Green Chemistry and Textile Industry

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1. concept of Green chemistry

The 2005 Nobel Prize awarded to Y Chauvin, R. H. Grubbs and R. R. Schrock for the development of metathesis reactions involving breaking and rearrangement of carbon bonds in the presence of specialised catalysts – typical example of green reactions. Every year U.S. Presidential award is given for achievements in various aspects of green chemistry.

Green Chemistry is the chemistry that

- Doesn't hurt nature,
- Reduce or eliminate the use or generation of hazardous substances [1],
- Provides more eco friendly alternative,
- Prevents formation of waste,
- Creates new knowledge based on sustainability i.e. sustainable chemistry [2],
- Takes a life cycle approach to reduce the potential risks throughout the production process.

The conventional chemical manufacturing processes are unsustainable because:

(a) Mostly carbon-based products are derived from fossil fuels, petroleum and coal which have limited supply.
(b) Large amounts of waste increasing burden on the environment.

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

Usage of nonconventional technologies is highly popular in India. The microwave chemists are working on microwave-assisted dry-media reactions in order to minimize solvent usage. Ultrasonic and photochemical reactions are also used as non-conventional reaction technology [3].

Principles

1) **Prevent waste:** Design chemical syntheses to prevent waste, thereby eliminate/minimise waste treatment processes.
2) **Maintain atom economy:** There should be few, if any, wasted atoms.
3) **Use safe chemical synthesis methods**
4) **Use low toxic products:** Use fully effective but safe or non-toxic chemicals and products.
5) **Choice energy efficient processes:** Prefer ambient temperature and pressure reactions.
6) **Use renewable feedstock:** Use non-depleting renewable raw materials and feedstock such as agricultural products or the wastes of other processes and not products derived from fossil fuels.
7) **Omit derivation steps:** Follow least number of sequential chemical steps, and choose direct reactions.
8) **Catalysis:** Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. Gold exhibits outstanding catalytic activity for oxidation processes [4].
9) **Safer solvents and auxiliaries:** Use aqueous or other safe media.
10) **Degradation of chemical products:** Design chemicals which break down to harmless substances.
11) **Real time analysis:** In-process real-time monitoring and control to minimise/eliminate formation of by-products
12) **Safety:** Minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

Challenges

The challenges for green chemistry are the identification of

1) Renewable feedstock, preferably non-food plants and its full conversion to useful products,
2) Reactions having minimum environmental impact e.g. use of eco-friendly organic catalysts or enzymes,
3) Industrial processes and reactors having maximum efficiency and minimum waste,
4) Products of reduced toxicity and increased biodegradability [5]. Perhaps the greatest challenge facing green chemists is the eventual elimination of all environmentally harmful chemical products. Chemists are still a long way from being able to predict the properties — both chemical and biological — of compounds from its chemical structure.
5) Most of the solvents are flammable, toxic and volatile organic compounds that pollute atmosphere. A variety of cleaner solvents have been evaluated as replacements [6]. The useful alternative to traditional solvents are supercritical carbon dioxide (compressed gas dense nearly as a liquid), ionic liquids (organic salts that are liquid at room temperature) and water. Water has been traditionally considered as a nuisance medium in most chemical reactions. However, recent works suggest that water will be better than many organic solvents in preventing side-reactions [7, 8].

Assessment

The easiest way to assess how green a chemical process is to measure the amount of waste generated. The processes can be assessed using their 'E-factor' i.e. the ratio of the mass of waste to that of the product [5]. All processes should aim for the lowest possible E-factor - for truly green processes, the E-factor should be zero. Large-scale manufacturing units for bulk chemicals may generate large amount of waste, but their E-factors may be smaller in comparison with small-scale units as the E-factor depends on the quantity of waste in relation to total production.

Misconception

Some misconceptions relating to green chemistry [9] are:

Cost Benefit

Green chemistry truly allows for increased profits by saving reagents, solvents, energy, waste disposal costs, personnel costs, and increasing production.

Perfection of the Systems

A perfectly green process may not be so green if it hasn't been applied in the right situations.

Fields of Application

The application of green chemistry is not restricted. It is applicable to various industrial sectors since all industrial processes involve one or more of the following basics: raw materials, chemical reactions, solvents, and separation/purifications.

Longevity

Green chemistry often remains unchanged for long periods of time.

Overall Performance

Traditional purification and separation methods both generate large amounts of acid, base, and solvent wastes, and are often energy intensive. New separation techniques such as carbon dioxide extraction, phase separation, evaporation, membrane separation, and reforming by-products into new products minimise waste generation.

Key Developments

Ryoji Noyori [10] identified three key developments in green chemistry namely:

1) The use of supercritical carbon dioxide as green solvent.
2) Aqueous hydrogen peroxide for clean oxidations and
3) The use of hydrogen in asymmetric synthesis or stereo-selective synthesis.

Supercritical Carbon Dioxide (scCO_2)

In the last two decades therefore, research has been done for the use of supercritical fluids as a dye solvent, rather than water. It can adopt properties midway between a gas and a liquid expanding to fill its container like a gas but with a density like that of a liquid. Such solvents have not yet been implemented in textile industry, but their use as dyeing medium has received considerable attention from researchers in the past two decades, as is illustrated by the 143 articles mentioned in the review by Bach et al. [11]. The most widely used supercritical fluid is carbon dioxide, because it 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. The CO_2 is a waste product of combustion, fermentation and ammonia synthesis, so that no CO_2 has to be produced especially for dyeing.

The main advantage is the easy separation of the CO_2 and the unused dye that remains after the dyeing process. Depressurization leads to precipitation of the excess dye and gives clean, gaseous CO_2, so that both compounds can be recycled and no waste is generated. Furthermore, the energy-intensive drying after dyeing is not required. As scCO_2 is a non-polar solvent, no dispersing agent is needed when polyester is dyed. As the process operates at conditions of typically 120ºC and 300 bar, high-pressure equipment is needed which results in high investment costs. The supercritical dyeing process was investigated [12] experimentally for both reactive and non-reactive dyeing.

2. Textile industry and pollution

The textile industry is considered as the most ecologically harmful industry in the world. The utilization of rayon for clothing affects fast depleting forests. Petroleum-based synthetic fibre and the dyes are not sustainable and not biodegradable [13]. During cultivation of cotton synthetic fertilizers are used to improve the yield, pesticides/herbicides are sprayed to protect from pests/weeds. Today, the conventional cotton crops occupy 3 % of the world cultivated areas. Nevertheless, it represents 25 % of pesticides and 10 % of insecticides bought in the world.

Water Consumption

Estimated total water used in wet processing of cellulosic fibres is 2.96 trillion litres considering water consumption of 100 l/kg of material. If we can reduce water consumption by ¾ (i.e. 25 l/kg), the saved water can provide drinking water for 2.34 billion people (assuming consumption of 2.6 litres per capita per day).

Water can be saved in dyeing in the following ways:

1) Reuse dyehouse water
2) Reduce reprocessing
3) Optimise rinsing and soaping processes
4) Reduce Liquor ratio

Wet Processing

The important environmental concerns related to textile wet processing are:

1) Chemical intensive wet processing– scouring, bleaching, mercerising, dyeing, printing etc.
2) Use of heavy metals – iron, copper, lead etc,

found in dyestuffs auxiliaries, binders etc.

3) Residual dyestuffs due to poor fixation of dyes and chemicals in effluent water.
4) PVC and phthalates used in plastisol printing paste.
5) Formaldehyde found in dispersing agents, resins, printing paste and colorant fixatives.
6) Dye effluent-wastewater issue.

Many of the chemicals used in textile processing can be recovered from waste water by membrane technology. The most problematic pollutant is the dye itself. Inherent to their purpose, dye molecules are designed to be resistant to degradation by light, water and many chemicals [14]. Dye molecules can be decomposed in water by a range of chemical, physical and biological treatments. The most widely used technique is the oxidative process, where hydrogen peroxide is added to the water and activated by ultra violet light to oxidise the dye molecules. However, toxic sludge is produced, which has to be disposed of or incinerated.

Adsorbable organic halogens (AOX)

It is a measured value for organically bound chlorine, bromine and iodine in a given substance. The AOX consent limit is likely to be as low as 2 ppm from a German drinking water directive (DIN 38409414, 1987) [15] and as such compounds having high AOX values are to be used carefully, a few such products used in the textile industry are:

1) Chlorine-containing bleaching agent.
2) Shrink-proofing of wool with chlorine, the most promising alternate being permonosulphuric acid.
3) Insect-proofing agent for wool.
4) Some types of carriers used in dyeing with disperse dyes.
5) Certain chromophores.
6) Some classes of reactive dyes.

Harmful Chemicals

Some of the toxic and harmful substances used in textile industries are listed below [16]:

1) Cotton growing – banned pesticides such as DDT, Dieldrin, Aldrin etc.
2) Sizing – pentachlorophenol used as preservative.
3) Scouring – chlorinated products.
4) Bleaching – sodium and calcium hypochlorite.
5) Dyeing and printing – azo dyes containing/ releasing banned (twenty in number aromatic amines and dyes containing traces of heavy metals (e.g. arsenic, lead, cadmium, mercury, nickel, copper, chromium, cobalt and zinc), formaldehyde-based auxiliaries.
6) Finishing - formaldehyde-based finishes, stain removers containing chlorinated products.
7) Packing – wooden boxes treated with insecticides.

3. Green Chemistry in textile industry

In paper and textile industries, efforts are being made to develop new greener methods, which result in reduction in energy, water usage, time in textile processing. Some examples of green approaches in various textile related industries are as follows:

Greener Fibres

Organic cotton is generally understood as cotton, from non-genetically-modified plants, that is certified to be grown without the use of any synthetic agricultural chemicals such as fertilizers or pesticides. The farmers undertake not to use chemicals, and to recycle as much as possible the waste stemming from their activity.

Lyocell fibres are produced by regenerating cellulose in an organic solvent, N-methylmorpholine-N-oxide (NMMO) hydrate. Non-toxic, biodegradable NMMO solvent used is almost completely recycled [17]. The fibre is significantly more sustainable than oil-derived synthetic fibres and natural fibres such as cotton (need pesticides and fertilisers to grow). Land required is more than the eucalyptus trees, from which lyocell is made [18].

Bamboo fibre has particular and natural functions of anti-bacteria, bacteriostasis and deodorization. It is validated by Japan Textile Inspection Association that, even after fifty times of washing, bamboo fibre fabric still possesses excellent function of anti-bacteria, bacteriostasis. Like chemical antimicrobial, it does not cause skin allergy.

The use of biopolymers – plastics made from corn, sugar, starch and other renewable raw materials – has exploded in recent years. Clariant announced the development of Biodegradable RENOL®-natur colorant from sustainable, mainly vegetable resources for use with these new-age plastics. [19].

Henry Ford first used soy plastic to construct various car parts. A new composite materials has been derived from soy flour and flax resin cross-linked with glutaraldehyde, derivable from bio-feedstocks. Materials produced have good mechanical properties and may be used for indoor applications [20]

Recycled Textiles

Because textiles are 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%), 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. [21].

Polyester fibre is one of the most non-biodegradable polymers which create environmental problems. Major revolution happened in 1993 when Wellman Inc. introduced the first polyester textile fibre made from post consumer PET packaging: Fortrel® EcoSpun®. There are two broad types of recycled polyester namely:

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

However, re-cycled polyester yarn is not always as good as virgin polyester. Colour consistency is difficult to achieve, particularly on pale shades [22].

If the carpet fibres are made of polypropylene and they're held together with a polypropylene Licocene back-coating, the product can be reused simply by melting [19].

Dye and auxiliaries

The greener approaches are:

1) Elimination of harmful azo dyestuffs
2) Alternative synthesis for eco-friendly products.
3) Search for sustainable source such as natural dyes. They, in general, have poor to moderate light fastness. It was found that the natural additives Vitamin C (ascorbic acid) and gallic acid (found in stomach, tea leaves, oak bark and many other plants) were most effective in reducing the rate of fading in madder, weld and woad dyed cotton [23].

Biodegradable surfactants

By reacting dextrins with fatty acids and their derivatives, new sustainable and biodegradable surfactants have been formed. They have highly desirable physical properties including low foaming, good wetting and whitening ability, as well as excellent biodegradability [24].

Queste reported [25] that the researchers in France and Germany have jointly developed a new class of so-called 'solvosurfactants' (which exhibit the properties of both solvent and surfactant and are commonly used in applications such as coatings and degreasing, as well as perfumery and inks) that are derived from glycerol, a renewable material from bio diesel.

Dyeing /printing/finishing

Bio-processing can simply be defined as the application of living organisms and their components to industrial products and processes, which are mainly based on enzymes.

The application of enzymes in various stages of textile processing may be listed as follows [26]:

Desizing:	amylase, lipase.
Scouring:	pectinase, cellulase.
Bleaching:	oxidoreductase. xylanase.
Dyeing:	oxidoreductase.
Finishing:	cellulase, oxidoreductase, lipase.
Composting	(biodegradation of textile wastes): cellulase, protease, nylonase, polyesterase.
Delignification,	decolourisation of dyes: laccases [27]

Greener Preparatory Processes

1) Purification of cellulose by extraction by carbon dioxide and ionic liquids,
2) High temperature water extraction of lignin,
3) Substitution of chlorine bleaching with non-polluting oxidants,
4) Carbon dioxide-based dry cleaning.
5) Elimination of ozone-depleting chemicals such as carbon tetrachloride (stain remover).

Greener Dyeing Processes

Improvement in the existing dyeing processes

1) Optimise processes (to reduce time and energy consumption)
2) Reduce consumption of water, electrical power, steam consumption
3) Optimise dye/chemical costs
4) Eliminate reprocessing and shade correction
5) Sulphur dyeing: substitution of hazardous sodium sulphide with sustainable, nontoxic, biodegradable, cost-effective reducing sugars [28].
6) Reactive dyeing: treatment of cellulose with cationic, nucleophilic polymers enables dyeing at neutral pH without electrolyte addition - 3-chloro-2-hydroxypropyl-trimethylammonium chloride (CHTAC) [29], Copolymer of diallyldimethylammonium chloride and 3-aminoprop-1-ene (PT1) and copolymer of 4-vinylpyridine quaternised with 1-amino-2-chloroethane (PT2) [30].
7) In chemical-free denim processing [31], laser technology is used to burn away the surface of the dyed denim fabric or a pair of jeans on a mannequin to replicate an authentic worn look. The laser system is very quick and a pair of jeans can take as little as 15 seconds to process.
8) Right-First-Time dyeing: It is also termed as 'no addition' dyeing or 'blind dyeing'. Elimination of the inspection stage made a significant saving [32]. Twenty factors which must be monitored or controlled to achieve RFT processing in the dyeing process have been identified [33].

New dyeing technologies with minimum environmental impact [34]

1) About 90% dye fixation on batchwise cellulose dyeing with polyfunctional dyes.
2) Cold pad-batch dyeing, rapid dyeing techniques and better machine design.
3) Economic continuous dyeing methods.
4) supercritical carbon dioxide dyeing

Formaldehyde-releasing finishing agents

The most widely used crosslinking agents in DP finishes, N-methylol agents or N-methylolamides fall in the category of formaldehyde reactants [35].

The release of formaldehyde vapours is a problem with those agents. It depends on the reactant types, the catalyst types, the condition of the treated fabrics, and the additives in the impregnating bath and most importantly the time and temperature of cure [36].

The Occupational Safety and Health Administration (OSHA) have set the upper limit for formaldehyde in air at 0.75 parts per million average over an eight-hour work shift [37]. Formaldehyde is a carcinogen to animals [36]. Some formaldehyde-free DP finishes are:

1) Cyclic addition of glyoxal with NN/dimethyl urea, namely DHDMI (1,3 dimethyl-4,5-dihydroxyethyleneurea)
2) Polycarboxylic acids (PCA) - their main drawback is loss of tensile strength due to acid-catalysed cellulose chain cleavage. The most important PCA reactants are butanetetra-carboxylic acid (BTCA) and citric acid (CA) [38]. BTCA, in the presence of sodium hypophosphite, provides the same level of durable press performance as conventional DMDHEU reactant, but it is quite costly [37].

Flame Retardants

An interesting development in the field of flame retardancy is the use of polymer nanocomposites as a substitute of toxic brominated flame retardants (BFR). Nanocomposites may be described as two-phase materials, consisting of a dispersion of appropriate filler (on a nanometre scale) through a polymer matrix. In the case of polymer-layered silicate (clay) nanocomposites, only a very small amount of filler (2-10 weight-%) is required for the material to be flame-retardant [39].

Automation

Pollution reduction is possible through automation in textile dyeing and printing. The steps are:

(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.

The most important steps depend on priorities:
Improvement in the quality: steps (a) and (c)
Man-power savings: steps (a) and (b)
Cost reduction: step (d)
Better customers' service (RFT production, *quick response* and *just-on-time* delivery): steps. (a) to (e) (full automation).

4. eco-legislation

REACH [40] is a new European Community Regulation on chemicals and their safe use. It is a new regulatory framework proposed by the EC on October 29, 2003. It is a single, coherent system for new and existing chemicals with the following three new elements:

1. Registration (30,000 substances traded in EU; 100,000 on EINECS)
2. Evaluation (5,000 substances)
3. Authorisation (1,350 substances)

CHemical Substances

Aims of REACH

- To improve the protection of human health and the environment
- To increase the competitiveness of the EU chemicals industry
- To increase transparency
- To achieve integration with global efforts
- To conform with EU international obligations under the WTO
- To promote non-animal testing.

5. Conclusion and future trends

Green Chemistry provides a technical solution to many environmental problems. It is effective due to design stage efforts, starting at the molecular level lets one to design out the hazardous properties and to design in environmentally appropriate features.

The 21st century philosophy for textile dyeing is follows:

- Minimum human/operator intervention,
- Process steps optimised for utility consumption,
- Decisions made strategically not on a daily routine basis,
- Processes devised and selected to produce the correct shade and quality as an expectation not just an intention,
- Digital shade passing and colour communication,
- Profits are made by doing it right - not just by doing it cheaply [41].

A systematic approach can ensure effective application. Systematic eco-plan can lead business to such an extent that by 2012 it should:

- Become carbon neutral,
- Send no waste to landfill,
- Develop sustainable sourcing routes,
- Set new standards in ethical trading,
- Help customers and employees to live a healthier lifestyle.

'Carbon neutrality', or having a 'net zero carbon footprint', refers to achieving net zero carbon emissions by balancing a measured amount of carbon released with an equivalent amount sequestered or offset [42].

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