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A REVIEW ON GREEN APPROACH IN CHEMISTRY

Jyoti Mathela* **and B.K Singh**

Department of Pharmaceutical Sciences, Kumaun University Nainital, 263136

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***Corresponding Author**
Jyoti Mathela
Department of Pharmaceutical Sciences, Kumaun University Nainital, 263136.

ABSTRACT

Green chemistry advocates the set of principles and methodologies that can reduce the generation of hazardious substances in the manufacture and application of chemical products. 1. By modification of the traditional synthesis reactions we can arrive at the same final product, yet reduce or eliminate toxic starting materials, by-products, and wastes. 2. Green chemistry tools include choosing alternate starting materials, reagents, solvents, process alternative process analytical chemistry and catalysts. Green chemistry focuses on the minimizing the environmental impacts of hazardous chemicals substances. It is based on the effective ways to reduce, remove or rectify the existing toxic effects of hazardous substances generated as a result of manufacture and the use of chemical substances. By using sustainable means of waste management and by limiting the existing use of hazardous substances, the devastating impacts of chemical substances can be prevented. This review covers subjects relating to reducing the environmental impacts of chemical substances and fuels by developing alternative and sustainable technologies that are non-toxic to living things and the environment .It shall also focus on Alternate Energy Technologies, Biofuels, Green engineering and Green solvents.The application of innovative technology to establish industrial procedure, designating greener, safer chemical synthesis, designing greener and safer chemical manufacturing processes, Microwave assisted and Ultrasound assisted synthesis,Green synthesis. This review focuses on the modification in some traditional reactions by changing the solvents b green solvents like water or by alterations in temperature which leads to better environment friendly products. This review is an attempt to compile all major work towards role of green chemistry to maintain the sustainability and environmental protection.

KEYWORDS: Microwave assisted reactions, Ultrasound assisted reactions, Biofuels.

INTRODUCTION

The Pollution Prevention Act of 1990 created awareness amongst the population regarding the burning issue of pollution and its impact on environment. The contribution of industries and factories, manufacturing the chemical substances and disposing the chemical waste directly into the nearby water bodies, was recognized as one of the prime factors of water pollution. The prevention of pollution at the source rather than the treatment of pollutants after they are formed became a formal objective of Environmental Protection Agency (EPA) in 1991.Anastas coined the term "green chemistry" in the same year. Anastas and Warner formulated the twelve principles of green chemistry in 1998.These principles serve as guidelines for the chemists seeking to lower the ecological footprint of the chemicals they produce and the processes by which such chemicals are made.

The Environment Protection Agency (EPA) and American Chemical Society (ACS) have played a key role in promoting research and development, as well as education and in green chemistry. Chemical societies around the globe have recognized the importance of green chemistry and promoted it through journals, conference, educational activities. This has now known as green chemistry, and is defined by Anastas and Warner.[1, 16]

We are living in the age where the adulteration in food items is very common and acceptable. The carcinogenic substances like KBr present in eatables like low grade breads, the attractive red color of seasonal fruits like watermelon due to injected chemicals, the genetically modified vegetables which are banned in other countries are easily sold in market, the adulteration of food items, all these are the unintentional means by which we ingest the harmful chemicals in our system. These hazardous chemicals accumulate in our system and act as a contributing factor to various diseases. It has been observed in recent times, that there has been a significant increase in the number of individuals suffering from diseases like diabetes and hypertension. These are the major issues our country is facing these times. It is the responsibility of each and every human being on this planet to do their part in creating a greener tomorrow which can be done by adopting the sustainable development techniques.

THE PRINCIPLES OF GREEN CHEMISTRY TO PRACTICE

1. Atom Efficiency: Diels-Alder reaction is an example of a potentially very atom efficient reaction.

2. Less Hazardous Chemical Synthesis: Replacement of amalgam cells with (mercury containing) with polymer membranes in chlor-alkali industry.

3. Designing Safer Chemicals: an environmentally accepltable alternative to organotin antifoulants.

4. Safer Solvents and Auxiliaries: Usage of bio-solvents, supercritical fluids ionic liquid and solvent less reactions.

5. Design for Energy Efficiency: Improving the energy efficiency of current polymerization systems through creating better stereospecific catalysts, biocatalytic reactions and condensation polymerization reactions.

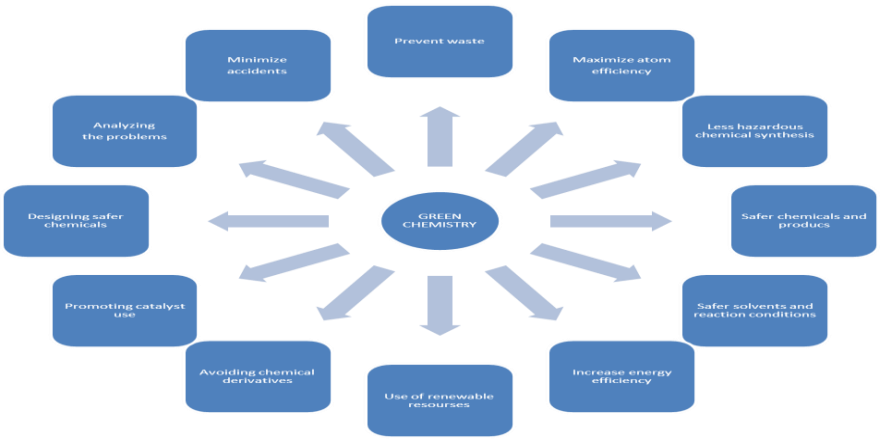
6. Renewable Feed stocks: Developments of new class of surfactants those which are readily biodegradable and are based on renewable resources.

7. Inherently Safer Chemistry for Accident Prevention: Dimethyl carbonate is so eco-friendly than dimethyl sulfate and methyl chloride in methylation reaction.

8. Use of visible light as reagent.

9. Alternative Synthetic Pathways.[1]

THE PRINCIPLES OF GREEN CHEMISTRY



INNOVATIONS IN GREEN CHEMISTRY

Chemists freom all over the world are using their creative and innovative skills to develop new processes, synthetic methods, reaction conditions, catalysts etc., under the new Green Chemisty concepts. Some of these are:

1. Historically, chlorofluorocarbons (CFCs) have been used as refrigerants in air conditioners and refrigerators. CFCS have the advantages of safe combustibility, high stability, and low toxicity, but unfortunately they destroy the ozone layer.

(HFCs) have replaced CFCs. HCFCs and HFCs are, indeed, safer for the ozone layer.

2. Chelates are complex that interact with metal ions, often increasing the solubility of the metal ion. They are used in many types of cleaners and industrial processes. Conventional chelates are based on amino carboxylic acids (e.g., ethylenediaminetetraacetic acid, EDTA) and phosphates (e.g., sodium triphosphate). Unfortunately, because EDTA is not readily biodegradable and because phosphates can cause pollution via eutrophication, these conventional materials are often viewed as environmentally unfriendly.

3. Spinosad is an environmentally safe pesticide but is not stable in water and so therefore cannot be used to control mosquito larvae. It is 15 times less toxic than the organophosphate alternative, does not persist in the environment, is non-toxic to wildlife and eliminates the use of hazardious materials.

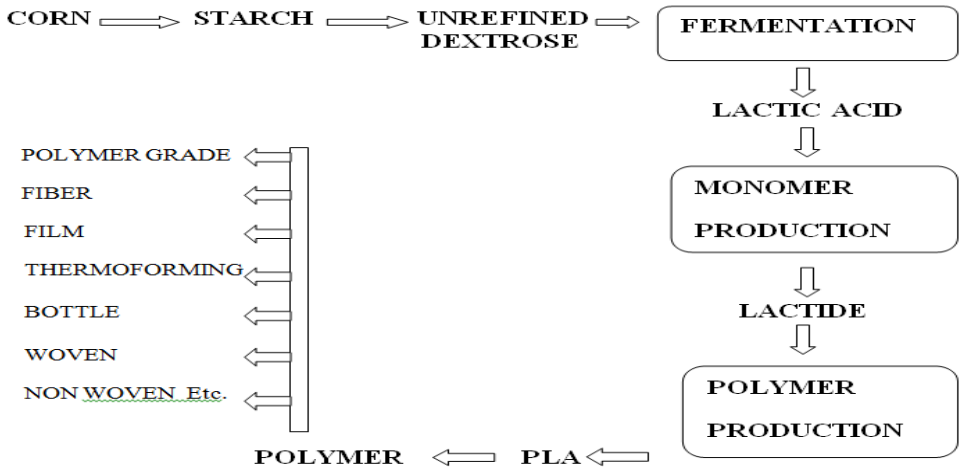
4. Converting waste glycerin from biodiesel production to propylene glycol with the use of a copper-chromate catalyst. Propylene glycol produced in this way will be cheap enough to replace the more toxic ethylene glycol that is the primary ingredient in automobile antifreeze.

5. Another approach towards protecting plants from pests and diseases is to activate their natural defense mechanism against pests and diseases it is known as **Harpin technology**. Harpin is a naturally occurring protein that is isolated from genetically altered bacteria. When applied to the leaves and stems of plants, this protein elicits their natural defense systems.

The EPA has classified harpin as Category IV, which is reserved for the materials with the lowest hazard potential. As an added benefit, Harpin also stimulates plant growth.

In order to decrease human consumption of petroleum, chemists have investigated methods for producing polymers from renewable resources such as **biomass**. Polylactic acid (PLA) is a polymer of naturally occurring lactic acid(LA) , and LA can be produced from the fermentation of corn. Another advantage of Polylactic acid is that, unlike most synthetic polymers which liter the landscape and pack landfills, it is biodegradable.PLA can also be recycled by conversion back to lactic acid. It can replace many petroleum-based polymers in products such as carpets, bags, cups and textile fibres.

- Using new less toxic chemicals for bleeching paper.
- Substituting yttrium for lead in paint.
- Using enzymes instead of a strong base for treatment of cotton fibres.



MODIFICATION

TRADITIONAL REACIONS AND THEIR GREEN APPROACH[5]

Let us consider a reaction of the type

A+B ⟹ (P) PRODUCT+ (W) WASTE

We will try to find alternate A or B to avoid W

EXAMPLE 1: Disinfection of water by chlorination. Chlorine oxidizes the pathogens by killing them, but at the same time forms harmful chlorinated compounds. A solution to this problem is to use another oxidant, such as O_3 or supercritical water oxidation.

EXAMPLE 2: Production of allyl alcohol CH_2=$CHCH_2OH$

TRADITIONAL ROUTE: Alkaline hydrolysis of allyl chloride, which generates acid as a by-product.

CH_2=$CHCH_2Cl + H_2O \longrightarrow CH_2$=$CHCH_2OH + HCL$

Problem **Product**

GREENER ROUTE: To avoid chlorine. Two step reaction using propylene CH_2= $CHCH_3$

CH_2= $CHCH_3 + CH_3COOH + ½\ O_2 \longrightarrow CH_2$=$CHCH_2OCOCH_3 + H_2O$

Propylene Acetic acid

CH_2=$CHCH_2OCOCH_3 + H_2O \longrightarrow CH_2$=$CHCH_2OH + CH_3COOH$

Allyl alcohol acetic acid

ADDED BENEFIT: Recovery of acetic acid in the final step, leaving no unwanted by-product

APPLICATIONS OF GREEN APPROACH IN CHEMISTRY

1. FLOW REACTORS

An alternate way to simplify organic syntheses into a single operation is to perform sequential reactions in a flow reactor. Ley and colleagues reported that a multistep synthesis of an alkaloid natural product (+)-oxomaritidine can be accomplished by using microfluidic pumping systems that pass materials through various packed columns containing immobilized reagents, catalysts, scavengers, or catch-and- release agents, combining seven separate synthetic steps linked into one continous sequence.[7]

2. LESS HAZARDOUS CHEMICAL SYNTHESIS

- The family of polycarbonates contains very important polymers which are used where high optical properties combined with strength are needed.
- The polycarbonate is manufactured by a condensation reaction between bisphenola and either carbonyl chloride or diphenyl carbonate.
- Carbonyl chloride is a very poisonous gas, manufactured from other hazardous gases, carbon monoxide and chlorine. On the other hand diphenyl carbonate is produced from dimethyl carbonate, which is readily manufactured from methanol, carbon monoxide and oxygen in the liquid phase, in presence of copper(II) chloride, $CuCl_2$.
- Dimethyl carbonate, when heated with phenol in the liquid phase, forms the diphenyl carbonate.

The overall process for the production of polycarbonate that uses diphenyl carbonate is less hazardous than that using carbonyl chloride.

For example: One process used in the manufacture of the most widely used herbicide, glyphosates uses the sodium salt of 2,2'-iminodiethanoic acid as one of the intermediates. This is made in a series of reactions from ammonia, methanol (formaldehyde) and hydrogen cyanide. Although hydrogen cyanide is a very useful reagent, it is extremely toxic. A recent innovation has been the introduction of a new route to the sodium salt.[21, 22]

1. RENEWABLE FEEDSTOCKS

There are many developments aiming to reduce the dependence on oil. Surfactants are made which are readily biodegradable **Polyols**, from soya, which are used to make **polyurethanes**.

- Ethene from bioethanol and which is used to make poly (ethane)

- Propene is being produced from materials produced in turn from biodegradable resources it is used to manufacture poly (propene).[24]

2. CATALYTIC APPROACH TO GREEN CHEMISTRY

The choice of the catalyst is of prime importance in these environmentally conscious days. Green Chemistry demands the replacement of highly corrosive hazardous and polluting acid catalysts with ecofriendly and renewable solid acid catalysts. **Zeolites**, solid acids and especially those based on micelle-templated silicas and other mesoporous high surface area support materials are beginning to play a significant role in the greening of fine and specially manufacturing processes.[25] The advantages in developing and using catalysts for chemical reactions are

1. Reduction in energy demand by lowering the temperature and pressure used.

2. They enable alternative reactions to be used which have better atom economy and thus reduce waste.

3. It is possible to control reaction pathways more precisely, reducing unwanted side products and making it easier to separate and purify the required product.

4. For example, Aluminum chloride was used for many years in the production of alkyl benzene sulfonates, an active surfactant in many detergents. The aluminium chloride was needed to effect the reaction between benzene and long chain alkene. The aluminium chloride could not be recycled and became waste as aluminium hydroxide and oxide. Now a solid zeolite catalyst with acid groups is used and can be reused time and time again with no waste products.[26]

5. Similarily, benzene and propene are converted into cumene in the manufacture of phenol, using a zeolite in place of aluminium chloride.[1]

6. Another example is the manufacture of one of the most important polymer used to make fabrics, polyamide 6(known as nylon6). In this process cyclohexanone is converted into caprolactum via the oxime (produced by the reaction of ketone with hydroxylamine hydrogensulfate). The oxime is isomerised by sulfuric acid to caprolactum; the released sulfuric acid is converted to ammonium sulfate.However, again zeolite catalyst, with acidic sites, is now being used to effect the arrangement.

The zeolite is regenerated and saves the use and subsequent waste of sulfuric acid.[12]

3. DESIGNING SAFER CHEMICALS

- For example, polymers have been developed which are much less flammable than the more well known polymers but also retain properties such as toughness. They must be able to absorb severe impacts without cracking and breaking. One such polymer is polyphenylsulfone.

- Detergents used to be based on the sodium salts of alkylbenzene sulfonic acids, and the alkyl group was branched bt now these compounds have been replaced with sodium salts of linear alkylbenzene sulfonic acids, which are readily degraded.

4. REPLACEMENT OF HAZARDOUS SOLVENTS BY GREEN SOLVENTS:

The development of green chemistry redefines the role of solvent. An ideal solvent facilitates the mass transfer but does not dissolve. In addition, a desirable green solvent should be natural, non-toxic, cheap and readily available. More desirably, it should have additional benefits of aiding the reaction, separation or catalyst recycling.[3]

SOLVENTS

PREFERRED	USABLE	UNDESIRABLE
Water	Cyclohexane	Pentane
Acetone	Heptane	Hexane
Ethanol	Toulene	Di-isopropyl ether
2-Propanol	Methylcyclohexane	Diethyl ether
Ethyl acetate	Methyl t-butyl ether	Dichloroethane
Isopropyl acetate	Isooctane	Dichloromethane
Methanol	Acetonitrile	Chloroform
Methyl ethyl ketone	2-Methyl THF	Dimethyl formamide
1-Butanol	Xylenes	Pyridine
t-Butanol	Dimethy sulfoxide	Dimethyl acetate
	Acetic acid	Dioxane
	Ethylene glycol	Benzene
		Carbon tetrachloride

LATEST DEVELOPMENTS IN THE FIELD OF GREEN CHEMISTRY

MICROWAVE-ASSISTED ORGANIC REACTIONS:

The microwave-assisted organic reactions are proved to be eco-friendly with higher yields. Thus, it is one amongst the accepted fields in the green chemistry. Short reaction time, wide range of reactions, minimum exposure of hazardous chemicals and maximum utlilization of energy; these features enable microwave assisted synthesis as an effective and handy tool for theindustry as well as academic research.

ULTRASOUND-ASSISTED ORGANIC REACTIONS

Ultrasound assisted organic synthesis is another green methodology which is applied in many organic synthetic routes with great advantages for high efficiency, low waste, low energy requirements. Sonochemistry(in region of 20KHz to 1MHz) has many applications due to its high energy and the ability to disperse reagent in small particles and accelerate reactions.

Also, sonochemical engineering is a new field involving the application of sonic and ultrasound waves to chemical processing. Sonochemistry enhance or promotes chemical reactions and mass transfer. It offers the potential for shorter reaction cycles, cheaper reagents,chemistry –intensive, and an application of this novel means of reaction in environmental remediation and pollution prevention seem almost unlimited and is rapidly growing area.[7]

PROBLEMS AND THEIR SOLUTIONS

- Discouraging the purchase and use of plastic bags and containers and replacing them by paper bags and stainless steel containers, and also the plastic can be used to make the roads by using molten plastic mixed with bitumen. This is a beneficial technique that will help the Indian economy as well.

- Preventing the waste of solvents like acetonitrile, methanol, and acetone while washing the apparatus prior use in HPLC method development and validation trials.

- Preventing the solvent and drug abuse, by making people aware regarding the prominent adverse effects like irreversible brain damage, loss of consciousness ,hearing problems ,impairment of mental and physical balance. For example:- the cheap adhesive fevibond which contains toluene as solvent is abused by the young school and college going children .Due to its easy availability and cheap price it has become the most popular means of getting

high which provides a temporary euphoric feeling which serves as an escapism from the reality. The adhesive must be banned, as it has spoiled many lives and also led to the death of many teenagers.

- Promoting the microwave assisted reaction that reduces the multistep reaction to a single step which is very economic and less time consuming.

- The waste management must start right at our homes by separating the organic waste from the inorganic and by discouraging the practice of dumping waste in open. Besides this the sharp blades and broken glass must not be mixed with organic waste, as the stray dogs and cows which feed on this waste ingest these sharp blades and polybags which lead to choking and ultimately death of animals.

- Planting more and more trees is the ultimate solution of all the environmental proplems as it will maintain the balance of nature and keep a check on air pollution.

CONCLUSIONS

The aspiration can be summed up in one word "**sustainabilit**y" i.e., meeting the present requirements without compromising the ability of the future generations to meet their own needs. Green chemistry aims at reducing or completely eliminating the use of hazardous substances in the manufacture and application of chemical products, which can be done by modification of traditional routes of synthesis by using alternate feedstock, reagents, solvents and catalysts. The problems green chemistry addresses are

- The depletion of finite oil, gas and mineral resources.
- The production of waste, some of which is harmful to living organisms.
- Reagents and processes that present a risk to human health and environment.

Microwave assisted synthesis are faster, better and safer green chemistry approach for the traditional and applied named reactions. The time taken for the synthesis is drastically reduced by the microwave assisted reactions. The time take for the synthesis is drastically reduced by the microwave assisted synthesis. Several named reaction were carried out using microwave assisted synthesis, which complied in spectral assignments as that of those with products obtained from the conventional methods.[5]

Presently it is easy to find in the literature many interesting examples of the use of green chemistry rules. Green efforts are still undertaken to design an ideal process that starts from non-polluting materials. It is clear that the challenge for the future chemical industry is based on production of safer products and processes designed by utilizing new ideas in fundamental research. Furthermore, the success of green chemistry depends on the training and education of a new generation of chemists.

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