Topic:

Green chemistry: Optimization tool for research and its developments (Short review)

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Abstract:

Within our daily life, practically we are surrounded by products, which are chemistry's creation. Chemists not only create, furthermore innovates, and develops a new product for the entire world for enhancement and upgrading daily life. Chemicals used for the manufacturing of goods and products are toxic in nature. As a result, environment and humans receive some hazardous effects. To cope up hazardous effects of chemicals on environment, Paul T Anasthas developed the green chemistry. These concepts, when implemented world widely, the reduction in hazardous effects of chemicals by industry and environment as well as chemists heave been accepted globally. Later on, this concept was accepted and implemented by 'Environmental Protection Agency' in response to prevent environmental pollution by Pollution Prevention Act (1990). Now-a-days, further Green Chemistry concept is wishfully accepted and adopted by industrialists and academicians. Globally, this emerging trend is in boom in all fields such as pharmaceuticals, industrial, academics, cosmetics and so on.

Keywords; Green chemistry, Sustainable chemistry, atom economy, nanomaterials. Introduction:

There is no hesitation to say, creation of all over the world is the chemistry's creation and in the economy's heart, whether developed and developing countries across the world. In everyday life, practically chemistry puts an impact on our life in such a way that we never realized including ourselves. Food we eat and materials we used are made up of

chemistry's chemical composition aspects. ² In collaboration of science and technology, our researchers giving a shape to society on both regional and global levels. In short, chemistry is increasing as an interdisciplinary field that will result as an opportunity and leads to some novel innovation. ³ As an interdisciplinary, it emerged as a solution of major challenges for the world, and hazardous effects faced by 'Chemists' or 'Chemistry followers' because of chemicals. 4 Chemists not only create, but moreover innovates, and develops a new product for the entire world for enhancement and to carry out upgradations in life. Chemicals used for the manufacturing of goods and products are toxic in nature, as a result environment and humans receive some dangerous effects. To avoid or check the chemical's effects on environment, Paul T Anasthas developed the green chemistry. Green chemistry concept was developed, and term was coined by Paul T Anasthas. Later on, Paul T Anasthas and Warner explained the Green Chemistry's 12 principles in their book 'Green Chemistry: Theory and Practice'. Later on, this concept was accepted and implemented by 'Environmental Protection Agency' in response to prevent environmental pollution by Pollution Prevention Act (1990). The green concept, and its 12 principles were formulated to lessen (reduce), reuse, and eliminate the chemicals and develop a new alternative to hazardous chemicals by chemists and for environment protection. Over the last two decades, 'Environmental Protection Agency' and its conservation policy focuses on awareness and is in progress due to its advantages as 'Green Chemistry' or 'Sustainable Chemistry'. ⁵



Figure1: Principles of Green chemistry⁶

Principles of Green Chemistry:

Green chemistry's twelve principles developed and promulgated by Paul T. Anasthas & John Warner to reduce, reuse and recycle the chemicals as a alternative to chemicals use, have been explained in 1998 in their 'Green Chemistry Theory & Practice' book published. The 12 principles of green chemistry are as follows: ⁶.

1. Waste / by product prevention:

In terms of chemical synthesis, designing of process plays an important role and puts an impact on production. From transformation of reactants into products, minimum waste and by-products is major consideration of manufacturer, otherwise become a burden for production during its disposal and treatment. Furthermore, unreacted starting material and discharged (disposed of) material causes environmental pollution in the atmosphere, sea & land and require some expenditure for cleaning-up.

2. Maximizing the atom economy:

Design the synthesis, in such a way that maximum incorporation of reactants (starting material) into products is achieved. Globally, ideal reaction should attain 100% yield, which means one mole of reactants produces one mole of products but practically it is difficult to attain.

B.M. Trost developed the atom economy concept with consideration of 'Up to what extent reactants converted into final products.' R.A. Sheldon forwarded the same concept as:

% Atom economy = 100 x (FW of product /FW of reactants)

As per principle, the reaction/chemical synthesis is green if maximum amount of starting material produces exact final products without any waste. ⁷

3. Design the safer chemical & products:

The use of hazardous materials and the formation of hazardous products (by products/final products) which are toxic in nature or not ecofriendly should be avoided or if possible.

Hazardous materials affect the worker directly. To avoid these effects the use of protective clothing, engineering control, respirator etc. should be in use contrarily it increases the overall production cost. ⁸

4. Design the safer chemicals:

The chemicals are the backbone of synthesis. The compounds synthesized or developed should be safe to use. For example, the drug Thalidomide (introduced in 1961) was banned & withdrawn due to its effects as birth defects and nausea & vomiting during pregnancy and categorized as unsafe. ⁹

5. For synthesis energy requirement:

For all kind of organic synthesis, minimum energy requirement plays an important role and should be acknowledged by researchers in industrial sector and academics.

In majority of chemical reactions, catalyst lowers energy which is utilized by chemical reaction. In case of exothermic reaction, extensive cooling is required which adds overall reaction cost. Furthermore, impure product adds on cost as distillation, recrystallization & separation additionally. In addition to minimum energy, reaction time should be minimum. ¹⁰

6. Select an appropriate solvent:

In chemical synthesis, appropriate solvent should be selected for specific reaction. By using an appropriate solvent, the byproducts formation reduces and any kind of environmental pollution & health hazard may be minimized or eliminated.

7. Use of renewable (starting material):

Normally, starting materials selected for synthesis are from renewable or non-renewable source. Mostly used petrochemicals are of non-renewable source and millions of years for its formation from plant and animal remains. The initial materials should be renewable, obtained from biological or agricultural products such as: methane gas or carbon dioxide.

A renewable source (CO2 & methane) is available in abundance which can reduce the negative effect of non-renewable sources. Petrochemicals (non-renewable sources) are mostly used in chemical synthesis which are hazardous & toxic in nature. ¹¹

8. Appropriate protecting groups in use:

In organic synthesis, to obtain the desired product from two or more reactive one functional groups, one group should be masked by protecting groups (PG) and then deprotection is carried out safely and these protecting groups are not incorporated in to final products.

To perform green synthesis, atom economy is of great concern and by selecting protecting groups chemo selectivity problem are sorted out. With the 'protecting groups' introduction, molecular weight increases and boiling point too resulted to less atom-economical, but facilitates the drying process with ease. ¹²

9. Use catalyst instead of stoichiometric reagents:

The use of catalyst has a great advantage, catalyst speeds up reaction and increases the reaction rate and reduces reaction time & transformation of reactants into products instantly, without being consumed itself.

Some advantages by using catalyst are:

1. Better yield:

Reduction or halogenation of olefins in nickel(catalyst) presence

2. Selectivity enhancement:

Selectivity C-methylation over O-methylation

3. Make reaction possible when reaction is not feasible in normal conditions.¹³

10. Design the product of biodegradable type:

In chemical synthesis, reaction must be harmless to environment. Design the chemical compound as biodegradable type which breakdown into innocuous degraded products.

Such as use of diacylhydiazines (Rohm and Hass company developed) in pesticides (insecticides) is in working processes or conditions.

11. Minimize the accidents in manufacturing plant:

During chemical synthesis, use the chemicals which are safe and by its use, occurrence of accidents reduced throughout operation and must be ecofriendly. Hazardous effects as explosions, fire, mis happenings, toxic fumes and associated disease occurrence should be reduced.

12. Strengthening of analyzed techniques:

Design the analytical techniques by minimum use of chemicals & recycle the unreacted reagents upon completion of reaction. To monitor, unreacted or byproducts (hazardous) generation, accurate sensors placement is also advantageous in order to monitor hazardous products monitoring. ¹⁴

Designing a Chemical Synthesis

In any synthesis, targeted molecules are reacted with chemicals for attaining of desired final products. Sometimes by modifying the conditions, same products can also be obtained. Following point to be taken in consideration to eliminate products formation & non-toxic starting material.

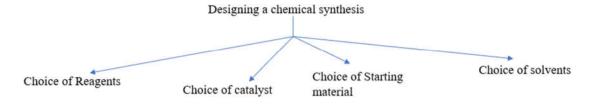


Figure 2: Points for designing of green laboratory 15

1. Reagents selection (Choice of reagents):

Reagents availability, efficiency & impact on environment's impact are the basic criteria for the selection in production, selection of appropriate reagent is beneficial for chemists and environment. The selection of appropriate reagent can directly affect byproducts nature, & percentage yield etc.

2. Choice of Catalyst:

On the addition of catalyst, the higher reaction rate, faster the reaction and lower temperature range is to be noted. Heavy metal catalysts are toxic in nature & cause environmental problems so it should be avoided in use for all reactions. In chemical transformation, visible light use must be explored. Alternative approach to synthetic catalyst, biocatalyst (Enzymes) will be beneficial and improves the yield, regiospecificity, stereospecificity.

e.g.

By Gibberella fujikuroi oxidation of oesterone gives 75% yield of 15α -hydroxyoesterone. ¹⁶

Figure 3: Conversion of oesterone to 15α-hydroxyoesterone.¹⁶

The conversion of 11α -hydroxyprogesterone into progesterone in the presence of several microorganism as *Aspergillus ochraceus* and *Rhizopus nigrioans*. This is method of

manufacturing the 11α -hydroxyprogesterone as a raw material on commercial scale and having a medicinal importance as a steroid.¹⁷

Figure 4: Conversion of 11α-hydroxyprogesterone into progesterone¹⁷

Now-days, Biocatalysis is in use by fermentation industries and chemically used in order to exhibits the regioselectivity, chemiselectivity, stereoselectivity.

3. Starting Material Choice:

In chemical synthesis, synthetic pathway will depend on appropriate starting material and is the backbone of chemical synthesis to attain maximum yield. Otherwise, workers will face the hazardous effects of chemicals during handling & transportation in addition to less yield.¹⁸ Yet, most synthesis used petrochemicals (non-renewable) so starting material must be from agriculture/biological origin as:

Corn, molasses, potatoes, soya (Agricultural products) Xylene, resorcinol, glucose, furfural, furan (biological origin)

4. Choice of Solvents:

Mostly solvents such as benzene cause cancer, aromatic hydrocarbons cause brain damage, halogenated solvents are carcinogenic in nature & CFC (Chlorofluorocarbon) depletes the ozone layer. Green solvent is the one of the best alternatives to eliminate these hazardous effects. In green synthesis, best alternative are solventless reactions, use of supercritical CO₂, reactions proceed in aqueous conditions or renewable solvents. Additionally, for proper mixing reactions can be performed in molten state. ¹⁹

Applications of Green Chemistry:

1. Green Chemistry in Pharmaceutical Industry:

Now-a-days, pharmaceutical industries use the green chemistry approach on practical purposes and makes a revolutionary change in terms of production of drugs. BASF (chemical company) synthesizes an Ibuprofen (pain killer) in just one step instead of 6 steps carried out in conventional method. Another, Simvastatin (Zocor), cholesterol lowering drug now applies green approach in synthesis by considering the hazardous effects of chemicals. Codexis (biocatalyst company), carried out development in technique for drug synthesis by using enzyme & low-cost feed stock.

Paclitaxel (Chemotherapeutic drug) obtained from tree yew's bark. Now, drug is formulated by budding the tree cells in a fermentation vat. ²⁰

2. Eco Friendly Clothes Dry Cleaning:

Traditionally, PERC (Per chloroethylene) used in dry cleaning & pollutes the water as well as cancer causing agent. To overcome the toxic effects, super critical CO₂ (a) and surfactants are used for cleaning the garments (Joseph De Simons, Timothy Romack & James developed). To replace the halogenated solvents, micelle technology developed a metal cleaning framework by utilization of CO₂ & surfactants. ²¹

3. For Cleaning the Water (Municipal/Industrial) Waster):

By conventional methods, for cleaning the turbid water, alum was used but it intensifies poisonous ions in treated liquid (water) & was the reason for occurrence of Alzheimer's disease. Now municipal/industrial uses tamarind seeds, kernel powder (not poisonous perishable & cheap) for purification of wastewater purified & reused again.

4. Energy as a science:

Normally, the gentle source of power is organic solar cells due to its low cost & ecofriendly nature. With the advance of organic solar cells (OSC), conjugated molecules & polymers are synthesized. Now scientist prefers the method for polymerization in lesser steps & by bio feed stock in use.

5. Design a Catalyst for Next Generation:

Lot of efforts was put off for improving the industrial processes. Now-a-days, to develop a Nylon 6,6 precursor-o-caprolactam carried out in open step, solvent free & eliminates the use of hazardous reagents. Within synthesis, catalyst nonporous alumina

phosphate used with the distribution of active site of acidic & redox charge distribution. This reaction reduces the generation of waste/by products. ^{22,23}

6. In Nano Science:

Nanomaterial's exhibits intense applications in all disciplines. Due to multipurpose technical applications, researchers are curious to develop a low dimensional material in addition to environmental aspects.

Nano filtration techniques are developed & used for the purification of wastewater & air. Green chemical synthesis reduces agent selection, size distribution & solvent choice, avoiding surfactants which are used as new generation techniques/materials. Such as Ag nanoparticles synthesis is carried out by sucrose ester micelle mediated method & to accelerate the formation/development of Ag nanoparticles, NaOH is added. Another CMC derivatives plays dual role as reducing agent (for Ag ions) & stabilizing agents (in silver nanoparticles formation). Furthermore, for the generation of cube octahedral magnetite iron oxide nanoparticles, plant fungus, verticillium species was involved with 24hr is of 100-400nm size. 24,25,26.

Green Chemistry's benefits:

For human health:

- 1. Cleaner and purified air: By using greener chemicals, the release of less hazardous chemicals into air, resulted to fewer damaging effects on lungs.
- 2. Cleaner and purified water: Less hazardous chemicals affect minutely to water, and increase the quantity of water for drinking and recreational purposes.
- 3. Increased worker's safety in industrial sector: By using less toxic material, non-flammable chemicals ultimately provide a safe environment for workers and no need of protective clothing and equipment's during and after completion, that increases the overall production cost.
- 4. Safer Products: Novel and safer products made by valorization of waste and make byproducts free generation, will be in favor of purchasers and industries too in terms of economy.

Environment:

1. Minimizes the possibility of ozone depletion, global warming, and smog formation.

- 2. Fewer chemical interactions to the environment or ecosystem.
- 3. Mini usage of landfills, especially lethal waste landfills
- 4. Green chemicals are recyclable and degraded into innocuous products. As in pesticides (diacylhydrazines, halofenozide, methoxyfenozide), otherwise unintentional release or by disposal many chemicals affect environment directly.

Economy and business:

- Increases the yield of chemical reactions and consuming little feedstock in amount to obtain quantity of product.
- By reducing the synthetic steps, product manufacturing will be faster, resulted to increasing plant capacity, and saving water and energy.
- Switch to safer chemicals from petroleum products, in order to slow down ozone depletion and preventing their hazardous effects and other price variations.
- Reduction in size of manufacturing plant or footprint via increased throughput
- Increases the competition among chemical manufacturers and their customers.²⁷

Recent trends in Green Chemistry:

- ✓ Novel research developments in Degradable and Recycled Polymers
- ✓ Targeted Evolution- Biocatalysis, Green chemistry
- ✓ Development of polymers from carbon Dioxide
- ✓ Green Chemistry and Oil-Based Paints
- ✓ Energy sources developments.
- ✓ Planning and Designing of Electrochemical Storage Systems. ²⁸

Current Research in Green and Sustainable Chemistry

✓ Biodegradable Plastics:

✓ Biodegradable plastics having a benefit as compared to standard plastics as proper waste management(composting), reduced carbon dioxide impacts on environment.

✓ Optimization of Lactic Acid Production:

✓ For poly-lactic acid, lactic acid is the starting material and the use of lactic acid from agro-industrial waste due to low- cost, renewable substrate in addition to control the environmental pollution is the primary goal of researchers. By using 16S rRNA, lactic acid yield increases as discovered.²⁹

Future trends of green chemistry in research:

As per the Nobel Laureate Professor Ryoji Noyori "Green Chemistry is not just a mere catch phrase; it is the key to the survival of mankind."³⁰ Primarily, the dependency of chemical reaction in the synthesis, the search for discovering the new solvent mixture (Supercritical CO₂) and appropriate solvent whether from hidden treasure of chemistry and alternative approaches for the forthcoming future of the green chemistry.^{31, 32}

Additionally, recently great attention has been drawn by supramolecular aspects of micellar aggregation within the field of green synthesis. In all types of chemical transformations, the contribution of catalyst, surfactants are mandatory for transformation of reactants in to products. To increase the outcome of reaction, sophisticate optimization of chemicals, concentration and molar ration of surfactants is required. Recently, unique amalgamation of substrate, catalyst and surfactant resulted to molecular tablet by adding novel surfactants and its photoactive microencapsulation that shows remarkable applications in catalysis and drug delivery system.³³

Another widely advancement in the research is the discovery of suitable reversible biosurfactants, to upgrade biocatalysis and for mimic the green metabolic reactions in saturated medium within living organisms.^{34,35,36}

Conclusion:

Green chemistry, also sustainable chemistry, and used in the production of biodegradable plastic and optimization of production to increase the yield and polymerization. Now-adays, it is emerging as a hope for the researchers, and alternative approach against conventional methods, which cause global warming and ozone depletion. The 12 principles of green chemistry are applicable theoretical, as well as practical concern.

Human participants and/or animals required in research:

No human or animal was involved in this study.

Informed consent

There was no human participant and consent was not required.

Funding

None

Data availability statement

The supporting data if needed, must be provided on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors request to thank Department of Pharmaceutical Sciences and Drug Research, Punjabi University Patiala.

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