

Utilization and characterization of natural products pretreatment and dyeing wool fabric by natural dyes with economical methods

Abstract

Natural dyes are eco-friendly and they used in dyeing textile fabrics. This requires recent researches for application of natural dyes to obtain smart textile fabrics. Natural dyes extracted from plants, insects and microorganisms, they help to reduce health hazards and pollution to the environment and extend the sustainable use in textile. This review interested in using green chemistry application in dyeing textile fabrics with economic methods. It is also interested in application of nanotechnology in pre-treatment of wool fabric and dyeing with natural dyes. There is a great demand for antimicrobial textiles based on non-toxic and eco-friendly bioactive compounds. Consequently the review aimed to use natural compounds for treatment of textile fabrics before dyeing with natural dyes to enhance dyeing quality and antimicrobial activity.

Keywords: textile, natural dyes, nanotechnology, green chemistry, antimicrobial activity

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Introduction

Natural dyes are renewable, safe for environment eco-friendly and not cause pollution. Natural dyes used in dyeing textile materials instead of synthetic dyes. They are nontoxic and not carcinogenic. Natural dyes are used in dyeing different textile fabrics.¹

Natural dyes are environmentally friendly. It is gentle on the skin and flattering the eyes. Natural dyes are suitable for all types of fabrics used in industries due to its specialty of natural origin.² Natural dyes obtained from plants, vegetables, and many sources. They are characterized by their antimicrobial activity, it is not allergic for the skin, and it protect the body against ultraviolet.³

Natural dyes are coloring agents obtained from vegetables, plants, minerals or insects. The trend of using natural dyes has gained about the environmental friendliness of different textile industries. The use of natural dyes on textiles are increasingly being reported worldwide.³

Several researches have also concluded the medicinal and antibacterial characters of natural dyes. It has been found that yellow dye from the turmeric is traditionally used in medicine as an antibacterial agents.⁴⁻⁶

Several researchers investigated that some natural dyes are suitable to various fibers and textiles. It is an environmentally friendly and require inexpensive methods to produce different colors for textiles. Different extraction processes are carried out from plants and then colored with different stains. Some of plants or vegetables also it has high medicinal properties and pharmaceutical uses and are devoid of toxicity.⁷

In recent years the using of natural dyes has increased interest due to their growing resuscitation phase due to people's concerns about reducing pollution and safety and thereby avoiding more chemicals used in synthetic dyes. On the export market, the demand for naturally dyed natural textiles for future work is increasing now a day. This review interested in natural dyes extracted from natural sources and used for used for dyeing of wool fabric.

Applications

Using microwave energy technology in textile dyeing

Microwave dyeing takes place according to influences the vibration energy in the water molecules and the dye molecules. The heating mechanism depend on the ionic conduction, Affecting on the acceleration of the ions through the dye solution, This cause collision between the dye molecules and the molecules of the fiber. The mordant enhance the penetration of the dye and also the depth in the fabric. Thus microwave dyeing is more effective than conventional technique.⁸ Dyeing using microwave enhance the dyeing properties. It save time and energy ,it is also increase the dyeing rate.⁹

Using plasma technology in textile dyeing and finishing

Plasma technique is environmentally friendly. The advantages of plasma technique related to the drastic decrease in pollutants and a also decrease the cost for effluent treatment. Atmospheric pressure plasmas treatment is important for the polymers which difficult to dyeing by conventional technique

Using supercritical fluids method in textile dyeing and self-cleaning

Carbon dioxide used in different application in industry because it characterized by its low critical point. As a super critical fluid. Carbon dioxide is a cheap, inert, non-combustible, non-toxic and easily available. Super critical carbon dioxide used in textile industry.^{10,11} It is used for dyeing polyester, poly amide and polyester/cotton fabric.

Using of combined enzymatic processes technology in the pre-treatment of textiles

The possibilities of enzymatic processes have been discussed in detail in the literature.¹² It has been suggested that using various types of enzymes, namely amylase, protease, lipase, pectinase, laccase, glucose oxidase, catalase and cellulase, from the beginning to the end of the preparatory processes of textile substrates could be achieved .The combined enzymatic processes of textile materials were also achieved by several researchers.¹³ The use of enzymes enhances the

process efficiency, shortens the process time and requires the use of less energy, compared to the conventional methods which are carried out separately. In the Turkish textile companies, the enzymes, namely amylase, pectinase and catalase are widely used in the preparatory processes.

Using of ultrasonic technique in dyeing textile fabric

The frequency of ultrasonic waves ranges from 20kHz and 500MHz frequencies. The mechanism of ultrasound depend on the cavitations that takes place in water as the micro bubbles when a negative pressure applies to it. A large amount of energy produced due to the collision between the bubbles. Ultrasonic technique leads to decrease in time and energy in dyeing processing. Ultrasonic energy for pre-treatment of textile fabric to enhance the dyeing properties.^{14,15}

Green chemistry technology for textile

Basic principles of green chemistry:

- Minimal waste production.
- Minimal energy consumption.
- Least utility of hazardous chemicals.
- Least time consumption.

In the light of these requirements chemists developed several new directions.

Minimization of time consumption

Utility of microwaves as a quick way to conduct chemical reactions is now at frontiers of organic synthesis

Minimal utility of hazardous chemicals

In the 19th century plenty of the extensively used reactions had employed hazardous and toxic chemicals thus nitrations were performed in presence of excess of $\text{HNO}_3/\text{H}_2\text{SO}_4$ Friedal-Craft acylations used AlCl_3 and thus both reactions produced plenty of hazard methyl methacrylate produced in tons during Second World War. Green chemists have already replaced these process thus nitration and Friedal-Craft acylations are preformed now in acidic zeolites. Methacrylic acid is prepared from propylene by a transition metal catalyst. Catalysis are also wasted is not recyclable and this interest in heterogeneous catalysis have grown, and recognized that Myrobolan is fertile in tannin, hence we applied it in dyeing wool by the aid of Iranian madder natural dyes. Yellow and Black Myrobolan were extracted and used as biomordant for treatment of wool fibers before dyeing with natural dyes. The color strength, color coordinates, wash, light and rubbing fastness of wool fibres dyed in the presence of combination of Yellow and Black Myrobolan extracts are evaluated with and without mordanting and the results are investigated. The approach implemented the fastness properties and the colour strength for the treated and untreated fabrics were assessed. The comparison between them was then evaluated.¹⁶

Application of Natural compounds used in textile

Chitosan

Chitosan can prepared by deacetylation of chitin. It fight microorganisms, capable of being decomposed by bacteria or other living organisms and it is not toxic. There are different factors affected the antimicrobial activity of chitosan as the kind of chitosan, the deacetylation degree degree and the molecular weight It is also affected by pH, ionic strength and aqueous solvents. Chitosan used as antimicrobial agent for textile processing.¹²

Sericin

Sericin is a natural macromolecular protein produced from silkworm *Bombyx mori* which contain 25-30% of the silk protein. It is a biomolecule of large value since it has antibacterial characters. It resist to ultraviolet. It also has resistance to oxidize and has hydrating characters. It has enormous applications. It is used as moisturizing agent in shampoos and creams. It is also used as biomaterial for different applications textile processing.

Materials and methods

Textile processing other than dyeing and finishing is the pre-treatment process. It has been used in the textile processing conventionally or specifically which depends on the end-uses of the products. For example bleaching needs for light shade woolen yarn, carbonizing requires for burr-free products, enzyme treatment requires for softness.¹⁷ Pre-treatment can also used in a textile processing to save energy and to reduce the amount of chemicals to be used in the subsequent processing. Wool, is an animal based natural fibre has distinct properties like warmness, reactivity, moisture regain, elasticity and flame resistant. However, it has demerits like felting shrinkage, hydrophobicity and prone to moth attack due to presence of surface cuticle and cysteine based amino acids.¹⁸

Natural dyes are extracted from different sources. They are extracted from animal or vegetable materials without any chemical procedure. Natural dyes are derived from natural origins as plants (e.g., curcumin and saffron); insects (e.g., cochineal beetles and lac scale insects); fungi and algae without chemical processing.¹

Natural dyes are important for pharmaceutical, food industry, cosmetics and textile dyeing,

Extraction procedure

The coloring material are grinded into and then immersed in water and left during night. Then the solution was heated till boiling and undergo filtration to exclude the non colored components and the impurities non-dye materials.. This method is suitable only for the dyes which not decompose on boiling.

Consequently the dye must be water soluble. There are other suitable and economic methods of extractions as ultrasonic and microwave and do not cause decomposition of the dye.¹

Extraction procedure of yellow and black Myrobolan

Natural dye is extracted from the fruits of myrobolan plant. It is used as natural coloring agent. The dried fruits constitute one of the most important vegetable tanning materials and have been used in India form a long time. The Myrobolan fruits were grinded into small pieces and reserved in glass bottles at temperature (26-28°C). The colored material (50g) was extracted using 200 mL ethanol on shaker for 22 h. The residue was extracted three more times to complete the extraction. The extract was heated to boil and left during night and then filtered.

The cleared filtrate was then concentrated under vacuum in rotatory instrument (heidolph, Germany) and the semi-solid mass obtained was diluted with distilled water. The precipitate was subsequently dried in an oven and turned into powder. $\lambda_{\text{max}}=480\text{nm}$; FTIR (KBr) (Cm-1): 3624: OH str., 3010: CH str. Ar., 1608, 1492: C=C str. Ar. In this study yellow and black Myrobolan named YM and BM, respectively.

Madder is an important source of natural dyes extracted from vegetable used for dyeing wool fabric. Madder is an old natural dye. It is named as the queen of red colors with common name of Rubiaargy

that related to Rubiaceae family. Natural dyes (Madder), Yellow and Black myrobolan are natural mordants produced from underbrush grown in Iran.

FTIR-ATR spectra were measured on a spectrometer (Perkin Elmer, USA) equipped with a ZnSe to exhibit qualitative evaluation of changes in the main functional group absorption bands in the mordanting wool and the dyed wool fibers.¹

Dyeing of wool fabrics

Dyeing wool with madder natural dye was carried out using IR dyeing machine (Xiamen Rapid) by lacquer ratio 1:50 at different concentrations (10,20,30,40%). The temperature raised from 40 to 100°C at a heating rate of 2°Cmin⁻¹, for 60 min and then cooling down to 70 °C at a rate of 3°Cmin⁻¹. The fastness properties was measured using ISO105-C10:2006, ISO105-B02:2014 and ISO105-X12 2016 protocols, respectively.

Pretreatment of wool and silk fibers by neem oil

Wool and silk fibers treated by pad-dry-cure techniques. The wool fibers treated by neem oil extract at different concentrations (20-50%) and silk fibers treated by neem oil extract at concentrations (2-10%), then padded to 100% wet pick up, dried at 80°C for 5 min. then cured at 120°C for 3 min (Figure 1).

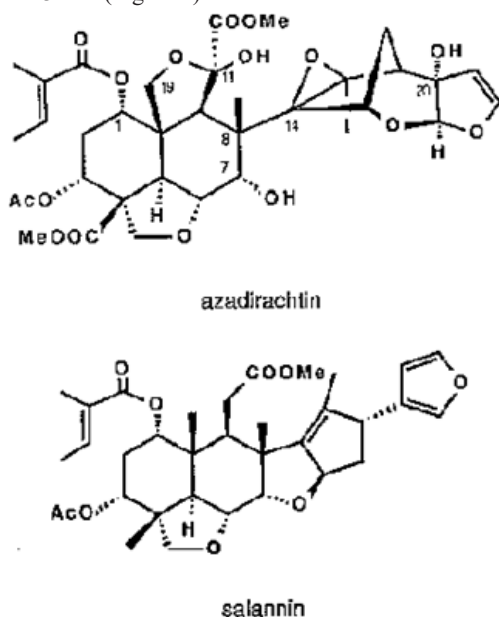


Figure 1 Chemical structures of main constituents of neem oil extract.

Neem (*Azadirachta indica*) is an evergreen tree of India, which belongs to the plant family *Meliaceae*. It is one of the most important compounds has antimicrobial activity. The active ingredients of neem are found in all parts of tree. It is used textile industry as an antimicrobial agent. Neem can be used for pretreatment of textile fabric dyed with natural dyes instead of mordant.¹³

The extract of neem has been widely used in pesticide formulations that due to their pest repellent properties have the potential to inhibit the growth of Gram-positive and Gram-negative bacteria. At present, little has been reported of its use in textiles as an antimicrobial agent. Dyeing is a main process in textile technology and dye applied the important role in dyeing of textile, fibers or fabrics. Natural and synthetic dye can be used in dyeing process and recently was increased the use of natural dye due to their renewability and biodegradability. The majority of natural dyes could not be directly used in dyeing process due to their low affinity. The mordanting process could be solved

this limitation. Mordants are materials having tendency towards both fibers and dyes molecule, whenever there is low affinity between dye and fibers.

This review interested in using modern technology in dyeing fabrics by economical and eco-friendly methods to avoid health hazards and environmental pollution. The review also interest in the application of green strategy and to obtain smart textile by using microwave and ultrasonic in dyeing fabrics.

These studies have focused primarily on application of new methods for dyeing textiles resulting in:

- i. Excellent dyeing efficiency.
- ii. Excellent fastness properties
- iii. Outstanding functional finishing.
- iv. High color strength.

There has been a revival of interest in natural dyes throughout the world as some synthetic dyes are being banned by the Western countries due to their toxic, carcinogenic and polluting nature. There has been a manifested interest in natural dyes. The reasons are manifold, including the ecological movement, biodegradability and higher compatibility of natural dyes with the environment

The present review is interested with green chemistry applications for natural dyes. So that environmentally friendly pre-treatment with chitosan were used instead of using mordants.

In this review wool fibres will be dyed with natural dyes extracted from some natural dyes as Saffron (*Crocus sativus*) powder, curcumin, Indigo, Madder, cassia fistula and chlorophyll using a traditional and microwave heating methods.

Chlorophyll is a green compound found in leaves and green stems of plants. Due to the green color of chlorophyll, it has many uses as dyes and pigments. It is used in coloring soaps, oils, waxes and confectionary. The problem of the use of a natural pigment, chlorophyll, as ecologically pure dye for textile fibers was discussed. Chemical transformations of chlorophyll and physicochemical properties of its derivatives are considered.

Hina dye (*Lawsonia inermis* L)

Hina dye is extracted from the leaf of the plant. It is traditionally used for coloring the design on the hands of women. The extraction of the dye carried out by boiling of the leaf of the plant after drying and crushed it. The Addition of mordant change the color of the fabric from brown to mustard yellow. It considered as disperse dye; hence, polyester and nylon can be dyed by hina. However, it stains wool and silk by a lighter brown colour. Hina is called as lawsone. The main constituent of hina leaves is hennotannic acid; its color is red orange. The chemical name of hennotannic acid is 2-hydroxy-1,4-naphthoquinone. The coloring material have strong substantivity for protein fiber used as coloring agent in textile (Figure 2).¹⁶



Figure 2 Hina dye (*Lawsonia inermis* L).

Saffron dye (*Crocus sativus*)

Saffron dye obtained from the stigma of flower. It is extracted by boiling in water. It produce a bright yellow color to the textile fabrics. It is used for dyeing wool, silk and cotton. Alum mordant give orange yellow shade which is also known saffron yellow. This is coloration of food. Saffron belongs to the Iridaceae family. The aqueous extract of saffron petals constitute 12% colorant. The coloring component of saffron include phenolic compounds, flavonoids and anthocyanins. Anthocyanidins (pelargonidin) is considered as the color in saffron petals. The oxidation of anthocyanidins produces flavone used as natural dye for textiles (Figure 3).¹³



Figure 3 Saffron dye (*Crocus sativus*).

Flavones dye

Flavon dye is a yellow shade. The natural dye graft related to this series. Most of the dyes are substituent of hydroxyl and methoxy flavones or isoflavones. Plant-based carotenoids are obtained from microalgal pigment which is organic pigments called carotenoids belongs to tetraterpenoids are hydrophobic molecules located within cell membranes and contain α carotene, β carotene, γ carotene used as natural dye for textile and fibers (Figure 4).¹⁶



Figure 4 Flavones dye.

Carotenoids dye

Carotenoids are red, yellow and orange pigments extracted from plants. It has a polyisoprenoid structure with chains which bonded with conjugated bonds. Carotenoids are responsible for the bright colors of many fruits and vegetables. The conjugated double bonds, which make as chromophore and responsible for characteristic absorption spectra used also for dyeing textile.¹⁶

Tumeric (*Curcuma longa*) dye

Turmeric (*Curcuma longa*) is a plant present in south India. Indonesia. China and the whole of South East Asia. It known as "Haldi". Curcumin from *Curcuma longa* contain antioxidant, anti-inflammatory, anticancer and hepato-protective agent. It has anti-inflammatory effects in arthritis, capable of inhibits prostaglandin synthetic way of Cox-2 and do not cause ulcers in the GI tract¹⁰.

it has used as anti-platelet, antiviral, antifungal, anti-bacterial effects (inhibits *Helicobacter Pylori*) and good antiseptic material and it also as coloring agent and antimicrobial agent for textiles (Figure 5).⁵



Figure 5 Tumeric (*Curcuma longa*) dye.

Marigold flower dye

Marigold plant present in Americas, cultivated also in United States into South America. Small species have produced and naturalized the world over. Most species contain pinnate green leaves. Sprouts colors are brilliant, orange, yellow, and white tones, commonly with maroon aberrance used as coloring agent for textile (Figure 6).⁵



Figure 6 Marigold flower dye.

Turkish red pine dye

Turkish pine generally cultivated in the eastern Mediterranean areas. The bulk of its range is in Turkey, but it also present in Bulgaria, Jordan, Iran, Crete, Georgia, and Iraq, Syria, Lebanon, and Cyprus. The bark color are orange-red, thick and deeply fissured at the base of the trunk, and thin and flaky in the upper crown. The leaves are bright green to slightly yellowish green color used for textile (Figure 7).⁵



Figure 7 Turkish red pine dye.

Indigo natural dye

Indigo plants are found in China, Taiwan, Netherland and Japanese. Dying with indigo is based on a single color, and it give a bright blue color, and different levels of meddle colors, and produce different chromaticity of blue coloration. Indigo gave lighter colors and have a shorter biodegradation time, and darker colors take

longer. Clothing with different indigo dyes is recycled process; it will not have different biodegradation time due to the differ degrees of chromaticity and many materials-saving. As eco-friendly because natural dyes having good biodegradability and almost having larger compatibility with the environment. Using natural dyes have become one of the world's future trends of natural dye. Indigo colors are used for sustainable design as natural resources depending to the important of the sustainable design of indigo dyeing is natural dye for textiles and as finishing product. Indigo-dyed fabrics can be de- composed by a different microorganisms which gave light-colors in a short time, from light to dark-colored for textiles (Figure 8).⁵



Figure 8 Indigo natural dye.

Discussion

Antimicrobial activities for textile fabric

To decrease hazards accompanied with the use of antimicrobial agents, there is a great need for antimicrobial textile depending on non-toxic and ecofriendly bioactive materials. Relative reversible reactions occur as a result of using natural compounds compared to synthetic pharmaceuticals. Consequently scientists can be hard done by an attractive ecofriendly substitute of textile application.

There are several researches in textile industry for new technology to satisfy the consumers demands. Functionalized and smart textiles are produced which have the ability of sensing to the changes in environmental factors or body operations and sensing to these changes, yarns of antimicrobial activity has increased considerably now a day.

Bacteria and fungi, may be pathogenic or not, are essentially present on human skin. Microbial shedding from our body participate to microorganism spreading into a textile fabric either directly in fabric or on surrounding clothes. Development researches highly support that contamination of clothes in clinical settings may participate to the dispersal of pathogens to the air which then infect the surrounding and the environment. It is one of the most probably causes of hospital infections. Typically, pathogenic microorganisms as *Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, *Staphylococcus epidermidis*, *Staphylococcus aureus* and *Candida albicans* have been present on fabrics.¹²

Microorganism can effect on malodors, stains and destroy the mechanical characters of the fibres which cause a product to be less effective. Also, may cause skin contamination, inflammation for sensitive people, atopic dermatitis. The use of antimicrobial fabrics may significantly reduce the risk of infections especially when they are used in close contact with the patients or in the immediate and non-immediate surroundings.¹³

Antimicrobial agents for textile

Antimicrobial agents are natural or synthetic materials that cause inhibition of the growth of bacteria and fungi (bacteriostatic or fungi

static) as they can be protein, lipid synthesis or enzyme inhibitors, all of which are common for cell survival; or kill (biocidal) the microorganisms by destroying the cell wall. Mainly all antimicrobial synthetic agents using textiles are biocides.¹²

Nanotechnology for textiles and their application

Nanotechnologies are very important for nanostructure materials used in various materials and nano sciences, for the development of technologies and new approaches of new material synthesis with applications in various industries. Nanotechnology is the technology based on nanostructure, atoms and molecules of the products of smaller and faster and more reliable materials. The application of nanotechnology in industrial fabrics is important for development of textile characters as high tensile strength, unique surface structure, soft feel, durability, antimicrobial properties; further advances have produced different chances and challenges for textile.

Nano materials are characterized by a decrease from macro size to nano size with changes in chemical reactivity, mechanical properties, physical properties, surface properties and thermal properties and transform into Nano scale and nanostructured materials. Nanomaterial depends on their nanostructures and the characterization of nano-compounds. Nanotechnology is a multidisciplinary field of application in research and industry that depends on the generation of information and communication technologies.^{19,20}

Textile nanotechnology in the use and characterization of Nano fibers and nanofabrication technology for use as garment water, wrinkle-free properties, fibers materials with nanotechnology Applications to achieve new properties with less washing time at low temperatures are now increasing in industries around the world.

While the textile industry is due to advances in nanotechnology, the development of the roles of textile and the fulfillment of action of textiles are the results of nanotechnology. The key of nanotechnology depend on the nanostructure, nanomaterial and nano scale compounds can be efficiently obtained by nanotechnology are more durable, lighter, high conductive, and stronger and can have many other individual properties and increased special and extraordinary properties of textiles and clothing.^{21,22}

The improvement of the action of textiles and the fulfillment of extraordinary characters of textiles are the results of nanotechnology in textiles. Smart textiles are also playing a role in interior design. They give the interior products exclusive properties, as Optical and acoustic properties. Nanotechnology, which is used in textiles, also it is effective in the medical field. Such as, ultraviolet rays have a very negative action on people and the environment. They can cause serious health problems such as skin cancer, blisters, bumps, red spots, eye damage, sunburn, and premature wrinkling.^{23,24}

Metal oxide nanoparticles are made to minimize the interaction of UV rays with the skin. Titanium oxide, magnesium oxide, zinc oxide and aluminum oxide are the metal oxides that inhibit UV absorption, photocatalytic, electrical conductivity and photooxidizing ability. Nanoparticles of these metal oxides act against biological and chemical toxins. Zinc oxide and titanium oxide nanoparticles are usually used as UV blockers. Silver nanoparticles coated on cotton fibers using the Pad-Dry-Cure process exhibited high wash resistance and retained the antibacterial and antifungal characters against different pathogens even after washing several times.^{25,26}

The characters of silver nanoparticles leads to the use of nanoparticles on textiles worthwhile. Organic or inorganic titanium oxide and titanium dioxide influence the characters of fabrics. photo-

stabilize of wool, super hydrophobic, photo catalyst, co-catalyst for cotton crosslinking, antibacterial, gas sensor, self-cleaning, hydrophilic, dye broking. Clay nanoparticles are used as UV absorbers, antibacterial and flame retardants. Gold nanoparticles are electrically conductive and antibacterial agents that are used for different types of finishing agents for textiles.^{27–30}

Conclusion

Natural dyes are known as environmentally friendly dyes as a result of their unique properties of natural origin, but synthetic mordants are not very environmentally friendly and some are toxic, which are not effective for natural dyes. The consumption of naturally colored fabrics in the industry will increase rapidly. Applications and improvements needs to be done to enhance the performance of natural dyes to reduce the cost, using natural stains and increase industrial uses. Application of nano technology in textile is very important in industries for the future work.

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Conflicts of interest

The authors declare no conflict of interest.

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