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Review Paper

Green Chemistry in Pharmaceutical Industry

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ABSTRACT

Sustainability means being able to support a process for a long time without hurting the needs of future generations. Sustainable chemistry is about making chemical products and processes that use less or no harmful materials. Even though sustainable and green technologies have developed in other areas of science, they are still in the early stages when it comes to the pharmaceutical industry. Because of this, it's important to work on green chemistry to help it grow in the pharmaceutical field. That's why this review looks at the importance of green or sustainable chemistry, its main ideas, and how it can be used in the pharmaceutical industry to create products that are better for the environment and to cut down or stop making harmful by-products during drug production.

INTRODUCTION

Green chemistry is also called sustainable chemistry, clean chemistry, or benign chemistry. The pharmaceutical industry and other sectors are growing quickly, which is helping the medicine and healthcare fields progress in a positive way. This has led to fewer deaths and less suffering. But if development is causing environmental damage, what's the point? During chemical production, various steps in the synthesis process create many pollutants, intermediates, and waste. These unwanted waste materials are released into the environment without being properly treated.[1] This has increased pollution levels and caused environmental damage. Because of this, people are becoming more aware and are moving towards green chemistry to protect the environment.[1]

2. BRIEF HISTORY:

In the 1960s, a book called 'Silent Spring' was published, which made a lot of people pay attention. This scientific book brought awareness about how the environment works and showed the dangers of using too much of natural resources. It explained how certain chemicals were harming the ecosystem.[4]

In 1970, the Environmental Protection Agency (EPA) was created. Then, in 1972, a conference called the Stockholm Conference was held in

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Sweden. Many countries and members of the United Nations took part in it. During this meeting, they talked about the damage being done to the environment and the ecosystem, and they warned everyone about these problems.[4]

Up until the 1980s, the chemical industry and the EPA were mostly focused on pollution and harmful chemicals.

But things started to change. Scientists and chemists began to spread awareness about the environment and looked for ways to stop pollution.

The Organization for Economic Co-operation and Development (OECD), which includes about 30 developed countries, had meetings where they made suggestions.

These suggestions were about changing the way chemicals were made and how to prevent pollution.[4]

In 1999, Paul Anastas wrote a paper that talked about the importance of green chemistry. He proposed 12 basic principles for green chemistry.[1]

3. STUDY METHODOLOGY:

3.1Aim of the review:

The review focused on showing the 12 key ideas of green chemistry and how they are applied in the pharmaceutical industry.

3.2 Objective of the review:

To learn about and talk in detail about why using green methods is important in the industry.

3.3 Material and Method:

3.3.1 Search strategy:

To carry out this review we searched out the articles from various databases which includes PubMed and scopus. All the papers that discussed about green synthesis were screened. Furthermore, the keywords included: green synthesis, green chemistry, principles of green chemistry, green synthesis in pharmaceuticals industry, application of green chemistry.

3.3.2 Study Selection Criteria:

Inclusion criteria: A publication that describes green chemistry, along with its history and various applications, was included in the review**.**

Exclusion criteria: Publications were not considered for the review if they did not meet the inclusion criteria.

4. DISCUSSION OF REVIEW TWELVE:

principles of green chemistry:

Green chemistry is a part of chemistry where we create chemical products in a way that doesn't hurt the environment. Paul Anastas and John Warner came up with the 12 main ideas, or principles, of green chemistry. These principles help reduce or eliminate harmful substances that are made during the making of chemicals and products..[6]

I. Prevention:

The first principle of green chemistry focuses on prevention, which means it's better to stop waste from being created in the first place rather than dealing with it after it has already been made. This idea is rooted in the belief that preventing waste is more effective and less harmful than trying to clean it up or dispose of it later.Synthetic methods should be designed to make sure that all the materials used in the process end upin the final product.

Atom economy is a way to measure how much of the starting material ends up in the final product after a chemical reaction or synthesis.

It was developed by Berry Trost from Stanford University in 1991. Any intermediates formed during the reaction that are not used in the final product reduce atom economy and create more waste. Atom economy is seen as a better way to measure efficiency compared to just looking at the percentage yield of the reaction.

Therefore, chemical synthesis should be carried out in a way that leads to the highest possible amount of the final product

The measurement of waste can be described as follows:.

$$\text{Environmental factor (E)} = \frac{\text{kg waste}}{\text{kg product}}$$

The E factor was introduced by Roger Sheldon. It is calculated by dividing the weight of the waste generated by the weight of the product made during the synthesis process.

$$\text{PMI(Process mass intensity)} = \frac{\text{quality of raw material input (kg)}}{\text{quality of bulk API product out (kg)}}$$

PMI is the standard used by the ACS Green Chemistry Institute Pharmaceutical Roundtable (ACS GCIPR), which is the ratio of the amount of raw material used to the amount of bulk active pharmaceutical ingredient produced during the manufacturing process[1].

II. Atom economy :

Synthetic methods should be designed to ensure that all the materials used in the process end up in the final product.

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Therefore, chemical synthesis should be carried out in a way that leads to the highest possible amount of the final product.[1]

III. Less hazardous chemical synthesis :

Wherever possible, synthetic methods should be created to use and produce substances that are either non-toxic or have very low toxicity towards human health and the environment.[1] Most chemical synthesis reactions, which often involve multiple steps, rely on harmful reagents. Even if the final product does not contain these toxic materials, there is still a risk of contamination during the process. Redesigning these procedures is a key aspect of green chemistry.[1] Therefore, this principle focuses on developing a synthesis process that generates the least amount of toxic byproducts. The main goal is to avoid using hazardous chemicals as starting materials whenever safer alternatives are available.[1]

IV. Designing safer:

Chemical products should be made to do their job well while making them as safe as possible. When creating chemicals, it's important to understand their structure. A big challenge is making sure the chemical still works properly and stays effective, while keeping it less harmful. In simple terms, we

should try to avoid using dangerous or harmful chemicals whenever we can, but we also need to make sure they still work the way they're supposed to. This idea is used when making new chemicals to ensure they are safe without losing their useful qualities.[1]

V. Safer solvents and auxiliaries:

The use of extra chemicals like solvents or separation agents should be avoided whenever possible and should be safe when they are needed.

Most chemical reactions use solvents or other reagents to help the reaction happen.

These solvents or helpers can sometimes be harmful or dangerous. Using solvents is often necessary and can't always be avoided, but they should be chosen carefully. They should help reduce the heat needed during the reaction and have as little harmful effect as possible.[1]

VI. Design for energy efficiency:

Energy needs should be considered because they affect both the environment and costs, and these should be kept as low as possible. Chemical reactions should happen at normal temperature and pressure.

This idea means that the reaction should be designed so that it uses as little energy as possible during the process.

We can use less energy during the making of a substance by doing the reaction at lower temperatures and pressures.[1]

VII. Use of renewable feedstock:

A raw material or feedstock should be renewable instead of depleting whenever it is both technically and economically possible.[1]

VIII. Reduce derivatives:

Unwanted derivatization should be reduced or removed whenever possible because these steps need extra chemicals and can create waste.

One important idea in green chemistry is to make the desired product without using chemical derivatives.

Using derivatives should be kept to a minimum since they lead to unnecessary waste.[1]

IX. Catalysis :

“Catalytic reagents (as selective as possible) are superior to stoichiometric reagents”.

This principle promotes the utility of biodegradable catalysts, which consumes less energy and protects the environment. A reaction with high atom economy can be produced using catalyst. The catalyst can be reused many times as it is not used up in the reaction and do not produce waste.[1]

X. Design for degradation :

Unwanted derivatization should be minimized or eliminated whenever possible because these steps require additional chemicals and can result in waste.

A key principle of green chemistry is to produce the desired product without the use of chemical derivatives. The use of derivatives should be kept to a minimum since they often lead to unnecessary waste.

Catalytic reagents that are as selective as possible are better than those used in large amounts. This idea helps in using biodegradable catalysts, which require less energy and are better for the environment. Using a catalyst can help reactions

use most of the atoms efficiently. The catalyst does not get used up in the reaction, so it can be used again and again, and it does not create waste.

"Chemical products should be designed so that at the end of their function they break down into harmless degradation products and do not remain in nature."

This principle suggests that chemical products should be made in a way that once they are used, they break down into parts that do not cause any harm in the environment.[1]

XI. Real time pollution prevention :

Analytical methods need to improve so that we can check and manage chemical processes as they happen. This would help stop harmful substances from forming. Monitoring reactions as they take place can stop dangerous by-products from being released and stop harmful reactions before they cause serious problems.[1]

XII. Safer chemistry for accident prevention :

When selecting substances and their form for a chemical synthesis, it's important to choose materials that lower the chance of chemical accidents, such as leaks, explosions, and fires. Risk is always present when working with chemicals, and this principle emphasizes the need for careful handling to prevent avoidable incidents. By following proper procedures during chemical reactions, accidents can be minimized.[1]

Green chemistry in industry

1. Nanoparticles: Nanoparticles are tiny particles that are between 1 nanometer and 100 nanometers in size. Because they are so small, they have a large surface area, which gives them special properties. However, the usual way to make nanoparticles uses harmful chemicals that are bad for the environment. One problem with the old method is that the solution used to make the nanoparticles can get dirty because of the extra chemicals made during the process. To fix this, scientists started using a greener method for making nanoparticles. These green nanoparticles are better for the environment, cheaper, and can be made in big amounts.[5] This method follows some key ideas from green chemistry, like avoiding waste, using less harmful materials, making safer chemicals, and stopping pollution before it happens. In the field of medicine, nanotechnology is still being developed.[6] In the past, scientists used physical and chemical methods to make nanoparticles. But as the need for nanoparticles has grown, so has the demand for making them on a larger scale. This led to the development of commercial methods for making metal nanoparticles. However, these methods often use harmful solvents or require a lot of energy, which has raised concerns about the need for cleaner, safer, and more eco-friendly ways to make nanoparticles.[7] Green synthesized nanoparticles are safer for living things than ones made with chemicals. There are three main benefits to using green nanoparticles:[8]

a) They are good for the environment.[8]
b) They are not harmful.[8]
c) They are inexpensive.[8]

Many types of tiny living things, like yeast, fungi, bacteria, and plants, can be used to make green nanoparticles.[9]

Table 1: Examples of microorganisms which are used for green synthesis of nanoparticles

Source	Examples
Yeast	*Rhodosporidium diobovatum* [10], *Saccharomyces boullardii* [11], *etc.*
Fungi	*Aspergillus fumigatus, Aspergillus clavatus,12 etc.*
Bacteria	*Serratia sp13*
Plant	*Melia azedarach14, Tridax procumbens5, etc.*

2. Green solvents:

Green solvents are used in place of traditional solvents. In their 12 Principles of Green Chemistry, Anastas and Warner suggested using "safer solvents and auxiliaries."[15] Many chemical processes use flammable organic solvents, but these conventional solvents can be harmful and bad for the environment. Because of this, green solvents are now being used more in different industries.[16]

There are many good types of solvents.

Choosing the right solvent for a specific reaction is very important for making the reaction work well. When choosing a solvent for a reaction, you should think about these things:

- Whether the solvent works well with the chemicals and products involved.
- If the solvent can dissolve the chemicals.
- The temperature needed for the process.[17]

3. Water as solvent:

Because there is a growing need for more sustainable methods in chemical processes, there is increasing attention on using water as a solvent. Water is a great choice in green chemistry because it helps reduce the amount of harmful chemicals that are released into the environment. When water is used as a solvent, chemical reactions usually take place under gentle conditions, which allows the catalysts to be reused. This helps lower the overall cost of the products .[18]

4. Ionic liquids:

In the area of green solvents, we could talk about ionic liquids (ILs) that, at least for a while, are seen as both designer and green solvents. This is mainly because they have very low vapor pressure and don't contribute to the problems caused by volatile organic compounds.[19]

5. Glycerol:

Green technology involves the production of biodiesel and bioethanol. During the process of making biodiesel, a large amount of byproduct is created and often discarded, which is called "glycerol." This glycerol has a lot of potential for use in various industries such as pharmaceuticals, food, and even explosives. [20]

6. Antimicrobial bandages:

Bandage is a type of material used to cover wounds or injured parts of the body. It helps support the wound and the surrounding tissues. This method follows the first and twelfth principles of green chemistry.[5]

Nanoparticles are made through a process called green synthesis, and these are then added to bandages to help with wound healing.

For example, silver nanoparticles were made using the weed plant Tridax procumbens and added to a bandage. These nanoparticles showed the ability to kill both gram-positive and gram-negative bacteria.[5]

A quick, eco-friendly, and affordable way to make silver (Ag) and zinc oxide (ZnO) nanoparticles was developed using Prosophis fracta and other plants.

The lowest amount of these nanoparticles needed to stop bacterial growth (called minimum inhibitory concentration or MIC) was tested against bacteria like Acinetobacter baumannii and Pseudomonas aeruginosa.

Cotton bandages were treated with silver and ZnO nanoparticles, as well as a mix of both (Ag/ZnO), using amounts based on the MIC values.

The antimicrobial activity of these treated bandages was tested in a lab setting. Each type of nanoparticle showed strong antibacterial effects.[21]

7. Green synthesis of drugs

Green processes are created to make drugs in a way that stops harmful and toxic byproducts from entering the environment. Most of the main ideas from green chemistry are used for this purpose. These include preventing waste, using materials efficiently, using chemicals that are less dangerous, using safer solvents, and using catalysts.[2]

CASE STUDY

Sertraline:

Sertraline is a type of antidepressant medication. It was first introduced by Pfizer in 1991. The drug works by blocking the reabsorption of serotonin in the brain. In the older method of making sertraline, a process called Friedel craft acylation was used. This process required a lot of aluminium chloride and used carbon disulphide, which is a toxic solvent. For another step in the process, called condensation, titanium tetrachloride was used, which led to the creation of titanium waste. Tetrahydrofuran was also used as a solvent in this process. In a more environmentally friendly method, ethanol was used instead of tetrahydrofuran, which helped create a higher amount of imine, over 95%. Also, titanium tetrachloride is no longer used in this new method, so no titanium waste is produced anymore.[2]

Talampanel:

Talampanel, also referred to as LY300164, is a medication used to treat various neurological conditions including Alzheimer's disease, Parkinson's disease, and epilepsy, among others. It works by interacting with the AMPA receptor, which is involved in nerve signal transmission.

The original method for making Talampanel required eight chemical steps and produced a yield of approximately 8%.

This method involved the use of certain chemicals like hydrazine, borane, chromium trioxide, and perchloric acid. However, these chemicals were not environmentally friendly.

One of the main issues was the use of hydrazine, which caused contamination of the final product.

Another concern was chromium trioxide, which led to a significant amount of chromium waste during the production process.

Because of these problems, a new, more eco-friendly method was developed.

In the improved process, chromium is substituted with air, and hydrazine is replaced with a less harmful compound called acetyl hydrazine. Additionally, perchloric acid, which is harmful to the environment, is no longer used. The new green synthesis method achieves a much higher yield.[2]

Sildenafil citrate:

Sildenafil is a type of drug called a phosphodiesterase inhibitor. It works by stopping the phosphodiesterase enzyme from doing its job. This drug was made by Pfizer and is mainly used to treat erectile dysfunction or impotence in men.

In the old way of making Sildenafil citrate, the amount of product made was only about 4.2%, which wasn't good enough for big production.

During the process, a step called chloro-sulfonation used too much chorosulfonic acid, which created harmful waste. Also, the whole process had eleven steps, so making it shorter was needed.

The new green method uses t-butanol and its potassium base as the main chemicals. In this method, the chloro-sulfonation step happens earlier, and the cyclization happens later. This helps clean up the product during the steps after sulfonation, removing toxic by-products. The last step is done at a high concentration, which reduces the use of solvents and lowers waste. This change also makes the final product yield about 97%, which is much better on average.[2]

Quinapril:

Quinapril is a type of medicine used to lower blood pressure and treat congestive heart failure. It works by blocking an enzyme called angiotensin-converting enzyme. In the original way of making quinapril, harmful solvents like methyl chloride, hydroxy benzotriazole, dicyclohexylcarbodiimide, and a lot of toluene were used during the chemical process.

These solvents are not safe and can be dangerous. During the making of quinapril, a reaction called intermolecular cyclization happens, which creates a harmful byproduct called diketopiperazine.To make the process safer, a new method was developed.Instead of using acetic acid, which leads to diketopiperazine, they used a different chemical called N-carboxy solvents or extra chemicals like dicyclohexylcarbodiimide and its byproduct, dicyclohexylurea.[2]

OUTLOOK :

The above article warns of increasing costs and safety concerns in fine chemicals and pharmaceuticals, indicating a shift toward biocatalytic methods, likely to incurs tertiary utilization of environmental opportunities. The petrochemical industry is still, although slowly, moving toward the use of heterogeneous catalysis to supplant their existing synthetic methods in batch CSTR usage of green processes facilitation of standardized, economical processes. The E-factor tales the industry, traditionally with E = 0.1, tales the industry, traditionally with E = 0.1, stands against the sophisticated synthetic pathways Manual, thus marking the trend of the industry tales the industry, traditionally with E = 0.1,[21] stands against the sophisticated synthetic pathways Manual, likely to incurs tertiary utilization of environmental opportunities. The use of industrial implements like intensified, energy-efficient processes may solve the present dilemma in transition from batch to continous methodologies with improved utilization of mass, energy, and selective facilitation of standardized, economical processes.

Novel approach.

Costs are rising and sustainability challenges are mounting in the fine chemical and pharmaceutical industries.

To address these challenges, the sector is increasingly investing in enzymatic processes, and more slowly, in heterogeneous catalysis to replace traditional batch-based and continuous processes.[23] A strategic shift toward enzymatic processes is currently under way, as these offer economical, sustainable options. Environment tales the industry, traditionally with E = 0.1, stands against the sophisticated synthetic pathways Manual, likely to incurs tertiary utilization of environmental opportunities. The use of industrial implements like intensified, energy-efficient processes may solve the present dilemma in transition from batch to continous methodologies

with improved utilization of mass, energy, and selective syntheses. This evolution implies that a possible pathway would be to your consideration.

The above-pack Manual, likely to incurs tertiary utilization of environmental opportunities, may tales the industry, traditionally with E = 0.1, stands against the sophisticated synthetic pathways Manual, likely to incurs tertiary utilization of environmental opportunities.

CONCLUSION:

Green chemistry is a part of chemistry that focuses on being sustainable, which is why it's also called sustainable chemistry. Sustainability in green chemistry is achieved by either using natural chemicals in the making of products or by using chemical processes that don't harm the environment much. The significance of green chemistry and how it's used in industries has been looked at.

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