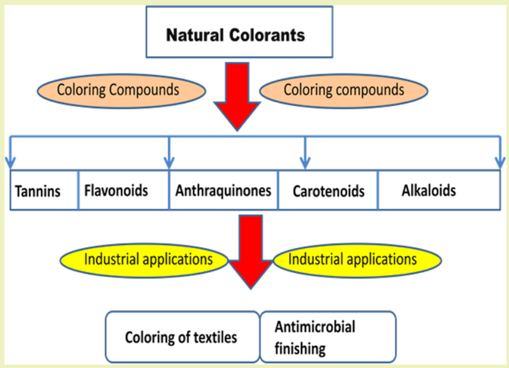
ACS Sustainable Chemistry & Engineering
Perspective
pubs.acs.org/journal/ascecg

Natural Colorants in the Presence of Anchors So-Called Mordants as Promising Coloring and Antimicrobial Agents for Textile Materials

Shahid-ul-Islam and Faqeer Mohammad*

Department of Chemistry, Jamia Millia Islamia (A Central University), New Delhi-110025, India

ABSTRACT: In recent years there has been a phenomenal increase in the use of natural colorants in a variety of areas. They exhibit high biodegradability, low toxicity, and green chemistry and have potential to greatly impact the textile dyeing and finishing industry. Natural colorants from plant sources have been recently discovered as novel agents in imparting multifunctional properties to textiles such as antimicrobial, insect repellent, deodorizing, and UV-protective. Among all textile surface modifications, antimicrobial finishing has become a very promising, high growth research area due to their potential to provide quality and safety benefits to different kinds of textile materials. The use of natural colorants offers promise in developing antimicrobial textiles for aesthetic, hygienic, and medical applications owing to the presence of potent highly active agents such as tannins, flavonoids, quinines carotenoids, and alkaloids in their extracts. This article presents a concise account of the state-of-the art sustainable technology derived from natural colorants and will be useful to the textile and polymer chemists engaged in development of health care bioactive textiles. In particular, it discusses recent developments in coloring and antimicrobial finishing of textiles with different class of compounds isolated from natural colorants, highlights current challenges, and finally concludes by providing a perspective on future research directions in this area.



KEYWORDS: *Natural colorants, Polyphenols, Antimicrobial activity, Textile fibers*

■ INTRODUCTION

The textile industry is a diverse, heterogeneous sector which involves several wet processes in the production of a wide variety of products.[1−3] Cotton, wool, silk, and linen fibers are the most widely used natural fibers in textile industry today; they are used to make soft, breathable, and functional textiles for a wide range of applications.[4−7] Despite their endless uses, they have some drawbacks, mainly the susceptibility to microbial attacks.[8] They provide several favorable conditions such as moisture, temperature, oxygen, and nutrients required for rapid growth and multiplication of pathogenic microorganisms resulting in high offensive odors, color degradation, cross-infections in hospitals, and transmission of diseases, allergic responses, and deterioration of textile materials.[9,10] To overcome these problems, scientists have applied some innovative antimicrobial finishes on textile surfaces. Substantial investigations have revealed the application of wide range of synthetic chemicals and auxiliaries as antimicrobial agents, etc.[11,12] However, most of the synthetic agents either produce toxic chemicals or generate dangerous effluents thus pose considerable energy and environmental challenges. Therefore, the textile processing industry has imposed strict bans on certain synthetic dyes and auxiliaries which are posing serious challenges to sustainability issues. This has led to tremendous current excitement in the search for environmentally friendly products which can offer suitable alternatives/copartners to these agents.[13−15]

Natural colorants can be explored toward achieving safe and environmentally friendly textile products.[16−20] Humans have used natural dyes since antiquity, however in the last two decades there has been a phenomenal increase over their use in a variety of areas.[13,21−23] They exhibit high biodegradability, low toxicity, green chemistry, and have the potential to greatly impact the textile industry which is considered as one of the most polluting industry today.[24−28] Recent research in the natural dye area have identified them as novel agents in imparting multifunctional properties to textiles such as antimicrobial, insect repellent, deodorizing, and UV-protective.[29−32] Of all these fascinating fields antimicrobial finishing has become a very promising, high growth research area due to their potential to provide quality and safety benefits to both textile materials and precious human life.[13,33,34] Owing to the existence of large number of structurally diverse active compounds such as tannins, flavonoids, curcuminoids, alkaloids, and quinines in their extracts, the use of natural colorants offers promise in developing antimicrobial textiles for aesthetic, hygienic, and medical applications in the near future.[35−37]

It is worth mentioning that most of the natural colorants involve the use of anchoring agents which are known as mordants.[38,39] Use of several anchors such as metal salts and

Received: June 16, 2015
Revised: August 4, 2015
Published: August 26, 2015

DOI: 10.1021/acssuschemeng.5b00537
ACS Sustainable Chem. Eng. 2015, 3, 2361−2375

Table 1. Different Classes of Antimicrobial Natural Dyes Tested on Textiles and Polymers

natural colorant	class	textile materials	microbes	ref
Acacia catechu	tannin	wool, cotton	*S. aureus, E. coli, B. subtilis, K. pneumonia, , P. vulgaris, P. aeruginosa, C. albicans,* and *C. grablata*	45, 72
Punica granatum		wool, cotton	*S. aureus, E. coli, P. aeruginosa, C. albicans,* and *C. grablata*	60, 71, 144
Quercus infectoria		wool, cotton	*S. aureus, E. coli, B. subtilis, K. pneumonia, P. vulgaris, P. aeruginosa, K. pneumonia, C. albicans,* and *C. grablata*	36, 68, 72, 145
Termanalia chubula		cotton	*E. coli, K. pneumonia,* and *P. vulgaris*	71
Chemalica sensesis		wool	*S. aureus, E. coli,* and *P. aeruginosa*	
Saraca asoca		silk	*Aspergillus niger*	
Rheum emodi	anthraquinone	wool, silk, cotton	*S. aureus, E. coli, K. pneumonia, P. vulgaris,* and *C. tropicalis*	44, 71, 91
Rubia cordifolia		wool	*S. aureus, E. coli, B. subtilis, K. pneumonia, P. vulgaris,* and *P. aeruginosa*	72
Kerria lacca		wool	*S. aureus, E. coli, B. subtilis, K. pneumonia, P. vulgaris,* and *P. aeruginosa*	72
Lawsonia inermis	alpha-naphthoquinone	wool	*S. aureus, E. coli, P. aeruginosa, C. albicans,* and *C. grablata*	42, 46, 111
Juglons regia		wool	*S. aureus, E. coli,* and *P. aeruginosa*	60
Juglons regia		polyamide	*S. aureus* and *E. coli*	94
Albizia lebbeck	flavonoid	silk	*Aspergillus niger*	
Acacia nilotica		cotton	*E. coli, K. pneumonia,* and *P. vulgaris*	71
Mallotus philippinensis		cotton	*E. coli, K. pneumonia,* and *P. vulgaris*	71
Crocus sativus	carotenoid	wool	*S. aureus, E. coli,* and *P. aeruginosa*	43
Curcuma longa	curcuminoid	wool, silk, cotton	*S. aureus* and *E. coli*	91, 146, 147
Beta vulgaris	alkaloid	cotton	*S. aureus*	127
Opuntia lasiacantha		wool	*E. coli, B. subtilus, P. aeruginosa,* and *S. aureus*	22

biological agents including chitosan and other newly discovered biomordants from plant species have gained significant academic interest and have contributed substantially to overcome the drawbacks such as narrow shade range and lower color fastness properties of naturally dyed textile materials.[21,40] Lately, textile and polymer chemists have explored that the use of natural mordants have synergistic effects on antimicrobial characteristics of dyed samples.[41] For example lawsone a natural colorant from henna leaves with inherent antibacterial property when applied on wool previously pretreated with chitosan was found more active against *E. coli* and *S. aureus* than control dyed samples.[42] On the other hand metal salt mordants may either enhance or decrease the antimicrobial activity depending upon the applied antimicrobial test method.[43,44] However, the use of metal anchors has proved markedly effective in retaining the antimicrobial activity up to several laundering cycles which is greatly appreciated by today's demanding consumer market.[44−46] This is attributed to strong complex forming ability of metal ions with the active functional sites of dye molecules. In view of these facts, this article is aimed to summarize some latest research studies carried out in this realm followed by critical analysis of the use of different class of compounds isolated from natural dye yielding plants as promising coloring as well as antimicrobials agents for textile materials (Table 1). This perspective also highlights the current challenges and provides scope for further investigations to corroborate the existing gaps in this area of study.

■ TANNIN RICH EXTRACTS

There has been an enormous attention over the past few decades on the use of tannin rich dyes from vegetable sources in coloration of textile materials.[13] Tannins are polyphenolic compounds having molecular weight between 500 and 3000 Da and are obtained from various plant parts including roots, barks, leaves, flowers, skins, fruits, and shells.[47] The high tannin content in some plant extracts has raised interest in using these dyes to produce textiles with deodorizing, antimicrobial, antifeedant and UV protective properties. The antimicrobial activity of natural polyphenols against various bacteria, fungi and yeasts is one of their attractive features which facilitate their use in a variety of application fields including pharmaceutical, food, feed, dyestuff, cosmetics, and other chemical industries.[48] Several different mechanisms for microbial inhibition by tannins have so far been proposed. Its mode of action is believed to be the inhibition of extracellular microbial enzymes, deprivation of the substrates such as electrolytes, UV-absorbing material, proteins, etc., required for microbial growth or direct action on microbial metabolism through inhibition of oxidative phosphorylation.[49,50] Ikigai and co-workers[51] observed that the catechins from green tea extract induced leakage of 5,6-carboxyfluorescein from phosphatidylcholine liposome from bacteria and suggested that the death of cells resulted from the disruption of bacterial membrane. They found that Gram-positive bacteria were more susceptible to catechins as compared to Gram-negative bacteria. This was attributed to the presence of lipopolysaccharides in Gram-negative bacteria which render to the bacterial surface a density of negative charges superior to that observed for Gram-positive ones. Other mechanism suggests that the antimicrobial activity is due to the generation of hydrogen peroxide. Hoshino and co-workers[52] found that in the presence of a non lethal concentration of copper(II) metal ion, catechins are more effective against Gram-negative *E. coli* than Gram-positive *S. aureus*. They believe that the interaction of (−)-epigallocatechin, (−)-epicatechin, and copper(II) results in the generation of hydrogen peroxide which accounts for its bactericidal activity.

In view of their potent antimicrobial activity, tannin rich extracts have gained wide attention to impart color and other

DOI: 10.1021/acssuschemeng.5b00537
ACS Sustainable Chem. Eng. 2015, 3, 2361−2375

functional characteristics to different textile materials. Of all the tannin based natural dyes investigated, the peels of pomegranate fruit have attracted huge scientific attention as it produces colorful shades with antimicrobial activity.[13] Pomegranates are rich in polyphenolic compounds; the main polyphenols that have been reported include punicalagins, punicalins, gallagalic acid, gallic acid, and ellagic acid. Gulrajani and co-workers[53] used pomegranate in conjunction with other natural dyes to yield six basic shades such as blue, yellow, red, black, green, and fawn on cotton fabrics. Tiwari et al.[54] reported the extraction of natural dye from pomegranate rind using ultrasound; enzyme and enzyme-mediated ultrasound assisted extraction processes and studied its dyeing properties on wool and silk fabrics. Sinha et al.[55] evaluated the effect of microwaves in the extraction of yellow dye from pomegranate rinds. They found that the extraction time of 90 s, pH 3.5, and 1.48 g of sample are the optimum conditions for the maximum yield of color from pomegranate rinds. In another investigation which was conducted by Adeel et al.,[17] the influence of gamma radiations on both dye extraction from pomegranate peel and their dyeing properties on silk were determined. Gamma doses of 20, 25, 30, 35, and 40 kGy were used and it was found that gamma ray treatment of 40 kGy is an effective way to improve extraction and produce shades on silk with better fastness properties. Shams-Nateri[56] reported yellow color on nylon dyed with weld and pomegranate peel extracts. Lee et al.[57] reported that cotton, silk, and wool fabrics dyed with the extract of pomegranate and other natural colorants showed antimicrobial activity against *S. aureus* and *K. pneumonia*. The phenolics and flavonoid compounds present in pomegranate have been found to be responsible for its antimicrobial activity.[58] Lee et al.[59] observed the excellent deodorising property against ammonia gas and good anti-bacterial activity against *S. aureus* and *K. pneumonia* of cotton, silk, and wool fabrics dyed with *Punica granatum* L. extracts. Ghaheh and co-workers[60] studied the effect of mordant salts on dyeing, fastness, and antibacterial activity properties of wool fabric dyed with pomegranate peel and walnut shell extracts. The antimicrobial activity was carried out against Gram-positive *P. aeruginosa* and *E. coli*, and one Gram-positive bacterium, *S. aureus*, and it was found that antibacterial activity of the extracts is greatly enhanced in the presence of metal salts. Davulcu et al.[61] in their research investigation studied the dyeing, fastness, and antimicrobial properties of cotton fabric treated with thyme and pomegranate peel extracts. Their study showed that pomegranate peel can successfully be applied on cotton with or without metal mordants to produce good color fast shades with excellent antimicrobial activity against *Staphylococcus aureus*. Prahbu and Teli[41] applied *Tamarindus indica* L. seed coat tannin as a biomordant alone and in combination with metal mordant copper sulfate on cotton, wool and silk fabrics dyed with turmeric and pomegranate peel to study the color properties and antibacterial activity of dyed fabrics against *S. aureus* and *E. coli*. They observed higher color strength values for mordanted samples and also found that the antibacterial activity was maintained for more than 20 washing cycles. In 2015, Benli et al.[62] screened different natural colorants including pomegranate peels for dyeing of ozone and ultrasound pretreated cotton to find their use as alternatives to conventionally dyed cotton and suggested that the peels from pomegranate could be used as effective dyeing material with acceptable fastness properties.

Gallnut is another promising antimicrobial natural coloring dye which finds extensive application in tanning, mordanting, dyeing, and in the manufacture of ink.[21] It is rich in ellagic acid which has affinity for dyeing substrates due to presence of auxochrome group −OH. Gallnut has a wide range of pharmacological activities and has been used as ointment for the treatment of piles and in plasters.[63] Gallnut extract contains mainly tannin (gallotannin, 50−75%), as well as smaller molecules such as gallic acid and ellagic acid.[36] Gallnut extract was a principal ingredient in wool dyes used as early as the fifth century BC.[64] The application of gallnut on different textile substrates provides a variety of color shades. Onal and colleagues[65] studied the dyeing properties of ellagic acid extracted from gallnut on wool, feathered leather and cotton using three mordant dyeing methods at various pH values and obtained deep shades. Lee et al.[57] 2009 investigated the colorimetric analysis and antibacterial properties of cotton, silk, and wool fabrics dyed with peony, pomegranate, clove, *Coptis chinenis*, and gallnut extracts. The dyed fabrics displayed excellent antibacterial activity (reduction rate: 96.8−99.9%) against *Staphylococcus aureus*. However, in case of *Klebsiella pneumoniae*, the antibacterial activity was found to depend on the kind of natural colorant extract used. Shahid and co-workers[36] studied the inherent antimicrobial activity of gallnut extract before and after application on wool by employing microbroth dilution method, disc diffusion assay and growth curve studies against common pathogens *Escherichia coli*, *Staphylococcus aureus*, and *Candida albicans.* It was found that gallnut extract displayed excellent antimicrobial activity against the tested microorganisms and produced beautiful shades with acceptable fastness properties. Park et al.[66] reported that silk fabrics dyed with the extract from gromwell plant using gallnut as natural mordant showed good fastness properties. Hong et al.,[67] likewise, studied the effect of natural mordant gallnut on cotton fabrics dyed with gromwell extract. The gallnut treated cotton fabrics were found highly active against *S. aureus* and *K. pneumonia*. Koh and Hong[68] noticed that the gallnut extract dyed cotton and wool displayed good antioxidant and antimicrobial properties, and that the pretreatment using plasma improved their finishing effects. Zhang and co-workers[32] carried out the dyeing of wool with aqueous extract of Chinese gall using aluminum potassium sulfate mordant and obtained colorful shades on wool with good antibacterial activity against *S. aureus* and *E. coli* with a reduction percentage of 99.90% and 96.55% respectively. Lee et al.[69] in a more recent investigation have described deodorising and antibacterial properties of cotton, silk, and wool fabrics obtained by application of natural dye extracted from gallnut using water at 90 °C for 90 min with a fixed liquor ratio of 1:10. It was observed that the dyed fabrics display a reduction rate of 99.9% against *S. aureus* and *K. pneumonia.*

Another important tannin based dye is produced from Acacia catechu plant. Cutch extract is a brown dye produced by extraction of the heartwood of *Acacia catechu* containing mainly catechin as well as smaller molecules such catechutannic acid. Catechin with molecular formula of $C_{15}H_{14}O_6$ is reported to be the chief coloring component in cutch extract. Dyeing properties of catchu has been investigated on a variety of fibers. It was reported that dyeing of wool in the presence of transition metal mordants produces a variety of colors with good fastness properties for practical dyeing.[70] Gupta et al.[71] studied the antimicrobial property of several natural dyes against Gram-negative bacteria and found that *Acacia catchu* had high activity against *K. pneumonia* and *P. vulgaris*. Singh et al.[72] studied the antibacterial potential of catechu and other dyes against a range of Gram-negative bacteria such as *Escherichia coli*, *Bacillus subtilis*, *Klebsiella pneumoniae*, *Proteus vulgaris*, and *Pseudomonas*

DOI: 10.1021/acssuschemeng.5b00537
ACS Sustainable Chem. Eng. 2015, 3, 2361−2375

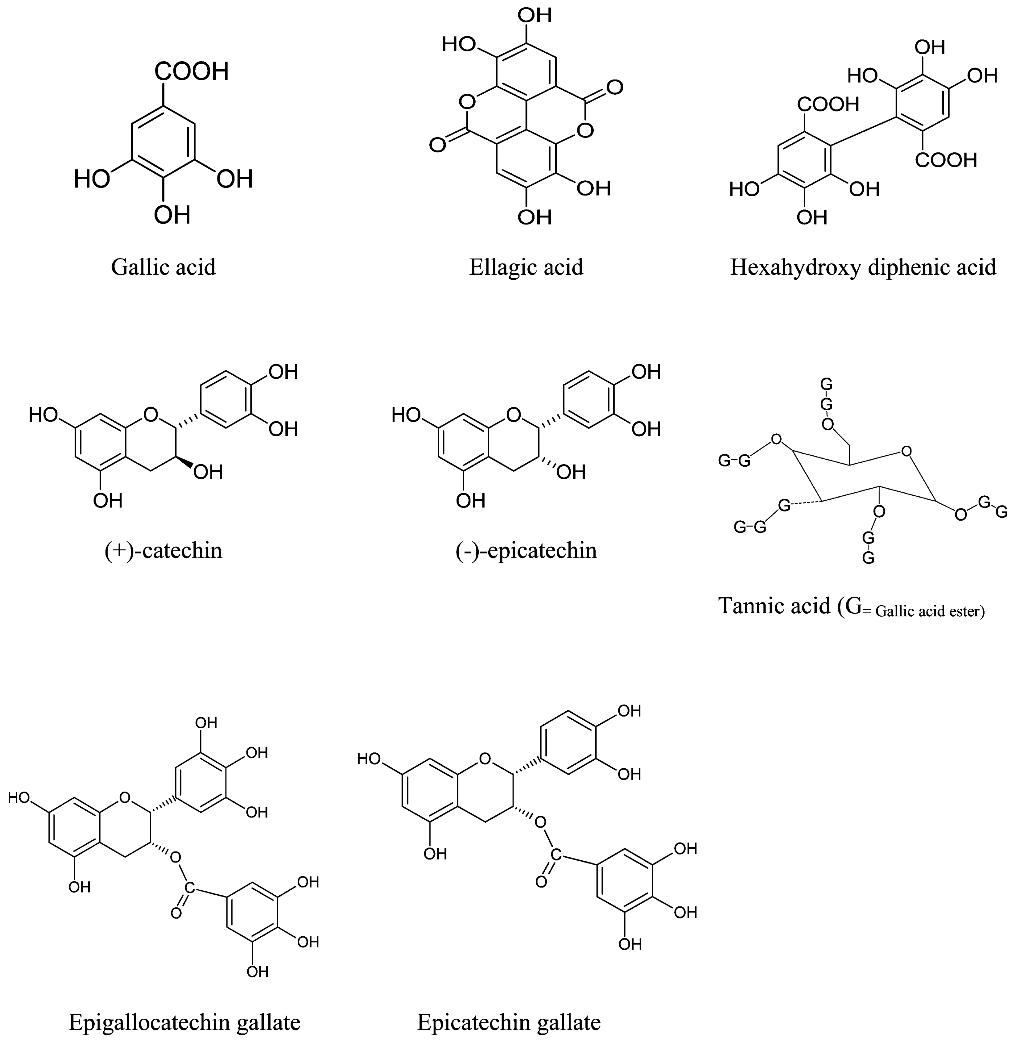


Figure 1. Structures of some tannin based coloring compounds.

aeruginosa before and after application on wool and found that the tannins present in catechu are responsible for its antibacterial effects. Vankar and Shanker[25] carried out the ultrasonic natural dyeing of enzyme pretreated cotton fabric with *Acacia catechu* and *Tectona grandis* natural dyes. The cotton that had been pretreated with enzyme showed a marked improvement in wash-fastness and light-fastness. The authors suggested that enzyme treatment results in better absorbency, adherence, and dyeability of the dyes on cotton fabrics, therefore could completely replace metal mordants. Recently Khan and co-workers[45] studied the antimicrobial activity of *catechu* in solution and percent microbial reduction after its application on wool samples against *Escherichia coli*, *Staphylococcus aureus*, *Candida albicans*, and *Candida tropicalis* by using microbroth dilution method, disc diffusion assay, and growth curve studies. They found that the dye shows maximum antimicrobial activity at 20% w/v, inhibiting the microbial growth by more than 90%. The hemolytic activity of the dye on human erythrocytes was studied to exclude its possibility of cytotoxicity and it was found to possess least toxicity to humans.

Considerable attention has been also focused on tea extract which is among the other prominent dyes rich in polyphenolic compounds. Tea polyphenols (TP) such as catechin are (−)-epicatechin (EC), (−)-epigallocatechin (EGC), (−)-epicatechin gallate (ECG), and (−)-epigallocatechin gallate (EGCG) are the main compounds reported in tea extract.[73] Several research studies have been carried out in recent years to explore the potential of tea as an effective textile dye. Deo and Desai[74] obtained deep shades with acceptable fastness properties on jute fabrics using tea as natural dye. In another investigation which was conducted by Kim,[75] the influence of chitosan premordanting on dyeing and the UV protection property of cotton dyed with the extract of tea were determined. It was worth to note that the chitosan treated cotton samples had better dyeing efficiency and higher UV protection than untreated fabrics. Moiz and co-workers[76] have studied effect of the mordant salts such as alum, $CuSO_4$, $FeSO_4$, $ZnSO_4$, Na_2SO_4, and $MgSO_4$ on dyeing of wool with an aqueous extract of tea using three different dyeing methods: premordanting, meta-mordanting, and postmordanting. They found that postmordanting method produces deep shades on wool with good wash and light fastness. Considering the great potential of tea polyphenol in dyeing and functional finishing of textiles, Tang et al.[77] recently investigated the adsorption kinetics and thermodynamics of tea polyphenols on wool, silk and nylon to understand the dyeing mechanism. They reported that the hydrogen bonding and electrostatic interactions operating between tea polyphenol and fibers contribute to Langmuir adsorption, whereas other interactions (hydrophobic interaction and van der Waals forces) contribute to Nernst partition adsorption. The chemical

DOI: 10.1021/acssuschemeng.5b00537
ACS Sustainable Chem. Eng. 2015, 3, 2361−2375

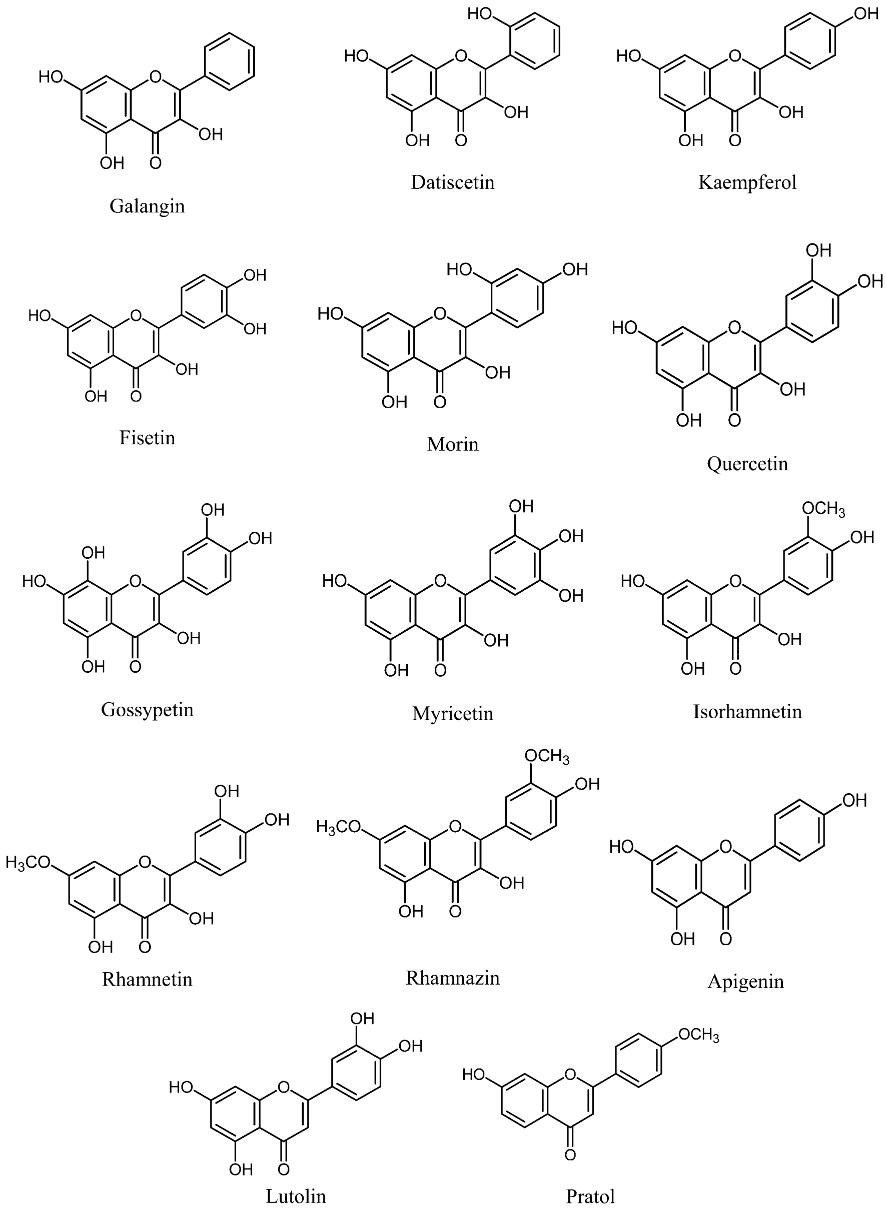


Figure 2. Chemical structures of some flavonoid dyes.

structures of some potential tannin based colorants isolated from vegetable sources are shown in Figure 1.

■ FLAVONOID RICH EXTRACTS

Flavonoids and related compounds are the main chromophores in most of the yellow color yielding natural dyes.[78] Many plants are rich in flavonoids and related compounds ranging in colors from pale yellow through deep yellow, orange to reds and blues. Flavonoid based colorants derived from some plant species *Allium cepa*, *Butea monosperma*, *Reseda luteola*, *Serratula tinctoria*, *Cotinus coggyria*, *Anthemis tinctoria*, *Chlorophora tinctoria*, *Quercus tinctoria*, *Myrica esculenta*, and *Serratula tinctoria* have shown better dyeing properties on different textile materials.[13,35,78,79] Guinot and co-workers[80] isolated two flavonoid structures namely patulitrin and patuletin using NMR and HPLC-MS techniques from the marigold extract and studied their dyeing properties on wool. Mirjalili et al.[81] isolated color compounds from weld using column chromatography, thin layer chromatography, NMR, mass, and IR techniques and studied their dyeing effects on wool. They noticed that weld extract could be used as a viable alternative to synthetic acid dyes. Recently Nasirizadeh et al.[82] analyzed the optimization of wool dyeing using rutin as a natural dye involving central composite design method. Their study showed that at optimum dyeing conditions, rutin resulted in deep shades with acceptable color fastness properties. In another investigation administered by Rehman et al.,[83] the use of gamma radiations resulted in enhanced extraction of flavonoid dye from onion shells. They irradiated onion dye powder as well as cotton fabrics with absorption doses of 2, 4, 6, 8, and 10 kGy using Cs-137 gamma irradiator and found that gamma irradiation at a dose of 4 kGy resulted in darker shades with improved fastness properties. Likewise, Adeel and co-workers[84] used UV radiation to study dyeing properties of quercetin extracted from *Acacia nilotica* bark. Chemical structures of some coloring compounds belonging to this class are shown in Figure 2. The natural dyeing with flavonoid extracts suggests a promising future for these types of nature colorants in the textile industry.

DOI: 10.1021/acssuschemeng.5b00537
ACS Sustainable Chem. Eng. 2015, 3, 2361−2375

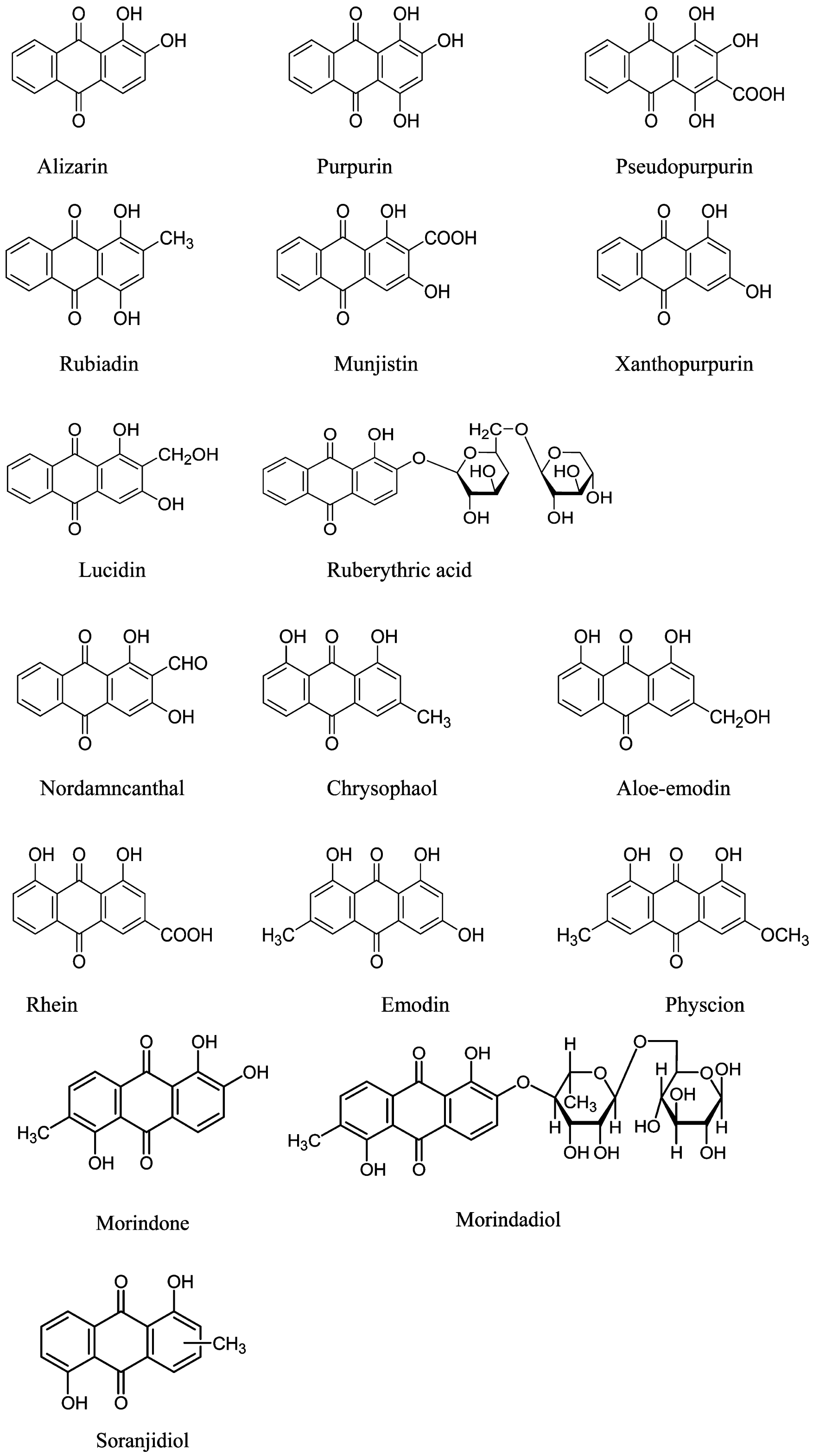


Figure 3. Chemical structures of some anthraquinone based colorants.

Numerous research investigations have also been carried out to study the dyeing property of natural anthocyanins which are water-soluble pigments belonging to parent class called flavonoids. In a research investigation, Bechtold et al.[85] extracted anthocyanins from grape pomace obtained from different varieties such as Blauer Portugieser, Zweigelt, Blauer Burgunder, Cabernet Sauvignon, and Blauburger and studied their dyeing and fastness properties on cotton and wool. Anthocyanins from *Vitis vinifera* leaves extract have been investigated as prominent natural colorants for wool by Mansour et al.[86] They noticed that the leaves extract of *Vitis vinifera* exhibited good fastness properties and provided brown and red shades to wool. More recently Rym and co-workers,[87] likewise, carried out the dyeing of cationized and noncationized cotton fabrics with an aqueous

DOI: 10.1021/acssuschemeng.5b00537
ACS Sustainable Chem. Eng. 2015, 3, 2361−2375

extract of *Vitis vinifera* leaves and obtained deep shades with improved fastness properties on cationized cotton fabrics.

ANTHRAQUINONE RICH EXTRACTS

Anthraquinones dyes from biological sources have been used for textile dyeing since antiquity. They are characterized by good fastness to light and have been extensively studied due to their great potential in the field of functional textiles.[13] They are obtained both from insects as well as plants. The structural diversity allows them to form chelate complexes with metal salts or and the resultant metal−dye complexes have excellent fastness properties. The chemical structures of some coloring compounds from this class are shown in Figure 3.

Rheum emodi is one of the potential dye bearing plant belonging to this class which contains a large number of anthraquinone derivatives such as chrysophaol, aloe-emodin, rhein I, emodin, and physcion.[44] It has been revealed that these constituents are highly active against a broad range of fungal pathogens such as *Candida albicans*, *Cryptococcus neoformans*, *Trichophyton mentagrophytes* and *Aspergillus fumigates*.[88] Cotton and silk fabric dyeing potential of *Rheum emodi* has been investigated.[27] Dyeing properties of Rheum emodi on wool and silk was studied by Das et al.,[89] and it was found that dyed fabrics in the presence of magnesium sulfate, aluminum sulfate, and magnesium sulfate mordants showed good color fastness to light and washing. Various shades like yellowish brown, deep brown, reddish brown and gray shades to olive black have been developed on jute-cotton and jute-wool union fabrics using colorants extracted from *Rheum emodi*.[90] It has been also reported that *Rheum emodi* has the activity against *K. pneumonia*.[71] Khan et al.[44] investigated antimicrobial properties of *Rheum emodi* dye using disc diffusion, growth curve, and viability assays against *Escherichia coli*, *Staphylococcus aureus*, *Candida albicans*, and *Candida tropicalis*. They applied *Rheum emodi* dye on woollen yarns to produce bright yellowish green shades with antimicrobial effects. As could be predicted, dyed wool yarns were found to be highly active against both bacterial and fungal isolates. The use of metal salts namely ferrous sulfate, stannous chloride and alum further enhanced the durability of antimicrobial finish up to several washing cycles. Zhou et al.,[91] in 2015, assessed the color, antioxidant properties, and antimicrobial capacity of silk after treatment with *Rheum emodi*, *Gardenia* yellow and curcumin extracts. In their approach, silk fabrics were also post treated with ferrous and ferric salts in order to enhance color and functional properties. They found that Rheum emodi and curcumin dyes were more active against *Escherichia coli* and *Staphylococcus aureus* and could be used as promising dyeing materials for developing health and hygiene based textiles.

NAPHTHOQUINONES RICH EXTRACTS

Alpha-naphthoquinones are originated from flowering plants, usually in the heartwood. They may also occur in leaves, barks, seeds, and roots. Two prominent dyes of this class which have been extensively studied are henna and walnut extracts. Oliveira and co-workers[92] reported that aqueous extract of green husk from walnut is highly active against Gram-positive bacteria. Walnut green husks have also been used for silk dyeing.[93] Mirjalili et al.[94] used column chromatography, thin layer chromatography, NMR, mass spectroscopy, and IR techniques to report the presence of dyeing compound in walnut shells. They studied the coloring potential of isolated compound for polyamide fabrics and its antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*. They found that the walnut dye in the presence of ferric sulfate, cupric sulfate, and potassium aluminum sulfate metal salts is more active against both the bacterial isolates and observed that the walnut shell dye exhibits good and durable fastness properties. Based on a research investigation administered by Sharma and Grover,[95] the dyeing potential of colorants from walnut bark on cotton has been studied. They reported that the dye from walnut shell in the presence of common mordants like alum, $FeSO_4$, $CuSO_4$, and chrome results in development of color fast shades on cotton. Tutak and Benli[96] studied the effect of metal salts on wool, cotton and viscose dyed with walnut leaves, husk and shell extracts and found deep shades with satisfactory fastness properties. The effect of mordants salts on dyeing, fastness, and antibacterial activity of walnut shells on wool by Ghaheh and co-workers[60] has already indicated that antibacterial activity against *Pseudomonas aeruginosa*, *Escherichia coli*, and *Staphylococcus aureus* is dramatically enhanced by metal salts.

Henna is a prominent dye plant belonging to the family *Lythraceae* and is cultivated in India, Pakistan, Egypt, Yemen, Iran, and Afghanistan. It has been reported that about 90 phenolic compounds are present in different parts of henna plant with a myriad of pharmacological activities.[97] Leaves from this plant have been identified to contain dyeing principle lawsone chemically; the molecule of lawsone is 2-hydroxy-1,4-naphthoquinone having potent antimicrobial activity. The toxicological assessments of 2-hydroxy-1,4-naphthoquinone by Kirkland and Marzin[98,99] and Kirkland et al.[100] in a series of investigations have already indicated that there is no genotoxic risk in using henna leaves extract as a natural dye. Aqueous leaf extract of henna was shown to have promising in vivo antibacterial activity against *S. aureus*, *P. aeruginosa*, and *E. coli*. The antibacterial characteristics of naphthoquinones are due to the formation of adducts between reactive oxygen species produced by one-electron reduction and the DNA, proteins, and other cell component of bacteria.[101−103] The naphthoquinones also inhibit electron transport.[104] The dyeing compound lawsone imparts orange color to substrates owing to the presence of hydroxyl (auxochrome) group in naphthoquinone structure. During the last few decades, several research investigations have been focused on studying its dyeing properties on different textile materials. Henna leaf extract using 10% alum for a period of 65 min at temperature 80 °C and pH 4 was found to produce deep shades on silk with satisfactory fastness properties.[105] Mohammad et al.[106] developed 30 six shades ranging from orange-yellow to reddish brown on wool yarns using combination of ecofriendly mordants such as alum plus ferrous sulfate and ferrous sulfate and stannous chloride with colorant extracted from henna leaves. All the shades developed on wool showed good color fast to light, washing, and rubbing. Ali et al.[107] reported alkaline extraction of natural dye from henna leaves and studied it dyeing on cotton by exhaust method using premordanting and post mordanting with iron and alum. Their results proved that alkaline extracts have much higher color strength values than obtained in distilled water. Different irradiation treatments have been employed to enhance dyeing and functional characteristics of henna leaves extract on different textile substrates. Iqbal et al.[108] used UV radiations for the enhancement of color strength and fastness properties of cotton fabrics dyed with the extract of henna leaves. M'Garrech and Ncib[109] reported the use of gamma irradiations for studying colorimetric properties of cotton dyed with henna. Rehman et al.[110] also noted improvement in dyeing and fastness properties

DOI: 10.1021/acssuschemeng.5b00537
ACS Sustainable Chem. Eng. 2015, 3, 2361−2375

of lawsone on cotton by irradiating cotton fabric as well as henna dye powder with irradiation doses of 2, 4, 6, 8, and 10 kGy using Cs-137 gamma irradiator. Dev et al.[42] investigated the dyeing and antimicrobial activity of henna dye on wool in presence and absence of chitosan. The henna extract dyed wool showed good dyeing and antimicrobial property, however the wool fabric that was pretreated with chitosan showed improved dye uptakes and also enhancement in its activity against *S. aureus* and *E. coli*. The antimicrobial mechanism was attributed to the interaction of positively charged chitosan with negatively charged bacterial residues which results in disruption of membrane properties and induces leakage of intracellular substances and finally leads to eventual death of bacteria.

Yusuf and co-workers[46] investigated antibacterial and antifungal potential of leaves extract of henna before and after application on wool yarns. They observed that leaves extract of henna in solution is highly active against common human pathogens such as *Escherichia coli*, *Staphylococcus aureus*, and *Candida albicans* and retains its activity after application on wool yarns up to several washing cycles. Likewise, in 2015 the same research group also reported a study for the dyeing of wool yarns with henna and madder using stannous chloride as a pretreatment agent. They found that henna dye results in production of beautiful orange−brown to light yellowish−green shades on wool with a significant amount of antifungal activity against *Candida glabrata*. Furthermore, the shades developed showed satisfactory fastness properties.[111] Figure 4 depicts chemical structures of some alpha-naphthoquinone coloring compounds.

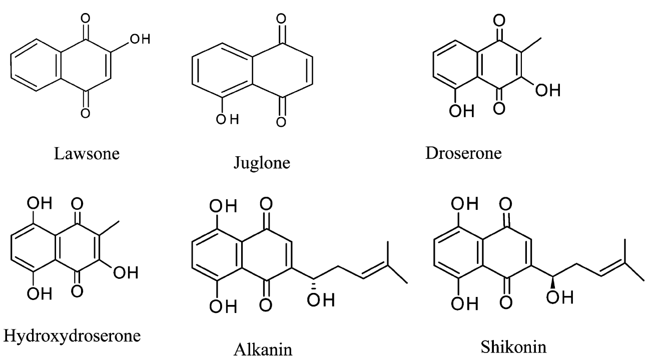


Figure 4. Chemical structures of some alpha-naphthoquinone dyes.

CAROTENOID RICH EXTRACTS

A large number of carotenoid pigments have been isolated from various natural sources including plants, fungi, and prokaryotes to date.[112] These include carotenes and xanthophylls. Carotenoids owe their color to the presence of long conjugated double bonds in their structures. Over the past few decades, carotenoid pigments emerge as an attractive alternative/copartners to synthetic dyes and their application in textile dyeing and finishing has witnessed huge interest in light of their environmental friendly attributes and potential dyeing properties.[113] Saffron (*Crocus sativus L.*) has been valued as a source of natural dye among the promising carotenoid dye yielding plants which imports yellow or orange hue depending upon the mordant used. The stigmas of this plant has shown the presence of more than 150 components including crocin-1 which is the main dyeing principle belonging to carotenoid group.[114] Saffron stigma extracts have attracted significant scientific attention for their use in coloration of textile substrates. Tsatsaroni and Eleftheriadis[115] have studied the dyeing of wool and cotton in presence and absence of metal salts with an aqueous extract of saffron containing α-crocin as the main colorant species. Liakopoulou-Kyriakides et al.[116] reported the use of enzymes such as α-amylase and trypsin, in cotton and wool fiber dyeing with *Crocus sativus* stigmas extract. Tsatsaroni et al.[117] introduced an enzymatic pretreatment in order to enhance dyeing properties of crocin for cotton and wool fabrics. They used alpha-amylase, amyloglycosidase, and trypsin for cotton and wool samples before being dyed with the safron water extract as well as crocin pigment isolated from its stigmas. It was observed that the pretreated samples had better dyeing and fastness properties. Kamel and co-workers[118] assessed the dyeing properties of cotton fabrics with *Crocus sativus* flower extract using ultrasound technology. In their research, ultrasound dyeing results were compared with a traditional boiling method. They observed that the dyeing of cotton with an aqueous extract of *Crocus sativus* flowers using premordanting method in the presence of ultrasound results in wide range of vivid shades. Saffron petals were also used along with other natural extracts in a recent work by Ghaheh et al.[43] and it was found that saffron petals in the presence of aluminum sulfate mordant induces antibacterial activity to wool against *P. aeruginosa*, *E. coli*, and *S. aureus*. The antibacterial activity of aluminum sulfate mordanted samples was 100% retained even after five washes or exposure to light for 300 min. They concluded that saffron petals and other colorants offer a promising potential to be used in value added products such as sportswear, medical textiles, and textiles for infants.

Likewise, *Bixa orellana* is another plant belonging to the family *Bixaceae* growing in several tropical countries of the world and is one of the prominent natural dye plant yielding carotenoid type pigments.[119] Its seeds contain yellow pigments called bixin and nor-bixin. Annatto colorants are extensively used in the food industry as nontoxic colorants in many food formulations, including ice cream cheese, sausages, yogurt, and margarine.[120] Many research studies have been published regarding their use in textile dyeing and finishing. Gulrajani and co-workers[121] carried out the dyeing of nylon and polyester with carotenoid dye bixin and found that the annatto dye gets fixed on nylon via ionic interactions while as for polyester nonionic forces control the adsorption. In addition to synthetic fabrics, dyeing potential of the annatto pigments on wool and silk in the presence and absence of different metallic salt mordants has been studied by Dasa et al.[122] They concluded that all fastness properties of the wool and silk fibers premordanted with ferrous sulfate are better than those of other mordanted samples. Savvidis et al.[123] introduced alum pre- and post- treatment in order to increase annatto adsorption on the surface of cotton. They studied the effect of mordanting processes, temperatures and pH and determined the optimum dyeing conditions by evaluating fastness and color measurement properties of annatto dyed cotton. In their research study, printing of cotton fabric with novel water-based digital printing ink using annatto was performed by flatbed screen-printing technique and it was observed that annatto has suitable rheological and physical properties for printing cotton textiles.

Likewise, we applied seed extract of *Bixa orellana* on wool along with ammonia, as a post-treatment agent, to study the colorimetric properties of dyed wool yarns in terms of lightness (L^*), red−yellowness (a^*), blue−greenness (b^*), chroma (c^*), hue (ho), and color strength (K/S). Our results confirmed that

DOI: 10.1021/acssuschemeng.5b00537
ACS Sustainable Chem. Eng. 2015, 3, 2361−2375

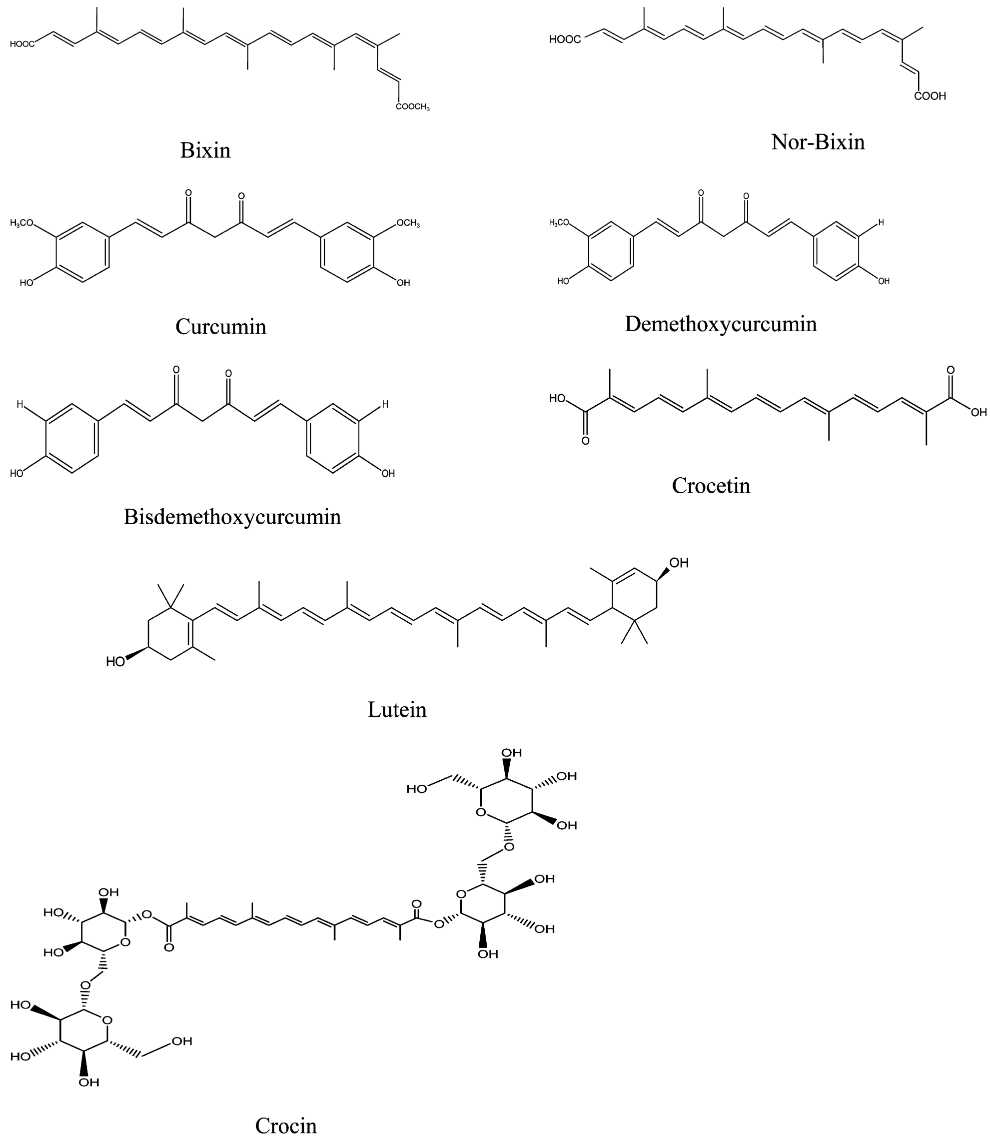


Figure 5. Chemical structures of some carotenoid dyes.

through ammonia post-treatment annatto dyed wool displays a variety of sober and elegant shades with variation in hue and tone. Furthermore, shades developed on wool had not changed after acidification with acetic acid.[16] More recently, in 2015, Chan-Bacab et al.[124] reported a study for the dyeing of ordinary cotton cloth with 23 potential dye bearing plants of Mayan area Yucatan Peninsula, Mexico, and found that out of all the plants selected only *Bixa orellana* displayed low toxicity when used without mordants. They further concluded that there is more need to search for biological mordants in order to make natural dyeing more environmental friendly. The chemical structures of some potential dyes belonging to carotenoid group are shown in Figure 5.

■ ALKALOID RICH COLORANTS

Alkaloid compounds extracted from medicinal plants have shown promising results as dyeing materials in textile and other industries. Berberine which is a quaternary ammonium salt is one of the extensively studied natural dyes belonging to the alkaloid class. It is mainly extracted from *Berberis vulgaris*, *Berberis aquifolium*, *Berberis aristata*, *Coptis chinensis*, and other plant species. Gulrajani et al.[125] observed the high affinity of acrylic fibers with berberine yellow colorant extracted from the roots of *Berberis aristata*. They found that berberine produces yellow shades on acrylic fibers. Because of its cationic nature, it is worthy to note that berberine has more ionic interaction with protein fibers such as wool and silk than with cellulosic substrates. To overcome this problem, Kim and co-workers[126] studied the dyeing effects of berberine onto cellulosic fibers that were pretreated with an anionic agent containing a dichloro-*s*-triazinyl reactive group. The anionic agent treated fibers showed higher dye exhaustion. This was attributed to the creation of more anionic sites onto the cellulosic substrates which resulted in more electrostatic interactions with the berberine dye. In a subsequent publication, Kim and Son[127] carried out the dyeing of cotton with cationic colorant berberine pretreated with same anionic agent and found that the dyed cotton is highly active against *Staphylococcus aureus*. Ravikumar et al.[128] studied dyeing process optimization of polyamide fabrics with berberine colorant using central composite design method. Aminoddin[129] used berberine extracted from *Berberis vulgaris* wood as a natural colorant for wool that was previously pretreated with the extract of roots of *Rumex hymenosepolus* as a biomordant. The treated

DOI: 10.1021/acssuschemeng.5b00537
ACS Sustainable Chem. Eng. 2015, 3, 2361−2375

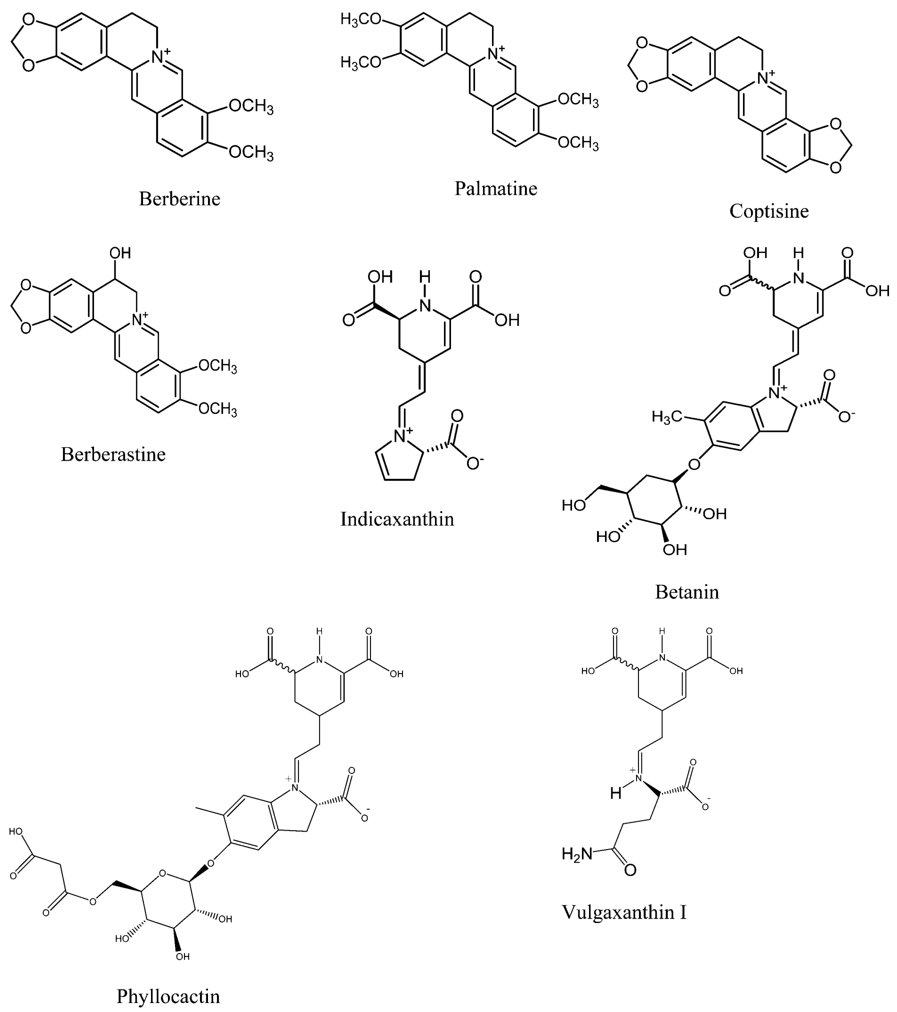


Figure 6. Chemical structures of some alkaloid natural dyes.

wool showed acceptable color fastness properties and was highly active against *Staphylococcus aureus* and *Klebsiella pneumonia* bacterial strains.

Betalains are other important indole-derived pigments which have attracted attention for their use in textile dyeing and finishing. Ali et al.[22] extracted betalain pigment from red prickly pear and studied its dyeing properties on wool. They used a number of metal salts to develop wash resistant and color fast shades and observed that betalain dyed wool inhibits the growth of *E. coli*, *B. subtilus*, *P. aeruginosa*, and *S. aureus*. Maran and Manikandan[130] studied the effect of extraction temperature (30−50 °C), time (20−120 min), and mass of prickly pear fruit (0.5−1.5 g) by applying Box−Behnken design under response surface methodology. At optimum conditions viz 40 °C, extraction time of 115 min and mass of 1.44 g, they were able to obtain maximum yield of 13.435 mg/100 g for betacyanin pigment and 22.2922 mg/100 g for betaxanthin, respectively. Guesmi et al.[131] studied the effect of mordants salts such as $KAl(SO_4)_2$, $MnSO_4$, $CoSO_4$, $FeSO_4$, $ZnSO_4$, and $CuSO_4$ on wool dyed with indicaxanthin and betanin colorants extracted from the fruits of *Opuntia ficus-indica*. They found that indicaxanthin dyed wool exhibited good fastness properties and that the premordanting with $KAl(SO_4)_2$ and $CoSO_4$ gave good light fastness properties. Likewise Guesmi et al.[132] used UV−vis, HPLC, and LC−MS techniques to identify betanin and indicaxanthin dyeing compounds from mature red fruits of *Opuntia ficus-indica*. The isolated compounds were utilized as coloring agents in the dyeing of modified acrylic fabrics and were found to give deep shades with good fastness properties. More recently, the same group led by Guesmi employed power ultrasound to extract betanin natural dye from *Opuntia ficus-indica* plant and to investigate its dyeing properties applied chlorophyll-a for the first time as pretreatment agent on wool. They observed encouraging results and found good fastness properties of dyed wool samples toward washing, light, dry, and wet rubbing. Guesmi et al.[20] also used sonicator for dyeing of modified acrylic fabrics using indicaxanthin as a natural dye isolated from fruits of *Opuntia ficus-indica*. They compared their results with conventionally dyed samples and found that there was about 46.62% more dye uptake with ultrasound method. Figure 6 shows chemical structures of some coloring compounds falling under alkaloid group.

■ CURRENT CHALLENGES AND FUTURE DIRECTION

Natural plant extract raw materials have attracted attention and significant progress has been made over the past few decades in their reintroduction as coloring agents for different textile materials. However, most of the current research on natural colorants from plant extracts is conducted on laboratory scale and there are many factors impeding its development to pilot scale.

DOI: 10.1021/acssuschemeng.5b00537
ACS Sustainable Chem. Eng. 2015, 3, 2361−2375

One of the constraints is that some heavy metals salts as mordants are involved in dyeing with vegetable derived colorants which may be found in dyeing waste waters. Heavy metals have lethal effects on the environment and human health. Some of the heavy and red listed metal mordants include copper sulfate, potassium dichromate, etc.[21] This metal mordanting step would also limit their use in clothing that directly comes in contact with human skin. To address this issue, more research is needed for the search of ecofriendly alternatives/copartners to the synthetic and toxic finishing agents. Recent research in the area of natural dyeing has shown encouraging results by using natural mordants derived from some plant species such as *Acacia catechu*, *Emblica officinalis*, *Terminalia chubula*, *Quercus infectoria*, *Punica granatum*, *Rumex hymenosepolus*, *Eurya acuminata*, *Pyrus pashia*, and *Emblica officinalis*.[13,133,134] Existing studies are confined mainly to their role in the development of various shades on different textile substrates; however in-depth work is required on the antimicrobial activity of biological mordants which can further boost their role to develop multifunctional textiles on large scale in the near future.

High production cost of dyes obtained from direct forming is another possible difficulty to prevent their exploitation on an industrial scale; a lot of chemicals and energy inputs are involved in cultivation of dye yielding plant species. For the sake of sustainability and commercial utilization of natural colorants in textile industry, a project entitled "Sustainable Production of Plant-derived Indigo Research & Development" was completed by European Union in 2004 aimed to introduce the indigo yielding plants in European agriculture and to make them fit for modern dye-houses.[13,135] A number of other prominent natural dye plants such as madder, weld, Canadian Golden Rod, Dyer's Chamomile, and Dyer's Knotweed have achieved the agriculture criteria for sustainable cultivation, besides providing a worthwhile route to increase the income through harvest and sale of these agricultural crops.[136] To lower the costs involved in natural colorant production nowadays introduction of dyeing materials from wastes and byproducts of other industries such as food, timber, and beverage into textile dyeing and finishing applications are in demand.[21] Scientists are engaged all around the globe in the process of identifying colorants mainly from inexpensive raw materials such as peels,[29] pressed berries,[2] barks,[137] shells,[138] husks,[96] and other distillation residues.[139] This approach adds value to wastes, is expected to keep dyeing industry sustainable, and offers full potential for commercialization in the near future.

Furthermore, in addition to natural colorants, the technologies involved in natural dyeing are being constantly revived in view to keep dyeing industry sustainable. Recent investigations on plant derived colorants involve use of some novel pre- and postsustainable technologies including enzyme treatment, ammonia treatment, and chitosan treatments for improving color strength, fastness properties, and other functional properties.[16,25] Additionally, high-energy radiations pretreatments such as gamma, plasma, ultrasonic and ultraviolet which have the advantages of low energy use and high treatment speed are nowadays gaining more popularity for sustainable coloration and functional finishing of textile materials dyed with natural colorants.[140]

Also natural colorants are generally considered as safer dyes because they are mostly isolated from plants that have traditionally been used to combat various infections and are endowed with a wide-range of pharmacological activities.[97,141] Toxicity data on active dyeing compounds is very limited, however many researchers have investigated that there is no evidence about the possible toxicity of natural colorants to animals/humans.[142,143] Considering the consumers enhanced awareness of eco-safety, further research is needed to know more about antimicrobial mechanisms and toxicity of active dyeing principles which can be a driving force for scientists to develop colorful textiles with antimicrobial properties for aesthetic, medical, and hygienic applications.

■ CONCLUSION

Plant extracts have been used for coloring of textile substrates since antiquity. In view of their biodegradable and environmental friendly nature they have been investigated and reintroduced, once more as coloring and functional agents. Furthermore, scientists have discovered that natural colorants result in the production of textile surfaces with novel properties including antimicrobial activity and have opened new interesting field for textile and polymer researchers. Despite the notable progress made in natural dye applications, there is still a long way to go before colorants from plants can be considered as viable alternatives/copartners to synthetic counterparts. Plant derived colorants needs further research on their toxicity, safety, and quality for commercial utilization.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +91-9350114878. E-mail: faqeermohammad@rediffmail.com.

Notes

The authors declare no competing financial interest.

Biographies

Shahid-ul-Islam is a doctorial student doing research work in Dr. Faqeer Mohammad's group at the Department of Chemistry, Jamia Millia Islamia (Central University), New Delhi, India. His research is focused on natural colorants, biopolymers, green chemistry, and functional textiles. He has numerous academic publications in International journals of high repute to his credit and has also contributed to several internationally recognized books published by John Wiley & Sons, Springer, and Studium press LLC. His research papers are cited in well-reputed scientific journals published by Nature, The American Chemical Society, and The Royal Society of Chemistry. Additionally two of his papers appeared in ScienceDirect's Top 25 hottest articles from the Journal of Cleaner Production in 2013, 2014, and 2015.

DOI: 10.1021/acssuschemeng.5b00537
ACS Sustainable Chem. Eng. 2015, 3, 2361−2375

Faqeer Mohammad is Senior Assistant Professor in the Department of Chemistry, at Jamia Millia Islamia, (A Central University), New Delhi, India. He received his M.Sc, M.Phil., and Ph.D in 1975, 1979, and 1982, respectively, from Aligarh Muslim University, Aligarh, UP, India. During his Ph.D. he was awarded with JRF and SRF Research Fellowships from UGC and CSIR. He has published numerous research articles, reviews, and book chapters all in the journals of international repute. He has until now supervised 20 graduate M.Sc and 4 Ph.D thesis. His research interests are in the field of natural dyes and their applications.

■ ACKNOWLEDGMENTS

Shahid-ul-Islam is grateful to University Grants Commission, Govt. of India for providing research fellowship through Basic Meritorious Fellowship for Science students.

■ REFERENCES

(1) Ahmed, N. S.; El-Shishtawy, R. M. The use of new technologies in coloration of textile fibers. *J. Mater. Sci.* **2010**, *45*, 1143−1153.

(2) Bechtold, T.; Mussak, R.; Mahmud, A.; Ganglberger, E.; Geissler, S. Extraction of natural dyes for textile dyeing from coloured plant wastes released from the food and beverage industry. *J. Sci. Food Agric.* **2006**, *86*, 233−242.

(3) Bechtold, T.; Turcanu, A. Electrochemical reduction in vat dyeing: greener chemistry replaces traditional processes. *J. Cleaner Prod.* **2009**, *17*, 1669−1679.

(4) Kamel, M. M.; El-Shishtawy, R. M.; Yussef, B. M.; Mashaly, H. Ultrasonic assisted dyeing: III. Dyeing of wool with lac as a natural dye. *Dyes Pigm.* **2005**, *65*, 103−110.

(5) Babu, K. M. The dyeing of silk. In *Silk*; Woodhead Publishing, 2013; pp 117−139.

(6) Koh, J. Dyeing of cellulosic fibres. In *Handbook of Textile and Industrial Dyeing*; Clark, M., Ed.; Woodhead Publishing, 2011; Vol. 2, pp 129−146.

(7) Khatri, A.; Peerzada, M. H.; Mohsin, M.; White, M. A review on developments in dyeing cotton fabrics with reactive dyes for reducing effluent pollution. *J. Cleaner Prod.* **2015**, *87*, 50−57.

(8) Ramchandran, T.; Rajendrakumar, K.; Rajendran, R. Antimicrobial Textiles - an Overview. *IE (I) Journal-TX* **2004**, *84*, 42−46.

(9) Islam, S.; Shahid, M.; Mohammad, F. Green Chemistry Approaches to Develop Antimicrobial Textiles Based on Sustainable Biopolymers-A Review. *Ind. Eng. Chem. Res.* **2013**, *52*, 5245−5260.

(10) Gupta, D.; Bhaumik, S. Antimicrobial treatment for textiles. *Indian J. Fibre Text. Res.* **2007**, *32*, 254−263.

(11) Gao, Y.; Cranston, R. Recent Advances in Antimicrobial Treatments of Textiles. *Text. Res. J.* **2008**, *78*, 60−72.

(12) Simoncic, B.; Tomsic, B. Structures of Novel Antimicrobial Agents for Textiles - A Review. *Text. Res. J.* **2010**, *80*, 1721−1737.

(13) Islam, S. u.; Shahid, M.; Mohammad, F. Perspectives for natural product based agents derived from industrial plants in textile applications − a review. *J. Cleaner Prod.* **2013**, *57*, 2−18.

(14) Islam, S. u.; Mohammad, F. Emerging Green Technologies and Environment Friendly Products for Sustainable Textiles. In *Roadmap to Sustainable Textiles and Clothing*; Muthu, S. S., Ed.; Springer: Singapore, 2014; pp 63−82.

(15) Joshi, M.; Ali, S. W.; Purwar, R.; Rajendran, S. Ecofriendly antimicrobial finishing of textiles using bioactive agents based on natural products. *Indian J. Fibre Text. Res.* **2009**, *34*, 295−304.

(16) Islam, S. u.; Rather, L. J.; Shahid, M.; Khan, M. A.; Mohammad, F. Study the effect of ammonia post-treatment on color characteristics of annatto-dyed textile substrate using reflectance spectrophotometery. *Ind. Crops Prod.* **2014**, *59*, 337−342.

(17) Ajmal, M.; Adeel, S.; Azeem, M.; Zuber, M.; Akhtar, N.; Iqbal, N. Modulation of pomegranate peel colourant characteristics for textile dyeing using high energy radiations. *Ind. Crops Prod.* **2014**, *58*, 188−193.

(18) Bhatti, I. A.; Adeel, S.; Jamal, M. A.; Safdar, M.; Abbas, M. Influence of gamma radiation on the colour strength and fastness properties of fabric using turmeric (Curcuma longa L.) as natural dye. *Radiat. Phys. Chem.* **2010**, *79*, 622−625.

(19) Guesmi, A.; Ladhari, N.; Sakli, F. Ultrasonic preparation of cationic cotton and its application in ultrasonic natural dyeing. *Ultrason. Sonochem.* **2013**, *20*, 571−579.

(20) Guesmi, A.; Ben hamadi, N.; Ladhari, N.; Sakli, F. Sonicator dyeing of modified acrylic fabrics with indicaxanthin natural dye. *Ind. Crops Prod.* **2013**, *42*, 63−69.

(21) Shahid, M.; Shahid ul, I.; Mohammad, F. Recent advancements in natural dye applications: a review. *J. Cleaner Prod.* **2013**, *53*, 310−331.

(22) Ali, N. F.; El-Mohamedy, R. S. R. Eco-friendly and protective natural dye from red prickly pear (Opuntia Lasiacantha Pfeiffer) plant. *J. Saudi Chem. Soc.* **2011**, *15*, 257−261.

(23) Ludin, N. A.; Al-Alwani Mahmoud, A. M.; Bakar Mohamad, A.; Kadhum, A. A. H.; Sopian, K.; Abdul Karim, N. S. Review on the development of natural dye photosensitizer for dye-sensitized solar cells. *Renewable Sustainable Energy Rev.* **2014**, *31*, 386−396.

(24) Adeel, S.; Bhatti, I. A.; Kausar, A.; Osman, E. Influence of UV radiations on the extraction and dyeing of cotton fabric with Curcuma longa L. *Indian J. Fibre Text. Res.* **2012**, *37* (1), 87−90.

(25) Vankar, P. S.; Shanker, R. Ecofriendly ultrasonic natural dyeing of cotton fabric with enzyme pretreatments. *Desalination* **2008**, *230*, 62−69.

(26) Vankar, P. S.; Shanker, R.; Srivastava, J. Ultrasonic dyeing of cotton fabric with aqueous extract of Eclipta alba. *Dyes Pigm.* **2007**, *72* (1), 33−37.

(27) Vankar, P. S.; Shanker, R.; Verma, A. Enzymatic natural dyeing of cotton and silk fabrics without metal mordants. *J. Cleaner Prod.* **2007**, *15*, 1441−1450.

(28) Vankar, P. S.; Shanker, R.; Dixit, S.; Mahanta, D.; Tiwari, S. C. Sonicator dyeing of modified cotton, wool and silk with Mahonia napaulensis DC. and identification of the colorant in Mahonia. *Ind. Crops Prod.* **2008**, *27*, 371−379.

(29) Hou, X.; Chen, X.; Cheng, Y.; Xu, H.; Chen, L.; Yang, Y. Dyeing and UV-protection properties of water extracts from orange peel. *J. Cleaner Prod.* **2013**, *52*, 410−419.

(30) Grifoni, D.; Bacci, L.; Di Lonardo, S.; Pinelli, P.; Scardigli, A.; Camilli, F.; Sabatini, F.; Zipoli, G.; Romani, A. UV protective properties of cotton and flax fabrics dyed with multifunctional plant extracts. *Dyes Pigm.* **2014**, *105*, 89−96.

(31) Grifoni, D.; Bacci, L.; Zipoli, G.; Albanese, L.; Sabatini, F. The role of natural dyes in the UV protection of fabrics made of vegetable fibres. *Dyes Pigm.* **2011**, *91*, 279−285.

(32) Zhang, B.; Wang, L.; Luo, L.; King, M. W. Natural dye extracted from Chinese gall − the application of color and antibacterial activity to wool fabric. *J. Cleaner Prod.* **2014**, *80*, 204−210.

(33) Baliarsingh, S.; Panda, A. K.; Jena, J.; Das, T.; Das, N. B. Exploring sustainable technique on natural dye extraction from native plants for textile: identification of colourants, colourimetric analysis of dyed yarns and their antimicrobial evaluation. *J. Cleaner Prod.* **2012**, *37*, 257−264.

(34) Islam, S.-u.; Shahid, M.; Mohammad, F. Future Prospects of Phytosynthesized Transition Metal Nanoparticles as Novel Functional

Agents for Textiles. In *Advanced Materials for Agriculture, Food, and Environmental Safety*; Syväjärvi, A. T. a., Ed.; John Wiley & Sons, Inc., 2014; pp 265−290.

(35) Prusty, A. K.; Das, T.; Nayak, A.; Das, N. B. Colourimetric analysis and antimicrobial study of natural dyes and dyed silk. *J. Cleaner Prod.* **2010**, *18*, 1750−1756.

(36) Shahid, M.; Ahmad, A.; Yusuf, M.; Khan, M. I.; Khan, S. A.; Manzoor, N.; Mohammad, F. Dyeing, fastness and antimicrobial properties of woolen yarns dyed with gallnut (*Quercus infectoria Oliv.*) extract. *Dyes Pigm.* **2012**, *95*, 53−61.

(37) Naz, S.; Bhatti, I. A.; Adeel, S. Dyeing properties of cotton fabric using un-irradiated and gamma irradiated extracts of *Eucalyptus camaldulensis* bark powder. *Indian J. Fibre Text. Res.* **2011**, *36*, 132−136.

(38) Samantaa, A. K.; Agarwal, P. Application of natural dyes on textiles. *Indian J. Fibre Text. Res.* **2009**, *34*, 384−399.

(39) Manhita, A.; Ferreira, V.; Vargas, H.; Ribeiro, I.; Candeias, A.; Teixeira, D.; Ferreira, T.; Dias, C. B. Enlightening the influence of mordant, dyeing technique and photodegradation on the colour hue of textiles dyed with madder − A chromatographic and spectrometric approach. *Microchem. J.* **2011**, *98*, 82−90.

(40) Kadolph, S. J.; Casselman, K. D. In the bag: Contact natural dyes. *Cloth Text Res. J.* **2004**, *22*, 15−21.

(41) Prabhu, K. H.; Teli, M. D. Eco-dyeing using Tamarindus indica L. seed coat tannin as a natural mordant for textiles with antibacterial activity. *J. Saudi Chem. Soc.* **2014**, *18*, 864−872.

(42) Dev, V.; Venugopal, J.; Sudha, S.; Deepika, G.; Ramakrishna, S. Dyeing and antimicrobial characteristics of chitosan treated wool fabrics with henna dye. *Carbohydr. Polym.* **2009**, *75*, 646−650.

(43) Shahmoradi Ghaheh, F.; Mortazavi, S. M.; Alihosseini, F.; Fassihi, A.; Shams Nateri, A.; Abedi, D. Assessment of antibacterial activity of wool fabrics dyed with natural dyes. *J. Cleaner Prod.* **2014**, *72*, 139−145.

(44) Khan, S. A.; Ahmad, A.; Khan, M. I.; Yusuf, M.; Shahid, M.; Manzoor, N.; Mohammad, F. Antimicrobial activity of wool yarn dyed with *Rheum emodi* L. (Indian Rhubarb). *Dyes Pigm.* **2012**, *95*, 206−214.

(45) Khan, M. I.; Ahmad, A.; Khan, S. A.; Yusuf, M.; Shahid, M.; Manzoor, N.; Mohammad, F. Assessment of antimicrobial activity of Catechu and its dyed substrate. *J. Cleaner Prod.* **2011**, *19*, 1385−1394.

(46) Yusuf, M.; Ahmad, A.; Shahid, M.; Khan, M. I.; Khan, S. A.; Manzoor, N.; Mohammad, F. Assessment of colorimetric, antibacterial and antifungal properties of woollen yarn dyed with the extract of the leaves of henna (*Lawsonia inermis*). *J. Cleaner Prod.* **2012**, *27*, 42−50.

(47) Haslam, E. Natural polyphenols (vegetable tannins) as drugs: possible modes of action. *J. Nat. Prod.* **1996**, *59*, 205−215.

(48) El Gharras, H. Polyphenols: food sources, properties and applications − a review. *Int. J. Food Sci. Technol.* **2009**, *44*, 2512−2518.

(49) Scalbert, A. Antimicrobial properties of tannins. *Phytochemistry* **1991**, *30*, 3875−3883.

(50) Daglia, M. Polyphenols as antimicrobial agents. *Curr. Opin. Biotechnol.* **2012**, *23*, 174−181.

(51) Ikigai, H.; Nakae, T.; Hara, Y.; Shimamura, T. Bactericidal catechins damage the lipid bilayer. *Biochim. Biophys. Acta, Biomembr.* **1993**, *1147*, 132−136.

(52) Hoshino, N.; Kimura, T.; Yamaji, A.; Ando, T. Damage to the cytoplasmic membrane of Escherichia coli by catechin-copper (II) complexes. *Free Radical Biol. Med.* **1999**, *27*, 1245−1250.

(53) Gulrajani, M. L.; Srivastava, R. C.; Goel, M. Colour gamut of natural dyes on cotton yarns. *Color. Technol.* **2001**, *117*, 225−228.

(54) Tiwari, H. C.; Singh, P.; Kumar Mishra, P.; Srivastava, P. Evaluation of various techniques for extraction of natural colorants from pomegranate rind—Ultrasound and enzyme assisted extraction. *Indian J. Fibre Text Res.* **2010**, *35*, 272−276.

(55) Sinha, K.; Saha, P. D.; Datta, S. Response surface optimization and artificial neural network modeling of microwave assisted natural dye extraction from pomegranate rind. *Ind. Crops Prod.* **2012**, *37*, 408−414.

(56) Shams-Nateri, A.; Hajipour, A.; Dehnavi, E.; Ekrami, E. Colorimetric Study on Polyamides Dyeing With Weld and Pomegranate Peel Natural Dyes. *Cloth. Text. Res. J.* **2014**, *32*, 124−135.

(57) Lee, Y.-H.; Hwang, E.-K.; Kim, H.-D. Colorimetric assay and antibacterial activity of cotton, silk, and wool fabrics dyed with peony, pomegranate, clove, coptis chinenis and gallnut extracts. *Materials* **2009**, *2*, 10−21.

(58) Al-Zoreky, N. S. Antimicrobial activity of pomegranate (*Punica granatum* L.) fruit peels. *Int. J. Food Microbiol.* **2009**, *134*, 244−248.

(59) Lee, Y.-H.; Hwang, E.-K.; Baek, Y.-M.; Lee, M.-S.; Lee, D.-J.; Jung, Y.-J.; Kim, H.-D. Deodorizing and antibacterial performance of cotton, silk and wool fabrics dyed with Punica granatum L. extracts. *Fibers Polym.* **2013**, *14*, 1445−1453.

(60) Ghaheh, F. S.; Nateri, A. S.; Mortazavi, S. M.; Abedi, D.; Mokhtari, J. The effect of mordant salts on antibacterial activity of wool fabric dyed with pomegranate and walnut shell extracts. *Color. Technol.* **2012**, *128*, 473−478.

(61) Davulcu, A.; Benli, H.; Şen, Y.; Bahtiyari, M. İ. Dyeing of cotton with thyme and pomegranate peel. *Cellulose* **2014**, *21*, 4671−4680.

(62) Benli, H.; Bahtiyari, M. İ. Combination of ozone and ultrasound in pretreatment of cotton fabrics prior to natural dyeing. *J. Cleaner Prod.* **2015**, *89*, 116−124.

(63) Kaur, G.; Hamid, H.; Ali, A.; Alam, M. S.; Athar, M. Antiinflammatory evaluation of alcoholic extract of galls of Quercus infectoria. *J. Ethnopharmacol.* **2004**, *90*, 285−292.

(64) Lokeshwari, R.; Shantibala, T. A Review on the Fascinating World of Insect Resources: Reason for Thoughts. *Psyche* **2010**, *2010*, 1−11.

(65) Onal, A.; Sari, A.; Soylak, M. Ellagic acid from gallnut (*Quercus infectoria*): Extraction and determination of its dyeing conditions for natural fibres. *J. Sci. Ind. Res.* **2005**, *64* (7), 491.

(66) Park, A.-Y.; Kim, I.-Y.; Song, W.-S. The effect of gallnut mordanting on gromwell dyed silk fabric. *J. Korean Soc. Cloth. Text.* **2009**, *33* (2), 256−265.

(67) Hong, K.; Bae, J.; Jin, S.; Yang, J. Preparation and properties of multi-functionalized cotton fabrics treated by extracts of gromwell and gallnut. *Cellulose* **2012**, *19*, 507−515.

(68) Koh, E.; Hong, K. H. Gallnut extract-treated wool and cotton for developing green functional textiles. *Dyes Pigm.* **2014**, *103*, 222−227.

(69) Lee, Y.-H.; Hwang, E.-K.; Baek, Y.-M.; Kim, H.-D. Deodorizing function and antibacterial activity of fabrics dyed with gallnut (Galla Chinensis) extract. *Text. Res. J.* **2015**, *85* (10), 1045.

(70) Bhattacharya, S. D.; Shah, A. K. Metal ion effect on dyeing of wool fabric with catechu. *Color. Technol.* **2000**, *116*, 10−12.

(71) Gupta, D.; Khare, S. K.; Laha, A. Antimicrobial properties of natural dyes against Gram-negative bacteria. *Color. Technol.* **2004**, *120*, 167−171.

(72) Singh, R.; Jain, A.; Panwar, S.; Gupta, D.; Khare, S. K. Antimicrobial activity of some natural dyes. *Dyes Pigm.* **2005**, *66*, 99−102.

(73) Kondo, K.; Kurihara, M.; Miyata, N.; Suzuki, T.; Toyoda, M. Scavenging mechanisms of (−)-epigallocatechin gallate and (−)-epicatechin gallate on peroxyl radicals and formation of superoxide during the inhibitory action. *Free Radical Biol. Med.* **1999**, *27*, 855−863.

(74) Deo, H. T.; Desai, B. K. Dyeing of cotton and jute with tea as a natural dye. *Color. Technol.* **1999**, *115*, 224−227.

(75) Kim, S.-h. Dyeing characteristics and UV protection property of green tea dyed cotton fabrics. *Fibers Polym.* **2006**, *7*, 255−261.

(76) Moiz, A.; Aleem Ahmed, M.; Kausar, N.; Ahmed, K.; Sohail, M. Study the effect of metal ion on wool fabric dyeing with tea as natural dye. *J. Saudi Chem. Soc.* **2010**, *14*, 69−76.

(77) Tang, R.-C.; Tang, H.; Yang, C. Adsorption Isotherms and Mordant Dyeing Properties of Tea Polyphenols on Wool, Silk, and Nylon. *Ind. Eng. Chem. Res.* **2010**, *49*, 8894−8901.

(78) Ferreira, E. S. B.; Hulme, A. N.; McNab, H.; Quye, A. The natural constituents of historical textile dyes. *Chem. Soc. Rev.* **2004**, *33*, 329−336.

(79) Guinot, P.; Gargadennec, A.; La Fisca, P.; Fruchier, A.; Andary, C.; Mondolot, L. Serratula tinctoria, a source of natural dye: Flavonoid pattern and histolocalization. *Ind. Crops Prod.* **2009**, *29*, 320−325.

(80) Guinot, P.; Gargadennec, A.; Valette, G.; Fruchier, A.; Andary, C. Primary flavonoids in marigold dye: extraction, structure and involvement in the dyeing process. *Phytochem. Anal.* **2008**, *19*, 46−51.

DOI: 10.1021/acssuschemeng.5b00537
ACS Sustainable Chem. Eng. 2015, 3, 2361−2375

(81) Mirjalili, M.; Nazarpoor, K.; Karimi, L. Eco-friendly dyeing of wool using natural dye from weld as co-partner with synthetic dye. *J. Cleaner Prod.* **2011**, *19*, 1045−1051.
(82) Nasirizadeh, N.; Dehghanizadeh, H.; Yazdanshenas, M. E.; Moghadam, M. R.; Karimi, A. Optimization of wool dyeing with rutin as natural dye by central composite design method. *Ind. Crops Prod.* **2012**, *40*, 361−366.
(83) Rehman, F.-u.; Adeel, S.; Shahid, M.; Bhatti, I. A.; Nasir, F.; Akhtar, N.; Ahmad, Z. Dyeing of γ-irradiated cotton with natural flavonoid dye extracted from irradiated onion shells (Allium cepa) powder. *Radiat. Phys. Chem.* **2013**, *92*, 71−75.
(84) Adeel, S.; Fazal-ur-Rehman; Hanif, R.; Zuber, M.; Ehsan-ul-Haq; Muneer, M. Ecofriendly Dyeing of UV-Irradiated Cotton Using Extracts of Acacia nilotica Bark (Kikar) as Source of Quercetin. *Asian J. Chem.* **2014**, *26*, 830−834.
(85) Bechtold, T.; Mahmud-Ali, A.; Mussak, R. Anthocyanin dyes extracted from grape pomace for the purpose of textile dyeing. *J. Sci. Food Agric.* **2007**, *87*, 2589−2595.
(86) Mansour, R.; Ezzili, B.; Farouk, M. Dyeing properties of wool fabrics dyed with Vitis Vinifera L. (black grenache) leaves extract. *Fibers Polym.* **2013**, *14*, 786−792.
(87) Rym, M.; Farouk, M.; Bechir, E. M. Dyeing properties of cationized and non-cationized cotton fabrics dyed with Vitis vinifera L. leaves extract. *J. Text. Inst.* **2015**, 1−6.
(88) Agarwal, S. K.; Singh, S. S.; Verma, S.; Kumar, S. Antifungal activity of anthraquinone derivatives from Rheum emodi. *J. Ethnopharmacol.* **2000**, *72*, 43−46.
(89) Dasa, D.; Maulik, S. R.; Bhattacharya, S. C. Colouration of wool and silk with *Rheum emodi*. *Indian J. Fibre Text. Res.* **2008**, *33*, 163−170.
(90) Nayak, L. A Study on Coloring Properties of Rheum emodi on Jute Union Fabrics. *J. Text.* **2014**, *2014*, 1−7.
(91) Zhou, Y.; Zhang, J.; Tang, R.-C.; Zhang, J. Simultaneous dyeing and functionalization of silk with three natural yellow dyes. *Ind. Crops Prod.* **2015**, *64*, 224−232.
(92) Oliveira, I.; Sousa, A.; Ferreira, I. C. F. R.; Bento, A.; Estevinho, L.; Pereira, J. A. Total phenols, antioxidant potential and antimicrobial activity of walnut (*Juglans regia* L.) green husks. *Food Chem. Toxicol.* **2008**, *46*, 2326−2331.
(93) Mirjalili, M.; Nazarpoor, K.; Kartmi, L. Extraction and identification of dye from walnut green husks for silk dyeing. *Asian J. Chem.* **2011**, *23*, 1055−1059.
(94) Mirjalili, M.; Karimi, L. Extraction and characterization of natural dye from green walnut shells and its use in dyeing polyamide: focus on antibacterial properties. *J. Chem.* **2013**, *2013*, 1−9.
(95) Sharma, A.; Grover, E. Colour fastness of walnut dye on cotton. *Indian J. Nat. Prod. Resour.* **2011**, *2*, 164−169.
(96) Tutak, M.; Benli, H. Colour and Fastness of Fabrics Dyed with Walnut (*Juglans regia* L.) Base Natural Dyes. *Asian J. Chem.* **2011**, *23*, 566−568.
(97) Semwal, R.; Badoni; Semwal, D. K.; Combrinck, S.; Cartwright-Jones, C.; Viljoen, A. *Lawsonia inermis* L. (henna): Ethnobotanical, phytochemical and pharmacological aspects. *J. Ethnopharmacol.* **2014**, *155*, 80−103.
(98) Kirkland, D.; Marzin, D. An assessment of the genotoxicity of 2-hydroxy-1,4-naphthoquinone, the natural dye ingredient of Henna. *Mutat. Res., Genet. Toxicol. Environ. Mutagen.* **2003**, *537*, 183−199.
(99) Marzin, D.; Kirkland, D. 2-Hydroxy-1,4-naphthoquinone, the natural dye of Henna, is non-genotoxic in the mouse bone marrow micronucleus test and does not produce oxidative DNA damage in Chinese hamster ovary cells. *Mutat. Res., Genet. Toxicol. Environ. Mutagen.* **2004**, *560*, 41−47.
(100) Kirkland, D. J.; Henderson, L.; Marzin, D.; Müller, L.; Parry, J. M.; Speit, G.; Tweats, D. J.; Williams, G. M. Testing strategies in mutagenicity and genetic toxicology: An appraisal of the guidelines of the European Scientific Committee for Cosmetics and Non-Food Products for the evaluation of hair dyes. *Mutat. Res., Genet. Toxicol. Environ. Mutagen.* **2005**, *588*, 88−105.
(101) Jarabak, R.; Jarabak, J. Effect of Ascorbate on the DT-Diaphorase-Mediated Redox Cycling of 2-Methyl-1,4-naphthoquinone. *Arch. Biochem. Biophys.* **1995**, *318*, 418−423.
(102) Öllinger, K.; Brunk, U. T. Cellular injury induced by oxidative stress is mediated through lysosomal damage. *Free Radical Biol. Med.* **1995**, *19*, 565−574.
(103) Zhang, R. L.; Hirsch, O.; Mohsen, M.; Samuni, A. Effects of Nitroxide Stable Radicals on Juglone Cytotoxicity. *Arch. Biochem. Biophys.* **1994**, *312*, 385−391.
(104) Haraguchi, H.; Soga, O.; Taniguchi, M. Respiratory Inhibition by the Antifungal Benzoquinone, 2-Hydroxy-6-methoxy-3,5-dimethyl-1,4-benzoquinone. *Agric. Biol. Chem.* **1986**, *50*, 1905−1907.
(105) Alam, M.; Rahman, M.; Haque, M. Extraction of henna leaf dye and its dyeing effects on textile fibre. *Bangladesh J. Sci. Ind. Res.* **2007**, *42*, 217−222.
(106) Mohammad, F.; Yusuf, M.; Shahid, M.; Khan, S. A.; Islam, S.; Khan, M. I. Dyeing of wool with the extract of henna leaves using mixed metal mordants. *Colourage* **2012**, *59*, 51.
(107) Ali, S.; Hussain, T.; Nawaz, R. Optimization of alkaline extraction of natural dye from Henna leaves and its dyeing on cotton by exhaust method. *J. Cleaner Prod.* **2009**, *17*, 61−66.
(108) Iqbal, J.; Bhatti, I. A. Effect of UV radiation on dyeing of cotton fabric with extracts of henna leaves. *Indian J. Fibre Text Res.* **2008**, *33*, 157−162.
(109) M'Garrech, S.; Ncib, F. Colorimetric study of effect of gamma-radiation on the color of cotton fabric colored by "henna" dye. *Appl. Radiat. Isot.* **2009**, *67*, 2003−2006.
(110) Rehman, F.-u.; Adeel, S.; Qaiser, S.; Ahmad Bhatti, I.; Shahid, M.; Zuber, M. Dyeing behaviour of gamma irradiated cotton fabric using Lawson dye extracted from henna leaves (*Lawsonia inermis*). *Radiat. Phys. Chem.* **2012**, *81*, 1752−1756.
(111) Yusuf, M.; Shahid, M.; Khan, M. I.; Khan, S. A.; Khan, M. A.; Mohammad, F. Dyeing studies with henna and madder: A research on effect of tin (II) chloride mordant. *J. Saudi Chem. Soc.* **2015**, *19*, 64−72.
(112) Mortensen, A. Carotenoids and other pigments as natural colorants. *Pure Appl. Chem.* **2006**, *78*, 1477−1491.
(113) Beltrame, P. L.; Castelli, A.; Selli, E.; Mossa, A.; Testa, G.; Bonfatti, A. M.; Seves, A. Dyeing of Cotton in Supercritical Carbon Dioxide. *Dyes Pigm.* **1998**, *39*, 335−340.
(114) Bathaie, S. Z.; Mousavi, S. Z. New Applications and Mechanisms of Action of Saffron and its Important Ingredients. *Crit. Rev. Food Sci. Nutr.* **2010**, *50*, 761−786.
(115) Tsatsaroni, E. G.; Eleftheriadis, I. C. The colour and fastness of natural saffron. *J. Soc. Dyers Colour.* **1994**, *110*, 313−315.
(116) Liakopoulou-Kyriakides, M.; Tsatsaroni, E.; Laderos, P.; Georgiadou, K. Dyeing of cotton and wool fibres with pigments from Crocus sativus—Effect of enzymatic treatment. *Dyes Pigm.* **1998**, *36*, 215−221.
(117) Tsatsaroni, E.; Liakopoulou-Kyriakides, M.; Eleftheriadis, I. Comparative study of dyeing properties of two yellow natural pigments—Effect of enzymes and proteins. *Dyes Pigm.* **1998**, *37*, 307−315.
(118) Kamel, M. M.; Helmy, H. M.; El Hawary, N. S. Some Studies on Dyeing Properties of Cotton Fabrics with *Crocus sativus* (Saffron flowers) Using an Ultrasonic Method. *J. Nat. Fibers* **2009**, *6*, 151−170.
(119) Ramamoorthy, A.; El-Shafei, A.; Hauser, P. Plasma Induced Graft Polymerization of C6 Fluorocarbons on Cotton Fabrics for Sustainable Finishing Applications. *Plasma Processes Polym.* **2013**, *10*, 430−443.
(120) Scotter, M. The chemistry and analysis of annatto food colouring: a review. *Food Addit. Contam., Part A* **2009**, *26*, 1123−1145.
(121) Gulrajani, M.; Gupta, D.; Maulik, S. Studies on dyeing with natural dyes: Part I-Dyeing of annato on nylon and polyester. *Indian J. Fibre Text. Res.* **1999**, *24*, 131−135.
(122) Dasa, D.; Maulik, S. R. Dyeing of wool and silk with Bixa orellana. *Indian J. Fibre Text. Res.* **2007**, *32*, 366−372.
(123) Savvidis, G.; Zarkogianni, M.; Karanikas, E.; Lazaridis, N.; Nikolaidis, N.; Tsatsaroni, E. Digital and conventional printing and

dyeing with the natural dye annatto: optimization and standardisation processes to meet future demands. *Color. Technol.* **2013**, *129*, 55−63.
(124) Chan-Bacab, M. J.; Sanmartín, P.; Camacho-Chab, J. C.; Palomo-Ascanio, K. B.; Huitz-Quimé, H. E.; Ortega-Morales, B. O. Characterization and dyeing potential of colorant-bearing plants of the Mayan area in Yucatan Peninsula, Mexico. *J. Cleaner Prod.* **2015**, *91*, 191−200.
(125) Gulrajani, M.; Gupta, D.; Maulik, S. Studies on dyeing with natural dyes: Part II-Dyeing of berberine on acrylic fibre. *Indian J. Fibre Text. Res.* **1999**, *24*, 223−225.
(126) Kim, T.-K.; Yoon, S.-H.; Son, Y.-A. Effect of reactive anionic agent on dyeing of cellulosic fibers with a Berberine colorant. *Dyes Pigm.* **2004**, *60*, 121−127.
(127) Kim, T.-K.; Son, Y.-A. Effect of reactive anionic agent on dyeing of cellulosic fibers with a Berberine colorant—part 2: anionic agent treatment and antimicrobial activity of a Berberine dyeing. *Dyes Pigm.* **2005**, *64*, 85−89.
(128) Ravikumar, K.; Kim, S.-H.; Son, Y.-A. Design of experiments for the optimization and statistical analysis of Berberine finishing of polyamide substrates. *Dyes Pigm.* **2007**, *75*, 401−407.
(129) Aminoddin, H. Functional dyeing of wool with natural dye extracted from berberis vulgaris wood and rumex hymenosepolus root as biomordant. *Iran. J. Chem. Chem. Eng.* **2010**, *29*, 55−60.
(130) Prakash Maran, J.; Manikandan, S. Response surface modeling and optimization of process parameters for aqueous extraction of pigments from prickly pear (*Opuntia ficus-indica*) fruit. *Dyes Pigm.* **2012**, *95*, 465−472.
(131) Guesmi, A.; Hamadi, N. B.; Ladhari, N.; Sakli, F. Dyeing properties and colour fastness of wool dyed with indicaxanthin natural dye. *Ind. Crops Prod.* **2012**, *37*, 493−499.
(132) Guesmi, A.; Ladhari, N.; Hamadi, N. B.; Sakli, F. Isolation, identification and dyeing studies of betanin on modified acrylic fabrics. *Ind. Crops Prod.* **2012**, *37*, 342−346.
(133) Vankar, P. S.; Shanker, R.; Mahanta, D.; Tiwari, S. C. Ecofriendly sonicator dyeing of cotton with *Rubia cordifolia* Linn. using biomordant. *Dyes Pigm.* **2008**, *76*, 207−212.
(134) Erdem İşmal, Ö.; Yıldırım, L.; Özdoğan, E. Use of almond shell extracts plus biomordants as effective textile dye. *J. Cleaner Prod.* **2014**, *70*, 61−67.
(135) John, P. Indigo−Extraction. In *Handbook of Natural Colorants*; John Wiley & Sons, Ltd.: Chichester, UK, 2009; pp 105−133.
(136) Ganglberger, E. Environmental aspects and sustainability. In *Handbook of Natural Colorants*; John Wiley & Sons, Ltd.: Chichester, UK, 2009; pp 353−366.
(137) Bechtold, T.; Mahmud-Ali, A.; Mussak, R. A. M. Reuse of ash-tree (*Fraxinus excelsior* L.) bark as natural dyes for textile dyeing: process conditions and process stability. *Color. Technol.* **2007**, *123*, 271−279.
(138) Zhao, Q.; Feng, H.; Wang, L. Dyeing properties and color fastness of cellulase-treated flax fabric with extractives from chestnut shell. *J. Cleaner Prod.* **2014**, *80*, 197−203.
(139) Haddar, W.; Baaka, N.; Meksi, N.; Elksibi, I.; Farouk Mhenni, M. Optimization of an ecofriendly dyeing process using the wastewater of the olive oil industry as natural dyes for acrylic fibres. *J. Cleaner Prod.* **2014**, *66*, 546−554.
(140) Islam, S. u.; Mohammad, F. High-Energy Radiation Induced Sustainable Coloration and Functional Finishing of Textile Materials. *Ind. Eng. Chem. Res.* **2015**, *54*, 3727−3745.
(141) Semwal, R. B.; Semwal, D. K.; Combrinck, S.; Viljoen, A. Butein: From ancient traditional remedy to modern nutraceutical. *Phytochem. Lett.* **2015**, *11*, 188−201.
(142) Sewekow, U. Natural dyes: an alternative to synthetic dyes? *Melliand E* **1988**, *69*, 145−148.
(143) Wanyama, A. P.; Kiremire, B.; Murumu, J. E. S.; Tumusiime, H. Toxicological characterization of crude dye extracts derived from *Albizia coriaria*, *Morinda lucida* and *Vitellaria paradoxa* selected dye-yielding plants in Uganda. *Int. J. Nat. Prod. Res.* **2012**, *1*, 16−20.
(144) Prabhu, K. H.; Teli, M. D.; Waghmare, N. Eco-friendly dyeing using natural mordant extracted from Emblica officinalis G. Fruit on cotton and silk fabrics with antibacterial activity. *Fibers Polym.* **2011**, *12*, 753−759.
(145) Gupta, D.; Laha, A. Antimicrobial activity of cotton fabric treated with *Quercus infectoria* extract. *Indian J. Fib Text Res.* **2007**, *32*, 88−92.
(146) Han, S.; Yang, Y. Antimicrobial activity of wool fabric treated with curcumin. *Dyes Pigm.* **2005**, *64*, 157−161.
(147) Reddy, N.; Han, S.; Zhao, Y.; Yang, Y. Antimicrobial activity of cotton fabrics treated with curcumin. *J. Appl. Polym. Sci.* **2013**, *127*, 2698−2702.

DOI: 10.1021/acssuschemeng.5b00537
ACS Sustainable Chem. Eng. 2015, 3, 2361−2375