Effect of Bleach Pretreatment on Surface Discoloration of Dyed Wood Veneer Exposed to Artificial Light Irradiation

Yi Liu,[a,b,c,d] Hongwu Guo,[a,b,c,]*Jianmin Gao,[a,b,c,]* Fan Zhang,[a,b,c] Lingmin Shao,[a] and Brian K. Via [d]

To investigate the effect of bleach pretreatment on the surface photo-discoloration of dyed wood, two kinds of bleached and unbleached dyed wood veneers were irradiated in a xenon light source accelerated aging tester. The exposed surfaces' color, spectral reflectivity, chemical functional groups, and microstructure were characterized. Bleach pretreatment improved the dyeing effect of the wood veneers. However, it decreased the light fastness of the samples, and as adsorption between the dyes and wood components was reduced, some chromophoric chemical structures of the wood lignin and dyes were degraded, and some extractives (which can function as antioxidants to protect wood surfaces from discoloration) were removed. After light irradiation, the reflectance curves of dyed wood veneers was shifted toward longer wavelengths and noticeable yellowing was observed. Some parenchyma tissue, such as pit membranes in wood cell walls, suffered serious deterioration, as indicated by SEM.

Keywords: Dyed wood veneer; Bleach pretreatment; Surface photo-discoloration; Extractives; Reflectance spectrum

*Contact information: a: MOE Key Laboratory of Wooden Material Science and Application, Beijing Forestry University, Beijing 100083, China; b: Beijing Key Laboratory of Wood Science and Engineering, Beijing Forestry University, Beijing 100083, China; c: MOE Engineering Research Center of Forestry Biomass Materials and Bioenergy, Beijing Forestry University, Beijing 100083, China; d: Forest Products Development Center, School of Forestry and Wildlife Sciences, Auburn University, Auburn, AL 36849, USA; *Corresponding authors: ghw5052@163.com; jmgao@bjfu.edu.cn*

INTRODUCTION

Wood is a natural, renewable biomass source primarily consisting of cellulose, hemicellulose, lignin, and extractives. It is an ideal material for furniture manufacture, timber construction, and interior decoration. Wood's color is an important indicator of its value. In some cases, consumers select species that exhibit superior decorative properties. Bleach treatment can eliminate color differences and remove contamination from the wood surface. After bleaching, the wood surface color becomes lighter but retains its original texture. Additionally, because of the effects of oxidation and reduction, decolorizers can change the active chemical structure associated with the wood color in lignin and extractives. They can destroy some chromophoric groups (C=O, C=C) and stabilize some auxochromic groups (-OH). This results in wood decoloration and improves its light resistance. As a result, bleach treatment is commonly used on lesser-valued wood for color modulation and modification (Duan 2002).

Wood dyeing is an emerging technology used to achieve more efficient use of plantation wood *via* treatment. It can be optimized to yield decorative colors and enrich the patterns within the wood veneer (Zhuang 2004; Guo and Liu 2012; Liu *et al*. 2015a). Dyed wood products have been used in the manufacture of furniture, interior decoration, plywood secondary finishes, and handicrafts. However, as a polymeric composite, dyed wood veneer, like native wood, is prone to discoloration when exposed to light irradiation because the major photosensitive chemical constituents in dyes and wood contain unsaturated groups such as carbonyl groups and carbon-carbon double bonds. These unsaturated groups can facilitate various complex photochemical reactions, leading to dyed wood surface discoloration, and chemistry and microstructure degradation (Guo and Liu 2012; Fu *et al*. 2014; Liu *et al.* 2015b).

It is thought that bleach pretreatment, which is used in wood veneer dyeing, can be used to eliminate the color difference between earlywood and latewood to obtain a light color substrate, make the dyeing color more uniform, and reduce variance within the same batch. Additionally, it can improve the light fastness of dyed wood veneers. Although bleach pretreatment is commercially employed for wood modification, abundant studies have been performed analyzing the effects of bleaching on improving the color of wood. There are no publications available regarding the photo-discoloration of bleached dyed wood veneers. Detailed studies of bleached dyed wood veneer color changes with reflectance spectra and scanning electron microscopes (SEM) are also scarce in current literature. Furthermore, there is not any published study available regarding the chemical analysis of the photooxidation of bleached dyed wood veneers during accelerated aging. Changes to the color and affiliated properties of bleached dyed wood veneer surfaces as a result of light irradiation are not completely understood.

The aim of this study was to investigate the effects of bleach pretreatment on the color variation and surface property changes of dyed wood veneers exposed to artificial light. The exposed surface color, reflectivity curve, chemical functional groups, and microstructure changes during accelerated aging were also characterized.

EXPERIMENTAL

Materials

Fast-growing birch wood (*B. platyphylla* Suk.) veneers measuring 85 mm × 55 mm × 0.7 mm were prepared. The air-dried density of the veneers was 0.607 g/cm^3. Azo Acid Red GR (*C. I. Acid Red 73*) dye and three aryl methane Acid Blue V (*C. I. Acid Blue 1*) dye, commonly used in the wood dyeing industry, were provided by the Second Plant Dye Chemical Company in Tianjin, China. All other chemicals were purchased from Beijing Chemical Works and were of reagent grade.

Methods

Bleach pretreatment

A 4% (w/v) hydrogen peroxide solution was prepared containing 1% (w/v) $NaSiO_3$•$9H_2O$ as a buffering agent. The pH of the liquor was adjusted to 10.0 with 20% NaOH (w/w) solution. A bath ratio of 1:15 (V_{veneer}:$V_{bleach\ liquor}$) was used, and the wood veneers were placed into an electrically heated, temperature-controlled water bath. The bleaching process was carried out at 65 °C for 2 h. After bleaching, the raffinate of all veneers was washed away with treated water (3 mL, 30% (w/v) glacial acetic acid per liter of water) and then air-dried to a moisture content of 8%.

Dyeing treatment

An atmospheric-pressure impregnation method was used for wood veneer dyeing. Acid Red GR and Acid Blue V dyes with concentrations of 0.05% and 0.15% (w/v) were prepared with 0.15% (w/v) anhydrous Na_2SO_4 as a buffering agent. The pH of the liquor was adjusted to 4.0 with 10% H_2SO_4 (w/w). The bleached and unbleached wood veneers were inserted vertically into the groove of a dye vat with gaps between the samples to avoid overlap. A bath ratio of 1:15 ($V_{\text{wood veneer}}$:$V_{\text{dye liquor}}$) was used, and the veneers were placed into a temperature-controlled water bath dye vat. The dye liquor was stirred clockwise every 20 min to ensure even penetration. The dyeing process was carried out at 90 to 95 °C for 4 h. After dyeing, the raffinate of all dyed wood veneers was washed away with tap water. The dyed wood veneers were then air-dried and kept in a cool, dark place until use.

Xenon light irradiation

The wavelength domain of xenon light is from 300 nm to 800 nm, which is very close to the spectral distribution of light from the sun. It contains UV light, visible light, and infrared light. Accelerated ageing with artificial xenon light was performed to test the surface light resistance of the samples. Bleached and unbleached dyed wood veneers were exposed to a 42-W xenon light source for 100 h at a black panel thermometer (BPT) temperature of 55±2 °C and 65% relative humidity in an accelerated aging tester (Xenon Fade Meter, X25F, Japan). In order to provide contrast, the central region of the samples was covered with an aluminum sheet (2 mm thick). The chromatic indices and chemical changes of the samples were analyzed after irradiation for 0, 1, 2, 5, 10, 20, 40, 60, 80, and 100 h.

Color parameters and reflectance measurement

The color changes of the dyed wood veneer surfaces after light irradiation were evaluated using the CIE $L^*a^*b^*$ color system according to the standard of DIN EN ISO 11664-4-2011 (Pandey 2005a; Chen *et al.* 2012c). The color parameters L^*, a^*, and b^* were measured with a colorimeter (Datacolor SF600 Plus-CT. USA) using a D65 standard illuminant and 10° standard observer. Equipment calibration was carried out with standards provided by the supplier. All parameters were measured using three replicates each at two locations on each sample. The average value of each parameter was calculated. The overall color difference (ΔE^*) was used to describe the level of discoloration of the wood veneer. Normally, a greater ΔE^* value represents greater color change. ΔE^* was calculated according to Eq. 1,

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \tag{1}$$

where ΔE^* is the degree of total color change, L^* is the lightness (ranging from 0, black, to 100, white), a^* represents the red-green chromaticity coordinate ($+a^*$ indicates red color and $-a^*$ indicates green), and b^* denotes the yellow-blue chromaticity index ($+b^*$ indicates yellow color and $-b^*$ indicates blue). ΔL^*, Δa^*, and Δb^* are the differences in the values of L^*, a^*, and b^* before and after treatment, respectively.

The reflectance spectrum was used to identify the surface reflectance of wood samples, which were also recorded by the colorimeter. The reflectance was converted into K-M spectra according to the Kubelka-Munk equation,

$$F(R) = K/S = (1-R)^2/2R \qquad (2)$$

where $F(R)$ is the ratio of K-M units, R is the measured reflectance, and K and S are the absorption and scattering coefficients, respectively. The K/S spectrum, as a function of wavelength, is used to identify the apparent absorption maxima. Typically, based on the Kubelka-Munk theory, it can be assumed that a unit of K/S is approximately linearly related to the variation of chromophores in this range of absorption values (Chen *et al.* 2012b; Huang *et al.* 2012).

ATR-FTIR and SEM analysis

Chemical structure changes on the irradiated, dyed wood veneer surfaces were characterized by attenuated total reflectance-Fourier transform infrared spectrometry (ATR-FTIR; Nicolet Nexus 670, USA). All samples were directly placed on the diamond crystal of the ATR-FTIR spectrometer. The spectra were collected at a resolution of 8 cm^{-1} in the range of 4000 to 400 cm^{-1}, and 64 scans were recorded. An SEM (JSM 5900, Japan) was used to observe the micromorphology of the samples.

RESULTS AND DISCUSSION

Surface Color Changes after Bleach Pretreatment and Dyeing

Birch wood is considered light-colored, as it has high lightness, with L^* above 85 and a low red-green chromaticity, a^*, of almost 0 (Table 1). The apparent color changes were determined after bleach pretreatment (Fig. 1). There was a decrease in a^* values at the samples' surfaces after bleaching. The yellow-blue chromaticity b^* exhibited the same decreasing trend as a^*. This indicates that the surface color of the birch wood veneer faded and became less saturated, or had a lower hue.

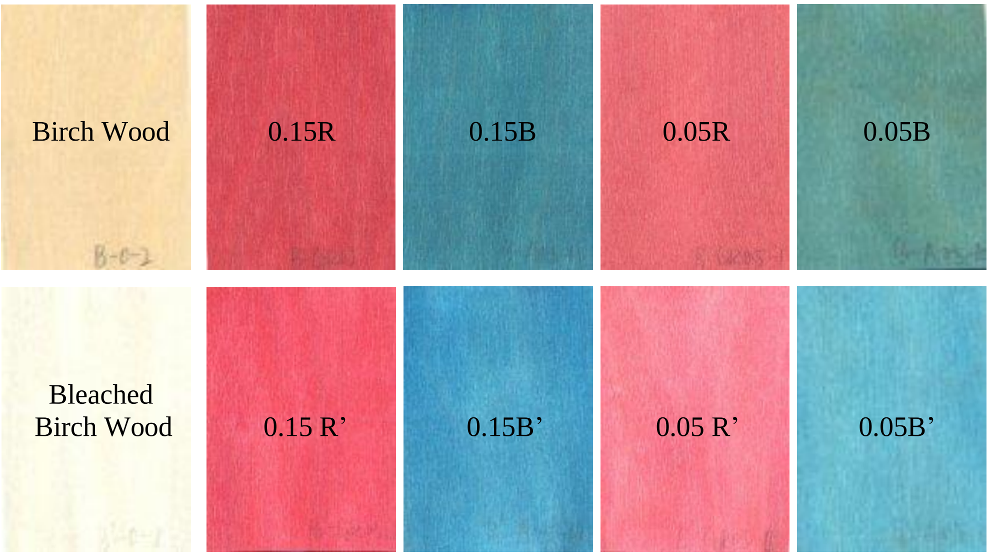

Fig. 1. Visual assessment of birch wood veneer and bleached birch wood veneer and their visual assessment after dyeing treatment (0.15 indicates that the concentration of dye liquor was 0.15%, 0.05 represents the concentration of dye liquor was 0.05%; R represents the Acid Red GR dye and B represents the Acid Blue V dye; ' represents bleach pretreatment)

Additionally, the L^* values accompanying the color difference ΔE^* (ΔE^* was 13.6) of the bleached veneers were noticeably increased compared to those of the unbleached control. Previous research has shown that the extractives in solid wood, such as flavone-glycosides, quinone-glycosides, and tannins, are active in hydrolysis and oxidation reactions in extracted solvent systems (Bekhta and Niemz 2003; Nzokou and Kamdem 2006; Ates *et al.* 2009; Fan *et al.* 2009; Chen *et al.* 2014). It is thought that the accumulation of these oxidation products results in color changes on the birch wood veneer surface (Friman *et al.* 2004; Kishino and Nakano 2004).

Table 1. Color Index of Wood Veneer before and after Bleach Pretreatment

	Birch Wood Veneer	Bleached Birch Wood Veneer
L^*	85.9 (1.10)[a]	92.1 (0.80)
a^*	2.4 (0.27)	-2.3 (0.33)
b^*	21.0 (0.84)	9.8 (0.97)
ΔE^*		13.6 (0.37)

[a] Numbers in parentheses represent the standard deviation of six replicates.

The color indices L^*, a^*, and b^* changes of bleached and unbleached wood veneers after dyeing are shown in Fig. 1 and Table 2. Compared with the undyed samples in Table 1, there was a clear decrease in the L^* values and apparent enhancement in ΔE^* of wood veneers after dyeing, regardless of the dye type or the concentration of dye liquor applied. On the other hand, compared with the unbleached samples, the bleached wood veneers dyed with Acid Red GR dyes exhibited increases in a^* values. Larger positive changes (the absolute value increase but from a mathematical point of view the values decreased) in a^* and b^* values were observed in the samples dyed with Acid Blue V dyes. Thus, bleach pretreatment influenced the dyeing effect of wood veneers, resulting in brighter-colored dyed wood veneers.

Table 2. Color Indices Changes of Bleached and Unbleached Wood Veneers after Dyeing

	0.05B	0.05B'	0.05R	0.05R'	0.15B	0.15B'	0.15R	0.15R'
L^*	63.2(2.20)[a]	72.4(2.20)	61.1(1.84)	66.7(2.35)	59.3(1.07)	63.6(1.91)	54.2(2.03)	57.2(1.18)
a^*	-26.0(0.96)	-32.2(1.08)	36.4(0.83)	36.7(1.21)	-30.9(1.01)	-35.0(0.89)	43.9(1.31)	48.7(1.07)
b^*	-1.2(0.04)	-10.7(0.81)	15.9(0.76)	9.7(0.14)	-7.5(0.73)	-17.6(1.31)	18.5(0.40)	15.8(0.55)
ΔE^*	42.6(1.95)	48.8(1.57)	42.4(1.84)	40.9(1.48)	51.3(2.01)	58.2(1.36)	52.3(2.20)	54.7(2.75)

[a] Numbers in parentheses represent the standard deviation of six replicates.

Surface Color Changes during Light Irradiation

The effect of the bleach pretreatment on the surface color changes of the dyed wood veneers exposed to xenon light is shown in Fig. 2 and Table 3. The color difference ΔE^* of all samples subjected to various treatments increased considerably with prolonged irradiation, especially during the initial 40 h. Bleach pretreatment had a dramatic influence on the ΔE^* value of the dyed wood veneer, yielding a substantial increase in ΔE^*. It should be noted that, after 100 h of irradiation, the ΔE^* values of the two kinds of bleached dyed wood veneers increased by 27.25 and 24.65%, respectively, relative to those of unbleached veneers dyed at a concentration of 0.05%. The increases were 41.23% and 29.90%, respectively, when the samples were dyed with 0.15% concentration dye liquor. This indicates that bleach pretreatment decreased the light fastness of the dyed wood veneer, causing greater discoloration on the sample surface, and that dye type and liquor concentration played a combined role.

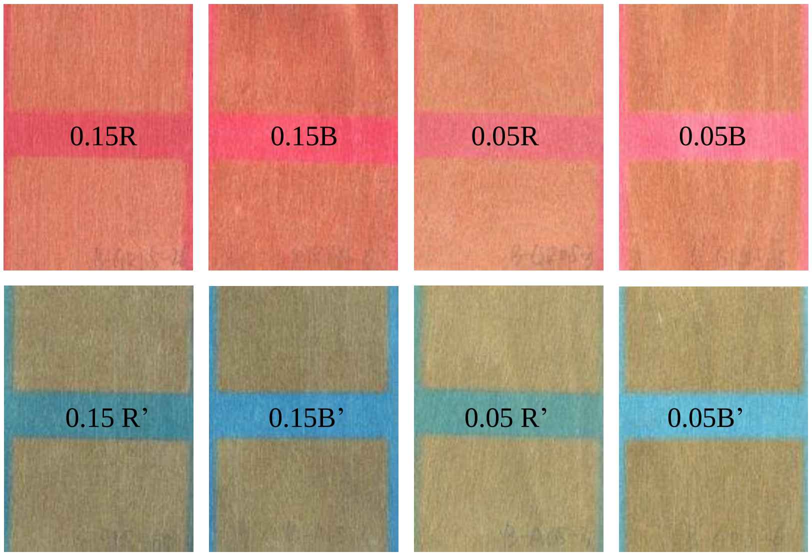

Fig. 2. Visual assessment of bleached and unbleached dyed wood veneer after 100 h of xenon light irradiation

Table 3. ΔE^* Changes of Bleached and Unbleached Dyed Wood Veneer during Xenon Light Irradiation

Time(h)	0.05B	0.05B'	0.05R	0.05R'	0.15B	0.15B'	0.15R	0.15R'
0	0	0	0	0	0	0	0	0
1	2.7(0.48)[a]	2.9(1.23)	0.9(1.08)	2.1(0.08)	2.2(0.26)	5.9(0.47)	1.5(0.94)	2.5(0.03)
2	4.5(0.74)	6.6(1.26)	2.1(0.89)	3.6(0.61)	3.8(0.34)	8.2(1.08)	2.9(1.36)	4.3(0.74)
5	8.4(1.27)	13.4(0.78)	3.7(0.83)	6.7(1.88)	7.2(0.54)	14.4(.099)	4.6(0.81)	8.0(1.18)
10	15.0(1.12)	21.6(1.06)	7.7(1.31)	10.8(1.06)	13.1(0.83)	21.9(1.02)	8.3(1.40)	12.7(1.06)
20	22.6(1.36)	30.8(0.68)	11.4(1.40)	16.3(1.46)	19.6(1.03)	30.6(1.59)	12.2(1.51)	17.9(0.68)
40	31.1(1.64)	40.4(1.57)	15.8(1.51)	20.6(1.57)	27.4(1.57)	39.6(1.47)	16.6(1.67)	22.6(2.05)
60	35.6(1.52)	46.1(1.46)	17.9(1.55)	23.6(1.45)	31.0(1.68)	44.8(1.52)	18.6(1.83)	25.2(1.57)
80	38.4(0.97)	49.2(1.65)	21.1(1.63)	25.4(1.56)	33.6(2.05)	47.8(2.06)	20.4(1.57)	26.5(1.48)
100	41.1(1.55)	52.3(1.89)	21.5(1.78)	26.8(1.19)	35.9(2.15)	50.7(2.12)	21.4(2.14)	27.8(1.19)

[a] Numbers in parentheses represent the standard deviation of six replicates.

Surface Chemical Structure Changes

Bleach pretreatment with hydrogen peroxide degraded or oxidized some unsaturated functional structures present in lignin and extractives (Fig. 3). This was evident in the complete disappearance of the C=O non-conjugated carbonyl bond peak at 1735 cm^{-1} and the significant decrease in intensity at 1234 cm^{-1}, assigned to -OH phenol hydroxyl stretching vibrations (Pandey 2005b; Chen *et al.* 2014). It is thought that the disappearance of carbonyl groups is consistent with the changes in a^* shown in Table 1. This indicates that the red-green hue of birch wood veneers can be largely attributed to the C=O groups they contain. Additionally, the decreased absorption of -OH phenol hydroxyl functional groups may be correlated with the lower b^* of the wood veneers obtained after bleach pretreatment compared to that of the unbleached ones. The characteristic absorption peak of aromatic vibrations, at 1595 cm^{-1} (also assigned to C=C unsaturated linkages), slightly changed in intensity after bleaching. These chemical changes destroyed the original surface chromophoric system of the birch wood veneer and increased the surface lightness, L^* (Table 1). The chemical functional group changes of the dyed wood veneers before and after light irradiation are shown in Fig. 4.

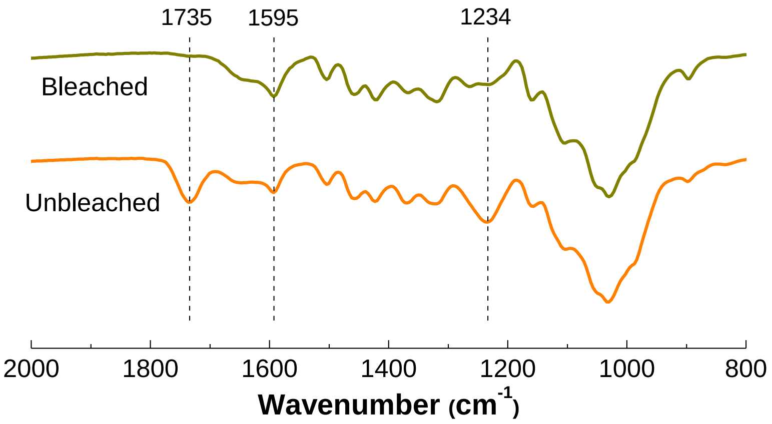

Fig. 3. ATR-FTIR spectra of bleached and unbleached birch wood veneers

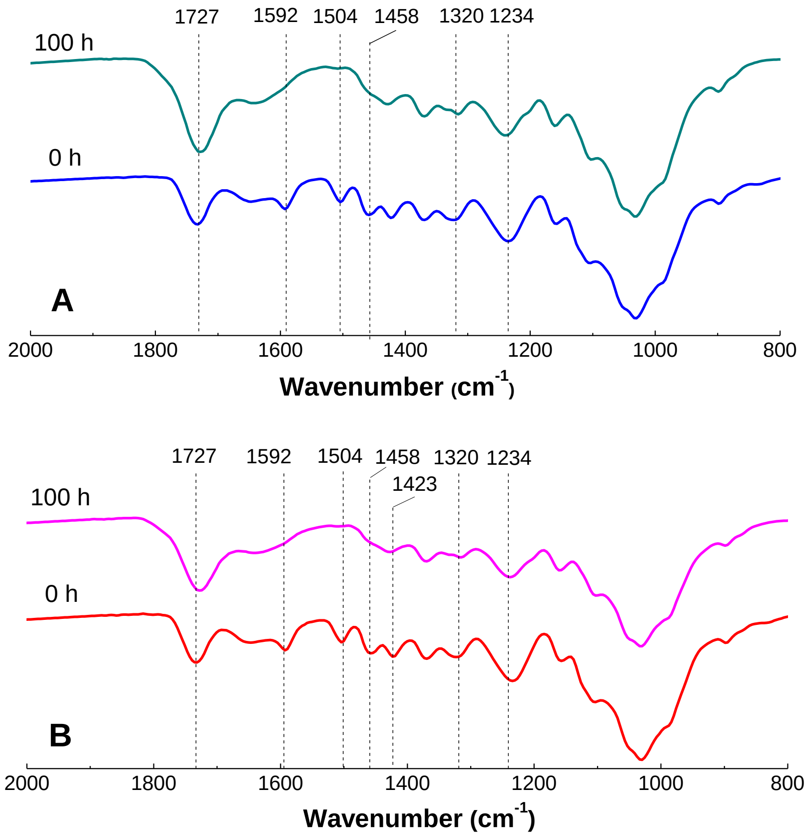

Fig. 4. ATR- FTIR spectra of (A) Acid Blue V- and (B) Acid Red GR-dyed wood veneer before and after light irradiation (the mass fraction of dye liquor was 0.15%)

Noticeable changes were observed in the fingerprint region from 800 to 1800 cm^{-1}. Some unsaturated groups initially present in wood lignin and/or dyes were degraded *via* photo-oxidation. The peak at 1727 cm^{-1}, assigned to the C=O bond of lignin and dyes, was enhanced considerably. The intensity of the C=C stretching of the aromatic skeleton at 1592 and 1504 cm^{-1} gradually disappeared after irradiation. Additionally, the transmittance bonds at 1458 and 1423 cm^{-1}, representing $-CH_3$ and $-CH_2$ asymmetric bending vibrations, considerably decreased in intensity, likely because of the reaction of the methoxy group of the benzene ring. Furthermore, the hydroxyl group on the benzene ring was also oxidized, as shown by the medium reduction at 1234 cm^{-1}. These results indicate that the structures of the dyes and wood lignin were degraded to a considerable extent, inducing undesirable discoloration of the dyed wood veneers.

Surface Spectral Reflectance Changes

Wood color is an important surface attribute determined by the spectral composition of visible light (350 to 780 nm) reflected from the wood surface (Rowell 2005; Guo and Liu 2012). The reflectance curves obtained were used to characterize the trends of wood color changes with respect to bleach pretreatment and light irradiation.

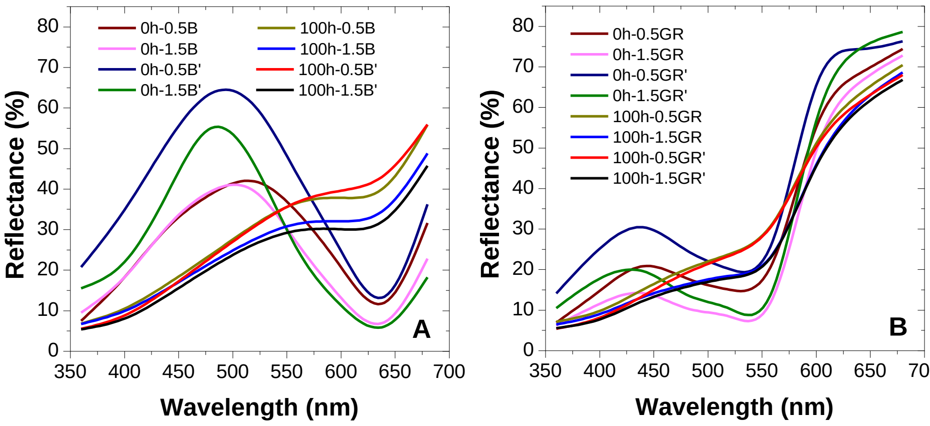

Fig. 5. Reflectance spectra of (A) Acid Blue V- and (B) Acid Red GR-dyed, bleached and unbleached dyed wood veneer before and after light irradiation

Compared with that of the unbleached dyed wood veneer, the color of the Acid Blue V-dyed samples became more saturated following bleach pretreatment, if compared with that of the unbleached dyed wood veneer. In fact, the reflectance in the 450 to 560 nm (blue-green light) wavelength region increased prominently (Fig. 5A). This result suggests that bleach pretreatment improved the dye absorption and consequently the dyeing effect in wood veneers. However, by observing the spectra in the Fig. 5A, it is evident that the reflectance of both bleached and unbleached dyed wood veneer underwent a significant change after 100 h of irradiation. In fact, the reflectance band in the 450 to 560 nm was almost disappeared whereas the reflectance in the long wavelength region, from 580 to 700 nm (yellow-orange-red light), substantially increased. These results suggest that the surface of the samples suffered serious color fading. The lightness of the samples' surfaces increased primarily toward yellowing. A similar trend was observed for Acid Red GR-dyed samples (Fig. 5B), albeit to a lesser extent. This is an indication that Acid Red GR-dyed wood veneers exhibit better light fastness than Acid

Blue V-dyed samples.

The above results are consistent with the analysis using the CIE $L^*a^*b^*$ system (Table 2 and Fig. 1), indicating that reflectance curves can be used to evaluate the color changes of wood veneers.

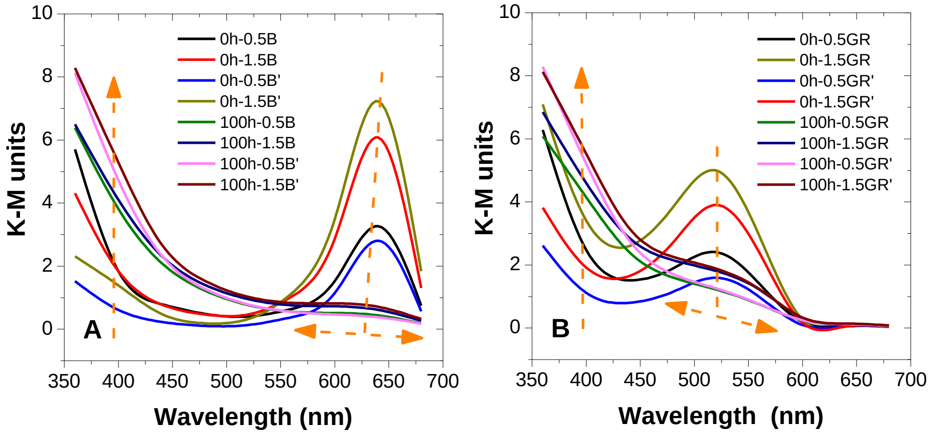

Fig. 6. K-M spectra of (A) Acid Blue V and (B) Acid Red GR bleached and unbleached dyed wood veneer before and after light irradiation

The K-M spectra (ratio of *K*/*S*) before and after bleach pretreatment and light irradiation display the visible light absorption changes and suggest that the generation of some types of chromophores in photo-degradation, condensation, or oxidation processes occurred (Chen *et al.* 2012a; Huang *et al.* 2012; Liu *et al*. 2015b).

Before xenon light irradiation, all Acid Blue V-dyed birch wood veneers exhibited characteristic absorption maxima at 640 nm, while Acid Red GR-dyed birch samples had absorption peaks near 520 nm (Fig. 6). Additionally, wood veneers dyed with higher-concentration dye liquor (0.15%) exhibited much higher absorptions in the visible light region. However, Huang *et al.* (2012) reported that the absorption maximum of pure birch wood was around 420 nm. This suggests that the chromophore system of the dyed wood veneer is different from that of pure wood.

Bleached and unbleached samples changed slightly when they were dyed with low-concentration dye liquor (0.05%). This suggests that the absorption of wood components played a dominant role in this case. On the other hand, the absorption of bleached dyed wood veneers was prominently improved compared to the unbleached samples when they were dyed with higher-concentration dye liquor (0.15%). The absorption of dyed wood veneers was determined to be a function of both wood composition and the properties of the dyes applied.

The absorption curves for the two kinds of dyed wood veneers changed after light irradiation. The characteristic absorption peak of both dyed wood samples decreased in intensity, almost disappearing, and the K-M unit in the region of 350 to 450 nm was dramatically increased (Fig. 6). This result is different from those observed by Huang *et al.* (2012) and Pastore *et al.* (2004), who reported that the K-M unit of pure birch and marupa solid wood increased across the whole visible light region with UV irradiation prolonged up to 100 h. The reasons for this difference were, primarily, as follows. First, it is believed that the surface discoloration of dyed wood veneers is due to changes in chromophores caused by light-induced degradation of dyes and lignin during accelerated aging. Pastore *et al.* (2004) reported that the absorption increase near 410 nm for marupa was due to the photo-degradation of lignin. This is because lignin is the most active component involved in photooxidation and the photochromic degradation of wood (Colom *et al.* 2003; Müller *et al.* 2003; Azadfallah *et al.* 2008; Rosu *et al.* 2010). Furthermore, the combination of acid dyes and wood occurs *via* physical adsorption. Under xenon light radiation, the dye molecules adsorbed on the wood cell wall are the first constituent to fade or discolor (Guo and Liu 2012), which can also influence the absorption spectrum of dyed wood surfaces. Therefore, the absorption features of dyed wood veneers are different from those of pure solid wood as they are related to dye photo-degradation products.

The effect of wood extractives on veneer appearance has not received sufficient attention in previous literature. As shown in Fig. 6, the bleached and dyed wood veneers suffered a slightly more degradation after light irradiation than those unbleached, due to the pre-treatment removing most of the extractives. This result is important in that it confirms the hypothesis that some extractives, such as phenols, contained in wood act as antioxidants and provide some protection against weathering degradation to the wood surface (Nzokou and Kamdem 2006). This result is inconsistent with previous findings indicating that the presence of extractives causes an increase of wood discoloration rate during the initial period of light irradiation (Pandey 2005a). However, more work is required to understand the complex chemistry behind these extractives' action to practically use their protective properties. Another reasonable explanation is that the dye molecules would be attach to the lignin and not to cellulose or hemicelluloses (Zhuang 2004; Guo and Liu 2012). During bleach pretreatment, hydrogen peroxide generated free radicals such as HOO•, O^-, and HO_2^- under alkaline conditions (Ek *et al.* 2009). These free radicals can oxidize and destroy the chemical structure of hydroxyl and carboxyl groups in the wood veneer, weakening the van der Waals binding force between the dye molecules and the wood components. As a result, the photosensitive wood components were more exposed, inducing more serious oxidation and degradation of lignin. Consequently, the photo-stability of the dyed wood veneer decreased and the surface fading was accelerated.

Surface Microstructure Changes

Bleach pretreatment removed most of the extractives in the wood tracheid *via* hydrolysis and oxidation, leaving the longitudinal permeability channel relatively unobstructed during wood veneer dyeing. Comparing Figures 7A and 7B, it can be concluded that bleach pretreatment improved the dispersivity of the dyes and reduced the accumulation of dye particles. This resulted in increased dyeing uniformity and dye adsorption, thereby improving the dyeing effect of the wood veneer.

Removing extractives could reduce adsorption between dyes and wood photosensitive components. This phenomenon caused the dyed wood veneer to become more sensitive to discoloration and degradation. Figures 7C and 7D demonstrate that, after light irradiation, some microstructures of the wood surface were degraded. Part of the parenchyma tissue, such as the pit membrane in the wood cell wall, suffered serious deterioration. Under the effects of long-term radiation, the changes in the microstructure increased the roughness of the wood veneer surface, affecting the surface color fastness and coating performance.

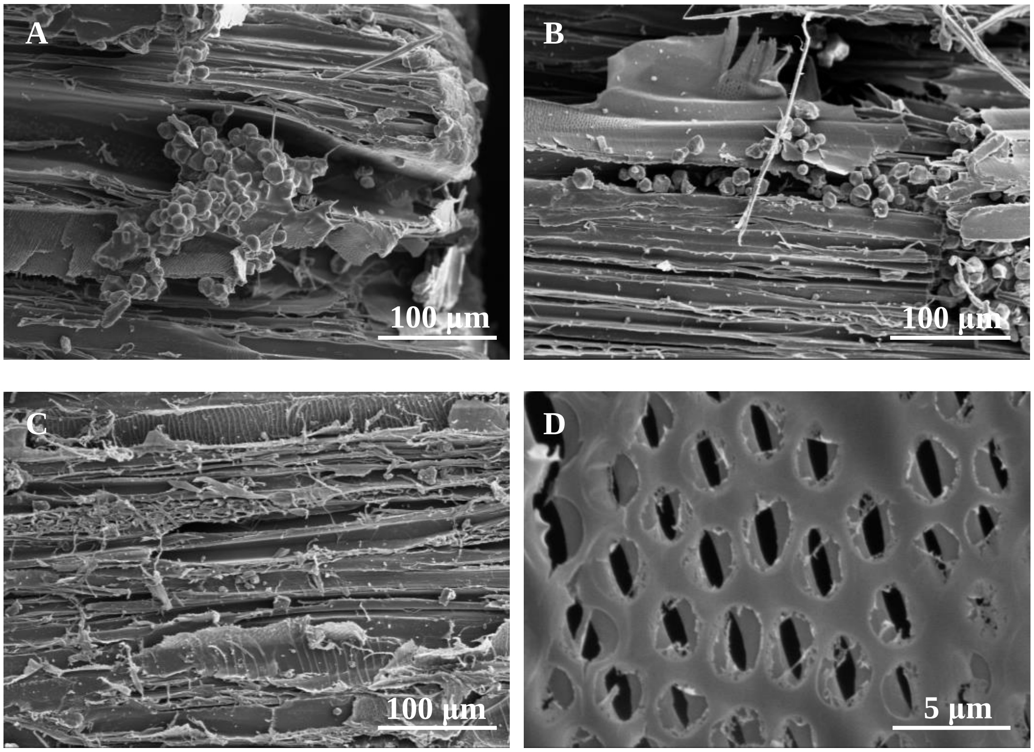

Fig. 7. Microstructure of (A) unbleached and (B) bleached dyed wood veneer and (C, D) the surface morphologies after light irradiation

CONCLUSIONS

1. Bleach pretreatment removed most of the extractives from the wood tracheid, improved the dispersivity of dyes, and reduced the accumulation of dye particles. These factors together resulted in improved dyeing of the wood veneer.
2. Bleach pretreatment decreased the light fastness of dyed wood veneers, as the adsorption between dyes and wood components was weakened, some chromophoric chemical structures in lignin and the dyes were destroyed, and some extractives (which can function as antioxidants and protect the wood surface from discoloration) were removed.
3. After light irradiation, the reflectance curves were shifted toward longer wavelengths. Sample surfaces suffered serious yellowing.
4. The reflectance curve is suitable for estimating the color change in wood veneers.
5. Some parenchyma tissue, such as the pit membrane in wood cell walls, suffered serious deterioration after light irradiation.

ACKNOWLEDGMENTS

The authors are grateful for the support of the Beijing Municipal Education Commission Joint Project for Scientific Research and Graduate Training, the Special Fund for Forest Scientific Research in the Public Welfare (No. 201204702), the China

Scholarship Council (No. 201306510015), and the Forest Products Development Center within the School of Forestry and Wildlife Sciences. Regions Bank is also acknowledged for their financial support for value-added products from wood.

REFERENCES CITED

Ates, S., Akyildiz, M. H., and Ozdemir, H. (2009). “Effects of heat treatment on Calabrian pine (*Pinus brutia* Ten.) wood,” *BioResources* 4(3), 1032-1043. DOI: 10.15376/biores.4.3.1032-1043 Azadfallah, M., Mirshokraei, S. A., Latibari, A. J., and Parsapajouh, D. (2008). “Analysis of photodegraded lignin on cellulose matrix by means of FTIR spectroscopy and high pressure size exclusion chromatography,” *Iranian Polymer Journal* 17(1), 73-80.

Bekhta, P., and Niemz, P. (2003). “Effect of high temperature on the change in color, dimensional stability and mechanical properties of spruce wood,” *Holzforschung* 57(5), 539-546. DOI: 10.1515/HF.2003.080

Chen, Y., Fan, Y., Gao, J., and Stark, N. M. (2012a). “The effect of heat treatment on the chemical and color change of black locust (*Robinia pseudoacacia*) wood flour,” *BioResources* 7(1), 1157-1170. DOI: 10.15376/biores.7.1.1157-1170

Chen, Y., Fan, Y., Gao, J., Tshabalala, M. A., and Stark, N. M. (2012b). “Spectroscopic analysis of the role of extractives on heat-induced discoloration of black locust (*Robinia pseudoacacia*),” *Wood Material Science and Engineering* 7(4), 209-216. DOI: 10.1080/17480272.2012.669407

Chen, Y., Gao, J., Fan, Y., Tshabalala, M. A., and Stark, N. M. (2012c). “Heat-induced chemical and color changes of extractive-free black locust (*Robinia pseudoacacia*) wood,” *BioResources* 7(2), 2236-2248. DOI: 10.15376/biores.7.2.2236-2248

Chen, Y., Tshabalala, M. A., Gao, J., Stark, N. M., and Fan, Y. (2014). “Color and surface chemistry changes of pine wood flour after extraction and delignification,” *BioResources* 9(2), 2937-2948. DOI: 10.15376/biores.9.2.2937-2948

Colom, X., Carrillo, F., Nogués, F., and Garriga, P. (2003). “Structural analysis of photodegraded wood by means of FTIR spectroscopy,” *Polymer Degradation and Stability* 80(3), 543-549. DOI: 10.1016/S0141-3910(03)00051-X

Duan, X. (2002). *Wood Color Control Technology*, China Building Materials Industry Press, Beijing.

Ek, M., Gellerstedt, G., and Henriksson, G. (2009). *Pulping Chemistry and Technology*, Walter de Gruyter, Berlin. DOI: 10.1515/9783110213423

Fan, Y., Gao, J., and Chen, Y. (2009). “Colour responses of black locust (*Robinia pseudoacacia* L.) to solvent extraction and heat treatment,” *Wood Science and Technology* 44(4), 667-678. DOI: 10.1007/s00226-009-0289-7

Fu, Z., Liu, Y., Xing, F., and Guo, H. (2014). “Changes in chemistry component structure and microstructure characterization of acetylated wood before and after UV radiation,” *Spectroscopy and Spectral Analysis* 34 (11), 2944-2947. DOI: 10.3964/j.issn.1000-0593(2014)11-2944-04

Friman, L., Höglund, H., Högberg, H.-E., and Agnemo, R. (2004). “Tannin-iron impregnated thermomechanical pulp Part II: Bleachability and brightness reversion,” *Nordic Pulp and Paper Research Journal* 19(4), 525-531. DOI: 10.3183/NPPRJ-2004-19-04-p525-531

Guo, H., and Liu, Y. (2012). *Photochromic of Coated Dyeing Wood*, China Environmental Science Press, Beijing.

Huang, X., Kocaefe, D., Kocaefe, Y., Boluk, Y., and Pichette, A. (2012). “A spectrocolorimetric and chemical study on color modification of heat-treated wood during artificial weathering,” *Applied Surface Science* 258(14), 5360-5369. DOI: 10.1016/j.apsusc.2012.02.005

Kishino, M., and Nakano, T. (2004). “Artificial weathering of tropical woods. Part 2: Color change,” *Holzforschung* 58(5), 558-565. DOI: 10.1515/HF.2004.085

Liu, Y., Hu, J., Gao, J., Guo, H., Chen, Y., Cheng, Q., and Via, B. K. (2015a). "Wood veneer dyeing enhancement by ultrasonic-assisted treatment," *BioResources* 10(1), 1198-1212. DOI: 10.15376/biores.10.1.1198-1212

Liu, Y., Shao, L., Gao, J., Guo, H., Chen, Y., Cheng, Q., and Via, B. K. (2015b). "Surface photo-discoloration and degradation of dyed wood veneer exposed to different wavelength of artificial light," *Applied Surface Science* 311,353-361. DOI: 10.1016/j.apsusc.2015.01.091

Müller, U., Rätzsch, M., Schwanninger, M., Steiner, M., and Zöbl, H. (2003). “Yellowing and IR-changes of spruce wood as result of UV-irradiation,” *Journal of Photochemistry and Photobiology B: Biology* 69(2), 97-105. DOI: 10.1016/S1011-1344(02)00412-8

Nzokou, P., and Kamdem, D. P. (2006). “Influence of wood extractives on the photo-discoloration of wood surfaces exposed to artificial weathering,” *Color Research and Application* 31(5), 425-434. DOI: 10.1002/col.20248

Pandey, K. K. (2005a). “A note on the influence of extractives on the photo-discoloration and photo-degradation of wood,” *Polymer Degradation and Stability* 87(2), 375-379. DOI: 10.1016/j.polymdegradstab.2004.09.007

Pandey, K. K. (2005b). “Study of the effect of photo-irradiation on the surface chemistry of wood,” *Polymer Degradation and Stability* 90(1), 9-20. DOI: 10.1016/j.polymdegradstab.2005.02.009

Pastore, T. C. M., Santos, K. O., and Rubim, J. C. (2004). “A spectrocolorimetric study on the effect of ultraviolet irradiation of four tropical hardwoods,” *Bioresource Technology* 93(1), 37-42. DOI: 10.1016/j.biortech.2003.10.035

Rosu, D., Teaca, C. A., Bodirlau, R., and Rosu, L. (2010). “FTIR and color change of the modified wood as a result of artificial light irradiation,” *Journal of Photochemistry and Photobiology B: Biology* 99(3), 144-9. DOI: 10.1016/j.jphotobiol.2010.03.010

Rowell, R. M. (2005). *Handbook of Wood Chemistry and Wood Composites*, CRC Press, Boca Raton, FL.

Zhuang, Q. (2004). *Engineered Wood-Reconstituted Decorative Lumber*, China Forestry Publishing House, Beijing.

Article submitted: November 15, 2014; Peer review completed: April 4, 2015; Revised version received and accepted: July 2, 2015; Published: July 21, 2015.
DOI: 10.15376/biores.10.3.5607-5619