# Evaluation of Copper Leaching in Thermally Modified Southern Yellow Pine Wood Impregnated with ACQ-D

Wang Wang, Yuan Zhu, and Jinzhen Cao*

Thermally-modified wood is not sufficiently durable for exposure to environments in which severe biological deterioration is likely. So in this study, samples of southern yellow pine sapwood were first subjected to thermal modification and then impregnated with the alkaline copper quat-type D (ACQ-D) wood preservative. Three heating temperatures (180, 200, and 220 °C) and two concentrations of ACQ-D solution (0.90% and 1.35%) were used in the experiments. The copper retention, percentage of copper leaching, and concentrations of copper ions in the leachates collected during the leaching tests were evaluated using inductively coupled atomic emission spectrometry (ICP-AES). Fourier transform infrared spectroscopy (FTIR) analysis was also used to interpret the differences in leaching performance between thermally-treated and unheated wood samples. The pseudo-second-order model of copper leaching was developed with the experimental leaching data, which could determine the amounts of copper ion leaching and predict the final percentage of copper leaching during the leaching process. As a result, compared to the control group, the copper retention of the thermally-modified wood samples was lower, while the percentage of copper leaching was higher. This observation could be explained by the lower number of copper ion fixation sites in the thermally-treated wood.

*Keywords: Thermally-modified wood; Alkaline copper quat-type D(ACQ-D); Copper retention; Copper leaching; Pseudo-second- order model*

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## INTRODUCTION

In recent years, thermal treatment has become widely used in wood modification. During the thermal treatment, the chemical composition of the wood changes (Weiland and Guyonnet 2003). The hemicellulose is most susceptible to thermo-chemical degradation, even at low temperatures (Sivonen *et al.* 2002). Degradation of the hemicelluloses is manifested as polysaccharide decomposition (Nuopponen *et al.* 2004), which is responsible for the decrease in hydroxyl groups (Mitsui *et al.* 2008). Crosslinking reactions between the lignin molecules may occur, leading to the formation of methylene lignin linkages during the treatment (Tjeerdsma and Militz 2005).

The chemical transformations occurring during thermal treatment decrease the equilibrium moisture content of wood, which in turn enhances its dimensional stability (Sinkovic *et al.* 2011; Srinivas and Pandey 2012). After the thermal modification, the surface color of the wood becomes darker (Mitsui *et al.* 2001; Hu *et al.* 2012), and the color change seems to appeal to more consumers.

The decomposition of the nutrient contents of wood during thermal modification leads to an improvement in resistance against wood-rotting fungi (Bazyar 2012; Mohareb *et al.* 2012). However, the improvement turns out to be insignificant for use in ground contact (Kamdem *et al.* 2002). Moreover, the influence of thermal modification on mold and termite resistance was not shown to be important (Kocaefe *et al.* 2007; Surini *et al.* 2012). Therefore, thermally-modified wood is unsuitable for an environment with severe biological deterioration hazard. To explore the application field of thermally-modified wood, low toxicity preservatives or biocides have been proposed to improve its biological resistance in Europe (Ahmed *et al.* 2013).

Alkaline copper quat-type D (ACQ-D), a copper-based water-borne wood preservative, is widely used in the market. The results of our previous studies indicated that ACQ-D impregnation barely influences the mechanical properties of thermally-modified wood, while mold resistance increases significantly (Wang *et al.* 2013). A study of the copper leaching performance of ACQ-D-treated wood products is essential to determine its long-term biological performance, as well as any environmental issues (Yu *et al.* 2010). Previous studies have shown that the copper ions react with functional groups such as carboxyl groups, carbonyl groups, and phenolic hydroxyl groups (Jin and Archer 1991) and then become immobile in the wood. However, after thermal treatment, wood undergoes various changes, which might influence the amount of copper ions leached from the treated wood.

Researchers have used diffusion models to simulate the leaching performance of copper-based preservatives in wood (Ra *et al*. 2001; Waldron *et al*. 2005). But in fact, the copper leaching process is not the same as copper ions diffusion. Copper ions could be chemically reacted with wood or physically attached to wood by ion-ion or dipole-dipole interactions (Craciun *et al.* 2009). These circumstances suggest limited ability of the copper ions to diffuse in the wood. Therefore, another leaching mode was sought to simulate this condition appropriately. Ho *et al.* (2005) developed a second-order model for the leaching of water-soluble compounds from *Tilia* sapwood, and such a model could be referenced for the copper leaching process. Because mass loss of wood is one of the most important features in thermally-modified wood, it can be a suitable performance indicator for the intensity of thermal modification. Hence, mass loss has been used for the quality classification of heat-treated beech wood (Repellin and Guyonnet 2003). Therefore, in this study, mass loss was taken as a variable in building a predictive model for copper leaching.

The objective of this study was to investigate the effects of thermal modification on the copper leaching performance. A pseudo-second-order model was employed for analyzing the thermally-modified wood impregnated with ACQ-D solutions. The mechanism of the different leaching performances was interpreted by Fourier transform infrared spectroscopy (FTIR) analysis.

## EXPERIMENTAL

### Materials

Southern yellow pine sapwood with an air-dry density of 0.4 g/cm$^3$ and an average growth ring width of 0.6 cm was purchased from the market and cut into samples of 19 mm (longitudinal) ×19 mm (tangential) ×19 mm (radial) for the leaching test. Before being subjected to thermal modification, wood samples were oven-dried at 80 °C to constant mass. The ACQ-D concentrate used in this study was about 15% (66.7% CuO and 33.3% didecyldimethylammonium chloride (DDAC)), produced by Guangzhou

Xingyue Wood Preservation Co., Ltd., China. To achieve different preservative retentions, ACQ-D was diluted with deionized water to two different concentrations, 0.90% and 1.35%, prior to impregnation.

## Thermal Modification

The wood samples were thermally modified at 180, 200, and 220 °C for 6 h in a modified drying oven connected with a water vapor supplying system. After 6 h of heat treatment, wood samples were naturally cooled and dried at 80 °C to constant weight, then weighed. The percentage of mass loss was calculated, and the mass of the wood samples decreased by 1.17%, 3.11%, and 7.82% for heat treatments at 180, 200, and 220 °C, respectively.

## ACQ-D Impregnation

After thermal modification, wood samples were impregnated with ACQ-D solutions using a full-cell process. Wood samples were exposed to a vacuum at -0.1 MPa for 30 min, and the pressure for impregnation was maintained at 0.5 MPa for 30 min. After the impregnation, samples were taken from the treating cylinder, wiped with tissue paper, covered with plastic film, and kept under room conditions for 2 days. Then, samples were oven-dried at 80 °C for 2 days to constant mass.

## Copper Leaching Test

Twelve replicates of each treated group were used to test the copper leaching performance according to AWPA (2010) E11-06 standard. Six of the treated wood blocks were immersed in deionized water (0.3 L for each group) for 14 days. Deionized water was changed and leachates were collected after 6, 24, and 48 h and thereafter at 48-h intervals. ICP-AES (Perkin 5300V, USA) was used to analyze the leachates, which contained copper ions leached from the treated wood. The other six treated wood blocks were used for determining the initial copper content. When the leaching tests were finished, all samples were ground to pass a 20-mesh (85-$\mu$m) sieve and dried at 80 °C to constant mass. A pre-weighed sample of 0.15 g of powder from both leached and unleached samples was digested with acids, and then the digestate was diluted to 100 mL, followed by the analysis of copper content using ICP-AES. The copper retentions ($R_i$ (kg/m$^3$)) were calculated according to Eq. (1),

$$R_i(kg/m^3) = \frac{c_u \times \rho_u}{0.15 \times 100} \tag{1}$$

where $c_u$ (mg L$^{-1}$) is the copper ion concentration of the digested liquid obtained from unleached samples and $\rho_u$ (g cm$^{-3}$) is the average oven-dry density of unleached samples.

## Modeling of Copper Leaching

In order to build the leaching model, two assumptions have been made as follows: (1) the concentration of copper ions in the wood is distributed uniformly; (2) the cumulative water spray time was equivalent to continuous soaking. With the assumptions mentioned above, to model the copper ion loss from the samples during the leaching tests over time, a pseudo-second-order differential equation (Ho and Macay 1999), which demonstrated how the rate depended on the copper ion concentration in leachates, was described as follows,

$$\frac{\mathrm{d}c_t}{\mathrm{d}t} = k\left(c_f - c_t\right)^2 \qquad (2)$$

where $k$ (L mg$^{-1}$ h$^{-1}$) is the pseudo-second-order leaching rate constant, $c_f$ (mg L$^{-1}$) is the total copper ion concentration when all the unfixed copper ions leached out from the wood, and $c_t$ (mg L$^{-1}$) is the cumulative copper ion concentration of leachates collected at time $t$ (h).

Equation (2) was integrated utilizing the boundary conditions of $t = 0$ to $t$ and $c_t = 0$ to $c_f$, respectively, to yield Eq. (3), which could be rearranged to yield Eq. (4):

$$c_t = \frac{c_f^2 kt}{1 + c_f kt} \qquad (3)$$

$$\frac{t}{c_t} = \frac{1}{kc_f^2} + \frac{t}{c_f} \qquad (4)$$

Therefore, the parameters $c_f$ and $k$ can be determined experimentally from the slope and intercept by plotting $t/c_t$ against $t$.

## Percentage of Copper Leached

The realistic percentage of copper leached after a 14-day leaching test could be calculated in two ways. The first calculation, which was based on the copper ion concentration of the digested liquids obtained from the leached sample ($\mathrm{L_d}$ (%)), was carried out in accordance with Eq. (5),

$$\mathrm{L_d}(\%) = \left(1 - \frac{c_l \times \rho_l}{c_u \times \rho_u}\right) \times 100\% \qquad (5)$$

where $c_l$ (mg L$^{-1}$) is the copper ion concentration of the digested liquid obtained from leached samples and $\rho_l$ (g cm$^{-3}$) is the average oven-dry density of leached samples.

The second calculation, based on the cumulative copper ion concentration in leachates collected during the 336-h leaching test ($\mathrm{L}_l$ (%)), was carried out in accordance with Eq. (6),

$$\mathrm{L}_l(\%) = \frac{0.3 \times c_{336}}{R_i \times V_t} \qquad (6)$$

where $V_t$ (cm$^3$) is the total volume of the six wood samples in each group and $c_{366}$ (mg L$^{-1}$) is the cumulative copper ion concentration of leachates collected at time $t$ = 366 h.

Moreover, the final percentage of copper leaching ($\mathrm{L}_{max}$ (%)) could be predicted by the copper leaching model in accordance with Eq. (7):

$$\mathrm{L}_{max}(\%) = \frac{0.3 \times c_f}{R_i \times V_t} \qquad (7)$$

## FTIR Analysis

Wood samples were ground to pass through a 100-mesh (149-$\mu$m) sieve, and FTIR spectra were recorded with the samples, which were first formed into a KBr pellet, on a FTIR spectrophotometer (Bruker Vertex 70v, German) in transmission mode within the wavenumber range of 1800 to 800 $\text{cm}^{-1}$.

# RESULTS AND DISCUSSION

## Copper Retention

The results of copper retention for the thermally-modified wood and the untreated wood are shown in Fig. 1. Samples treated with the 1.35% ACQ-D solution displayed much higher copper retention than samples treated with the 0.90% ACQ-D solution. According to ASTM U1-08 (2008) and P29-08 (2008) standards, samples treated with 0.90% ACQ-D met the requirement of category UC3B (above ground, exterior, exposed or poor water run-off), while the samples with 1.35% ACQ-D impregnation met the requirement of category UC4A (ground contact or fresh water). Increased copper ion concentration from the impregnation fluid significantly elevated the copper retention in both the control groups and the thermally-modified groups. The difference of copper retention between control groups and 180 $^{o}$C treated thermally-modified groups was not significant ($P$>0.05). But when the heating temperature was higher than 180 $^{o}$C, the thermally-modified samples showed lower copper retention, and this trend was more evident with increasing thermal treatment temperature. The percentages of retention decrease of two different treating concentrations were roughly the same. This result can be ascribed to the modification of wood components during the thermal treatment.

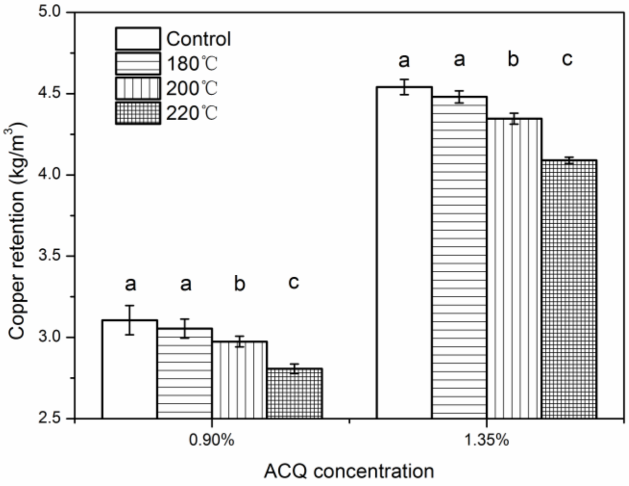

**Fig. 1.** Copper retention of ACQ-D-treated thermally-modified wood. In each ACQ-D concentration group, means under the same letter are not significantly different at $P$=0.05 (Tukey's HSD multiple comparison).

## Modeling of Copper Leaching Process

The plots of the accumulative copper ion concentration in leachates versus time for the ACQ-D treatment of the thermally-modified wood are shown in Fig. 2. The experimental data are plotted together with the predicted theoretical curves from the model. The leaching rate was fast at the beginning of the leaching process; afterwards, the rate rapidly decreased over time and tended to level out at the end of the process for all treatment groups. The initial rapid copper leaching rate can be attributed to the high content of unfixed copper ion in the unleached samples. As the leaching process continued, the content of unfixed copper ions in the samples significantly diminished, giving a smaller driving force (by lower concentration gradient pressure) for copper ion release. The $c_t$ of the 1.35% ACQ-D-treated samples was higher than that of the 0.90% ACQ-D-treated samples; also, $c_t$ significantly increased when the thermal treatment temperature increased.

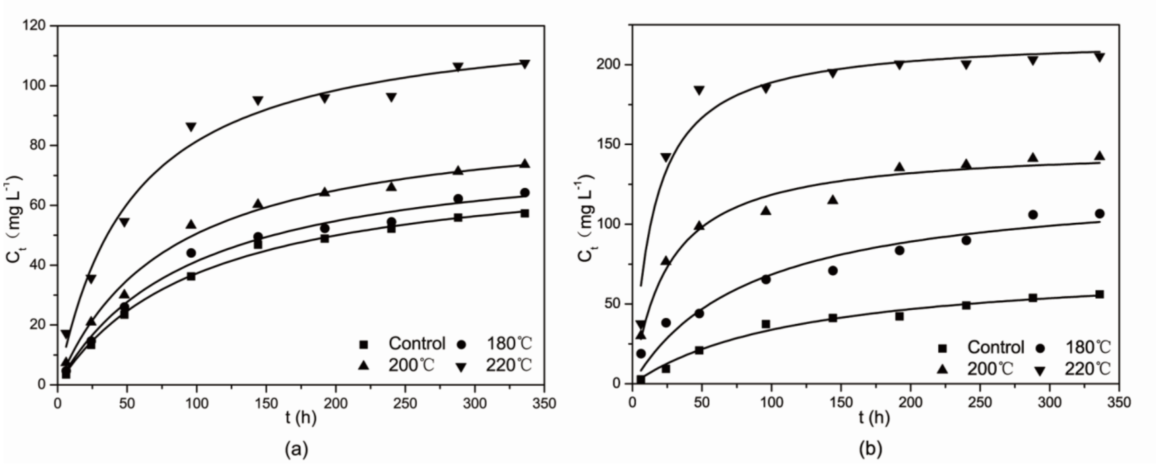

**Fig. 2.** Plot of accumulativecopper ion concentration ($c_t$) in leachates versus time for the ACQ-D treatment of thermally-modified wood: (a) 0.90% ACQ-D impregnation and (b) 1.35% ACQ-D impregnation

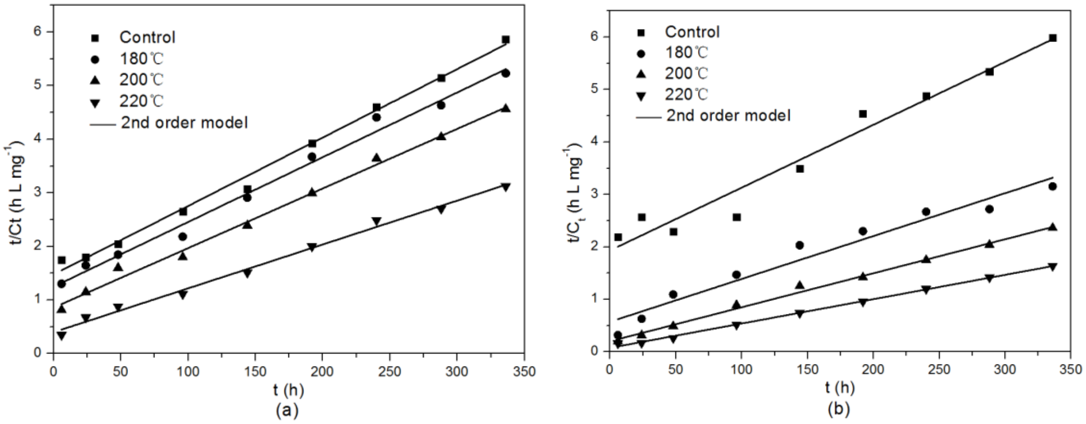

**Fig. 3.** Pseudo-second order copper leaching kinetics of ACQ-D treatment of thermally-modified wood at various heating temperatures: (a) 0.90% ACQ-D impregnation and (b) 1.35% ACQ-D impregnation

Figure 3 shows the plots of the linearized forms of the integrated pseudo-second-order model of Eq. (4) for the cumulative copper ion leaching of all wood samples. The correlation coefficient for the linear plots of $t/c_t$ against time were higher than 0.95 for all wood samples for the 336-h leaching time (Table 1); this indicated that the experimental data fitted the pseudo-second-order model well. The slopes and intercepts shown in Fig. 3 gradually decreased as the thermal treatment temperature increased for both ACQ-D impregnation concentrations.

**Table 1.** Constants and Correlation Coefficients of the Pseudo-Second-Order Copper Leaching Model

| ACQ-D Concentration (%) | Heating Temperature (°C) | $k$ (L mg$^{-1}$ h$^{-1}$) | $c_f$ (mg L$^{-1}$) | $r_1^{2\,a}$ | $r_2^{2\,b}$ |
|---|---|---|---|---|---|
| 0.90 | control | $1.11\times10^{-4}$ | 78.13 | 0.9962 | 0.9939 |
| | 180 | $1.17\times10^{-4}$ | 82.64 | 0.9890 | 0.9903 |
| | 200 | $1.44\times10^{-4}$ | 90.09 | 0.9900 | 0.9935 |
| | 220 | $1.69\times10^{-4}$ | 121.95 | 0.9810 | 0.9930 |
| 1.35 | control | $7.46\times10^{-5}$ | 83.33 | 0.9830 | 0.9644 |
| | 180 | $1.18\times10^{-4}$ | 121.95 | 0.9353 | 0.9579 |
| | 200 | $2.11\times10^{-4}$ | 153.85 | 0.9677 | 0.9948 |
| | 220 | $2.82\times10^{-4}$ | 217.39 | 0.9477 | 0.9979 |

[a] $r_1^2$, the correlation coefficient for the pseudo-second-order model as shown in Fig. 2.
[b] $r_2^2$, the correlation coefficient for the linearized form of the pseudo-second order model as shown in Fig. 3.

The constants in Eq. (4) were obtained from the plots of Fig. 3 for all the wood samples and are given in Table 1. The values of the pseudo-second-order leaching rate constant, *k*, increased from $1.11\times10^{-4}$ to $1.69\times10^{-4}$ L mg$^{-1}$ h$^{-1}$ as the thermal heat treatment temperature increased for the samples impregnated with 0.90% ACQ-D, and from $7.46\times10^{-5}$ to $2.82\times10^{-4}$ L mg$^{-1}$ h$^{-1}$ for the 1.35 % ACQ-D-treated samples. The total copper ion concentration that leached out from the wood, $c_f$ , increased as the thermal heat treatment temperature increased.

Figure 4 shows the change in $k$ and $c_f$ of all the wood samples with mass loss during the thermal treatment. At this point, mass loss was used as an index of the intensity of the thermal modification. Increases in $k$ and $c_f$ were observed as the mass loss increased, which indicated higher copper ion loss from the wood after thermal treatment. Special attention should be paid to the intersection of the two trend lines at the mass loss of approximately 1% in Fig. 4 (a), below which $k$ of 0.90% ACQ-D treated wood was slightly higher than that of 1.35% ACQ-D treated wood. In addition, it was found that the variation of $k$ and $c_f$ with mass loss could be well fitted linearly by Eqs. (8) and (9) for 0.90% ACQ-D and Eqs. (10) and (11) for 1.35% ACQ-D,

$$k_{0.90}(\mathrm{L\ mg^{-1}h^{-1}}) = 8.00\times10^{-6}M_l + 1.12\times10^{-4} \tag{8}$$

$$c_{f0.90}(\mathrm{L\ mg^{-1}}) = 5.70M_l + 75.97 \tag{9}$$

$$k_{1.35}(\mathrm{L\ mg^{-1}h^{-1}}) = 2.60\times10^{-5}M_l + 9.25\times10^{-5} \tag{10}$$

$$c_{f1.35}(\mathrm{L\ mg^{-1}}) = 16.22M_l + 95.08 \tag{11}$$

where $M_l$ (%) is the percentage of mass loss of wood samples after thermal modification. Inserting the parameter values calculated from Eqs. (8) to (11) into Eq. (3), the rate law for the pseudo-second-order copper leaching can be represented in terms of $c_t$, $M_l$, and $t$. Equation (3) for 0.90% ACQ-D becomes:

$$c_{t0.90}(\mathrm{L\ mg^{-1}}) = \frac{(2.59\times10^{-4}M_l^3 + 1.06\times10^{-2}M_l^2 + 0.143M_l + 0.646)\times t}{1 + (4.56\times10^{-5}M_l^2 + 1.25\times10^{-3}M_l + 8.51\times10^{-3})\times t} \tag{12}$$

and for 1.35% ACQ-D:

$$c_{t1.35}(\mathrm{L\ mg^{-1}}) = \frac{(6.84\times10^{-3}M_l^3 + 0.105M_l^2 + 0.520M_l + 0.836)\times t}{1+(4.22\times10^{-4}M_l^2 + 3.97\times10^{-3}M_l + 8.80\times10^{-3})\times t} \qquad (13)$$

Equations (12) and (13) represent the generalized predictive model for copper ion leaching, which could be used to obtain the amount of copper ion leached from the thermally modified, ACQ-D-treated wood for any given leaching time and mass loss.

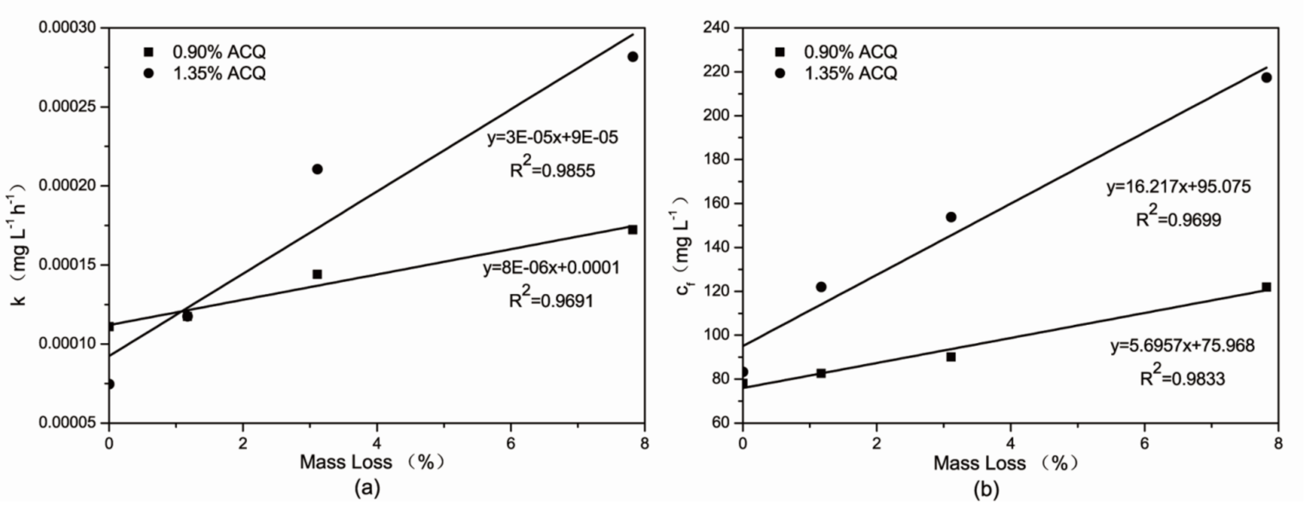

**Fig. 4.** Variation in *k* (a) and $c_f$ (b) with mass loss of thermally-modified wood samples

## Percentage of Copper Leached

The realistic percentage of copper leached from the ACQ-D treated, thermally-modified wood is shown in Fig. 5. The results of the two methods indicated that the thermal treatment significantly increased the percentage of copper leached from the wood samples. The total copper leaching increased with increasing temperature of the thermal treatment. An explanation for this result is the decomposition of cell wall components decreasing the reactive sites for copper fixation during the thermal modification, which is similar to interpretation for the reduction of copper retention.

In addition, it should be noted that the copper leaching of samples treated with different concentrations of ACQ-D seemed to show an inconsistent response to heating temperature. For the control groups, more copper leaching was observed at low impregnation concentrations; for the thermally-modified groups, a reverse trend was apparent that was even more pronounced with high heating temperature. Lee *et al.* (1993) reported that for samples that have many unfixed copper ions, higher percentages of copper leaching could be observed at higher retentions, whereas for well-fixed samples, the reverse result was observed. Therefore, the difference between the control and thermally-modified groups could be explained by the presence of more unfixed copper ions in the thermally-modified wood. In addition, the percentage of copper leaching calculated using two different methods showed similar results for different ACQ-D treatment concentrations and thermal treatment temperatures; however, the differences in the numerical values might be caused by the variability of the initial copper retention of the samples.

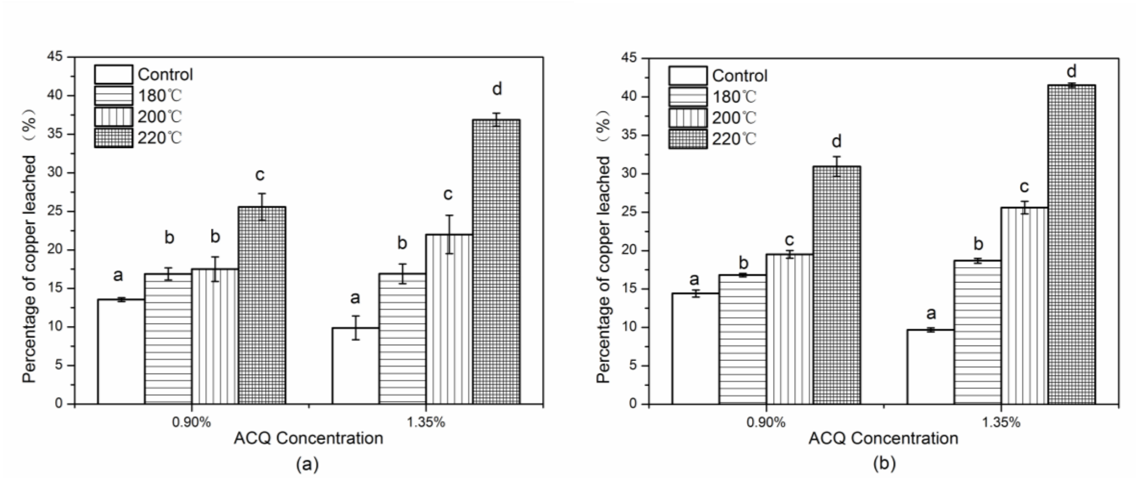

**Fig. 5.** Realistic percentage of copper leached from ACQ-D-treated, thermally-modified wood. In each ACQ-D concentration group, means under the same letter are not significantly different at *P*=0.05 (Tukey's HSD multiple comparison); (a) calculation based on the copper ion concentration of the digested liquids obtained from leached samples during the 336-h leaching test; and (b) calculation based on the cumulative copper ion concentration in leachates collected during the 336-h leaching test

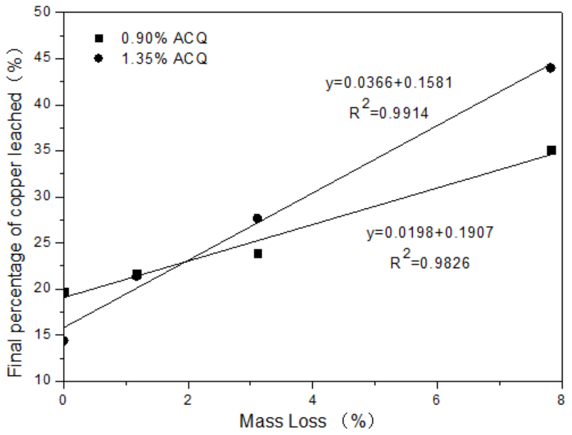

**Fig. 6.** Final percentage of predicted copper leached from ACQ-D-treated, thermally-modified wood

Figure 6 illustrates an excellent linear relationship between the percentage of mass loss from thermal treatment and the final percentage of predicted copper leaching. These linear relationships are described by Eqs. (14) and (15) for 0.90% and 1.35% ACQ-D, respectively:

$$L_{max0.90}(\%) = 0.0198M_l + 0.1907 \tag{14}$$

$$L_{max1.35}(\%) = 0.0366M_l + 0.1581 \tag{15}$$

The fitted curve of the final percentage of predicted copper leaching showed similar trends to the experimental copper leaching. Consequently, the final percentage of copper leaching of ACQ-D-treated, thermally-modified wood can be predicted using Eqs. (14) and (15).

## FTIR Analysis

FTIR analysis of the wood samples is presented in Fig. 7, and the bands are assigned to the vibrations of various groups in southern yellow pine wood (Table 2) (Kocaefe *et al.* 2008; Aydemir *et al.* 2011). Thermal modification led to an obvious decrease of the carbonyl band at 1738 cm$^{-1}$, indicating the cleavage of hemicellulose acetyl groups that occurred during the thermal treatment (Eq. (16)) (Tjeerdsma and Militz 2005):

$$\text{Polyose—}\,\mathrm{OCOCH_3} + \mathrm{H_2O} \xrightarrow{\mathrm{H^+}} \text{Polyose—}\,\mathrm{OH} + \mathrm{CH_3COOH} \qquad (16)$$

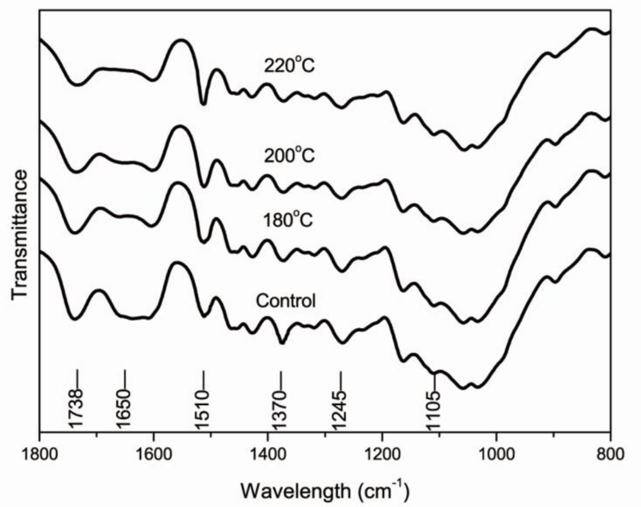

**Fig. 7.** FTIR spectra of thermally-modified southern yellow pine

**Table 2.** Infrared Absorption Bands of Southern Yellow Pine

| **Observed band** (cm$^{-1}$) | **Band assignment** | **Attribution** |
|---|---|---|
| 1738 | C=O stretching (unconjugated) | Hemicellulose |
| 1650 | C=O stretching (conjugated) | Lignin |
| 1602 | Aromatic skeletal vibration | Lignin |
| 1510 | Aromatic skeletal vibration | Lignin |
| 1370 | C-H deformation | Cellulose and hemicellulose |
| 1245 | CO-O stretching | Hemicellulose |
| 1105 | Aromatic skeletal vibration and C-O stretching | Lignin |
| 895 | C-H deformation | Cellulose |

Acetic and formic acids released during this reaction catalyzed the degradation of the polysaccharides and lowered the pH value of the wood (Sundqvist *et al.* 2006; Wang *et al.* 2012). The decrease in the bands at 1370 cm$^{-1}$ and 1245 cm$^{-1}$ also indicated the degradation of hemicellulose. Comparing the spectra of the unheated and the thermally-modified wood, the sharply decreasing intensity of the peak at 1650 cm$^{-1}$ can be attributed to the formation of diphenylmethane structures resulting from the condensation of lignin during the thermal treatment (Funaoka *et al.* 1990). Further cross-linking of disaggregated aliphatic side chains in lignin during the heat treatment contributed to the increasing intensity of the peaks at 1510 cm$^{-1}$ and 1105 cm$^{-1}$ (Ercin and Yurum 2003). The FTIR analysis results showed that the degradation of the hemicellulose and the condensation of lignin were the main reactions during the thermal treatment, and these reactions became more intense at higher treatment temperatures.

In Fig. 8, the differences between the FTIR spectra of control samples with and without 1.35% ACQ-D treatment are shown. After ACQ-D treatment, the band at 1738 $cm^{-1}$ was diminished, while the band at 1602 $cm^{-1}$ increased, probably due to the copper complexation with the wood. This implies that one of the main fixation reactions that occurred in the wood can be represented in the following equation (Craciun and Kamdem, 1997):

$$\mathrm{Wood-COOH+Cu^{2+}\rightarrow(Wood-Coo^{-})_{2}Cu^{2+}+H^{+}} \tag{17}$$

The changes of the peaks at 1738 $cm^{-1}$ and 1602 $cm^{-1}$ were attributed to the dissociation of wood carboxylic acid and the formation of Cu-carboxylate salt. The reduction of the intensity of the peak at 1510 $cm^{-1}$ could be attributed to the interaction between lignin and copper ions within the wood. No obvious alteration was found at the peak of 895 $cm^{-1}$, indicating that the cellulose did not significantly interact with preservatives. Zhang and Kamdem (2000) found that only a small amount of copper (approximate 0.06%) was absorbed by the cellulose after copper-ethanolamine treatment, while the copper absorption of hemicellulose and lignin was 0.50 and 0.95%, respectively. These authors concluded that hemicellulose and lignin were primarily responsible for copper absorption, which was consistent with our FTIR results.

For the thermally-modified wood, the same functional groups for copper fixation were observed from the FTIR spectra (Fig. 8). As mentioned above, the peaks at 1738 $cm^{-1}$, 1650 $cm^{-1}$, 1510 $cm^{-1}$, 1370 $cm^{-1}$, 1245 $cm^{-1}$, and 1105 $cm^{-1}$ manifested the chemical changes during the thermal heat treatment.

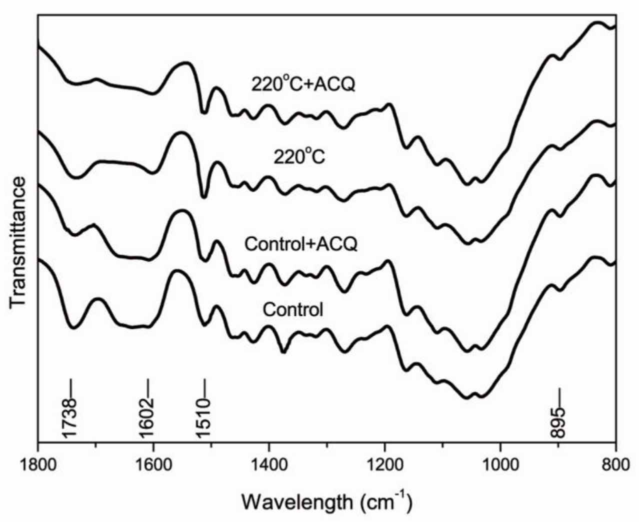

**Fig. 8.** FTIR spectra of ACQ-D-treated, thermally-modified wood

The reduction of hemicellulose and the transformation of lignin caused by the thermal modification led to a change of the adsorptive environment inside the wood. Moreover, the embrittled structure of the cell wall attributed to heat-treatment made it more likely to be depolymerized by ethanolamine in ACQ-D treated samples (Humar *et al.* 2007). The amount of functional groups in wood that can complex with the copper ions greatly influences the fixation capacity of the wood. Therefore, the fixation capacity for copper ions was reduced, which could explain the low copper retention and high copper leaching of ACQ-D-treated thermally-modified wood. Based on this, the intersection of the two lines in Fig. 6 could be explained as follows. More functional groups were needed for copper fixation in the samples treated with high concentrations of ACQ-D. For the control and thermally-modified wood with low mass loss, there were sufficient functional groups in the wood for copper fixation, while for the thermally-modified wood with high mass loss, the number of fixation sites for copper ions was obviously reduced. This reduction could have a great impact on copper leaching in samples treated with 1.35% ACQ-D solution.

Moreover, previous studies have noted that the cation exchange capacity of the copper ions decreased with increasing acidity (Yu *et al*. 2009, Lee and Copper 2010, Pankras *et al.* 2012), as manifested by lower pH values for the thermally-modified wood. This was another reason for the high percentage of copper leached from the ACQ-D-treated, thermally-modified wood.

## CONCLUSIONS

1. The negative effect of thermal modification on copper fixation was found from the experimental data and the predictive model. In addition, this effect was more obvious for samples treated with higher concentrations of ACQ-D. Therefore, the preferential treating condition for exterior application was 0.90% ACQ-D concentration and 180 $^{o}$C heating temperature on the basis of its lower copper leaching.

2. A copper leaching model based on the assumption of a pseudo-second-order mechanism was developed to evaluate the capacity of copper ion leaching at any given time and to predict the final percentage of copper leaching of the ACQ-D-treated, thermally-modified wood for any given mass loss.

3. As determined in the FTIR analysis, the change in copper leaching performance can be attributed to the degradation and depolymerization of cell wall components during the treatment. These reactions diminished the number of fixation sites for copper ions in wood.

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