PERIODATE AND HYPOBROMITE MODIFICATION OF SOUTHERN PINE WOOD TO IMPROVE SORPTION OF COPPER ION

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Milled southern pine wood was modified with sequential treatments of sodium periodate and sodium hypobromite for the purpose of improving copper ion (Cu^{2+}) sorption capacity of the wood when tested in 24-h equilibrium batch tests. The modified wood provided additional carboxyl groups to those in the native wood and substantially increased Cu^{2+} uptake over that of unmodified wood. Sorption capacity (q_e) measured with an unbuffered standard solution increased to a maximum of 7.8 mg Cu^{2+} ion per gram of wood (treated) from 3.1 mg Cu^{2+} ion/g wood (untreated). Samples tested were first sodium ion exchanged to keep the pH of the standard solution from declining during the sorption test. The treatment necessary for maximum q_e was 3% (w/v) periodate for 24 h and 0.8% (w/v) bromine (as hypobromite) for 24 h; both treatments were at room temperature. These conditions corresponded to the maximum periodate concentration and treatment times tested. To further evaluate the efficacy of modification treatments, weight change after each treatment was determined. Weight loss after the periodate stage for any concentration and time used was minor, indicating the selective nature of this reaction. However, most of the weight loss was incurred after hypobromite treatment. Weight loss corresponding to the greatest increase in sorption capacity was 12.6% total from the combined periodate and hypobromite stages. The increase of carboxylate functional groups in the wood was monitored using FTIR/ATR spectroscopy.

Keywords: Periodate; Hypobromite; Selective oxidation; Copper ion sorption; Southern pine wood

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INTRODUCTION

Carbohydrate chemists traditionally have used periodate compounds as an analytical tool for differentiation of ring sizes in sugars. The first documented use was the discovery by Malaprade (1928a,b) that periodic acid would readily cleave and oxidize the α-glycol groups on mannitol. Notably, Fleury and Lange (1932) reported that the periodate reaction was selective for hydroxyl groups attached to adjacent carbon atoms. These early and subsequent uses of periodates utilized the measurement of periodate consumed and formaldehyde and formic acid produced. The relative quantities of these assayed compounds can be useful in determining carbohydrate structure.

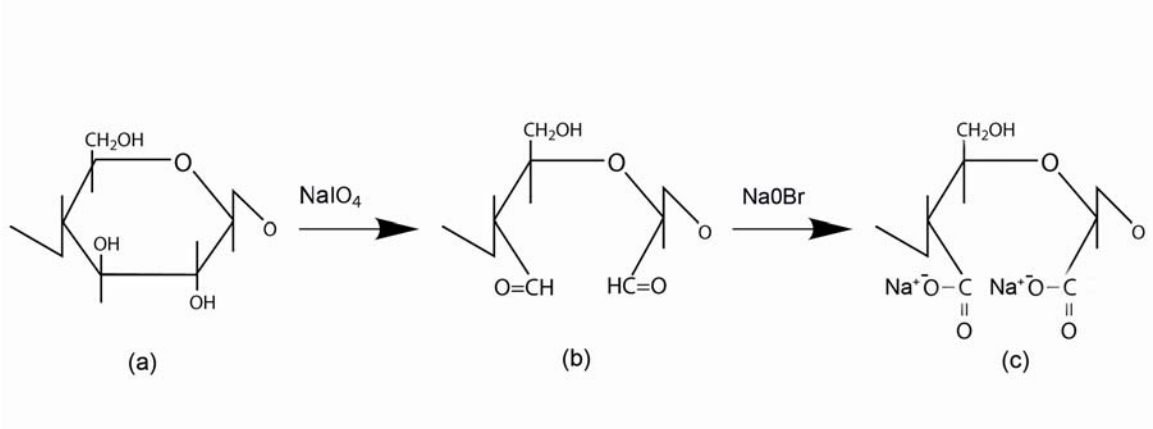

Fig. 1. Reaction of sodium periodate with cellulose glucose sugar unit (a) to produce dialdehyde (b). Sodium hypobromite oxidation of dialdehyde to dicarboxylate (c).

Because of the selective nature of the periodate reaction, we were intrigued by the prospect of employing it as part of a process to increase the carboxylic content of wood, thus improving wood's metal ion sorption capacity. Because polysaccharides constitute the largest fraction of the wood cell wall constituents and they contain a large number of hydroxyl groups, the potential for substantially increasing the number of carboxylate functional groups was expected to be high. Another interesting attribute of the periodate reaction was that it apparently will react with the crystalline as well as amorphous regions of the cellulose (Guthrie 1961). If crystalline regions were inaccessible, as might be expected, then the periodate reaction would be restricted to the amorphous fraction of cellulose, limiting its practical utility.

In addition to the abundance of modifiable functional groups in the wood polysaccharides, the selective nature of the periodate reaction is an important advantage. Glycosidic linkages between sugar units are unaffected by periodate oxidative reactions, avoiding a major decrease in degree of polymerization and loss of the wood substrate.

Periodate was also used as a reactant with the diols of wood polysaccharides by Chen and Rowell (1989). However, their purpose was to modify the wood to improve its resistance to attack by fungi and termites.

The treatment process in our study is a two-step oxidative process. The first step is periodate reacting with the carbohydrate polymers, resulting in ring scission and the formation of a diadehyde within the monomeric units (Figure 1). The resulting aldehydes can then be oxidized to carboxylates in a second step with any number of oxidants; hypohalites are commonly used for this purpose. We are using hypobromite in the second oxidative step because it is a mild oxidant. Our intent is to avoid degradation of the modified wood that can result from an oxidant stronger than hypobromite.

Another study (Maekawa and Koshijima 1984) took a similar approach to ours, in this case using selective oxidation of cellulose powder to enhance its ability to bind with metal ions. In their study, periodate was used in the first oxidation step, and the second oxidation step utilized acid chlorite. They also studied the properties of these modified powders when combined with metal ions. Martin-Dupont et al. (2004) utilized periodic acid as part of a process to modify Douglas-fir bark to increase its binding capacity for

lead ion. Their process differed from ours in that they utilized a reductive amination in a second step to derivatize the dialdehydes with acid-containing groups.

This study is part of a larger research program by our laboratory that is seeking to improve the inherent metal ion sorption characteristics of wood and bark. Our objectives in this study were (1) to test the selective oxidation of southern pine wood and evaluate the results with respect to weight losses from the treatment steps and effect on metal ion sorption capacity as measured with a copper ion test protocol and (2) to monitor increases of carboxylate functional groups in the wood with Fourier transform infrared/attenuated total reflectance (FTIR/ATR) spectroscopy.

MATERIALS AND METHODS

Southern Pine Wood

One inch square by one-half inch thick pieces of wood were processed in a Wiley mill to pass through a 5-mm mesh size screen attached to the mill. The milled wood was sorted into size fractions by the use of 10-, 20-, 30-, and 40-mesh sieve screens in a shaker apparatus. The largest quantity fraction captured was between 10- and 20-mesh screen sizes and was the fraction used for testing. The 10- to 20-mesh wood fraction was oven dried for 4.5 h at 105°C, then stored in a desiccator containing anhydrous calcium sulfate.

Sodium Periodate

ACS reagent sodium periodate (99%) was prepared as an aqueous solution immediately before each use. A glass stirring rod was used to mix dry wood (25 g) in 500-mL periodate solution contained in a 1-L beaker. Separate experiments were conducted with three different concentrations of sodium periodate: 1%, 2%, and 3% (w/v) of reagent in de-ionized water (DI H_2O). Wood and reagent at each concentration level were reacted in separate timed experiments for periods of 6 and 24 h. These reactions were conducted at room temperature. The pH of the sample reaction mixture was checked periodically during each reaction period using a pH meter equipped with a double junction electrode. The target pH range was 3–5, and all samples remained in this range without the need for adjustment.

At the end of each reaction period, the mixture was filtered using vacuum and the filtrate set aside for analysis. Samples then were rinsed with a total of approximately 3 L of DI H_2O. The rinsed samples were placed in approximately 850 mL of DI H_2O and allowed to soak for 24 h to remove entrained periodate. After soaking, the filtered samples were rinsed with approximately 500 mL of DI H_2O and then air dried. Air-dried samples were dried for about 16 h in a 45°C vacuum oven, and then stored in a desiccator.

Sodium Hypobromite

ACS reagent bromine (99.5%) was used to prepare the sodium hypobromite solution immediately before each use. This was accomplished by dispensing with volumetric pipettes 3 mL of bromine in 50 mL Deionized (DI) H_2O containing 5 g

NaOH. From this solution, 5, 10, and 15 mL were transferred with pipettes to 10 g of the 1%, 2%, and 3% periodate-treated samples, respectively, in 300 mL DI H_2O contained in a 500 mL beaker. Samples and reagent were mixed with a glass stirring rod. The three levels of hypobromite (5, 10, and 15 mL) also were mixed with untreated wood to serve as periodate controls. During the reaction period, pH levels of the mixtures periodically were checked with the meter and small amounts of 2 N NaOH added to maintain a pH range of 10–11. Reactions were carried out 24 h at room temperature. At the end of each reaction period, the mixture was filtered using vacuum and the filtrate set aside for analysis. Samples were then rinsed with a total of approximately 3 L of DI H_2O. The rinsed samples were then placed in approximately 700 mL of DI H_2O and allowed to soak for 24 h, to remove entrained hypobromite. After soaking, the filtered samples were rinsed with about 500 mL of DI H_2O and then air dried. Air-dried samples were dried for approximately 16 h in a 45°C vacuum oven, and then stored in a desiccator.

Analysis of Oxidants

Consumption of periodate and hypobromite at the end of the reaction period was determined titrimetrically.

Periodate Consumption

A 5-mL volume of the filtrate from the filtered reaction mixture was added to 10 mL of 0.5 N KI and 20 mL of 1 N HCl in a beaker with magnetic stirring bar. The I_2 formed was titrated with 0.2 N $Na_2S_2O_3{\cdot}5H_2O$ until the endpoint marked by disappearance of the I_2 was visualized by the addition of soluble starch. The following equations from Lange (1961) described the reactions involved in the analysis (except for the periodate cation being K): $KIO_4 + 7KI + 8HCl = 8KCl + 4I_2 + 4H_2O$, therefore $I = KIO_4/8$; $I_2 + 2Na_2S_2O_3{\cdot}5H_2O = 2NaI + Na_2S_4O_6$, therefore $Na_2S_2O_3{\cdot}5H_2O = KIO_4/8$. A similar titration of 5 mL of the starting concentration of periodate also was performed to calculate the change in oxidant concentration. The following calculation was used:

$$\text{Percent change} = [(\text{end mL } Na_2S_2O_3{\cdot}5H_2O - \text{start mL } Na_2S_2O_3{\cdot}5H_2O)/\text{start mL } Na_2S_2O_3{\cdot}5H_2O] \times 100$$

Hypobromite Consumption

Change in hypobromite concentration was determined as its bromine equivalent by acidification of the solution to be analyzed. The filtrate from the filtered reaction mixture was added to 10 mL of 0.5 N KI and 20 mL 1 N HCl in a beaker with magnetic stirring bar. Concentrated HCl was added to the solution until pH was about 0.5 as measured with a pH probe. This shifted the equilibrium of the predominantly hypobromite species in solution to bromine, which readily oxidizes KI to I_2. The I_2 formed was titrated with 0.2 N $Na_2S_2O_3{\cdot}5H_2O$ as in the periodate analysis. The following equations from Lange (1961) described the reactions involved in this analysis: $Br_2 + 2KI = 2KBr + I_2$; $I_2 + 2Na_2S_2O_3{\cdot}5H_2O = 2NaI + Na_2S_4O_6$, therefore $I = Na_2S_2O_3{\cdot}5H_2O$ and $Br = Na_2S_2O_3{\cdot}5H_2O$.

When calculating the percentage change in oxidant at the end of the reaction, the starting concentration of oxidant in the reaction mixture needs to be determined. First, a determination of milliequivalents per milliliter (meq/mL) of Br in the Br_2 stock solution is accomplished using the above titration method and calculating Br(meq/mL) = mL $Na_2S_2O_3 \cdot 5H_2O$ × 0.2 N/mL Br_2 titrated. Then the starting concentration of oxidant in NaOBr is calculated: NaOBr (meq/mL) = mL Br_2 × meq mL^{-1}/mL NaOBr. A measured volume of the NaOBr is added to the reaction mixture (wood + H_2O) and starting oxidant concentration is NaOBr (meq/mL) = mL NaOBr added × meq mL^{-1}/reaction mixture volume (mL). With the starting concentration of oxidant in each reaction mixture known, the following calculation is used to determine the change in oxidant concentration: %change = [(end meq/mL – start meq mL^{-1})/start meq/mL] × 100.

Weight Loss

The selectivities of treatments were compared by measuring recovered weights of the treated samples after each treatment and rinsing, air-drying, and drying in a vacuum oven for 16 h at 45°C. The percentage change in weight was calculated with the following formula:

$$\text{Percent change} = [(\text{end weight} - \text{start weight})/\text{start weight}] \times 100$$

Sodium Ion Exchange

Samples that were not subject to a treatment under alkaline conditions (untreated and periodate-treated only) were sodium ion exchanged before Cu^{2+} ion sorption testing to prevent pH decline during the test. Samples (2.5 g) were placed in 150-mL beakers containing approximately 71 mL of DI H_2O and 4 mL of 0.05 M NaOH. The samples were mixed with a glass stirring rod and adjusted to about pH 11. During the 24-h reaction period at room temperature, sample pH was checked occasionally, and the pH was maintained at 10–11 with small additions of 0.05 M NaOH. After the 24-h reaction, samples were rinsed, air dried, and vacuum oven dried for 4.5 h at 45°C and stored in a desiccator until sorption testing.

Copper Ion Sorption

The efficacy of each modifying treatment was evaluated by testing sorption capacities of unmodified and modified wood with copper ion solutions. Each treatment regime tested (including periodate, hypobromite controls, and untreated) was triplicated. The copper ion standard acquired was 1000 mg/L atomic absorption standard solutions consisting of copper nitrate in 1% nitric acid. Before using in the sorption experiments, the standard solution was diluted to 50 mg/L and pH was adjusted with sodium hydroxide to pH 4.6. Samples were tested for sorption capacities in 24-h equilibrium experiments.

Approximately 100 mg of sample with weight recorded was placed in a 60-mL screw cap bottle, and 50 mL of the diluted standard was added. Bottles were shaken for 24 h at 150 revolutions per minute at room temperature on an oscillator. Shaking was alternated in both clockwise and counter-clockwise directions. After the shaking period, pH of the sample was checked with a pH meter equipped with a double junction electrode. To ensure a particle-free sample for copper ion analysis, 10 mL of the liquid

from the sample bottle was removed with a syringe and filtered through a 0.45-µm nylon syringe filter. Filtered samples were then analyzed for copper ion (Cu^{2+}) concentration with an inductively coupled plasma–atomic emission spectrometer instrument. Equilibrium sorption capacities were calculated by the following formula:

$$q_e = V(C_0 - C_e)/M$$

where V is volume of Cu^{2+} ion solution (L), M is mass of sample (g), C_0 is starting concentration of Cu^{2+} ion solution (mg/L), and C_e is end concentration of Cu^{2+} ion solution with wood sample after 24 h (mg/L), and q_e is Cu^{2+} sorption (mg/g sample).

FTIR Spectroscopy

Carboxylate functional groups in the wood samples were characterized using an FTIR spectrometer equipped with a single reflection attenuated total reflection (ATR) accessory. The carboxylate carbonyl band absorbance (approximately 1600 cm^{-1} band) depicted was normalized against the approximately 1320 cm^{-1} band associated with the cellulose C–H bending mode.

RESULTS AND DISCUSSION

Oxidative Treatment Effects on q_e and FTIR Spectra

Table 1 shows the effects of the oxidative treatments with regard to oxidant consumption, wood sample weight loss, and Cu^{2+} ion sorption (q_e). For periodate treatments only, smaller (than with second oxidation step) increases in q_e were apparent with increasing concentration of oxidant (samples 1–7). These reactions are expected to result in mainly the formation of aldehyde end groups from the scission of adjacent hydroxyl groups in sugar molecules. Without the subsequent hypobromite oxidation step to a carboxylic acid/carboxylate, the end group lacks the ability to exchange a metal ion for H^+/Na^+. The q_e increase from periodate-only treatment could be partially due to the polar nature of the newly created aldehyde carbonyls chelating Cu^{2+} ions (in contrast to ion exchange). However, FTIR scans of the 24-h periodate-treated samples (Fig. 2) indicated that the absorbance bands in the approximately 1600 cm^{-1} region corresponding to carboxylate follow a pattern of increase with periodate level (similar to the increases of q_e), as compared with the untreated sample; the 6-h spectra are not shown but are very similar to the 24-h spectra. This would seem to indicate that some of the aldehyde groups have undergone oxidation to carboxylate groups. It is known that some aldehydes present in carbohydrates are capable of being oxidized to carboxyls by air oxidation. In fact, the aldehyde group is one of the most easily oxidized groups in carbohydrates (Green 1957).

Table 1. Oxidative Treatments on Milled Southern Pine Wood

Sample	Treatment[a,b,c]	Change in oxidant (%)	Weight change after treatment (%)	q_e[d] (mg Cu^{2+} per g sample)	2 x std. dev. of q_e
1	Untreated			3.1	0.6
	Single-stage treatments				
2	1% periodate for 6 h	–20.3	–2.9	3.8	0.3
3	2% periodate for 6 h	–19.8	–2.8	4.0	0.2
4	3% periodate for 6 h	–22.6	–3.3	4.2	0.9
5	1% periodate for 24 h	–29.2	–1.9	3.7	0.3
6	2% periodate for 24 h	–29.2	–2.6	4.2	0.2
7	3% periodate for 24 h	–18.1	–2.5	4.2	0.8
8	0.3% Br_2 for 24 h	–45.8	–2.1	3.7	0.2
9	0.6% Br_2 for 24 h	–25.9	–1.4	4.0	0.4
10	0.8% Br_2 for 24 h	–22.9	–0.9	4.1	0.3
	Two-stage treatments				
11	1% periodate for 6 h, 0.3% Br_2 for 24 h	–20.3, –90.9	–2.9, –2.8 Total: –5.7	4.5	0.7
12	2% periodate for 6 h, 0.6% Br_2 for 24 h	–19.8, –89.8	–2.8, –5.9 Total: –8.7	5.9	0.1
13	3% periodate for 6 h, 0.8% Br_2 for 24 h	–22.6, –89.1	–3.3, –14.0 Total: –17.3	6.9	0.3
14	1% periodate for 24 h, 0.3% Br_2 for 24 h	–29.2, –82.6	–1.9, –3.4 Total: –5.3	4.7	0.6
15	2% periodate for 24 h, 0.6% Br_2 for 24 h	–29.2, –85.3	–2.6, –5.6 Total: –8.2	7.0	0.7
16	3% periodate for 24 h, 0.8% Br_2 for 24 h	–18.1, –87.7	–2.5, –10.1 Total: –12.6	7.8	0.5

[a] Oxidant percentage is w/v.
[b] Percentage Br_2 as sodium hypobromite.
[c] Untreated and single-stage periodate-treated samples Na^+ exchanged.
[d] q_e sorption values an average of three replicates.

Similar to periodate-only, the hypobromite-only treated samples exhibited increases to q_e (samples 1, 8–10) and the FTIR 1600 cm^{-1} region, indicative of the formation of new carboxyl groups (Fig. 3). It is known that hypobromite is capable of oxidation of the polysaccharide primary and secondary hydroxyl groups directly to carboxyl groups; however, the yield is low (Green 1957).

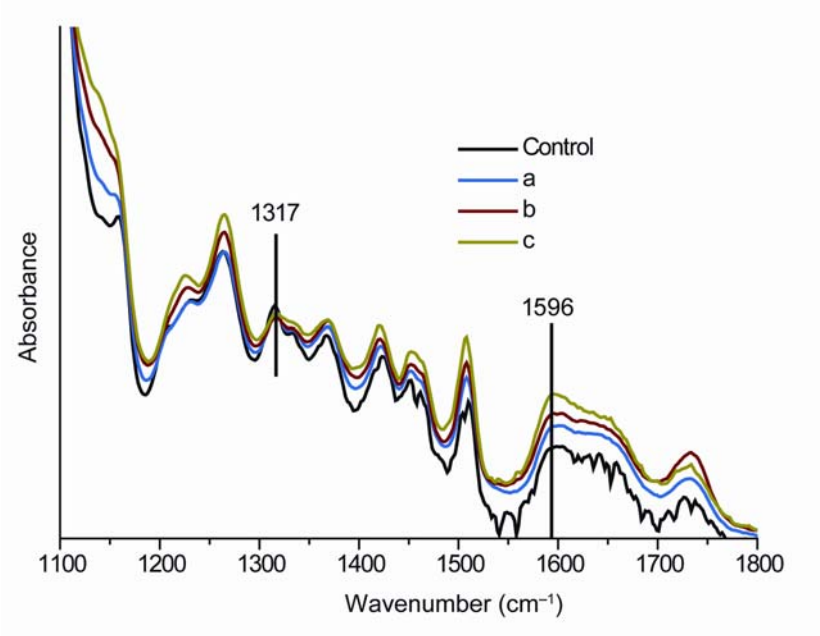

Fig. 2. FTIR scan of 24-h periodate-treated and Na-exchanged southern pine; Na^+-exchanged untreated southern pine, showing carboxylate absorption region (1596 cm^{-1}). Baseline normalized at 1317 cm^{-1}. Control, untreated; a, 1% periodate for 24 h; b, 2% periodate for 24 h; c, 3% periodate for 24 h.

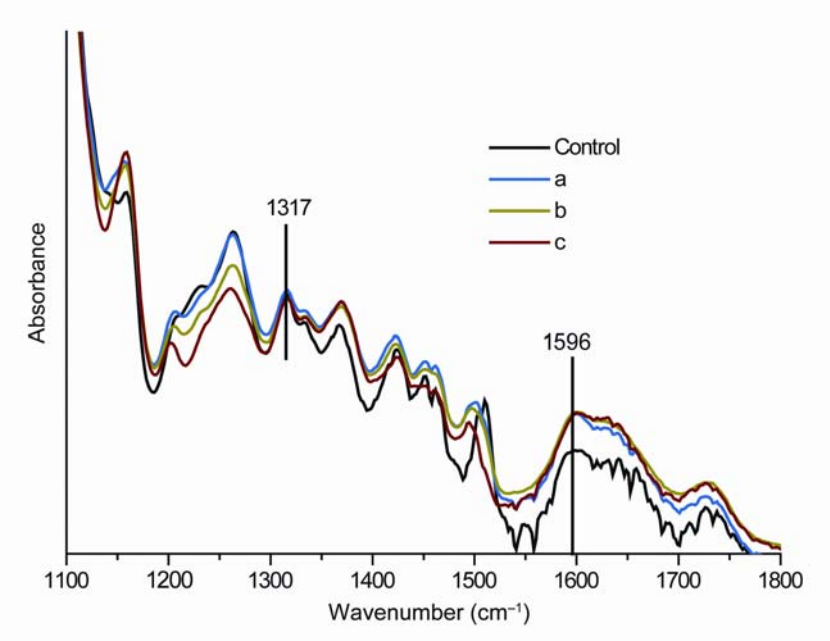

Fig. 3. FTIR scan of Br_2-treated (as sodium hypobromite) southern pine; Na^+-exchanged untreated southern pine, showing carboxylate absorption region (1596 cm^{-1}). Baseline normalized at 1317 cm^{-1}. Control, untreated; a, 0.3% Br_2 for 24 h; b, 0.6% Br_2 for 24 h; c, 0.8% Br_2 for 24 h.

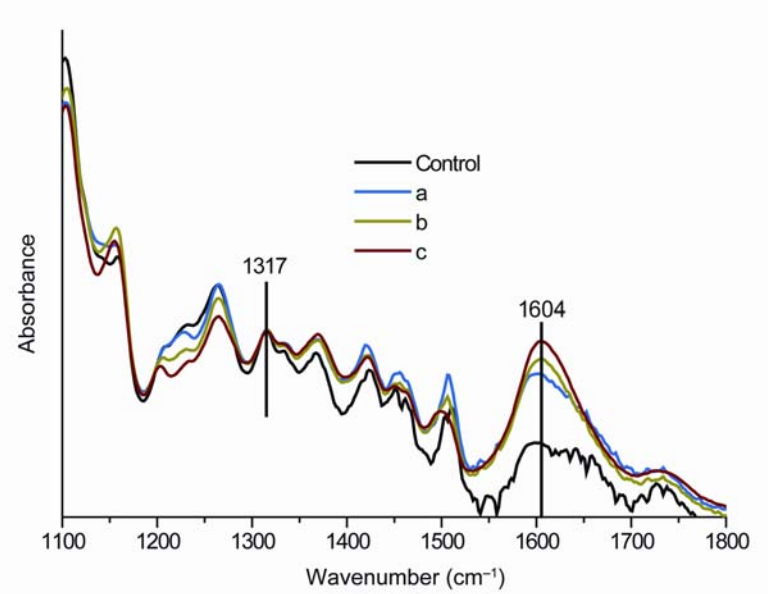

Fig. 4. FTIR scan of 6-h periodate-treated and Br_2-treated (as sodium hypobromite) southern pine; Na^+-exchanged untreated southern pine, showing carboxylate absorption region (1604 cm^{-1}). Baseline normalized at 1317 cm^{-1}. Control, untreated; a, 1% periodate for 6 h, 0.3% Br_2 for 24 h; b, 2% periodate for 6 h, 0.6% Br_2 for 24 h; c, 3% periodate for 6 h, 0.8% Br_2 for 24 h.

The effect of a two-stage oxidative sequence (periodate and hypobromite) was apparent even at the lowest oxidant (1% periodate, 0.3% Br_2) level, and particularly at the two highest oxidant (2% and 3% periodate, 0.6% and 0.8% Br_2) levels. This effect is evident when viewing the q_e values (samples 1, 11–13) and the FTIR 1600 cm^{-1} region absorbance (Fig. 4) for 6-h periodate treatment sequences, as compared with the periodate- or hypobromite-only treatments. The effect of time of the longer (24 h) periodate treatments is apparent (samples 1, 14–16; Fig. 5), yielding further increases to sorption values and the carboxylate functional groups of the modified wood. The FTIR scans for the 24-h periodate treatment sequence give perhaps the most sensitive indication of the differential effects of the three periodate levels used (1%, 2%, and 3%).

Weight Loss

The single-stage oxidation treatments had only minor weight losses of approximately 1% to 3% (samples 2–10). Weight losses began to increase noticeably after the second oxidative (hypobromite) stage, particularly at the 2% and 3% periodate levels. At these higher periodate levels, the shorter treatment time of 6 h did not appear to be a mitigating factor with respect to weight loss (samples 11–16; Figs. 6 and 7). However, the higher weight loss for sample 13 as compared to sample 16 seems anomalous and likely is an error. Clogging of the filter paper pores was a problem with sample 13 after the hypobromite stage, causing some sample loss. A switch in filter paper brand with sample 16 decreased the clogging problem.

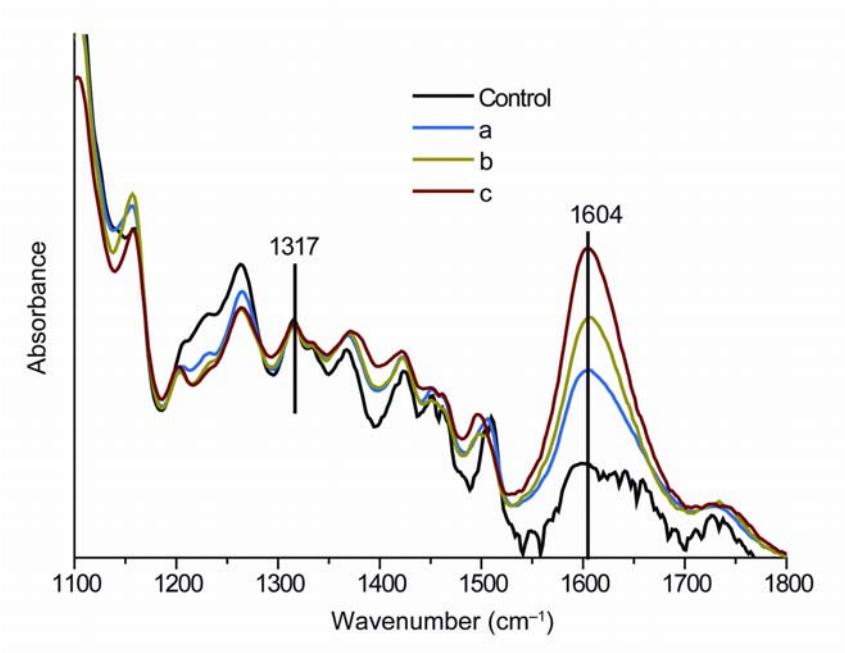

Fig. 5. FTIR scan of 24-h periodate-treated and Br_2-treated (as sodium hypobromite) southern pine; Na^+-exchanged untreated southern pine, showing carboxylate absorption region (1604 cm^{-1}). Baseline normalized at 1317 cm^{-1}. Control, untreated; a, 1% periodate for 24 h, 0.3% Br_2 for 24 h; b, 2% periodate for 24 h, 0.6% Br_2 for 24 h; c, 3% periodate for 24 h, 0.8% Br_2 for 24 h.

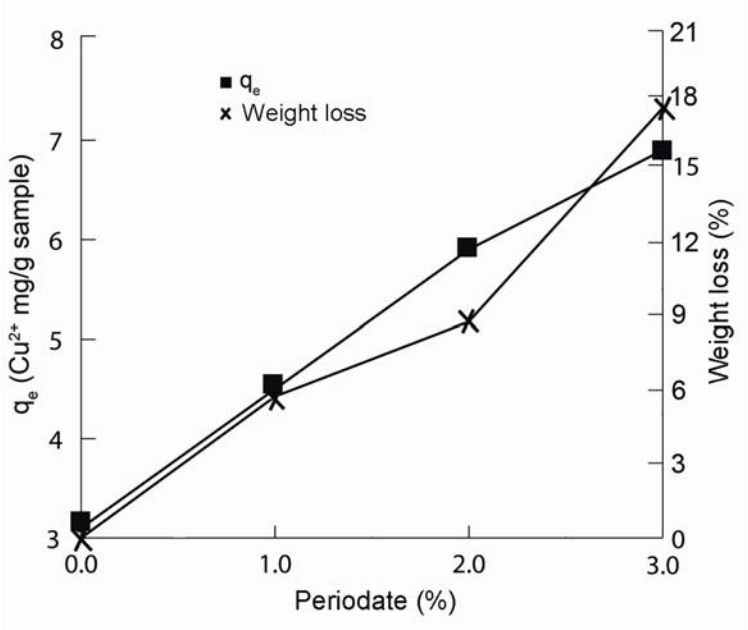

Fig. 6. Six-hour periodate and hypobromite treatments on southern pine wood showing effect of percentage periodate on Cu^{2+} sorption capacity and weight loss of sample. The point at 0% periodate and 0% weight loss is Na^+-exchanged untreated wood.

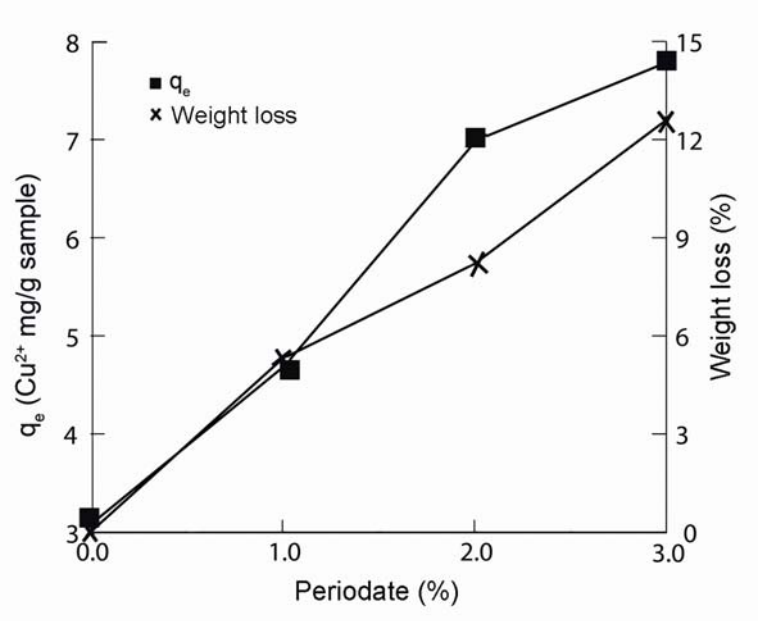

Fig. 7. Twenty-four-hour periodate and hypobromite treatments on southern pine wood showing effect of percentage periodate on Cu^{2+} sorption capacity and weight loss of sample. The point at 0% periodate and 0% weight loss is Na^{+}-exchanged untreated wood.

It is reasonable to infer that these higher periodate levels began to show a loss of selectivity that has been described as "over-oxidation," with cleavage of other types of carbohydrate bonds (Bobbitt 1956). This could occur when periodate levels are much greater than what is needed to react with just the available α-glycol groups. In Table 1, it can be seen that periodate consumed was only 20% to 30%, for either the 6- or 24-h reactions. It is interesting that the 2% and 3% periodate levels used in a single treatment stage did not result in similarly notable weight losses, as when combined with the second hypobromite stage. A possible explanation for this is that the alkaline pH conditions used in the hypobromite stage swell the fibers and allow washing out of the oxidative cleavage fragments. Because the weight loss was not observed in the hypobromite-only treatments (with alkaline pH), fragmentation must occur during the periodate stage.

Oxidation of lignin structures could be a minor contributor to weight loss of periodate-treated wood. However, we did not expect this reaction to be a major source of weight loss because periodate has been used to isolate lignin (retaining its polymeric structure) from the carbohydrate fraction of the wood. For example, Eisenbraun and Purves (1961) accomplished this by reacting a large quantity of sodium periodate (30% w/w) with spruce wood meal at pH 3.6 to 4.0 and then removing the carbohydrate fragments with a 0.1 N sodium hydroxide solution. This oxidation/extraction procedure was repeated four or five times.

It may be that a weight loss of more than 10% is a necessary trade off to produce a large number of new carboxyl groups from the modified wood. However, it may be

possible to attain higher yields of carboxyl groups while avoiding the effects of over-oxidation by increasing the reaction time at room temperature, while keeping the levels of periodate used less than 2%.

Another potential improvement in efficiency might be found by utilizing the solubilized oxidative fragments lost to the water rinse after treatment that may also contain some carboxyl groups. This might be done by treating the reaction mixture after each oxidation stage with a reducing compound to quench the excess oxidant; the excess base in the hypobromite stage could then be neutralized with acid. Finally, the excess water would need to be evaporated from the mixture.

An added benefit from recovery of the fragments is a reduction of organic compounds in waste water. This step reduces oxygen-consuming materials before they are added to the environment.

An alternative method to contain the filtration media would need to be used to avoid the loss of the smaller fragments when the modified materials are contained in a porous envelope or filter apparatus. This laboratory is currently testing a method to address the loss of fine media and avoid clogging of the filter apparatus by employing an extruder to make the wood or bark media into pellets. Very fine materials and those that are easily lost when contained within a porous envelope or filter mat can be utilized with this method.

CONCLUSIONS

1. Wood carbohydrates can be modified with room-temperature sequential oxidative treatments utilizing sodium periodate to convert α-glycol groups to dialdehydes, and sodium hypobromite to convert the dialdehydes to carboxylates, thereby substantially increasing the wood's Cu^{2+} ion sorption capacity and improving its utility as a heavy metal filter material.
2. The highest experimental treatment level of periodate (3% w/v followed by 0.8% Br_2 w/v as sodium hypobromite) increased the wood's Cu^{2+} ion sorption capacity by 148% and also resulted in a 12.6% weight loss from the water washing loss of soluble fragments.
3. To realize the full benefit of the selective nature of periodate oxidation, the level of periodate used may need to be adjusted close to a stoichiometric quantity for the number of glycol groups reacted.

REFERENCES CITED

Bobbitt, J. M. (1956). "Periodate oxidation of carbohydrates," In: M. L. Wolfram (ed.), *Advances in Carbohydrate Chemistry, 11.* Academic Press, Inc., New York, pp. 1-41.

Chen, G. C., and Rowell, R. M. (1989). "Fungal and termite resistance of wood reacted with periodic acid or sodium periodate," *Wood Fiber Sci.* 21, 163-168.

Eisenbraun, E., and Purves, B. (1961). "Condensation of spruce periodate lignin with formaldehyde," *Can. J. Chem.* 39, 1518-1529.

Fleury, P. F., and Lange, J. (1932). "The oxidation of acid alcohols and sugars by periodic acid," *Comptes Rendus.* 195, 1395-1397.

Green, J. W. (1957). "Acids and oxidation products," In: Pigman, W. (ed.), *The Carbohydrates. Chemistry, Biochemistry, Physiology*. Academic Press, Inc., New York, pp. 299-366.

Guthrie, R. D. (1961). "The 'dialdehydes' from the periodate oxidation of carbohydrates," In: Wolfrom, M. L. (ed.), *Advances in Carbohydrate Chemistry, 16*. Academic Press, Inc., New York and London, pp. 105-158.

Lange, N.A. (ed.) (1961). *Handbook of Chemistry, 10th edn*. McGraw-Hill Book Company, Inc., New York, Toronto, London. 1969 pp.

Maekawa, E., and Koshijima, T. (1984). "Properties of 2,3-dicarboxy cellulose combined with various metallic ions," *J. Appl. Polymer Sci.* 29, 2289-2297.

Malaprade, L. (1928a). "Oxidation of some polyalcohols by periodic acid—applications," *Comptes Rendus*. 186, 382-384.

Malaprade, L. (1928b). "Action of polyalcohols on periodic acid. Analytical application," *Bulletin de la Societe Chimique de France* 43, 683-696.

Martin-Dupont, F., Gloaguen, V., Granet, R., Guilloton, M., and Krausz, P. (2004). "Chemical modifications of Douglas fir bark, a lignocellulosic by-product—enhancement of their lead (II) binding capacities." *Separation Sci. Technol.* 39(7), 1595-1610.

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