

Greener developments in the process of textile dyeing: A Review.

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The textile industry, which uses hundreds of chemicals in production, from raw material to disposal, is generally regarded among the most polluting industries. Some 72 toxic chemicals have been identified in water solely from textile dyeing, 30 of which cannot be removed. Increasing demand for sustainable dyeing processes is evident due to such environmental concerns, opening the door for exploitation of various new techniques of coloration with the help of modern scientific inputs so that modified naturally available dyes and colourants can offer themselves as effective ecologically benefiting alternative in various traditional and advanced application disciplines. In this review, we discuss various such advancements taken to adopt a greener step in the ladder of textile coloration and dyeing along with some newly discovered applications of natural dyes.

1. Introduction

The textile industry produces and uses approximately 1.3 million tons of dyes, pigments and intermediates, valued at around US\$23 billion, almost all of which is manufactured synthetically. Until the second half of the 19th century, all dyes used in textiles were naturally obtained. However, with the synthesis of mauveine by Perkin in 1856 [1], the synthetic dye industry has grown at a dynamic rate which led to total eradication of the use of natural dyes. The large number of synthetic dyes in use today bear witness to the creativity and innovation of textile chemists in successfully satisfying the dyer's demands for simple and reproducible application methods, and the consumer's demand for quality products at an equitable price. There are many limitations of synthetic pigments. The precursors, used in the production process of synthetic pigment, have many carcinogenic hazardous effects on the workers. The wastes from the production process are also harmful. And above all, they are not environment friendly or biodegradable. Under the current situation where environmental friendliness of the process is highly stressed on, the use of synthetic dyes has become a constraint. To counter these hazardous effects of synthetic colourants, there is global interest in development of processes for the production of pigments from natural sources. The application of natural pigments in foodstuff, dyestuff, textile and pharmaceutical manufacturing processes has

been increasing in recent years based on the demand. Of all the available resources for exploiting natural colourants, plants and microorganisms are the two major sources. Despite overcoming the disadvantages of synthetic dyes, the natural pigments from plants also have their own drawbacks such as: instability against light, heat or adverse pH, low water solubility and frequent non-availability throughout the year. Such factors have led to research into new methods involving micro-organisms as source as well as catalyst in the procedure of textile dyeing. Also, to overcome some of the disadvantages of naturally occurring colourants, the natural dyes have also been modified to suit the need of the process and the substrate without the use of metals for mordanting and complexing.

2. Discussions

2.1 Modified Natural Dyes

Natural dyes are dyes or colorants derived from plants, invertebrates, or minerals. The majority of natural dyes are vegetable dyes from plant sources—roots, berries, bark, leaves, and wood—and other biological sources such as fungi and lichens. Since the dawn of synthetic dyes, focus has completely shifted away from the application of natural dyes in textile dyeing.

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However, due to the stringent environmental standards imposed by many countries in response to the hazardous effluent generated during synthesis of synthetic dyes, the textile researchers have once again been enthralled by natural dyes. Today, many are rediscovering the joy of achieving colour through the use of renewable, non-toxic, natural sources by using natural dyes as available or by modifying them by various methods [2]. Since coupling with metal ions also reduced the naturalness of the so-obtained dyes, only the work involving dye modification without metal ion coupling has been considered.

Pawar et al studied dyeing of 100% polyester fabric with an ancient source of natural dye (KasimKaaram) [3]. This ancient source of natural dye was chemically modified to substantivity and tinctorial capacity to overcome the inherent limitations of natural dyes by coupling it with diazonium salts of three different primary amines. Its assessment of the fabric dyed with this colourant was done in terms of CIELAB colour space values and colour strength was determined using K/S values. The results so obtained showed that they were in agreement with the spectral data of all three modified natural dyes. Higher K/S value implied greater depth on fabric. Excellent all-round fastness properties for the three modified natural dyes were shown. Wash fastness showed “very good” to “excellent” on the scale, rubbing fastness results were in the range “very good” to “excellent” and light fastness properties were also found to be excellent for all the dyed fabrics. Also, in case of sublimation fastness for all the three dyes, excellent fastness properties were obtained.

Availability of very limited data on the use of modified natural dyes is facilitated by the fact that this method is relatively very new and no commercial scale progress of this process has been observed. Nevertheless, research on this method still continues based on the advantages offered by this process and its future prospects.

2.2 Microbial Colourants

Microorganisms are known to be a potential source for bio-pigment production due to their advantages over plants in terms of availability, stability, cost efficiency, labor, yield and easy downstream processing. The pigment production from microorganisms is an efficient and intensified process as compared to chemical synthesis of pigments. Varieties of bio pigments have been obtained such as carotenoids, melanins, flavins, quinines, monascins,

Dye	Hue on polyester	Dyed sample
NA1	Bright brown	
NA2	Bright grey	
NA3	Dark brown	

Figure 1: This figure represents the hue dyed on polyester and a visual of the dyed sample. [3]

and violacein using microorganisms [4,5]. Cultivation of microorganisms can be accomplished through solid state and submerged fermentation on natural raw material or industrial organic waste. Microbes can grow easily and at a very fast rate in the cheap culture medium and their growth is independent of the weather conditions. Many of the microbial pigments not only act as colourants, but also possess anticancer, antioxidant, anti-inflammatory, anti-microbial properties. Hence, microbial pigments are of great interest owing to the stability of the pigments produced and the availability of cultivation technology. Microbial colours are available in different shades. These colours are biodegradable and environment friendly. Only limited research studies are available on exploration of microorganisms for colour/pigment production especially in the Indian scenario, which really points towards exploring microbial pigments in more detail.

Practically, fermentation of microorganisms such as fungi and bacteria could be an appreciated source of

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manufacturing colorants. Microorganisms produce a large variety of stable pigments such as carotenoids, flavonoids, quinones, and rubramines, and the method of fermentation gives higher yields of pigments and lower residues compared to the use of plants and animals as raw material [6].

Alihosseini et al. characterized the bright red pigment prodigiosin from *Vibrio spp* [7]. Their study suggested that this pigment could be used to dye many fibres including wool, nylon, acrylics and silk.

Yusof reported the capability of using pigment from *Serratia marcescens* [8] to colour five types of fabric, namely, acrylic, polyester microfibre, polyester, silk and cotton, using tamarind as mordant. The study concluded that the dyeing performances are different, depending on the types of fibre and the dyed fabrics also have the ability to maintain their colour under several external conditions such as perspiration, washing, and rubbing/crocking.

A similar study was also reported for *Janthinobacterium lividum* [9] which gave a good colour tone when applied on silk, cotton and wool (bluish purple) and nylon (dark blue). Dyeing was performed by a simple procedure consisting of either plunging in the pigment extract or boiling with the bacterial cells. Colour variation was achieved by changing the dipping time and the temperature of the dye baths.

Ahmad et al. characterized the red pigment prodigiosin (*Serratia marcescens*) [10] and the violet pigment violacein (*Chromobacterium violaceum*) and tested their dyeing efficiency on different fabrics – pure cotton, pure silk, pure rayon, jacquard rayon, acrylic, cotton, silk satin and polyester. Their results suggested that prodigiosin could be used to dye acrylic and for violacein, intense colorations were observed in pure rayon, jacquard rayon and silk satin.

Ahmad et al. noted the applications of prodigiosin and violacein in batik making [11]. The chosen pattern was first drafted onto the fabric by a “Batik-Tulis” maker i.e., the painter, using pencil. Then, a mixture of beeswax and paraffin wax was spread over the drafted motifs by a technique called “canting”. After the waxing process, the fabrics were dyed using the bacterial pigments using the brushing technique. The colour tone was adjusted by adding either ethyl acetate (for red and purple pigment) or acetone (yellow pigment). This was followed by immersing the fabrics into boiling water containing fixating agents to remove excessive wax as well as fixing the bacterial

pigments onto the fabrics. The “batik” was then allowed to dry under mild sunlight (Fig. 2).

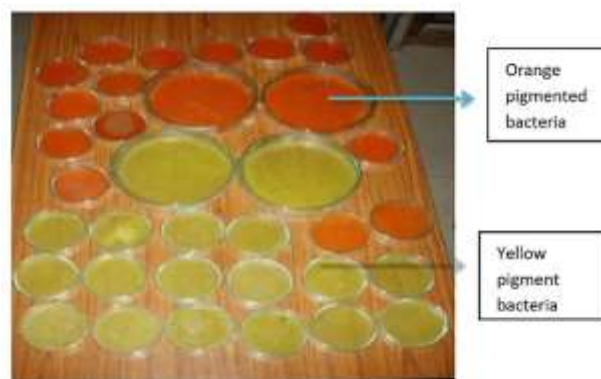


Figure 2: Application of microorganism-based pigments on various wool samples done in a company targeting the launch of microbial pigments on a commercial scale for textile coloration. (Source: MICOLOR [15])



Figure 3: Coloured multifiber fabric with red pigments from *Vibrio spp*. (Source: Process Biochemistry 48 (2013))

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S. No.	Name of dye	Source	Application
1.	Prodigiosin44	<i>Vibrio</i> spp.	Wool, nylon, acrylics and silk
2.	Red Prodigiosin45	<i>Serratiamarcescens</i>	Acrylics, polyester, polyester microfiber, silk and cotton
3.	Pigments from	<i>Jaethinobacterium lividum</i>	Silk, cotton and wool (bluish-purple, all-natural fibres) and nylon and vinylon (both synthetic fibres)
4.	Violacein (violet pigment)46	<i>Chromobacterium violaceum</i>	Pure cotton, pure silk, pure rayon, jacquard rayon, acrylic, cotton, silk stain and polyester
5.	Pink pigment	<i>Roseomonasauri</i>	Cotton fabrics
6.	Pigments from	<i>Fusariumoxysporum</i> , <i>Trichoderma viride</i> and <i>Alternaria</i> spp.	Cellulosic fibres
7.	Anthraquinone	<i>Demodice sanguine</i>	Wool fibres.
8.	Pigment from	<i>Trichoderma</i> spp.	Wool and silk fibres.

Figure 4: Sources and uses of microbial colourants in textile industry

2.3 Enzyme Catalysed Dye Synthesis

With the increasing demand for textile manufacturers to reduce pollution in production processes, the use of enzymes in the chemical processing of fibres and textiles is rapidly gaining wider recognition because of their non-toxic and eco-friendly characteristics. They can be safely used in wide varieties of textile processes such as de-izing, scouring, bleaching, dyeing and finishing, as an alternative to the very harsh chemicals currently used, the disposal of which into the environment causes many complications. Textile processing has benefitted greatly in both, environmental impact and product quality, through the use of enzymes. From the 7000 enzymes known, only about 75 are commonly used in textile industry processes [12]. There are already some commercially successful applications, such as amylases for desizing, cellulases and laccases for denim finishing, and proteases incorporated in detergent formulations.

Textile dyeing with enzymes aims at the application of colours obtained from various enzymes onto the textile substrates by either in situ development of colour on the substrate or by preparation of colourants from the enzyme and then transferring it onto the substrate.

Sun et al. studied the enzymatic dyeing of cotton, silk and wool fibres by the use of ferulic acid (FA) through polymerization [13]. FA possesses many physiological functions, and it acts as an antioxidant, antimicrobial, anti-inflammatory, anti-thrombosis, and anti-cancer agent.

FA was used to dye fabrics using two methods – simultaneous enzymatic polymerization of FA and dyeing (one-step method), and enzymatic polymerization of FA followed by dyeing (two-step method). In the case of enzymatically treated fabrics, remarkable changes in colour parameters were found. This is especially true for silk and nylon fabrics. The reason for this phenomenon is the laccase-catalysed polymerization of phenolic FA, the formation of an intensive yellow colour and the uptake of Polymerized Ferulic Acid (PFA) by fibres. Indeed, the enzymatically dyed fabrics show obviously increased a^* and b^* indices, and obviously decreased lightness (L^*). The enzymatic dyeing with FA increases the UV-protection properties of the fabrics although the increment depends completely on the fibres. This phenomenon is especially remarkable for viscose and cotton fabrics.

R. Bai et al. worked on laccase-catalysed in-situ dyeing of wool fabric [14]. In this study, wool fabrics were treated with laccase/phenol via a one-step or two-step treatment, and polymers synthesized in-situ were used to dye wool fabrics. The K/S values of the wool fabrics were evaluated under different treatment conditions, including the dosages of laccase and dye precursor, temperature, pH, mediator type, and mechanical agitation. The surface of wool fibres was examined using a scanning electron microscope (SEM). Wool fabrics were treated with laccase in the presence of monomer (catechol) using three different processing methods. The first method was named as a one-step method in which enzymatic polymerization and in-situ dyeing of wool fabric was simultaneously undertaken. The second was denoted as the two-step method (1) as shown in Fig 5. In this method, the reaction solution containing laccase and catechol was incubated for the first 1 h for enzymatic catalysis and polymerization of colour followed by addition of wool fabric into the solution for further 4 h for textile dyeing at the same treatment conditions. The third was denoted as the two-step method (2). In contrast to the two-step method (1), wool fabric was immersed in the reaction solution containing catechol but in the absence of laccase at the same liquor ratio and 50 °C for the first 1 h and then laccase was added to the mixture and continued for 4 h treatment. Post dyeing, all the dyed wool fabrics were washed thoroughly with water. The results showed that the dyeing effect of the wool fabric samples using the single step processing method of in-situ colour synthesis and fabric dyeing was better than those dyed using the two-step methods of colour synthesis and fabric dyeing under the same conditions. The colour depth of the dyed wool

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fabrics increased gradually with increasing concentration of laccase, and also depended on other process parameters, such as dosage of catechol, temperature, and pH.

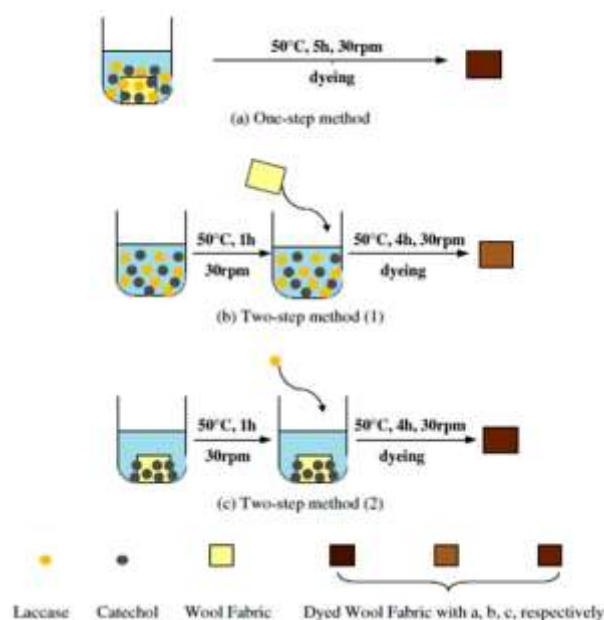


Figure 5: A schematic representation of one step and two step methods for laccase-catalysed in situ dyeing of wool fabrics. [14]

3. Conclusion

Natural dyes which have the advantages of being less expensive, non-hazardous and sustainable have caught the attention of research scientists all over the world. All the methods described above are greener and ecofriendly methods of dyeing textile fabrics hence reducing the amount of damage done to the environment. With increasing attention to the environment and the need of shifting towards lesser polluting methods of textile processing, it is imperative to adopt such developing technologies. A lot of research is going on currently to make these processes even more efficient.

The usage of enzymes in the textile industry to help improve fabric quality is a step towards environment friendly methods of processing of fibres. Various enzymes are used owing to the different steps of fibre processing for the preparation of dyes and colourants before dyeing and in-situ as well. Different methods using natural colorants and enzymes have been used in the processing of cotton, silk, wool and other fibres. Results obtained show that such

methods give better dye uptake and higher total adsorption than normal methods. The color measurement values (e.g. K/S) also showed significant improvements.

Among the natural Sources, pigment producing microorganisms hold a promising potential to meet present day challenges. Furthermore, natural colours not only improve the marketability of the product but also add extra features like anti-oxidant, anti-cancer properties etc. These microbial pigments have broad area of application, mainly in food industries, pharmaceutical industries and textile industries. Food grade pigments such as β -carotene, Arpink Red, Riboflavin lycopene and Monascus pigments are used in food industry. In pharmaceutical industry pigments like treat diseases. Several microbial Pigments are also used in textile industry.

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