Application of ZnO nanoparticles for Producing Antibacterial Batik

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Abstract. The government of Indonesia has launched a program of ‘Making Indonesia 4.0’ since April 4th 2018. The program is an integrated roadmap to implement a number of strategic action to enter the 4.0 Industrial era. One of the strategic initiatives is the development of functional clothing by producing a cloth that has multifunctional properties, such as antibacterial clothing. Batik, a traditional cloth is originally from Indonesia. It is fabricated by applying hot wax onto a fabric to create a pattern before colouring process which is then removed in the final stage. Since people use batik in daily life for clothing and household appliances, it is worth to produce antibacterial batik. This research aimed to make antibacterial batik by applying zinc oxide (ZnO) nanoparticles to the material of batik i.e. cotton. Colouring process was conducted by synthetic dyes of indigosol. To see the effect of ZnO application, the antibacterial activity, the colour fastness to washing, the colour strength (K/S) and surface morphology of batik have been examined. The results showed that the batik exhibited antibacterial activity due to the incorporation of ZnO onto the fabric. The colour strength was also enhanced. To maintain the colour fastness to washing, the ZnO should be applied to the fabric before the batik process.

1. Introduction

Industry 4.0 refers to a new phase in the Industrial Revolution that emphasizes on interconnectivity, automation, machine learning, and real-time data. Indonesia has launched a program of ‘Making Indonesia 4.0’ since April 4th 2018. The program is an integrated roadmap to implement a number of strategic action to enter the 4.0 Industrial era. Five industrial sectors that have been selected for Making Indonesia 4.0 are: Food and beverages, textile and apparel, automotive, electronics and chemicals. In the textile and apparel sectors, Indonesia is targeted to become a leader of functional clothing producer in 2030. Functional clothing exhibits multi-functional properties, including hydrophobicity, enhanced thermal stability, antibacterial, UV-protection, anti-wetting and laundering performance [1].

In recent years, nanotechnology has become one of the most important and exciting fields in chemistry, physics, biology and engineering [1]. Nanotechnology deals with particles at the atomic level (1–100 nm). Structures on this scale have been shown to have unique and novel functional properties. Nano materials in various forms such as metal nanoparticles, nano composites and metal oxides have been used for functional finishing of textiles, such as UV protection, conductive, water repellent, antibacterial, and deodorizing functionalization of textiles [2]. They can be applied onto textile surfaces by different means like in situ synthesis, spraying and pad-dry-cure method. One of the most studied
nanoparticles is zinc oxide (ZnO). Zinc oxide (ZnO) nanoparticles are preferred because of their unique properties such as electrical, photo catalytic, optical, and antibacterial [3]. The antibacterial properties of ZnO are excellent because they are heat-resistant and stable in a harsh conditions [4]. ZnO exhibits significant antimicrobial activities when particle size is reduced to the nano meter range. The nano-sized ZnO can interact with bacterial surface where it enters inside the cell, and subsequently exhibits distinct bactericidal mechanisms [5]. Different methods have been adopted for investigation of antibacterial activity. The agar diffusion method is the most frequently used method and has been standardized as an official method for detecting bacteriostatic activity by the American Association of Textile Chemists and Colourists (ATCC).

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 as a result of resist dyeing technique using a hot wax that attached onto media (textile or non-textile) using the batik stamp (called a canting) [6]. The fabrics commonly used for batik are silk and cotton. Cotton fabric has several advantages including high absorption, smooth and comfortable to wear [7]. However, they certainly lack easy-care, dimensional stability, antibacterial, UV-blocking and self-cleaning properties [8]. Application of ZnO nanoparticles on cotton fabrics is expected to improve batik performance, especially providing antibacterial properties. The process of batik fabrication is carried out by attaching a hot wax onto fabric, which acts as a color barrier using a batik canting. Then the dyeing process may be carried out by natural dyes or synthetic dyes. Furthermore, the wax is removed by boiling the cloth in water. The batik cloth is then washed thoroughly and dried in the shade place [9].

The application of zinc oxide onto the fabric is not only able to provide antibacterial properties but also improve its coloring quality. These have been investigated by a number of researchers [8] [10]. Cotton fabrics that have previously been carboxymethylated and then applied using zinc oxide and titanium isopropoxide have good antimicrobial properties and color fastness [8]. Tavanaie (2017) applies ZnO-TiO2-PET (Polyethylene Tereptalat) to the fabric and has excellent color absorption and color fastness [10]. To the best of author knowledge, there has been no research yet about application of ZnO nanoparticles for producing antibacterial batik, therefore this research was conducted to apply ZnO nanoparticles for producing antibacterial batik with good coloring quality.

2. Experimental

2.1. Materials and Equipments

Batik wax, cotton fabric, synthetic dye of Indigosol, aluminium sulphate (Al(SO₄)₂·12H₂O), non-ionic detergents (TRO), soda ash (Na₂CO₃), natrium nitrit (NaNO₂), and HCl were purchased from Prawoto Shop, Yogyakarta. ZnO nanoparticles powder (average particle size of 67 nm) was obtained from Sigma Aldrich. Analytical balance (Fujitsu), oven (Memmert), magnetic stirrer (SCILOGEX MS7-H550-Pro) and standard laboratory glassware were used for the experimentation. The experiments were carried out at the laboratory of Centre for Craft and Batik Yogyakarta.

2.2. Methods

2.2.1. Making the batik. The batik processes includes an application of the batik wax onto fabric, dyeing process and removal of the wax. Initially, the white cotton fabric was immersed in a non-ionic detergent (TRO) solution (0.1%) in order to clean it up. To apply the batik wax onto fabric, the melted wax was applied onto the fabric by batik stamp to create desired pattern. The dyeing process was carried out by the following procedures: the indigosol dye solution was prepared by dissolving 5 g/l of dyes with 10 g/l of NaNO₂. Dyeing of the fabric was conducted by immersing the fabric in the indigosol solution for 5 minutes and then it was dried under sun light for 10 minutes. The dyeing process was repeated twice. Then the fabric was immersed in the acid solution (15 cm³/l of HCl) and it was neutralized with soda ash solution (1 gr/l of Na₂CO₃). At last the fabric was rinsed thoroughly in tap water and exposed to the
sun to get dried. To remove the wax, fabrics was immersed in the boiling water until the wax was removed. Soda ash (2 gr/l) was added in the water to help removing the wax.

2.2.2. *Application of ZnO nanoparticles onto fabric*. ZnO nanoparticles was applied onto the fabric by the pad-dry-cure method. To investigate the effect of ZnO concentration, temperature and order of the ZnO application, the research was carried out at a concentration of ZnO of 1% and 2%, temperature of 25°C and 80°C and the coating of ZnO conducted before and after the batik process. Initially, the fabric was immersed in a non-ionic detergent (TRO) solution (0.1%) in order to clean it up. Thereafter ZnO was applied to the fabric using the pad-dry-cure method. When it was applied before the batik process, white cotton fabric (330 mm x 350 mm) was dipped into ZnO solution (1% and 2%) at the temperature variation of 25°C and 80°C. The cotton fabric was then padded at room temperature to reduce moisture content. Afterward the fabric was dried at 80°C for 5 minutes. The dipping-padding-drying processes were repeated 3 times. Then the fabric was cured at 140°C for 3 minutes. The batik process was then subsequently carried out. When ZnO was applied after the batik process, the batik process was carried out first and then followed by the application of ZnO using the same procedures.

2.3. *Characterizations*

2.3.1. *Antibacterial Activity*. Antibacterial activity of the ZnO coated fabric was examined against Gram-positive bacteria Staphylococcus aureus and Gram-negative bacteria Eschericia coli using agar diffusion method. The bacteria were prepared in nutrient broth medium. Test organisms diluted x100 from a 3 hour culture, were wiped on the surface of Isosensitest agar plates. The batik 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 batik was indicated by the inhibition zone diameter (mm) compared to the control fabric [7].

2.3.2. *Colour Strength*. Color strength (K/S value). Color strength of the batik were evaluated using a UV-vis Spectrometer. The reflectance (R) of the samples were measured so the K/S value were calculated using equation 1. The K/S value indicates the color intensity of dyed samples [8].

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

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

2.3.3. *Color fastness to washing*. Washing fastness was carried out in accordance to ISO 105-C10:2006 standard. The change in color and stains of the adjacent batik were assessed by grey scale.

3. *Result and Discussion*

Antibacterial activity of white fabric and batik with ZnO treatment have been examined using the agar plate method. The results are shown in Figure 1 and 2. Figure 1 shows inhibition zone around the sample fabric of white fabric and batik with ZnO treatment against E.coli bacteria compared to antibacterial drug (Chloramphenicol) and batik without ZnO treatment. Figure 2 shows inhibition zone of the same sample against S. aureus bacteria. As can be seen in Figure 1, ZnO application affect the ability of the fabric to inhibit the growth of E. coli bacteria, since the value of inhibition area of fabric without ZnO is zero. The inhibition area of coated fabric is approximately 60% of inhibition zone of the antibacterial drug (Chloramphenicol). The treated white fabric exhibit slightly greater antibacterial effect than the treated batik. This indicates that the batik process reduce slightly the antibacterial activity against E. coli of the treated fabric. The order of ZnO treatment (before and after the batik process), the difference of ZnO concentration and temperature did not significantly affect the antibacterial activity against E. coli bacteria.
Figure 1. Antibacterial activity against E. coli of batik with ZnO treatment and the control, C1: ZnO concentration 1%, C2: ZnO concentration 2%, Tk: temperature of ZnO application at 25°C, T80: temperature of ZnO application at 80°C

The same trend of antibacterial activity is shown by the sample fabric against S. aureus as can be seen in Figure 2. The inhibition area of coated fabric against S. aureus bacteria is approximately 60% - 75% of inhibition zone of the antibacterial drug (Chloramphenicol), slightly greater than the inhibition zone against E. coli bacteria. This is in line with the study of some researchers which state that gram-negative E. coli bacteria are more resistant to the antibacterial activity of ZnO compared to gram-positive S. aureus bacteria [4][12][9]. In this case the effect of temperature, concentration of ZnO solution and the order of ZnO treatment are also insignificant. Even though the effect of the ZnO application order is insignificant, there was a slight decrease of antibacterial activity against both E. coli and S. aureus when ZnO was applied before the batik process. This is due to the batik process, mainly dyeing and wax removal process. The dyeing and wax removal process caused the ZnO separated from the fabric thus providing less antibacterial activity. The mechanism of antibacterial activity of ZnO nanoparticles was studied by
Mishra which states that ZnO nanoparticles can generate Reactive Oxygen Species (ROS) that damage bacterial membranes, DNA, and mitochondria, resulting in the death of bacterial cells [13].

The inhibition area due to the effect of ZnO application were photographed and shown in Figure 3 and 4. In Figure 3b, the white cotton cloth applied by ZnO shows the zone of inhibition around the fabric. Whereas the zone of inhibition not seen in Figure 3a, indicates no antibacterial activity on the untreated white fabric. This result corresponds with Rajendran’s study on producing antimicrobial cotton fabric using ZnO nanoparticles [11]. Figure 4b also shows the zone of inhibition of the batik fabric applied by ZnO whereas there is no inhibition area around the untreated batik fabric in Figure 4a. It can be seen that the zone of inhibition of treated batik is smaller than the zone of inhibition of white fabric applied by ZnO, indicates that the process of batik causes a decrease in antibacterial activity of the fabric, due to the reduction of ZnO during the batik process.

![Figure 3. The inhibition area of (a) untreated white fabrics and (b) white fabrics treated with 2% ZnO at temperature of 25°C](image)

The assessment of surface morphology by Scanning Electron Microscope (SEM) shows the presence of ZnO nanoparticles on the fabric. Figure 5 shows that the ZnO nanoparticles were imparted on the white fabric before being applied with wax (batik process). Figure 6 shows the presence of ZnO nanoparticles on the fabric after the batik process. It can be seen that ZnO in the fabric after the batik process is less than in the white fabric. This shows the ZnO loss during the batik process. But from the assessment of antibacterial activity previously discussed, although there is a reduction of ZnO during the batik process, the batik fabric still exhibit antibacterial activity. This indicates that ZnO nanoparticles is suitable for producing antibacterial batik, and the proof of Dimapilis’s study which states that the antibacterial properties of ZnO is excellent because they are heat-resistant and stable in a harsh conditions [4].

![Figure 4. The inhibition area of (a) untreated batik fabric and (b) batik fabric treated with 2% ZnO at temperature of 25°C](image)
The assessment of colour strength and washing fastness of ZnO-treated batik fabric is seen in Table 1. The colour strength is shown by the K/S value that indicates the colour intensity of the dyed fabric, calculated using equation 1. In all ZnO-treated batik fabrics gives a K/S value that are greater than the batik fabric without ZnO application. The higher K/S value indicates a high intensity of the colour. The higher K/S values of ZnO-treated batik fabric indicate that the presence of ZnO nanoparticles increases the dye affinity towards the fabric[12]. When ZnO was applied after the batik process, the K/S value is higher, but the colour fastness to washing value is lower than untreated batik fabric. Meanwhile, when ZnO was applied before the batik process, the value of colour fastness to washing is the same as untreated batik fabric and the K/S values are still higher than untreated batik fabric. So to increase the K/S value and to maintain colour fastness to washing, ZnO application should be carried out before the batik process.

| Samples                  | Colour Strength | Colour fastness to washing |
|--------------------------|-----------------|----------------------------|
| ZnO-treated batik fabric dyed with indigosol |                 |                            |
Application of ZnO before batik process:
C1T80ᵇ 1.10  4-5
C2T80ᵇ 1.03  4-5
C1Tkᵇ 1.05  4-5
C2Tkᵇ 0.86  4-5

Application of ZnO after batik process:
C1T80ᵃ 4.09  4
C2T80ᵃ 3.50  4
C1Tkᵃ 3.20  4
C2Tkᵃ 4.30  4

Synthetic dye batik without ZnO
White fabric 0  4-5

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

4. Conclusions
The ZnO application can provide antibacterial activity of synthetic dye batik against E. coli and S. aureus. The antibacterial activity of treated batik fabric against S. aureus is greater than that against E. coli. The order of ZnO treatment (before and after the batik process), the difference of ZnO concentration and temperature did not significantly affect the antibacterial activity of batik fabric against E. coli and S. aureus bacteria. However, there was a slight decrease of antibacterial activity against both E. coli and S. aureus when ZnO was applied before the batik process. This is due to the batik process, mainly dyeing and wax removal process that caused the ZnO separated from the fabric thus providing less antibacterial activity. The ZnO application also enhance color strength that indicate the presence of ZnO nanoparticles increases the dye affinity towards the fabrics. To maintain the value of color fastness to washing, the ZnO application should be carried out before the batik process.

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