Introduction

Humanity has been blessed by nature with brilliant and eye-catching colors of eco-friendly origin [1-2]. These natural gifts of colors have always been used by humans to dye clothing and other items. A considerable decline in the utilization of natural colorants has been observed since the discovery of the first synthetic dye [3-4]. There is an increasing awareness that natural dyes are a good alternative to synthetic dyes due to their biodegradability and sustainability, as well as soothing nature [7-8]. Hence, the demands for

Original Research

Sustainable Dyeing of Cotton Fabric Using Black Carrot (Daucus carota L.) Plant Residue as a Source of Natural Colorant

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Abstract

Rising environmental concerns toward the use of synthetic chemicals as well as global acceptance of natural products has emphasized the need for exploring novel and sustainable sources of eco-friendly dyes for the textile sector. Our study was conducted to explore the natural colorant potential of black carrot (Daucus carota L.) plant residue for textile processing and optimizing conditions for cotton dyeing. Cotton fabric was dyed using black carrot-based dye, extracted in varying media. The results revealed that black carrot colorants produced darker shades when extracted in acidified methanol media. Excellent color strength of cotton fabrics were found at 70°C by coloring for 55 minutes using 4.0 g of salt (NaCl) as an exhausting agent. The bio mordants as well as chemical mordant were employed to improve color strength properties. In the case of chemical mordanting, 6% tannic acid and 8% iron sulphate as pre-mordant and 8% tannic acid and 2% iron sulphate as post-mordant showed maximum color strength values. Similarly, using bio mordanting, 2% of turmeric (Curcuma longa L.) and 6% of henna (Lawsonia inermis L.) extracts as pre-mordant, as well as 8% of turmeric and 4% of henna extracts as post-mordant showed maximum color strength values. Dyed cotton fabrics exhibited best color fastness properties in term of light, washing, dry and wet rubbing fastness.

Keywords: black carrot, color fastness, color strength, cotton fabric, mordanting

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eco-friendly natural colorants have risen again around the globe due to increasing health hazards associated with the use of synthetic dyes [5-6].

The color strength and shades of dyes derived from different natural sources depends on the nature of extraction media as well as dyeing conditions [9-11]. Finding optimum extraction and dyeing conditions is the pre-requisite for natural dyes to be used in coloring of food substrate, leather, wood, plastics, paints and pharmaceutical products [12-13]. Different parts of plants such as the outer shell of bulbs [14], flowers [15], fruit peels [16], barks [17] and vegetative organs [18-19] are being used to extract natural dyes for textile processing. While using the natural source of colorants, the trimmed and surplus plant material has been gaining considerable attention from researchers and consumers over the last decade [18-20]. This is a sustainable approach because utilization of leftover plant material in natural dye extraction does not disturb ecological balance and biodiversity.

Black carrot (Daucus carota L.), the root vegetable belonging to the Apioaceae family, is cultivated all around the world [21]. Carrots are a rich source of different active photochemicals such as phenolics, flavonoids, carotenoids, chlorophylls and anthocyanins [22-23]. The darker color of black carrot is due to the presence of anthocyanin [24-25], which are mainly distributed among flowers, fruits and vegetative parts and impart bright colors such as purple, red and blue to these plant organs [26-27]. These have antioxidant [28], anti-fungal, anti-bacterial and anti-cancerous properties [29], and are widely used in food, drugs and in pharmaceutical products [30].

The present investigation is an attempt to utilize black carrot that is left over from extracting natural colorant for cotton dyeing. The objective of the current study is to provide a cheap and ecofriendly source of dye for the textile industry as well as characterize natural colorants obtained from black carrot leftovers.

**Material and Methods**

Black carrot (Daucus carota L.) leaves were collected from the Vegetable Research Institute, AARI, Faisalabad, Pakistan. The fresh leaves were washed; sun dried and then kept in an oven at 70°C for five days. The dried plant material was ground to a fine powder and stored in a plastic jar to be used as dye for cotton dyeing. Mercerized cotton fabrics used for dyeing with black carrot powder were produced by Noor Fatima Textile Faisalabad.

Extracting natural dye from black carrot plant residue was carried out by boiling a small amount of dye powder, keeping the solid-to-liquor ratio of 1:25. Suitable media are given below.

1. Aqueous medium.
2. Alkaline medium: Potassium hydroxide and sodium hydroxide were used as alkaline medium in the range 1-10%
3. Organic medium: Ethanol and methanol were used in a range of 20, 40, 60, 80 and 100%. Methanolic KOH (1-5%) was prepared by dissolving KOH in 100% methanol.
4. Acidic medium: Hydrochloric acid (HCl), acidified methanol and acidified ethanol were used in a range of 1, 2, 3, 4 and 5% (this medium was employed to compare the results with conventional solvents; acidified methanol or ethanol was prepared by dissolving 1-5 ml of conc. HCl in 99-95ml of methanol and ethanol).

After boiling, the crude material was filtered and each extract was used for cotton dyeing. The best extraction medium was further used for optimizing and mordanting studies. Dyeing of cotton fabric was carried out by employing 25 ml of respective extract for 1g of fabric at 60°C for 60 min, keeping the extract-to-fabric ratio of 1:25.

Different dyeing parameters such as temperature, time, salt concentration, pH and material-to-liquor ratio were optimized. In order to achieve optimum dyeing temperature, the dye extract was treated with cotton fabric at varying temperatures, such as 40, 50, 60, 70, 80 and 90°C for one hour. Various dyeing times such as 25, 35, 45, 55, 65, 75 and 85 minutes were employed to achieve optimum dyeing time interval. To determine the influence of salt concentration on dyeing behavior of black carrot, varying levels of NaCl salt (1-10%) were used. To find out optimum pH for dyeing.

To improve color strength and color fastness properties of dyed cotton fabrics, pre- and post-mordanting were employed at optimum dyeing conditions using black carrot dye extract. Bio mordants, such as turmeric (Curcuma longa L.), henna (Lawsonia inermis L.), pomegranate (Punica granatum L.) rind, golden shower plant (Cassia fistula L.) bark and onion (Allium cepa L.) peel as well as chemical mordants such as tannic acid, copper sulphate, iron sulphate and potassium dichromate were employed. Based on the results, two best chemicals as well as biomordant were selected for further study. For preparing the biomordants, 1-10 g of respective plant material was boiled separately in water for one hour, filtered and used for further study. Similarly, 1-10% of metal salt solutions of respective chemical mordants were used.

The color strength values (K/S) of all dyed fabrics were determined with the help of Spectra flash SF 600 at the Department of Applied Chemistry, Government College University, Faisalabad. Color fastness properties of dyed fabrics were determined using ISO methods such as ISO 105 BO2 for light fastness, ISO105-CO3 for washing fastness and ISO 105 X-12 for rubbing fastness.
Results and Discussion

The results given in Tables 1-3 showed that 2% of acidified methanol was the best medium to obtain maximum colorants from black carrot leftovers. Depending on the colorant polarity, acidified methanolic extract produced a higher value of color strength (K/S) as compared to aqueous, alkaline or organic media used in the study. The higher level of colorant extraction from black carrot residues in acidified medium indicated that during boiling, this medium helped to transfer more mass kinetics as compared to aqueous or other medium used in the study [31, 32]. The concentration of acidified methanol also played a role in isolating the colorant from black carrot residues. The low concentration of acid was not helpful to increase the extraction, while too-high levels mediated the extraction of other phytochemicals along with the desired colorant [33].

The current experimental results indicated that darker color shades of black carrot leftovers extracting treated fabric could be achieved by keeping dyeing bath at 70ºC as compared with all other temperature regimes applied during the study (Fig. 1). A dyeing time with a duration of 55 minutes was proven to be more useful in creating good color depth of black carrot leftovers extract-treated fabric than those of other time intervals used during current experimentation (Fig. 2). The results given in Fig. 3 also showed that 4.0 g of salt as an exhausting agent produced good color strength compared with all other salt levels tested during the current investigation, indicating that the appropriate contact time of dye extract with fabric helped maintain the strike rate of colorant onto fabric. The optimum contact time to raise the kinetic energy of colorant resulted in good K/S value [34]. The optimum dyeing interval of 55 minutes to produce darker shades of high K/S values as observed during the present investigation revealed the efficacy of black carrot-based colorant to produce darker shades within less time.

The addition of salt during dyeing helped to achieve maximum exhaustion and acceptable color characteristics. This exhausting agent had led the colorant towards fabric with in short range of attractive forces [35]. The higher salt levels, above the optimal amount, may result in over-exhaustion, leading to

<table>
<thead>
<tr>
<th>Organic media</th>
<th>Methanol (%)</th>
<th>Ethanol (%)</th>
<th>Methanolic KOH (%)</th>
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<tbody>
<tr>
<td>20 40 60 80 100</td>
<td>20 40 60 80 100</td>
<td>1 2 3 4 5</td>
<td></td>
</tr>
<tr>
<td>Color strength</td>
<td>1.05 1.62 1.24 2.12 2.30</td>
<td>1.42 3.28 3.74 2.04 2.58</td>
<td></td>
</tr>
<tr>
<td>(K/S ) values</td>
<td>2.06 1.73 1.55 1.32 1.24</td>
<td></td>
<td></td>
</tr>
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<tr>
<th>Alkaline media</th>
<th>NaOH (%)</th>
<th>KOH (%)</th>
</tr>
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<tbody>
<tr>
<td>1 2 3 4 5 6 7 8 9 10</td>
<td>1 2 3 4 5 6 7 8 9 10</td>
<td></td>
</tr>
<tr>
<td>2.26 2.29 2.20 1.29 1.88 2.12 1.59 1.06 0.88 0.68</td>
<td>1.36 1.40 1.52 1.79 1.6 1.06 1.54 1.95 1.52 1.43</td>
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<table>
<thead>
<tr>
<th>Acidic media</th>
<th>Acidified methanol (%)</th>
<th>Acidified ethanol (%)</th>
<th>Aqueous medium</th>
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<tbody>
<tr>
<td>HCl (%)</td>
<td>Acidified methanol (%)</td>
<td>Acidified ethanol (%)</td>
<td>100 ml</td>
</tr>
<tr>
<td>1 2 3 4 5</td>
<td>1 2 3 4 5</td>
<td>1 2 3 4 5</td>
<td>1.06</td>
</tr>
<tr>
<td>Color strength</td>
<td>1.89 1.79 1.06 0.91 1.04</td>
<td>3.31 4.32 2.24 3.18 2.55</td>
<td>2.21 2.65 2.27 0.30 0.30</td>
</tr>
</tbody>
</table>
Hence good color characteristics were obtained by dyeing cotton fabric at 70ºC for 55 minutes using 4.0g of salt as an exhausting agent.

The dyeing results from mordanting experiments revealed that varying concentrations of chemical mordants produced different shades and variable rating of fastness properties on black carrot leftover-treated cotton fabrics (Table 4). Among different chemical mordants used in the study, tannic acid and iron sulphate produced darker shades than all others. A tannic acid level of 6% produced darker shades when treated before dyeing of fabric with black carrot extract compared with all other levels of this mordant used in the study. The treatment of black carrot extract-dyed cotton fabric with tannic acid gave darker shades when this mordant was applied in a concentration of 8% as compared to all other concentrations. Comparatively, tannic acid post-mordanting showed the highest color strength as compared to pre-mordanting iron sulphate formed stable complexes with dye molecule and cotton fabric and exhibited excellent fastness properties when applied in concentrations of 8 and 2% as pre- and post-mordanting agent, respectively. The data shown in (Table 4) suggested that color strength and color fastness properties of iron post-mordanting were higher in contrast to pre-mordanting.

Based on the results of bio-mordanting experiments, turmeric and henna powder were selected for mordanting of black carrot leaves extract-treated fabric. By employing different concentrations (1-10%) of two bio mordants, turmeric and henna powder, multiple color strength values were recorded (Table 4). In bio pre-mordanting of cotton fabrics with turmeric powder, 2% was the optimum concentration, which resulted in higher K/S color strength values. In bio post-mordanting with turmeric, 8% powder showed higher color strength by the formation of a strong linkage between cotton and dye molecules. The treatment of black carrot leaves extract dyed fabric with 4% henna powder produced darker shades, whereas, pre-mordanting with 6% henna powder was more beneficial in producing good color strength (Table 4).

The higher color strength values at optimum concentrations of mordants indicate strong bonds of applied chemicals and fabric. The decreased color strength at other levels might be due to the aggregation of dye molecules and mordant onto cotton fabric, leading to low color strength [34-37]. The concentration of mordant below the optimum level had less affinity to fabric and led to poor color strength values [36-37]. Above optimum mordant concentration, the applied chemical caused unevenness, resulting in low color strength values of dyed fabric.

Dyeing of fabrics with natural colorant along with bio mordanting could be a good alternative to chemical mordanting [38]. The turmeric powder containing coloring component (curcumin) was firmly bound to anthocyanin and formed a strong linkage onto cotton fabric, resulting in a dark yellow color with excellent color strength. More than optimum concentrations of turmeric powder might have caused precipitate formation and showed minimum color strength, while less concentration was insufficient to form a strong bond formation and exhibited low color strength [39]. Henna was another excellent bio mordant that produced excellent color strength (K/S) on dyed fabric. In pre-mordanting, color strength (K/S) was increased up to 6% henna extract, indicating the strong coordination between the colorant (lawsone), anthocyanin and cellulosic fabric. Overall, 4% henna as post bio mordant showed relatively good color strength properties [40]. The bio mordanting displayed higher K/S values in comparison to chemical mordanting and yielded multiple color shades, thereby making the process more eco-friendly and sustainable.

Fastness properties estimation results revealed that 6 or 8% of tannic acid and iron sulphate produced excellent rating of fastness (Table 4). This was because the iron having low reduction potential formed good metal dye complex onto fabric before or after dyeing, whereas tannic acid via H-bonding produced a strong shade [11]. Similarly, bio-mordants produced excellent
| Mordant type | Mordant conc. (%) | Tannic Acid |  |  | Bio-mordant |  |  |  |
|--------------|------------------|-------------|-------------------------------------------------|-------------------------------------------------|-------------|-------------------------------------------------|-------------------------------------------------|
|              |                  | K/S LF WF D RF W RF | K/S LF WF D RF W RF | K/S LF WF D RF W RF | K/S LF WF D RF W RF | K/S LF WF D RF W RF | K/S LF WF D RF W RF |
|              | 2 | 1.5448 3 3 3 3 | 0.702 3/4 3 3/4 4 | 4.6634 4/5 4/5 4 4 | 1.9431 3 3/4 3 3/4 | 2.034 4 3 4/5 4 |
|              | 4 | 2.2474 4 4 4/5 4 | 0.839 3 3 3/4 3/4 | 4.2298 4/5 4 4/5 4 | 2.121 4/5 4 4/5 4/5 |
|              | 8 | 2.4363 4 4/5 4/5 4 | 1.0095 4 4/5 4 4 | 3.445 4 4 4/5 4 | 1.4859 3 4 3 4/5 |
|              | 10 | 2.73 5 4/5 4/5 5/5 | 0.8374 3 3/4 3 4 | 4.2456 4/5 4/5 4 4 | 1.342 4 3/4 4 4/5 |
| Post mordanting | 1 | 1.3163 3 3/4 4 ¾ | 0.844 3 3/4 3/4 3 | 1.8837 3 4 3/4 4/5 | 2.5668 3 4 4/5 4 |
|              | 2 | 1.0977 4 4 4 4 | 1.2409 4 4 5 4/5 | 1.8646 4 4 4 4/5 | 4 4/5 4/5 4 |
|              | 6 | 3.0422 4/5 4/5 4 4 | 0.8478 3 4 3/4 3 | 1.8344 4 4/5 4/5 4/5 | 1.9578 3/4 4 3/4 4 |
|              | 8 | 3.8258 4/5 4/5 5 4/5 | 0.9103 3/4 4/5 4 4 | 2.8777 4/5 4 4/5 4 | 1.2814 3 3/4 4 4/5 |
|              | 10 | 1.5842 3 4 3 3/4 | 0.7873 3 4 4/5 4 | 2.6816 3/4 4 4/5 4 | 1.9656 3 3 4 4/5 |

k/s = colour strength; LF = light Fastness; WF- = wash fastness; DRF = Dry rub fastness; WRF = Wet Rub fastness
results for fastness properties. The conjugation sites present in functional moiety of bio mordant (curcumin from turmeric and lawsone from henna) formed extra H-bond with –OH of colorant and –OH of cellulosic fabric, thus producing a stronger shade as compared to metal dye complex [41]. Upon treatment of mordanted fabrics to heat, light, and washing, a high rating was observed.

Conclusion

Black carrot plant residues could be an eco-friendly and cost-effective natural dye source for textile dyeing. The optimized dyeing parameters were 70°C temperature, 55 minutes dyeing time and 4.0g NaCl salt as exhausting agent. In the case of chemical mordanting, 6% tannic acid and 8% iron sulphate as pre-mordant and 8% tannic acid and 2% iron sulphate as post-mordant showed maximum color strength values. Bio mordanting experiments revealed that 2% turmeric and 6% henna as pre-mordant as well as 8% turmeric and 4% henna as post-mordant showed maximum color strength values. Mordanted cotton fabrics showed best color fastness properties in terms of light, washing dry and wet-fastness.

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Conflict of Interest

The authors declare no conflict of interest.

References