Continuous Dyeing of Cellulose Electrospun Nanofibrous Mat with Synthetic Indigo Dyes

Awais Khatri (awais.khatri@faculty.muet.edu.pk)
Mehran University of Engineering and Technology

Shamshad Ali
Mehran University of Engineering and Technology

Alishba Javeed
Mehran University of Engineering and Technology

Research Article

Keywords: Cellulose, electrospun nanofibrous mats, synthetic indigo dyes, aniline-free, continuous method

Posted Date: November 28th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-2296541/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License.
Read Full License
Abstract

In our study, cellulose electrospun nanofibrous mats (ENMs) were dyed with synthetic indigo dyes by continuous method. We have used the industrial scale dyeing procedure (pre-wetting, dyeing and washing-off steps). The effect of pH, concentration of sodium hydrosulphite, dye bath temperature and concentration of indigo dyes on the color yield (K/S) were optimized. Excellent K/S of dyed cellulose ENMs were achieved (reached to 13) with good colorfastness properties. For comparison, aniline-free synthetic indigo dyes were applied on the cellulose ENMs. The dyeing effluent was measured for pH, TDS and COD results. Considerable ecological merits have been found for dyeing effluent of aniline-free synthetic indigo dyes in comparison to the synthetic indigo dyes. Furthermore, the dyed samples were characterized by SEM analysis, ATR-FTIR spectroscopy.

Introduction

Nanofibers are getting attention for prominent apparel applications (Khatri et al., 2014, Khatri et al., 2013c, Khatri et al., 2013b, Khatri et al., 2013a, Mehdi et al., 2018) due to their better breathability, thermal insulation, antibacterial, antimould properties (Kim et al., 2011) as compared to conventional textiles due to the small pore size in between the fibers and high porosity (Greiner and Wendorff, 2007). They also exhibits excellent durability, without loss of mechanical properties when subjected to laundering. Therefore, electrospun nanofibrous mats (ENMs) have been produced on a mass scale successfully (Ali et al., 2019). The coloration of polymeric nanofibers is continuously evolving as novel colorant, processes and techniques are introduced from time to time. The motivating factor is to get higher dye fixation with minimal effluent pollution discharge at economical price. During the recent years, various technologies for the coloration of polymeric nanofibers have been developed (Khatri et al., 2019). Particularly dyeing of cellulose nanofibers with reactive dyes has been reported by dual-pad (Khatri et al., 2013a), cold-pad-batch (Khatri et al., 2014) and ultrasonic-assisted (Khatri et al., 2016) methods. Batchwise dyeing of cellulose nanofibers with vat dyes is also reported (Khatri et al., 2017).

Aspland (1992) reported that vat dyes possess affinity towards cellulose. Indigo dye is one of the well know carbonyl class of dyes having coplanar and multi-ring sing system. These rings contribute in strengthening the Van-der-Waals forces between dye and the substrate (Shore, 2002). This is the main reason why indigo dye offers better colorfastness than the reactive dyes (Khatri et al., 2017). Indigo, a vat dye, is practically insoluble in water, alcohol, ether and dilute acids. In order to apply indigo to a textile, therefore, it has been necessary to reduce the dye to its soluble leuco form using a suitable reducing agent with an alkaline material, e.g. sodium hydroxide. After a given textile has been impregnated with the reduced dye, the textile has been exposed to air or oxygen in order to oxidize the dye back to its insoluble color. This is one of the oldest known coloring agent that has been used to dye cellulosic textiles, such as cotton, for centuries. The dark blue dye is still employed extensively today for dyeing cotton yarn in the manufacture of denims and ‘blue jeans’ (Fono and Patton, 1979). The chemical structures of indigo dye and its leuco form (C_{16}H_{10}N_{2}O_{2}) are shown in Fig. 1.
In our work, for the first time, we analyze the comparison of dyeability of cellulose electrospun nanofibrous mat with CN synthetic indigo dye and aniline free synthetic indigo dye in order to produce colored nanofibrous mat for apparel applications. The major toxicity issue with synthetic indigo dye is the presence of aniline compound which is highly carcinogenic and also toxic to aquatic life. Therefore Archroma Pakistan Ltd. developed an alternative system that is aniline free indigo dye. Cellulose nanofibers were electrospun from polymer solution and resultant mat were dyed with both type of synthetic indigo dye using continuous dyeing method. The dyed nanofibrous mat were evaluated for color yield (K/S), colorimetric values, colorfastness, tensile properties and scanning electron microscopy (SEM) analysis.

**Experimental**

**Materials**

Cellulose acetate (39.8% acetyl content having average \( M_w = 30 \text{ kDa} \)) was obtained from Aldrich Chemical Company Japan. Commercial synthetic indigo dye (liq.) and aniline-free synthetic indigo dye (as claimed by the manufacturer) was acquired from Archroma Pakistan Ltd. and other auxiliaries include sodium hydroxide (NaOH), sodium hydrosulphite (\( \text{Na}_2\text{S}_2\text{O}_4 \)), Leonil and Mercerol was provided by Textile Wet Processing Lab of Mehran University Jamshoro. For all the experiments deionized water was used.

**Preparation of cellulose nanofibers**

For the preparation of CEL nanofiber, the precursor cellulose acetate was used for electrospinning in order to obtain CEL ENM’s. Polymer solution of 17% was prepared in 2:1 of acetone/dimethyl formamide solvent, supplied through a two plastic syringes of 5ml with the applied voltage of 15kV. Electrospun nanofibers were collected on a rotatory drum which rotates at 1 rpm. The polymer solution of 17% was prepared by dissolving the precursor cellulose acetate in acetone/dimethyl formamide (2:1). To obtain cellulose ENM’s, polymer solution was supplied through a two plastic syringes of 5ml with the applied voltage of 15kV and the distance from needle tip to the rotatory collector was fixed at 15 cm. CA solutions were delivered via a syringe pump to control the mass flow rate which was fixed at 1.040 mL/h. Follow-on the resultant cellulose nanofibers were collected on to the rotatory collector which rotates at 1 rpm and dried at room temperature for 48 h after then deacetylation process was carried out until the pH was reached to neutral.

**Dyeing of nanofibers**

The coloration of CEL ENM using CN and aniline free synthetic indigo dye was studied for the very first time therefore the dyeing parameters optimization is a key step of this research. CEL ENM’s were dyed with commercial synthetic indigo (Liq.) at given dyeing parameters. Initially the effect of pH on color yield was studied at (10.5, 11, 11.5, 12, and 12.5), effect of sodium hydrosulphite concentration at (3, 4, 5, 6, 7 g/L) and effect of dye bath temperature was studied at (22 C, 32 C, 42 C, 52 C, 62 C). Also the effect of
dye concentrations (1.11, 2.22, 3.33, 4.44 5.55 g/L) on color yield was investigated. Continuous dyeing method was carried out in three steps, reduction, oxidation and washing. Before dyeing, samples was pre-wetted in order to increase the absorbency. Web of CEL nanofibers were dyed by padding (multiple nip and multiple dip at 80% wet pick up) using HF horizontal padder (Mathis). Initially the samples were padded by pre-wetting solution containing 10 g/L caustic soda, 5 g/L Leonil-EHC and 1 g/L Mercerol, after then the gentle washing was done for 3 min. Samples were then dyed with dyeing liquor containing required concentration of synthetic indigo dye, 1.5 g/L caustic soda (48%), and 5 g/L sodium hydrosulphite. After each 4 to 5 dips, oxidation was carried out for 90 s. The padded samples was washed out gently for 3 min then squeeze and dry out the samples at room temperature.

Testing

Color measurement and testing

Color yield ($K/S$) values using Kubelka-Munk equation (Eq. 1); and CIE $L^* a^* b^* C^*$ and $h^o$ coordinates were measured on an X-Rite CE-7000A spectrophotometer (illumination D65, 10° standard observer, UV and specular component included) at the maximum absorption peak.

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

1

Where $R$ is reflectance value at maximum absorption peak, $K$ is absorption coefficient and $S$ is scattering coefficient.

Colored samples were tested for colorfastness to light (ISO 105 B02:2013, 20 h) on a light fastness tester (SDL Atlas, UK); and colorfastness to washing (ISO 105 C10:2006) on a Gyrowash (James H. Heal, UK). Further, the dye solution (5.55 g/L) as the representative effluent was evaluated for pH, TDS contents with digital TDS meter (Oakton, USA) and COD value (HACH method).

Characterization

The surface morphology of ENMs was examined on a SEM (JSM 6380L, JEOL Japan) at an accelerating voltage of 10 kV. All the samples were sputtered with gold under vacuum before SEM test. Chemical structure analysis of ENMs was carried out on an ATR-FTIR spectroscopy HATR Spectrum Two Spectrometer equipped with an ATR accessory (Perkin Elmer, USA) in the range 4000–800 cm$^{-1}$. Transmission spectrum of the dye solution was obtained using a UV-Vis Spectrophotometer (Specord 200 Plus, Germany).

Results And Discussion

Chemical structure of CEL ENMs
Figure 2 shows the IR-spectrum of the electrospun nanofibers. For neat CA NFM, the FTIR spectrum showed absorption bands present at 1368 cm$^{-1}$ (symmetric C-CH$_3$ bending), 1231 cm$^{-1}$ (asymmetric stretching of carboxylate group) and 1046 cm$^{-1}$ (asymmetric C-O-C stretching) from the pyranose ring. Additionally, the peak located at 1745 cm$^{-1}$ is assigned to the carbonyl band (C = O) of the acetate group in the CA ENM (Khatri et al., 2016). The results are in agreements with previous reports (Khatri et al., 2013a, Khatr et al., 2014).

After deacetylation process, the typical absorption bands of CA were disappeared, and one absorption peak appeared significantly at around 3400 cm$^{-1}$ (-OH group) (Fig. 2). This shows a complete conversion of CA ENM into CEL ENM (Khatri et al., 2013a, Khatr et al., 2013c). The IR-spectrum of dyed CEL ENM has retained its chemical structure (result is not shown here), the interaction in between the CEL ENM and the dye molecules is not evident in the IR-spectrum. This is possibly due to the small amount of dye molecules used in during the experiments.

**UV-Vis spectrophotometry of dye solution**

Figure 3 shows the UV-vis transmittance spectra of indigo dye solution. It is evident that the transmittance spectra of CN indigo dye solution exhibited 55% transmittance peak at 500nm wavelength, and aniline free indigo dye exhibited 62% transmittance peak at the same wavelength.

**Effect of dye solution pH**

The pH is the most impacting parameter in order to get maximum color yield during dyeing of CEL ENM’s with synthetic indigo. The dyeing of pre-wetted CEL ENM’s was carried out using dye concentration of 3.33 g/L, sodium hydrosulphite 5 g/L during variation in pH at (10.5, 11, 11.5, 12, and 12.5). Figure 4 exhibits the effect of pH on color yield during dyeing process. The result shows that by increasing the pH of the dye solution from 10.5 to 12.5, color yield of the dyed samples was increased and the maximum color yield obtained at pH of 12.5. Further increase in the pH, reduced the color yield of the dyed samples because at higher pH, CEL ENM when dipped in alkaline bath acquires more negative charge and more is the repulsion occurs between dye and fiber, resulting in reduced dye uptake (Chakraborty and Chavan, 2004). Therefore, we considered the 12.5 pH as optimized value for further experiments.

**Effect of sodium hydrosulphite concentration**

To investigate the effect of sodium hydrosulphite concentration, dyeing of pre-wetted samples of CEL ENM’s was carried out at optimized pH of 12.5 by using 3.33 g/L dye concentration during variation in sodium hydrosulphite concentration (3, 4, 5, 6, 7 g/L). Figure 5 represents the effect of sodium hydrosulphite concentration on color yield and it reveals that by increasing the amount of sodium hydrosulphite concentration, color yield of the dyed samples was increased gradually. The maximum color yield was obtained at 7 g/L and was considered for further experiments.

**Effect of dyebath temperature**
For the optimization of dye bath temperature we consider the optimized value of pH and sodium hydrosulphite concentration by using 3.33 g/L dye concentration throughout the variation in dye bath temperature (22, 32, 42, 52, 62 °C). Figure 6 reflects the effect of dye bath temperature on the color yield of dyed samples and reveals that the color yield increased by increasing the dye bath temperature from 22 °C to 52 °C. Further increment in the dye bath temperature slightly decreases the color yield of the dyed samples may be due to the affinity of the solubilized dye for CEL ENM decreases with the increase in temperature. Hence we selected 52 °C dye bath temperature for further trials.

**Effect of dye concentration**

Figure 7 shows the effect of dye concentration on color build up property of the dyed CEL ENM were investigated using the previously optimized conditions. Five differing dye concentrations (1.11, 2.22, 3.33, 4.44, 5.55 g/L) were used and the color build up properties were measured in terms of K/S values. As expected, the color yield increased with increasing dye concentration. However, further increment in the dye concentration has slightly reduced the K/S of CEL ENM. Hence, 5.55 g/L may be the saturation level for dyeing of CEL ENM with synthetic indigo dye by continuous method.

**Comparison between the conventional (CN) and aniline free synthetic indigo dye**

Effect of dye concentration on color build up property of the CN and aniline free synthetic indigo dye were investigated using the previously optimized conditions. Five differing dye concentrations (1.11, 2.22, 3.33, 4.44, 5.55 g/L) of both dyes were used and the color build up properties were measured in terms of K/S values. The results reported in Fig. 8 demonstrate an increase in the K/S with increasing dye concentration for both dyes. The K/S values for dyed CEL ENMs by aniline free indigo dye are slightly higher in comparison to the CN indigo dye during continuous dyeing method. The profiles of K/S results for both dyes were same demonstrating the uniform behavior of both dyes at the optimized conditions.

**Effect of dye concentration on colorimetric values of dyed CEL ENMs**

Figure 9 shows the images of the undyed and dyed samples for shade visualization. It can be seen that the dye have been applied uniformly on the ENMs.

In addition to K/S values, the calorimetric coordinates (L*, a*, b*, C* and h°) were measured for each dye concentration and the results are compiled in Table 1. It can be observed that with the increased concentrations of dye, the lightness values (L*) were decreased which shows that the dyed webs became darker. This trend supports the results shown in Fig. 7, as negative a* designate for greenness, and negative b* designated for blueness. Hence, the obtained results indicate that the dye is bluer in tone; this can be proved by hue angle h° which shows all values within the bluer region.
Table 1
Effect of CN synthetic indigo dye concentration on calorimetric values of dyed CEL ENMs

<table>
<thead>
<tr>
<th>dye conc. g/L</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>h°</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.11</td>
<td>40.63</td>
<td>-1.36</td>
<td>-23.65</td>
<td>23.69</td>
<td>266.71</td>
</tr>
<tr>
<td>2.22</td>
<td>30.11</td>
<td>-2.26</td>
<td>-20.35</td>
<td>20.47</td>
<td>276.34</td>
</tr>
<tr>
<td>3.33</td>
<td>31.85</td>
<td>-2.49</td>
<td>-18.50</td>
<td>18.67</td>
<td>262.34</td>
</tr>
<tr>
<td>4.44</td>
<td>31.18</td>
<td>-1.19</td>
<td>-20.60</td>
<td>20.64</td>
<td>266.69</td>
</tr>
<tr>
<td>5.55</td>
<td>30.22</td>
<td>-0.16</td>
<td>-22.51</td>
<td>22.51</td>
<td>270.41</td>
</tr>
</tbody>
</table>

The calorimetric values ($L^*, a^*, b^*, C^*$ and $h^o$) were also measured for aniline free synthetic indigo dye concentration; and the results are compiled in Table 2. It can be observed that with the increased concentrations of dye, the lightness values ($L^*$) were decreased which shows that the dyed webs became darker. This trend supports the results shown in Fig. 8, as positive $a^*$ designate for redness, i.e. with increasing dye concentration the dyed ENMs are moving towards redder region, and negative $b^*$ designated for blueness. Hence, the obtained results indicate that the dye is bluer in tone; this can be proved by hue angle $h^o$ which shows all values within the bluer region.

Table 2
Effect of aniline free synthetic indigo dye concentration on calorimetric values of dyed CEL ENMs

<table>
<thead>
<tr>
<th>dye conc. (g/L)</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>h°</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.11</td>
<td>36.26</td>
<td>1.58</td>
<td>-26.39</td>
<td>26.43</td>
<td>273.42</td>
</tr>
<tr>
<td>2.22</td>
<td>28.63</td>
<td>2.82</td>
<td>-19.78</td>
<td>19.98</td>
<td>278.11</td>
</tr>
<tr>
<td>3.33</td>
<td>27.20</td>
<td>4.70</td>
<td>-21.50</td>
<td>22.01</td>
<td>282.34</td>
</tr>
<tr>
<td>4.44</td>
<td>24.43</td>
<td>5.05</td>
<td>-14.01</td>
<td>14.89</td>
<td>289.84</td>
</tr>
<tr>
<td>5.55</td>
<td>24.05</td>
<td>5.20</td>
<td>-14.72</td>
<td>15.62</td>
<td>289.46</td>
</tr>
</tbody>
</table>

Dye Solution Analysis as Effluent

Table 3 shows the properties of CN and aniline free synthetic indigo dyeing effluent used in this study. The results revealed that the effluent is basic in pH with high TDS content. In Pakistan, the untreated effluent discharge from dyeing industries has TDS content up to 2500 mg/L. During the testing everything performed exactly the same as it would with conventional indigo, there was just one important difference is no aniline and that aniline impurities are toxic to humans, causing skin allergies, damage to
major organs and genetic defects, as well as being linked to cancer. Aniline is also toxic to aquatic life, which is an issue as two-thirds of the 400 metric tons of aniline waste on an annual basis ends up in the environment as wastewater discharge. Therefore, we used an alternative system that is aniline free indigo dye which make our industry sustainable by removing a hazardous impurity and to protect the workers, consumers and the environment with cleaner waterways.

<table>
<thead>
<tr>
<th>Dye</th>
<th>pH</th>
<th>TDS (mg/L)</th>
<th>COD (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN synthetic indigo dye</td>
<td>12.3</td>
<td>1641</td>
<td>1940</td>
</tr>
<tr>
<td>Aniline free synthetic indigo dye</td>
<td>12</td>
<td>1193</td>
<td>1635</td>
</tr>
</tbody>
</table>

### Colorfastness Properties

Table 4 presents the effect of colorfastness to washing and light of CEL ENM dyed with CN and aniline free synthetic indigo at optimum conditions. The colorfastness to washing (change in color) was excellent, and the results of colorfastness to washing (staining on multiber) ratings were also excellent probably. The results of colorfastness to light test was excellent with no color change of the dyed sample. The excellent colorimetric properties demonstrate that the novel CEL ENM (colored and breathable) can potentially be deliberated as future apparels for casual and fashion.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Washing fastness</th>
<th>Light fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change in color</td>
<td>Staining on Multiber a</td>
<td>Blue wool reference</td>
</tr>
<tr>
<td>CN synthetic indigo dye (Liq.)</td>
<td>4 4.5 4.5 4.5 5 4.5</td>
<td>4.5 7</td>
</tr>
<tr>
<td>Aniline free synthetic indigo dye</td>
<td>4 4.5 4.5 4.5 5 4.5</td>
<td>4.5 7</td>
</tr>
</tbody>
</table>

a CT, cellulose triacetate; CO, cotton; PA, polyamide; PES, polyester; PAC, polyacrylonitrile; WO, wool

### Morphology of Electrospun Fibers

The surface morphology of ENMs is demonstrated in Fig. 10. CEL ENM displayed a smooth morphology without beads suggesting that the electrospinning parameters (solution and process) used were optimum (Fig. 10a). Significantly, dyed CEL ENMs displayed almost similar morphology (Fig. 10b-c) in comparison to the undyed CEL ENM revealing good resistance to indigo dyeing conditions used. Similar findings were reported in previous studies for dyeing of CEL ENMs (Khatri et al., 2013a, Khatri et al., 2013c).
Conclusion

CEL ENMs can effectively be dyed with CN and aniline free synthetic indigo dye by continuous dyeing method. The results of dyeing were mainly dependent on addition of alkali and reducing agent, dyebath temperature and dye concentration. CEL ENMs have successfully prepared from the CA ENMs as confirmed by the ATR-FTIR analysis. SEM images showed that the dyed CEL ENM have almost similar morphology in comparison to the undyed CEL ENM revealing good resistance to dyeing conditions used. Moreover, \(K/S\) enhanced gradually with a simultaneous increase in the dye concentrations up to 5.55 g/L, indicating good color build up on CEL ENM. The maximum \(K/S\) obtained for CN synthetic indigo dye was 13.07 and for aniline free synthetic indigo dye was 13.50 at 5.55 g/L dye concentration. The colorfastness to light and washing showed excellent ratings. Increased wrinkle resistance as well as tensile strength of dyed CEL ENMs was revealed in comparison to the undyed CEL ENMs.

Declarations

We declare that:

- This study does not involve human or animal participation, data and/or tissue.
- We allow the journal (Cellulose) to publish this work in any of its issues to come.
- We have all the experimental data available with us.
- We have no competing interests as defined by Springer, or other interests that might be perceived to influence the results and/or discussion reported in this paper.

Authors’ Contribution

Shamshad Ali and Awais Khatri were the projects leads. They planned the research, prepared experimental plan, conducted analysis of the results, and reviewed/edited the final manuscript draft. Whereas Alishba Javeed did the literature review, conducted experiments and wrote the initial manuscript draft.

ACKNOWLEDGEMENT

We acknowledge the Higher Education Commission Pakistan for funding this research work.

References


Figures
Figure 1

Chemical structure of indigo dye and its leuco form (Buscio et al., 2014)

Figure 2

ATR-FTIR spectra of CEL ENMs
Figure 3

UV-Vis transmittance spectra of indigo dye solution
Figure 4

Effect of pH on $K/S$ of CEL ENM dyed with synthetic indigo dye
Figure 5

Effect of hydro concentration on $K/S$ of CEL ENM dyed with synthetic indigo dye
Figure 6

Effect of dyebath temperature on $K/S$ of CEL ENM dyed with synthetic indigo dye
Figure 7

Effect of dye concentration on *K/S* of CEL ENM dyed with synthetic indigo dye
Figure 8

Effect of dye concentration on $K/S$ of CEL ENM dyed with CN and aniline free synthetic indigo dyes

Figure 9

Photographic images of the undyed and dyed CEL ENMs with CN synthetic indigo dye and aniline free synthetic indigo dye in the sequence
Figure 10

SEM images of CEL ENMs (a) CEL ENM (b) dyed with CN synthetic indigo dye (c) dyed with aniline free synthetic indigo dye by continuous method