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Green revolution in chemistry: Chemistry for a sustainable environment

Churala Pal¹, Prabal Giri^{2*}

¹Department of Chemistry, Basanti Devi College, (Affiliated to University of Calcutta), 147B, Rash Behari Avenue, Kolkata 700029, West Bengal, (INDIA)

²Department of Chemistry, Guskara Mahavidyalaya, (Affiliated to University of Burdwan), Guskara, Burdwan 713128, West Bengal, (INDIA)

E-mail: prabalgiri@yahoo.co.in; churalapal@yahoo.co.in

ABSTRACT

Chemistry has improved quality of life making thousands of products possible. Unfortunately, this achievement has come at a price: collective human health and the global environment are threatened. Green chemistry can be defined as the use of chemistry for pollution prevention by use of alternative and renewable materials including the use of agricultural waste or biomass and non-food-related bioproducts. It also focused on prevention of waste, less hazardous chemical synthesis, and designing safer chemicals including safer solvents and design of chemical products to safely degrade in the environment and efficiency and simplicity in chemical processes. This study describes the principles and progress of green chemistry and its industrial applications.

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KEYWORDS

Green chemistry;
Biomass;
Resources;
EcoWorx;
Biocatalysis.

INTRODUCTION

Chemistry has improved our quality of life, and made thousands of products possible^[1]. Unfortunately, this achievement has come at a price, our collective human health and the global environment are threatened. Our bodies are contaminated with a large number of synthetic industrial chemicals, many of which are known to be toxic and carcinogenic while others remain untested for their health effects. They come to us from unlabeled products, chemically contaminated food, air, water and dust while the developing fetes is exposed directly to chemicals in the womb. Many chemicals work their way up the food chain and circulate

round the globe: pesticides used in the tropics are commonly found in the Arctic; flame retardants used in furniture and electronics are now commonly found in marine mammals. Yet as cancer rates rise and evidence increases about the link between certain chemicals and birth defects and learning disabilities our regulatory system has been unable to make chemical producers provide full testing information or promote inherently safer chemicals. Green chemistry aims to eliminate hazards right at the design stage. The practice of eliminating hazards from the beginning of the chemical design process has benefits for our health and the environment, throughout the design, production, use/reuse and disposal processes. In 1998, two US chemists, Dr Paul Anastas

Tutorial Review

and Dr John Warner outlined Twelve Principles of Green Chemistry to demonstrate how chemical production could respect human health and the environment while also being efficient and profitable. One of the principles of green chemistry is to prioritize the use of alternative and renewable materials including the use of agricultural waste or biomass and non-food-related bioproducts. In general, chemical reactions with these materials are significantly less hazardous than when conducted with petroleum products. Other principles focus on prevention of waste, less hazardous chemical syntheses, and designing safer chemicals including safer solvents. Others focus on the design of chemicals products to safely degrade in the environment and efficiency and simplicity in chemical processes^[2-4].

The terms 'Environmental Chemistry' and 'Green Chemistry' are two different aspects of environmental pollution studies. The former is the study of chemical pollutants in natural environment while the latter is an attempt to design chemical products and processes to reduce the harm they cause to the environment. Green chemistry seeks to reduce pollution at source, whereas environmental chemistry focuses on the study of pollutant chemicals and their effect on nature. On the other hand, environmental chemistry, as taught today, is largely the study of what man has put into the environment and its effect, as well as how to remediate contaminated sites.

PRINCIPLES OF GREEN CHEMISTRY^[5-8]

Prof. Anastas and Prof. John C Warner have postulated twelve principles of green Chemistry.

Prevention of waste

It is better to prevent waste than to treat or clean up waste after it is formed.

It is most appropriate to carry out a synthesis by following a pathway so that formation of waste is minimum or absent. One type of waste product common and often avoidable is the starting material or reagent that remains unreacted. In universities and colleges, the cost of disposal of waste from chemical laboratory can be reduced by carrying out experiments on a much smaller scale.

Maximize atom economy

Atom Economy is a concept that evaluates the effi-

ciency of a chemical transformation, and is calculated as a ratio of the total mass of atoms in the desired product to the total mass of atoms in the reactants.

$$\% \text{ Atom Economy} = \{(\text{Mol. wt of desired product}) / (\text{Mol. Wt of all products})\} \times 100$$

Choosing transformations that incorporate most of the starting materials into the product are more efficient and minimize waste, e.g., Diels–Alder reaction is 100% Atom Economy reaction as all the atoms of the reactants are incorporated in the cycloadduct. If one mole of the starting material produces one mole of the product, the yield is 100%. However, such a synthesis may generate significant amount of waste or by product which is not visible in the above calculation. Such a synthesis, even though gives 100% yield is not considered to be green synthesis. In order to find, if a particular reaction is green, the concept of atom economy was developed. This considers the amount of starting materials incorporated into the desired final product. Thus by incorporation of greater amounts of the atoms contained in the starting materials (reactants) in to the formed products, fewer waste by products are obtained.

Less hazardous chemical syntheses

This principle focuses on choosing reagents that pose the least risk and generate only benign by-products. Wherever practicable, synthetic methodologies should be designed to use and generate substances that poses little or no toxicity to human health and the environment. Redesigning existing transformations to incorporate less hazardous materials is at the heart of Green Chemistry.

Metathesis

Developed by Grubbs, Schrock and Chauvin, metathesis is a major advance for green chemistry. It is a reaction in which double bonds are broken and made between carbon atoms in ways that cause atom groups to change places, with the help of special catalyst molecules. It is used in the development of pharmaceuticals and advanced plastic materials, and is a great step forward for green chemistry, reducing hazardous waste through smarter production.

Designing safer chemicals

New products can be designed that are inherently

safer for the target application. Pharmaceutical products often consist of chiral molecules, and the difference between the two forms can be a matter of life and death—for example, racemic thalidomide when administered during pregnancy, leads to horrible birth defects in many new borns. Evidence indicates that only one of the enantiomers has the curing effect while the other isomer is the cause of severe defects. That is why it is vital to be able to produce the two chiral forms separately. Catalysts that can catalyse important reactions that produce only one of the two mirror image forms are used. Chemical properties of a molecule, such as water solubility, polarity etc. so that they can manipulate molecules to the desired effects.

Safer solvents and auxiliaries

Widely used solvents in syntheses are toxic and volatile—alcohol, benzene (known carcinogenic), CCl_4 , CHCl_3 , perchloroethylene, CH_2Cl_2 . Purification steps also utilize and generate large amounts of solvent and other wastes. These have now been replaced by safer *green solvents* like ionic liquids, supercritical CO_2 , supercritical H_2O etc.

Use of renewable feedstocks

Chemical transformations should be designed to utilize raw materials and feedstocks that are renewable. For green synthesis, the feedstock should replace the traditional petroleum sources, e.g., benzene used in the commercial synthesis of adipic acid has been replaced to some extent by the renewable and nontoxic glucose and the reaction is carried out in water.

Use of catalysts

Catalysts are used in small amounts and can carry out a single reaction many times and so are preferable to stoichiometric reagents. They can enhance the selectivity of a reaction, reduce the temperature of a transformation, reduce reagent-based waste and potentially avoid unwanted side reactions leading to a clean technology. Apart from heavy metal catalysts softer catalysts like zeolites, phase transfer catalysts like crown ethers, are finding increasing industrial applications.

Biocatalysts – microorganisms and enzymes

Enzymes are the most efficient and commonest of the catalysts found in nature. Enzymes have been used

as important tools in organic syntheses. In pharmaceutical industry, the largest scale biocatalytic process is the conversion of the fermentation product of Penicillin G into 6-amino penicillanic acid by enzyme penicillin acylase. Many chemically modified penicillins, amino acids, vitamins, fructose syrup and many biopharmaceuticals are obtained by this method. Biocatalysed reactions are advantageous as they are performed in aqueous medium, all conversions are single step, and protections of functional groups are not necessary, reactions are fast, stereo-specific. Such transformations are either impossible or extremely difficult to achieve by conventional chemical methods.

Design synthesis for energy efficiency

Energy requirements of the chemical processes should be recognized for their environmental and economic impacts.

(a) Microwave irradiation

Reactions with microwave sources have been carried out in a solid support like clay, silica gel, etc., eliminating the use of solvents or with minimum amount of solvents. The reactions take place at a faster rate than thermal heating.

(b) Sonochemistry (Ultrasound energy)

Reactions using ultrasound energy are carried out at RT with excellent yields.

Design for degradation

Chemical products should be designed so that at the end of their function, they do not accumulate and persist in the environment but break down into innocuous harmless substances. It is now possible to place functional groups in a molecule that will facilitate its biodegradation. Functional groups which are susceptible to hydrolysis, photolysis or other cleavage have been used to ensure that products will be biodegradable.

Inherently safer chemistry for accident prevention

Design chemicals to minimize the chemical accidents including explosions, fires and releases to the environment eg cancercausing benzene Nanoscience and nanotechnology is another important contribution to green chemistry. Nanotechnology provides huge savings in materials by development of microscopic and

Tutorial Review

submicroscopic electronic and mechanical devices. It has been found that in an attempt to recycle solvents from a process increases the potential for a chemical accident or fire.

AREAS FOR THE DEVELOPMENT OF GREEN CHEMISTRY

Use of alternative feedstock

The use of feedstocks^[9] those are renewable rather than depleting and less toxic to human health and the environment. The synthesis and manufacture of any chemical substance begins with the selection of a starting material from which the final product will be built. In many cases the selection of a starting material can be the most significant factor. If the substance itself does not pose any hazard to human health or the environment, for example, but the retrieval and/or isolation of the substance causes significant risk to either, then this factor must be taken into account in the selection.

Employing natural processes

Use of biosynthesis, biocatalysis, and biotech-based chemical transformations for efficiency and selectivity. Biocatalysis harnesses the catalytic potential of enzymes to produce building blocks for the pharmaceutical and chemical industry. While fermentations use the carbon source for *de novo* product synthesis, biocatalytic processes employ a different strategy^[10].

Use of alternative solvents

The design and utilization of solvents that have reduced potential for detriment to the environment and serve as alternatives to currently used volatile organic solvents, chlorinated solvents, and solvents that damage the natural environment^[11].

Design of safer chemicals or use of enzymes

Use of molecular structure design and consideration of the principles of toxicity and mechanism of action to minimize the intrinsic toxicity of the product while maintaining its efficacy of function^[11]. Enzymes play important roles in food and beverage industry and have already been recognized as valuable catalysts for organic transformations and production of fine chemicals and pharmaceuticals. Enzymes catalyze reactions in a

selective manner, not only regio- but also stereo selectively and have been used both for asymmetric synthesis and racemic resolutions.

Minimizing energy consumption

The design of chemical transformations that reduce the required energy input in terms of both mechanical and thermal inputs and the associated environmental impacts of excessive energy usage.

Renewable resources

In addition to the direct hazard associated with a particular chemical substance, the implications of using a renewable versus a depleting feedstock need to be included in the selection of that substance as a starting material in a synthetic transformation^[12]. To ensure a high degree of product safety for consumers and the environment, renewable resources have often been shown to have advantages.

(a) Oleochemistry

Oleochemistry is a branch of chemistry that uses vegetable oils and fats as renewable resources. Together with carbohydrates and proteins, fatty oils are important renewable resources compared to fossil and mineral raw materials.

(b) Light

Light is another emerging feedstock in a broad sense, a safe alternative to toxic catalysts in many synthetic transformations. Beside UV light, the most renewable and environmentally ideal energy source is sunlight

GREEN CHEMISTRY EDUCATION^[13]

In order to allow for the full potential of green chemistry to explore the scientific and economic advances the scientific community needs to provide educational opportunities to train chemists of the future. Since green chemistry requires the same skills and abilities of traditional chemistry, students of all ages can learn fundamental concepts in ways that are more environmentally benign. This educational endeavour can take several forms, including traditional courses in chemistry for students at primary, secondary, and university levels, as well as professional training for practicing chemistry in industry. In addition, nonscience students and profes-

sionals (especially those involved in the business/ finance communities) need to be aware of the recent developments and advances green chemistry.

GREEN CHEMISTRY IN PHARMACEUTICAL SCIENCES^[14]

After numerous Acts and Rules, the current economic situation is forcing managements to re-think their stand on Environmental, Health & Safety policies of how pharmaceutical companies can go green. After a long struggle pharma manufacturers have recognized the economic and environmental value of Green Chemistry. Although various Act and Rules such as

i. The Environmental (Protection) Act, 1986 and Rules, ii. the Water (Prevention & Control of Pollution) Act, 1974 and Rules.,iii. the Air (Prevention & Control of Pollution) Act, 1982 and Rules have been introduced by the Indian government, these have been followed for compliance and for obtaining licenses rather than realising the importance and value of green chemistry. The importance and self realisation has now come to mean economic value also. Pharma companies have to take responsibility for two major issues: energy efficiency and solvent reduction.

GREEN GUIDELINES FOR TEACHERS AND STUDENTS IN LABORATORY^[14]

It is most appropriate to carry out a synthesis by following a pathway so that formation of waste is minimum or absent. In universities and colleges, the cost of disposal of waste from chemical laboratory can be reduced by carrying out experiments on a much smaller scale. Many do not have such a scheme so that all this goes in the sewage untreated If you don't use a chemical, you don't have to buy it and you can't lose it. green chemistry need not be expensive. If the whole chemical process is rethought and modified, the result may be cheaper. It may be not be possible to green every step of the process at once.

1. Experiments should involve the use of alternative reagents which are not only eco-friendly but also be easily available at very cheap price. They should not preferably involve the use of organic solvents ethanol and methanol.

2. Modified Experiments, if possible should not involve sophisticated instrumentation techniques like high -pressure system, evacuated system, inert atmosphere using argon, *etc.*
3. Experiments should avoid tedious experimental procedure like longer reaction time, reaction at high temperature *etc.*
4. All organic chemistry experiments should preferably be conducted in semimicro or micro-scale. Thin-layer chromatography (TLC), spectroscopic techniques (UV, IR and NMR) should be methods of choice for determining purity, functional groups and structure elucidation.
5. One can use ethyl chloroformate as a substitute for PCl_5 , PCl_3 , POCl_3 or SOCl_2 . The acid is converted to anhydride which can be used for the same purpose.

Inorganic analysis

The conditions of the laboratories for doing inorganic analysis by conventional methods in the under graduate level are at all not eco -friendly. The gases are toxic – causing health-hazards. Sometimes experiments are carried out in closed doors – in hot, humid conditions. Students often fall victim of this infrastructure. The acid fumes, which are toxic, pollute the atmosphere. So, a change in outlook must be brought about with the existing systems. Inorganic analysis mainly deals with the detection and estimation of basic and acid radicals. For the detection of radicals “Spot -tests” may be introduced.

Physical chemistry experiments

1. In distribution experiment, the use of chemicals like carbon tetrachloride, benzene should be avoided and can be substituted by toluene or acetic acid in butanol.
2. Experiments involving conductometry, polarimetry, potentiometry, pH-metry, colorometry, polarography, spectrophotometry, requires chemicals in very low concentrations and have no negative influence on the health or environment, hence these expt. may not need any change or alterations.
3. If possible, instrumental methods may be introduced from the UG level.

(a) How to design safer chemicals

The more we know about how a chemical's struc-

Tutorial Review

ture causes a toxic effect, the more options are available to design a safer chemical. Chemists now have access to many sources of information to determine the potential toxicity of the molecules they design and the ingredients they choose. Green chemists are trained to integrate this information into the design of molecules to avoid or reduce toxic properties. For example, they might design a molecule large enough that it is unable to penetrate deep into the lungs, where toxic effects can occur. Or, they might change the properties of a molecule to prevent its absorption by the skin or ensure it safely breaks down in the environment.

(b) Green paints in all colours

Many now recognize that volatile organic compounds (VOCs), the source of “new paint smell,” are harmful to health and the environment. Old-fashioned, water-soluble “milk paints” in powder form have been around for decades, but are still not widely available. Great strides have been made to bring home paints to the market that contain low or no VOCs, and are just as attractive. One company, Archer RC paint, won a 2005 Presidential Green Chemistry Award with a bio-based paint which in addition to lower odor, has better scrub resistance and better opacity.

GREEN CARPETS IN ALL SORTS OF PLACES^[15]

In 2003, Shaw Carpet won a Presidential Green Chemistry Challenge Award with its carpet tile backing, EcoWorx. EcoWorx replaces conventional carpet tile backings that contain bitumen, polyvinyl chloride (PVC), 11 or polyurethane with polyolefin resins which have low toxicity. This product also provides better adhesion, does not shrink, and can be recycled. Carpets with EcoWorx backing are now available for our homes, schools, hospitals and offices.

GREEN CHEMISTRY CONTEXT IN INDIA

India in the way to green

(a) Green strategies

In developing green synthetic strategies, Indian scientists are mainly concentrating on avoiding environmentally noncompatible reagents, solid-phase synthe-

ses, modification of synthetic routes to decrease the number of steps and increase overall yield, usage of newer catalysts and simplification of classical procedures of reaction. Reagent chemists in India are working toward development of more benign and selective reagents that require ambient conditions. The elimination of hazardous solvents is one of the prime concerns among them. Enzymes have emerged as biotechnological tools, which can offer solutions to the major problems of the chemical industry in India. Over the years, chemists in India are engaged in enhancement of an application base of enzymes to develop new alternative sweeteners such as high fructose corn syrup (HFCS), synthetic honey, and other food products such as polysaccharide gums, thickeners, and flavour enhancers.

Usage of nonconventional technologies is highly popular in India. First in this list is the usage of microwaves, which is also the field of my research work. Further, the microwave chemists are turning their attention toward microwave-assisted dry-media reactions in order to minimize solvent usage, an added advantage to already established microwave chemistry. In addition to microwave-assisted reactions, ultrasonic and photochemical reactions are also used as nonconventional reaction technology.

Analytical chemistry has been at the center of the green chemistry movement. Advances in analytical chemistry are key to environmental protection. In India, the focus for analytical chemistry is mainly on extraction technologies such as solid phase, ultrasound and microwave, supercritical fluid extraction, and automated soxhlet extraction. Monitoring and analysis of heavy metals and pesticides is very important for an agro-economy-based country like India, and chief governmental institutes like the Indian Agricultural Research Institute (IARI) and the Defence Research and Development Organisation (DRDO) are working extensively in this field.

(b) Non-academic initiatives

Industry in India still needs to make significant improvement from the environmental point of view. Most of the industrial R&D is mainly concerned with cost effectiveness rather than eco-effective methods. Although there has been some collaborative work between

academia and industries, still there is ample opportunity for increased collaboration. The textile industry is one of the highly revenue generating industries in India, and they are now switching over to microbial decolorization and degradation. There is an increasing need of exploring biodiversity for natural dyes and developing eco-friendly methodology for synthetic dyes. All these require more funding in the R&D of respective fields and greater interaction and coordination between industry, academia, and government.

One of the recent examples of government initiative is the conversion of diesel vehicles to compressed natural gas (CNG) in order to reduce pollution in the capital city Delhi. Relocation of industries into industrial areas away from residential parks is another bold step taken by the Delhi government. Further, the government is also concentrating on new projects such as fuel pellets from municipal waste, aspirated H-cylinder engines for light commercial vehicles (LCVs), meeting India 2000 emission norms, battery-powered cars for pollution-free driving, hydrogen energy and energy towers for new environment-friendly fuel, development of traditional herbal drugs as adaptogens and immune modulators. The government should also increase funding to encourage research in green chemistry.

CONCLUSIONS

In conclusion, the practicing of green chemistry in India is a necessity rather than an option. The future of green India is in the hands of young researchers and students, as the practice of green chemistry is a moral responsibility for them. Government agencies should enforce the laws strictly to practice green chemistry. Industries should also understand their moral responsibility toward the fragile environment. The research and development and the science and technology agencies that are responsible for the funding of scientific activities in the country must encourage and give preference to the development of greener science and technology. Though it is true that many industries and research organizations are yet to implement the principles of Green chemistry, nevertheless some of them have begun to realize that the 'think green' culture is more than just a fashion. In fact, the winds of changes have already started blowing and the more successful chemistry re-

searchers and chemical technologists will like to appreciate and apply the values of Green chemistry in innovation, application and teaching.

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Tutorial Review

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