Effect of Citric Acid Modification of Aspen Wood on Sorption of Copper Ion

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ABSTRACT. Milled aspen wood was thermochemically modified with citric acid for the purpose of improving the copper (Cu^{2+}) ion sorption capacity of the wood when tested in 24-hour equilibrium batch tests. The wood-citric acid adducts provided additional carboxyl groups to those in the native wood and substantially increased Cu^{2+} ion uptake of the modified wood compared with that of the unmodified wood. Sorption capacity (q_e) measured with an unbuffered standard solution increased to a maximum of 7.9 mg Cu^{2+} ion/g of wood (treated) from 1.3 mg Cu^{2+} ion/g wood (untreated). When measured with a buffered standard solution, the q_e increased to a maximum of 13.8 mg Cu^{2+} ion/g of wood (treated) from 4.1 mg Cu^{2+} ion/g wood (untreated). The treatment necessary for maximum q_e was 2 hours at 130°C. Modification treatments included three time periods (2, 4, 6 hours) and three temperature regimes (110, 120, 130°C). To further evaluate the efficacy of modification treatments, weight change after treatment was monitored as an indirect measure of bound citric acid. It was found that increases to the original mass of greater than about 30% were associated with no further increase or a decline in q_e. The contribution of citric acid ester linkages to increasing mass at longer reaction times was monitored with ATR/FTIR. *[Article copies available for a fee from The Haworth Document Delivery Service: 1-800-HAWORTH. E-mail address: <docdelivery@haworthpress.com> Website: <http://www.HaworthPress.com>]*

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INTRODUCTION

The development of filters to clean our water supply is a big business. It is estimated that global spending on filtration will increase from \$17 billion in 1998 to \$75 billion by 2020 (Noble 2000). The fastest-growing non-industrial application for filter media is to generate clean water.

It has been shown that lignocellulosics such as wood and bark can remove heavy metals from water. Wood and bark structures are very porous and have a very high free surface volume that allows aqueous solutions to access cell wall components. Laszlo and Dintzis (1994) showed that wood's ion exchange capacity and general sorptive characteristics are derived from their constituent polymers and structure. The polymers include extractives, cellulose, hemicelluloses, pectin, lignin and protein. These polymers adsorb a wide range of solutes, particularly divalent metal cations (Lee and Rowell 2004, Kmiecik et al. 2005). Tannin and lignin, polyphenolic compounds contained in wood, are believed to be the active sites for attachment of heavy metal cations. Reddad et al. (2002) showed that the anionic phenolic sites in lignin had a high affinity for heavy metals. Mykola et al. (1999) also showed that the galacturonic acid groups in pectins were strong binding sites for cations.

A facet of our research program involves experimental protocols for modifying and ultimately increasing the metal sorption capacities of wood and bark. In this study, the feasibility of bonding citric acid to aspen wood was evaluated to increase its ion exchange potential and thus its capacity for metal cation sorption. Aspen was selected because it has a lower Cu^{2+} ion sorption capacity compared with some other hardwood species (Šćiban and Klašnja 2004). Aspen is also plentiful because it is often managed by even-aged large-scale harvesting. We employed a thermochemical reaction that results in an ester bond formed between a carboxylic acid group of citric acid and a hydroxyl group on the wood. This method has the advantages of using a low toxic and low-cost reactant and it is simple to effect–evaporation of water and heating of reactant and substrate are all that is required. These advantages should enable its use in an environment removed from the laboratory, such as close to where the wood is harvested and where the modified wood is employed for water clean-up.

Others have used this thermochemical method with citric acid on non-wood lignocelluloses such as agricultural by-products. Wing (1996a,b, 1997) showed that reacting citric acid with corn fibre, ground corn cobs, starch, and cellulose fibre greatly increased sorption of Cu^{2+} ion by these materials. Other agricultural by-products including corn distillers' grains, soy protein isolates, and soybean hulls were similarly modified by citric acid for enhanced copper ion sorption (Wing et al. 1997; Sessa and Wing 1998; Marshall et al. 1999). Vaughan et al. (2001) found that corn cobs could be effectively modified with either citric acid or phosphoric acid, and sorption properties were enhanced for heavy metal ions such as cadmium, nickel, zinc, and copper. However, availability of the wood cellulose hydroxyl groups to citric acid is limited, since wood cellulose has crystalline regions that are relatively impervious to liquid penetration. Low et al. (2004) showed that pine wood could be modified with citric acid and demonstrated an increase in sorption of Cu and Pb ions.

There has been an interest in using citric acid and other multifunction carboxylic acid compounds to improve mechanical properties of paper and textile products, without using formaldehyde (Trask-Morrell, Kottes-Andrews et al. 1991; Yang and Xu 1998). The methods that have been studied usually employ a compound with three or more acid groups that are reacted thermochemically to esterify cellulose hydroxyls. In these cases, the objective was to create two or more ester crosslinkages per acid molecule between the cellulose units. The crosslinkages improve wet strength for paper products and enhance permanent press properties in textiles. A compound consisting of a minimum of two acid groups such as maleic acid and succinic acid could be used; however, it is difficult to achieve a second esterification reaction necessary for a crosslink. This is thought to be due to the need to form a 5 or a 6-member anhydride ring intermediate for a facile reaction, which would not be available after the first esterification reaction (Welch and Kottes-Andrews 1989) (Choi 1992). In our case, this would not be a concern since a crosslink is undesirable as it removes an available ion exchange site. We did not evaluate the di-acids or multifunction acids larger than citric acid, because of greater toxicity and cost considerations. In addition, another consideration favors the citric acid compound. While any other larger acid, for example, butanetetracarboxylic acid, should present more ion exchange sites, than citric acid, this may not be the case in actual practice. There is evidence that the larger acid will crosslink to a greater extent because of its ability to form simultaneous anhydride intermediates, thus losing the potential additional ion exchange sites (Caulfield 1994).

The citric acid modification mechanism has two steps. The first involves formation of a reactive internal anhydride (5-member ring formation) between two adjacent carboxylic acid groups of the citric acid molecule, resulting in the loss of one molecule of water. In the second step, the anhydride reacts with a wood hydroxyl group to form an ester linkage between the two substrates and leaves two acid groups remaining on the citric acid molecule. Every molecule of bound citric acid thus has potentially two available exchange sites for metal cations to bind if the thermochemical reaction does not proceed any further. If the reaction temperature is sufficiently high and/or the reaction time is long enough, a second carboxylic acid on the citric acid can form another bond with the wood (crosslink) (Figure 1). Finally, the remaining carboxylic acid can form an external anhydride with an acid group of the wood resulting in another crosslink with no remaining acid functions of the citric acid molecule. This may reduce the ion exchange capacity of the wood.

The heavy metal cation copper was used to evaluate the modified and unmodified wood because water analyses indicated it was a common pollutant in the streams near the area of the collected wood.

MATERIALS AND METHODS

Aspen Wood. Wood for citric acid treatments was prepared from aspen tree cross-section cuttings taken from the Beaverhead-Deerlodge National forest in Southwest, Montana. The bark was removed with a

FIGURE 1. Reactions of citric acid with wood hydroxyl groups.
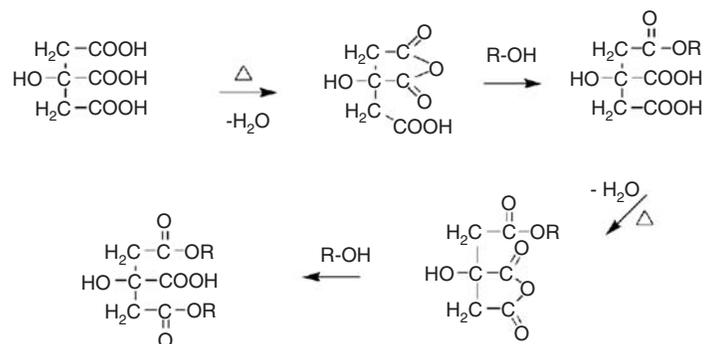
chisel from these sections before comminuting the wood into an easily treated form. Bark was not included for treatment due to its different sorption capacity from the wood and varying bark thickness could complicate results. In addition we have found that bark exhibits a significantly different response to modifying treatments to increase metal ion sorption. Debarked sections were cut with a band saw into approximately 2 inch cube size material that was ground in a Wiley mill to pass through a 5 mm mesh size screen. The milled wood was oven dried for 3 hours at 105°C, then stored in a desiccator containing anhydrous calcium sulfate until use in experiments.

Citric Acid Treatments. ACS Reagent citric acid (anhydrous) was prepared as an aqueous solution. Aliquots of 10 ml of the aqueous solutions of citric acid (200 g/l) were dispensed into 50 ml beakers, each containing 2 g of milled wood. Samples were mixed with a glass stirring rod and the mixtures allowed to equilibrate at room temperature for one-half hour. Water was removed from the samples by placing them in a forced air oven at 60°C for a period of 4 hours. Raising the oven temperature caused a thermochemical reaction bonding the citric acid to wood. Time and temperatures tested were 2, 4, and 6 hours at 110, 120, and 130°C, respectively. After the reaction period, 25 ml of de-ionized water was added to the sample, mixed with a glass stirring rod, and equilibrated for one-half hour. The excess water containing unreacted citric acid was removed by a vacuum flask and funnel equipped with paper filter. Samples were then rinsed with a volume of about 600 ml of de-ionized water. The final volume of rinse water used was checked with short-range pH paper (3-5.5) to ensure excess citric acid had been removed. Dewatered reacted samples were air dried, and remaining moisture removed by placing in a 45°C vacuum oven for 16 hours.

In addition to the normal citric acid treated samples, a citric acid control sample was treated according to the above procedure but without the elevated thermochemical reaction temperature.

Mass Balance. The effectiveness of bonding citric acid to wood was estimated by comparing the recovered weights of the treated samples and control. The wood samples were left in pre-weighed filter papers after the post-treatment water rinse and the two together were vacuum oven dried in order to eliminate or minimize handling losses. The percentage change in weight was calculated with the following formula:

$$\% \text{ Change} = (\text{End weight} - \text{Start weight/Start weight}) \times 100$$

Copper Ion Sorption. The efficacy of citric acid reactions with aspen wood was evaluated by testing the modified wood sorption capacities with copper ion solutions. Each treatment regime tested (including control and untreated) was done in triplicate. In addition to the citric acid control, the untreated wood (without citric acid soak and water rinse) was included for comparison. We assumed that exposing the wood to a citric acid solution and water rinse, could affect the apparent sorption capacity of unmodified wood. The copper ion standard used was 1000 mg/l of 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 with NANOpure™ water and pH was adjusted with sodium hydroxide. Testing was done with one standard adjusted to pH 4.6 (unbuffered) and another adjusted to pH 5.1, buffered to 0.01 M sodium acetate. Samples were tested for sorption capacities in 24-hour equilibrium experiments. Approximately 100 mg of weight recorded sample was placed in a 60 ml screwcap bottle and 50 ml of the diluted standard added. Bottles were shaken for 24 hours at 150 revolutions per minute at room temperature on a Thermolyne oscillator. Shaking was alternated in both clockwise and counter-clockwise directions. After the shaking period, pH of the sample was checked with an Accumet® AR25 pH meter equipped with a double junction electrode. To assure 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 micron nylon syringe filter. Filtered samples were then analyzed for copper ion (Cu^{2+}) concentration with a Jobin Yvon, Ultima, inductively coupled plasma–atomic emission spectrometer instrument. Equilibrium sorption capacities were calculated by the following formula:

$q_{e = V (Co-Ce)/M}$ where, V = Volume of Cu^{2+} ion solution (l), M = Mass of sample (g);

C_o = Starting concentration of Cu^{2+} ion solution (mg/l);

C_e = End concentration of Cu^{2+} ion solution with wood sample after 24 hours (mg/l); and

q_e = mg Cu^{2+} ion/g wood.

FTIR Spectroscopy. Citric acid ester linkages in the wood samples were characterized using a Nicolet Nexus 670 Spectrometer equipped with a Thermo Nicolet Smart Golden Gate MKII Single Reflection ATR accessory. Samples were prepared for analysis by base treatment

of 125 mg of sample in 2 ml of 0.1M NaOH for 5 minutes. The base treated samples were transferred in to a few ml of water to a filter and the liquid was removed. The filtrate was checked with short range pH paper (8-9.5) to assure a pH of 8 or above. Base treated samples were air dried for the ATR/FTIR scans. The ester carbonyl band absorbance ($1730 \ cm^{-1}$ band) depicted is normalized against the $1320 \ cm^{-1}$ band associated with the cellulose C-H bending mode.

RESULTS AND DISCUSSION

In Table 1, the percentage weight gains were determined for the modification treatments and the control. The control had an anticipated minor loss (-2.4%) from the citric acid soak and water rinse. The majority of mass loss was most likely from the hemicellulose portion of the polymeric structure of the wood. Goldstein (1984) showed that hemicelluloses are susceptible to removal even by mild acid treatments. Weight gains with treated samples increased with higher temperatures and longer reaction times, and a limit was not reached in this series.

Figure 2 shows the results of citric acid treatment conditions on aspen wood particles and their equilibrium copper ion sorption capacities at 110, 120 and 130°C, using the lower pH (4.6), unbuffered Cu^{2+} ion standard. Maximum sorption of 7.9 mg Cu^{2+} ion/g of modified wood is reached when treated for 2 hours at 130°C. This result compares favorably with the untreated wood (1.3 mg Cu^{2+} ion/g wood) and is over a sixfold increase. Even more encouraging is the comparison with the cit-

TABLE 1. Effect of citric acid treatment conditions on wood weight gain or loss.

Time (hrs)	Temp (°C)	% Gain or Loss ($-$)
Control	$-$	-2.41
2	110	4.66
4	110	16.51
6	110	24.07
2	120	10.71
4	120	28.11
6	120	38.94
2	130	28.54
4	130	52.55
6	130	58.43

FIGURE 2. Cu^{2+} ion sorption capacity (mg/g) of treated wood as a function of treatment time at 110°C, 120ºC, and 130ºC using unbuffered standard with initial pH of 4.6. Y-axis values are an average of 3 replicates. The point at zero hour is untreated wood.
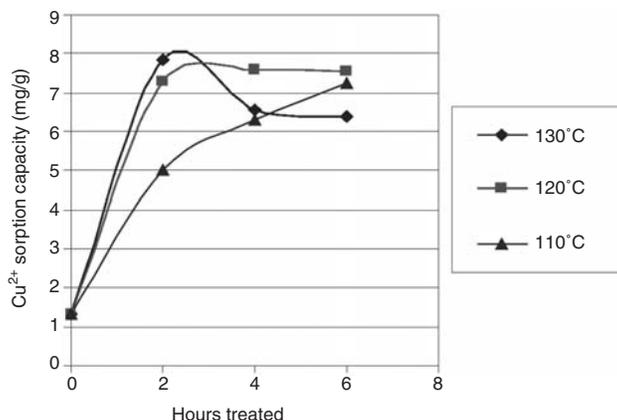

ric acid control. The sorption capacity of the treated sample is increased almost nine times over that of the control (0.9 mg Cu^{2+} ion/g wood). An examination of the measured pH of sample solutions at the end of the 24-hour copper ion sorption tests provides a possible explanation for the lower capacity of the control from that of untreated wood. The final solution pH of the untreated wood (4.0) is somewhat lower than that of the initial solution pH (4.6). By comparison the final pH values for the control and the citric acid treated samples were significantly lower at about 3.1. The pH differences may be explained by the fact that some of the acidic groups of the wood's cell wall components are associated with alkali metal ions such as calcium and potassium that are extractable with dilute acid (Buchanan 1975). In the case of the untreated sample, the wood has not been exposed to an acid extraction and the acidic groups on the wood do not contribute a proton to the solution when a copper ion is exchanged, but instead exhibit a buffering effect from the displaced alkali metal ions. The citric acid treated samples and the citric acid control should have the metal ions removed from wood by the concentrated citric acid solutions (pH 1.9) and subsequent de-ionized water rinses. This leaves the acidic groups in the free acid form that can contribute a proton during copper ion exchange, thus lowering solution pH. This phenomenon is comparable to the regeneration of an ion exchange resin

by acid washing to remove the positively charged counter-ions. Citric acid pK_2 and pK_3 values are 4.77 and 6.39, respectively (CRC 1972). Since the pK values of the acid groups of wood-citrate are probably similar to citric acid, this is an indication that the sorption experiments at the lower pH levels reached here may be in an environment where the carboxyl groups are not fully ionized, making them less readily available to ion exchange. In addition, lower pH environments reduce metal ion sorption by the increased competition of protons for these sites (Low 1993). The modified wood samples tested with the Cu^{2+} standard and with a final solution pH of about 3.1 might benefit from either buffering the solution, or raising the initial pH, to increase carboxyl group ionization and reduce proton competition. For this reason we decided to test the wood samples with another Cu^{2+} standard incorporating these changes. Testing the modified samples for an optimal pH range for Cu^{2+} sorption capacities had constraints. Raising the standard solution pH is limited to approximately 5.4; or the copper ion would begin to form an insoluble hydroxide when above this pH at the concentration used here. This would change the metal removal mechanism from chemical ion exchange to that of a solubility effect with physical removal of the metal precipitate, thus complicating any comparisons. An added buffer to control pH would seem to be the best alternative but it has been shown that increasing the ionic strength of a Cu^{2+} ion solution (such as with the added buffer) can have a negative impact on sorption by carboxyl groups (Reddad et al. 2002). Preliminary testing with an unbuffered standard that was adjusted to a pH of slightly more than 5, did not substantially diminish pH drop or change sorption capacities. Testing with two concentrations of sodium acetate buffers (0.01 M and 0.05 M), confirmed that despite slightly better pH control, the more concentrated buffer of the two tested produced lower indicated sorption capacities for the tested samples. The lower buffer concentration (0.01 M) was sufficient to largely control pH drop of the buffered Cu^{2+} standard during ion exchange with the samples. From an initial pH of 5.1, final pH of tested sample's standard solutions was about 4.6 for modified wood samples, 4.8 for the control, and 5.0 for the untreated wood sample.

In Figure 3, results of equilibrium sorption testing with the samples and the higher pH/buffered standard can be observed. As expected, the indicated sorption capacities of the samples were substantially higher when compared with the results from the unbuffered standard. The maximum value of 13.8 mg Cu^{2+} ion/g of modified wood is reached with the same citric acid reaction conditions (2 hours at 130°C) as with the other (unbuffered) standard solution. The unmodified samples simi-

FIGURE 3. Cu^{2+} ion sorption capacity (mg/g) of treated wood as a function of treatment time at 110°C, 120°C, and 130°C using 0.01 M sodium acetate buffered standard with initial pH of 5.1. Y-axis values are an average of 3 replicates. The point at zero hour is untreated wood.
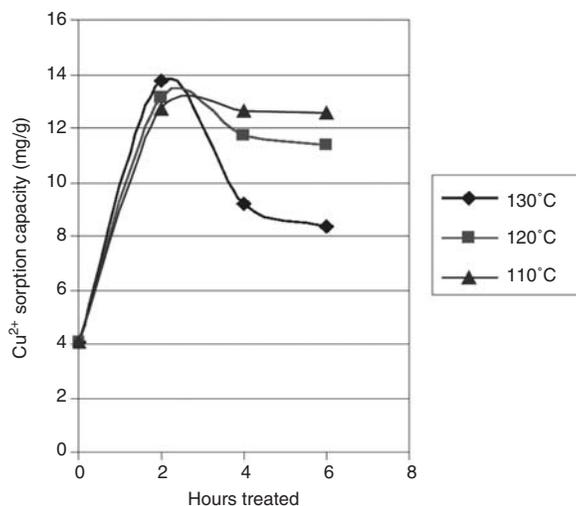
larly exhibited higher sorption levels of 4.1 mg Cu^{2+} ion/g and 2.9 mg Cu^{2+} ion/g for the untreated and control samples, respectively.

When comparing the samples for weight gain from the citric acid adduct with the effect on equilibrium sorption capacity, it is clear that a point of diminishing return is eventually reached. In Figure 4, at longer times of 4 and 6 hours at the highest temperature (130°C), sorption capacity begins to go down even though these samples had higher weight gains. Even at the 120°C level, sorption capacity increase levels off at the longer treatment times. The same pattern of declining sorption capacities at the longer reaction times and higher weight gains is seen when comparing the sorption capacities attained with the buffered standard (Figure 5). However, with this standard, the longer reaction times at 110°C appear to reach a plateau in sorption capacity, whereas the unbuffered results were still increasing at 4- and 6- hour reaction times. It is believed that increasing the severity of treatment conditions eventually leads to crosslinking reactions of the non-bonded acid groups with wood hydroxyl groups and the net number of free carboxylic acid groups available for ion exchange decreases.

FIGURE 4. Cu^{2+} ion sorption capacity (mg/g) of treated wood (using un-buffered standard, initial pH 4.6) as a function of weight gain (%) from bound citric acid. Y-axis values are an average of 3 replicates. The point at 0% weight gain is untreated wood.
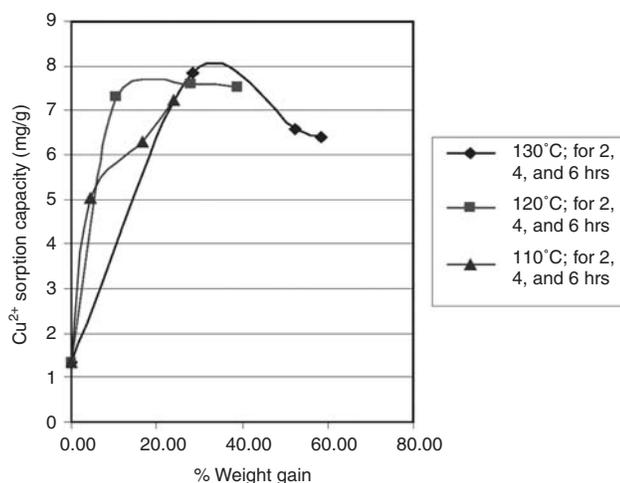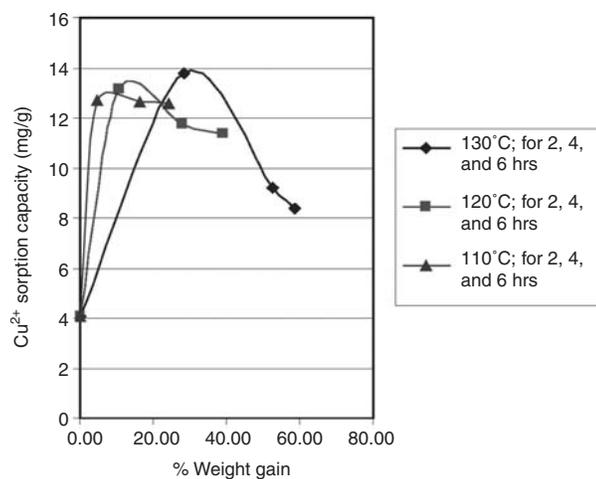

FIGURE 5. Cu^{2+} ion sorption capacity (mg/g) of treated wood (using 0.01 M sodium acetate buffered standard, initial pH of 5.1) as a function of weight gain (%) from bound citric acid. Y-axis values are an average of 3 replicates. The point at 0% weight gain is untreated wood.

Evidence for increasing the number of ester linkages at longer reaction times is seen in Figure 6(a-c). The FTIR spectra depict the ester group region of the cellulose for base treated control and base treated modified wood samples. Prior to a base treatment, the 1730 cm^{-1} region consisted of both the ester carbonyl and carboxylate ions. Base treating the samples leaves the 1730 cm^{-1} region consisting of ester carbonyl and shifts carboxylate ion to the 1580 cm^{-1} region. With in each of the temperature regimes, the 1730 cm^{-1} region increases with additional reaction time, indicating an increase in ester formation. This increase can be due to added singly bonded citric acid or crosslinking of previously bound citric acid, or a combination of both. Some researchers have used different peak ratio techniques to distinguish the degree of crosslinking of polycarboxylic acid modified cellulose. Yang (1991) used the ratio of 1730 cm^{-1} to 1580 cm^{-1} peak heights on base treated modified fabrics. Morris et al. (1995) used the ratios of the 1730 cm^{-1} peak heights of base treated to acid treated, modified fabric. Both of these ratio techniques were attempted with our citric acid modified wood samples. Neither method provided a high degree of correlation of increasing ratios

FIGURE 6a-c. FTIR scans of 1730 cm^{-1} (ester) region with baselines normalized to 1320 cm^{-1}. Samples are treated with 0.1 M NaOH. Scans are of control and wood reacted with citric acid for 2, 4, and 6 hours at 110°C (a), 120°C (b), and 130°C (c).
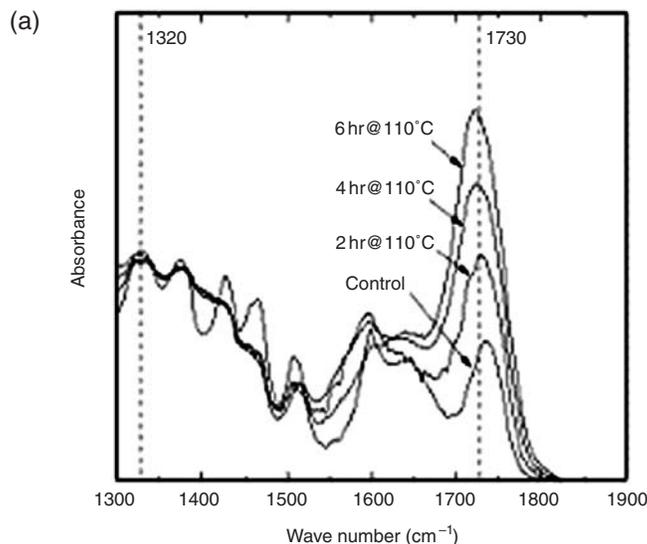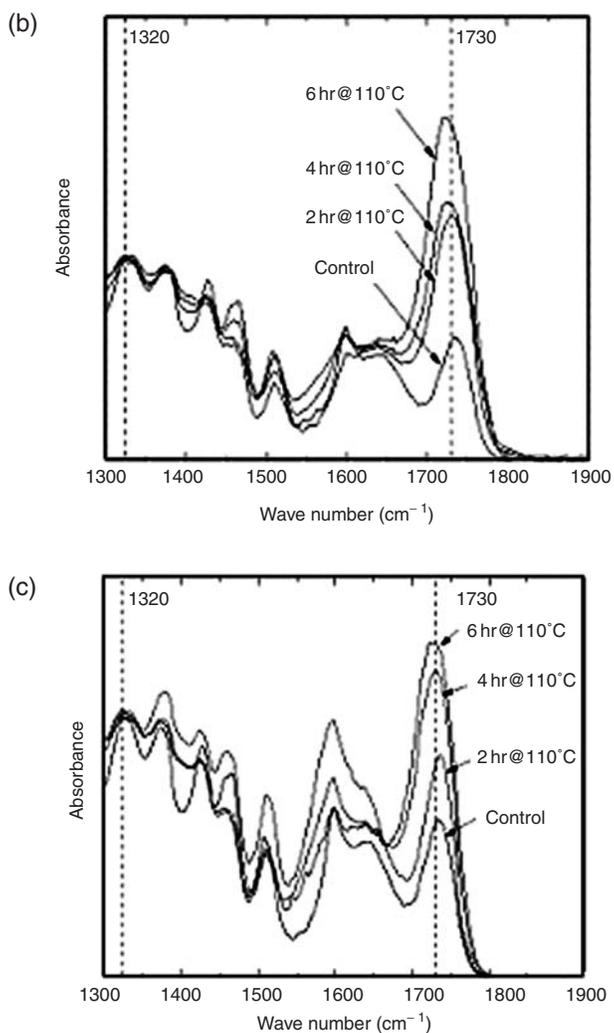
FIGURE 6 (continued)

(b)

(c)

with severity of reaction conditions. However, using the Yang technique did show a modest degree of association of the 1730 cm^{-1} to 1580 cm^{-1} peak height ratio with longer reaction times at 110 and 120°C. This was not the case with the 130°C treated samples, which had higher weight gains than the lower temperature reactions. Morris et al. (1994) found a similar lack of linearity of FTIR 1730 cm^{-1} peak measure-

ments, when quantifying citric acid on modified cellulose at higher weight gain levels (> 8%). Weight gains for our 130°C series ranged from 28.54 to 58.43%. A study that measured the effect on metal ion sorption, of esterifying algal carboxyl groups, showed large reductions in the sorption of Cu and Pb ions (Gardea-Torresdey et al., 1990). In our study, the fact that mass increases with lengthened reaction times indicates that the addition of citric acid is in part responsible for the increase in ester bonds seen in the 1730 cm^{-1} peak heights. At longer reaction (4 and 6 hours) times, static or declining sorption values indicate that crosslinking reactions are also occurring.

CONCLUSIONS

1. Aspen wood can be readily modified with citric acid to increase its Cu^{2+} ion sorption property, with a simple thermochemical procedure and conditions similar to those used in the modification of agricultural by-products. This improvement in wood sorption property could increase its utility for contaminated water treatment, particularly in areas of acid mine drainage where Cu^{2+} ion is prevalent, and aspen wood is harvested.

2. Citric acid treatments at the concentration used in this study (2 g of 5 mm or smaller milled aspen wood in 10 ml of 200 g/l citric acid), heated for 2 hours at 130°C, effected a maximum increase in Cu^{2+} ion sorption capacity. Untreated, treated wood and a citric acid control were tested in 24 hour equilibrium sorption tests with 100 mg of sample in 50 ml of 50 mg/l Cu^{2+} ion solution. Two Cu^{2+} standard solutions were used to test the samples; one had a starting pH of 4.6 and was unbuffered, the second had a starting pH of 5.1 and was buffered to 0.01 M with sodium acetate. Testing with the unbuffered standard, Cu^{2+} ion sorption capacity of untreated wood increased from 1.3 mg Cu^{2+} ion/g to 7.9 mg Cu^{2+} ion/g for the treated sample. The control sample tested is slightly lower at 0.9mg Cu^{2+} ion/g, than the untreated sample. Testing with the buffered standard, sorption capacity of the untreated wood increased from 4.1 mg Cu^{2+} ion/g to 13.9 mg Cu^{2+} ion/g for the treated sample. The control sample tested also lower at 2.9 mg Cu^{2+} ion/g. The lower values for the control sample is thought to be due to the loss of buffering metal ions removed during the citric acid soak and water rinse, and the consequently lower pH at the end of the sorption test.

3. Maximum sorption capacity increase occurred at lower than the highest level of bound citric acid; this corresponded to a weight

gain of 28.54% for maximum sorption capacity and a 58.43% weight gain for maximum bound citrate for the highest temperature and longest treatment period tested here (6 hrs at 130°C). The crosslinking reactions of the free acid groups of bound citrate with other wood hydroxyl groups could account for this behavior.

4. Future research should explore ways to increase the metal ion sorption efficiency of the modified wood. One approach could involve testing the use of smaller particle sizes of the milled wood, for modification treatments. Another approach would be to explore the use of catalysts to enable milder reaction conditions to minimize ester crosslinks.

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