Green chemistry and its applications

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Introduction to green chemistry:

Environment is a sphere around us which comprises of some physical and chemical components with which we are interacting and are a part of it. Due to development in science (chemical science), the use of chemicals has become a quantity; same is the case with our environment. The chemical components in our environment are increasing day by day of which some can be degraded but most of them are undegradable. This is termed as pollution.

The addition of undegradable substances that causes instability, disorder, harm or discomfort to the ecosystem is termed as pollution. Pollution is creating a risk to the environment. Thus in order to reduce the risk of pollution a system should be introduced that must reduce the risk by not changing the effect but by changing the cause. Thus a concept named green chemistry was introduced.

Green Chemistry or environmentally benign chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. [1]

Rather than focusing only on those undesirable substances that might be inadvertently produced in a process, green chemistry also includes all substances that are part of the process. Therefore, green chemistry is a tool not only for minimizing the negative impact of those procedures aimed at optimizing efficiency, although clearly both impact minimization and process optimization are legitimate and complementary objectives of green chemistry. Green chemistry applies to industrial prospects organic chemistry, inorganic chemistry, biochemistry, analytical chemistry, and even physical chemistry.[2]

Green chemistry works on risk and hazard factor. That means risk can be minimized by reducing hazard and then the cost and potential of exposure can be maintained.

The calculating the risk associated to hazards of a substance we use;

Risk= f(exposure X hazard)

Collectively, Green chemistry works on:

Evaluation of methods to design safer chemicals:

- Mechanism of action analysis:
- Structure activity relationship:
- Avoidance of toxic functional groups:
- Minimizing bioavailability:
- Minimizing auxiliary substances.

Evaluation of reaction types:

- Addition reactions
- Substitution reactions &
- elimination reactions

Evaluation and design of energy efficient processes.

- The best way of waste disposal.

Principles of green chemistry:

Beyond these green chemistry works on certain principles for making environment safe. These 12 principles are[4]

1. Waste Prevention
2. It is better to prevent waste than to treat or clean up waste after it has been created.
3. Atom Economy
4. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
5. Designing Less Hazardous Chemical Syntheses
6. wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

7. Designing Safer Chemicals
8. Chemical products should be designed to affect their desired function while minimizing their toxicity.
9. Safer Solvents and Auxiliaries
10. The use of auxiliary substances (e. g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
11. Design for Energy Efficiency
12. Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
13. Use of Renewable and degradable Feedstock
14. A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
15. Reduce Derivatives
16. Unnecessary derivatization (use of blocking groups, protection, deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
17. Catalysis
18. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
19. Design for Degradation

20. Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

21. Real-time analysis for Pollution Prevention

22. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

23. Inherently Safer Chemistry for Accident Prevention

24. Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Examples and applications of green chemistry:

- As starting materials:
  - Polysaccharides polymers: polymers are a very important class of compounds that have broad applications and a wide array of compounds can be exploited. They have their hazardous effects. In order to use starting materials more environmentally we must use polysaccharides as the feedstock. These are biological feedstock, and as such have the advantage of being renewable, as opposed to those feedstock which are the product of petroleum. On the other hand these have no chronic toxicity to human health and environment.
  - Commodity chemicals from glucose: glucose is another alternative for commodity chemicals. Using biotechnological techniques to manipulate the schkimic acid pathway (responsible

for making aromatic compounds), compounds such as hydroquinone, catechol, and adipic acid, all of which are important, can be synthesized. Benzene is the starting material for these substances, by using glucose in place of benzene, can help in minimizing the use of certain reagents with certain toxicity. The conduction of synthesis in water instead of organic solvents is more beneficial.

- Some reactions are:
- Green chemical reactions:
    - Atom economy and homogeneous catalysis: Atom economy was developed by Trost. The goal of this work is to reduce the number of atoms that are produced as unwanted by-products. Aldol condensation reactions are examples where little or no by-products are formed.
    - Halide free synthesis of aromatic amines: Traditional synthesis of aromatic amines involves chlorination of benzene followed by nitration and nucleophilic displacement of the chlorine with a new substituting group. The synthesis of 4-amino-diphenylamine illustrates this process. Monsanto has developed a new synthesis of 4-aminodiphenylamine that utilizes nucleophilic substitution for hydrogen (fig. 4). The process avoids the use of halogenation intermediates. In this process nitrobenzene and aniline are heated in presence of tetramethyl ammonium hydroxides to give tetramethyl-ammonium salts of thew condensation products.
- As green reagents:

    - Green oxidative transmission complexes: many oxidative processes have negative ecological consequences. The metal ion contamination can be minimized by using molecular oxygen as the primary oxidant. Many ligands which are stable towards oxidative decomposition in oxidizing environments have been developed. Now, stable high oxidation state transition metal complexes can be synthesized.
    - Liquid oxidation reactor: it allows safe oxidation of organic chemicals with pure oxygen. The amount of vent gas has been reduced because of use of oxygen. The use of can make reaction to occur at low temperature is beneficial.
    - Non phosgene isocynate synthesis: polyurethanes are important polymers that are widely used for variety applications. These are generally prepared with the help of phosgene. But phosgene is an extremely toxic gas whose acute end point is lethality. A method of synthesis is developed in which poly-urethanes and their isocyanate precursors are synthesized without using phosgene.

- Green solvent and reaction conditions:
- Super critical fluids: the use of co2 as a substitute for organic solvents already represents a tool of waste reduction in chemical industry. Of the wide range of supercritical carbon dioxide reactions that have been explored, one class of reaction has shown exceptional promise, it was found that asymmetric catalytic reactions, particularly hydrogenation and hydrogen transfer reactions, can be carried out in supercritical

carbon dioxide with selectivity compared or superior to those observed in conventional solvents.

- Immobilized solvents: With solvents being of extremely high volume and very broad breadth of applicability, their potential for negative impact on human health and the environment is very large. Therefore, the immobilization of such solvents helps in reduction of hazards. Immobilized solvents or solvent molecules tethered to a polymeric backbone follow the same logic as the ionic liquids. By creating a system where a known solvent, e. g., THF, is tethered properly, it can still maintain its solvency but is incapable of manifesting any hazard by exposing humans or the environment. These types of solvents are expensive and difficult to handle.[5]
- aqueous reaction conditions
- Irradiative reaction conditions:

- Green chemical products:
  - Design of alternative nitrites: toxicological structure activity relationships of a compound are explored and synthetic modifications that reduce toxicity are found. The mechanism of acute toxicity is proposed to be elimination of hydrogen cyanide from cyanohydrins, depending on the nature of the substitution at alpha carbon position can be slowed or accelerated.
  - Donlar’s polyaspartic acids:
  - Polaroid’s complexed developers:
- Manufacture of drugs:

- Oligonucleotide drugs: Synthetic oligonucleotides are an emerging class of drug molecules with a broad spectrum of therapeutic application.

Currently, our manufacturing process uses HL-30™, a polystyrene bead support loaded at 90 mmol/g. The HL-30 bead has several limiting characteristics: (a) nonbiodegradable,(b) nonrenewable (c) it contributes ~40% of raw material costs, and (d) it is a single-source raw material. Therefore, effective regeneration of spent solid supports and their reuse is done in Oligonucleotide synthesis. The reusable solid-support technology is based on use of a Q-linker™ (hydroquinone diacetic acid) spacer arm between the 3′-end of the first nucleoside and a hydroxyl- functionalized support (in fig). In summary, the method allows used support to be quickly rederivatized with protected nucleoside and reused, without opening and recharging the synthesis column. The solid-support bed may be used up to six times in this manner.

- In agriculture:
  - Management of the soybean cyst nematode by using a biorational strategy: Soybean cyst nematode infestation continues to be a serious agricultural problem. As part of an interdisciplinary effort to identify a biorational solution to the problem, analogs of glycinoeclepin A, a natural hatching stimulus of the nematode, were prepared and tested. Several of the analogs were discovered to inhibit the hatching of soybean cyst nematode eggs. The eggs are now so protected in the female that it can last for eleven to twelve days in soil.[7]

- Potential of entomo-pathogenic Fungi as Biological Control agents against the Formosan subterranean Termite: Control of colonies of pest species of termite can be achieved by treatment of conidia applied directly to the nest, although the time of elimination may vary depending on factors such as the target species, time of year and colony vigour. Spores will remain active in nests for at least two years. The repellency of conidia can be used to protect timber. Spores can be sprayed directly onto sound timber or into termite-infected timber to provide protection at least for a period of time. Conidia are capable of proving protection from termite attack for timber in ground contact. A soil barrier created by mixing conidia of M. anisopliae has given protection to susceptible timber for up to three years under cool, dry conditions in the Canberra region, but only for less than six months at a site near Darwin in the tropics. With a " trap-and-treat" system, one of the approaches in bait technology, it is possibe to introduce the conidia to a termite colony. The major factor limiting the efficacy of M. anisopliae with the currently available isolates is the behavioral response of healthy termites to the applied conidia, to foraging termites bringing conidia

Future trends in green chemistry:

- Oxidation reagent and catalysis: historically, many of the oxidation reagents and catalysts have been comprised of toxic substances such as heavy metals. Since these substances were often used in extremely large volumes required to convert millions of pounds of petrochemicals, there was a significant legacy of these metals being released to the environment and having substantial negative effect on human health and environment. It can be changed by the use of benign substances.

- Non covalent derivatization: use of chemicals is dependent upon formation and breaking of covalent bond. chemistry happening without bond making physical, chemical properties are modified and performance measures are enhanced by utilization of dynamic complexation which allows for the temporary formations of modified chemical structures, the properties of molecules can be changed for the period of the necessary to carry out a particular function without all of the waste that would be generated if full derivatization is implemented.
- Supramolecular chemistry: Research is currently ongoing in the area of supramolecular chemistry to develop reactions which can proceed in the solid state without the use of solvents. The cycloaddition of trans-1, 2-bis(4-pyridyl)ethylene is directed by resorcinol in the solid state. This solid-state reaction proceeds in the presence of UV light in 100% yield.
- Biometric multifunctional reagents: while synthetic catalysis and reagents for the most part have centered on carrying out one discrete transformation. The manipulations may include activation, conformational adjustments, and one or several actual transformations and derivitizations.
- Combinatorial green chemistry: it is the chemistry of being able to make large numbers of chemical compounds rapidly on a small scale using reaction matrices. The example is lead that has a large no of

derivatives. This chemistry has enabled large no of substances to be made and their properties assessed without the magnitude of the effects of waste disposal.

- Energy focus: The environmental effect of energy usage are profound but have not been as visible and as direct as some of the hazards that have not been posed by materials used in manufacture, use and disposal of chemicals. The benefit of catalysis is dramatic in photochemistry. There is a need to design substances and materials that are effective, efficient and inexpensive at the capture, storage and transportation.
- Proliferation of solvent less reactions: one of the ‘ solvent alternatives’ that is being: it is one of the solvent alternatives that is being developed in green chemistry is that of solvent less reaction system. The carrying of manufacturing process in solvent-less condition utilizes some non-traditional conditions. This helps in development of product isolation, separation and purification that will be solvent-less as well in order to maximize the benefits.

Some environmental laws[8]:

Also the late sixties and early seventies were times when the environment received a great deal of attention including the formation of the Environmental Protection Agency (EPA) and the celebration of the first Earth Day, both of which occurred in 1970. In the intervening years in excess of 100 environmental laws have been passed. These include the twelve major laws listed below.

- 1970 Clean Air Act. Regulates air emissions.

- 1972 National Environmental Policy Act.
- 1972 Clean Water Act.
- 1972 Federal Insecticide, Fungicide & Rodenticide Act. Governs distribution, sale and use of pesticide products.
- 1972 Ocean Dumping Act. Regulates the intentional disposal of materials into ocean waters.
- 1974 Safe Drinking Water Act. Establishes primary drinking water standards.
- 1976 Toxic Substances Control Act. Requires the testing, regulating, and screening of all chemical produced or imported in the U. S.
- 1976 Resource Conservation & Recovery Act. Regulates solid and hazardous waste form " cradle to grave."
- 1976 Environmental Research & Development Demonstration Act. Authorizes all EPA research programs.
- 1980 Comprehensive Environmental Response, Compensation & Liability Act.
- 1990 Pollution Prevention Act. Seeks to prevent pollution by encouraging companies to reduce the generation of pollutants through cost-effective changes in production, operation, and raw material use.

All of these act, deal with pollution after they were formed. These laws are in general focused on the treatment or abatement of pollution and have become " command and control" laws. Risk associated with a toxic chemical is a function of Hazard and Exposure.

While these laws have accomplished a great deal in terms of improving work for the coming years in pollution prevention.

Conclusion:

As we design new chemical syntheses and improve the manufacture of GMP oligonucleotides, decisions about whether hazardous substances will be used, whether toxic materials must be handled. Whether hazardous waste will require special disposal and the overall environmental issues associated with these processes must be seriously considered. Green synthesis protocols for oligonucleotides manufacture will yield less costly drug products when all direct and indirect costs are accounted.

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