ZnO Nanoparticles Synthesized by Green Chemistry Methods for improvement of Cotton Fabric Dyeing with Natural Dye

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Abstract: The study investigated the synthesis of ZnO nanoparticles by green chemistry methods using extracts from Dialium cochinchinense Pierre, Cleoma viscosa L., Morinda citrifolia, Moringa oleifera, Piper nigrum L. and Cassia fistula. The extracted extracts were converted into ZnO nanoparticles by heating at 400 °C for 1 hour. The SEM, XRD and FTIR analyses were performed to characterize the synthesized nanoparticles. The absorbance of UV-Vis of the synthesized ZnO nanoparticles was measured at 347 nm. The SEM images showed that the nanoparticles were spherical in shape. The K/S values of the cotton fabrics dyed with natural dyes were higher than those of the cotton fabrics dyed without nanoparticles. The antibacterial activity of the cotton fabrics dyed with nanoparticles was higher than those of the cotton fabrics dyed without nanoparticles.

Keywords: ZnO nanoparticles, green chemistry, cotton fabric, natural dye.
Abstract

The study aimed to investigate the modification on cotton fabric with the zinc oxide nanoparticles synthesized using green chemistry by the local plants extract such as Kheng (Dialium cochinchinense Pierre), Wild spider flower (Cleoma viscosa L.), Cheese fruit (Morinda citrifolia), Moringa (Moringa oleifera), Gam chum (Tamarindus indica L.), Lakoocha (Artocarpus lacucha), Piperaceae (Piper nigrum L.) and Golden shower (Cassia fistula). Zinc nitrate was transformed from zinc ion to Zn complex formation by using plants extract as template. ZnO nanoparticles were performed by the calcination of Zn complex at 400 °C for 1 h. Among the plant extract, Kheng leaf was the best source of extracts because it gave the highest amount of the as-synthesized zinc oxide nanoparticles than the others. The as-synthesized ZnO nanoparticles were characterized by UV-Visible spectroscopy, scanning electron microscopy (SEM), x ray diffraction diffractometry (XRD) and Fourier transform infrared spectroscopy (FTIR). The UV-Visible absorption spectrum shows a strong resonance centered on the surface of zinc oxide particles at 347 nm. SEM image illustrated that the resulting products were an aggregation of the ZnO spherical like shape of calcinated ZnO nanoparticles was matched well with ICDD no. 00-0361451 indicating that the products were ZnO crystallized in wurtzite structure. The average crystallite size of ZnO was estimated according to Scherrer’s equation is 26.05 nm. Fourier transform infrared spectroscopy (FTIR) shows that the bands corresponding to (Zn–O) appeared at 1025 and 415 cm⁻¹. The cotton fabric was modified with the ZnO nanoparticles prior to dyeing with coconut coir fiber dye which obtained brown color. Results of the dyeing showed that the color intensity (K/S), the color fastness of sunlight and color fastness to washing and antibacterial activity Staphylococcus aureus of the modified cotton fabric were higher than that of unmodified one.

Keywords: ZnO nanoparticles, green chemistry, cotton fabric, natural dye

1. Introduction

Using natural dyes in coloring cotton fabric have been presented a greater attention because they are more environmental friendly than synthetic dye (Mongkholrattanasit, 2014; Mitra & Das, 2015). However, natural dyes are less permanent and wash out easily. Therefore, in many research, cotton fabric samples were treated with finishing agents having different compositions such as chitosan, or
metal nanoparticles for natural dyes improvement (Chattopadhyay & Inamdar, 2013; Elela, 2016). In addition, surface coating of textiles with nano-sized particles of metal oxides can also help improve imparting self-cleaning property and UV protection (Press, 2011). Recently, biomaterials have been used in synthesis of ZnO-nano particles such as plant extracts and derivatives because they are biodegradable and bioabsorbable with degradation products that are non-toxic (Devi & Gayathri, 2014; Gunalan, Sivaraj, & Rajendran, 2013; Vimala, et al., 2014). The plants extracted were utilized as template for transformation of zinc ion from zinc nitrate to Zn complex formation with plants extract. After the complex formation, they were calcined at the high temperature as ZnO nanoparticles. Addition, ZnO-nano particles produced by plants are more stable, and the rate of synthesis is faster than that in the case of other organisms (Devi & Gayathri, 2014). The present investigation was carried out to green synthesis of zinc oxide nanoparticles by using the local plants. The synthesized samples were then characterized using UV–vis spectroscopy SEM, XRD and FT-IR. The efficiency and physical properties of dyeing of ZnO nanoparticles-treated cotton fabric with natural dye (coconut coir fiber) were evaluated. This method is eco-friendly, low cost, and can consequently be used as a valuable alternative for the large-scale of textile production.

2. Materials and Methods

2.1 Materials

Coconut coir fiber (Cocos nucifera L.), Kheng (Dialium cochinchinense Pierre), Wild spider flower (Cleoma viscosa L.), Cheese fruit (Morinda citrifolia), Moringa (Moringa oleifera), Gam chum (Tamarindus indica L.), Lakoocha (Artocarpus lacucha), Piperaceae (Piper nigrum L.), Golden shower (Cassia fistula) and cotton fabric were purchased from the local community in Sakon Nakhon, Thailand. Zinc nitrate hexahydrate was purchased from Sigma-Aldrich, Germany. Distilled water was used throughout the experiments.

2.2 Preparation of dye solution

The dye solution was prepared by chop coconut coir fiber into small pieces and put in a pot. Double the amount of water to plant material was added. The suspension was heated to boil and then simmer for about 1 h. The dye solution was filtered for further use.
2.3 Pretreatment of cotton fabric

A 100 g of cotton fabric sample was cleaned to remove the wax and impurities using a mixture of 7 g of soap flakes and 3 g of sodium carbonate in 2 L of water and heated at 100°C for 1 h. Repeated rinsing with distilled water was followed, after that the cotton fabric was dried in air.

2.4 Preparation of the leaf extract

The leaves from local plant were used in this study such as Kheng, Wild spider flower, Cheese fruit, Moringa, Gam chum, Lakoocha, Piperaceae, Golden shower. These leaves were washed dried fine cut leaves in beaker along with 100 mL of water. The mixture was then boiled for 1 h. until the color of the aqueous solution changes from watery to light yellow. The extract was cooled to room temperature and filtered using filter paper (Whatman No. 1). The extract was stored in a refrigerator used for further experiments.

2.5 Preparation of zinc nanoparticles

The 50 ml of leaf extracts was taken and boiled to 90°C using hot plate and magnetic stirrer. Add 10 g of zinc nitrate hexahydrate to the solution. This mixture is then boiled until it reduced to a deep yellow colored paste. Furthermore the solvent was evaporated to get the Zn-complexes followed by washing with methanol. Zn-complexes heated in an air furnace at 400°C for 3 h. The results from calcination are designated as ZnO particles. The samples were characterized by using UV-Visible (UV-1601, Shimadzu, Japan) and FTIR spectrophotometers (Shimadzu 8900, Japan) XRD diffractometer (XRD 6100 2kW, Shimadzu. Japan) and SEM(JSM 5800LV, JEOL, Japan).

2.6 Modification of ZnO nanoparticles on cotton fabric

Erlenmeyer flasks containing 100 mL of ZnO nanoparticle solution (in distilled water) were placed in ultrasonic bath for 20 min. Then the cotton fabric at material to liquor ratio (MLR) of 1:100, which had been pre-warmed in water bath for 15 min, was immersed in ZnO nanoparticle solution. The modified cotton fabric samples were heated in hot air oven at 100°C for 30 min and then increase the temperature to 160°C for 10 min. The modified ZnO nanoparticle cotton fabric was then washed with in distilled water and dried at room temperature.

2.7 Dyeing method

Erlenmeyer flasks containing 100 mL of the dye solution were placed in a water bath at controlled temperature of 30 °C. Then the cotton fabric modified at MLR of 1:100, which had been pre-warmed in the water bath for 15 min, was
immersed in the dye solution for 15 min. The dyed cotton fabricsample was washed in distilled water until the rinsed water was neutral, then dried at room temperature.

2.8 Measurements

Color measurement
The color strength, tones (a* and b*) and light/darkness (L*) were measured using CIELAB system (mini scan XE plus, hunter lab, USA).

The wash and the light fastness
The wash and the light fastness of cotton fabrics dyed were evaluated according to ISO 105- C06: 1994 and ISO 105- B02: 1994, respectively.

2.9 Antibacterial activity of Staphylococcus aureus

The antibacterial activity of the cotton fabrics dyed was determined using the agar diffusion method. The experimental technique was as follows: the cotton fabric dyed swatch of known diameter was put in the center of an agar plate. The plates were incubated at 37°C for 24 h. After incubation, a growth free “zone of inhibition” around the cotton fabric appeared as the antibacterial agent migrated from the cotton fabric onto the agar, and diffused outward. Diameters of the inhibition zones were determined according to AATCC Test Method 147.

3. Results

For the preparation of ZnO nanoparticles from leaf extracts, it was found that Kheng was the best extract because it gave the highest amount of the calcined ZnO nanoparticles than the others (Figure 1). The plant extract as active agent in some of these syntheses are believed to be polyphenols, it is found that the efficiency and size of nanoparticles are depend on the kind of plant extract (Is, Rizqi, & Annisa, 2016).
Figure 1. The amount of ZnO nanoparticles using different types of the plants studied.

**X Ray Diffractometer (XRD) analysis**

The nanoparticles were characterized by powder X-ray diffractometer. The XRD pattern shows a significant amount of line broadening which is a characteristic of nanoparticles. Figure 2 shows XRD pattern which exhibits prominent peaks at 31.72°, 34.38°, 36.16°, 47.52°, 56.52°, 62.78°, 67.94°, 68.04°, 72.62° and 76.74° that were matched well with ICDD no. 00-0361451 indicating that the product is the ZnO crystallized in wurtzite structure. The average crystallite size of ZnO was estimated according to Scherrer’s equation $d = \frac{0.9\lambda}{\beta \cos \theta}$, where $d$ is average crystallite size, $\beta$ is Line broadening in radians, $\theta$ is the diffraction angle and $\lambda$ is X-ray wavelength (Devi & Gayathri, 2014). The mean crystallite size of ZnO nanoparticle is 26.05nm.

Figure 2. XRD pattern of calcined ZnO nanoparticles.
The calcined nanoparticle was characterized by UV-Visible spectroscopy. The UV visible absorption spectrum illustrates that a strong resonance is centered on the surface of ZnO nanoparticles at 347 nm (Vimala, et al., 2014) (Figure 3).

![Figure 3. UV-visible absorption spectrum of ZnO nanoparticles.](image)

**Scanning Electron Microscope (SEM) analysis**
The SEM was done to determine the morphology of the products formed. Figure 4 shows the SEM image ZnO nanoparticles which has magnified 20,000 times. The product showed an aggregation of the ZnO spherical-like shape.

![Figure 4. SEM image of ZnO nanoparticles](image)

**Fourier transform infrared spectroscopy (FTIR)**
The FTIR spectrum of ZnO nanoparticles (Figure 5) was recorded using KBr pellet. The bands correspond to (Zn–O) appeared at 1025 and 415 cm\(^{-1}\) which indicated that the product was composed of high purity zinc nanoparticles (Bindu & Thomas, 2014, Gunalan, Sivaraj & Rajendran, 2013).
Figure 5. FTIR spectrum of zinc oxide nanoparticles.

Color analysis

The cotton fabric was modified with the as-synthesized ZnO nanoparticles prior to dyeing with coconut coir fiber dye giving a brown color. The color intensity (K/S) can assess the efficiency of dying. The K/S of the modified ZnO nano-cotton fabric was higher than that of the unmodified one. The results indicated that the sample modified with ZnO nanoparticles was higher in dying efficiency than the unmodified one. Considering the results of the L*a*b* color space, L* indicates lightness (+ = lighter, - = darker), a* is the red/green coordinate (+ = redder, - = greener) and b* is the yellow/blue coordinate(+ = yellower, - = bluer). The results found that the modified ZnO nano-cotton fabric was changed to darker and yellower tones than that of the samples unmodified (Table 1).

Table 1. The color coordinates for cotton fabric dyed with ZnO nanoparticles compared with the unmodified one.

<table>
<thead>
<tr>
<th>Cotton fabric dyed</th>
<th>(K/S)</th>
<th>color coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>L*</td>
</tr>
<tr>
<td>Unmodified</td>
<td>2.614</td>
<td>69.3</td>
</tr>
<tr>
<td>ZnO nano</td>
<td>3.021</td>
<td>61.8</td>
</tr>
</tbody>
</table>

Wash and light fastness analysis

The cotton fabrics were compared with grey scale to obtain the color change compared with cotton fabric before testing. Grey scale is ranged between 1 and 5 that scale 1 indicates the most color difference and scale 5 means no color difference. The results of wash-fastness (WF) and light fastness (LF) of the cotton
Fabric dyed are shown in Table 2. Both LF and WF of the modified cotton fabrics with ZnO nanoparticles showed higher scale than those of the unmodified cotton fabric.

Table 2. Comparison of light fastness (LF) and wash fastness (WF) for modified and unmodified cotton fabric dyed

<table>
<thead>
<tr>
<th>Cotton fabric dyed</th>
<th>LF</th>
<th>WF / repeated washes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Unmodified</td>
<td>3/4</td>
<td>3/4</td>
</tr>
<tr>
<td>ZnO nano</td>
<td>4</td>
<td>4/5</td>
</tr>
</tbody>
</table>

Antibacterial activity of *Staphylococcus aureus* analysis

The antibacterial activity for *Staphylococcus aureus* of the modified cotton fabric with ZnO nanoparticles can be observed by using inhibition zones. Table 3 shows the inhibition zone (1.67 mm) of the modified ZnO-cotton fabric dyed, while that of the unmodified cotton fabric does not present.

Table 3. Antibacterial activity of *Staphylococcus aureus* of modified cotton fabric dyed

<table>
<thead>
<tr>
<th>Cotton fabric dyed</th>
<th>Diameter of inhibition zone (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified</td>
<td>-</td>
</tr>
<tr>
<td>ZnO nano</td>
<td>1.67</td>
</tr>
</tbody>
</table>

4. Conclusion

The results of this study conclude that the Kheng extracted was the best utilized as template for transformation of zinc ion from zinc nitrate to complex formation of Zn with Kheng extract. After the complex formation, ZnO nanoparticles were performed by calcination of the complexes at the high temperature. These mean crystallite size of ZnO nanoparticle was 26.05 nm. The ZnO nanoparticles modified cotton fabric prior to dyeing with coconut coir fiber dye gave the derived materials readily available in the local area. This modified cotton fabric is proved to have better the color intensity, the color fastness of sunlight, the color fastness to washing and antibacterial activity of *Staphylococcus aureus*. In conclusion, ZnO nanoparticles synthesis utilizing green chemistry gave high purity of ZnO. The modified cotton fabric is proved
to improve the color intensity, the color fastness and antibacterial activity of *Staphylococcus aureus*. It is appropriate for cotton fabric dyeing and finishing.

6. References


