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Introductory Chapter: Principles of Green Chemistry

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1. Introduction

New chemistry is required to improve the economics of chemical manufacturing and to enhance the environmental protection. The green chemistry concept presents an attractive technology to chemists, researchers, and industrialists for innovative chemistry research and applications.

Primarily, green chemistry is characterized as reduction of the environmental damage accompanied by the production of materials and respective minimization and proper disposal of wastes generated during different chemical processes. According to another definition, green chemistry is a new technique devoted to the synthesis, processing, and application of chemical materials in such manner as to minimize hazards to humankind and the environment.

Numerous new terms have been introduced associated with the concept of “green chemistry,” such as “eco-efficiency,” “sustainable chemistry,” “atom efficiency” or “atom economy,” “process intensification and integration,” “inherent safety,” “product life cycle analysis,” “ionic liquids,” “alternate feedstocks,” and “renewable energy sources.”

Hence, there is an essential need to improve the synthetic and engineering chemistry either by environmental friendly starting materials or by properly designing novel synthesis routes that reduce the use and generation of toxic substances by using modern energy sources.

2. Basic principles of green chemistry

Green chemistry is generally based on the 12 principles proposed by Anastas and Warner [1]. Nowadays, these 12 principles of green chemistry are considered the fundamentals to contribute to sustainable development. The principles comprise instructions to implement new chemical products, new synthesis, and new processes as illustrated in **Table 1**.

1	The “better to prevent than to cure” principle It is beneficial to a priori prevent the generation of waste instead of later on treating and cleaning up waste
2	The “atom economy” principle Synthetic production routes have to be planned in a way maximizing the incorporation of all the compounds used in the synthesis into the desired product
3	The “less precarious chemical syntheses” principle Wherever feasible, such synthetic methods have to be aspired, which resort to and generate compounds of no or only insignificant noxiousness to the environment and human health
4	The “designing safer chemicals” principle Chemicals should be developed in a way affecting their desired functionality, while, at the same time, considerably reducing their toxicity
5	The “safer solvents and safer auxiliaries” principle Expenditure of auxiliary substances, such as solvents, separation agents, and others, should be avoided wherever possible; if not possible, harmless auxiliaries should be used
6	The “design for energy efficiency” principle The environmental and economic impact of energy demands for chemical processes should be analyzed in terms of followed by optimizing the required energy input. Wherever practicable, chemical synthesis should be carried out under mild process conditions, hence, at ambient temperature and pressure
7	The “renewable feedstocks” principle Whenever feasible in technological and economic terms, synthetic processes should resort to such raw materials and feedstocks, which are renewable rather than limited
8	The “derivative reduction” principle Redundant derivatization, e.g., protection/deprotection, the use of blocking groups, or temporary modification of physical/chemical processes, requires additional reagents and often contributes to additional waste generation. Therefore, wherever possible, they should be avoided or reduced to a minimum
9	The “catalysis” principle Generally, catalytic reagents are intrinsically superior to stoichiometric reagents; these catalysts should be as selective as possible
10	The “degradation” principle Chemical products have to be designed in such a way that, at the end of their life span, they do not resist in the biosphere, but disintegrate into nontoxic degradation products
11	The “real-time analysis for pollution prevention” principle Advanced analytical methods have to be developed, which permit the real-time, in-line process monitoring and control well before hazardous substances are generated
12	The “accident prevention by inherently safer chemistry” principle Compounds and the compound’s formula applied in a chemical process should be chosen in a way minimizing the risk of chemical accidents, encompassing the release of chemicals, detonations, or fire formation

Table 1. The 12 principles of green chemistry proposed by Anastas and Warner (based on [1]).

2.1. It is better to prevent waste than to treat or clean up waste after its formation

This statement is one of the most popular guidelines in process optimization; it describes the ability of chemists to redesign chemical transformations in order to minimize the generation of hazardous waste as an important step toward pollution prevention. By preventing waste generation, the hazards associated with waste storage, transportation, and treatment could be minimized.

This principle is easy to understand and easy to apply, and examples from both industry and academia have proven its significance, relevance, and feasibility. This pillar of green chemistry is still valid; however, we have to conceive it in a broader context, switching from a restricted interpretation of waste based on its quantity to a universal approach to deal with the topic “waste”: (1) We have to take waste’s multidimensional nature into account. (2) We need to move from a “quantity of waste per quantity of product” principle toward a principle addressing the “quantity of waste generated per function provided by the product.” In this context, we have to aim at making both quality and functionality of products superior. (3) Considering the entire life cycle of a product, we have to address the fact that not only the production process itself generates waste but, moreover, “end-of-life waste” accrues after the product’s life span or its consumption. This encompasses firstly the conversion of such materials up to now considered as waste into valuable products and, secondly, their recyclability.

Generally, moving toward “zero-waste production” and “waste prevention” encompasses the modernization of industrial processes through clean production techniques. These techniques aim at the reduction of gaseous emissions, effluents, solid residues, and noise generation; generally, they are developed to contribute to the protection of climate and environment [2]. However, the most auspicious strategy to prevent waste generation would simply be not producing the desired product. In most scenarios, this will not be practicable; however, it might be reasonable to instead produce completely novel products, which display higher quality and longer durability. Lower quantities of such novel, superior products are sufficient to fulfill a desired function. An alternative approach is to avoid that the product can be transformed into precarious waste, e.g., by making plastics accessible toward biodegradation or by a priori switching toward biodegradable plastic instead of highly recalcitrant petrochemical plastics. According to these ideas, we need to fundamentally reconsider our understanding of waste as hazardous material that needs to be disposed by enhancing the status of waste to a valued resource, which can act as starting material for generation of new products [3].

2.2. Maximize atom economy

Atom economy is a concept developed in the early 1990s to evaluate the efficacy of chemical conversions on an element-by-element basis [4]. In analogy to well-established yield calculations, the concept of “atom economy” is based on the ratio of the entire mass of atoms in the target product to the entire mass of atoms in the starting materials. One option to reduce waste generation is to plan such chemical transformations, which maximize the integration of all materials used in the process into the final product, resulting in a number of wasted atoms as low as possible. Hence, selecting such chemical conversion routes, which incorporate the major share of starting materials into desired products, displays higher efficiency and contributes to waste reduction. This concept is nowadays widely implemented in new routes to generate various organic compounds, e.g., such substances that are used in the biomedical and pharmaceutical field [5–7].

One factor that is greatly speeding the incorporation of pollution prevention into industrial manufacturing processes is the development of green chemistry. According to an alternative

definition, chemical synthesis methods should be designed in such a way to maximize the incorporation of different potentially hazardous materials, such as spinning precarious waste with cement and sand to produce improved paste used in construction applications [8–9] or to incorporate radioactive wastes as immobilizing material to produce a safe stabilized form of waste [10, 11]. In a similar vein, combining recycled poly(ethylene terephthalate) (PET) waste with cement paste displays a viable strategy for immobilization of hazardous wastes, e.g., radioactive borates [12, 13].

2.3. Design less hazardous chemical synthesis

In synthetic organic chemistry, effecting a successful chemical transformation in a new way or with a new molecule or in a new order is what matters regarding the principles of green chemistry. Various researchers have clearly demonstrated the direct relation of toxicity and the associated hazards and risks allied with chemical reactions to the matrix of matter present in the reaction vessel. Generally, the holistic toxicity spectrum of products or processes, together with most other sustainability and green chemistry criteria, is highly impacted by the chemistry behind a process and the transformation contributing to a chemical synthesis chain. An exception is identified in such cases where a molecule is produced by purpose, which is designed to display toxicity and/or biologically activity. For example, this scenario is found in the case of various molecules synthesized for pharmaceutical or agricultural applications; such compounds exhibit toxicity and/or impact living organisms.

Selection of compounds and materials to be used to increase the efficacy of chemical transformations is a pivotal point in process development; chemists should dedicate increased attention to the decision on which materials to be put into reaction vessels. It is simple to disregard all the other materials and to dedicate all efforts exclusively to the chemosynthetic pathway, which provides us with the desired product. However, discounting all the other matter present in a production process ultimately results in a high price to be paid, and we finally have to get rid of this scenario. Sometimes, chemists actually produce hazardous molecules, and, therefore, the subsequent principle is dedicated to the design of molecules which are intrinsically safer in their nature [14].

2.4. Design safer chemicals and products

Chemical products should be designed to achieve their desired function with at the same time minimizing their toxicity. New products can be designed that are inherently safer, while highly effective for the target application. For example, the direct incorporation of radioactive spent liquid scintillation waste into cement combined with clay materials is considered an added value in the immobilization of the hazardous organic wastes in very cheap materials and natural clay to produce a safe stabilized product easy for handling, transformation, and disposal [15, 16].

2.5. Safer solvents and auxiliaries

This principle promotes the use of safer solvents and auxiliaries. It is about any substances that do not directly contribute to the structure of the reaction product but are still necessary for the

chemical reaction or process to occur. Mostly, reactions of organic compounds take place in liquid milieus, where the solvent acts in different ways: it can enable enhanced contact between the reactants, it can stabilize or destabilize generated intermediates, or it can influence transition states. In addition, the applied solvent also governs the selection of adequate downstream and regeneration processes and recycling or discarding techniques. By taking the ecological effect of chemical processes in consideration, innovative concepts for substitution of volatile organic solvents have become a great challenge in green chemistry. A green solvent should meet numerous criteria such as low toxicity, nonflammability, nonmutagenicity, nonvolatility, and widespread availability among others. Moreover, these green solvents have to be cheap and easy to handle and recycle [17, 18]. Prime examples are provided in the field of extractive recovery of microbial polyhydroxyalkanoate (PHA) biopolymers, typical intracellular storage materials, from biomass [19]. For this extraction process, which is typically carried out by the use of precarious halogenated solvents, one more and more resorts to less harmful greener solvents [20–22], or to new recovery methods which entirely do without any solvents [23].

2.6. Design for energy efficiency

Usually, energy is used to enhance the human life in important ways. The traditionally used energy sources like coal, oil, and gas are limited in supply, and their combustion releases greenhouse gases. For continuous improvement of life quality, both move toward renewable energy and design for energy efficiency are needed. Designing more efficient processes by choosing the most suitable technologies and unit operations has to go in parallel with selecting proper energy sources. Using an electric motor with energy sources generated from the sun and wind is more effective in ecological terms instead of using fossil fuels. How energy is converted to useful forms and where it gets lost are the most important questions for engineers and designers to help society use energy more effectively.

Consequently, green chemistry includes minimization of energy loss like mechanical friction, fluid drag, and unwanted heat transfer, by improving the layout and insulation of a refrigerator or designing lighter vehicles with enhanced aerodynamic characteristics and lower rolling resistance.

In addition, when developing a new production process, the effect of geographical location of production plants has to be taken into account: ecological comparison of different production scenarios for the same product, in this case bioplastics, clearly demonstrates that different energy production technologies, resources for energy production, and the effect of available energy mixes in different countries become significant for the ecological footprint of a new process [24].

2.7. Use of renewable feedstocks

According to the principles of green chemistry, a raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable. Using renewable resources like microbial or plant biomass, which are embedded into nature's closed carbon cycle, represents a real option to prepare functional bioproducts in a sustainable way and to contribute to energetic transition.

In the context of the Green Chemistry Principle #7, which addresses the renewable feedstock thematic, we nowadays witness a vast number of current multidisciplinary collaborations, involving the fields of, among others, agronomy, biochemical engineering, biotechnology, chemistry, microbiology, physics, toxicology, or engineering. These collaborations result in the development of next-generation fuels, polymers, and other materials pivotal for our today's society based on renewable resources and characterized by low impact on health and environment. The current global dynamic of these developments indeed gives reason to optimism for the future [25]. Finding a method to convert raw wastes such as spinney waste fibers into a mortar composite stabilized material could be an excellent application of this principal of green chemistry [8–11]. Whenever switching from fossil feedstocks to renewables, one has to consider that using renewable resources enlarges the process concept by incorporating resource provision, transportation, storage, and other aspects of logistics into the process design. Such a switch in feedstock provision, however, results in a fundamental change in the structure of processes, used technologies, and the economical concepts of industry and society [26].

2.8. Reduce derivatives

Many processes could be designed in such a way to reduce the use of additional reagents and the resulting wastes. It is commonly necessary to synthesize a derivative of a compound containing groups which are not needed in the final product, but which allow the synthesis or purification steps to proceed more easily. However, these derivatives result in lower atom economy, since they introduce atoms that are not incorporated into the final product, but finally end up as waste; this is in conflict with the atom efficiency principle according to **Table 1**. For many reactions that have traditionally required protecting groups, chemists are currently devoting research efforts to finding alternatives that do without them [27].

2.9. Catalysis

Catalysis is the chemical reaction enabled or accelerated by a catalyst. According to Ostwald, catalysts are substances that speed up a reaction by enabling an energetically favored transition state between reactants, but which are not consumed by it and do not appear in the net reaction equation [28]. Catalysts play an essential role in our modern industrial economy, in our stewardship of the environment, and in all biological processes. Saleh and others found that iron and copper sulfate as catalysts improved the mechanism of oxidative degradation of cellulosic wastes using 35% hydrogen peroxide. High weight reduction up to 95.2% in the presence of copper sulfate and 87.8% in the presence of ferrous sulfate was reported [8, 29, 30]. Recently, synthesis of nano-catalysts of specific size and shape was developed to allow facile movement of materials in the reacting phase and the control over morphology of nanostructures to tailor their physical and chemical properties. Nano-catalyst systems encompassing a paramagnetic core allow rapid and selective chemical transformations with excellent product yield coupled with the ease of catalyst separation and recovery [31].

Talking about catalysis, it is nowadays indispensable to spend some words on the topic biocatalysis; hence, the application of enzymes as highly selective and active catalysts

produced by Mother Nature. Not only do enzymes carry out the desired reactions under mild conditions of temperature and pressure, which is analogous to the above-discussed energy efficiency principle. Moreover, they are predestined to drive reactions of renewable materials (analogy to the renewable feedstock principle) and, in some cases, even enable reactions that are not accessible by using traditional catalysts, such as the generation of some enantio-pure products [32]. In addition, biocatalysts in a free or immobilized form are to an increasing extent applied for bioremediation, hence, the mitigation of pollutants from the ecosphere [33, 34].

In the context of catalysis, microwave-driven chemical reaction for organic chemistry is an emerging field to drastically reduce reaction times from days to only seconds. During the last decades, this technique has matured from a laboratory shenanigan to a well-established technology, now already industrially applied [35].

2.10. Design for degradation

One of the most important objectives of green chemistry is maximizing the production with minimizing unwanted by-products. Designing of products and processes that display reduced impact on humans and the environment, such as creating sustainable mortar composite that could be considered as an value-added product suitable for various applications as inert matrix for immobilization of some low and intermediate levels of radioactive wastes, decorative tiles, building bricks, and light concrete, is reported. In this case, highly reactive hydroxyl radicals react with the organic moieties of the spinning fiber wastes either by subtracting ions of hydrogen or by addition to the unsaturated site to yield organic radicals, which are readily oxidized by oxygen. Therefore, the end products of the degradation process were only carbon dioxide and water [8–11].

2.11. Real-time analysis for pollution prevention

With advancements in chemistry, the production of numerous toxic chemicals is a serious problem for the environment. One of the basic concepts of green chemistry is familiar to pollution prevention practitioners. Less hazardous materials in chemical formulations and reducing waste formation have been sounded for many years. Consequently, green chemistry aims at eliminating the usage and generation of hazardous substances by designing better manufacturing processes for chemical materials with minimum waste production by real-time monitoring of running processes. This consequently enables a timely intervention right before waste or toxins are generated [36].

2.12. Inherently safer chemistry for accident prevention

It is of outstanding importance to avoid highly reactive chemicals that could potentially cause accidents during the reaction. Substance and the form of a substance used in a chemical process should be chosen in such a way to minimize the potential for chemical accidents, including toxin releases, explosions, and fire formation. For example, the most abundant solution medium, water, could accidentally cause an explosion by flowing into a tank containing

methyl isocyanate gas, releasing a large amount of methyl isocyanate into the surrounding area. Other well-known materials, which undergo reactions of often disastrous outcome with water, are found among alkali metals. If an alternative reaction had been developed that did not use this reagent, the risk of explosion even causing death would have been minimized.

Intrinsically, safe chemistry can also be carried out in flow mode, using tubular microreactors with reaction channels of tiny diameter. Such flow chemistry approaches drastically reduce the reaction volume, the reaction time, and catalyst requirement, intensifies the processes by boosting the space/time yield, opens new process windows in terms of extreme temperature and pressure conditions to be applied, and, moreover, even allows to carry out highly dangerous reactions in a safe way [37, 38]. In addition, the application of flow chemistry in microreactors also displays a strategy to overcome classical drawbacks of microwave-driven processes, such as the restricted penetration depth of microwaves into absorbing media [39, 40].

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