Evaluation of the Effects of Transition Metal Ions on the Optical Aging and Whiteness of Chemimechanical Pulp

Mohammad Nemati and Ahmad Samariha *

The negative effects of metal ions were addressed relative to the whiteness characteristic of chemomechanical pulp samples prepared. Proper solutions were considered to mitigate this adverse effect. The chemomechanical pulp samples were supplied in an unbleached form. The samples were wetted using ethylene diamine tetra acetic acid (EDTA) chelating agent, and then each of the samples was wetted with EDTA after drying with solutions containing the transitional metal ions. The results showed that the greatest whiteness reduction resulted from Fe^{2+} ions, whereas the smallest effect resulted from Al^{3+} ions. Wetting of the samples in various concentrations of the chelating agent (EDTA) had an optimum value in improving the whiteness characteristic of the paper. Thereafter, no change was created in whiteness improvement and brightness stability by increasing the concentration of EDTA. Increasing the aging time reduced the whiteness characteristic of the chemomechanical pulp.

DOI: 10.15376/biores.17.3.4444-4451

Keywords: Hardwood CMP; Transition metal ion; EDTA; Accelerated optical aging; ISO whiteness

*Contact information: Department of Wood Industry, Technical and Vocational University (TVU), Tehran, Iran; * Corresponding author: a.samariha@gmail.com*

INTRODUCTION

Pulp and paper mills aim to increase the life and avoid degradation of brightness and physical/mechanical properties of chemomechanical pulps. As some paper used in Iran is produced *via* the chemimechanical pulp (CMP) process, some solutions must be considered to reduce the yellowing and aging of this paper. Transitional metal ions such as Fe^{2+}, Cu^{2+}, and Mn^{2+} lead to discoloring of the paper due to the formation of colored complexes (Yoon *et al*. 1999). Because transitional metal ions have a great tendency toward lignin and the formation of colored complexes, samples that are made from high lignin species will thus exhibit more potential for yellowing and bond formation. The water of the pulping process, equipment, and even wood chips can act as a source of the transition elements. Using distilled water is not economical for reducing the negative effect of ions. Therefore, some other methods have been proposed such as using chelating agents (*e.g.*, EDTA), decreasing pH of the pulp (Mirshokraei and Abd Alkhani 2005), or acetylation techniques (Carter 1996). As a result, some methods have also been considered for mitigation of the negative effect of ions.

One of these methods is using chelating materials (Mirshokraei and Abd Alkhani 2005). This material was investigated as a chelating material taking into account the lower price of EDTA and its economic advantages. Carter (1996) studied the discoloring of the pulps containing large amounts of lignin, finding that yellowing of the paper is intensified after years due to the effects of oxidation and photo-oxidation of the existing groups in the paper and formation of new colored groups upon exposure to light, heat, moisture, and active ions such as Ca^{2+}, Fe^{2+} and gas pollutants, especially SO_2 and NO_2. Paulson *et al*. (2001) investigated the effect of photo-yellowing on untreated chemical-thermomechanical pulp (CTMP) under argon, ambient, and oxygen atmospheres. They found that the degree of photo-yellowing in untreated CTMP decreases when the air in the surrounding atmosphere is replaced with the oxygen-free argon. Furthermore, they concluded that the atmospheric level of oxygen is not required for light-induced discoloration. A trace amount of oxygen is rather sufficient to cause discoloration. Saint-Cyr *et al*. (2002) studied the application of the yellowness inhibitors of the mechanical pulps. Stability and equilibrium of 2-benzo-triazole as an inhibitor of yellowing in the mechanical pulp were evaluated by investigation of changes in type and density of the inhibitor and salt concentration. Qiu *et al*. (2003) studied the effect of metal ions like Mn^{2+} on the decomposition of hydrogen peroxide by introducing DTPA as the stabilizer. Their results indicated that the addition of DTPA to the pulp containing Mn^{2+} is more effective than that of no DTPA addition. Mirshokraei and Abd Alkhani (2005) studied the effect of metal ions on optical properties of chemomechanical pulp prepared from hardwood trees. The chelating agent in this test was DTPA. For this purpose, the pulp was exposed to one pre-treatment step with DTPA. Afterward, it was bleached by hydrogen peroxide under special conditions. After bleaching and decreasing the pH, metal ion-containing water, municipal water, and industrial water were separately used for producing handmade papers from distilled water. The optical aging steps were implemented on the pulp samples then. Based on observations and results of this experiment, the maximum most adverse effect on degradation of the optical properties and further yellowing and optical aging belonged to the Fe^{2+} ion, while the smallest effect belonged to Al^{3+}. Moreover, the presence of the DTPA chelating agent is expected to enhance the stability of brightness. For chemical pulps, heat-induced yellowing is the fundamental type of brightness inversion. Lignin residues, carbonyl gatherings, xylan, hexenuronic corrosive (HexA) gatherings, and transition metal ions are associated with the yellowing responses (Borrega *et al*. 2013).

Vaysi and Ebadi (2021) examined the thermal yellowing of hornbeam chemi-mechanical pulps (CMP) subsequent to bleaching with hydrogen peroxide and sodium dithionite. The outcomes showed that from 0 to 40 h, the optical properties of paper increased with the exception of brightness and greenness. This increment was greater up to 15 h. Moreover, among the different medicines, DTPA treatment in long-term thermal aging and the utilization of sodium dithionite and hydrogen peroxide in the momentary maturing discernibly affected splendor durability and reduction in the variety inversion. In this manner, there was an increase in the resistance of the paper against thermal deterioration. Vaysi (2005) considered discoloration of the acetylated CMP that was prepared from two species of hornbeam and beech due to optical and thermal aging. The results were indicative of the fact that upon acetylation, the hydrogen in the phenol hydroxide group of lignin is readily replaced with the acetyl groups so that the electrons stop moving through the propane phenyl ring. Therefore, the stability of brightness will be increased because no light absorbent quinone is formed. The mechanism for the generation of chromophores and damaging of lignin is summarized below during photo-oxidation of the lignin and yellowing phenomenon:

The primary chromophores of lignin are known to develop *via* the following series of events: Absorption of light at 300 to 400 nm wavelength → breaking of etheric bonds and generation of free radicals →reaction of free radicals and lignin → generation of ketyl radicals →phenoxy and ketone radicals → generation of yellow quinones and yellow chromophores and secondary chromophores→ optical damaging of lignin and yellowing of paper (Vaysi 2005).

In long-term aging, DTPA spray has a considerable effect relative to the stability of brightness and improved durability against optical deterioration of hornbeam CMP pulp following an accelerated irradiation aging (Vaysi and Mirshokraei 2007). The catalytic activity of Mn^{+2} and Mn^{+3} relative to the decomposition of hydrogen peroxide was evaluated with DTPA as the only stabilizer. The addition of DTPA to an Mn^{+2} containing system is more effective than adding it to an Mn^{+3}-containing one. To decrease the catalytic effect of Mn^{+3}, sodium borohydride and DTPA were considered to reduce Mn^{+3} to Mn^{+2} under acidic conditions. This research determined the negative effect of metal ions on whiteness characteristic of the chemomechanical pulps. In addition, appropriate solutions to mitigate this undesirable effect were suggested.

EXPERIMENTAL

A mechanical print paper made from CMP with a base weight of 80 g/m^2 was supplied by Mazandaran Wood and Paper Industries in an unbleached form. EDTA was procured from Merck (Istanbul, Turkey) and used at different concentrations levels of 0, 0.25, 0.5, 0.75, and 1% in the pH range of 5.5 to 6. Deionized water was used in the experiments to avoid any error in the results and negative effects of existing ions in the municipal water. Solutions containing metal ions of Fe^{3+}, Fe^{2+}, Cu^{2+}, Al^{3+}, and Mn^{2+} were prepared in the laboratory with concentrations of 1, 0.3, 0.1, 25, and 1 ppm in deionized water (Abd Alkhani and Latibari 2004). Salts that were soluble in water were used to make metal ion-containing solutions as follows: $FeSO_4.7H_2O$, $CuSO_4.5H_2O$, $MnSO_4.H_2O$, $FeCl_3.6H_2O$, and $AlCl_3.5H_2O$.

After cutting the papers into dimensions of 5 × 5 cm, the existing ions in the paper samples were treated with the EDTA chelating agent and then wetted with each of the metal ion solutions. The samples were dried in an atmosphere away from light and moisture under the gentle flow of a fan. For the accelerated aging test, one simulated apparatus was utilized (Paulson and Ragauskas 2000; Pu *et al*. 2003). Six UV lamps of blacklight type (Philips, Amsterdam, Netherlands) and six conventional fluorescent lamps were used. The range of the output wavelength was between 300 and 400 nm. Optical treatments were arranged to be implemented in 0, 10, 20, 30, 40, and 50 h intervals. A spectrophotometer (Technibrite Micro TB-1C, New Albany, Indiana, USA) was utilized to measure the whiteness of the papers. A minimum number of 10 test runs were repeated for each sample to measure their whiteness characteristics according to TAPPI T560 om-05 (2010). The data were analyzed using SPSS statistical software (version 22, IBM, Armonk, NY) with one-way variance analysis, and grouping of the average values was done using Duncan's test at a 5% confidence level.

RESULTS AND DISCUSSION

The results of variance analysis showed that there was a statistically significant difference between the values of metal ion solutions, EDTA chelating agent, and aging time at a probability level of 5% (Figs. 1 to 3). Whiteness is defined as how close a color is to the absolute white, due to brightness, intensive light diffraction, and minimum noticeable back color (Vaysi 2005). As depicted in Fig. 1, Fe^{2+} had the greatest effect on the reduction of whiteness in the sample pulps, while minimum changes of whiteness were observed in the samples wetted with Al^{3+}. The Al^{3+} ion acts as a neutral and inert ion. Similar results have been reported previously (Abd Alkhani and Latibari 2004; Mirshokraei and Abd Alkhani 2005; Kasmani *et al*. 2013; Nemati *et al*. 2013). Whiteness is also affected by factors like the type of metal ion, the concentration of the chelating agent, optical aging time, and the lignin content of the samples. The most significant effect on the whiteness characteristic was observed for the Fe^{2+} ion as an effectively damaging ion. This ion has a greater negative effect on the whiteness due to the formation of oxygen-bearing radicals in comparison with the other ions, which is attributed to the accelerated formation of the phenoxy radicals by the Fe^{2+} ion.

As evident in Fig. 2, increasing the concentration of the EDTA chelating agent decreased the accelerated optical aging effect. In other words, adding to the concentration of the EDTA chelating agent increased the whiteness of CMP, which indicates the promising effect of this material in the improvement of the whiteness properties. Chelating agents are effective in changing the whiteness, and they cause a relatively smaller reduction in the whiteness over time. This is because of the more reactive features of EDTA as well as the greater stability constant with the metal ions. Chelating materials such as DTPA and EDTA enclose the ion and prevent its adverse function. However, the application of the chelating materials is subject to some scientific and economic limitations, as further increasing the concentration of these materials cannot guarantee their better performance. Their optimal range is between 0.5 and 1%. Moreover, using this material at high concentrations is not economically reasonable (Kasmani *et al*. 2013; Nemati *et al*. 2013).

The mechanism of the chelating materials is such that the metal ions form very stable complexes with phenolic compounds (Gupta and Mutton 1969), while the stability constant of these compounds is rather high. Nevertheless, the chelating agents reach greater stability constant with the metallic ions due to their more reactive features. Therefore, the formation of the ion complexes with EDTA attains a better thermodynamic equilibrium when the pulp samples are wetted by EDTA. Thus, increasing the concentration of EDTA reduces the effect of metal ions. There are some other factors in addition to time, the concentration of the chelating agent, and type of the metal ion that impact the aging process. Qiu *et al*. (2003) argued that even the behavior of various models of lignin is different against the effect and amount of aging. In this regard, even the behavior of metal salt including sulfates, chlorides, and nitrides may lead to a different aging process. For example, iron chloride forms a complex with phenols, but iron sulfate has a much slower regime. In this regard, even this behavior is different for the lignin models. Iron sulfate with catechol creates a colored complex, but this does not occur with apocynin. In the compound of copper metal with bizginol lignin, this complex readily forms because the two hydroxyl groups have the correct distance in the copper ions. As shown in Fig. 3, each of the optical aging times causes a significant reduction in the whiteness content, and each of them individually incorporates a considerable impact in the reduction of the whiteness. The unbleached samples have larger amounts of extractive and lignin materials. Because the role of oxidized cellulose and hemicellulose in creating yellowing and reduction of whiteness is almost negligible, the contribution of the coloring groups of lignin would be much greater, which means further degradation of whiteness (Yoon *et al*. 1999).

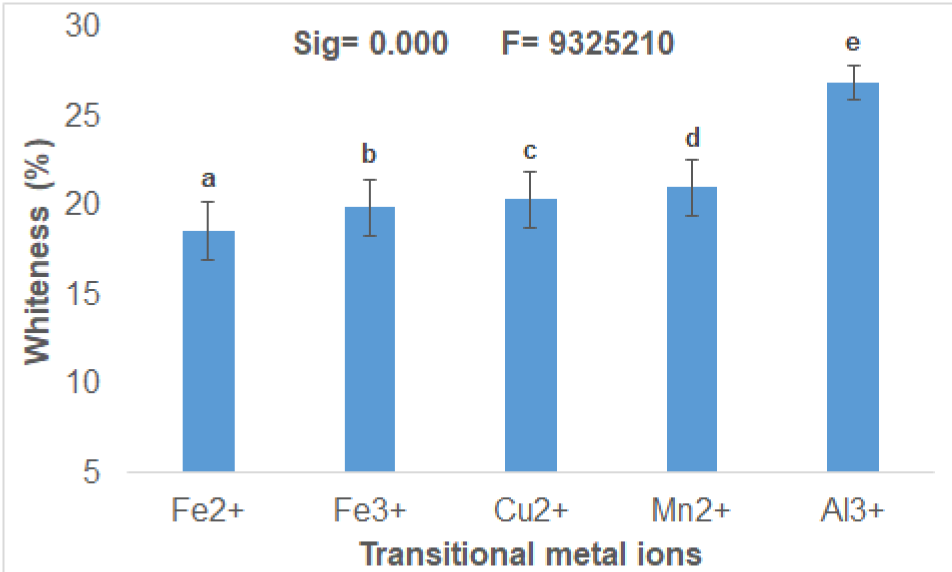

Fig. 1. Effect of metal ions on the whiteness of samples

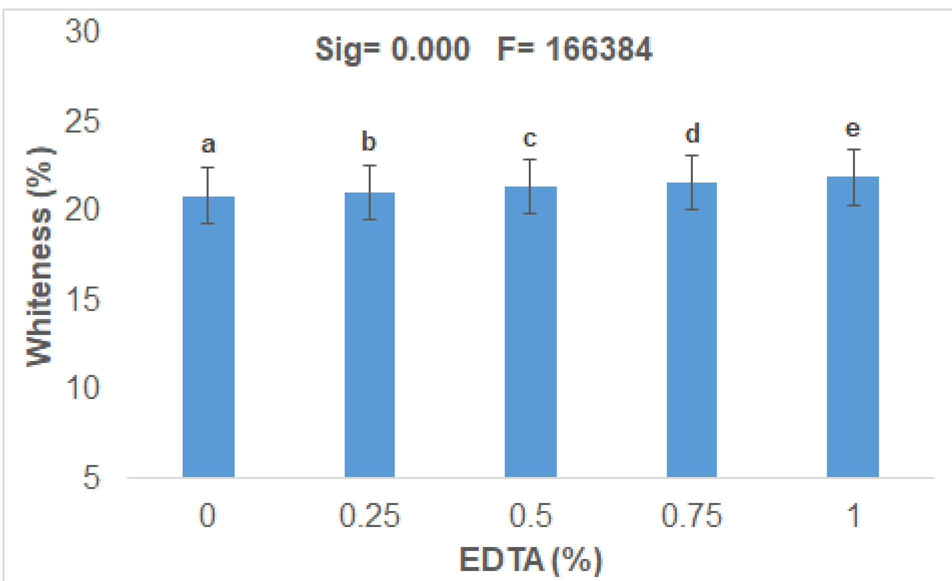

Fig. 2. Effect of EDTA on the whiteness of samples

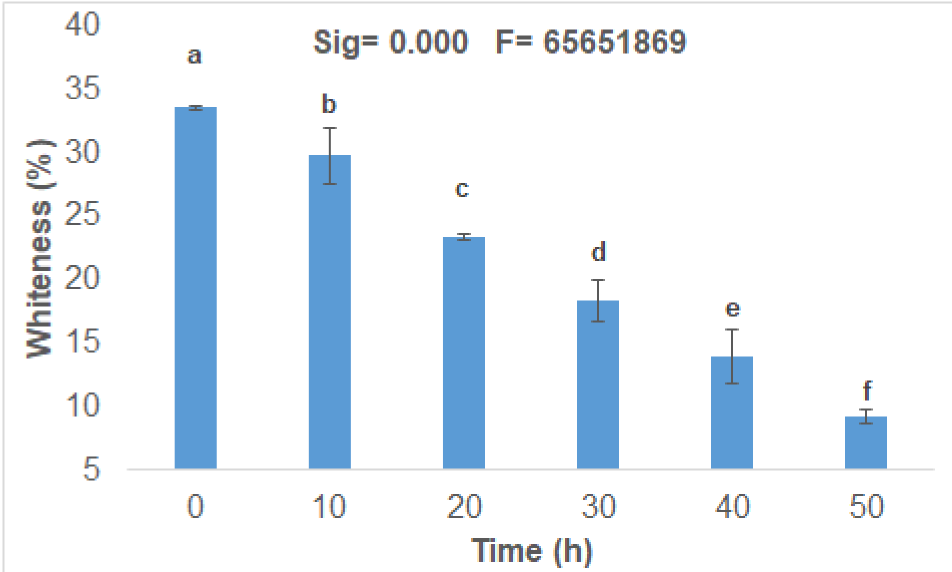

Fig. 3. Effect of time on the whiteness of samples

Cellulose chromophores and lignin chromophores have been introduced as reasons for yellowing and reduction of whiteness in the papers (Abd Alkhani and Latibari 2004). The yellowing of celluloses is believed to be brought about by three pressure factors: oxidative or potentially hydrolytic stress, photograph pressure (light and illumination), and thermal stress. These elements can either cause the yellowing individually or in a mixture. As an outcome of these physico-substance impacts, sub-atomic changes emerge in the cellulose material, which are reflected by losses in molecular weight (and frequently crystallinity) (Ahn *et al.* 2019). Tschirner and Dence (1988) argued that during oxidation or photo-oxidation, the carbonyl and carboxyl groups are formed from anhydrous-glucose units. Saint-Cyr *et al*. (2002) diagnosed oxidized chromophores of hemicellulose as aldehyde groups on carbon atoms of C_2 and C_3. Lignin is a polymer that is aromatic and comprised of phenyl propane units. The structure of lignin mainly contains etheric bonds, while C-C bonds are also evident in its structure to a limited extent. Haque *et al*. (2005) found that aromatic ketones, quinones, aldehydes, and acids can be generated due to photooxidation of the lignin.

CONCLUSIONS

1. The Fe^{2+} ion was found to have the most significant effect on the degradation of whiteness in different pulp samples. Variations of the whiteness characteristic were the least in the samples which were wetted using the Al^{3+} ions.
2. Increased concentration of the chelating agent of EDTA causes the whiteness of the chemimechanical pulp (CMP) samples to be decreased at a much smaller ratio.
3. Extension of the aging time reduces the whiteness of the CMP samples.

REFERENCES CITED

Abd Alkhani, A., and Jahan Latibari, A. (2004). "Effect of brightening agent on optical properties and photostability of chemimechanical pulp bleached with hydrogen peroxide and sodium borohydride," *Journal of Polymer Sciences and Technology* 72(4), 247-255.

Ahn, K., Sara Zaccaron, S., Zwirchmayr, N. S., Hettegger, H., Hofinger, A., Bacher, M., Henniges, U., Hosoya, T., Potthast, A., and Rosenau, T. (2019). "Yellowing and brightness reversion of celluloses: CO or COOH, who is the culprit?," *Cellulose* 26(1), 429-444. DOI: 10.1007/s10570-018-2200-x

Borrega, M., Niemelä, K., and Sixta, H. (2013). "Effect of hydrothermal treatment intensity on the formation of degradation products from birchwood," *Holzforschung* 67(8), 871-879. DOI: 10.1515/hf-2013-0019

Carter, H. A. (1996). "The chemistry of paper preservation: Part 2. The yellowing of paper and conservation bleaching," *Journal of Chemical Education* 73(11), 1068-1073.

Gupta, V. N., and Mutton, D. B. (1969). "User of sequestering agents in deionization and hydrosulfite bleaching of groundwood," *Pulp and Paper Canada* 70(6), 77-84.

Haque, M. N., Khalil, H. P. S. A., and Hill, C. A. S. (2005). "Chemical modification of wood flour and thermomechanical pulp fiber with acetic anhydride," *Journal of the Timber Development Association of India* 54(3), 2533.

Kasmani, J. E., Samariha, A., and Nemati, M. (2013). "Effect of optical aging on yellowness characteristics of soda paper made from bagasse," *Asian Journal of Chemistry* 25(3), 1587-1589.

Mirshokraei, S. A., and Abd Alkhani, A. (2005). "Studying the effect of metal ions on the brightness of CMP from hardwood trees of northern Iran," *Journal of Natural Resources* 58(2), 405-411.

Nemati, M., Hemmasi, A. H., Talaeipour, M., and Samariha, A. (2013). "Studying the effect of photo-yellowing on the brightness property of chemi-mechanical pulping paper," *Cellulose Chemistry and Technology* 47(1-2), 93-109.

Paulson, M., and Ragauskas, A. J. (2000). "Chemical modification of lignin-rich paper. Light-induced changes of softwood and hardwood chemithermomechanical pulps. The effect of irradiation source," in: *Lignin: Historical, Biological, and Material Perspective*, W. G. Glasser, R. A. Northey, and T. P. Schultz (eds.), Oxford University Press, Washington, DC, USA, pp. 490-504.

Paulson, M., Lucia, L. A., Ragauskas, A. J., and Li, C. (2001). "Photo-yellowing of untreated chemical-thermo-mechanical pulp under argon, ambient and oxygen atmosphere," *Journal Wood Chemistry and Technology* 21(4), 343-360. DOI: 10.1081/WCT-100108330

Pu, Y. Anderson, S., Lucia, L., and Ragauskas, J. A. (2003). "Fundamentals of photobleaching lignin. Part 1: Photobehaviours of acetylated softwood BCTMP lignin," *Journal of Pulp and Paper Science* 29(12), 401-406.

Qiu, Z., Ni, Y., and Yang, S. (2003). "Using DTPA to decrease manganese-induced peroxide decomposition," *Journal of Wood Chemistry and Technology* 23(1), 1-11.

Saint-Cyr, K., Van De Ven, T. G. M., and Garnier, G. (2002). "Adsorption of yellowing inhibitors on mechanical pulp," *Journal of Pulp and Paper Science* 28(3), 78-84.

TAPPI T 560 om-05 (2010). “CIE whiteness and tint of paper and paperboard (d/0 geometry, C/2 illuminant /observer),” TAPPI Press, Atlanta, GA.

Tschirner, U., and Dence, C. W. (1988). “Attempts to photo stabilization Norway spruce TMP by chemical modification,” *Paper Ja Puu* 36(4), 338-346.

Vaysi, R. (2005). *Studying Discoloring of CMP Prepared from Two Species of Hornbeam and Beech upon Acetylation and Optical/Thermal Aging*, Ph.D. Dissertation, Azad University, Sciences and Research Branch, Tehran.

Vaysi, R., and Mirshokraei, S. A. (2007). “Investigation on the optical behavior of acetylated and non-acetylated hornbeam CMP pulp following accelerated irradiation aging,” *Journal Science Techniques Natural Resources* 2(2), 79-88.

Vaysi, R., and Ebadi, S. E. (2021). “Thermal yellowing of hornbeam chemi-mechanical pulps bleached with hydrogen peroxide and sodium dithionite,” *BioResources* 16(4), 7635-7647. DOI: 10.15376/biores.16.4.7635-7647

Yoon, B. H., Wang, L. J., and Kim, G. S. (1999). “Formation of lignin-metal complexes by photo-irradiation and their effect on color reversion of TMP,” *Journal of Pulp and Paper Science* 25(8), 289-293.

Article submitted: February 17, 2022; Peer review completed: April 30, 2020; Revised version received and accepted: May 30, 2022; Published: June 3, 2022.
DOI: 10.15376/biores.17.3.4444-4451