DISCOLORATION OF OAK VENEER INDUCED BY METAL IONS

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ABSTRACT

The 3 mm thick oak veneers were discolored by single ions of Fe^{2+}, Cu^{2+}, and Mn^{2+} and mixed ions of Fe^{2+}-Cu^{2+}, Fe^{2+}-Mn^{2+}, and Cu^{2+}-Mn^{2+}. The brightness (L^*), red-green index (a^*), and yellow-blue index (b^*) of the veneers changed by varying degrees with the changes in ion mass fraction, temperature, heating time, ion species, and ion mass fraction ratio. The maximum values of total color difference ($\triangle E^*$) of the veneers were 38.94, 11.79, and 9.42 for Fe^{2+}, Cu^{2+}, and Mn^{2+}. Moreover, the total color difference ($\triangle E^*$) values of 24.07, 13.71, and 4.45 were observed for Fe^{2+}-Cu^{2+}, Fe^{2+}-Mn^{2+}, and Cu^{2+}-Mn^{2+} mixed ions. The veneers showed different degrees of vibrational peaks after discoloration. According to the ultraviolet spectrum, Fe^{2+} had a red shift in the ultraviolet absorption band of the unsaturated carbonyl compound and benzene ring compound. Moreover, the dark effect of Fe^{2+}, Fe^{2+}-Cu^{2+}, Fe^{2+}-Mn^{2+}, Mn^{2+}, Cu^{2+}-Mn^{2+}, and Cu^{2+} gradually decreased. The surface of the veneer was flat, without any rupture or deformation, and the pores were clear after treatment.

KEYWORDS: Oak veneers, metal ions, inducer, discoloration.

INTRODUCTION

In recent years, the number of oak veneer imports has increased sharply in China. However, oak veneers change color due to microorganisms, acids, alkalis, and temperature rise during transportation. In addition, the veneers during manufacturing and use undergo irregular color changes (Li 2002). Inducing discoloration in oak wood can make the common wood obtain the color of high-value tree species (Ma 2012). It also satisfies the difference in people's aesthetic perceptions (Tao 2016). In recent years, researchers have conducted research on inducing oak wood discoloration by using the chromatin and auxochrome groups contained in the wood (Yu 2012, Cao 2019, Xu and Qi 2019, Xiao et al. 2019, Ning 2019, Xu et al. 2021). Wood discoloration is mainly induced by heat treatment (Sundqvist 2002, Gao et al. 2005, Jiang

and Lu 2011), light (Nzokou 2006, Zahrl et al. 2007), changing of wood extracts (Chen et al. 2009, Chang et al. 2010, Li et al. 2020). Studies showed that the main reasons behind the change in the wood color are the degradation of lignin (Calienno et al. 2015, Wang et al. 2008), reduction of oxygen-containing functional groups, and increase of quinone structures (Luo and Yu 2012, Bonifazi et al. 2015).

Cao et al. (2020) studied the chemical discoloration process and mechanism of oak wood treated with $FeCl_2$ and concluded that the uniform discoloration of oak veneer surface after treatment with ferrous chloride solution was mainly due to the complex reaction between phenolic substances in wood and iron ions. Hong et al. (2020) used a single copper ion to induce the discoloration of oak veneer in solid wood composite flooring and analyzed the effects of the amount of metal ion inducer and drying temperature on the color spatial distribution and luster of oak veneer. This research on wood discoloration induced by metal ions only used a single metal ion to induce discoloration. The research on oak wood discoloration induced by multiple metal ions as inducers has not been reported.

In this study, various single and mixed metal ions were used as inducers to induce wood discoloration by chemical reaction of metal ions with aromatic compounds, extracts, and lignin. Another purpose of this study was to induce wood discoloration under different ion mass fractions, temperatures, heating time, ion species, and ion mass fraction ratios.

MATERIAL AND METHODS

Materials

Oak veneers (*Xylosma racemosum*) with the dimension of 65 × 65 × 3 mm were used as specimens in this study. The number of specimens was 12 pieces for each treatment. The brightness (L^*), red-green index (a^*), and yellow-blue index (b^*) were averaged by 3 measured values for each specimen. The density of the specimen was 0.71 $g \cdot cm^{-3}$, The moisture content of specimens was 9%. The inducers, Fe^{2+} ($FeSO_4$) and Cu^{2+} ($CuSO_4$) were purchased from the Tianjin Damao chemical reagent factory. The inducer Mn^{2+} ($MnSO_4$) was bought from the Tianjin Yongda chemical reagent factory.

Test instruments

A tristimulus color meter (CR-410, Konica Minolta of Japan) with an aperture of 60 mm was used in this study. A grinding machine (K1T-DS-100, Shanghai Tiandao Electric Appliance Co., LTD) was utilized for grinding work. Vacuum Oven (DZF, Shanghai Jizhong Instrument Co., LTD) and analytical balance (FA2104, Shanghai Hengping Precision Electronics Co) were also availed in this work. The extraction work was done by a spherical 250 mL Soxhlet extractor (Xinmingte Glass Instrument Co., LTD). Ultraviolet- visible- near- infrared (UV-Vis-NIR) spectrophotometer (Cary5000, Varian Corporation of America) and scanning electron microscope (Quanta 200, AmericaFEI) were used in this study.

Pretreatment of specimens

The surfaces of the specimens were sanded in order to expose the double-bonded benzene rings more on the surface. Then specimens were put into a vacuum oven, dried at 35℃ for 12 h, and numbered.

Solution configuration of metal ion inducer

Single ion mass fractions were selected with 1%, 4%, 8%, 12%, and 16% values. The 1 g, 4 g, 8 g, 12 g, and 16 g of single ion inducers were dissolved individually in 99 g, 96 g, 92 g, 88 g, and 84 g of corresponding water, respectively.

Tab. 1: Mass fraction ratios of mixed metal ions.

Mass fraction ratio	Fe^{2+}-Cu^{2+}		Fe^{2+}-Mn^{2+}		Cu^{2+}-Mn^{2+}	
	Ferrous sulfate (g)	Cuprum sulfate (g)	Ferrous sulfate (g)	Manganese sulfate (g)	Cuprum sulfate (g)	Manganese sulfate (g)
7:3	11.2	4.8	11.2	4.8	11.2	4.8
5:5	8.0	8.0	8.0	8.0	8.0	8.0
3:7	4.8	11.2	4.8	11.2	4.8	11.2

Mixed ion mass fraction ratios are shown in Tab. 1. The quantities of both types of single ion inducers were weighed according to Tab. 1. Both the single ion inducers were dissolved into 84 g of water to have the mixed ion inducer with a 16% mass fraction value.

Inducing discoloration of oak veneer

Test conditions of metal ion-induced discoloration are presented in Tabs. 2 and 3. The inducer was evenly coated along the grain direction on the surfaces of oak veneers using a short bristle moistened with the inducer to induce discoloration.

Tab. 2: Experimental parameters of discoloration induced by single metal ion.

Serial number	1	2	3	4	5	6	7	8	9	10	11
Mass fraction (%)	1	4	8	12	16	1	4	8	12	16	1
Temperature (℃)	50	50	50	50	50	70	70	70	70	70	90
Heating time (h)	1	1	1	1	1	1	1	1	1	1	1
Serial number	12	13	14	15	16	17	18	19	20	22	23
Mass fraction (%)	4	8	12	16	1	4	8	12	16	4	8
Temperature (℃)	90	90	90	90	50	50	50	50	50	70	70
Heating time (h)	1	1	1	1	2	2	2	2	2	2	2
Serial number	24	25	26	27	28	29	30	31	32	33	34
Mass fraction (%)	12	16	1	4	8	12	16	1	4	8	16
Temperature (℃)	70	70	90	90	90	90	90	50	50	50	50
Heating time (h)	2	2	2	2	2	2	2	3	3	3	3
Serial number	35	36	37	38	39	40	41	42	43	44	45
Mass fraction (%)	1	4	8	12	16	1	4	8	12	14	16
Temperature (℃)	70	70	70	70	70	90	90	90	90	90	90
Heating time (h)	3	3	3	3	3	3	3	3	3	3	3

Tab. 3: Experimental parameters of mixed metal ion-induced discoloration process.

Serial number	Temperature (℃)	Heating time (h)	Mass fraction ratio	Serial number	Temperature (℃)	Heating time (h)	Mass fraction ratio
1	50	1	7:3	14	70	2	1:1
2	50	1	1:1	15	70	2	3:7
3	50	1	3:7	16	90	2	7:3
4	70	1	7:3	17	90	2	1:1
5	70	1	1:1	18	90	2	3:7
6	70	1	3:7	19	50	3	7:3
7	90	1	7:3	20	50	3	1:1
8	90	1	1:1	21	50	3	3:7
9	90	1	3:7	22	70	3	7:3
10	50	2	7:3	23	70	3	1:1
11	50	2	1:1	24	70	3	3:7
12	50	2	3:7	25	90	3	7:3
13	70	2	7:3	26	90	3	1:1
				27	90	3	3:7

FTIR infrared spectroscopy

Oak veneers before and after treatment were oven dried under 35 . The discolored surface layer was scraped off and ground to a fine powder. The resulting powder was mixed with KBr and pressed into a tablet. The infrared spectroscopy was performed in the wave number range of 500~4000 cm^{-1}.

UV-Vis spectroscopy

After grinding, 5 g of oak powder was put into a circular disk with a diameter of 100 μm. This disk of 5 g of oak powder was then placed on filter paper. The powders were extracted in 10 h using absolute ethyl alcohol. The extractions were used for analytical analyses with the UV-Vis-NIR spectrophotometer. The UV-Vis-NIR spectroscopy was done in the wave number range from 200 to 500 nm.

Scanning electron microscopy (SEM)

Samples with 5 × 5 ×1.5 mm were cut from the specimens and fixed on EP pipe. Metal was sprayed on the surfaces of specimens for 1 min to increase electrical conductivity. Analysis was made using scanning electron microscopy (SEM) with a working voltage of 15 kV and a working distance of 9 mm. The images of specimens were magnified 1000 times.

RESULTS AND DISCUSSION

Discoloration of oak veneer induced by single metal ions

According to the standard chromaticity system CIE (1976), in the term "$L^*a^*b^*$" recommended by the International Lighting Commission, L^* denotes brightness, a^* denotes red-green index, b^* denotes yellow-blue index, and ΔE^* denotes total color difference. The effect of mass fraction, temperature, and heating time on the color of oak veneer induced by a single metal ion is shown in Fig. 1, Fig. 5, and Fig. 6, resp.

From Figs. 1a-c, it is clear that the values of L^*, a^*, and b^* with the same metal ion mass fractions are in the following order: $Mn^{2+} > Cu^{2+} > Fe^{2+}$. It indicates that the color of specimens after discoloration changes from light to dark, red to green, and yellow to blue for Mn^{2+}, Cu^{2+}, and Fe^{2+}, respectively. Moreover, as the mass fraction of the metal ion inducers, Fe^{2+} and Cu^{2+}, increased, the value of L^*, a^*, and b^* decreased. However, the value of L^*, a^*, and b^* increased with the mass fraction of the metal ion inducer Mn^{2+}. It indicates that the specimens' colors gradually get dark after inducing Fe^{2+} and Cu^{2+}. After that, it turns green and then blue. The overall tendency is towards dark and cold tints. In contrast, the colors of specimens become gradually brighter after inducing Mn^{2+}. The colors change to red and then yellow. The general tendency is towards bright and warm colors.

Fig. 1d shows that the values of ΔE^* of discolored veneer induced by single metal ions are in the following order: $Fe^{2+} > Cu^{2+} > Mn^{2+}$. It represents that the change in color of specimens on a scale from strong to weak is in the following order: Fe^{2+}, Cu^{2+} and Mn^{2+}. Moreover, with the increase of the mass fraction of metal ion inducer, the values of ΔE^* of specimens increase after inducing Fe^{2+}, Cu^{2+}, and Mn^{2+}. It shows that the change in color becomes significant for induced specimens. This trend can be mainly attributed to more colored substances inducing wood discoloration after inducing metal ions. The phenolic compounds, such as tannin in wood complexing with metal ions, produce varying degrees of discoloration of colored materials in wood (Chen et al. 2003, Yu and Jin 2015).

Figs. 2-4 show the color change of oak veneer induced by different mass fractions of inducers of a single metal ion.
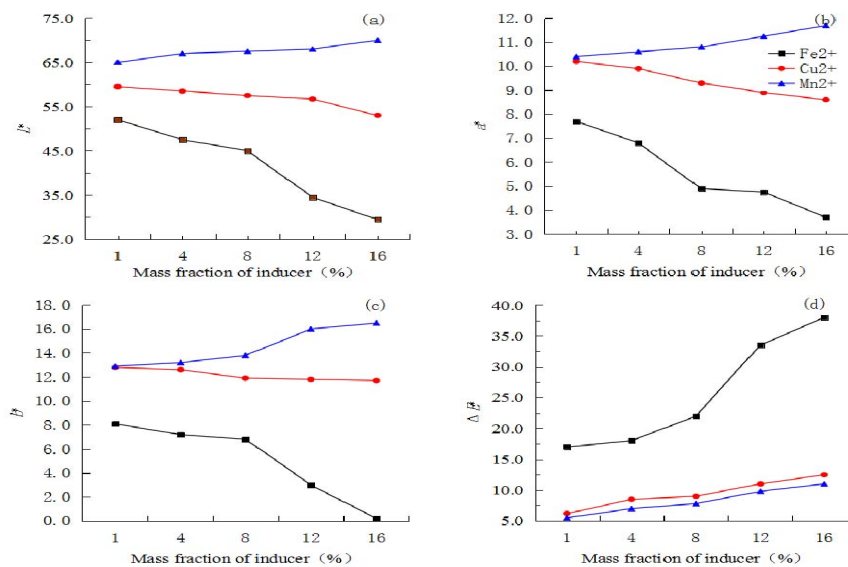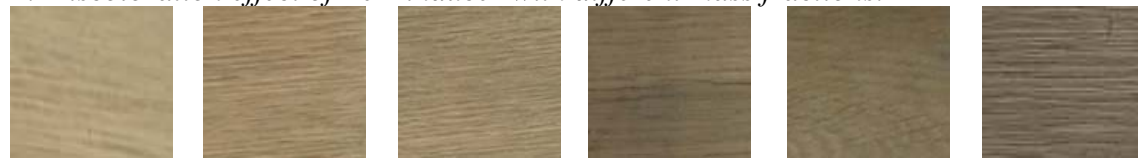

Fig. 1: Effect of mass fraction of metal ion inducer on the color of oak veneers.

| Untreated | 1% | 4% | 8% | 12% | 16% |

Fig. 2: Discoloration effect of Fe^{2+} inducer with different mass fractions.

| Untreated | 1% | 4% | 8% | 12% | 16% |

Fig. 3: Discoloration effect of Cu^{2+} inducer with different mass fractions.

| Untreated | 1% | 4% | 8% | 12% | 16% |

Fig. 4: Discoloration effect of Mn^{2+} inducer with different mass fractions.

Figs. 5a-c show that the magnitudes of L^*, a^*, and b^* of discolored veneer induced by Fe^{2+} and Cu^{2+} decreases as the temperature rises. However, the magnitudes of L^*, a^*, and b^* of discolored veneer, induced by Mn^{2+}, increase with the temperature rise. It presents that the color of specimens after introducing Fe^{2+} and Cu^{2+} gradually becomes dark, green, and then blue. The overall tendency is towards dark and cold tints with the temperature increase. On the contrary, the color of specimens, after inducing Mn^{2+}, gradually becomes bright, red, and then yellow with the temperature rise. The tendency is generally towards bright and warm colors with increased temperature. This trend can be mainly attributed to the occurrence of redox reactions and molecular rearrangements in wood components. A part of phenolic hydroxyl or substituent oxidation occurs, causing changes in color system structure and thus resulting in wood discoloration.

Fig. 5d shows that the values of ΔE^* of discolored veneer induced by single metal ions are in the following order: $Fe^{2+} > Cu^{2+} > Mn^{2+}$. It describes that the sensitivity of specimens, after inducing single metal ions, to temperatures from strong to weak is in the following order: Fe^{2+}, Cu^{2+}, and Mn^{2+}. Moreover, with the increase in temperature, the values of ΔE^* of specimens increase after inducing Fe^{2+}, Cu^{2+}, and Mn^{2+}. It suggests that the change in the color of specimens increases after the temperature has risen.
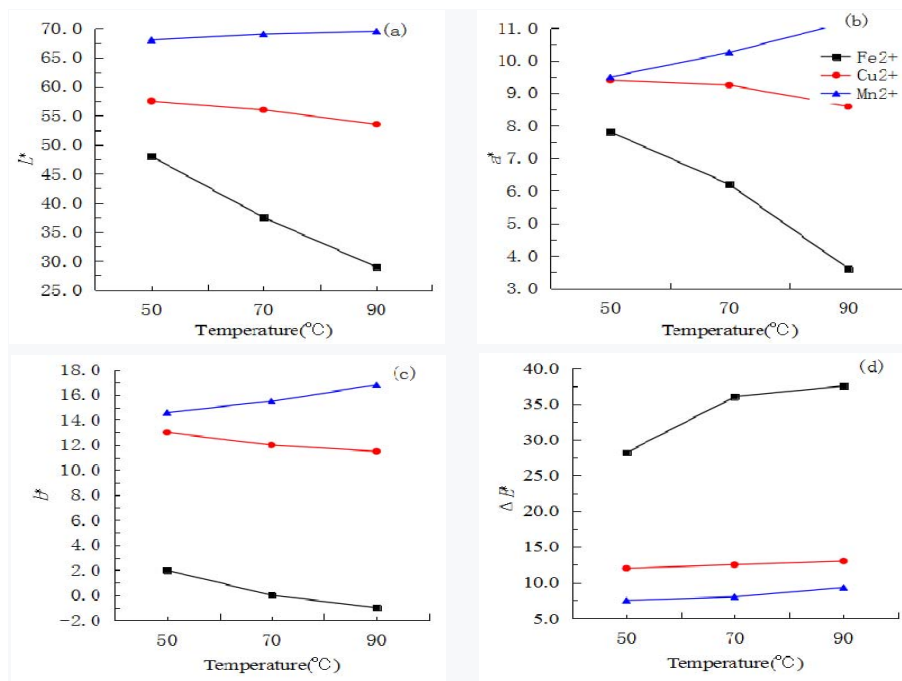
Fig. 5: Effect of temperature on the color of oak veneers induced by single metal ion.

From Figs. 6a-c, it can be observed that with the increase of heating time, the values of L^*, a^*, and b^* of discolored veneer are in the following order: Mn^{2+} **>** Cu^{2+} **>** Fe^{2+}. It describes that the colors of specimens with the increase of heating time change from light to dark, from red to green, and from yellow to blue for Mn^{2+}, Cu^{2+}, and Fe^{2+} samples. Moreover, as heating time increases, the values of L^*, a^*, and b^* of specimens after inducing Fe^{2+} and Cu^{2+} decrease, and this trend gradually increases. It tells that the color of specimens gradually darkens. It turns green and then blue. Mostly, the trend is toward dark and cold tints after inducing Fe^{2+} and Cu^{2+}.

However, the values of L^*, a^*, and b^* of specimens increase after inducing Mn^{2+}. It shows that the color of specimens gradually becomes bright. It turns red and then yellow. Overall, the tendency is toward bright and warm colors with increased heating time. This trend is mainly associated with the lignin and hemicellulose in wood being degraded by heat treatment. Moreover, with the extension of treatment time, the degree of reaction of lignin and hemicellulose is different. The effect of heat treatment temperature on the change in wood color is greater than that of heat treatment time (Chi 2005).

Fig. 6d shows that the magnitudes of ΔE^* of discolored veneer induced by single metal ions can easily be arranged in the following order: Fe^{2+} **>** Cu^{2+} **>** Mn^{2+}. It suggests that the effect of heating time on the change in color of specimens on a scale of high to low is in the given order: Fe^{2+}, Cu^{2+}, and Mn^{2+}. Moreover, with the increase of heating time, the value of ΔE^* of specimens increases after inducing Fe^{2+}, Cu^{2+}, and Mn^{2+}. It illustrates that the change in color of specimens is greatly enhanced after the increase in the heating time. The maximum values of ΔE^* of discolored veneer induced by Fe^{2+}, Cu^{2+}, and Mn^{2+} were 38.9, 11.8, and 9.4, resp., with the mass fraction of inducer equal to 16%, the temperature of 90 , and the heating time of 3 h.
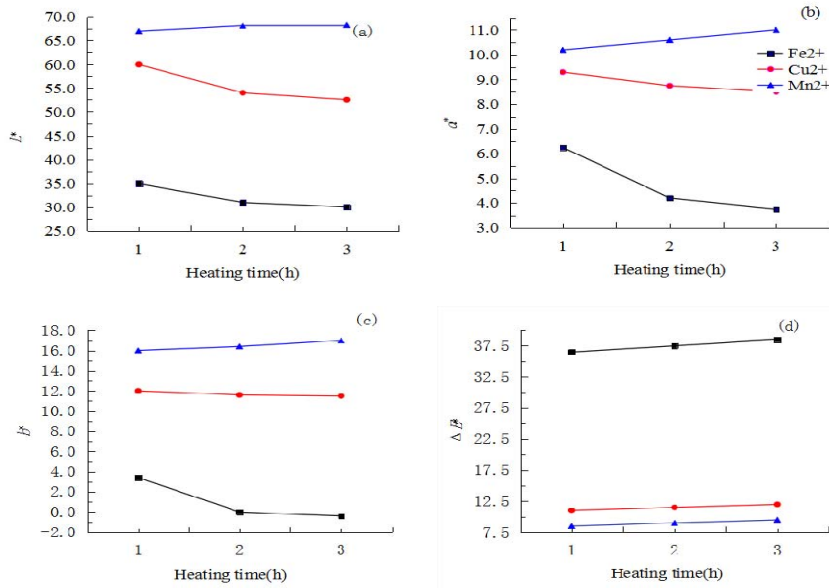
Fig. 6: Effect of heating time on the color of oak veneers induced by single metal ion.

Discoloration of oak veneer induced by mixed metal ions

The effects of mass fraction, temperature, and heating time on the color of oak veneer induced by mixed metal ions are shown in Figs. 7-12, resp. Magnitudes of L^*, a^*, and b^* of specimens after discoloration induced by mixed metal ions are in the following order: Cu^{2+}-Mn^{2+} > Fe^{2+}-Mn^{2+} > Fe^{2+}-Cu^{2+} (Figs. 7a-c). It shows that the colors of specimens after discoloration change from light to dark, red to green, and yellow to blue for the Cu^{2+}-Mn^{2+}, Fe^{2+}-Mn^{2+}, and Fe^{2+}-Cu^{2+} samples, resp. Moreover, as the proportion of Fe^{2+}, Fe^{2+}, and Cu^{2+} in the three mixed ion inducers increases, the value of L^*, a^*, and b^* decreases after inducing Fe^{2+}-Cu^{2+}, Fe^{2+}-Mn^{2+}, and Cu^{2+}-Mn^{2+}. Color of specimens gradually darkens, turns green, and then blue with the increase in the mass fraction ratio of Fe^{2+} and Cu^{2+}. The corresponding trend is towards the dark and cold tints with the increased mass fraction ratio of Fe^{2+} and Cu^{2+}.
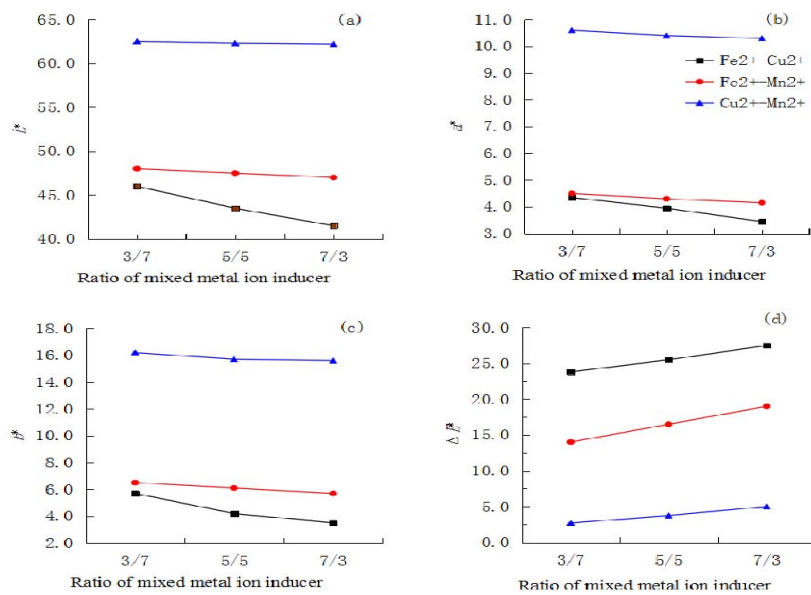
Fig. 7: Effect of mass fraction ratio of mixed metal ions on colors of oak veneers.

From Fig. 7d, it is clear that the magnitudes of ΔE^* of discolored veneer induced by mixed metal ions are in the following order: Fe^{2+}-Cu^{2+} > Fe^{2+}-Mn^{2+} > Cu^{2+}-Mn^{2+}. It indicates that the degree of change in colors of specimens from large to small is in the following order: Fe^{2+}-Cu^{2+}, Fe^{2+}-Mn^{2+}, and Cu^{2+}-Mn^{2+}. Moreover, as the proportion of Fe^{2+} and Cu^{2+} in the three mixed ion inducers increases, the values of ΔE^* of the specimens induced by Fe^{2+}-Cu^{2+}, Fe^{2+}-Mn^{2+} and Cu^{2+}-Mn^{2+} increase. It means that the change in color of specimens becomes large after inducing Fe^{2+}-Cu^{2+}, Fe^{2+}-Mn^{2+}, and Cu^{2+}-Mn^{2+}.

Figs. 8-10 show the color change of oak veneer induced by different mass fraction ratios of inducers of mixed metal ions.

Untreated   7:3   5:5   3:7
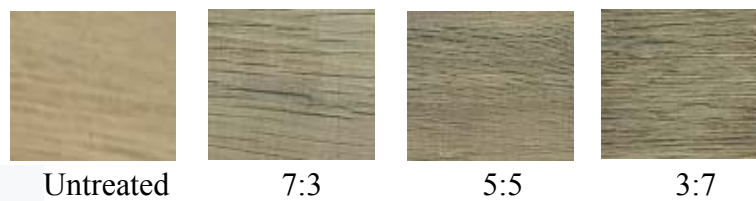
Fig. 8: Discoloration effect of Fe^{2+}-Cu^{2+} inducer with different mass fractions ratio.

Untreated   7:3   5:5   3:7
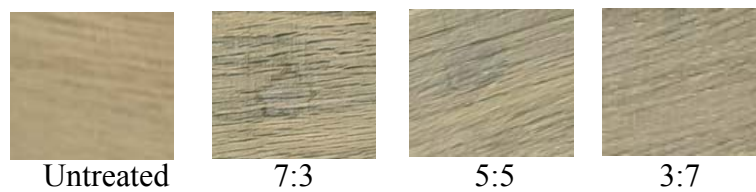
Fig. 9: Discoloration effect of Fe^{2+}-Mn^{2+} inducer with different mass fractions ratio.
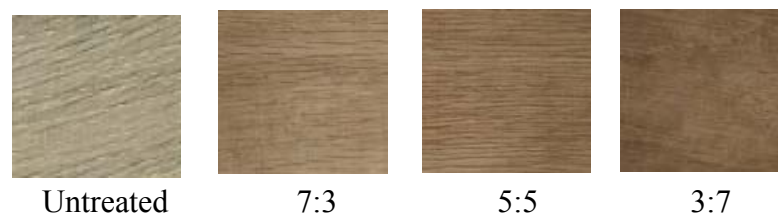

Untreated   7:3   5:5   3:7

Fig. 10: Discoloration effect of Cu^{2+}-Mn^{2+} inducer with different mass fractions ratio.

Figs. 11a-c show that the values of L^*, a^*, and b^* of discolored veneer induced by mixed metal ions are in the following order: Cu^{2+}-Mn^{2+} > Fe^{2+}-Mn^{2+} > Fe^{2+}-Cu^{2+}. It means that the colors of specimens after induced discoloration go from light to dark, red to green, and yellow to blue for the Cu^{2+}-Mn^{2+}, Fe^{2+}-Mn^{2+}, and Fe^{2+}-Cu^{2+} samples. Moreover, the values of L^*, a^*, and b^* of specimens after inducing Fe^{2+}-Cu^{2+} decrease with the temperature increase. It means that the color of induced specimens gradually darkens, turns green, and then blue with the temperature rise. In other words, the trend is toward a dark and cold tints. In contrast, the values of L^*, a^*, and b^* of samples, after inducing Fe^{2+}-Mn^{2+}, increase in the range 50 ~70 and decreases in the range 70 ~90 . In the range 50 ~70 , the colors of induced specimens brighten, turn red, and then yellow. The overall trend is toward bright and warm colors in 50 ~70 . In the range 70 ~90 , the colors of the induced specimen darken, turn green, and then blue. The general trend is toward the dark and cold tints in 70 ~90 . After

inducing Cu^{2+}-Mn^{2+}, the values of L^*, a^*, and b^* of specimens decreases with the temperature increase. It indicates that the colors of induced specimens brighten, turn red, and then yellow with an overall trend towards bright and warm colors.
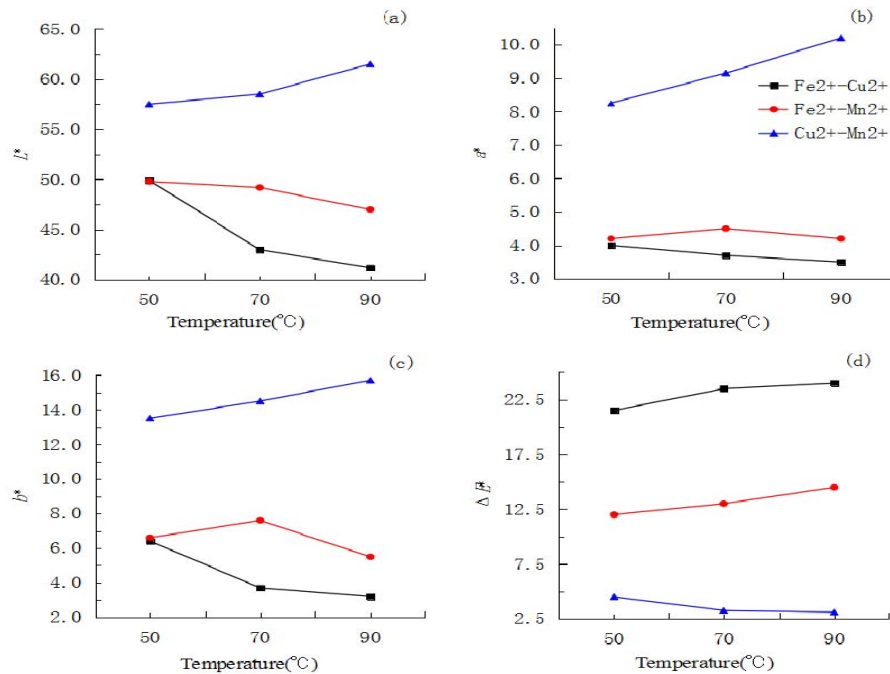

Fig. 11: Effect of temperatures on colors of oak veneers.

It is clear from Fig. 11d that the magnitudes of ΔE^* of discolored veneers induced by mixed metal ions are in the following order: Fe^{2+}-Cu^{2+} **>** Fe^{2+}-Mn^{2+} **>** Cu^{2+}-Mn^{2+}. It means that the sensitivity of specimens, after inducing mixed metal ions, to temperature is in the following order from strong to weak: Fe^{2+}-Cu^{2+}, Fe^{2+}-Mn^{2+}, and Cu^{2+}-Mn^{2+}. Moreover, with the temperature increase, the values of ΔE^* of specimens increase after inducing Fe^{2+}-Cu^{2+} and Fe^{2+}-Mn^{2+} ions. It means that the change in color of specimens increases with the temperature rise. On the contrary, the values of ΔE^* of specimens decrease after inducing Cu^{2+}-Mn^{2+} ions. It indicates that the change in colors of specimens decreases after the temperature has risen.

It is clear from Figs. 12a, 12b, and 12c that the magnitudes of L^*, a^*, and b^* of discolored veneer induced by mixed metal ions can be arranged in the following order: Cu^{2+}-Mn^{2+} **>** Fe^{2+}-Mn^{2+} **>** Fe^{2+}-Cu^{2+}. It indicates that the colors of discolored specimens change from light to dark, from red to green, and from yellow to blue for the Cu^{2+}-Mn^{2+}, Fe^{2+}-Mn^{2+}, and Fe^{2+}-Cu^{2+} samples, respectively. Moreover, as heating time increases, the values of L^*, a^*, and b^* of specimens, after inducing Fe^{2+}-Mn^{2+} and Fe^{2+}-Cu^{2+}, decrease. It indicates that induced specimens' colors gradually darken, turning green and then blue. The respective trend is towards dark and cold tints. However, the values of L^*, a^*, and b^* of the specimens, after inducing Cu^{2+}-Mn^{2+}, increase with the heating time. It shows that the colors of specimens gradually become bright, red, and yellow with the increase of heating time. The general trend is toward bright and warm colors.
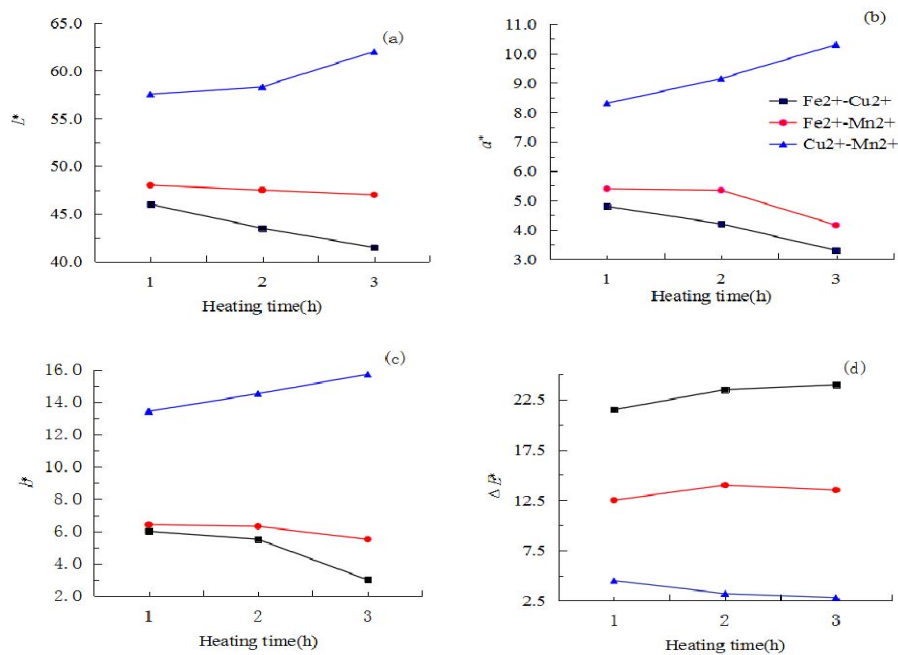
Fig. 12: Effect of heating time on colors of oak veneers.

It can be seen from Fig. 12d that the magnitudes of ΔE^* of discolored veneer induced by mixed metal ions can be arranged in the following order: Fe^{2+}-Cu^{2+} **>** Fe^{2+}-Mn^{2+} **>** Cu^{2+}-Mn^{2+}. It suggests that with the increase in the heating time, the degree of change in the colors of specimens from strong to weak is in the following order: Fe^{2+}-Cu^{2+}, Fe^{2+}-Mn^{2+}, Cu^{2+}-Mn^{2+}. Moreover, with the increase of heating time, the values of ΔE^* of specimens increase after inducing Fe^{2+}-Cu^{2+} and Fe^{2+}-Mn^{2+} ions. It illustrates that the effect of heating time on the change in colors of induced specimens is excellent. Similarly, the values of ΔE^* of specimens decrease after inducing Cu^{2+}-Mn^{2+} ions. It means that the effect of heating time on the change in color of induced specimens is small.

In summary, discoloration of oak veneer induced by mixed metal ions is relatively easy. However, discoloration of oak veneer is not that efficient by inducing single ions. However, mixed metal ions can supplement the colors induced by single ions, increasing color selectivity. The ANOVA showed that mass fraction, temperature, and time significantly affect metal ion-induced discoloration in Quercus Serrata.

Infrared spectroscopic analysis

Infrared spectroscopy of oak veneers before and after discoloration induced by the metal ion is presented in Fig. 13. Regarding the contrast between the infrared spectra before and after the color change, various peaks were observed accordingly. For different oak veneer samples, O-H characteristic vibrational peak at 3424 cm^{-1} after discoloration, vibrational peak at 1741 cm^{-1} after inducing non-conjugated C=O metal ions, and COOH vibrational peak at 1636 cm^{-1} after discoloration were enhanced. Moreover, a new C-H aromatic bending peak at 1122 cm^{-1} appeared after discoloration in the oak veneers. Similarly, another new C-H aromatic bending peak at 1124 cm^{-1} appeared after discoloration induced by Fe^{2+}-Mn^{2+} and Cu^{2+}-Mn^{2+} in the oak veneers. The reason behind these observations is that the discoloration induced by mixed metal ions is different from that of single metal ions because mixed ions form stable metal ion complexes with aromatic compounds and alkyl compounds. The C=O telescopic vibrational peak at 1035 cm^{-1} after inducing Fe^{2+} and Fe^{2+}-Cu^{2+} in oak veneers was enhanced. It indicates that Fe^{2+} and Fe^{2+}-Cu^{2+} react with C=O, resulting in a darker color of oak veneer with a significant color difference. A C-H bending vibrational peak at 810 cm^{-1} appears after inducing Cu^{2+} in the oak veneer.
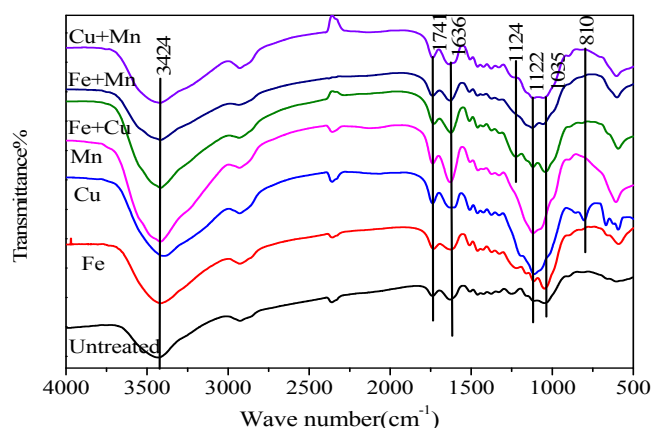

Fig. 13: Infrared spectra of metal ion inducer before and after discoloration treatment.

The observations mentioned above are due to the reaction of O-H, C=O, COOH, and other chemical groups on the wood surface with metal ions to form stable complexes. It alters absorption peak intensities or positions, generating new absorption peaks and indicating the generation of new chemical substances. The aromatic compounds in lignin of oak wood surface and acids, alcohols, and terpene compounds in tannins can easily make complexes with metal ions. A new C-O stretching vibrational characteristic peak at 1035 cm^{-1} appeared after treating the oak veneer with Fe^{2+} and Fe^{2+}-Cu^{2+}. It is because phenolic compounds were produced due to the reaction between phenolic substances and metal ions to form complexes. Phenolic compounds such as tannins were abundant in the extracts of oak veneer. These phenolic compounds can provide phenolic hydroxyl, carbonyl, carboxyl, and other structures needed to form complexes. In addition, acids, alcohols, and terpenes in aromatic compounds and lignin extracts contain many of the groups mentioned above, which are prone to complex

reactions with metal ions (Pandey 2015, Li et al. 2015, Chen et al. 2012). All the above reasons provide sufficient conditions for wood discoloration induced by metal ions.

UV-Vis spectrum analysis

Fig. 14 shows oak veneer's UV diffuse reflection absorption spectra before and after color-changing treatment. Fig. 14 shows that the absorption spectra of metal ions in the near ultraviolet and visible regions changed after the color-changing treatment. The changes in absorptivity in the visible region are due to the complexation reactions between metal ions and phenolic compounds such as tannin in oak wood veneer. After discoloration, the π orbital transition leads to different absorption lines in oak wood veneer. It is how the change in the color of wood happens. It can also be seen from Fig. 14 that the UV absorption spectra of the extracts from untreated oak veneer and oak veneer treated with metal ion inducer have three UV absorption peaks at 208 nm, 210 nm, and 257 nm. Lignin belongs to the guaiac-based E_1 absorption band in the UV band 200~208. The complexation reaction between chromatin unsaturated carbonyl compounds and metal ions changes the absorption peaks of oak veneer. The absorbance of tussah wood veneer treated with Fe^{2+}, Fe^{2+}-Cu^{2+}, and Fe^{2+}-Mn^{2+} inducers was significantly enhanced. The peak of the E_1 absorption band moved towards the long wavelength, forming an absorption peak at 210 nm. π orbital transition caused different absorption intensities of the samples at different bands. It changed the color of the wood and brought a redshift. The oak wood board, after induced discoloration, produces a dark effect.
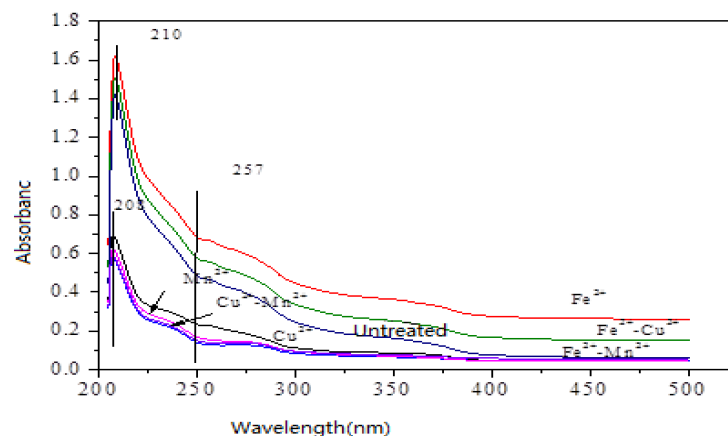

Fig. 14: UV absorption spectra of metal ion inducers before and after discoloration treatment.

The absorption peak at 257 nm is due to the E_2 absorption band between 227 nm and 233 nm. At this time, there is a chromophore substitution reaction of chromophore conjugates with the benzene ring. The chromophore substitution reaction on the benzene ring causes a redshift. The red shift in the ultraviolet absorption spectrum of oak wood veneer treated by a metal ion inducer agrees with the red shifting rule accompanied by a dark color effect under general conditions. The light absorption decreased successively for tussah veneers after treatment with Fe^{2+}, Fe^{2+}-Cu^{2+}, Fe^{2+}-Mn^{2+}, Mn^{2+}, Cu^{2+}-Mn^{2+}, and Cu^{2+} inducers. After metal ion-induced discoloration treatment, the absorption spectra of the oak wood panel in near ultraviolet and visible regions were significantly enhanced. It is mainly because of the complex reactions between aromatic compounds and metal ions, which change the peaks and

absorbances. That is why the metal ion-induced discoloration of oak wood panels shows different colors.

Surface morphology analysis

Fig. 15 shows the surface morphology of oak veneer before and after treatment with metal ion inducers by scanning electron microscope. Compared to untreated wood, oak wood's surface structure and pores are visible after metal ion inducer treatment. The surface of the treated oak veneer has no rupture or deformation, and the grain holes on the cell wall are evenly distributed. The cell walls, cell lines, and pores of oak veneer treated by metal ion inducer are clear and smooth as a whole after induced discoloration. It shows that the surface of oak wood treated by metal ion inducer is not damaged.
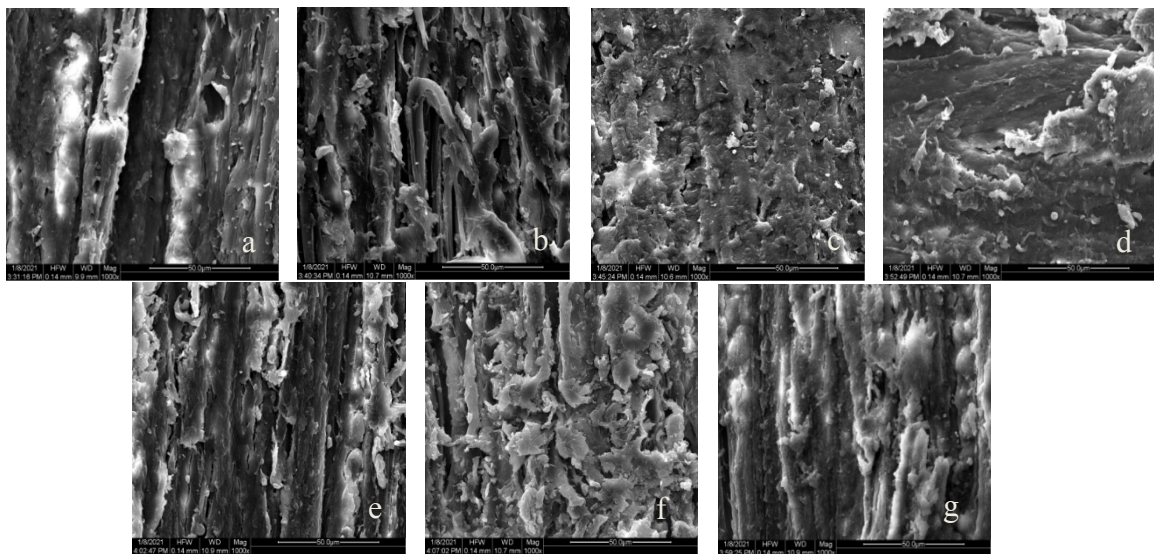

Fig. 15: Scanning electron microscopic images with 1000 times magnification of Xylosma racemosum surface plate before and after induced discoloration: a) untreated wood, b) Fe^{2+} induced, c) Mn^{2+} induced, d) Cu^{2+} induced, e) Fe^{2+}-Cu^{2+} iduced, f) Fe^{2+}-Mn^{2+} induced, g) Cu^{2+}-Mn^{2+} induced).

CONCLUSIONS

This work studied the discoloration trends and mechanism by changing the parameters like mass fraction, mass fraction ratio of inducer, temperature, and heating time of inducing metal ions in oak veneer.

With the increase in the mass fraction of the inducer, temperature, and heating time, after inducing Fe^{2+} and Cu^{2+}, the color of the oak veneer changes to dark and cold. However, with the same conditions, after inducing Mn^{2+}, the color of the oak veneer changes to bright and warm color. The discoloration of oak veneer induced by Fe^{2+}-Mn^{2+} and Fe^{2+}-Cu^{2+} mixed ion inducers tends to dark and cold tints with the increase of Fe^{2+} mass fraction ratio, temperature, and heating time. On the contrary, the discoloration of oak veneer induced by Cu^{2+}-Mn^{2+} mixed ion inducers tends to bright and warm colors with increasing Mn^{2+} mass fraction ratio, temperature, and heating time. According to infrared spectroscopy, O-H, C=O, COOH, and

aromatic C-H react with metal ions, causing discoloration of the oak wood panel. Mixed metal ions like Fe^{2+}-Cu^{2+}, Fe^{2+}-Mn^{2+}, and Cu^{2+}-Mn^{2+} react with aromatic C-H, resulting in different colors with discoloration effects. Fe^{2+} and Fe^{2+}-Cu^{2+} react with C=O causing a dark color of oak veneer and such a significant color difference. As per the ultraviolet spectrum analysis, the red shift occurred in the ultraviolet absorption band of the unsaturated carbonyl compound and benzene ring compound of Fe^{2+}, which led to the discoloration of oak veneer induced by metal ions. Fe^{2+} is complexed with unsaturated carbonyl and benzene compounds, resulting in dark wood color. Moreover, the dark wood effect of Fe^{2+}, Fe^{2+}-Cu^{2+}, Fe^{2+}-Mn^{2+}, Mn^{2+}, Cu^{2+}-Mn^{2+}, and Cu^{2+} gradually decreased. Scanning electron microscopic analysis showed that the surface of the oak veneer treated with metal ion inducer was smooth, without any cracking or deformation. In addition to that, the pores and holes were visible and remained intact.

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