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Enhancing Fastness and Ultraviolet Protection Factor of *Pelthophorum pterocarpum* Natural Dye by Titania Nanoparticles Modification

K.S. Budiasih[1,*], C. Kusumawardani[1] and I. Khoirunisa[2]

[1]Department of Chemistry Education, Universitas Negeri Yogyakarta, Yogyakarta, Indonesia
[2]Faculty of Mathematic and Natural Sciences, Universitas Negeri Yogyakarta, Yogyakarta, Indonesia

*Corresponding author: Tel: +62 8112638796; E-mail: kunsb@uny.ac.id

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The harmful effects of synthetic dyes on the environment can be mitigated through the use of natural dyes in textiles. However, textile dyeing with natural dyes has low brightness and colour resistance. TiO_2 nanoparticles modified copper pod (*Pelthophorum pterocarpum*) dye (TMCD) was studied to enhance the fastness and ultraviolet protection factor of fabrics dyeing. This study was conducted using a cotton fabrics which processed by some mordant agents. TiO_2 in various amount were dispersed in aqueous copper pod bark solution and produced a modified copper pod natural dye. Investigation of the dyed fabrics was conducted in 3 parameters *viz.* the colour direction, fastness values toward sunlight and ultraviolet protection factor (UPF). The results showed that the mordant agents affect the final colour palette and brightness, suggesting that TiO_2 improved the colour intensity and fastness value of copper pod dye. It also enhanced the ultraviolet protection factor (UPF) of dyed fabrics by 3-8 point higher than the control groups.

Keywords: Fastness, Natural dye, *Pelthophorum pterocarpum*, Titanium oxide, Ultraviolet protection factor.

INTRODUCTION

Fabric dyeing using natural dyes has become a highly established industry since it is safer for the environment and for humans [1]. Natural dyes come from plants, *i.e.* leaves, wood and even flowers or from animals which contain certain colour pigments and prepared through certain processes [2]. Natural dyes often exhibit themselves in earthy tones, such as a deep brown, which are widely seen in Yogyakarta, Indonesia's famed batik and other traditional garments. Natural brown from the soga plant, whose distinctive colour comes from the barks of copper pod (*Peltophorum pterocarpum*) tree is by far the most popular natural dye in Indonesia [3].

Chemical examination of several solvent extracts of both leaf and flowers of *P. pterocarpum* showed the presence of various phytochemicals such as terpenoids, alkaloids, saponins, phenols, steroids, tannin and phlobatannins [4]. Tannin usually present throughout the plant: in wood, bark, rhizomes, roots, leaves and fruits [5,6]. The disadvantages of natural dye colouring is the lower brightness and the fastness against washing and sunlight. Generally, natural dye coloured fabrics are not resistant to direct sunlight. The colouring product using natural dyes on fabrics tend to have a low colour resistance and stability. Therefore, the quality of colouring by natural dye need to be improved.

The quality of natural dye colouring on fabrics at least indicated by two parameters *viz.* brightness (chroma value) and resistance to sunlight (fastness value) [7]. Chroma (saturation) may be defined as the strength or dominance of the colour. The value of a colour describes its total intensity, which refers to its lightness or darkness. It defines a colour in terms of how close it is to white or black. The higher the chroma value of a colour, the closer it is to white. The darker a colour is, the closer its chroma value is to black [8].

To increase the brightness and resistance, some research applied certain material in order to give a thin layer which adsorb the sunlight [9]. Several materials such as metallic nanoparticles *e.g.* ZnO, TiO_2 and SiO_2 are well-matched to the criteria. The main characteristic is their low band gap so that a higher ability to absorb light well and protect the dye material from colour damage [10]. TiO_2 has several advantages, as the band gap of 3.2 eV, which is suitable for photocatalytic processes [10].

Titanium oxide also has certain properties as pigment absorber. It is also able to absorb ultraviolet light at wavelength about 277 nm [11]. In addition, TiO_2 has chemical stability in a large pH range (0-14) and has high photodegradation resistance. Titanium oxide (TiO_2) nanoparticles have been widely used as UV protection.

Addition of TiO_2 on the surface of fabrics has a potency to enhance the colour resistance and avoid the destabilization by UV light [11]. The fabrics which is coated by TiO_2 nanoparticles exhibit the antibacterial, UV protection and self-cleaning properties. The use of higher concentrations of TiO_2 nanoparticles on the fabric can increase the ultraviolet protection factor (UPF) value after 15 washing cycles [12]. The TiO_2-coated fabrics have a higher reflectance than raw fabrics and found that the TiO_2 pigmented layer increased the brightness of the sample and simultaneously decreased its chroma value [13]. In the form of nanoparticles, it has a larger surface area to provide effective UV protection [14].

In this research, TiO_2 nanoparticles modified copper pod (*P. pterocarpum*) dye (TMCD) was studied to enhance the fastness and ultraviolet protection factor of fabrics dyeing. The color fastness andUPF of fabrics dyed with TiO_2 modified dye were found to be significantly higher than those dyed with the conventional copper pod dye, indicating the efficacy of the modification.

EXPERIMENTAL

A bark of copper pod (*P. pterocarpum*) (Fig. 1) was purchased from a vendor in a local market in Yogyakarta, Indonesia, that specialized in batik colours. All the chemicals and solvents used in this study were procured from Merck, USA.

Fig. 1. Images of *Pelthophorum pterocarpum* bark

General procedure: The dye was prepared by boiling 1 kg of *P. pterocarpum* bark with 4 L of distilled water to produce 2 L of dye solution. The solution then divided into 4 parts, three parts as experiments groups of TiO_2 modified dye and 1 part as control. The dispersion technique was applied to incorporate TiO_2 nanoparticles in different amount *viz.* 0.1 (T1), 0.2 (T2) and 0.3 g/L (T3) into the copper pod dye by stirring the sample using magnetic stirrer at 1500 rpm for 30 min.

The resulting modified copper pod dye was then applied onto the cotton fabrics dyeing. The first step was scouring and followed by mordant processes on the fabrics. Scouring was carried out by using sodium carbonate or soda ash (5 g/L) in distilled water then heated until 80 ºC and stirred well. The cotton fabrics was then soaked in the scouring solution and allowed to stand for 30 min and then dried in the air.

The mordant process was carried out with six different mordant agents *e.g.*, 0.2 M solution of alum, lime (CaO), ferrous sulphate ($FeSO_4$), aluminium acetate, iron acetate and acetic acid. The scoured cotton fabrics were soaked into the mordant solution and allowed to stand for 1 h and then dried in air.

Four pieces of fabric were mordanted and then dyed in *P. pterocarpum* dye in both the standard/control solution and the TiO_2 modified dye solution. After 15 min, the fabrics piece then removed and dried. This step was repeated for 2 to 7 times. After a thorough drying process, the coloured materials were fixed in 0.2 M alum solution and then all the resulting fabrics were then characterized.

Detection method: The dry fabrics were characterized by the UV-visible spectrophotometer. The dyeing fabrics were also characterized for their chroma value, fastness and ultraviolet protection factor (UPF) value by chroma test equipment (CieLab), UPF test equipment and colour fastness resistant test equipment, respectively.

RESULTS AND DISCUSSION

Copper pod natural dye: Copper pod extract, also known as an extract of *P. pterocarpum* bark, is a brown solution. The solution of *P. pterocarpum* extract turned black when $FeCl_3$ was added to prove its quality, which is a benchmark qualitative standard testing for tannins [13]. Previous studies revealed that *P. pterocarpum* has a high concentration of tannin in its leaves and flowers [14].

UV-visible studies: Natural plant colours are typically composed of phenolic compounds. Tannin can be identified by the presence of polyphenol functional groups present in the molecule. In order to help their metabolism, plants produce a chemical called tannin, which is composed of polyphenolics structure. The feature is a bitter taste that is characteristic of tannin. Maximum UV-vis absorption was observed at 277 nm (Fig. 2) indicating that the phenolic compound was absorbed through its benzene rings. This is consistent with the absorption of

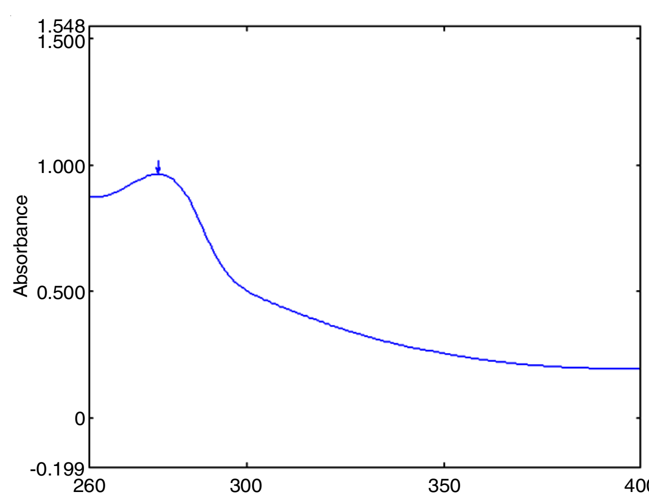

Fig. 2. UV-vis absorption of copper pod dye

transitions of $\pi \rightarrow \pi^*$ orbitals for a conjugated double bond system [15]. This finding was consistent with the reported work of Grasel *et al*. [16].

Colour stability: It is important to remember that the majority of natural dyes are unstable. The absorbance of copper pod natural dye extract was studied as a function of concentration over time to determine the dye solution's stability while being stored. The bark of copper pod, which can be used to make a natural brown dye, is rich in tannins. The dye-like qualities of the resulting colour are due to the presence of chromophore groups, that bind the fibres together, is causes colour to form [17].

The result showed that the absorbance of the dye solution remains constant until 3rd week. At week 4, there was an apparent decrease in absorbance, which correlated with an decrease in the concentration of the active component in the solution. It is recommended to use the dye solution in 1-3 weeks after the extraction. The results are shown in Fig. 3.

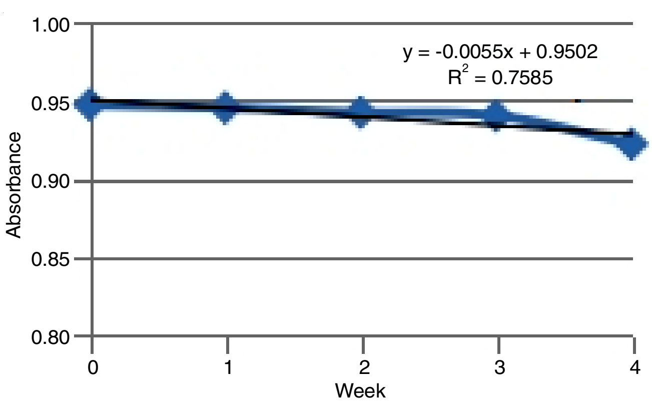

Fig. 3. Stability of copper pod dye in 4 weeks

The stability and brightness of natural dye affected by exposure to light, temperature, pH and other [8]. Some studies applied certain modification to increase the quality of natural dye. For example the addition of some metal oxide as ZnO and TiO_2 which act as the protection layer to absorb the sunlight. TiO_2 also applied in this research to cover it. The phase and particle size of TiO_2 powder was analyzed by X-ray diffraction technique. There are several peaks appeared in the diffractogram (Fig. 4). The highest peak appear at $2\theta = 25.44°$ is associated with anatase phase titania, while the two peaks at 25.44° and 48.14° also indicate the anatase phase [18]. Using the Debye-Scherrer formula, the average particle size of the TiO_2 sample was found to be 34.56 nm, which suggests that the titania powder meets the specification of nanoparticles (1-100 nm).

Modification of copper pod extract by TiO_2: In this study, a microemulsion approach was used to develop a titania-modified copper pod dye (TMCD). UV-vis analysis of TMCD showed a change in the maximum absorption wavelength. The higher the TiO_2 added the higher the wavelength. The results are shown in Table-1, which is in agreement with the previous research that the TiO_2 coated fabric has a higher reflectance than the raw fabric. In addition, it was found that the TiO_2 pigmented layer increased the brightness of the sample and

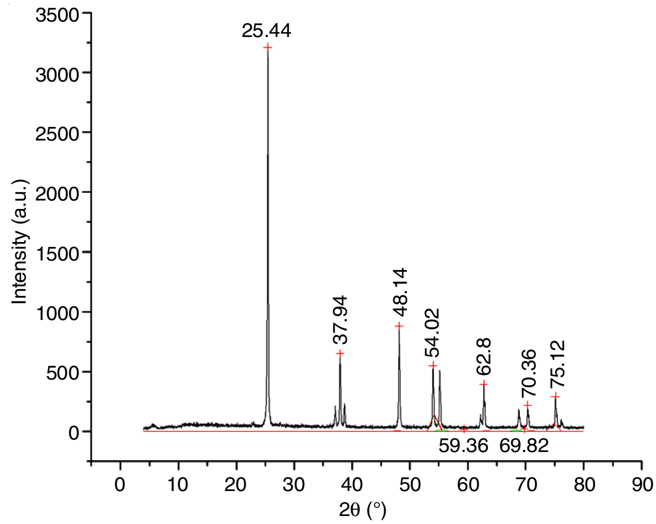

Fig. 4. XRD pattern of titania (TiO_2) nanoparticles (anatase)

TABLE-1
THE MAXIMUM ABSORPTION WAVELENGTH OF COPPER POD AND TMCD (TITANIA MODIFIED TANNIN DYE)

Material	Copper pod	TMCD 0.1 mg/kg	TMCD 0.2 mg/L	TMCD 0,3 mg/L
λ_{max} (nm)	277	278	278,5	279

simultaneously decreased it's chroma [11]. The concentration of TiO_2 nanoparticles had the most significant effect on the colour change of the dyed fabric through the coating process. The dye concentration and TiO_2 particle size also, to the same extent, have an influence on the colour change [15].

Application of copper pod and titania modified dye on cotton fabrics: In dyeing process, the fabric fibers, which dipped in the dye solution was swollen and caused the opening of the fiber pores. The opened pores make the dye easier to enter the fiber and form a bond. This bond is formed between the reactive groups of cellulose in cotton fibers (hydroxyl or OH groups). The hydrogen bond causes the dye retain in the fiber. The illustration of dyeing is shown in Fig. 5.

Colour intensity: The dyed fabrics was investigated by testing the brightness level of the colour by CIE-Lab method. The colour analysis method uses the CIE-Lab method developed by the Commission International de l'Eclairage (CIE) using the parameters L* (brightness), a* (red-green) and b* (yellowish blue) [19]. The performance of fabric colouring, a colour difference test was determined which included the L* value indicating the difference between light (L* = 100) and dark (L* = 0), a * difference between green (-a *) and red (+a *) and b * the difference between yellow (+b *) and blue (–b *).

As shown in Fig. 6, the more immersion, the lower the value of L* which indicates the decreasing level of brightness on the fabrics. In other words, the more immersion will increase the intensity of the colour and it becomes darker. The value of L produced in each mordant is different. Iron mordant (M2) produces the lowest brightness level or the darkest colour. This is due to the presence of a complex salt of Fe(III)-tannin which is formed from a strong reaction between mordant ions, Fe(III) ions and tannin [20]. The reaction is shown in Fig. 7.

Fig. 5. Illustration of cotton fabrics dyeing by copperpod dye (M = mordant agent, T = Titania, C = immersion)

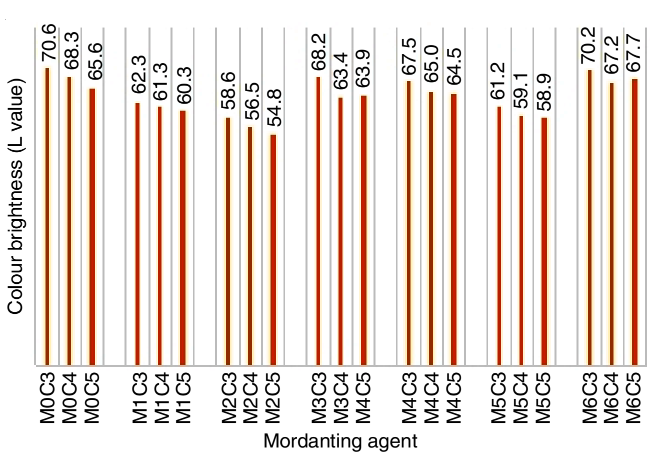

Fig 6. Effect of mordant agent to the colour brightness (L value), from 3-5 immersion samples

The effect of immersion/dipping frequencies to the colour brightness of dyed fabrics also shown in Fig. 6. The higher freq-uencies of dipping, the lower the "L" value indicates the decreasing level of brightness of the fabric. This is the result of the higher amount dyes are bound to the fabrics so it will produce a darker colour.

Measurement results of L, a and b showed the chroma value of the measured coloured fabric. Chroma value is an analysis of colour measurement based on the brightness level on one colour basis. Chroma is depicted in a lighter or darker colour. A higher chroma value indicates a lighter colour level, while a lower chroma value indicates a darker colour level [20]. The chroma level of the resulted samples showed at Fig. 8.

As shown in Fig. 8, the more the immersion frequencies, the higher the chroma value produced. This indicates that the

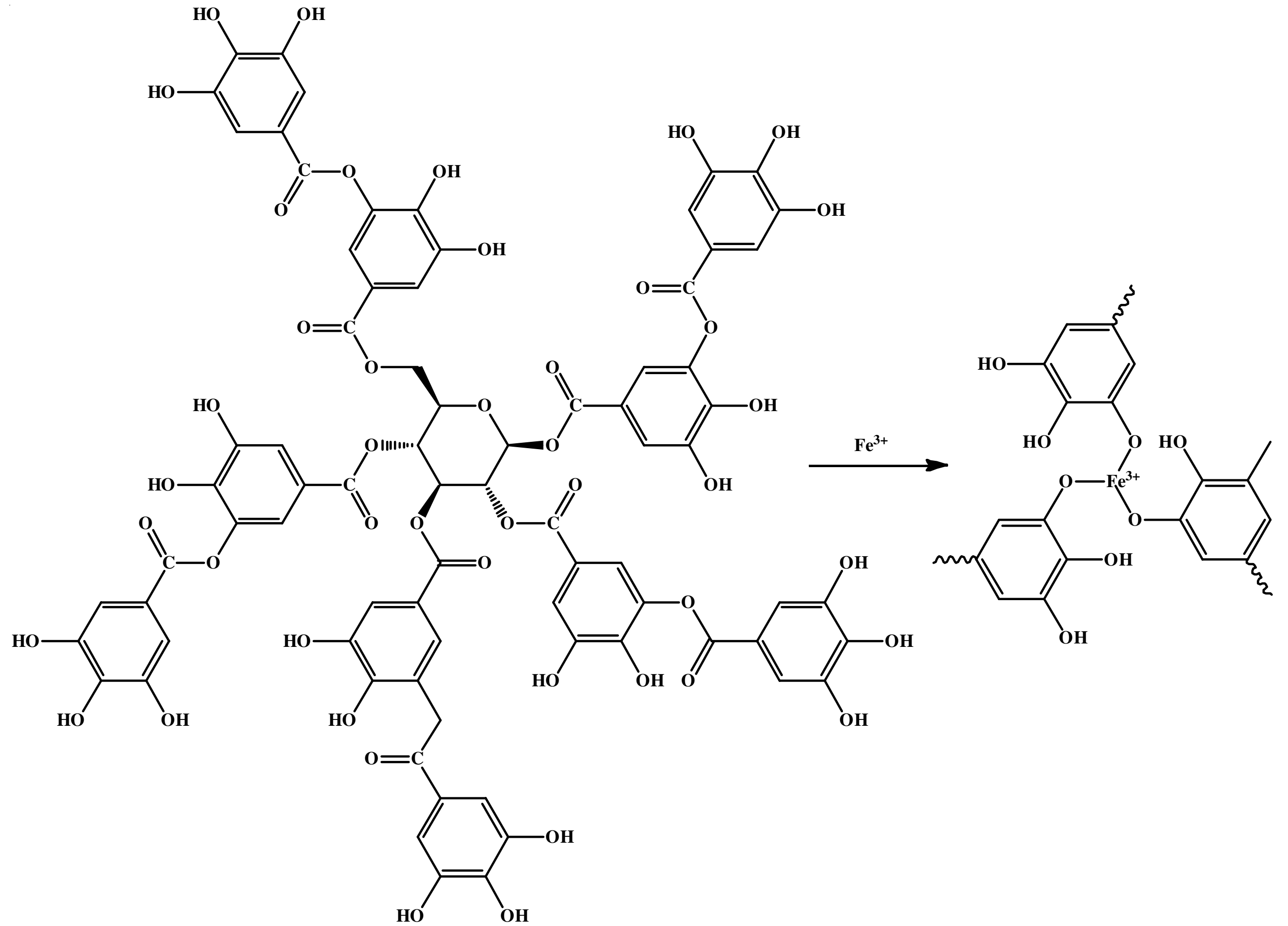

Fig. 7. Reaction of complex formation between tannin and iron (Fe^{3+})

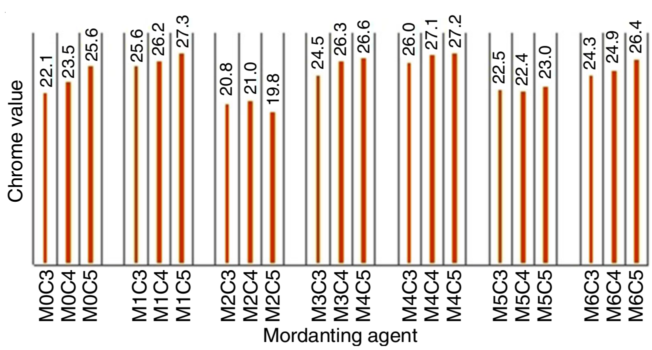

Fig. 8. Effect of mordant to the chroma value on fabrics dyed by copper pod dye

more dyes the resulting colour direction is getting brighter. The chroma level resulted in each mordant was different each other. The mordant was responsible for leading the colour direction based on their distinct properties of the metal ion serving as the centre of the complex [21]. The effect of mordant agent from M1 to M6 indicated the differences in colour brightness. The colour brightness was adjusted from 50 to 70 and a little higher. The dyed fabrics with Fe(III) mordant (M2) produced the darkest brightness level compared to other mordant. Both iron mordants (Fe-sulphate and Fe-acetate) resulted in dyed fabrics with a lower chroma value than the other mordant, illustrating the effect of Fe(III) as the centre ion in complex formation.

TiO_2 can improve the colour saturation and protect the quality of the fabrics. In terms of improving dye-resistance in cotton fabrics, it is comparable to the previous studies involving functionalized titania [10,22,23]. These fact lead the positive effect in development of natural dye on cotton fabrics.

Estimation of ultraviolet protection factor (UPF): The UV-VIS spectrophotometer was used to record the absorbance of the dyed fabric so that the UPF value could be calculated. The average UPF value was found to be highest for 0.3 g/L TiO_2 modified group (Fig. 9), with the exception of the ferrous acetate mordant group. The effectiveness of titania as an ultraviolet protection agent in coloured fabrics has been demons-

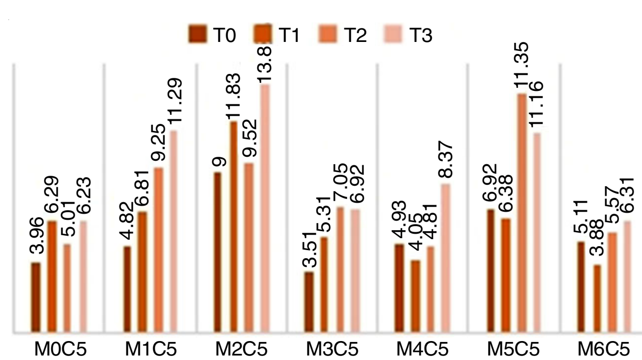

Fig. 9. UPF value of titania-copper pod dyed fabrics (M = mordant agent, C = immersion, T = Titania)

trated. The higher the amount of titania, the stronger UPF. The immordant fabrics has a lower UPF value but also influenced by TiO_2. Samples with aluminium sulphate, iron sulphate, aluminium acetate and acetic acid mordant, affected the UPF values by 11.29, 13.84, 8.37 and 6.31, respectively.

The role of TiO_2 in UPF is decreasing the energy gap, so that the absorption of UV light in the dye layer is lower. As shown in Table-1, the higher the concentration of TiO_2, the longer the wavelength or the lower the energy, which is in the agreement with the other reported study [11,24].

Resistance of colour fastness to sunlight: The quality of colour absorption of TiO_2-copperpod dyed fabrics is evaluated by the fastness value, which indicate the colour resistance to sunlight. Fig. 10 showed the effect of TiO_2 addition on copper pod dye to the fastness value of TMCD dyed fabrics. The control group or fabrics without addition of TiO_2 gave an average resistance value of 4 which means good, except for fabrics with Fe(III) ion mordant giving a value of 5, which means in the very good category. The fabrics dyed by titania modified copper pod dye showed the fastness value 4-5, which means in good and very good category. It indicates that the modification of titania on copper pod have significant effect in the quality of dyeing in cotton fabrics [25].

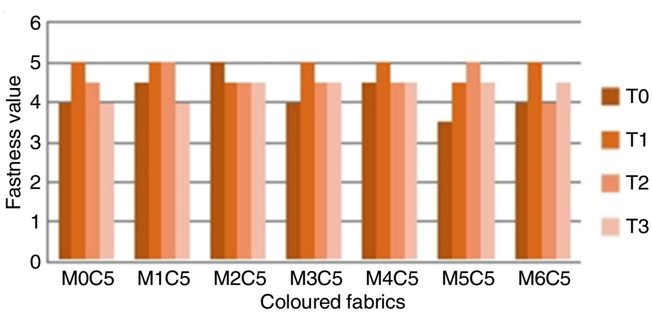

Fig. 10. Sun fastness value of fabrics with TiO_2-copperpod dyes on various mordant (1 = very bad; 2 = bad; 3 = fair; 4 = good; 5 = very good)

Conclusion

Titania modifed copper pod (*Pelthophorum pterocarpum*) dye has a significant effect on the chroma and the ultraviolet protection factor (UPF) value. The higher the concentration of TiO_2, the greater the UPF value being produced. Mordant variations on dyeing with copper pod dye lead the colour direction, including beige, light brown, medium brown and dark brown and also affected the chroma value. Titania modified copper pod dye enhanced the fastness and ultraviolet protection factor (UPF) value as compared to standard copper pod dye.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. S. Yadav, K.S. Tiwari, C. Gupta, M.K. Tiwari, A. Khan and S.P. Sonkar, *Results Chem.*, **5**, 100733 (2023); https://doi.org/10.1016/j.rechem.2022.100733
2. K. Amutha, S.G. Annapoorani and N. Sudhapriya, *Ind. Crops Prod.*, **148**, 112303 (2020); https://doi.org/10.1016/j.indcrop.2020.112303
3. S. Sudarmin, W. Sumarni, S.N. Azizah, M.H.H. Yusof and P. Listiaji, *J. Phys.: Conf. Ser.*, **1567**, 042046 (2020); https://doi.org/10.1088/1742-6596/1567/4/042046
4. S.K. Jash, R.K. Singh, S. Majhi, A. Sarkar and D. Gorai, *Int. J. Pharm. Sci. Res.*, **5**, 25 (2014).
5. M. Fraga-Corral, P. Otero, L. Cassani, J. Echave, P. Garcia-Oliveira, M. Carpena, F. Chamorro, C. Lourenço-Lopes, M.A. Prieto and J. Simal-Gandara, *Foods*, **10**, 251 (2021); https://doi.org/10.3390/foods10020251
6. Z. Dehghanian, K. Habibi, M. Dehghanian, S. Aliyar, B.A. Lajayer, T. Astatkie, T. Minkina and C. Keswani, *Heliyon*, **8**, e09094 (2022); https://doi.org/10.1016/j.heliyon.2022.e09094
7. C. Harsito, A.R. Prabowo, S.D. Prasetyo and Z. Arifin, *Open Eng.*, **11**, 548 (2021); https://doi.org/10.1515/eng-2021-0055
8. J. Koenderink, A. van Doorn and K. Gegenfurtner, *i-Perception*, **11(6)** 204166952095843 (2020); https://doi.org/10.1177/2041669520958431
9. T.M.A. Elmaaty, H. Elsisi, G. Elsayad, H. Elhadad and M.R. Plutino, *Polymers*, **14**, 4273 (2022); https://doi.org/10.3390/polym14204273
10. M.M. Rashid, M. Zorc, B. Simonèiè, I. Jerman and B. Tomšiè, *Catalysts*, **12**, 1330 (2022); https://doi.org/10.3390/catal12111330
11. H. Rabiei, S.F. Dehghan, M. Montazer, A.G. Koozekonan and S.S. Khaloo, *Front. Public Health*, **10**, 929095 (2022); https://doi.org/10.3389/fpubh.2022.929095
12. M. El-naggar, T.I. Shaheen, S. Zaghloul, M.H. El-rafie and A.A. Hebeish, *Ind. Eng. Chem. Res.*, **55**, 2661 (2016); https://doi.org/10.1021/acs.iecr.5b04315
13. A.S. Nateri, S. Zandi, V. Mottaghitalab and N. Piri, *Pigment Resin Technol.*, **47**, 431 (2018); https://doi.org/10.1108/PRT-08-2017-0072
14. L.C. Mohr, A.P. Capelezzo, C.R.D.M. Baretta, M.A.P.M. Martins, M.A. Fiori and J.M.M. Mello, *Polym. Testing*, **77**, 105867 (2019); https://doi.org/10.1016/j.polymertesting.2019.04.014
15. H. Kim, S. Jo and T.S. Lee, *Mater. Design*, **203**, 109630 (2021); https://doi.org/10.1016/j.matdes.2021.109630
16. F.S. Grasel, M.F. Ferrão and C.R. Wolf, *Ind. Crops Prod.*, **91**, 279 (2016); https://doi.org/10.1016/j.indcrop.2016.07.022
17. M.V. Limaye, Z. Bacsik, C. Schütz, A. Dembelé, M. Pléa, L. Andersson, G. Salazar-Alvarez and L. Bergström, *Text. Res. J.*, **82**, 1888 (2012); https://doi.org/10.1177/0040517512452955
18. T.M.A. Elmaaty and B. Mandour, *Asian J. Chem. Sci.*, **4**, 1 (2018); https://doi.org/10.9734/AJOCS/2018/40329
19. B. Becerir, *J. Textile Eng. Fashion Technol.*, **1**, 240 (2017); https://doi.org/10.15406/jteft.2017.01.00039
20. Zhaofeng Fu and Rui Chen, *J. Anal. Methods Chem.*, **2019**, 3894571 (2019); https://doi.org/10.1155/2019/3894571
21. Y. Ding and H.S. Freeman, *Color. Technol.*, **133**, 369 (2017); https://doi.org/10.1111/cote.12288
22. D. Cheng, M. He, J. Ran, G. Cai, J. Wu and X. Wang, *Cellulose*, **25**, 1413 (2018); https://doi.org/10.1007/s10570-017-1606-1
23. M.M. Rashid, B. Simoncic and B. Tomšic, *Surf. Interfaces*, **22**, 100890 (2021); https://doi.org/10.1016/j.surfin.2020.100890
24. M.F. Sojka, P.G. Cummins, L.A.G. Declercq, C.G. Fthenakis, M.C. Ionita-Manzatu, W.A. Lee, D.H. Maes, M.A. McKeever-Alfieri, L.J. Najdek, N. Pernodet, I.M.E. Sente, L.P. Teta, K. Van Rillaer, D.B. Yarosh and P.U. Giacomoni, *Photochem. Photobiol. Sci.*, **10**, 1146 (2011); https://doi.org/10.1039/c0pp00327a
25. R. Ghafarzadeh, A. Shams-nateri and A.F. Shojaie, *Indian J. Fibre Textile Res.*, **43**, 363 (2018).