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Original Research Article

Greener approaches in textile industry

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ABSTRACT
Green reactions are sustainable, highly efficient (fewer steps, fewer resources, less waste), much easy-to-use (stable under ambient conditions) and very much eco-friendly (non-hazardous solvents and less hazardous minimized waste). The textile industry is considered as ecologically one of the most polluting industries in the world. Recently a number of steps have been taken to make textile processing greener. These include use of greener fibre, greener dyes and auxiliaries, greener solvents, eco-friendly, optimized and efficient processing, bio-processing, recycling of textile, water and chemicals and elimination of hazardous chemicals.

1. Introduction

Fast growing environmental threats are largely triggered by manmade chemistry which is trying to reverse the rhythm of mother earth. Lead, for example, used to be found mostly in deposits so isolated and remote that nature never folded it into living organisms. But now lead is everywhere, primarily because our paints, cars and computers have spread it around. Some of the new synthetic molecules in medicines, plastics and pesticides are so different from the products of natural chemistry as if they are dropped in from an alien world [1]. Two types of materials are available in nature are:

1. Renewable materials which grow, get biodegraded and re-grow,
2. Non-renewable finite materials which do not grow and may exhaust if used intensively.

Unsustainable conventional chemical manufacturing processes depend on non-renewable carbon-based fossil fuels (petroleum and coal) and they generate large amounts of waste polluting the environment.

"Sustainability" is the capacity to endure. For humans, sustainability is the long-term maintenance of well being, which has environmental, economic, and social dimensions, and encompasses the concept of stewardship, the responsible management of resource use. In ecology, sustainability describes how biological systems remain diverse and productive over time, a necessary precondition for human well-being. Long-lived and healthy wetlands and forests are examples of sustainable biological systems.

2. Non-ecofriendly substances

"Green" is a very subjective term that could be interpreted in different ways by different people. The green or eco-friendly goods, services, and practices, however, assure that [2]:

1. They are made of environmentally friendly materials.
2. They are free from harmful chemicals and compounds.
3. They do not deplete the environment during production and transportation.

Non-biodegradable organic materials, hazardous and accident-prone substances may harm on human being.

Non-biodegradable material is not broken down by microbes and has an oxygen demand only if it is a chemical reducing agent. It has no biochemical oxygen demand [3].

A hazardous substance is one which is health hazard and a physical hazard [4].

Health hazard means a chemical for which there is statistically significant evidence that acute or chronic health effects may occur in exposed humans. Two important sub-groups of hazardous chemicals are: (i) toxic heavy metals, and (ii) toxic volatile organic chemicals.

Physical hazard means a chemical which is a combustible liquid, a compressed gas, explosive, flammable, an oxidizer, pyrophoric, unstable (reactive) or water-reactive.

Toxic metals/Heavy metals: Heavy metals are defined as metals which have a large atomic number. They have specific gravity 4-5 times greater than that of water [5]. The heavy metals may enter the body through food, water or air or by absorption through skin and tend to bio-accumulate. Many of them form lipid soluble organo-metallic compounds that accumulate within the cells and organs impairing their functions. Lead (Pb), mercury (Hg), cadmium (Cd), chromium (Cr) and arsenic (As) may cause cancer and damage to brain, nervous system, lungs and kidneys [6].

Toxic volatile organic compounds: Volatile organic (VOCs) are organic chemicals that have high vapour pressure at ordinary, room-temperature conditions due to their low boiling points. VOCs may cause several health disorders namely eye, nose, and throat irritation, headaches, loss of coordination, nausea, damage to liver, kidney, and central nervous system. Some VOCs can cause cancer in animals; some are suspected or known to cause cancer in humans. VOCs include both man-made and naturally occurring chemical compounds. Respiratory, allergic, or immune effects in infants or children are associated with man-made VOCs and other indoor or outdoor air pollutants [7].

***Accident prone substances*:** Of the carriers that carry hazardous goods, the majority of them carry flammable petroleum products including kerosene, petrol, LPG, naphtha etc. When involved in a road accident, they may cause disastrous consequences like fire, explosion, injuries, in addition to property loss and environmental pollution.

3. Green Chemistry

'Green Chemistry' is essentially a way of thinking rather than a new branch of chemistry and is about utilizing a set of principles that seek to reduce the adverse environmental impact of chemical processes and products and to contribute to sustainable development [8].

Environmental chemistry studies the effect of environmental pollutants, whereas green chemistry deals with new sciences and technologies to prevent the formation of any waste.

The green issues are being confused with 'organic' sourcing and production. Indeed, many people are unaware that some of the most known toxic chemicals (for example, ricin and botulin) are not manufactured but are natural proteins [9].

3.1 Life cycle assessment

A life cycle assessment (LCA), life cycle analysis or cradle-to-grave analysis is an environmental assessment tool that accounts for the use and emission of various raw materials at all stages in the product chain from raw material extraction through production, use and final disposal [10].

LCAs enable a manufacturer to quantify how much energy and raw materials are used, and how much solid, liquid and gaseous waste is generated, at each stage of the product's life. LCAs might be conducted by an industry sector to enable it to identify areas where improvements can be made, in environmental terms.

Cleaner production is the conceptual and procedural approach to production demanding all phases of the life-cycle of a product or of a process should prevent or minimize short- and long-term risks to humans and the environment.

3.2 Principles of green chemistry

Green chemistry recommends [11] use of the reactions with the following twelve objectives:

1. Elimination or minimization of waste.
2. No or fewer wastage of atom (atom economy).
3. Catalysts are preferred to stoichiometric reagents.
4. Direct reactions with minimum or fewer steps. More steps require additional reagents and generate more waste.
5. Use of fully effective, yet safer and non-toxic products
6. Safe chemical synthesis routes.
7. Renewable and not depleting feedstock.
8. Easy and harmlessly degradable chemicals – no accumulation in the environment.
9. No solvent or safer solvents and reaction conditions.
10. Energy efficient processes preferably at ambient temperature and pressure reactions.
11. Real-time monitoring and control of by-products.
12. Avoiding hazardous chemicals – no changes of explosions, fires and harmful releases.

3.3 Advantages of green reactions

The advantages of adopting green chemistry [12] are:

1. It assures a series of reductions leading to economic, environmental, and social improvements.
2. Cost saving leading to environmental benefit by reducing
   (a) Waste and its disposal costs,
   (b) Energy consumption.
   (c) Materials consumption due to more efficient processes.
3. The industry becomes sustainable due to increasing use of renewable resources.
4. The reduction in hazardous incidents providing additional social benefit.

3.4 Implementation of green reactions

Six major classes of barriers to the implementation of green chemistry are [13]:

1. Occasionally *Green Chemistry* is more expensive and the future benefits are uncertain.
2. Lack of global harmonization, insufficient funding for research and regulatory incentives.
3. Non-availability of suitable substitute reactions and trained chemists and engineers
4. Other barriers include intra-organizational conflicts, poor awareness and wrong conception about green reactions
5. Poor guidance on best practice and sufficient teaching on sustainable chemistry;

3.5 Evaluation of green reactions

The general efficiency of a chemical transformation can be judged by assessing atom economy which is the molecular weight of desired product expressed as percentage of total molecular weight of all reactants [14]. The concept was introduced by Trost [15]. Atom economy can be poor even when chemical yield is near 100%. The concept of atom economy can be illustrated in general by the reaction shown in Eq. (1).

$$(\text{reagent})_1 + ... + (\text{reagent})_n \rightarrow \text{product} + \text{by-product} \quad (1)$$

The ultimate in atom economy is achieved when there is no or negligible by-product

$$\text{by-product} \ll \text{product} \quad (2)$$

A high degree of atom economy assures high efficiency of a chemical reaction (e.g. addition reactions).

While atom economy focuses on the reaction only, Sheldon factor of environmental acceptability, E factor, assesses greenness of the chemical process by measuring the ratio of the mass of waste to that of the product [16]. For truly green processes, the E factor should be zero. Table 1 shows environmental acceptability (E factor) of some established chemical production processes [17].

Table 1: Environmental Acceptability (E Factor) of Various Industries

Industrial chemical process	E factor
Oil refining	0.1
Commodity chemicals	< 1.5
Special chemicals	5 – 50
Drugs	25 - >100

3.6 Traditional vs. green solvents

Most solvents are volatile and tend to escape into the workplace and atmosphere. Benzene causes blood disorders and is suspected of causing leukaemia. Volatile C5-C7 alkenes damage nerves and can result in a condition known as peripheral neuropathy. The possibility of causing cancer is always a consideration in dealing with solvents in the workplace. Numerous N-nitroso compounds, many produced as by-products of industrial operations and food and alcoholic beverage processing, are found to be carcinogenic [18].

Carbon tetrachloride causes lipid peroxidation in the body and severe damage to the liver [19] and also causes stratospheric ozone destruction. As production of chlorofluorocarbons (CFCs) is phased out under the Montreal Protocol, carbon tetrachloride emissions will continue to decline [20].

Green solvents should not be flammable, toxic to any life form, carcinogenic, or able to contribute to smog formation, ozone depletion, or eutrophication of natural waters. Green solvents should not require a large amount of energy for their production (from renewable raw materials) or for the separation of the solvent from solutes or products. Unfortunately, there is currently no perfect green solvent that can meet all of these requirements. However, some solvents are clearly greener than others. The greenest solvent is sometimes no solvent at all.

The examples of green solvents are:

1. Ester solvents (volatile and non-volatile) such as isopropyl laureate, rapeseed methyl ester (biodiesel), glycerol triacetate and dibasic ester.
2. Specialty solvents for example, glycerol carbonate, dioctyl ether, ethyl lactate and 2-ethylhexyl lactate.
3. Supercritical gases, for example, supercritical carbon dioxide.
4. Fusible solids namely:
   (a) Waxes, e.g., hydrogenated castor oil, stearyl stearate
   (b) Ionic liquids, for example, tricaprylmethyl ammonium chloride and 1-butyl-3-methyl imidazollum methyl sulphate.

Ionic liquids (ILs) are liquids composed entirely of ions. Thus, molten sodium chloride is an ionic liquid while a solution of sodium chloride in water (a molecular solvent) is an ionic solution [21].

The green solvents recommended by Ash and Ash [22] are acetic acid, acetophenone, benzyl benzoate, diethylene glycol, dibutyl ether, diethylene glycol, dimethyl ether, dimethyl sulfoxide, ethyl acetate, ethylene glycol, dimethyl ether, glycerol, hexane, methanol, polyglycol E 200, propylene glycol, *t*-Butanol and tetrahydrofuran.

Nature's solvent, water has great appeal as a green solvent. Water is obviously non-flammable, non-toxic, and quite inexpensive. However, it is not a good solvent for a wide range of organic substances.

3.7 Greener energy

The processes like heating, cooling, stirring, distillation, compression, pumping and separation require electrical energy which is obtained by burning of fossil fuel. This results in release of carbon dioxide in the atmosphere causing global warming. Green chemistry aims at developing alternative energy generation such as photovoltaic, hydrogen, fuel cells and bio-based fuels.

4. Textile industry and sustainability

The textile industry has been condemned as being one of the world's worst offenders in terms of pollution as it uses more than 2000 types of chemicals and over 7000 types of dyes. Dyeing and finishing one ton of fabric can result in the pollution of up to 200 tons of water with a suite of harmful chemicals and consume tremendous amounts of energy for steam and hot water. With the industry now centred in countries with still developing environmental regulatory systems, such as China, India, Bangladesh, and Vietnam, textile manufacturing has a huge environmental footprint [23].

Besides displeasing colour visibility, heavy metal constituents in the textile effluent also resulted in negative ecological impacts. Some of the heavy metals commonly exist in textile effluent are arsenic, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel, silver, tin, titanium and zinc. Many of them are widely used for the production of pigments and dyes [24]. Among the possible sources of heavy metals in textile operations are incoming fibre, water, dyes, auxiliaries, finishing, plumbing and chemical impurities [25].

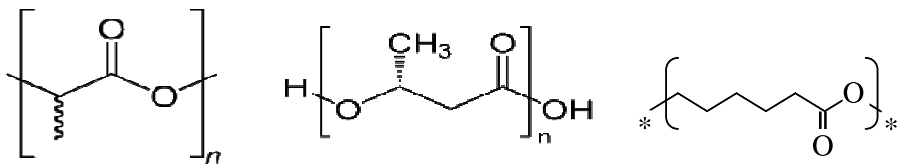
The following six issues make the life cycles of textiles and clothing unsustainable [26]:

1. Chemicals - as many as 2,000 different chemicals are used in the textile industry, a large portion of which is discharged with effluent after use.
2. Water - the textile industry is the highest consumer and polluter of clean water (after agriculture).
3. Energy - textile production consume a large quantity of non-renewable energy sources. Even textile consumers use electrical energy to heat water for running laundry and to dry materials after laundering. For textile industry, data on energy usage are relatively readily available, but the estimation of the CO_2 emissions that arise from the sources of energy (coal, electricity, natural gas or other sources) is difficult.
4. Waste - textile industry generates a huge quantity of waste. For greener processes, non-renewable wastes are to be recycled and the renewable are to be composted as much as possible.
5. Transportation - Excessive consumption of non-renewable fuel in transportation as the labour-intensive textile production units are generally far away from the consumer point to utilize cheap labour and land.

6. The sustainability of textile products is further tarnished when packed with huge quantity of plastics and layers of foam. Sustainability can be improved by the use of recyclable and reusable packaging materials.

4.1 Bio-polymers

The use of biopolymers, i.e., biodegradable plastics made from corn, sugar, starch and other renewable raw materials, has exploded in recent years. Advantages include production from fully renewable resources, fast and complete biodegradable, excellent strength and stiffness, which favours this material as a polymer for future.



(a) (b) (c)

Figure 1: Chemical Structures of Biopolymers. (*a*) polylactic acid, (*b*) Poly-(R)-3-hydroxybutyrate (P3HB), (*c*) polycaprolactone (Source: http://en.wikipedia.org, accessed on 5.8.11).

Polylactic acid or polylactide (PLA) (Figure 1(a)) is a thermoplastic aliphatic polyester derived from renewable resources, such as corn starch (in the United States), tapioca products (roots, chips or starch mostly in Asia) or sugarcanes (in the rest of world). It can biodegrade under certain conditions, such as the presence of oxygen, and is difficult to recycle.

The medical applications of this polymer arise from its biocompatibility. The fibres may be fabricated into various forms and may be used for implants and other surgical applications such as sutures. Tissue engineering is the most recent domain where PLA is being used and is found to be one of the most favourable matrix materials [27].

The route of manufacture is as follows [28]:

Corn → starch → unrefined dextrose → fermentation → D- and L-lactic acid → monomer production → D-, L- and *meso*-lactides → polymer (PLA) production → polymer modification → fibre, film, plastic, bottle etc. [29].

The most active current area of research in natural polymers involves bacterial polyesters polyhydroxyalkanoates (PHAs) with Poly-(R)-3-hydroxybutyrate (P3HB) as the first homologue (Figure 1(b)). Their production has now been achieved in transgenic (genetically engineered) plants. However, serious drawbacks of these polymers include highly thermal degradability and brittleness with consequent difficulty in processing, and high price [30].

Polycaprolactone (Figure 1(c)) is a synthetic polymer prepared by ring opening polymerisation of caprolactone. The mechanical properties are similar to polyolefin. It is similar to PHAs and fully biodegradable, but degrades at a lower rate compared to PHAs. Due to lower melting temperature of about 60°C, the polymer is mainly used in polymer blend or as a matrix for biodegradable composites.

4.2 Greener fibres

Cotton represents almost 38% of the world's textile consumption, second only to polyester. It is highly susceptible to pests, especially in humid areas. Though cotton production is restricted to 2.4% of cultivable land globally, an estimated 25% of global insecticide and 11% of global pesticide are consumed in cotton cultivation. This 'thirsty' crop also requires 7000-29000 litres of water to produce one kg of cotton fibre [31].

Organic cotton [32] and organic linen [33] are cultivated from non-genetically-modified plants that are certified to be grown without the use of any synthetic fertilizers or pesticides.

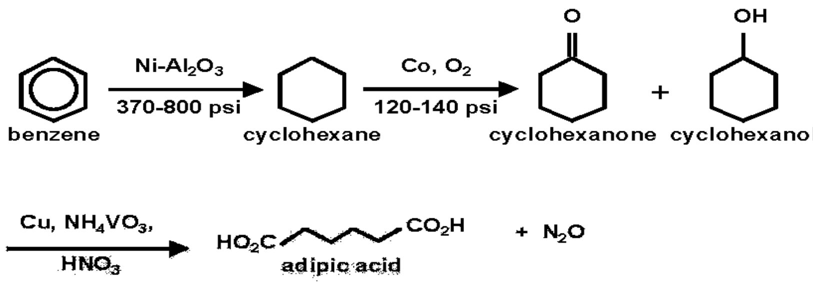
The preparatory processes required before dyeing and printing are similar for organic and conventional processing. However, some chemicals such as substances with high AOX (harmful adsorbable organic halogens) values, bluing agents, chelating agents, chlorine compounds, formaldehyde etc. are prohibited to use for organic textiles. All dyes should conform to ETAD [34] restriction regarding residual heavy metals and banned aromatic amines. The first choice for dyeing organic fabric, where, applicable, could be plant-based natural vegetable dyes. However, their commercial availability is limited.

Lyocell fibres are produced by regenerating cellulose in an organic solvent, N-methylmorpholine-N-oxide (NMMO) hydrate. Non-toxic, biodegradable NMMO solvent is almost completely recycled [35]. The lifecycle of a lyocell fibre has minimal environmental impact. The cultivation of cotton requires significant areas of land, irrigation, pesticides and fertilizers to grow as compared to eucalyptus trees, from which lyocell is made [36].

The process of regenerating cellulose can be greatly simplified by the use of ionic liquids which serve as the solvent and can be almost entirely recycled [37]. Cellulose can be dissolved, without derivation, in some hydrophilic ionic liquids, such as 1-butyl-3-methylimidazolium chloride (BMIMCl) and 1-allyl-3-methylimidazolium chloride (AMIMCl). Microwave heating significantly accelerates the dissolution process. Cellulose can be easily regenerated from its ionic liquid solutions by addition of water, ethanol or acetone. After its regeneration, the ILs can be recovered and reused.

A large quantity of adipic acid ($HOOC(CH_2)_4COOH$) is used for the production of nylon, polyurethanes, lubricants and plasticizers. Conventionally it is produced from carcinogenic benzene, steps of which are shown in Eq. (3).

Natural glucose can be converted into adipic acid by an enzyme discovered in genetically modified bacteria as shown in Eq. (4) [38].



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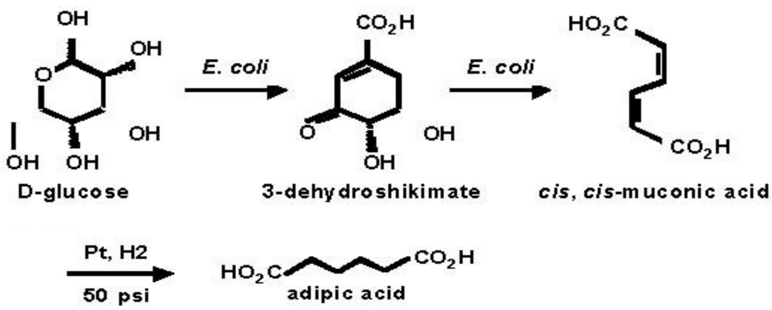

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4.3 Recycled textiles

After use, much of the painfully achieved textile products are thrown away, buried or burned. Landfill sites may release ozone-depleting methane gases because of improper decomposition of fibres and incomplete burning. Air-born particulates caused by improper incineration of the material may result asthma in human bodies [26].

The textiles being nearly 100% recyclable, nothing in textile and apparel industry should be wasted. The textile recycling industry is one of the oldest and most established recycling industries in the world. Textile recycling materials may be pre-consumer or post consumer (i.e. used garments or articles). The sorting categories of textile recycling by volume is represented by a pyramid structure, the base of which consists of used cloth market (48%), followed by conversion to value added new materials (29%), cut into wiping and polishing cloths (17%) and landfill and incineration for energy (<7%). The peak of the pyramid is represented by 'Diamonds' (1-2%) which have high value for antique quality or for other reason [39].

Non-biodegradable polyester fibre can be recycled in two ways:

1. Simply melted and re-extruded into fibres and
2. A multi-stage de-polymerization and re-polymerization to produce better quality yarn.

4.4 Greener colorants

Health and safety were absent from the list of priorities in the early decades of the synthetic dyes industry. Practical experience in the primitive working conditions of the time made workers aware of the more obvious dangers, such as corrosive acids, flammable solvents and potentially explosive nitro compounds [33].

Harmful Azo Dyestuffs

Azo groups (-N=N-) are not available in nature. Azo groups incorporated in benzenoids form the basis of majority of synthetic dyes. Approximately 70% of all dyes (belonging to various dye-classes) used in textile industries are azo dyes.

It has been estimated that less than 4 % of known azo dye structures would release the corresponding amines. Under reductive conditions (pH 6) using sodium dithionite these azo groups may be cleaved to form two amines as shown in Eq. (5).

$$A\text{-}N{=}N\text{-}B \xrightarrow{Na_2S_2O_4} A\text{-}NH_2 + B\text{-}NH_2 \qquad (5)$$

A small number of the aromatic amines are classified as being carcinogenic or potentially carcinogenic to humans. Only a few azo dyes can release these amines upon reductive cleavage [40]. The regulation, EU Directive 2002/61/EC identified twenty-two aromatic amines as harmful and has prohibited their use [41]. For OEKO-TEX standard 100, two more arylamine substances, are added to the list of harmful amines (total 24 amines). The detectable concentrations of any amine should not exceed 30 ppm in the finished articles or in the dyed parts thereof.

Natural Dyes

In recent years, interest in natural dyes has been revived due to increasing demands on manufacturers to produce more environment friendly alternatives to petrochemical derived dyes, but they have poor to moderate light fastness. The major types of natural dyes and their origin have been tabulated by Hill [42]. Natural dyes may be sustainable, but need more water and land to produce. There is not enough dye yields per acre of plant material to sustain industrial-scale fabric production.

Reactive dyes

The most obvious deficiency in the conventional reactive dyes lies in the fact that their dyeing efficiency is not more than 70% even in printing application. The remainder undergoes hydrolysis instead of reaction with the fibre increasing pollution load. More recently bifunctional reactive dyes have been developed which provide much higher degrees of fixation (above 90%) than the conventional reactive dyes.

Unfortunately, reactive dyes require a large quantity of common salt and moderate quantity of soda ash for their application. High electrolyte concentration in dyebath discharges is undesirable, as increased salinity in rivers upsets the delicate balance of aquatic flora and fauna. The most notable low-salt reactive dye ranges are Cibacron LS (CIBA) and Remazol EF (Hoechst). Cellulose may also be cationised so that it can be dyed with no or minimum amount of salt [43].

Synthetic dyes are difficult to remove from effluent due to poor biodegradability. A few easy degradable dye structures are being developed [44].

4.5 Greener Auxiliaries

Due to their complexity and the variety of compounds in use, textile auxiliaries, (TA) are an interesting subset of the broader category of industrial chemicals. Standard testing protocols for determining the environmental properties of chemicals are available from the Organization for Economic Cooperation and Development (OECD) [45]. Some of the harmful textile chemicals and their eco-friendly substitutes are shown in Table 2 [43].

Table 2: Some harmful textile chemicals and their eco-friendly substitutes

Existing Chemicals	Uses	Proposed substitutes
Polyvinyl alcohol (PVA)	size	Potato starch or carboxymethylcellulose (CMC)
Pentachlorophenol, formaldehyde	Size preservative	Sodium silicofluride
Carbon tetrachloride (CTC)	stain removers	• Detergent stain-removers • Detergent (non-ionic, ethoxylates) and water miscible solvent (glycol ethers) mixtures • Enzymatic stain-removers.
Calcium and sodium hypochlorite	Bleaching	Hydrogen peroxide, ozone at cold
Sodium silicate, phosphorous-based compounds	Peroxide stabiliser	Nitrogenous stabilisers
Nonyl phenyl ethylene oxide adducts (APEO)	Detergent, emulsifier	Fatty alcohol ethylene oxide adducts, alkylpolyglycosides (36)
Synthetic non-biodegradable surfactants	Various purposes	Sustainable and highly biodegradable surfactants from dextrin
Synthetic non-biodegradable surfactants + solvent	Coatings and degreasing	'Solvo-surfactants' acting both solvent and surfactant, derived from glycerol (bio diesel) (35)
Dichloro and trichloro benzene	Carriers in dyeing	Butyl benzoate, benzoic acid
Kerosene	Pigment printing	Water-based thickeners
Formaldehyde	Finishing, dye fixing	Polycarboxylic acid, non-formaldehyde products
Sodium dichromate	Oxidation in dyeing	Hydrogen peroxide
Silicones and amino-silicones + APEO emulsifier	Softener	Eco-friendly softeners, wax emulsions
Functional synthetic finish	Finishing	Bees wax, aloe vera and Vitamin A (46)

4.6 Greener preparatory process

The most important application of green chemistry is the use of enzymes in textile preparatory processes.

Enzyme Processing: The enzymes are applied in various stages of textile processing namely desizing, scouring, bleaching, dyeing, finishing and composting [43].

Desizing: Conventionally starch desizing is done by hydrolysis with water, mineral acids or by oxidation with sodium bromite or peroxy compounds. Alternate eco-friendly method is to treat with amylase enzymes in presence or absence of lipase.

Scouring: Conventionally scouring is done by prolonged boiling (atmospheric or high pressure) with caustic soda and other chemicals. For enzyme scouring, pectinase is the only enzyme needed for wettability/dyeability, while other enzymes like cellulase may have beneficial effects [47].

Bleaching: Conventionally bleaching is carried out by sodium hypochlorite, sodium chlorite and hydrogen peroxide. However, the former two compounds can generate AOX and therefore being substituted with non-polluting oxidant, hydrogen peroxide.

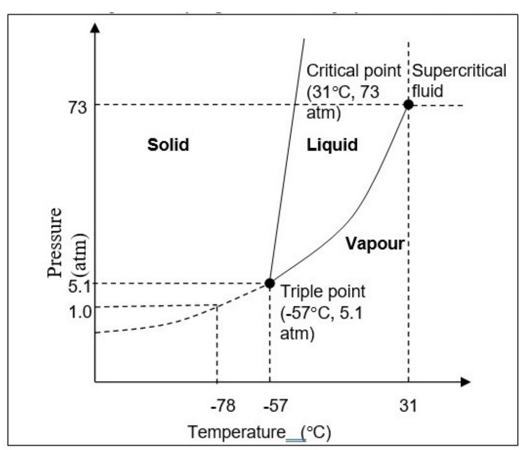

Figure 2. Various physical states of carbon dioxide

The cellulosic fabrics can be effectively photo-bleached using various excimer lasers (KrF, XeCl, XeF), a low-pressure mercury lamp, and a black-light fluorescent lamp in the presence of sodium peroxocarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$) or mixtures of sodium carbonate and hydrogen peroxide aqueous solutions at room temperature. The efficiency of the photochemical bleaching was found to be comparable to that of the commercial thermal bleaching [48].

Other promising green preparatory processes are the use of supercritical carbon dioxide and ionic liquids in purification of cellulose and dry cleaning.

4.7 Modification of dyeing processes

The following are some of the process modifications for making dyeing processes greener:

1. Process optimization to reduce process time and energy consumption.
2. Ultra low liquor ratio dyeing - 3:1 to 4:1 for polyester and 6:1 for cotton)
3. Low electrical power and steam consumption in general.
4. Substitution of hazardous sodium sulphide with sustainable, nontoxic, biodegradable, cost-effective reducing sugars in sulphur dyeing. The sugars tried as reducing agent by Blackburn and Harvey [49] are D-arabinose, D(-)-fructose, D(+)-galactose, α-D-glucose, β-D-lactose and D-maltose.
5. The dyeing of cationized cotton with reactive dyes with low or no salt and alkali addition [50].
6. Rapid dyeing of polyester using selected better levelling, low molecular weight disperse dyes and optimized design of dyeing machines.
7. Minimize reprocessing and shade correction. Twenty controllable factors [51] have been identified for Right-First-Time dyeing, no addition dyeing or blind dyeing (5). Continual refinement of textile machine design and its control equipment, together with dye selection and reliable recipe prediction systems in the laboratory have contributed to a high proportion of *right first-time* dyeing [5].
8. Multiple savings are possible through automation in textile dyeing and printing such as [52].
   (a) Process control - 10-30% saving in water and energy as well as 5-15% saving in dyes and chemicals.
   (b) Auto-dispensing - 5-10% savings in dyes, pigments and chemicals.
   (c) Computer-controlled weighing and stock-taking - 10-15% savings in dyes, pigments and chemicals.
   (d) Colour measurement and matching - significant improvement in quality and 30-40% savings of dyes and pigments.

4.8 New greener coloration processes

Some new coloration processes with lower environmental impact [5] are discussed below.

Ways for Savings of Energy, Water and Chemicals

1. Continuous preparatory and dyeing methods instead of batchwise methods minimizing consumption of the energy, water and chemical to less than half.
2. Semi-continuous cold pad–batch dyeing processes with reactive dyes instead of batchwise or pad-steam methods [53].
3. Sustainable digital printing and heat transfer printing which require far less water and produces far less waste than the traditional printing methods.
4. Cold transfer printing process (Cooltrans) of reactive dyes at room temperature on pretreated cotton, viscose, linen and silk thereby saving water and heat [54].
5. Supercritical carbon dioxide dyeing or waterless dyeing.

4.9 Supercritical carbon dioxide dyeing

A supercritical fluid, a substance above its supercritical temperature and pressure (31.1°C and 73.8 atm. respectively, for CO_2 as shown in Figure 2 [55], has the properties midway between a gas and a liquid. Considerable attention on supercritical carbon dioxide ($scCO_2$) as dyeing medium has been received from researchers. This is apparent from the fact that 143 articles on the topic have been reviewed by Bach et al. [18]. However, it has not been commercialized yet. Carbon dioxide combines a relatively mild critical point with non-flammability, non-toxicity and a low price. Because of its green and safe character, it is the best supercritical solvent for textile dyeing. It is obtained as waste product of combustion, fermentation and ammonia synthesis and need not to be produced especially for dyeing.

The carbon dioxide and the residual dye (after dyeing) can be easily separated by depressurization and both the compounds can be recycled. No waste is generated. The supercritical dyeing process was investigated experimentally for both reactive and non-reactive dyeing [56, 57]. Water-soluble dyes are insufficiently soluble in $scCO_2$. The method is, therefore, mostly suitable for dyeing of synthetic fibres with disperse dyes.

4.10 Greener finishing agents

Formaldehyde-free Finishes

The release of formaldehyde vapour is a problem with the most widely used cross-linking agents in textile finishing, N-methylol agents or N-methylolamides [58].

A number of formaldehyde-free cross-linking agents have been developed recently such as:

1. Cyclic addition of glyoxal with NN$^{/}$dimethyl urea, namely DHDMI (1,3 dimethyl-4,5-dihydroxyethyleneurea)
2. Polycarboxylic acids (PCA), but there may be loss of tensile strength due to acid-catalyzed cellulose chain cleavage. Butanetetracarboxylic acid (BTCA), in the presence of sodium hypophosphite, provides the same level of durable press performance as conventional DMDHEU reactant, but it is quite costly [59, 60].

Savings of Water

The water and energy consumption in finishing can be reduced by lowering %pick-up using modern machinery and methods such as low pick-up padding and minimum application techniques (e.g. kiss-roll, spray and foam application systems) which are gaining importance as substitutes for conventional padding systems.

Plasma Treatments

Water-based finishes require energy-intensive drying process after application. Plasma treatment, an eco-friendly technique, is essentially a dry process avoiding generation of waste as in case of wet-chemical processes.

Plasma treatment is carried out by excited partially ionized gas with negligible consumption of water and low consumption of energy. Plasmas can interact with polymer surface within milliseconds without heating the substrate. The treatment may be utilized for surface cleaning, ablation or etching, grafting, polymerization of the most external layer of the substrate. In principle, plasma treatment can be carried on all polymeric and natural fibres for the following purposes [61]:

1. Desizing,
2. Change in hydrophobicity or hydrophilicity of fibres,
3. Improvement of affinity and levelling properties of dyes,
4. Wool degreasing.
5. Anti-felting finish of wool,
6. Sterilisation of textile materials.

Atmospheric plasma modules can be easily scaled to the working width of textile machines, usually 0.2 and 10 meters. Investment and maintenance costs are also moderate. Prolonged exposure to atmospheric air pressure plasma (AAPP) causes abaca, flax and sisal fibres hydrophilic. The exception is the hemp fibre [62].

4.11 Green composites

Environment-friendly, fully biodegradable, 'green' composites based on plant-based fibres and resins are increasingly being developed for various applications as replacements for the prevailing non-biodegradable materials derived from petroleum. These green composites may be easily composted after their life, completing nature's carbon cycle. Flax yarn reinforced cross-linked soy flour (CSF) composites are fully biodegradable, environment friendly green composites which can be used in secondary and, in some cases, primary structures in indoor applications [63].

4.12 Greener effluent treatment

Wastewater treatment is essential to allow human and industrial effluents to be disposed without bringing danger to human health as well as to prevent unacceptable damage to the natural environment [64]. Conventional wastewater treatment consists of combination of several processes namely physical, chemical and biological, to remove solids, organic matter and, sometimes nutrients from the wastewater.

Porter and Snider [65] showed that most of the textile dyes are non-biodegradable. Extensive tests indicate that the dyes are generally absorbed to the extent of 40-50% by the bio-mass and are thus partially eliminated in sewerage plants; practically no biodegradation takes place. The large dye molecules have high affinity for various materials and some are only sparingly water-soluble.

The chemical coagulation of effluent water by alum and poly-aluminium chloride (PAC) is well known. This may cause several health problems, besides the possibility of Alzheimer's disease due to the presence of aluminium [66, 67]. There is circumstantial evidence linking this metal with Alzheimer's disease, but no causal relationship has yet been proved. As evidence for other causes continues to grow, a possible link with aluminium seems increasingly unlikely [68].

Biodegradable natural polyelectrolytes [69] such as *Cassia angustifolia* (CA) seed gum extracted from plant or animal life can be workable as alternative to synthetic polyelectrolytes [70].

Cationized cotton is sometimes used for the removal of anionic dyes from aqueous effluent produced by the textile industry as it is derived from natural product, inexpensive and renewable [71]. Although the sorption capacity of the sawdust is not very large, experimental results provide promising perspective for the utilization of sawdust as bio-sorbent in reducing pollution of textile effluents [72].

Coal ash, abundantly available from power plants, is a strong choice for economic means of removal of dyes. After adsorption it may be disposed off by burning after drying [73].

Hydrogen peroxide and oxygen can safely and powerfully destroy many pollutants, but in nature the process usually requires an enzyme, peroxidase. Peroxidase from fenugreek (FSP, Trigonella foenum-graecum) seeds is highly effective in the decolonization of textile effluent, especially hazardous aromatic pollutants in the presence of various redox mediators [74].

Chemists have recently created enzyme-like catalysts called tetra-amido macrocyclic ligand activators (TAMLs) that can destroy stubborn pollutants by accelerating cleansing reactions with hydrogen peroxide. Synthetic TAMLs, peroxide-activators (with iron as the central metal atom) decompose peroxide on timescales ranging from minutes to hours. The tiny TAML activators are easier and cheaper to make, and much more versatile in their reactivity, than their natural counterparts [1].

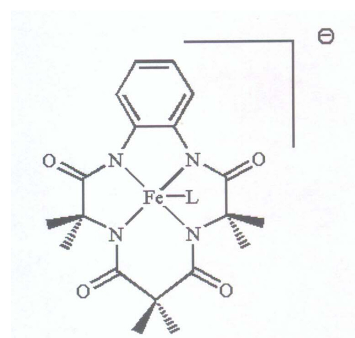

Figure 3: Tetra-amido macrocyclic ligand activators (TAMLs)

At the centre of each TAML (Figure 3) [75] is an iron atom bonded to four nitrogen atoms. In its solid state, the TAML has one water molecule called ligands attached to the iron atom. When a TAML dissolves in water, another water molecule connects to the catalyst. If hydrogen peroxide (H_2O_2) present in the solution, it can easily replace one of the loosely attached water ligands leaving one oxygen atom attached to the iron. The oxygen pulls electrons farther away from the iron atom, turning the TAML into a reactive intermediate.

Collins [1] showed that Fe-TAML/hydrogen peroxide catalytic system is capable oxidative breaking down carcinogenic Pentachlorophenols (PCPs) and trichlorophenols (TCPs) into environmentally benign products in aqueous solution at ambient temperatures and pressures.

The solid waste, called 'Sludge', obtained from wastewater treatment processes is categorized under toxic substances by statutory authorities. The conventional disposal methods like land-filling and incineration are not entirely satisfactory as the leakage and residue from the respective processes may induce secondary pollution.

The use of sludge as construction and building material not only convert waste into useful products but also eliminate disposal problems. As an additive to brick, heavy metals are immobilised in the fired matrix, oxidizing organic matter and destroying any pathogens during the firing process [76].

4.13 Eco-label

According to Global Eco-labelling Network, an Eco-label is 'a label which identifies overall environmental preference of a product within a product category based on life cycle consideration'. Eco-labels are very important to the development of a sustainable and a credible textile industry.

Eco-labels are of two categories - Governmental and commercial. The examples of Government administered eco-labels (country) are Blue Angel (Germany), Green Seal (USA), Eco-mark (Japan, India), European Flower (EU), NF Environment (France). A few commercial eco-labels are OEKO-TEX Standard 100 (Austria/Germany), GuT (Carpet, Germany), GuW (Furnishing, Germany) and Global Organic Textile Standard (GOTS, www.global–standard.org).

It is the European Community Regulation on chemicals and their safe use. It deals with the Registration, Evaluation, Authorization and Restriction of Chemical substances. Manufacturers and importers are required to gather information on the properties of their chemical substances, which will allow their safe handling, and to register the information in a central database run by the European Chemicals Agency (ECHA) in Helsinki [77].

4.14 Best available techniques (BAT) and practices

The main environmental advantages achievable by systematic performance of optimised housekeeping and management measures are savings in the consumption of chemicals, auxiliaries, fresh water and energy and the minimisation of solid waste and pollution loads in waste water and off-gas. Best available techniques (BAT) applicable in textile mills are listed below [78]:

1. Education and training of employees
2. Equipment maintenance and operations audit.
3. Chemicals storage, handling, doing and dispensing
4. Improved knowledge of chemicals and raw materials used
5. Minimisation/optimisation of chemicals used
6. Use of water and energy
7. Management of waste streams.

Ten best practices for textile mills to save water and energy and to reduce pollution as suggested by NRDC (79) are:

1. Leak detection, preventive maintenance, improved cleaning
2. Reuse cooling water: from singeing, air compressor system and preshrink
3. Reuse condensate
4. Reuse process water: from bleaching and mercerizing
5. Recover heat from hot rinse water
6. Pre-screen coal
7. Maintain steam traps
8. Insulate pipes, valves and flanges
9. Recover heat from smokestacks
10. Optimize compressed air system.

5. Conclusions and future trends

As globalization of the wet processing industry continues, it is clear that the textile industry can continue to 'green' its processes and chemistry. The communities in which these industries relocate can work together to provide an optimum situation where industrial growth and prosperity can be maximized without a negative impact on local water quality. The best news is that it can work, not only by using sophisticated toxicological and chemical technology, but also by dialogue and commonality of purpose [80, 81].

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