Modification of cotton fabric by ZnO nanoparticles for producing an antibacterial natural dyed batik

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Abstract. Batik is a traditional Indonesian cloth that has been recognized by UNESCO as the Intangible Cultural Heritage of Humanity on October 2, 2009. Nowadays batik with natural dyes is preferred because it is unique, natural and environmentally friendly. The disadvantage of natural dyed batik, especially those using cotton cloth, is easily overgrown with bacteria. This paper presents the results of research on the application of ZnO nanoparticles on cotton fabrics that produce batik with antibacterial activity. The application of ZnO nanoparticles was carried out with variations on concentration (1% and 2%), temperature (25°C and 80°C), and application stages, i.e before and after the batik process. Colouring process was conducted by natural dyes of Tungi (Ceriops tagal). To see the effect of ZnO application, the antibacterial activity, the colour fastness to washing, the colour strength (K/S) of natural dye batik have been examined. The results showed that the ZnO application before and after the batik process can provide antibacterial activity and enhance colour strength on natural dye batik. To maintain the colour fastness to washing, the ZnO application can be carried out before the batik process at temperature 80°C or after the batik process at 25°C.

1. Introduction

Batik is a traditional Indonesian cloth that have been recognized by UNESCO as the Intangible Cultural Heritage of Humanity on October 2, 2009. According to SNI 0239: 2014 the term batik is a handicraft produced by resist dyeing technique using a hot wax that attached onto media (textile or non textile) using a canting (stamp or written) to create desire pattern[1]. The batik processes are attaching a hot wax onto fabric using a canting to create pattern, then the dyeing process is carried out. Furthermore, the wax is removed by boiling the fabric in water. The batik fabric is then washed thoroughly and dried in the shade place [2]. Batik has become a part of life of the Indonesian people since ancient times. People use batik from the birth to the death ceremony. The Indonesian government, both central and regional, has tried to protect batik, one of which is by issuing regulations on the obligation to use batik for employees and school students on certain days. Batik protection efforts can also be conducted by various research and development technologies to improve the quality of batik.

In recent years, nanotechnology has been used in various fields including health, food, electronics, waste treatment, chemical sensors, pharmaceuticals and textiles. The development of nanotechnology in the field of textiles produces new innovations related to the function of multifunctional textiles [3]. Including functional properties are protection against microorganisms or
as antibacterial [4]. Natural dyed batik is currently preferred by consumers because it looks more ethnic, safe to use and environmentally friendly. The disadvantage of natural dyed batik, especially those using cotton cloth, is easily overgrown with bacteria. Staphylococcus aureus bacteria on cotton cloth fibres cause odour, damage to fabric fibres, changes in colour and reduced mechanical properties of textiles[3]. The development of nanotechnology provides solutions to various problems above with the discovery of nano metal oxides that can improve the performance of textile products, including ZnO, TiO$_2$, SiO$_2$ and MgO. Zinc oxide (ZnO) nanoparticles are favoured because of their unique properties such as photocatalytic, electrical, optical, and antibacterial [5]. The antibacterial properties of ZnO are excellent because they are heat-resistant and stable in a variety of operating conditions [6]. The antibacterial activity of ZnO nanoparticles is due to their ability to induce oxidative stress. Zinc oxide nanoparticles released Zn$^+$ ions which interact with the thiol group of respiratory enzymes of bacteria and inhibiting their action. Thus, when bacterial cells contact with ZnO nanoparticles, they absorb Zn$^+$, which inhibits the action of respiratory enzymes, generates Reactive Oxygen Species (ROS), and produces free radicals, causing oxidative stress. ROS irreversibly damage bacterial membranes, mitochondria and DNA, causing in the death of bacterial cells [7].

The application of ZnO nanoparticles onto fabrics is not only providing antibacterial properties, but also improving fabric colour fastness [8]. Many studies on the application of nano metal oxides to provide antibacterial properties on fabrics has been conducted, but none has applied it to batik, especially natural dyed batik. Therefore this research was conducted to apply ZnO nanoparticles to natural dyed batik which is expected to improve the quality of colouring and also provide antibacterial activity on batik.

2. Materials and methods

2.1. Materials and equipments
Cotton fabric, batik wax, natural dye of Tingi (Ceriops tagal), aluminium sulphate (Al(SO$_4$)$_2$·12H$_2$O), non-ionic detergents (TRO), soda ash (NaCO$_3$), ZnO nanoparticles powder (Sigma Aldrich, average particle size of 67 nm) were the materials used for the experimentation. Magnetic stirrer (SCILOGEX MS7-H550-Pro), oven (Memmert), analytical balance (Fujitsu), and standard laboratory glassware were used in this research. The experiments were conducted at the laboratory of Centre for Handicraft and Batik Yogyakarta.

2.2. Methods

2.2.1. Extraction of Tingi (Ceriops tagal)
Natural dye of Tingi tree bark was used for colouring the batik. The extraction was conducted by heating 1 kg Tingi with 5 litre of water at 100$^\circ$C for 1 hour. The extract was cooled at room temperature and filtered to remove the insoluble residues. The resulting filtrate was then used as dye solutions for the subsequent dyeing experiments.

2.2.2. Application of ZnO nanoparticles onto fabric
The application of ZnO nanoparticles is carried out with the pad-dry-cure method. The research variables are concentration (1% and 2%), temperature (25$^\circ$C and 80$^\circ$C) and ZnO application stages (before and after the batik process). First of all, cotton fabric was immersed in a non-ionic detergent/TRO solution (0.1%). When ZnO was applied before the batik process, white cotton fabric (330 mm x 350 mm) was dipped in ZnO solution (1% and 2%) with a temperature variation of 25$^\circ$C and 80$^\circ$C. Then it was padding at room temperature to reduce moisture content. Afterward it was dried at 80$^\circ$C for 5 minutes. The dipping-paddling-drying process was repeated 3 times. Then the cotton fabric was cured at 140$^\circ$C for 3 minutes. Afterward, the cotton fabric was processed (batik process). When ZnO was applied after the batik process, the batik process was conducted first, i.e applying the wax
onto cotton fabric, dyeing and then removing the wax and then the ZnO was applied onto the fabric in the same way.

2.2.3. Applying the wax onto fabric
This is the main process of batik. The wax was melted and then applied on the cotton fabric with batik stamp to create desire pattern.

2.2.4. Dyeing
When ZnO was applied before the batik process, the cotton fabric was treated with ZnO first, then the wax was applied onto fabric with batik stamp to form motifs. Dyeing was carried out by immersing the fabric in the natural dyes of Tingi solution for 5 minutes then it was dried in the shading place. The dyeing process was repeated at least 5 times, then the fabric was immersed in the aluminium sulphate solution. Afterward the fabric was rinsed thoroughly in tap water and dried.

2.2.5. Removing the wax
The Fabric was immersed in the boiling water until the wax was removed. Soda ash (2 g/L) was added in the water to help removing the wax. Sample with application of ZnO after the batik process, ZnO was applied onto fabrics after the wax was removed.

2.3. Characterizations

2.3.1. Antibacterial Activity
Antibacterial assessment of the ZnO coated batik fabric against Gram-positive bacteria *Staphylococcus aureus* and Gram-negative bacteria *Eschericia coli* was carried out with agar diffusion method. The bacteria were grown in nutrient broth medium. Test organisms diluted x100 from a 3 hour culture, were swabbed on the surface of Isosensitest agar plates. The batik fabric of 15 mm diameter were then slightly pressed on to the surface of one plate and the control fabric was onto another plate. The incubation of the plates were carried out at 37°C for 18 – 24 hours. The antibacterial activity of fabrics was demonstrated by the diameter of the zone of inhibition (mm) compared to the control fabric [9].

2.3.2. Colour strength (K/S value)
Color strength of the batik were evaluated using a UV-vis Spectrometer. The reflectance of the samples were measured, the K/S value were calculated that indicate the color intensity of dyed samples using equation 1[10].

$$K/S = \frac{(1 - R)^2}{2R}$$

K: absorption coefficient, S: scattering coefficient, and R: reflectance at complete capacity

2.3.3. Colour fastness to washing
Washing fastness was carried out in accordance with ISO 105-C10:2006 standard. The change in color and stains of the adjacent fabrics were assessed with grey scale.
3. Results and Discussion

Antibacterial activity assessment of ZnO treated fabric was carried out with agar diffusion method. The agar diffusion method (Kirby-Bauer) is a easily executed semi-quantitative test to determine antibacterial activity of diffusible antimicrobial agents on treated textile material. The results of antibacterial activity assessment are shown in table 1. The application of ZnO onto white fabric without batik process gives a high inhibition zone, even for the inhibition of *S. Aureus* showing a higher value than the antibacterial drug Chloramphenicol. When the fabrics was treated with ZnO first and then being applied with wax (batik process), the value of inhibition zone against both bacteria are smaller, this shows that the batik processes reduce the ZnO content in the fabric. When the ZnO was applied on to the fabric before the batik process, the highest inhibition zone of 17.77 mm against *E. coli* was shown by the C2T80 sample, which is a fabric treated with ZnO before the batik process with a concentration of ZnO 2% at 80°C. Then the large inhibition value was also shown by the C1T80 sample, which is the sample treated with ZnO before the batik process with a concentration of ZnO 1% at 80°C.

| Samples | Zone of inhibition (mm) |
|---------|------------------------|
|         | *E. coli* | *S. aureus* |
| Application of ZnO onto white fabric (without batik process): |
| C1T80w | 20.47 | 26.85 |
| C2T80w | 21.38 | 25.32 |
| C1Tkw | 19.15 | 23.73 |
| C2Tkw | 20.53 | 25.18 |
| Application of ZnO before batik process: |
| C1T80b | 17.67 | 16.25 |
| C2T80b | 17.77 | 16.2 |
| C1Tkb | 16 | 16.07 |
| C2Tkb | 16 | 16.03 |
| Application of ZnO after batik process: |
| C1T80a | 16 | 18.21 |
| C2T80a | 16 | 18.41 |
| C1Tk | 18.31 | 18.2 |
| C2Tk | 18.03 | 18.2 |
| Natural dye batik without ZnO | 0 | 0 |
| Chloramphenicol (antibacterial drug) | 32.6 | 23.4 |

C1 : ZnO concentration 1%
C2 : ZnO concentration 2%
Tk : temperature of ZnO application at 25°C
T80 : temperature of ZnO application at 80°C
a : application of ZnO after batik process
b : application of ZnO before batik process
w : application of ZnO onto white fabric
In general, it can be seen that the ZnO application before the batik process gives good results when done at 80°C, while the concentration difference does not have a significant effect. When the ZnO was applied after the batik process, the application at room temperature can provide a high inhibitory value for both bacteria, showed by C1Tk and C2Tk samples. This is due to the batik processes, especially dying and wax removal process, so that if ZnO was applied before the batik process, it must be carried out in conditions that can absorb more ZnO to anticipate ZnO loss during the wax removal process, i.e at a higher temperature (80°C). At higher temperatures (80°C), the pores of the fabric are opened so that more ZnO is absorbed in the fabric. Whereas if ZnO was applied after the batik process, there is no process afterwards so that the existence of ZnO is fixed. The control, natural dye batik samples without ZnO application, showed no inhibition zone (value 0). The overall sample showed that the application of ZnO before and after the batik process could provide antibacterial activity on batik fabric. Figure 1 and 2 show the antibacterial activity of treated white fabric and natural dyes batik fabric.

![Figure 1](image1.png)

**Figure 1.** Antibacterial activity of white fabrics treated with ZnO 1% at 80°C to *E. coli* (a) and *S. aureus* (b)

![Figure 2](image2.png)

**Figure 2.** Antibacterial activity of natural dyes batik treated with ZnO 2% at 25°C to *E. coli* (a) and *S. aureus* (b)

The assessment of color strength and washing fastness of ZnO treated batik fabrics are shown in table 2. The higher K/S value indicates a stronger/thicker color. In all ZnO-treated batik fabrics give a K/S value that is greater than the sample without ZnO application. The higher K/S values of ZnO-treated samples indicate that the presence of ZnO nano particles increases the dye affinity towards the
fabric. The ZnO nanoparticles in the fabric thus act as mordant [11]. The difference in temperature and concentration of ZnO applications did not significantly affect colour differences, as seen in figure 4 and 5. Fabrics treated with ZnO before and after the batik process at a concentration of 2% temperature 80°C, in appearance has the same colour as the sample applied by ZnO at a concentration of 1% temperature 25°C. When the ZnO was applied onto fabric before the batik process, it gave a smaller colour fastness to washing values than fabric without ZnO, except for the C2T80 sample that has the same value of 3-4. While the ZnO application after the batik process gave the same value to the fabric without ZnO if the application was carried out at room temperature. So that to maintain the value of colour fastness to washing, the ZnO application can be done before the batik process at temperature 80°C or after the batik process at temperature 25°C.

Table 2. Colour strength and colour fastness to washing of treated fabric dyed with natural colour of Tingi (Ceriops tagal)

| Samples                  | Colour Strength | Colour Fastness to washing |
|--------------------------|-----------------|-----------------------------|
|                          | %R             | K/S                         |
| Application of ZnO before batik process: |                 |                             |
| C1T80 b                  | 1.93           | 24.92                       | 3                           |
| C2T80 b                  | 2.89           | 16.32                       | 3-4                         |
| C1Tk b                   | 3.11           | 15.09                       | 3                           |
| C2Tk b                   | 2.72           | 17.40                       | 3                           |
| Application of ZnO after batik process: |                 |                             |
| C1T80 a                  | 2.50           | 19.01                       | 3-4                         |
| C2T80 a                  | 2.04           | 23.50                       | 3                           |
| C1Tk a                   | 3.47           | 13.43                       | 3-4                         |
| C2Tk a                   | 2.77           | 17.06                       | 3-4                         |
| Natural dye batik without ZnO | 19.67           | 1.64                        | 3-4                         |
| White fabric             | 102.11         | 0.0002                      |                             |

C1 : ZnO concentration 1%
C2 : ZnO concentration 2%
Tk : temperature of ZnO application at 25°C
T80 : temperature of ZnO application at 80°C
a : application of ZnO after batik process
b : application of ZnO before batik process

Figure 3. Natural dyed batik without ZnO
Figure 4. ZnO treated-natural dyed batik with application of ZnO before the batik process, (a) ZnO concentration 1% at 80°C, (b) ZnO concentration 2% at 80°C, (c) ZnO concentration 1% at 25°C, (d) ZnO concentration 2% at 25°C

Figure 5. ZnO treated-natural dyed batik with application of ZnO after the batik process, (a) ZnO concentration 1% at 80°C, (b) ZnO concentration 2% at 80°C, (c) ZnO concentration 1% at 25°C, (d) ZnO concentration 2% at 25°C
4. Conclusion
The ZnO application at concentration of 1% and 2% can provide antibacterial activity and enhance the colour strength on natural dyed batik. To give better antibacterial activity and colouring, if the application of ZnO is carried out before the batik process, it must be carried out in conditions that can absorb more ZnO to anticipate ZnO loss during the wax removal process, i.e. at a higher temperature (80°C). If the application of ZnO is carried out after the batik process, it can be done at temperature 25°C.

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