



## Photofading of Natural Indigo Dye in Cotton Coated with Zinc Oxide Nanoparticles Synthesized by Precipitation Method

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**Abstract.** Blue dye (indigo) from *Indigofera tinctoria* leaves is a popular natural dye used worldwide. The lower light fastness of natural indigo dyes compared to that of synthetic blue dyes is one of the drawbacks of the former, limiting its utilization in the textile industry. In this study, zinc oxide nanoparticles (ZnONPs) were synthesized and characterized, and their effect on the photofading of cotton fabric dyed with natural indigo was investigated. ZnO was produced by simple precipitation. Fourier transform infrared spectroscopy (FTIR), X-ray powder diffractometry (XRD), and Brunauer–Emmett–Teller analysis were employed to characterize the composition, shape, crystallinity, size, and surface area of the resulting NPs. The optical characteristics and bandgap energy of the ZnONPs were also determined using a UV-Vis spectrophotometer. XRD and scanning electron microscopy (SEM) confirmed the synthesis of ZnONPs. The ZnONPs were applied to cotton fabrics via the dip-coating method. The transmittance of cotton coated with ZnONPs was lower than that of the uncoated sample. Photofading tests with UV-A irradiation were conducted, and the fading rate of natural indigo dye in cotton showed first-order kinetics. Overall, the synthesized ZnONPs provided excellent UV protection to reduce the photofading of cotton dyed with natural indigo.

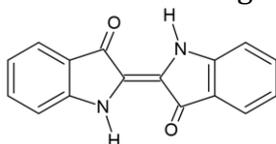
**Keywords:** *Indigofera tinctoria*; Natural Dye; Photofading; UV-protection; Zinc Oxide Nanoparticle

### 1. Introduction

Ecofriendly natural dyes with minimal impacts on the environment have gained increased research attention. Natural dyes present the advantages of high renewability, biodegradability, and nontoxicity (Rahayuningsih et al., 2019). Indigo is a popular natural dye that can be extracted from various plants, such as *Indigofera tinctoria*, *Indigofera arecta*, *Strobilanthes flaccidifollus*, *Isatis tinctoria*, and other indigoid plants. The indicans and isatans present in these plants are converted to colorless indoxyl and glucose by enzymatic hydrolysis or fermentation. Indoxyl forms indigotin pigment under alkali conditions by oxidation. Indigotin must be reduced into a soluble leuco form that bonds with cloth fibers

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and oxidizes back to its original insoluble form to develop color (Degani et al., 2015). Because this insoluble pigment is trapped within fibers, indigo has better wash fastness compared with most other natural dyes. Unfortunately, compared with different dyes, the light fastness of natural indigo dye is poor or moderate. According to ISO standard method, where grade 1 represents poor fastness and 5 represents excellent fastness, the light fastness values of natural indigo dye in cotton is rated Grade 3 to 3/4 (Comlekcioglu et al., 2015). Figure 1 shows the chemical structure of indigotin.



**Figure 1** Chemical structure of indigotin in natural indigo dye

Exposure to visible and UV light can promote the photofading of color. Because shorter wavelengths of light have higher energy, UV light is generally more harmful than visible light. The quantum energy of UV light is similar to the bond energies of organic molecules. Thus, UV light can cause undesirable degradation. Dye fading occurs because of the loss of conjugation of double bonds in whole molecules. The initial step of indigo fading may involve C=C double bond cleavage because the central C=C double bond is highly reactive (Iuga et al., 2012).

The addition of a UV protection agent is a suitable approach to reduce the photofading of colors on the fabric. UV protection agents are usually composed of organic or inorganic compounds with strong absorption in the UV range (i.e., wavelengths below 400 nm). Organic UV protection agents absorb UV rays throughout the spectra and dissipate the absorbed energy to avoid color degradation (Yang & Naarani, 2006; Latif et al., 2015). However, these agents are prone to reductions in efficiency over time. Compared with organic agents, inorganic UV protection agents are generally preferred because the latter are nontoxic, stable under UV exposure and high temperature, and insoluble in neutral pH. The mechanism of inorganic UV protection agents involves the absorption, reflection and scattering of UV rays through their high refractive index (Fajzulin et al., 2015).

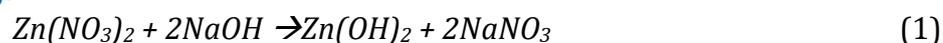
Nanosized zinc oxide (ZnO) has recently received great attention for its application as a UV protection finish in textile. Nanosized ZnO has a wide energy band gap of approximately 3.3 eV, which means it can absorb UV rays with wavelengths below 375 nm (Li et al., 2012). The material has a high surface-area-to-volume ratio, which endows it with excellent effectiveness in blocking UV radiation when compared with the bulk material. Nanoparticles tend to have a better affinity to fabric surfaces and, thus, provide greater durability compared with bulk materials (Yadav et al., 2006). Additionally, ZnO is generally recognized as safe by the Food and Drug Administration. Also, ZnO is commonly applied in cosmetics as UV sunscreen (Smijns and Pavel, 2011). In vitro and in vivo studies of sunscreen with ZnONPs applied on UV-B damaged porcine skin showed that ZnO did not enter into the viable epidermis and remained on the skin surface (Monteiro-Riviere et al., 2011). Therefore, the application of ZnONPs in textile is considered safe. ZnONPs are also inexpensive, making them suitable for use in the textile industry (Karthik et al., 2017).

On the other hand, nanoscale ZnO is known to possess the photocatalytic ability. Several studies show that ZnONP enhanced the degradation of dye solution in wastewater (Zafar et al., 2019; Agustina et al., 2020). Following light absorption, electrons in the valence band of ZnO nanoparticles (ZnONPs) are promoted to the conduction band, which produces a positive hole in the valence band. Photogenerated holes and electrons induce oxidation-reduction reactions with water and oxygen on the ZnONP surface and form hydroxyl radicals and ROS (Das et al., 2019). These radicals and ROS can promote the oxidative degradation of

organic compounds. Hence, there is a concern that, applying ZnONPs in dyed fabrics, especially in naturally dyed fabrics might accelerates photofading of dye molecules.

Many researchers utilized ZnONP as UV protection in fabric; however, they focus on investigating ZNONPs as anti-UV as skin protection (Román et al., 2019; Tania & Ali, 2020). Moreover, ZnONPs were applied in undyed fabric. Kathirvelu et al., (2009) studied the synthesis of ZnONPs and their application on cotton and polyester/cotton dyed with reactive dye. The result shows that the UV absorbing activity of ZnO-treated fabrics was significantly improved. However, the effect of ZnONPs on dye fastness was not discussed. To the best of our knowledge, no report on the application of ZnONPs as inorganic anti-UV to protect dyed fabrics is yet available. Investigations that address the photofading kinetics of natural dye are also rare. This study aims to study the effect of ZnONPs on photofading characteristics of natural indigo-dyed cotton coated with ZnONPs.

In the present work, ZnONPs were synthesized via a simple precipitation method using zinc nitrate ( $Zn(NO_3)_2$ ) and sodium hydroxide (NaOH) according to the reactions in Equations 1 and 2. Precipitation is a cost-effective, scalable, repeatable, and highly controllable method that has been used to synthesize a wide variety of ZnO nanostructures (Raoufi & Raou, 2013).



The synthesized ZnONPs were characterized by scanning emission microscopy (SEM), X-ray powder diffractometry (XRD), Fourier transform infrared (FTIR) spectroscopy, and UV-Vis spectrophotometry. The kinetics of the fading rates of indigo-dyed cotton with and without the ZnONP coating under UV-A irradiation were also calculated, and the durability of the ZnONP coating on the cotton substrate was tested.

## 2. Methods

### 2.1. Materials

Zinc nitrate tetrahydrate ( $Zn(NO_3)_2 \cdot 4H_2O$ ) and sodium hydroxide (NaOH), were purchased from Merck. Natural indigo dye powder was obtained from Gama Indigo (Indonesia). Commercial-grade sodium dithionite and sodium carbonate were used as reducing agents for indigo dyeing. Cotton fabric (mercerized sanforized with warp 106 and weft 92, Ne1 50) was purchased from PT. Primatexo, soaked with 2% nonionic detergent, washed several times and air-dried before further treatment.

### 2.2. Synthesis of ZnONPs

The ZnONPs were prepared by precipitation following a procedure reported by Talam et al. (2012) with some modification (Figure 2a). A solution of 0.05 M  $Zn(NO_3)_2 \cdot 4H_2O$  (6.54 g, 500 mL) was placed in a glass beaker under continuous stirring. After complete dissolution, 0.1-M NaOH (2 g, 500 mL) solution was added drop-wise to the beaker so that the solution gradually transformed into a milky white slurry. The reaction was allowed to proceed at room temperature (30 °C) for 2.5 h and then left under constant stirring for 0.5 h to complete the reaction. The  $Zn(OH)_2$  precipitate was allowed to settle overnight and then separated from the supernatant by sedimentation. The white precipitate was washed three times with 100 mL of deionized water, dried in an air oven at 100 °C for 3 h, and then ground to a fine powder. Heat treatment under 200°C can only eliminate residual water while the other impurities still exist, which can suppress the formation of crystals (Karthik et al., 2017). Salahuddin et al. (2015) report that the particle size of ZnNPs increased from 14.58 nm up to 91.44 nm by increasing calcination temperature from 250 °C up to 600 °C. From the XRD analysis, the peak of impurities in ZnONP calcined at 250 °C was not

observed. The thermogravimetric analysis showed no further weight loss after heating at around 320 °C up to 600 °C, indicating the complete loss of impurities at around 320 °C. Based on the information above, in this study, the  $\text{Zn}(\text{OH})_2$  powder was converted into ZnO by calcination at 300 °C for 3 h. The resulting fine powder was grounded for a second time and then stored in an airtight container for further use.

### 2.3. Dyeing with natural indigo

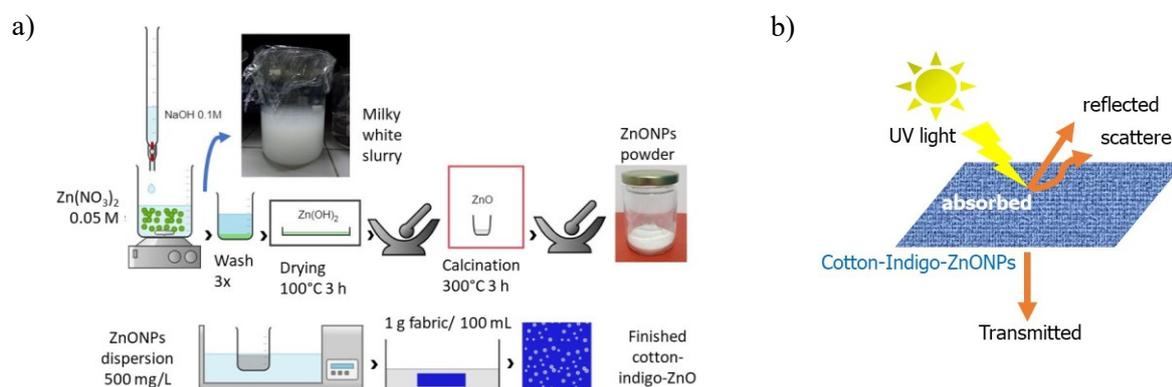
Indigo powder (50 g), sodium carbonate (14 g), and sodium dithionite (18 g) were dissolved in 1 L of water at 70 °C. The solution was allowed to stand for 15 min under closed conditions to prevent oxidation. After 15 min, the solution was combined with 9 L of a solution of sodium carbonate (3.5 g) and sodium dithionite (4.5 g). The mixture was allowed to stand for 1 h under closed conditions. Cotton fabric was dipped for 5 min in a dye bath (1:20 mass-to-liquid ratio) and then air-dried for 5 min to achieve contact with oxygen. The dipping process was repeated seven times to maximize dye uptake. The dyed cotton was washed with tap water to remove the unreacted dye and then air-dried. This sample was named cotton-indigo.

### 2.4. Coating of cotton with ZnONPs

A 100-mL dispersion of ZnONPs (500 mg/L) was irradiated for 20 min in a 300 W, 50/60-Hz bath sonicator (Elmasonic S 300 H). Cotton-indigo measuring 10 cm × 10 cm ( $\pm 1$  g) was dipped in the dispersion for 5 min and then air-dried. This sample was named cotton-indigo-ZnO. All samples were kept in the dark chamber for further analysis.

### 2.5. Photofading Test

Photofading tests were performed in a closed chamber with dimensions of 60 cm × 50 cm × 30 cm and equipped with a UV-A lamp (20 W, Sankyo Denki). A fan was installed in the chamber to ensure a homogenous temperature. Samples were laid parallel to the longitudinal axis of the lamp. The distance from the lamp to the sample was 25 cm. The radiant flux was measured as 0.206 mW cm<sup>-2</sup> by using a Lutron UV light meter (YK-35UV).



**Figure 2** Preparation of ZnONPs and their application onto cotton-indigo (a) and UV protection mechanism of ZnONPs in cotton-indigo (b)

### 2.6. Durability Test

Washing durability was assessed using a Launder-O-Meter (Limites Bulkert type Original Hanau, 18-L capacity), according to ISO 105-C06: 2010 (40 °C, 45 min). One wash cycle provides an accelerated washing treatment corresponding to five home washes (Krishnaveni & Thambidurai, 2013). The samples were washed twice, which is equivalent to 10 cycles of home washing.

### 2.7. Characterization and color measurement

The XRD patterns of the ZnO powder were determined using a Rigaku Smartlab instrument with Cu K $\alpha$  radiation at 40 kV, 30 mA, a scan speed of 3° min<sup>-1</sup>, a step width of 0.01°, and a scan range of 3°–90°. Crystal sizes were estimated using 'Scherrer's formula, as shown in Equation 3:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (3)$$

where  $D$  is the crystallite size,  $K$  is a dimensionless shape factor (0.89, in the assumption of spherical crystal with  $k$ -l),  $\lambda$  is the X-ray wavelength (0.154 nm),  $\beta$  is the full-width at half maximum, and  $\theta$  is the half diffraction angle (Monshi et al., 2012).

The FTIR spectra of the developed ZnONPs over the wavelength range of 4000–400 cm<sup>-1</sup> were recorded at 303 K by using a Shimadzu IRPrestige-21 instrument. The absorbance of the ZnONPs was analyzed by UV–Vis spectrophotometry (Shimadzu UV-1700 Pharma Spec). The morphology of the treated cotton fabric was characterized by SEM-energy dispersive X-Ray spectroscopy (Quanta 650). ZnO's elemental analysis in the treated cotton fabric was performed via energy dispersive X-Ray (EDX) analysis.

The color changes of the samples were measured at various intervals (i.e., 0, 24, 48, 96, and 144 h). The color was evaluated in terms of the CIELAB values  $L^*$ ,  $a^*$ , and  $b^*$  by using a UV–vis spectrophotometer (Shimadzu PC 2401;  $L^*$  = brightness;  $a^*$  = green  $-a^*$  to red  $+a^*$ ;  $b^*$  blue  $-b^*$  to yellow  $+b^*$ ). The level of color fading was evaluated in terms of color difference,  $dE$ , as shown in Equation 4 (AATCC Evaluation Procedure 7-2009).

$$dE = [(L^* - L^*)^2 + (a^* - a^*)^2 + (b^* - b^*)^2]^{1/2} \quad (4)$$

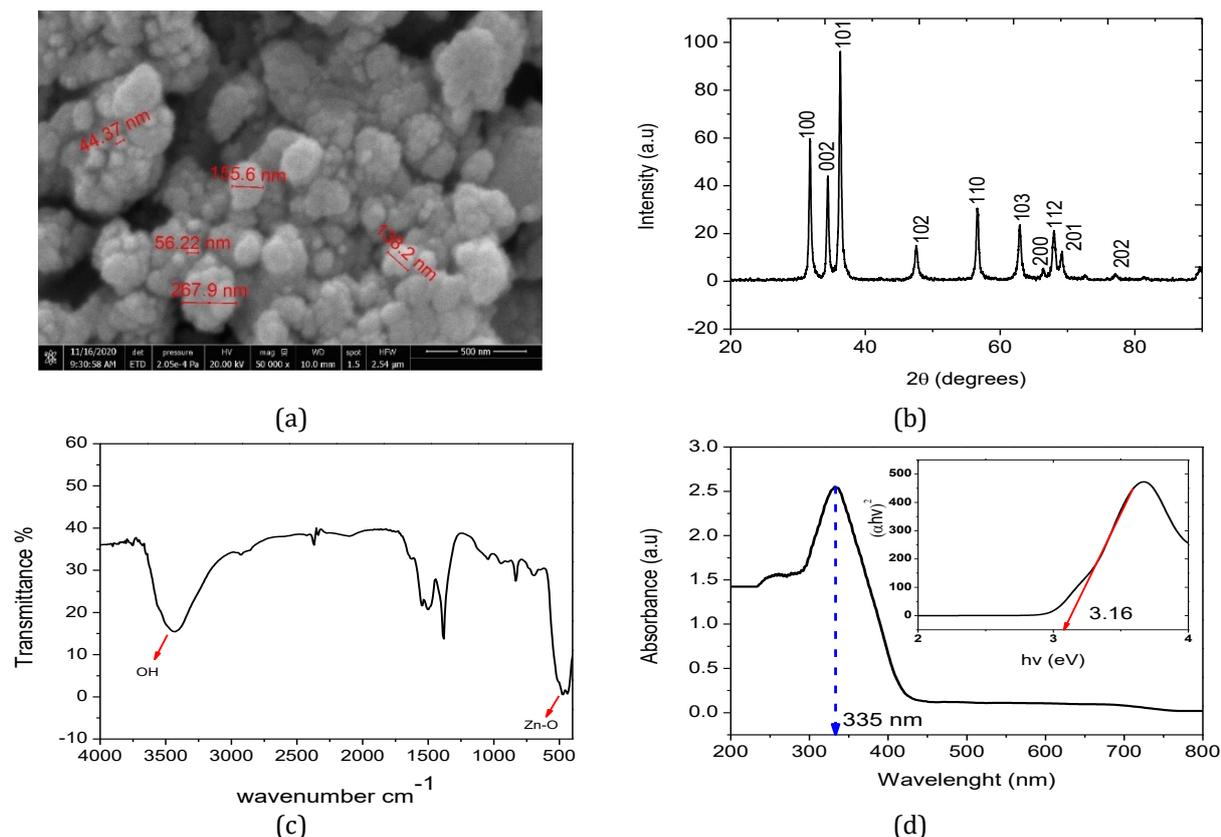
The  $dE$  of the samples was calculated after each period of irradiation; here,  $L^*$ ,  $a^*$ , and  $b^*$  are the color values of the sample after a certain period of irradiation, and  $L^*$ ,  $a^*$ , and  $b^*$  are the color values of the reference cotton.

## 3. Results and Discussion

### 3.1. ZnONP characterization

The synthesized ZnO was characterized, as shown in Figure 3. The SEM analysis in Figure 3a reveals that the individual ZnONP particles are in the nanoscale range but clump together in an agglomerated state. ZnO form aggregate due to 'nanoparticles' high surface energy, and heat treatment leads the aggregate to form agglomeration. The particles are spherical in shape and have diameters of approximately 40 nm. The agglomerates range in size from 100 nm to the micron scale. The spherical shape of ZnONPs synthesized from zinc nitrate, and sodium hydroxide was also reported by Romadhan et al., (2016).

The specific surface area of the ZnONPs was characterized via the Brunauer–Emmett–Teller (BET) method, and pore size were calculated according to Barrett–Joyner–Halenda (BJH) method. The BET surface area of the ZnONPs was 16.57 m<sup>2</sup> g<sup>-1</sup>, and their pore size was approximately 26.54 nm. According to IUPAC classification, the material with a pore width of 2 nm to 50 nm is called mesoporous (Thommes et al., 2015). Suntako (2015) prepared ZnONPs through the precipitation method using zinc nitrate hexahydrate and sodium hydroxide as precursors. The precipitates were calcined at 200 °C, and a surface area of 20.28 m<sup>2</sup> g<sup>-1</sup> g was achieved. In our experiment, ZnONP were calcined at 300 °C, hence, the smaller surface area is expected.



**Figure 3** SEM images of ZnONPs—magnification 50,000× (a), X-ray diffraction patterns of ZnONPs (b), FTIR spectra of ZnONPs (c), and UV–Vis Absorbance Spectra and Tauc plot for determination of bandgap energy of ZnONPs (d) (ZnONPs powder calcined at 300 °C)

Figure 3b shows the XRD patterns of the ZnONPs. The peaks of the NPS could be assigned to hexagonal ZnO (JCPDS Card 36-1451; Pandimurugan & Thambidurai, 2017). The crystal type of the ZnONPs was identified as wurtzite. The presence of sharp peaks indicates that the ZnONPs are crystalline in form and free of impurities. The crystal size of ZnO, according to the Debye–Scherrer's formula at  $2\theta$  36.248° ( $d_{101}$ ) was 23.33 nm. The calculated lattice parameters  $a$  and  $c$  of the ZnONPs were 5.205 and 3.249 Å, respectively, similar to those of pure ZnO powder ( $a = 5.207$ ,  $c = 3.250$  Å; Raoufi & Raou, 2013). This finding confirms that the simple precipitation method used in this study could produce pure ZnONPs.

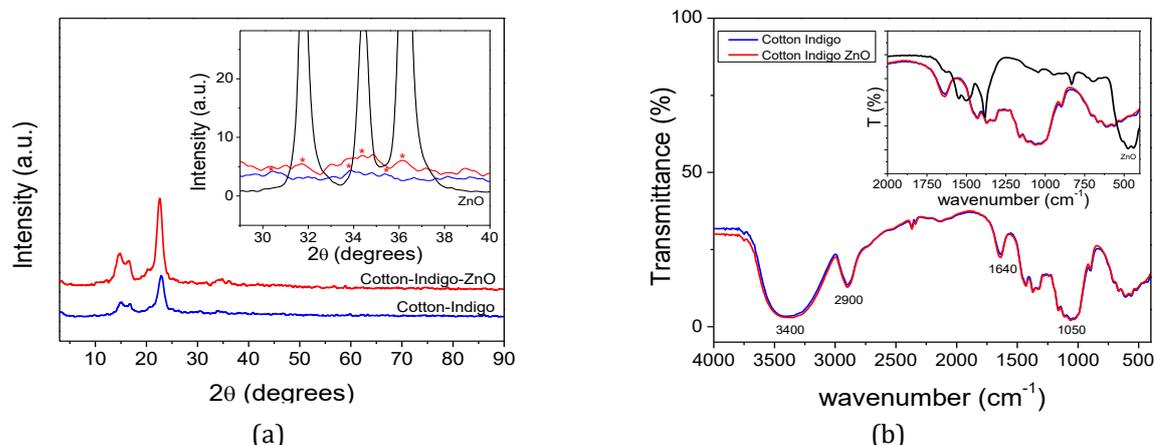
The FT-IR spectra of the obtained ZnONPs is presented in Figure 3c. The characteristic stretching vibration band of the Zn–O bond occurs at wavenumbers of approximately 405–470  $\text{cm}^{-1}$  (Pandimurugan & Thambidurai, 2017). Peak at 2350  $\text{cm}^{-1}$  corresponds to the  $\text{CO}_2$  absorbed from air. The peak at 3450  $\text{cm}^{-1}$  indicates the presence of –OH groups stretching vibration (Reghioua et al., 2021).

Figure 3d shows the UV–Vis absorbance spectra of the ZnONPs. The ZnONPs show absorption properties in the UV range, particularly at wavelengths below 400 nm, with a peak appearing at 335 nm. The band gap energies of the NPs were calculated using the Tauc plot method (Figure 2d), where  $\alpha$  is the optical absorption coefficient,  $h\nu$  is the photon energy,  $E_g$  is the direct band gap, and  $E_D$  is a constant. Our synthesized ZnONPs had an intrinsic optical band gap energy of 3.16 eV. This calculated energy is similar to the results of Alias et al. (2010), who synthesized ZnO using the precipitation method. Materials can absorb light when its  $h\nu$  matches or exceeds their band gap energy. The obtained band gap

energy lies in the UV range of the solar spectra; thus, the ZnONPs has UV protection properties.

### 3.2. Application of ZnONPs to cotton dyed with natural indigo

Figure 4 shows the XRD patterns and FTIR spectra of indigo-dyed cotton with and without the ZnONP coating. As can be seen in Figure 3a, the diffraction peaks at  $2\theta = 14^\circ$  ( $d_{101}$ ),  $16^\circ$  ( $d_{101}$ ), and  $22.5^\circ$  ( $d_{002}$ ) reveal the typical reflections of cellulose in cotton (Kartini et al., 2014). Compared with the XRD pattern of cotton-indigo, the peaks of the ZnONPs at  $2\theta = 31.677^\circ$ ,  $34.496^\circ$ , and  $36.275^\circ$  in the XRD pattern of cotton-indigo-ZnO are slightly higher. This result confirms the attachment of ZnONPs to cotton-indigo.



**Figure 4** (a) X-ray diffraction patterns and (b) FTIR spectra of cotton dyed with indigo and coated with or without ZnONPs (dip-coating mass to liquid ratio 1:100  $\text{g mL}^{-1}$  in a dispersion of ZnONPs 500  $\text{mg L}^{-1}$ )

The FTIR spectra of indigo-dyed cotton with and without the ZnONP coating are displayed in Figure 4b. The broad peak at  $3400 \text{ cm}^{-1}$  reflects  $-\text{OH}$  stretching vibrations, and the peak at  $2900 \text{ cm}^{-1}$  corresponds to cellulose's  $\text{C}-\text{H}$  stretching vibrations. The peak at  $1640 \text{ cm}^{-1}$  is associated with the  $-\text{OH}$  bending vibrations of physically absorbed water molecules. The peak at  $1050 \text{ cm}^{-1}$  is due to cellulose's  $\text{C}-\text{O}$  stretching vibrations (Shaheen et al., 2016). In the FTIR spectrum of cotton-indigo coated with ZnONPs (red color), the absorption band below  $500 \text{ cm}^{-1}$  is not appearing, likely because of the low concentration of ZnO in the samples. Covalent bonding between ZnO and cotton was not detected, which means the NPs are attached to the cotton substrate through van der Waals forces and hydrogen bonding.

The UV-protection properties of ZnO in cotton were evaluated in terms of % transmittance of UV light; in this test, undyed cotton was used as a reference. Figure 5a shows the % transmittance profile and average % transmittance of the samples. Light striking the cotton sample is absorbed, reflected, and transmitted (Figure 2b). The application of ZnONPs to cotton colored with natural indigo dye reduced the transmittance of UV light by up to 9.3%, which means some of the UV light was successfully absorbed, reflected, or scattered by the NPs. This result is in accordance with previous research findings (Kathirvelu et al., 2009; Cole et al., 2016; Attanayake et al., 2020). The unique ability of ZnONPs to absorb UV light, which is illustrated in Figure 3d, supports this result.

The effect of ZnONPs on the photofading of natural indigo-dyed cotton was investigated. The color change of natural indigo dyed cotton was determined by measuring the  $dE$  (Equation 4). The  $dE$  is assumed to equal the concentration ( $C$ ) of indigo in cotton fabrics. The proposed first-order kinetic reaction of indigo photofading within the cotton substrate is shown in Equation 5.

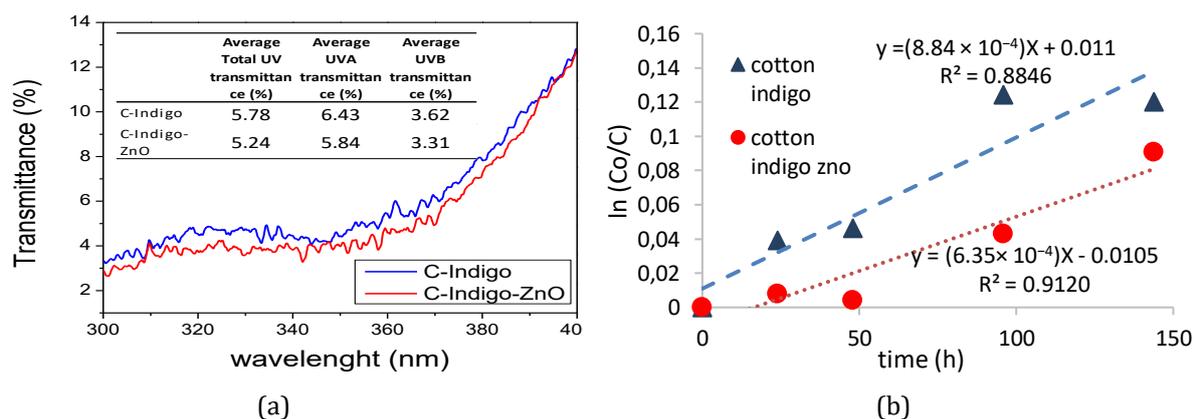
$$\ln\left(\frac{C_0}{C}\right) = k t \quad (5)$$

where  $C_0$  and  $C$  are the initial and remaining concentration of natural indigo in cotton at any time (Jawad et al., 2016). The rate constant ( $k$ ) was calculated from the slope of  $\ln(C_0/C)$  versus irradiation time ( $t$ ). Table 1 shows the  $dE$  of indigo-dyed cotton with and without the ZnONP coating after exposure to UV-A irradiation for different periods; Figure 5b shows the kinetics of photofading.

**Table 1** Effect of UV-A light exposure on the color difference ( $dE$ ) of indigo-dyed cotton with and without ZnONP coating

Irradiation time (h)	Cotton-Indigo				Cotton-Indigo-ZnO			
	$L$	$a^*$	$b^*$	$dE$	$L$	$a^*$	$b^*$	$dE$
0	41.89	-2.96	-16.98	61.90	41.39	-3.13	-14.96	61.86
24	44.00	-3.93	-15.44	59.51	42.26	-3.04	-16.37	61.38
48	44.35	-3.85	-15.11	59.08	41.40	-3.43	-13.82	61.60
96	48.62	-4.15	-13.82	54.65	43.94	-4.99	-13.88	59.26
144	48.79	-4.95	-15.06	54.89	47.29	-5.05	-15.67	56.49

As shown in Figure 5b, the photofading of natural indigo was fitted to first-order kinetics, indicated by a relatively high linear regression coefficient ( $R^2 = 0.8846$  and  $0.9120$ ). The photofading of indigo under UV-A irradiation follows first-order kinetics with a rate constant of  $8.84 \times 10^{-4} \text{ h}^{-1}$  in cotton-indigo and  $6.35 \times 10^{-4} \text{ h}^{-1}$  in cotton-indigo-ZnO. Cotton-indigo coated with ZnONPs shows significantly lower fading than the uncoated sample. In previous studies, the disappearance of solid indigo-TiO<sub>2</sub> under a high-pressure mercury lamp (Philips 125 W) also followed an apparent first-order kinetic mechanism with a rate constant of  $9 \times 10^{-3} \text{ min}^{-1}$  (Vautier et al., 2001).

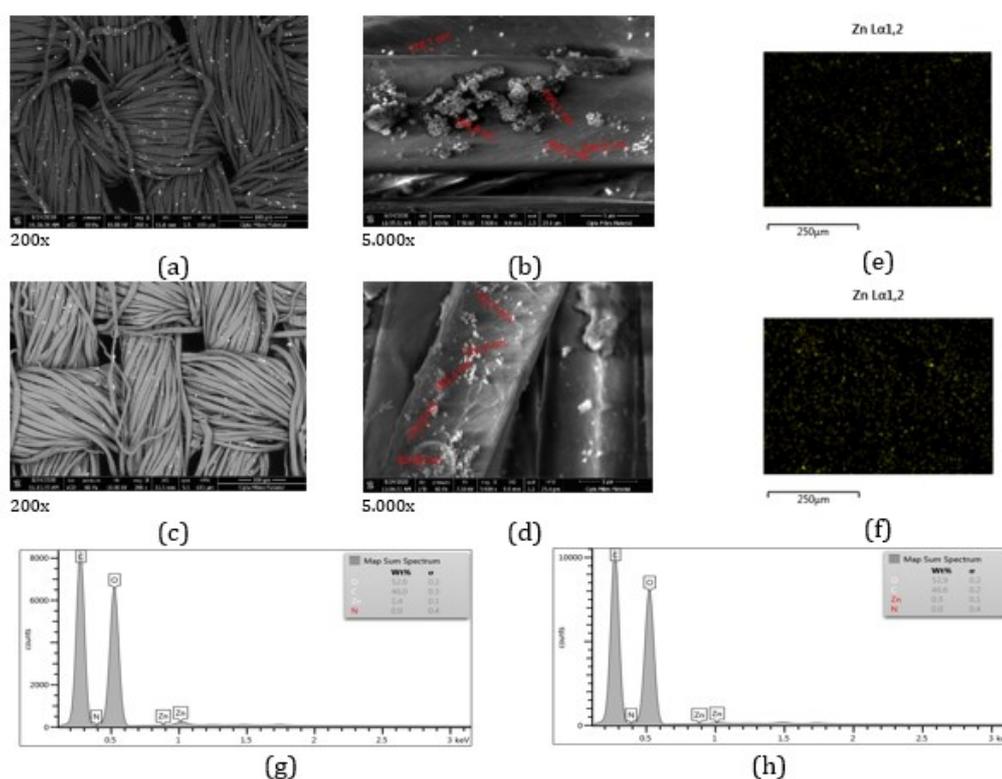


**Figure 5** UV-Vis spectra (a) and first-order kinetics (b) of cotton-indigo with and without the ZnONP coating (photofading test under UV-A irradiation 20 W)

Our results indicated that the ZnONPs provide UV protection to cotton and prevent color reduction. The role of ZnONP as a photocatalyst is minimal. The possible reason is that the lack of water in cotton surface prevents the formation of OH radicals, therefore, preventing the breaking of the various C-N and C-C bonds of chromophore groups. The low surface area of the synthesized ZnONPs may also impede photocatalytic reactions, which occur on the material's surface (Adiwibowo et al., 2018). This result is in accordance with the findings of Sani et al. (2019), who applied a ZnO/TiO<sub>2</sub> NP composite as a UV protection agent to cotton dyed with indigo.

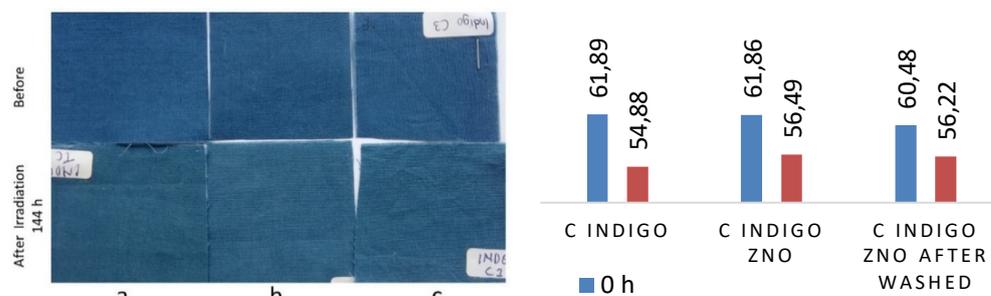
### 3.3. Durability of ZnONPs on cotton dyed with natural indigo

The durability of the ZnONP coating on cotton was investigated by washing the samples according to ISO 105-C06: 2010. SEM images of cotton–indigo–ZnO before and after two laundering cycles (equal to 10 hand washes) are shown in Figure 6a–d. The presence of ZnO could be clearly distinguished on the cotton surface even after washing. Individual ZnONPs were well dispersed on the cotton surface, but ZnONP aggregates attached to the fabric could also be observed. SEM images of washed cotton (Figure 6c–d) show that the aggregates are removed from the cotton surface. EDX analysis (Figure 6e–h) showed that cotton–indigo–ZnO contains C, O, and Zn. C and O could be attributed to cellulose, while Zn could be attributed to ZnO. Mapping calculations indicated a Zn concentration of 1.4% in cotton–indigo–ZnONP; after washing, ZnO remained in the cotton fabric but at a lower concentration of 0.5%. The reduction in Zn content following washing is likely caused by the loss of large aggregates of ZnO into the wash. The bond strength of aggregated ZnONPs to the cotton substrate is insufficient to prevent the NPs from falling off during washing. In this case, smaller NPs may provide better adhesion to the pores of the fabric.



**Figure 6** SEM mapping of cotton–indigo–ZnO (a, b, c) before and (d, e, f) after two cycles of washing—EDX spectra of the elements of cotton–indigo–ZnO (g) before and after (h) 2 cycles of washing (washing cycle according to ISO 105-C06: 2010)

Figure 7 illustrates the  $dE$  and the color of cotton fabric dyed with natural indigo before and after 144 h of UV-A lamp irradiation. The color of cotton–indigo–ZnO slightly decreased from 61.86 to 60.48 after washing. Mechanical action and temperature increases during washing could promote dye loss. Figure 7a shows that cotton-indigo without ZnONPs has some burnt color (more yellow and green), which is in accordance with the  $a^*$  and  $b^*$  values in Table 1. After UV-A irradiation for 144 h, the colors of cotton–indigo, cotton–indigo–ZnONP, and washed cotton–indigo–ZnO decreased by up to 7.01, 5.37, and 4.27, respectively.



**Figure 7** Color difference of indigo-dyed cotton (a), coated with ZnONPs (b), coated with ZnONPs after two cycles of washing ISO 105-C06: 2010 (c), before and after 144 h of UV-A irradiation

The obtained data indicate that the ZnONPs are able to reduce photofading. The ZnONPs showed good performance as an anti-UV agent and may help protect the color of textiles from fading. The ZnONPs remaining on the fabric after washing was still able to reduce photofading, but further research to enhance the durability of the ZnONP coating on the cotton fabric is necessary.

#### 4. Conclusions

In summary, ZnONPs with a crystallite size of 23.33 nm were successfully synthesized via a simple precipitation method. Incorporation of the obtained ZnONPs into cotton dyed with natural indigo decreased the sample's average transmittance of UV light up to 9.3%, which means the NPS confer excellent UV protection to the fabric. The photofading of natural indigo-dyed cotton with and without ZnONPs showed first-order kinetics with a rate constant of  $6.35 \times 10^{-4} \text{ h}^{-1}$  and  $8.84 \times 10^{-4} \text{ h}^{-1}$ . The lower fading rate indicates significant improvements in color protection after coating with the ZnONPs. The facile production of ZnONPs indicates their potential applicability to the textile industry, including in small-scale industries. However, research on methods to enhance the durability of ZnONP coatings on cotton fabric remains necessary.

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