and noting changes in frequency. Iron was found to interact with both lignin and hemicellulose irreversibly, chromium was found to interact with only hemicellulose irreversibly, whereas copper and arsenic were found to interact with hemicellulose with some reversibility.

1. Introduction

Weathering of wood is a surface degradation effect in response to environmental factors such as solar radiation, precipitation, temperature changes, abrasion, and atmospheric pollution [1]. Degradation is primarily initiated by the ultraviolet (UV) portion of solar radiation causing photooxidation of the surface [1]. The extent of weathering is subject to many factors of wood such as species density, growth rate, texture, and differs in early and late woods [1]. These factors will affect the ratio of wood components: cellulose (40-50 %), hemicellulose (25-35 %), and lignin (18-35 %), with small amounts of organic extractives (4-10 %) and inorganic trace elements (<1 %) [2].

The effects of weathering can be mitigated by applying a wood treatment process and/or wood finishing [3]. Currently, wood preservatives can be categorized into three types: (1) water-borne preservatives, (2) oil-borne preservatives, and (3) light organic solvent preservatives. Water-borne preservatives tend to be the least expensive and most widely used [1]. Today, the most common

components of these preservatives used for residential applications are copper-based preservatives. We also included chromium and arsenic in this study as they are main components of chromated copper arsenate (CCA)-type preservatives. Notably, CCA-treated wood has shown comparatively high weathering performance when exposed to long-term weathering [4].

Although water-borne preservatives have been around since the 1930s, there are still many limitations to our understanding of the interactions between preservative chemicals and individual wood components (e.g. hemicellulose and lignin). As a result, the efficacy of new preservative formulations in improving the weathering performance of wood remains difficult to predict and optimize. So far, the interactions between preservative components and wood fiber fractions have primarily been studied for CCA-type preservatives [5-10]. Copper-based interactions are also well studied and it is suggested that copper forms complex bonds with lignin [11-17]. Minimal work has been conducted to elucidate interactions of metal-azole preservatives and iron oxide pigments with wood fractions [18-20].

The objective of our study is to systematically investigate the interaction of wood preservative components with specific wood fiber fractions using a surface analysis technique. Specifically, quartz crystal microbalance with dissipation (QCM-D) monitoring is used to study the interaction of individual standard metal solutions (chromium, copper, arsenic, and iron) with well-characterized lignin and hemicellulose. A better understanding of these interactions can help optimize current formulations to extend the weathering performance of preservative-treated wood.

The use of quartz crystal resonators for quantitative mass measurement was first established by Sauerbrey in 1959 [21]. The piezoelectric properties of the thin quartz disc cause oscillation of the sensor when voltage is applied across the electrodes. The resonance frequency is dependent on the mass oscillating on the sensor. If a thin rigid film is adsorbed to the sensor, the change in resonance frequency ($\Delta \mathbf{f}$) will be directly proportional to the change in mass ($\Delta \mathbf{m}$), according to the Sauerbrey equation [21]:

$$\Delta \mathbf{m} = -(\mathbf{C} \cdot \Delta \mathbf{f})/\mathbf{n} \tag{1}$$

where $\mathbf{C}$ is 17.7 ng/Hz for a 5 MHz quartz crystal and $\mathbf{n}$ is the overtone number (1,3,5,7, etc.).
The effective thickness ($\mathbf{d_{eff}}$) of the adsorbed layer can be estimated by:

$$\mathbf{d_{eff}} = \Delta \mathbf{m}/\boldsymbol{\rho_{eff}} \tag{2}$$

where $\boldsymbol{\rho_{eff}}$ is the effective density of the adsorbed layer.

The sensor can be coated with a variety of materials for interaction and binding studies. The Sauerbrey equation provides a good estimation of mass and film thickness for thin and rigid adsorbed film on the sensor. However, during many QCM measurements water may add to the mass through entrapment, direct hydration, or viscous drag, which will create a thick soft layer that dampens the sensor's oscillation causing a dissipation effect. In this case, the Sauerbrey model will not apply [22].

Monitoring dissipation in addition to frequency changes can help in assessing the viscoelastic properties of the film. An increase in dissipation during the binding experiment is indicative of a viscoelastic film. The Kelvin-Voigt viscoelastic model can be used to describe the adsorbed film by a shear modulus [23]:

$$G = G' + iG'' = \mu_f + i2\pi f n_f = \mu_f(1 + i2\pi f \tau_f) \tag{3}$$

where μ_f is the elastic shear (storage) modulus, n_f is the shear viscosity (loss modulus), f is the oscillation frequency, and τ_f is the characteristic relaxation time of the film.

Under no-slip conditions and a Newtonian bulk fluid, the changes in frequency Δf and dissipation can be described by the following equations [23]:

$$\Delta f = Im(\beta)/2\pi t_q \rho_q \tag{4}$$

$$\Delta D = -Re(\beta)/\pi f t_q \rho_q \tag{5}$$

where

$$\beta = \xi_1 \frac{2\pi f n_f - i\mu_f}{2\pi f} \frac{1 - \alpha \exp(2\xi_1 d_f)}{1 + \alpha \exp(2\xi_1 d_f)}$$

$$\alpha = \frac{\frac{\xi_1}{\xi_2} \frac{2\pi f n_f - i\mu_f}{2\pi f n_1} + 1}{\frac{\xi_1}{\xi_2} \frac{2\pi f n_f - i\mu_f}{2\pi f n_1} - 1}$$

$$\xi_1 = \sqrt{-\frac{(2\pi f)^2 \rho_f}{\mu_f + i2\pi n_f}}$$

$$\xi_2 = \sqrt{i\frac{2\pi f \rho_1}{n_1}}$$

where ρ_1 is the bulk-liquid density and n_1 is the bulk liquid viscosity.

In this study, for each metal that has bound to the selected wood component (i.e., lignin and xylan) as indicated by a decrease in frequency, the applicability of the Sauerbrey and Kelvin-Voigt model will be assessed. The appropriate model will then be used to quantitatively measure the absorption of metal ions to lignin or xylan (hemicellulose).

2. Methodology

Sensor preparation

Biolin Scientific SiO$_2$ sensors (AT cut, 14 mm diameter, 0.3 mm thickness, frequency 4.95 MHz ± 50 kHz) were cleaned in an ozone UV cleaner for 10 minutes, then spin-coated with 30 μL of organosolv softwood lignin (0.5 % in 1,4-dioxane). The sensors were cured in an oven at 90 °C for 24 h to ensure tight binding of lignin to SiO$_2$. Similarly, clean SiO$_2$ sensors were spin-coated with 2x30 μL of beechwood xylan (2 % in water; purchased from Sigma, USA) and cured for 24 h at 90 °C. Sensors were allowed to cool to room temperature before placing in the Biolin Scientific QSense Analyzer.

Binding experiment

Two coated (either xylan or lignin) and two uncoated SiO_2 sensors were placed in the running chambers of the Biolin Scientific QSense Analyzer (Experiments were performed in duplicates for both uncoated and coated sensors). The changes in frequency and dissipation were monitored at n = 3, 5, 7, 9, and 11 overtones. A baseline measurement was established by flowing Milli-Q water over the sensors until the change in frequency over 30 minutes was less than 1 Hz. Once a steady baseline was reached, the Milli-Q water was replaced with a metal ion solution to observe the interaction with lignin or xylan. Each of the standard metal ion solutions tested (Cu (II), Fe (III), As, and Cr(VI)) were obtained from Inorganic Ventures and diluted 100X with Milli-Q water before running QCM-D experiment. In addition to the single metal ions tested, commercial CCA preservative concentrate was diluted 100X and the binding assessed for xylan and lignin. Once the frequency change had stabilized, the metal ion (or commercial) solution was replaced with Milli-Q water to wash the sensors and assess the reversibility of the binding.

3.   Results and discussion

The interaction of lignin and xylan with preservative components (Cu (II), Fe (III), As, and Cr(VI)) as well as a commercial CCA preservative was studied by monitoring the change in resonance frequency and dissipation with quartz crystal microbalance. A sample of the raw data in which arsenic was binding with xylan is shown in Figure 1.
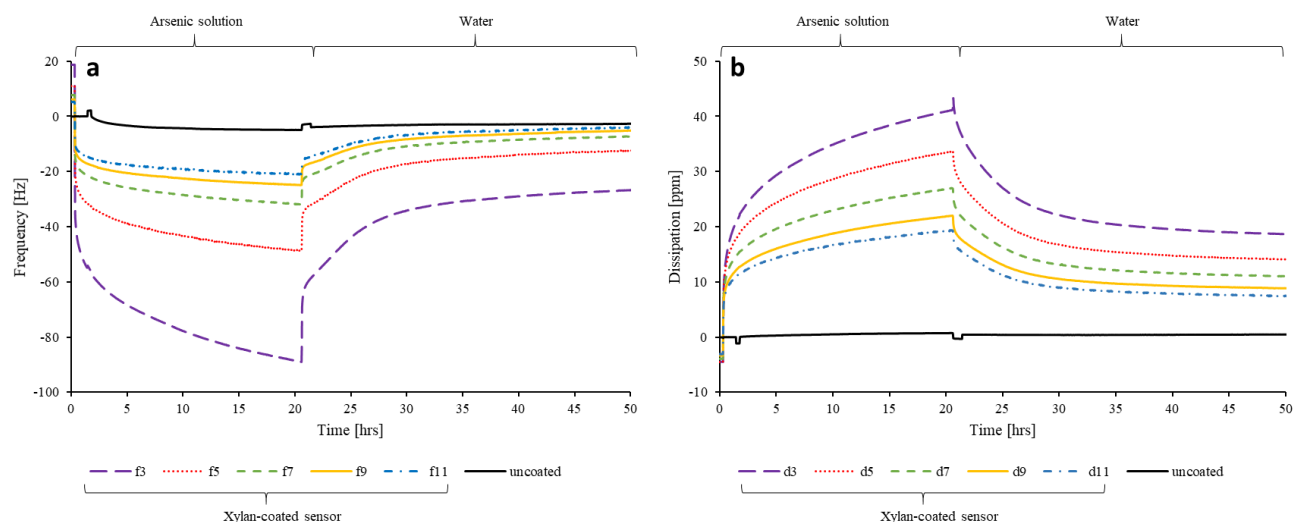

Figure 1. Xylan-coated SiO_2 QCM-D sensors were exposed to 100X diluted Inorganic Ventures Arsenic standard solution as indicated by the braces. After approximately 21 hrs, the sensors were washed with Milli-Q water to assess the reversibility of binding. The changes in frequency (a) and dissipation (b) were measured at n = 3, 5, 7, 9, and 11 overtones over time indicated in the legend. The black line represents the response of the uncoated sensor in which frequency and dissipation values for all overtones overlapped. Experiments were performed in duplicates for both uncoated and coated sensors.

The decrease in resonance frequency observed during exposure to arsenic solution in Figure a was indicative of an increase in mass on the oscillating sensor. Since the mass on the sensor increased, we can deduce that arsenic interacted and adhered to the xylan-coated surface. When the sensors were washed with water, an increase in the frequency was observed, indicating that some of the arsenic on the xylan surface was removed. Since the frequency did not return to the baseline value, the binding of arsenic to xylan was not fully reversible. Uncoated sensors (shown by the black line in Figure 1) did not exhibit these changes in frequency, indicating that the binding was indeed due to interactions with the xylan coating and not interactions between SiO_2 and the metal ion.

The dissipation was monitored over the course of the binding and washing experiment (Figure b). An increase in the dissipation was observed when the xylan-coated sensors were exposed to the arsenic solution. During the water washing step, the dissipation decreased as was expected if some of the arsenic was removed from the surface.

A sample of the raw data in which iron was binding with lignin is shown in Figure 2 below. Similarly to the arsenic example (Figure), a decrease in frequency was observed upon exposing the lignin-coated sensors to an iron solution, indicating that the iron (III) solution was adsorbed onto the surface. Minimal changes in frequency were observed when the sensors were washed with water indicating that the interaction between iron (III) and the lignin was not reversible. Uncoated sensors (shown by the black line in Figure 2) did not exhibit large shifts in frequency compared to lignin-coated sensors, therefore, the adsorbance of the iron solution was likely due to interactions with the lignin coating and not interactions between SiO_2 and the iron. The dissipation was also monitored, however, contrary to the arsenic-xylan example, minimal changes in dissipation occurred throughout the experiment.
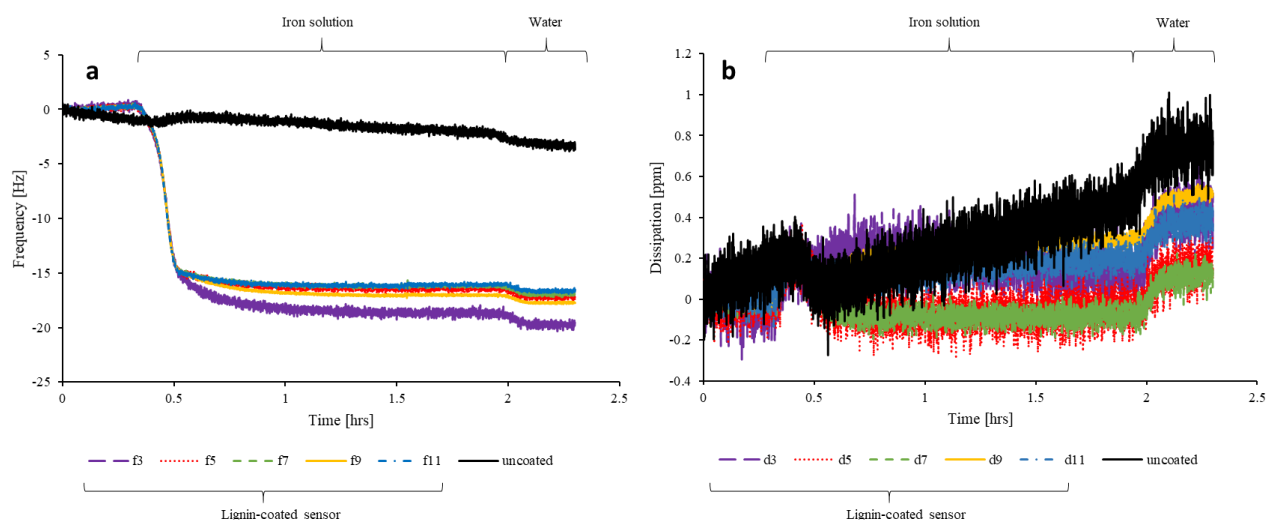

Figure 2. Lignin-coated SiO_2 QCM-D sensors were exposed to 100X diluted Inorganic Ventures Iron standard solution as indicated by the braces. After approximately 2 hrs, the sensors were washed with Milli-Q water to assess the reversibility of binding. The changes in frequency (a) and dissipation (b) were measured at n = 3, 5, 7, 9, and 11 overtones over time indicated in the legend. The black line represents the response of the uncoated sensor in which frequency and dissipation values for all

overtones overlapped. Experiments were performed in duplicates for both uncoated and coated sensors.

Monitoring of the dissipation was essential in determining the applicability of the Sauerbrey model, which describes a linear relationship between the change in resonance frequency and change in mass (*Equation 1*). The Sauerbrey model is only applicable for thin, rigid, and evenly distributed films. It should only be used when there are no significant dissipation shifts and the frequency shifts do not spread between overtones. Since Figure shows an increase in dissipation during exposure to arsenic; thus the Sauerbrey model does not apply. Biolin Scientific's QSense DFind software was used to confirm that the Sauerbrey model poorly fit the data ($R^2 = 0.0$). In the case of the iron-lignin experiment (Figure 2), minimal changes in the dissipation were observed during the experiment, however, the large amount of noise could indicate uneven distribution of iron on the sensor. Using the Biolin Scientific's QSense DFind software, the Sauerbrey model was applied to the data which yielded an R^2 of 0.15 indicating that the Sauerbrey model was not a good fit in this case.

The data in Figure shows an increase in dissipation as the adhering layer was formed meaning a viscoelastic model would better describe the data. Biolin Scientific's QSense DFind software was used to model the binding of arsenic to xylan using the Kelvin-Voigt model (*Equation 3, 4, 5*). The model was used to estimate the mass adsorbed to the surface and the thickness of the layer created during the binding of arsenic to xylan and the subsequent washing step as shown in Figure 2 **Error! Reference source not found.** (R^2=0.73).
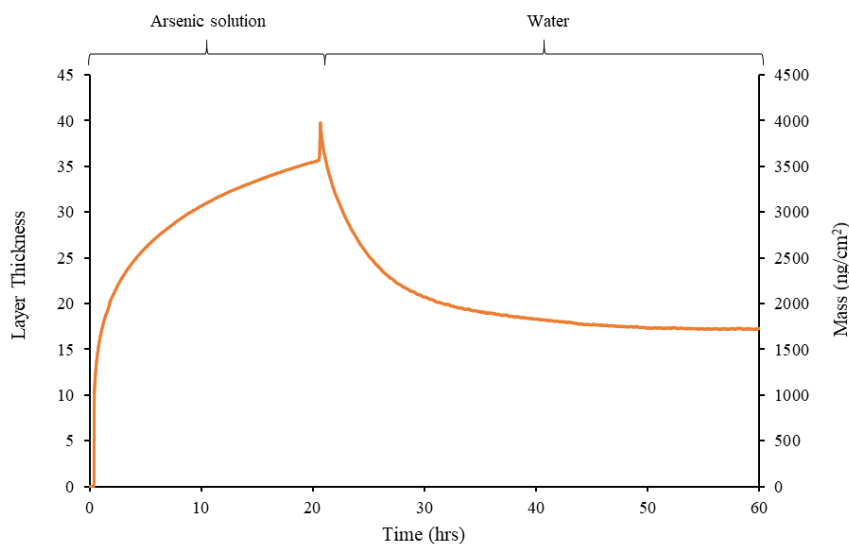

Figure 3. Kelvin-Voigt viscoelastic modelling of layer thickness and mass changes over time. Xylan-coated SiO$_2$ QCM-D sensors were exposed to 100X diluted Inorganic Ventures Arsenic standard solution as indicated by the braces. After approximately 21 hrs, the sensors were washed with Milli-Q water to assess the reversibility of binding. Modelling was fit with Biolin Scientific's QSense DFind software (R^2=0.73).

The Kelvin-Voigt model was also applied to the iron-lignin data from Figure 2 The mass adsorbed to the surface and the thickness of the layer created during the binding and subsequent washing step was estimated (R^2=0.87). The results are shown in Figure 4
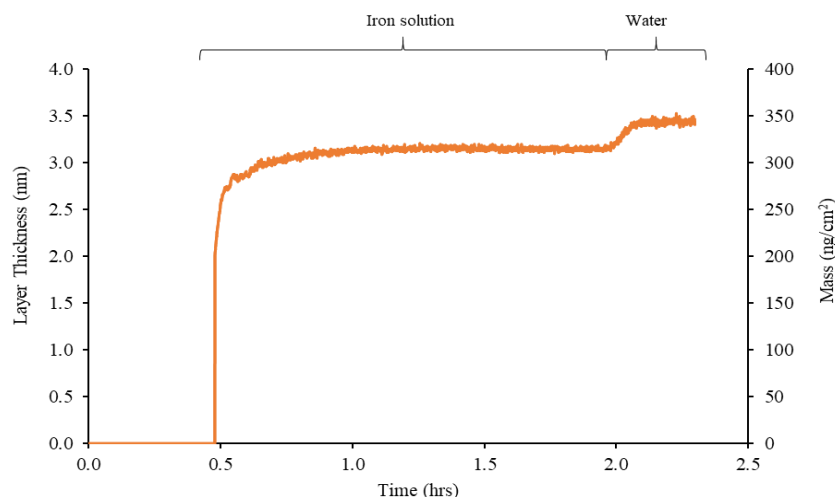
Figure 4. Kelvin-Voigt viscoelastic modelling of layer thickness and mass changes over time. Lignin-coated SiO_2 QCM-D sensors were exposed to 100X diluted Inorganic Ventures Iron standard solution as indicated by the braces. After approximately 2 hrs, the sensors were washed with Milli-Q water to assess the reversibility of binding. Modelling was fit with Biolin Scientific's QSense DFind software (R^2=0.87).

Similarly to the two examples described above, the adsorption of xylan or lignin by other metal ion solutions and the commercial CCA solution was explored by QCM-D. In all cases, the Sauerbrey model was a poor fit to the data and the Kelvin-Voigt viscoelastic model was used to estimate the mass adsorbed and the layer thickness. The results are summarized in **Error! Reference source not found.**Figure 5 below.
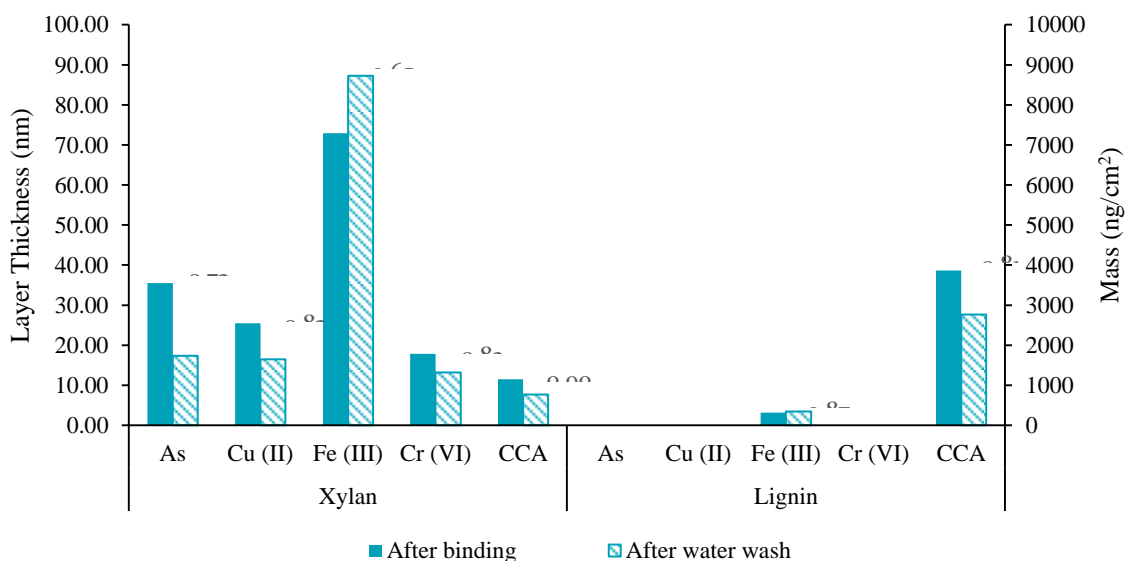

Figure 5. Thickness and mass of the adhering layer of preservative (CCA) or preservative component (Cu (II), Fe (III), As, and Cr(VI)) on xylan- or lignin-coated SiO_2 QCM-D sensors. The Kelvin-Voigt viscoelastic model was used to estimate the layer thickness after binding and after washing the

sensors with water. The R² for each model fit is indicated above the bars. No binding was observed for As, Cu (II), and Cr (VI) with lignin.

As mentioned, arsenic was found to adsorb to xylan, where adsorption was only partially reversible. By contrast, adsorption of arsenic to lignin was not detected.

Like arsenic, copper (II) also adsorbed to xylan, where adsorption was partially reversible. This observation is consistent with studies that show the carboxylic acids or uronic acids of glucuronoxylan bind to Cu(II) [12-13]. Past studies suggest that hydroxyl or methoxyl groups within lignin are potentially suitable for chelation with Cu(II) since complexes with the model compound, guaiacol, have been observed [14]; however, adsorption of copper to the organosolv lignin used in the current study was not observed.

Iron was found to irreversibly bind both xylan and lignin. Notably, the observed interaction between iron (III) and lignin is consistent with a previous study by Schmalzl *et al.*, in which interaction between the model compound, guaiacol, and iron (III) was observed [19].

The binding of chromium (VI) to xylan was partially reversible whereas binding to lignin was not observed. Chromium (VI) is found as CrO_4^{2-} in some preservative formulations, therefore, our study may not represent true interactions between chromium and wood components in preservative applications [1].

To compare interactions between wood components and individual preservative chemicals with a complete preservative formulation, the binding of a commercial CCA-type with lignin and xylan was studied. Figure shows the adsorbance of a CCA-type preservative to both lignin- and xylan-coated sensors. Binding had some reversibility in each case. All individual components of this preservative (copper, chromium, arsenic) bound xylan so it was expected that the CCA preservative would bind to xylan. However, the binding of lignin with these individual components was not observed. It should be noted that in CCA preservative solutions, chromium is found as trivalent chromium, arsenic as arsenic pentoxide, and copper as copper oxide. The oxidation of these metals may be affecting the interaction with xylan and lignin in our study. In addition, other chemicals in the preservative formulation could be affecting the interaction with wood components.

4. Conclusions

The interaction between preservative chemicals (Cu, As, Cr, and Fe) and wood components (lignin and xylan) was investigated using quartz crystal microbalance with dissipation (QCM-D) monitoring. Iron was found to interact with both organosolv softwood lignin and beechwood glucuronoxylan whereas copper, arsenic, and chromium were found to interact with the xylan only. This preliminary study did not consider the effect of pH, temperature, and interaction between metal ion solutions, which are known to be factors influencing binding of commercial preservatives. Future studies will implement Time of Flight- Secondary Ion Mass Spectroscopy (ToF-SIMS) to confirm metal ion distribution/interaction in copper-based preservative-treated wood. Since different wood types have different ratios of lignin, hemicellulose, and cellulose, deciphering the interaction between metal ions (preservative components) with lignin and hemicelluloses (xylan)

can help to extend the service life of preservative-treated wood by improving their performance when exposed to UV and rain in exterior applications.

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