Extraction of Natural Dyes, Characterizations, and their Ecofriendly Applications

Nandkishor B. Shirsath\textsuperscript{1}, Mayuri More\textsuperscript{2}, Hera Sajjad Ahmed\textsuperscript{3}, Tulshidas S. Savale\textsuperscript{4}

\textsuperscript{1,2,3,4}Department of Chemistry, Maharaja Sayajirao Gaikwad, Arts, Science and Commerce College Malegaon Camp Dist. Nashik

Abstract
Natural dyes produce an extraordinary variety of products and complex colors that complements each other. Straight off a day synthetic dye leads to high environmental pollution. In recent year, the interest of researchers has changed over on utilizing natural dyes in textiles, food and cosmetics industries. Natural dye sources are eco-friendly and permanent in fabrics. The present study focused on the extraction of dyes from plant materials such as leaves, tubers and flower plants. The obtained dyes yield a variety of colors and are processed with different types of mordants such as aluminum acetate and cream of tartar. In this article, our research focus on synthesis of azo dyes and compare it with natural dyes. We extracted number of natural dyes and find out of application in dying field. Natural dyes worldwide should be increased to prevent us from pollution and other harmful effects.

Keywords: Natural dyes, complex colors, azodyes, Eco-friendly

1. INTRODUCTION
The first systematic study of dyes that was suitable for application to cellulose acetate by a direct dyeing process was carried out by “Green”. In 1922, Green and Saunders made one type of colored azo compound in which a solubilizing group is attached to amino group [1]. Azo compounds are defined as compound containing at least one azo group attached to sp\textsuperscript{2} hybridized carbon atom such as benzene, naphthalene, thiazole, thiophene, etc. They bearing functional group R-N=N-R’, where, R & R’ can be either aryl or alkyl groups. IUPAC defines azo groups as ‘Derivatives of daizene (diimide)’, H-N=N-H, the name azo compound is from azote [2].

Azodyes are usually strongly colored compounds which can be intensively yellow, red, orange, brown, etc. As a result, they have huge importance as a dye and also as a pigment for a long time. Most importantly the groups that invariably confirm color are the azo (-N=N-) and nitroso (-N=O) groups [3]. Disperse dyes are the groups of compounds that have low solubility in water but they can interact with the fibres chains by forming disperse particles. Their main use is in the dyeing of hydrophobic fibers such as polyesters, cellulose acetate and polyamides[4]. The azo groups form links or bridges between organic residues of which one is usually an aromatic nucleus and being a chromophore, azo groups impart color to the textile fibers. The depth of shade is influenced by the number of azo groups present in structure of the azo dye [5].
Since prehistoric time natural dyes is used for coloring of food substrate, leather as well as fibers like wool, silk and cotton. The use of non-allergic, non-toxic and eco-friendly natural dyes on textiles have become a matter of significant importance due to the increased environmental awareness in order to avoid some hazardous synthetic dyes [6].

1.1 NATURAL DYED

In present scenario environmental awareness of people about natural products renewable nature of materials, less environmental harm and sustainability of the natural products has further revived the use of natural dyes in dying of textile materials [7,8]. Following are some advantages of natural dyes:

- No health hazard
- Easy extraction and purification
- No effluent generation
- Very high sustainability
- Mild dying condition
- Renewable sources

There are some technical issues and disadvantages related to the application of natural dyes.

- Poor colour fastness properties
- No standard method available for extraction of natural dyes
- Use of metallic mordant, some of which are not eco-friendly.

In India, Alps Industries Ghaziabad, (Uttar Pradesh, India) and later Ama Herbals, Lucknow and Bio dye, Goa done extensive work for industrial research and production of natural dyes [9-11]. The major carriers of natural dyes are the France, Germany, Italy and the UK [12]. Natural dyes are many advantages like non toxicity, eco friendliness, pleasing shades to the eye and having special aroma [12]. However natural dyes have some disadvantages to showing poor colour, reproducibility, poor composition, average washing fastness [13] and lesser availability in different regions, which are of great concern against its revival.

1.2 APPLICATIONS OF DYES

![Application of Natural Dyes](image)

**Fig. 1 Applications of natural dyes in different fields**
Different researchers had proposed different methods of dyeing of natural and synthetic fibres with natural dyes. The dyeing of textile substrates depends on dyeing parameters which are fibre structure, temperature, time and pH of the dye bath and dye molecule characteristics [15]. The fastness properties of dyes on textile substrates depend on bonding of dyes with fibre. Since natural dyes are lacking in the presence of active groups to make bonds with textile fibres, the fastness properties are not very good. The cellulosic fibres are difficult to dye with natural dyes as they have poor affinity and substantivity. The lack of bonding of natural dyes with cellulosic fibre requires mordanting treatment. Protein fibres have ionic groups and get bonded with natural dyes possessing ionic groups in dye structure [16].

The dyeing of proteins fibre can be done by exhaust method of dyeing. The dyeing process parameters in wool and silk dying is pH at 4.5–5.5 and dyeing temperature 80–90°C. The exhaustion % of dyes in dyeing is very poor. The longer liquor ratio may be preferred because of poor solubilities of natural dyes in water. Stainless steel-made dyeing machines are suitable in dyeing of wool and silk. Since natural dyes are having poor affinity for cellulosic fibre and due to poor exhaustion, mordanting treatment [17] is done to fix the dyes on cellulosic fibre. The dyeing of cellulosic fibre can be done at temperature of 80–90°C. The exhaustion of dyes can be increased by adding exhausting agents, sodium chloride or Glauber’s salt in dye bath. Most of the dyeing is done at neutral pH. Dyeing of cotton with natural indigo is done at alkaline pH in the presence of sodium hydrosulphite in a container made of stainless steel [18].

2. EXTRACTION PROCESS OF DYES

2.1 Turmeric (Curcuma longa):
The dye is obtained from the root of the plant. The turmeric root is dried, crushed in powder form and boiled with water to extract the dye. It can be used in the dyeing of cotton, wool, and silk. Proper mordanting treatment improves colour fastness to wash. The brilliant yellow shade is obtained after dyeing with turmeric natural dye. Turmeric is a rich source of phenolic compounds known as curcuminoids. The colouring ingredients in turmeric are called curcumin. Curcumin is diarylheptanoid existing in keto-enol form. Turmeric is a member of Curcuma botanical group.

![Turmeric molecule](image)

2.2 Onion (Allium cepa)
The papery skin of onion is the main source of the dye. Onion skin is boiled to extract the colour and subsequently can be dyed with or without mordanting the fabric. The resulting colour is from orange to brown. It contains colouring pigments called pelargonidin (5,5,7,4 tetrahydroxy antocyanidol). The amount of colouring pigment present varies from 2.0 to 2.25%.

![Onion molecule](image)
2.3 Hina (*Lawsonia inermis* L):
It is the leaf of the plant that is traditionally used in making the coloured design on the hands of women. The leaf of the plant is dried, crushed and subsequently boiled with water to extract the dye from leaf. The mordanted fabric gives colour from brown to mustard yellow. This is the dispersed dye type colour; hence, polyester and nylon can be dyed by hina. However, it stains wool and silk giving a lighter brown colour. Hina is commonly known as lawsone. The chief constituent of hina leaves is hennotannic acid; it is a red orange pigment. Chemically hennotannic acid is 2-hydroxy-1,4-naphthoquinone. The colouring molecules have strong substantivity for protein fibre.

![Henna molecule]

2.4 Beetroot (*Beta vulgaris*)
Chop the beets into 1inch pieces (no need to peel unless they are extremely dirty). Place the beets in a pot and cover with enough water to cover the beets by two inches. Bring to a boil then reduce heat, simmer 'til the beets have turned a lighter shade of red and are easily pierced with a fork. Let cool to room temperature and place the liquid and beets into a blender. Blend on high until the beets are fully processed. Place a fine mesh strainer over a large bowl and pour the beet slurry into the strainer. Press down on the beets to extract as much liquid as possible. You can discard the beets or save them for another purpose—we made a spicy beet & yogurt dip with pita and it was delicious. Pour the dye into squeeze bottles if you have them or just set the bowl to the side.

![Beetroot molecule]

**Fig.2 Method for extraction of dyes** Same methodologies are used for extraction of other dyes as per the literature data.
Fig. 3 Schematic representation of extraction of natural dyes from natural resources

Table 1: Different plants use for extraction of dyes

<table>
<thead>
<tr>
<th>Code</th>
<th>Common Name</th>
<th>Botanical Name</th>
<th>Part Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>a.</td>
<td>Haldi</td>
<td>Curcuma longa</td>
<td>Rhizome</td>
</tr>
<tr>
<td>b.</td>
<td>Onion</td>
<td>Allium cepa</td>
<td>Tunic</td>
</tr>
<tr>
<td>c.</td>
<td>Mehandi</td>
<td>Lawsonia inermis</td>
<td>Leaves</td>
</tr>
<tr>
<td>d.</td>
<td>Beet root</td>
<td>Beta vulgaris</td>
<td>Fruit</td>
</tr>
<tr>
<td>e.</td>
<td>Palak</td>
<td>Spinacia oleracea</td>
<td>Leaves</td>
</tr>
<tr>
<td>f.</td>
<td>Mayalu</td>
<td>Basella alba</td>
<td>Fruit</td>
</tr>
</tbody>
</table>

Table 2: Different moderates use in extraction process

<table>
<thead>
<tr>
<th>Mordants</th>
<th>Pre-mordants</th>
<th>Post-mordants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum acetate</td>
<td></td>
<td>5% FeCl₃</td>
</tr>
<tr>
<td>Cream of tartar</td>
<td></td>
<td>5% CuCl₃</td>
</tr>
</tbody>
</table>

3. MORDATING PROCESS
3.1 Pre-mordanting:
In premordanting process, mordanting is done before dyeing; subsequently the fabric is dyed with natural dye in aqueous media. It is a twobath process in which the first bath is used for mordanting of fabric and in the second bath, dyeing is done with natural dyes. Dyeing and mordanting are done at the same temperature of 60–70°C. The mordants are complexing agents, and if they are taken in the same bath, they
may react to each other, and precipitation of dyes may occur. That deteriorates fastness properties of dyed fabrics.

3.2 Meta-mordanting:
In metamordanting treatment, the mordant chemicals are added with natural dye in the same dye bath; dyeing and mordanting take place simultaneously. The mordanting and dyeing temperature are 80–90°C.

3.3 After- mordanting:
In after mordanting treatment, the dyeing of fabric is done first; after that in the same bath mordanting compounds are added. The temperature of chroming is 80–90°C. After chroming, the temperature is dropped to 60°C, and goods are run for 15 minutes after that liquor is drained. The application of natural dyes on cellulosic materials are done by the pad-drywashing and pad-dry-steaming-washing method. High-temperature curing is not suggested as dye molecules are susceptible to decompose. Fibre and yarn dyeing can also be done with natural dyes similar to synthetic dye application.

4. RESULTS AND DISCUSSION
The extracted dyes were characterized with help of different characterization techniques such as optimizations, UV analysis, FT-IR analysis, TGA analysis.

4.1 Optimization of system

![Graphs showing optimization of solvent, temp., & pH of process.](image)
The extraction process was optimized as shown in Fig 4 different solvents, temperature and pH of natural dyes. As seen from Fig. 4 absorbance versus solvent and from this graph it shown that ethanol show higher absorbance than other solvents. Same methodology applied in case of temperature parameter and it was seen that as temperature increases absorbance of natural dyes are also increases. pH is important parameter to analyse the application point of view and from graph seen that as pH increases the absorbance of natural dyes are also increase. For representative study we taken *Beta vulgaris* as it has more strong colorations.

The effect of dyeing temperature on colour strength is verified in Fig. 5 Maximum colour strength was obtained at 100°C. High temperature will lead to high value of entropy, increase the kinetic energy of dye molecule as well as increasing the pore size of the fiber, which allows dye molecules to speedily penetrate into the fabric and distribute themselves very easily all over the available dye sites. The increase in kinetic energy of the molecule lead to the molecule moving faster from the solution in to the fiber, and this carry about reduction in the time of dyeing.

The effect of salt concentration on colour strength is shown in figure 5. The colour strength was increased steadily by increasing the concentration of salt (sodium sulphate) from 0g/L to 100g/L as per the literature survey Saminu et al. (2022). It was seen that increase in salt concentration had sporadic effect because of increase in dye aggregation at high salt concentrations.

4.2 UV analysis

![UV-visible spectra of dyes](image-url)
The ultraviolet-visible spectroscopy (UV) is used to measure how much a substance absorbs light. As we can seen from UV spectra, Dyes shows absorbance at around 250 nm and 400-450 nm is due to n-π* transitions in compound.

4.3 FT-IR analysis

The FT-IR analysis of above compound is use to identify functionality in given organic compounds. The peaks observed at around 2500 cm⁻¹ is due to aromatic region and 1500-500 is due to -OH & -NH stretching and bending vibrations in dyes.

![FT-IR analysis of natural dyes](image)

**Fig.7 FT-IR analysis of natural dyes**

The FT-IR analysis of above compound is use to identify functionality in given organic compounds. The peaks observed at around 2500 cm⁻¹ is due to aromatic region and 1500-500 is due to -OH & -NH stretching and bending vibrations in dyes.

![Application of extracted natural dyes in fabrics, textiles and decoration](image)

**Fig.8 Application of extracted natural dyes in fabrics, textiles and decoration**
5. CONCLUSION
The current work indicated that natural dye may be successfully extracted from the plant material. The colour strength increases with increased in temperature, high salt concentration and increased dyeing time. The dye cotton fabric exhibit fairly good fastness properties. Extracted products may use social applications. Simple and effective protocol with green approach. This technique provides effective use of natural resources as eco-friendly technique and alternative of synthetic dyes.

6. ACKNOWLEDGEMENTS
An author acknowledges the DST-FIRST for financial support. We are sincere, thanks to principal and also HOD of M.S.G. College Malegaon for providing infrastructure and laboratory facilities.

7. REFERENCES


