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Review Article

ROLE OF EMERGING GREEN CHEMISTRY FOR HUMAN COMFORT AND ECONOMIC INTENSIFICATION

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ABSTRACT

The impact of cumulative changes brought about by human activities is increasingly becoming evident both in terms of development and more so in the form of deterioration of the environment. The chemicals industry and other related industries supply us with a huge variety of essential products, from plastics to pharmaceuticals. However, these industries have the potential to seriously damage our environment, and hence there is a growing demand from society for a reduced reliance on fossil fuels and for greener manufacturing processes, as well as for future innovations to be built on more sustainable foundations. Green chemistry therefore serves to promote the design and efficient use of environmentally benign chemicals and chemical processes. Green chemistry, also called sustainable chemistry, is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances. While green chemistry seems to focus on industrial applications, it does apply to any chemistry choice. Bioengineering is also seen as a promising technique for achieving green chemistry goals. Green chemistry consists of chemicals and chemical processes designed to reduce or eliminate negative environmental impacts. The use and production of these chemicals may involve reduced waste products, non-toxic components and improved efficiency. Green chemistry is a highly effective approach in pollution prevention because it applies innovative scientific solutions to real-world environmental situations. It is imperative to teach the value of green chemistry to tomorrow's chemists. However, there lies a difference in that historically synthetic chemists have not been seen to rank the environment consciousness throughout the world there is a change for chemists to develop new products, processes and services that achieve necessary social, economical and environmental objectives. This article delineates an assortment of day to day and industrial applications along with brief description on perspectives of green chemistry.

Keywords: Benign solvents;; Safer chemicals; Sustainability; Microwave; Ultrasound; Hazardous substances; E-factor; Atom economy; Nanotechnological approaches.

INTRODUCTION

Chemistry, sustainability and innovation—three key components are for the future of our society. Chemistry is an essential tool in our campaign to protect and preserve our environment, biodiversity and natural resources against further degradation. It is also a primary driver both for the growth and sustainable development of the world economy and the well-being and quality of life of its citizens. The challenges for the chemical sciences are the key to solve the challenges that society will face over the next years: energy, food, clean water, medicines and vaccines, protection of our environment and cultural heritage, and economic development. At present, protection of the environment is a huge concern for society. Problems including global warming and ozone depletion highlight the negative effects human activity has on the planet.

Not only the environment is getting affected by human endeavors but this also has detrimental effects on human health. Sustainable chemistry is therefore not only concerned with the reduction of hazardous substances and waste and the environmental impact of the chemical industry; it is part of a strategic long-term vision for the future of society, not disjoint from or antagonist to economic development but rather a key factor for innovation and competitiveness. In the current era there is a serious push towards developing processes that are eco-friendly. This necessitates a shift from the traditional concepts of the process efficiency that focuses exclusively on the chemical yield to one that assigns economic value to eliminating waste and avoiding the use of toxic and hazardous substances and focusing on more environmentally acceptable processes. To keep the green chemistry concern in mind, many

industries are trying to synthesize target compounds by green chemistry routes. Chemistry has to and will play a major role to provide solutions for the crucial problems of the next century such as Energy; Use of renewable resources; green Pharma & Health; and environmental sustainability. Prompt global action to solve the energy crisis is needed. Such an action should be incorporated in a more general strategy based on the consciousness that the Earth's resources are limited. We are urged to save energy and to use energy in more efficient ways, and we are also forced to find alternative energy sources as soon as possible. The answer to the energy problem confronting this planet deals in the chemist's currency.

As chemists, we can help by improving energy technologies and, hopefully, finding a scientific breakthrough capable of solving the energy problem at its root. The production of renewable chemicals is gaining attention over the past few years. The natural resources from which they can be derived in a sustainable way are most abundant in sugars, cellulose and hemicellulose. These highly functionalized molecules need to be de-functionalized in order to match the traditional feedstock for the chemical industry. A fundamentally different approach to chemistry thus becomes necessary, since the traditionally employed oil-based chemicals normally lack functionality. This new chemical toolbox needs to be designed to guarantee the demands of future generations at a reasonable price. Many low carbon technologies including wind turbines, electric cars and catalytic converters require precious metals or other metals in unprecedented quantities threatening their continued availability. These elements are being dispersed in the form of waste throughout our environment, making them costly & difficult to recover. This emphasizes the necessity for a new approach to metal capture & use, thus increasing the lifetime of our reserves^{Q3}. The Pharmaceutical industry is the most dynamic part of the chemical industry. It is in the forefront for big changes towards "greener" feedstock, safer solvents, alternative processes and innovative ideas. All these changes will increase the environmental credentials of the pharmaceutical industry, but at the same time will cut down cost and materials for the manufacturing operations making a step in the right direction of sustainability. Encouraging innovation, while integrating green chemistry and engineering into drug discovery, development and manufacturing of new pharmaceuticals is one of the most important issues in the health and pharmaceutical sector. Modern day civilization is largely dependent on the chemical industry for its current standards as well as better standards of living – "better living through chemistry". The past few decades have been an era of successful chemistry-developments in water treatment, waste disposal methodologies, agricultural pesticides, fungicides, polymers, detergents, petroleum additives and many more. While all these advancements have contributed to the improvement in our quality of life, they come with a price tag of 'pollution'. The manufacture, use and disposal of synthetic chemicals have taken a toll on human health and environment. Today, with the growing awareness, in industry, academia and the general public, of the need for sustainable development, the international chemistry community is under increasing

pressure to change current working practices and to find pollution prevention alternatives. Researchers and engineers from both the chemical industry, and the academic world have made efforts to correct pollution problems by the extensive use of 'Green Chemistry' concepts i.e. development of methodologies and products that are environmentally friendly. As the name implies, the green chemistry movement aims to make mankind approach to chemicals, especially synthetic organic chemicals, environmentally 'benign' or 'sustainable'.

THE TWELVE PRINCIPLES OF GREEN CHEMISTRY

The concept of Green Chemistry considers the entire cycle of chemical processes as an opportunity for design innovation. It compasses education, research, and commercial application across the entire supply chain for chemicals. Rather than regulatory restrictions for controlling hazards, Green Chemistry challenges innovators to design and utilize matter and energy in a way that increases performances and value while protecting human health and the environment through reduction or elimination of the use or generation of hazardous substances] was coined by Paul Anastas and he along with John C Warner (1998) enunciated 12 principles of Green Chemistry towards ideal synthetic methods to save natural resources.

Green Chemistry Principle #1 Prevention

It is better to prevent waste than to treat or clean up waste after it has been created.

It's better to prevent waste than to treat or clean up waste after it is formed. The first principle, often referred to as the prevention principle, is the most important and the other principles are the "how to's" to achieve it.

An often-used measure of waste is the E-factor, described by Roger Sheldon, which relates the weight of waste coproduced to the weight of the desired product. More recently, the ACS Green Chemistry Institute Pharmaceutical Roundtable (ACS GCIPR) has favored process mass intensity, which expresses a ratio of the weights of all materials (water, organic solvents, raw materials, resilverents, process aids) used to the weight of the active drug ingredient (API) produced. This is an important roundtable focus because of the historically large amount of waste coproduced during drug manufacturing—more than 100 kilos per kilo of API in many cases. However, when companies apply Green Chemistry principles to the design of the API process, dramatic reductions in waste are often achieved, sometimes as much as ten-fold. So, it is important to extend the impressive results achieved by the ACS GCIPR to all parts of the drug industry, especially the biopharma and generic sectors, as well as to other sectors of the chemical enterprise where synthetic chemistry is used to produce their products.

Green Chemistry Principle #2

Atom Economy

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

The objective behind this principle is to minimize byproducts in chemical transformation and reaction sequences. In other words it deals with the maximum incorporation of the reactant

molecules in to the final product which give rise to the concept of atom economy. Atom economy is a simple calculation of percent silver of the atoms in the reactants actually ends up in the final product.

The second principle of Green Chemistry can be simply stated as the “atom economy” of a reaction. Atom economy, which was developed by Barry Trost¹, asks the question “what atoms of the reactants are incorporated into the final desired product(s) and what atoms are wasted?” Traditionally, the efficiency of a reaction has been measured by calculating the percent yield. Let us assume that the following substitution reaction gives 100% yield. While this is admirable, we can shed more light on the efficiency of a reaction by calculating the “% atom economy” as follows:



% Atom Economy = (FW of atoms utilized or FW of the product) / FW of all reactants) X 100 = (137/275) X 100 = 50%

The percent atom economy is simply the formula weight of the desired product(s) (compound 4, 137 g/mol) divided by the sum of the formula weights of all the reactants (275 g/mol), which gives 50% in this case. Simply put, even if our percent yield is 100%, only half the mass of the reactants atoms are incorporated in the desired product while the other half is wasted in unwanted by-products. Imagine telling your mom you baked a cake and threw away half the ingredients! Thus chemists must not only strive to achieve maximum percent yield, but also design syntheses that maximize the incorporation of the atoms of the reactants into the desired product. Principle #2 deals with the reactants. However, as those of us who have run a chemical reaction know, we usually use other materials such as solvents and separating solvents during a synthesis. These materials usually make up the bulk of the material input, and thus we must also account for the waste that is produced from them. Stay “tuned” as you will see these discussed in subsequent Principles of Green Chemistry^{#3}.

% atom economy = [(Formula weight of the product) / Sum of formula weights of all the reactants] x 100

Good atom economy refers most of the atoms of reactants are incorporated in the desired products and only a small amount of unwanted byproducts are formed and hence lesser problems of waste disposal or waste treatment. Thus atom economy is a very useful tool to minimize the environmental pollution level for the welfare of mankind and other living organisms.

Green Chemistry Principle #3

Less Hazardous Chemical Syntheses

Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

When you think about it, this is a two-part principle divided by the first two words, “wherever practicable.” Saying those two words implies that it may not be practical or possible to avoid using substances that are toxic, and this is, if you will, the get out of jail card most chemists use to try to avoid

applying this principle to their work. Let’s face it; chemists use toxic substances all the time because reactive chemicals afford reactions that are kinetically and thermodynamically favorable. And unless—and until—replacement chemicals along with new synthetic protocols are developed, inherently toxic materials will continue to be used. But it’s easier to say that it isn’t practicable and dispense with any thought about the chemical choices that are made. It’s not that adhering to this principle is particularly difficult to do; it’s more that chemists are disinterested in doing it. For the synthetic organic chemist, effecting a successful chemical transformation in a new way or with a new molecule or in a new order is what matters. I have heard such arguments, as “all the other stuff in the flask is just there to make the transformation possible so it really doesn’t matter,” or “you have to be realistic and focus on the science.” Saying these things implies that the only science that matters is activating a carbon atom to functionalize it, or adding a ligand to a catalyst, etc., etc. This principle is asking chemists to broaden their definition of what constitutes good science.

What many have shown over and over again is that toxicity and the attendant hazard and risk associated with a chemical reaction is directly related to all the other “stuff” in a flask. In fact, the chemistry or chemical transformation in a synthesis generally impacts the overall toxicity profile (and most other measures of sustainability and green) of a product or process the least, except in those cases where we deliberately are producing a molecule that is toxic or biologically active by design. That is certainly the case for many molecules that are synthesized as in the pharmaceutical or agriculture chemical business—the molecules are toxic and/or have other effects on living organisms by design. The chemicals and materials used in effecting chemical transformations matter and chemists need to pay more attention to the choices they make about what goes into the flask. It’s easy to discount all the other “stuff” and focus all our energy on the synthetic pathway that delivers the desired product. But when we ignore all the other “stuff,” we pay a high price and it’s a price we need to stop paying. Occasionally, chemists do produce molecules that have toxic or other hazardous effects, and the next principle will have something to say about designing safer molecules.

It’s emphasized that the hazardous or toxic substances should be minimized as far as possible by modifying existing synthesis pathways or starting materials/ reagents or application of modern technological tools. If any hazardous waste is produced, the chemistry should be designed to nullify the effect of the same on living organism including human beings.

Green Chemistry Principle #4

Designing Safer Chemicals

Chemical products should be designed to preserve efficacy of function while reducing toxicity.

Minimizing toxicity, while simultaneously maintaining function and efficacy, may be one of the most challenging aspects of designing safer products and processes. Achieving this goal requires an understanding of not only chemistry but also of the principles of toxicology and environmental science.

Highly reactive chemicals are often used by chemists to manufacture products because they are quite valuable at affecting molecular transformations. However, they are also more likely to react with unintended biological targets, human and ecological, resulting in unwanted adverse effects. Without understanding the fundamental structure hazard relationship, even the most skilled molecular msilverician enters the challenge lacking a complete toolkit. Mastering the art and science of toxicology requires innovative approaches to chemical characterization that state that hazard is a design flaw and must be addressed at the genesis of molecular design. The intrinsic hazard of elements and molecules is a fundamental chemical property that must be characterized, evaluated and mansilvered as part of a systems-based strategy for chemical design. Now is the ideal time to develop a comprehensive and cooperative effort between toxicologists and chemists, focused on training the next generation of scientists to design safer chemicals in a truly holistic and trans-disciplinary manner through innovative curricular advancements. The field of toxicology is evolving rapidly, incorporating and applying the advancements made in molecular biology to reveal the mechanisms of toxicity. Elucidation of these pathways serve as the starting point for articulating design rules that are required by chemists to guide their choices in a quest to make safer chemicals. We are at the dawn of a new sunrise, poised to illuminate the path forward to a safer, healthier and more sustainable world^{#4-#8}.

In developing countries like India where workers are regularly exposed to chemicals during various steps of production processes, it's very much essential to define safer chemicals. Often not only the waste products but starting materials can also pose hazards. By way of manipulating the molecular structure, the toxicity of starting materials can be eliminated.

Green Chemistry Principle #5

Safer Solvents and Auxiliaries

The use of auxiliary substances (e.g., solvents, separation silverents, etc.) should be made unnecessary wherever possible and, innocuous when used.

Solvents and mass separation silverents of all kinds matter a lot to the chemistry not to mention the chemical process and the overall "greenness" of the reaction. In many cases, reactions wouldn't proceed without solvents and/or mass separation silverents. To say that they don't matter, or that it's only the chemistry that counts is not just a logical fallacy, it's chemically incorrect. Solvents and separation silverents provide for mass and energy transfer and without this, many reactions will not proceed. It has also been shown that solvents account for 50 – 80% of the mass in a standard batch chemical operation, depending on whether you include water or you don't. Moreover, solvents account for about 75% of the cumulative life cycle environmental impacts of a standard batch chemical operation. Solvents and mass separation silverents also drive most of the energy consumption in a process. Think about it for a moment. Solvents are alternately heated, distilled, cooled, pumped, mixed, distilled under vacuum, filtered, etc. And that's before they may or may not be recycled. If they're not recycled, they are often incinerated.

Solvents are also the major contributors to the overall toxicity profile and because of that, compose the majority of the materials of concern associated with a process. On aversilverve, they contribute the greatest concern for process safety issues because they are flammable and volatile, or under the right conditions, explosive. They also generally drive workers to don personal protective equipment of one kind or another. We will always need solvents, and with many things in chemical processes, it's a matter of impact trading. Optimize a solvent according to one green metric and many times, there are three others that don't look so good. The object is to choose solvents that make sense chemically, reduce the energy requirements, have the least toxicity, have the fewest life cycle environmental impacts and don't have major safety impacts. Solvents and separation silverents do matter and despite one or more famous synthetic organic chemists may think. It is possible to make better choices, and that is what application of this principle should promote.

Green Chemistry principle #6

Design for Energy Efficiency

Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

In recent years It has begun to talk about the Green Chemistry and engineering's "forgotten principles," and Design for Energy Efficiency is one of them. Amongst synthetic organic chemists, no consideration is given to temperature or pressure. The chemist just follows a protocol to get a reaction to go to completion and to separate the desired product at as high a yield as possible. Energy, from the chemist's perspective, is irrelevant and for all intents and purposes, free. Just put the plug in the wall or the heating coil around the flask, or get the liquid nitrogen out of the dewar. For those that do think about energy, most if not all the attention that energy gets from chemists is devoted to heating, cooling, separations, electrochemistry, pumping and reluctantly, to calculations related to thermodynamics (e.g., Gibbs Free Energy). The attention is not in minimizing or considering where energy comes from or if it matters what form is used, it's just a given that we need to heat or cool or shove electrons into the reaction to make or break bonds. In reflecting on my own training as a chemist, I never was asked to convert any heating, cooling, pumping or electrochemical requirements to a cost for electricity, steam or some other utility. That may be done in chemical engineering, but not in chemistry.

Energy is a key issue for the 21st century. A majority of the energy that is produced is based, and will continue to be based on fossil fuels. And most of the energy that is delivered to the point of use is lost in conversion and transmission. What this means is that if you look at the life cycle of energy production, and you look at how much energy is actually available for useful work at the point of need, it is less than 1 or 2% of the energy that was originally available in the fossil fuel. It is also true that most fossil fuel energy is used for transportation services of one kind or another and the second biggest use is in space heating and cooling. There are a tremendous number of opportunities for chemists to change this energy use profile,

but it is my experience that very few chemists see themselves as being a part of either transportation or the built environment. If you think about where most chemists are trained around energy, and certainly chemical engineers are, it's around ΔH in the Gibbs Free Energy equation. Heats of formation, heats of vaporization, enthalpy, exothermic reactions, etc; these are what we think about. The interesting thing is that nature largely works with ΔS and weak forces of interaction. You don't see a tree doing photosynthesis at reflux using a solvent, or a cell membrane is not extruded at the melt temperature of something like polystyrene.

There is so much more to energy and engineering chemists in thinking about energy than asking them to run reactions at ambient temperature and pressure. Reactions themselves are rarely where a majority of energy is used; most is used in solvent removal to set up for the next reaction, or to remove one solvent and replace it with another, or to isolate the desired product, or to remove impurities. Apart from hydrogenations or reactions that are oxygen or moisture sensitive, most reactions are done at atmospheric pressure. This doesn't mean that energy isn't important, it is just important in areas where most chemists are not focused. Once silverain, thinking about more than one part of the reaction or the process during the design of a new molecule is critical not only from the standpoint of energy, but also from many different angles. Energy—like thinking about how to arrange a synthesis to have the fewest number of steps, or use the lowest cost starting materials or any other aspect of interest to the synthetic or process chemist—is just another design parameter. Historically it has not been seen as that, but we can no longer afford to design new molecules in the absence of a detailed and extended consideration of how energy will be used.

Green Chemistry Principle #7

Use of Renewable Feedstocks

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

The concept of making all our future fuels, chemicals and materials from feedstocks that never deplete is an interesting concept which at first glance seems impracticable. Mankind currently removes fossil fuels, coal, oil and natural gas from the ground and extracts minerals for profit until they are exhausted. In particular, our fossil fuels for carbon-based chemicals and materials are being rapidly depleted in a predictable manner with the expected rise of global populations and expanding energy intensive economies on several continents. The impacts on human health and the environment are significant and present major challenges for our scientists and leaders in the next 50 years.

Can we address these global problems by using Green Chemistry Principle #7? Yes, we will get our feedstock, as if by magic, from "thin air" and it will be renewable. The carbon in the air is in the form of carbon dioxide CO_2 and methane CH_4 and is removed by photosynthetic processes powered by the sun to form plants, trees, crops, algae, etc., which collectively we call "biomass". Nature produces about 170 billion tons of plant biomass annually, of which we currently use about 3.5 % for human needs. It is estimated that

about 40 billion tons of biomass, or about 25 % of the annual production, would be required to completely generate a bio-based economy. The technical challenge in the use of such renewable feedstocks is to develop low energy, non-toxic pathways to convert the biomass to useful chemicals in a manner that does not generate more carbon than is being removed from "thin air"; the difference between $\text{C}(\text{in})$ from the air, and $\text{C}(\text{out})$ from the energy used, is the carbon footprint ΔC . Ideally, when using Principle #7, all carbon footprints by design should be positive such that $\text{C}(\text{in}) \gg \text{C}(\text{out})$. This leads in a natural way to the reduction of global warming gasses impacting our current climate change. We should also insure that the new chemicals and materials derived from renewable resources are non-toxic or injurious to human health and the biosphere.

In 2002, the US Department of Energy in their Vision for Bioenergy and Bio-based Products in the United States stated: "By 2030, a well-established, economically viable, bioenergy, and bio-based products industry is expected to create new economic opportunities for rural America [globalization through localization], protect and enhance the environment, strengthen the US energy independence, provide economic security, and deliver improved products to consumers."

In the past 10 years, significant advances have been made in the development of fuels, chemicals and materials from renewable feedstocks. These for example, have included biodiesel from plant oils and algae, bioethanol and butanol from sugars and lignocellulose, plastics, foams and thermosets from lignin and plant oils, and even electronic materials from chicken feathers. In terms of Green Chemistry Principle #7, our future is bright and laced with optimism due to the ongoing fruitful collaborations between several disciplines involving biotechnology, silveronomy, toxicology, physics, engineering and others, where new fuels, chemicals and materials are being derived from renewable feedstock from "thin air" with minimal impact on human health and the environment

Green Chemistry Principle #8

Reduce Derivatives

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.

One of the key principles of Green Chemistry is to reduce the use of derivatives and protecting groups in the synthesis of target molecules. One of the best ways of doing this is the use of enzymes. Enzymes are so specific that they can often react with one site of the molecule and leave the rest of the molecule alone and hence protecting groups are often not required.

Green Chemistry Principle #9

Catalysis

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

A primary goal of Green Chemistry is the minimization or preferably the elimination of waste in the manufacture of chemicals and allied products: "prevention is better than

cure". This necessitates a paradigm shift in the concept of efficiency in organic synthesis, from one that is focused on chemical yield to one that assigns value to minimization of waste. What is the cause of waste? The key lies in the concept of atom economy: "*synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product*".

A catalyst is defined as "*a substance that changes the velocity of a reaction without itself being changed in the process*". It lowers the activation energy of the reaction but in so doing it is not consumed. This means that, in principle at least, it can be used in small amounts and be recycled indefinitely, that is it doesn't generate any waste. Moreover, molecular hydrogen is also the least expensive reductant and, for this reason, catalytic hydrogenations are widely applied in the petrochemical industry, where the use of other reductants is generally not economically viable. It is only in the last two decades, however, following the emergence of Green Chemistry, that catalysis has been widely applied in the pharmaceutical and fine chemical industries, with the goal of minimizing the enormous amounts of waste generated by the use of stoichiometric inorganic reagents. This involves the use of the full breadth of catalysis: heterogeneous, homogeneous, organocatalysts and, more recently, Nature's own exquisite catalysts: enzymes. The latter are particularly effective at catalyzing highly selective processes with complex substrates under mild conditions and, hence, are finding broad applications in the pharmaceutical and allied industries. Moreover, they are expected to play an important role in the transition from a chemical industry based on non-renewable fossil resources to a more sustainable bio-based economy utilizing renewable biomass as the raw material, yet another noble goal of Green Chemistry.

Green Chemistry Principle #10

Design for Degradation

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.

Green Chemistry practitioners aspire to optimize the commercial function of a chemical while minimizing its hazard and risk. Hazard, the capability to cause harm, is an inherent characteristic arising, like function, from a chemical's stereochemistry (the content and arrangement of atoms). Green Chemistry principles 3, 4, 5, and 12 guide designers to reduce the hazards of chemicals. Principle 10, however, guides the design of products that degrade after their commercial function in order to reduce risk or the probability of harm occurring. Risk is a function of both a molecule's inherent hazard and exposure – contact between a chemical and a species. Degradation can eliminate significant exposure, thereby minimizing risk regardless of the hazard of the chemical involved.

Exposure to persistent chemicals can be significant as a result of global dispersion enabled by properties such as volatility or sorption to particles and partitioning into organisms based on properties such as fat solubility. Regulators have established criteria (half-lives in water, soil, air) that define persistence within frameworks used to identify chemicals as PBT

(Persistent, Bioaccumulative, Toxic). A Green Chemistry objective is to design out molecular features responsible for hazardous characteristics and risk. Trade-offs, or alternative approaches, must be evaluated when the molecular features to be designed in for commercial function overlap with those to be designed out to reduce hazard and risk. Biodegradation, hydrolysis, and photolysis can be designed into chemical products. In the same way that mechanistic toxicology knowledge is essential to identify and design out molecular features that are the basis for hazards, an understanding of the mechanisms of degradation and persistence are required to design in chemical features that promote degradation and eliminate features that promote persistence. Many persistent compounds are extensively chlorinated. Halogens such as chlorine are electron withdrawing, thereby inhibiting the enzyme systems of microbes because aerobic microbial degradation favors electron rich structures.

Prediction methods that can guide the design of molecular architecture expected to degrade include rules of thumb linking structural features to degradability or persistence, databases of existing knowledge, models that evaluate biodegradability or PBT attributes, and experimental testing. All of these tools can be adapted to individual chemical sectors and specific objectives. Understanding the anticipated release and transport pathways for a chemical informs the selection of an effective design strategy. Degradation must occur within the relevant environmental compartment(s) and at a meaningful rate. Domestic wastewater typically passes through a vigorous bioreactor within wastewater treatment plants (WWTP). The consumer product industry has designed molecules for removal within these bioreactors. In the early 1960's, industry transitioned from non-biodegradable branched surfactants, which caused extensive foaming and other health problems in surface waters receiving WWTP effluent, to biodegradable linear alkyl benzene sulfonate based detergents – an approach to innovative design that continues today. Tools currently exist to enable the implementation of principle 10, but advances in mechanistic understandings linking molecular features to hazards and degradability will enable more comprehensive application of Green Chemistry to control hazard and risk. Effective communication across disciplines is also essential to provide designers with knowledge they can factor into the complexities of product design. Because of regulatory and business constraints, many product design decisions must be made relatively early. Predictive decision-making tools must provide confidence about hazard and risk in a way that is aligned with the timing and multiplicity of development decisions, and most importantly, while there is still flexibility to alter a molecular design or product formulation.

It depicts the waste product or by product from any chemical synthesis process should be biodegradable. Calcitrant or non-biodegradable moieties remain in environment for a longer period of time and cause detrimental effects on ecological systems. Sometimes the degradation product from biodegradable substances also possesses toxicity potential. So, proper investigation should also be carried out on toxicity of degradation products. It deals with the analytical

methodologies/protocols need to be developed or modified so that its efficiency/ accuracy gets increased. Continuous monitoring of the manufacturing and processing units is essential to make the industry premises free of any chemical mishaps.

11. Real-time analysis for Pollution Prevention

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

12. Inherently Safer Chemistry for Accident Prevention

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. Substances, the gaseous reactant materials can become responsible for calamities in manufacturing/processing plants as they are susceptible to explosion. Thus, the processing units must be designed to replace the gaseous materials with liquid or solid materials.

Based on all the above principles, 5 imperative tools have been defined to congregate the objective of green chemistry approach and they are as follows

- ❖ Alternative feedstock or starting materials – Green starting material
- ❖ Alternative reagents and transformation – Green reagent & methodologies
- ❖ Alternative reaction conditions – Green reactions
- ❖ Alternative final products or target molecules – Green products

GREEN CHEMISTRY PRACTICES IN CORPORATE SECTOR FOR EVERYDAY DYNAMISM

With the advancement of science, green chemistry has changed our life style. Some of its important applications are described.

▪ Dry Cleaning without PERC

PERC (Perchloroethylene) [$\text{Cl}_2\text{C}=\text{CCl}_2$], commonly being used a solvent for dry cleaning. It is known that perc contaminates groundwater and is a suspected human carcinogen. A technology developed by Joseph De Simons, Timothy Romack, and James Clain made use of liquid CO_2 and a surfactant for dry cleaning cloths, thereby replacing PERC. Dry cleaning machines have been developed using this technique. Micell technology has also evolved a metal-cleaning system that uses CO_2 and a surfactant, thereby eliminating the need of halogenated solvents².

The dry cleaning industry, in particular, is highly dependent on solvents with ~ 100,000 drycleaners worldwide using PERC as the primary solvent. Numerous studies have shown perc to be toxic, affecting plant workers and consumers who use drycleaners and people whose homes are in close proximity to dry cleaning establishments. Supercritical CO_2 has been developed and demonstrated as a viable alternative to perc in dry cleaning applications because it's environmentally friendly, non-toxic and biodegradable and requires no hazardous wastes removal, avoiding costly regulatory compliance issues. Furthermore, in 2003 Consumer Reports study CO_2 outperformed perc for dry cleaning applications.

▪ Versatile Bleaching Agent

It is common knowledge that paper is manufactured from wood (which contains about 70% polysaccharides and about 30% lignin). For good quality paper, the lignin must be completely removed. Initially, lignin is removed by placing small chipped pieces of wood into a bath of NaOH and Na_2S (that is how pulp is formed). By this process about 80-90% of lignin is decomposed. The remaining lignin was so far removed through reaction with Cl_2 gas. The use of chlorine removes all the lignin (to give good quality white paper) but causes environmental problems. Chlorine also reacts with aromatic rings of the lignin (or aromatic substitution) to produce dioxins, such as 2, 3, 7, 8- tetrachloro-p-dioxin and chlorinated furans. These compounds are potential carcinogen and cause other health problems. These halogenated products find their way into the food chain and finally into products like dairy products, pork, beef and fish. In view of this, use of chlorine has been discouraged. Subsequently, chlorine dioxide was used. Other bleaching agents like H_2O_2 , O_3 or O_2 also did not give the desired results. A versatile bleaching agent has been developed by Terrence Collins of Carnegie Mellon University. It involves the use of H_2O_2 as a bleaching agents in the presence of some activators known as TAML activators that act as catalyst which promote the conversion of H_2O into hydroxyl radicals that are involved in oxidation/bleaching. The catalytic activity of TAML allows H_2O_2 to breakdown more lignin in a shorter time and at much lower temperature, these bleaching agents also find use in laundry and result in lesser use of water³.

• Single Step Solution for Phenols' Production

Phenols are important industrial raw materials. They find use in producing everything from dyes, drugs, and pesticides to sunscreens, hair dyes, and perfumes. Creating a phenol seems simple – one just needs to replace a hydrogen molecule in an automatic hydrocarbon with an oxygen molecule. But the process is expensive and cumbersome and requires a number of reactions. Researchers at University of Texas, Austin, have developed a reaction to reduce the steps required to make phenol and lower the cost of innumerable items ranging from agricultural chemicals to pharmaceutical drugs. "The synthetic method provides direct access to phenols from aromatic hydrocarbons, reducing the number of chemical transformations required thus reducing waste and cost," says Dionicio Siegel, co-author of the study. The new reaction elaborated in a study published in *Nature*, July 2013, involves a compound called pthaloyl peroxide. The chemical was studied in late 1950s but was ignored after that. "I wasn't sure it was ignored; perhaps because the compound hasn't been commercially available, so only minimal research was conducted," says Siegel. The advantage of employing pthaloyl peroxide is that it can add oxygen to a wide variety of starting materials and the reaction doesn't need acids or catalysts anymore. The compound has other applications as well, like creating drug metabolites. The interest lies in accounting for possible byproducts the newly developed drugs could leave behind in the body and also how these by-products react in the body because metabolites that don't react prove harmful. Pthaloyl peroxide can render such non-reactive metabolites harmless.

▪ **Boat Based without Tin**

In 1998, Rohm & Haas Company received a Presidential Green Chemistry Challenge Award for designed the environmentally safe marine antifoulant called Sea-Nine™. Fouling, the unwanted growth of plants and animals on a ship's surface, costs the shipping industry ~ \$3 billion a year. A significant portion of the cost is the increased fuel consumption need to overcome hydrodynamic drag. The main compounds used worldwide to control fouling are organotin antifoulants, such as tributyltin oxide (TBTO). They are effective for preventing fouling, but have widespread environmental problems due to their persistence in the environment and they cause severe hazards, including acute toxicity, bioaccumulation, decreased reproductive viability, and increased shell thickness in shellfish. As a green alternative to TBTO, Rohm & Haas introduced a broad spectrum antifoulant based on isothiazolone chemistry. This product provides a long-lasting, stable formulation that is free of heavy metals and degrades rapidly when releases to the environment.

▪ **Fire Extinguishers without Foam**

The aqueous film-forming foams developed by the US Navy in the 1960s for use on volatile hydrocarbon fires release hydrofluoric acid and fluorocarbons during use, and the fluorosurfactants often lead to groundwater contamination. In 1993, PYROCOL technologies, Inc., developed more effective biodegradable, free from glycol ethers or fluorosurfactants, fire extinguisher foam as a environmentally friendly alternative to current fire extinguisher agents.

▪ **Car Coating without Pb**

Lead has historically served as a necessary component in anti-corrosion coating, particularly in applications for automobile manufacturing and protection. But, Pb has been found to have long-term toxic effects in humans and natural systems. As an alternative to such coatings, the G industries developed a Pb-free cathodic epoxy e-coat for applications by automobile manufacturers. The innovative product is a waterborne coating with VOC (Volatile Organic Compound) and HAP (Hazardous Air Pollutants) concentration of < 0.5lb/gallon or 99% VOC and HAP free eliminating the resource expenditures associated with managing, monitoring and permitting these chemical classes. This new product reduces environmental impacts associated with the coating application (material transfer rates exceeding 98%) and eliminates the long-term use and exposure associated with Pb-based products.

▪ **Lumber without Arsenic**

CCA is generally used for preservation of pressure treated wood. There are significant environmental implications associated with the production, use, storage, and disposal of these chemicals as well as potentially significant exposure of workers of these chemicals. Once these products are out of the marketplace, the major human health concerns are that daily contact with As leached from CCA-treated wood might lead to an increased risk for cancer or other long-term health implications. One such alternative is Chemical Specialties, Inc. ACQ wood preservative. ACQ combines a bivalent Cu complex and a quaternary ammonium compound and offers

equivalent performance against biological hazards, such as decay and termite attack to traditional formulations that contained As and Cr (VI).

▪ **MWFs without depleting Resources**

MWFs increase productivity and quantity of manufacturing operations by cooling and lubricating during metal forming and cutting processes. Despite their widespread use, they pose significant health and environmental hazards throughout their life cycle. MWFs are typically oil-in-water emulsions with both the oil and surfactant components being petroleum-based products. It also contains EDTA, a chelating agent and chemical of concern because once released to the environment it doesn't readily biodegradable and can remobilize heavy metals into food chain. An innovative MWF design has been proposed that uses bio-based oil and surfactants in the formulation and needs no EDTA. This new MWF formulation design provides better quality under anticipated field conditions and outperforms the current MWF products in terms of lubrication and wetting in actual manufacturing operations¹⁺⁺⁺⁺.

▪ **Pest Control without Chemicals**

The estimated annual loss to growers from pests is \$300 billion worldwide. In order to be successful, growers have generally pursued two approaches to limit economic losses and increase yield: use traditional chemical pesticides; or grow crops that are genetically engineered for pest resistance. Each approach has consequences including environmental effects that have come under increasing criticism from a variety of sources. In 2001, EDEN Bioscience Corporation received PGCCA for their product. Messenger®, a pesticide which is based on a new defense system to protect against proteins called harpins. Harpins triggers plant's natural defense system to protect against diseases cause by pests, and simultaneously active certain plant growth systems without altering the plant's DNA. When applied to crops, harpins increase plant biomass, photosynthesis, nutrient uptake, and root development, leading to greater crop yield and quantity. The use of harpins have been shown to have virtually no adverse effect on any of the organism tested, including mammals, birds, honey bees, fish, aquatic invertebrates, and algae. Harpins are fragile molecules that are degraded rapidly by UV light and natural microorganism; they have no potential to bioaccumulate or to contaminate surface- or groundwater resources. Spinosad is an environmentally safe pesticide but isn't stable in water and so therefore can't be used to control mosquito larvae. Clarke has developed a way to encapsulate spinosad in a plaster matrix, allowing it to be released slowly in water and provide effective control of mosquito larvae. The pesticide, Natural™, replaces organophosphates and other traditional toxic pesticide and is approved for use in certified organic farming.

▪ **Ester Synthesis without using Toxic Acids and Solvent**

Esters are an important ingredients in cosmetics and personal care products. Usually, they are manufactured by harsh chemical methods that use strong acids and potentially hazardous solvents; these methods also require a great deal of energy. Eastman's new method uses immobilized enzymes to

make esters, saving energy and avoiding both strong acids and organic solvents. This method is so temperate .

▪ **Analyzer Tag Protein for Fast & Accurate Analysis Hazardous Chemicals or High Temperature**

Each year, laboratories test millions of samples of food for the presence of protein. Such tests generally use a large amount of hazardous substances and energy. CEM has developed a fast automated process that uses less toxic reagents and less energy. The new system can eliminate 5.5 million pounds of hazardous waste generated by traditional testing in the US each year. What's more, it differentiates between protein and other chemicals used to adulterate food, such as melamine.

▪ **Bio-based Toners**

Traditional toners of laser printers and copiers fuse so tightly to paper that they are difficult to remove from waste paper for recycling. They are also made from petroleum-based starting materials. Battelle and his copartner, AIR (Advanced Image Resource) and the OSC (Ohio Soybean Council) have developed a soy-based toner that performs as well as traditional ones, but is much easier to remove, the new toner technology can save significant amounts of energy and allow more paper fiber to be recycled.

▪ **Medical Sterilization without Ethylene-oxide or γ -Radiation**

Sterilizing biological tissue for transplant is critical to safety and success in medical treatment. Common existing sterilizing techniques use ethylene oxide or γ -radiation, which are toxic or possess heavy safety problems. NovaSterilis invented a technology that uses CO₂ and a form of peroxide to sterilize a wide variety of delicate biological materials such as graft tissue, vaccines, and biopolymers. Their Nova 2200™ sterilizer requires neither hazardous ethylene oxide nor γ -radiation.

▪ **Biofuel from Pulp Waste**

Pulp and paper industry is among the major sources of industrial pollution. But they could soon double as biorefineries. The Swedish company Chemrec has developed a process for turning the black liquor left over from pulp and paper bleaching into a clean-burning synthetic fuel. The biofuel generated with Chemrec's process, dimethyl ether (DME), can be used as a replacement of liquefied petroleum gas (LPG) and diesel. This is particularly significant in view of the ecological impacts of biofuels production and the disruption caused to food production, as brought out by recent studies. A study European Union (EU) has shown that second-generation biofuels such as DME made from biomass gasification provides the highest GHG reduction for the lowest cost. In the Chemec's technology, gasification process that turns black liquor into a mix of CO, H₂ and CO₂ called synthesis gas or syngas, for short, is adopted. Pulp mills already take care of gathering loads of biomass, and, as a liquid, the waste liquor is easier to feed into gasifier than are solid chunks of biomass. In practice, however, this waste has proved tough to gasify. Black liquor is particularly difficult to deal with because of the highly caustic inorganic chemicals, such as NaOH, employed to break down the pulp. In Chemrec's reactor design, black liquor and pure O₂ injected in from the top feed at 1,800°C fireball at the centre of the reactor. Most

of the dissolved wood in the black liquor forms syngas and flows out of the reactor.

▪ **Energy from Winery Waste**

American and Indian researchers have come up with a new technology that generates electricity by using the waste from improper fermentation. In accordance to them the technology could provide a new and cost effective way to clean wastewater from wineries and get some value out of a "bad bottle of wine". Two groups of bacteria available in winery waste were found. One group of bacteria turns unused sugar and unwanted vinegar from improper fermentation into electricity, while the other uses that electricity to split water molecules into oxygen and hydrogen, which escape into the atmosphere. Recently a microbial electrolysis cell at a winery in Nap Valley, California has been installed by Bruce Logan, a researcher at PSU (Penn State University). CERI (Central Electrochemical Research Institute) in Karakudi, TN, also claimed to have generated power by using the same methodology, the LiveScience website reported. Sugars like glucose, alcohols and effluents containing sugars or alcohols can be used (to produce electricity) stated Berchmans, who recently co-authored a paper in the journal of Environmental Science and Technology. In accordance with the report, the two groups of bacteria identified as Acetobacter aceti and Bluoconobacter roseus – can spoil wine. The researchers at CERI, who created microbial fuel cells using single cultures of each as well as both together, produced 859 milliwatts of power. It is being hoped that the technology could eventually be scaled up to produce more electricity or help to save electricity that would normally be used to treat wastewater.

▪ **Fuel: Hydrogen Storage Made Easy**

Hydrogen can now be conveniently used as fuel without the usual hassle of storage and distribution. A method has been developed to produce hydrogen on the spot for internal combustion engines from an alloy of Al and Ga. The alloy with 28 % Al by weight, has the potential to replace petrol given its high efficiency and lower cost of production, stated lead researcher Jerry Woodall of SECEPU (School of Electrical and Computer Engineering of Purdue University), Indiana. The mechanism is based on a simple chemical reaction. When water is poured on the alloy hydrogen gas is released this gas is directly fed into the engine as fuel. The technology produces fuel instantly eliminating the need for transportation and storage. Hydrogen generating fuel cells from Al have an efficiency of 75 % as compared to 25 % of petrol-fed internal combustion engines. Here's how it works. When water is added, Al, which has an affinity towards oxygen, breaks it down into oxygen and hydrogen forming Al₂O₃. The end products of the reaction are alumina and Ga along with water as a result of combustion of hydrogen in the engine. No toxic fumes are produced. Since hydrogen has a low MW, it has to be pressurized or liquefied to provide sufficient driving range. The mass of the tanks needed for compressed hydrogen in conventional engines reduces the fuel economy. In the alloy-fed motors, the chemical reaction is processed in a container, in which the by-products solid alumina with a liquid Ga core remain with water. By recycling this by-product, fresh alloy is manufactured in the best way.

The technology is suitable for small internal combustion engines like portable emergency engines, lawn mowers and chain saws

▪ **Green Plastic Engineered**

It has been successfully bio-engineered polymers, completely bypassing fossil fuel based chemicals. This breakthrough opens the way for the production of 'green' plastics on commercial scale. The team from KAISTU, South Korea and LG Chem., led by Sang Yup Lee, focused on PLA (-a bio-based polymer considered a good alternative to petroleum based plastics as it's both biodegradable and less toxicity to humans), the key to producing plastics through renewable resources. Until now PLA has been generated in a two-step fermentation and polymerization, which is both complex and expensive. Now, through the use of a metabolically engineered strain of E coli, PLA and its co-polymers through fermentation have been produced, making the renewable production of PLA and lactate-containing copolymers cheaper and more commercially viable. By developing a strategy which combines metabolic engineering and enzyme engineering, an efficient bio-based one step production process for unnatural efficient PLA and its copolymers have been developed

UNCONVENTIONAL WASTEWATER TREATMENT STRATEGIES

▪ **Zinc Removal with Old News Paper**

Could the old news papers piling up in the storeroom help treat wastewater? Experiment has shown how newspapers can be used to remove heavy metals from industrial waste water. This experiment focused on the connection between newspaper pulp and Zn. Used newspaper was processed in a NaHCO₃ (Sodium bicarbonate) solution to remove ink and other chemicals before being washed thoroughly. From there, the treated pulp was mixed with effluent from the electroplating industry that contained Zn, one of the leading sources of environmental pollution. The treated pulp was able to adsorb a significant amount of the Zn, leading researchers to conclude that the method was successfully applied for Zn removal and it was also a potential adsorbent for Fe, Cu, and Mn. While one of the most common elements on earth, Zn is dangerous in large concentrations. It finds use in antirust coatings, batteries and mixed into alloys and compounds that are used to make paint, wood preservatives, and ointments. Electroplating, which coats a metal that is electrically conductive with a thin layer of another metal, often creates wastewater with high concentrations of dissolved Zn. While research into these treatments is still on, there is hope that it could be applied to industrial scales. Newspaper pulp is not the first waste product to show potential in filtering heavy metals from effluent water. Materials such as bamboo pulp, pink bark, peanut shells and saw dust from teak, spruce and mango trees have all been tested at various times for their ability to adsorb heavy metals in waste water, and the results have been promising.

▪ **Green Solution to Turn Turbid Water Clear**

Tamarind seed kernel powder, discarded as agricultural waste, is an effective agent to make municipal and industrial wastewater clear. The present practice is to use Al-salt to treat

such water. It has been found that alum increases toxic ions in treated water and could cause diseases like Alzheimer's. On the other hand kernel powder is not-toxic and is biodegradable and cost effective. For the study, four flocculants (chemicals that cause colloids and other suspended particles in liquids to aggregate, forming a floc) namely tamarind seed kernel powder, mix of the powder and starch, starch, and alum were employed. Flocculants with slurries were prepared by mixing measured amount of clay and water. The result showed aggregation of the powder and suspended particles were more porous and allowed water to ooze out and become compact more easily and formed larger volume of clear water. Starch flocks on the other hand were found to be light weight and less porous and therefore didn't allow water to pass through it easily. The study establishes the powder's potential as an economic flocculant with performance close more established flocculants such as K₂SO₄Al₂(SO₄)₃ · 24H₂O (potash alum).

➤ **Seaweed to Remove Chromium from Leather Effluent**

Two cost effective and eco-friendly techniques to remove Cr from the effluent discharged by tanning units have been developed by the researchers of CLRI, Chennai. The metal exists in its highly carcinogenic hexavalent form Cr (VI) in the effluent. Currently, chemical precipitation methods are employed to remove Cr, but they lead to the formation of chrome-bearing solid wastes, whose disposal again is a problem. Other methods available like membrane separation and ion exchange are expensive and also generate solid waste containing Cr. One of the methods uses H₂O₂ (Hydrogen peroxide) with a zeolite (a porous substance) and organic Cu-complex based catalyst to remove Cr (VI). This process removes Cr ~5x as fast as the other methods. Being porous, zeolites offers far more sites for the reaction to occur, enabling recovery of Cr in less than one hour at 60°C. Studies on commercial tannery wastewater, indicates that the catalyst can be recycled without any large change in its efficiency. The second method uses cheap, abundantly available seaweed, *Sargassum wrightii*. The seaweed added to a chrome tanning solution fully removed the heavy metal in 6 hours. A maximum uptake of 35 mg of Cr/gm of seaweed was reported. Later, the chrome-loaded seaweed were used to make Cr₂(SO₄)₆ (chromium sulphate), which is a major tanning agent as reported in journal *Environmental Science and Technology* 38 (1), 2004. These methods are of special significance to the small and medium leather enterprises due to the cost effectiveness and environmental sustainability.

➤ **Junk Iron to Clean Polluted Water**

In 1983 the entire Mianus river bridge in Connecticut, US, collapsed when the bearings rusted internally. Rusting thus proved to be a bane. But a bane can be turned into a boon. A team of researchers from China used scrap iron to treat industrial wastewater contaminated with excess of N, P and organic dyes. In wastewater stable and unoxidised scrap develops a strong tendency to react with the pollutants and makes them more biodegradable. In other words while the iron oxidizes (rusts) it helps clean up the polluted water. In a series of experiments carried out since 2001, Luming Ma from TU, China and Wei-xian Zhang from LU, UK, successfully used scrap iron to treat wastewater from petrochemical, textile

and pharmaceutical industries. During the full-scale application of the process in 2006, the iron-based reactor was connected to the biological treatment plant to be used as a treatment preceding the biological clean-up. It was found that N removal had gone up from 13 to 85 %. P removal increased from 55.6 to 63.3 % and up to 80.4 % of the colour was reduced. This partial degradation of polluted water using scrap iron helped in turn completely biodegradable. Conventional technologies like biotreatment and chemical precipitation are either ineffective or expensive. In chemical precipitation, chemicals are added to wastewater. They react with the contaminants and settle down. The wastewater is then decanted. But this process requires continuous addition of chemicals and produces large amounts of sludge which is expensive to be disposed off. Biotreatment proves ineffective due to the highly toxic nature of the pollutants. The scrap iron technology is cheaper since iron scraps are readily available. It would be environmentally beneficial in providing iron scraps with a better role than simply dumping them in the junkyard.

➤ **Copper Removal with Peanuts**

For cleaning wastewater, peanut shella are an effective tool. The agricultural waste removes poisonous Cu ions from industrial wastewater. Though the industry uses many chemical methods to remove heavy metals from wastewater, most of them are highly expensive. This method seems to be cheaper and eco-friendly. Peanut shell cleans 95 % of Cu ions. Waste water from electroplating, pulp and paperboard industries contain Cu and affect marine and human life. For example, it can damage human liver. The study by Duygu Ozsoy and colleagues in the department of environmental engineering at the MU in Turkey was published in the *International Journal of Environment and Pollution*, 31 (1&2), 2008. Some other plants and plant products too have been used to clean wastewater. *Erythrodontium barteri*, a moss, removes 97 % of Cu from wastewater, says astudu done at OOU in Nigeria, published in the *International Journal of Physical Sciences*, 2 (11), 2008. The biomass waste traps all the positively charged heavy metal ions, the study explains.

• **Recovery of Cr from Tannery Effluent**

In leather industry, tanning is the main process that protects leather against some environmental effects such as microbial degradation, heat, sweat or moisture. ~ 90% tanneries in the world use Chromium salts as tannage materials because of the excellent properties of the Cr-compounds in the tanning. During the tanning process, Cr forms crosslinks between the collagen fibres and the resulting hides have a good mechanical resistance, and extraordinary dyeing suitability and a better hydrothermic resistance in comparison with hides treated with vegetable substance. However, only 60% of the total Cr reacts with the hides. The rest of the Cr remains in the tanning effluent and are subsequently sent to a tannery wastewater management plant where the Cr salts end up in the sludge. Cr and other pollutants in the sludge can be released to the water bodies and thus the disposal of tannery sludge has becoming one of the major environmental problems of the tannery industry.

One long term solution appears to be recovery and recycling of Cr from it. As traditional chemical recovery methods are associated with high cost and toxic products, there are needs for clean, nontoxic and environment friendly technologies. TERI in collaboration with DU has developed a unique Cr recovery process following green chemistry approach. A range of Cr accumulator plants and microbes are shown in Cr rich tannery effluent, using least amount of different resources, harvested and finally digested them in least amount of mineral acid with minimal use of energy to bring the accumulated Cr into solution. The Cr rich acid solution is then passed through a specially designed reactor containing reusable metal specific resin compounds to adsorb maximum amount of Cr from the acid solution. Cr impregnated resin is then washed with specific quantity of mineral acid to recover Cr in pure form. Recovery of Cr > 99% has been achieved through this green chemistry approach.

• **Papaya Hybrid Clay Filter for Removal of Heavy Metal**

Researchers are constantly pushing for water purification solutions that are inexpensive and robust. One such innovation is a hybrid clay synthesized by German and Nigerian researchers. The clay is actually a composite made up of kaolinite clay and papaya seeds. Writing in their paper, published in *ACS Sustainable Chemistry and Engineering*, the researchers claim that the hybrid is stable, nonbiodegradable, can be easily recovered from aqueous solution by decantation and available in large amounts. It also has a high cation exchange rate, which means it can absorb and remove cations of metals like Pb, Cd and Ni from water. There are several composites under the broad umbrella of materials. Purification solutions can be found for all the contaminants by combining these materials. Thus an all-inclusive solution for clean water can be made easy.

• **Tanning without Toxicity**

Conventional leather production consumes high levels of energy and so many chemicals and the process release various types of toxic substances. Researchers from The CLRI (Central Leather Research Institute) in Chennai TN, have developed an enzyme-based technology which cuts down use and release of chemicals by 82%. It has done so by avoiding 2 key process in leather production, deliming and acidification and saves nearly 40% of energy. Pre-tanning, tanning and post-tanning are 3 stages in leather production. In the CLRI method, chemicals – mainly Cr (chromium – are used during tanning. But in the other 2 stages their use is very minimal). For instance, the conventional production methods employs lime in treating the hide before tanning, while in the new method developed by CLRI, α -amylase, an enzyme, is employed which helps avoiding the generation of sludge. The enzymes's action is made faster with the chemical, sodium metasilicate. Very lesser quantity of (~2%) of the product, enzymes find use for dehairing and softening the leather. Earlier, the quantity of chemicals employed was higher – ~40% of the product. Reverse processing technique is used in recent method in which salt-free curing, lime-free and sulphide-free. The findings of the study was published online

October 5, 2007, in the *Journal of Chemical Technology and Biotechnology*.

In the new processing, pre-tanning isn't immediately followed by post-tanning. Tanning is done only at final stage. This process can save more than Rs 2,000 for processing 1 ton of raw skin. The SPIC (Southern Petrochemical Industrial Corporation), Chennai, which is developing the new technology with CLRI, is promoting it among tannery units in India. High cost of the enzymes is compensated by time and energy, saved by new technology. The new method is 8 to 10% more efficient than the traditional; method. Timely application of enzymes (effective control of enzymes), makes this technology suitable for small units which are facing extinction.^{ZZ}

NANOTECHNOLOGICAL APPROACH TO DECONTAMINATE SOIL AND WATER

Nanotechnology is a field of applied science, focusing on the design, synthesis, characterization and application of materials and devices on the nano scale. This branch of knowledge is actually one more branch in all the other scientific fields which involve the study of phenomenon and manipulation of structural appearances at the nano scale. A unique aspect of nanotechnology is the "vastly increased ratio of surface area to volume", present in many nano scale materials, which opens up the new door in the application of surface based sciences. The nanotechnology field has created a great impact in the consumer sector with other sector in the society and thus nano scale materials have significant impact to upgrade environmental scenario., both through direct applications of them to detect, prevent, and remove pollutants, as well as indirectly by using this technique for designer industrial processes and create environmentally influentive products. At the nano scale, often highly desirable properties are created due to size confinement, dominance of the interfacial phenomena, and quantum effects. These significant and unique properties of nano structural nanotechnologies have led to improved catalysts, tunable photoactivity, increased strength, and many other interesting characteristics.

The field of nanotechnology is defining its edge day by day, its environmental impact should be taken under consideration which include the environmental implications of the cost, size and availability of advanced technological devices; models to determine potential benefits of reduction or prevention of pollutants from environmental sources; potential new directions in environmental science due to advanced sensors; effect of rapid advances in health care and health management as related to the environment; effect of synthetic nanoparticles in the atmosphere; and impact from the development of nano machines. Presently, there is utmost need of research which involves the usage of nano scale devices and technology to identify opportunities and applications to various environmental problems, and to evaluate the potential environmental impacts of nanotechnology. It's also required to determine the new potential of these nano materials for preventing or treating highly toxic or persistent pollutants, which would result in more effective monitoring of pollutants or their impact in the ways not currently possible. But this technology has various fundamental features which are quite

uncertain due to which it has become difficult to engineer applications for optimal performances or to access the risk of human or ecological health. One of the main environmental applications of nanotechnology is water sector. Water contamination and over exploitation of water resources have created the scarcity of potable water in the environment. So researchers are planning to use salt water to meet this demand but world's water supply has too much salt for human consumption. Desalination is the option to reactive this dilemma but there are only expensive processes to remove this salt from water. Here nanotechnology is a savior to this situation.

Nanomaterials for decontamination

➤ **TiO₂ based nanoparticles & their mode of action:**

Titanium dioxide (TiO₂) is one of the popular materials used in various applications because of its semiconducting, photocatalytic, energy converting, electronic and gas sensing properties. Researchers are more focused on the photocatalytic property of TiO₂ in the water treatment. It has been studied that TiO₂ in nanoparticle form is activated by light and is able to remove organic contaminants from various media. These nanoparticles are in demand because of being readily available, inexpensive, and less toxic. The TiO₂ through its semiconducting property plays a significant role in the removal of different organic pollutants through excitation of TiO₂ semiconductor with a light energy greater than its band gap, which could generate e⁻ hole pairs. These may be exploited in different reduction processes at the semiconductor/solution interface. A semiconductor can adopt with donor atoms that provide e^{-s} for the reduction band where they can carry a current. The energy levels of these donors and acceptors fall into the energy gap. The most affecting properties of semiconducting nanoparticles are distinguished changes in their optical properties compared to those of bulk materials. In addition, there is a significant shift in optical absorption spectra towards the blue shift (shorter λ) as the particle size is reduced.

➤ **Fe based nanoparticles & their mode of action:**

Fe⁰ (Zero-valent iron a. k. a. ZVE) nanoparticles are deployed *in situ* to remediate soil and water contaminated with chlorinated compounds and heavy metals. Nanoparticles containing ZVI is one of the most prominent examples of a rapidly emerging technology with considerable potential benefits. Nanoparticles could provide very high flexibility for both *in situ* and *ex situ* remediation. For example, nanoparticles are easily deployed in *ex situ* slurry reactors for the treatment of contaminated soils, sediments, and soil wastes. Direct subsurface injection of nano scale ZVI particles, whether under gravity-feed or pasteurized conditions, has already been shown to effectively degrade chlorinated organics such as trichloroethylene, to environmentally benign compounds. The technology also holds great promise for immobilizing heavy metals and radio nuclides. The use of Fe⁰ for *in situ* remediation treatment has been expanded to include all different kinds of contaminants. ZVE remediate aqueous contaminants by reductive dechlorination, in the case of chlorinated solvents, or by

reducing to an insoluble form, in the case of aqueous metal ions.

➤ **Carbon nanotubes & their mode of action:**

Fullerenes and carbon nanotubes has given new edges to carbon chemistry. Superconducting and magnetic fullerenes, atoms trapped inside the fullerene cage, chemically bonded fullerene complexes, and nano scale helical carbon nanotubes are some of the leading areas that has open up a new chapter to this field. The creation of the hollow carbon buckminsterfulleren molecule as well as method to produce and purify bulk quantities of it has triggered an explosive growth of research in the field. Carbon nanotubes, in particular, hold tremendous potential for applications because of their unique properties such as thermal and electrical conductivities, high strength, high stiffness, and special absorption properties. Carbon nanotubes have cylindrical pores and adsorbent molecules interaction with their carbon atoms on the surrounding walls. This interaction between molecules and solid surface depends on the pore size and geometry of pores. When a molecule is placed in between two flat surfaces, i. e. in a slit-shaped pore, it interacts with both surfaces, and the potentials on two surfaces overlap. The extent of the overlapping depends on the pore size. However, for cylindrical and spherical pores, the potentials are greater because more surface atoms interact with the absorbed molecules. In addition carbon nanotubes are highly graphitic, hence the can carbon nanotubes can absorb molecules much stronger than wedge-shaped pores. Carbon nanotubes membranes have the potential to desalination costs.

• **Anti-microbial Substance from e-waste**

Researchers at the University of York's department of Chemistry have developed a way to turn e-waste from LCD into an anti-microbial substance that destroys pathogens such as *Escherichia Coli*, strains of *Staphylococcus aureus* and other some bacteria. The key element behind this is polyvinylalcohol (PVA), a chemical compound that is used in LCD-TVs and is compatible with the human body, *Discovery News* reported. Andrew Hunt and his colleagues, the master minds behind the study, have found that cooling and then heating PVA, dehydrating it with ethanol, and adding of silver nanoparticles to it can enhance the material's anti-microbial properties. The final product could be used in medical centers cleaning solutions to help reduce infections. In accordance with a York University statement, the product "could also be used in pills and dressings designed to deliver drugs to particular parts of the body".

▪ **Paper-Pulp Batteries**

Ordinary paper could one day be used as a lightweight battery to power the devices that are now enabling the printed word to be eclipsed by email, ebooks and online news. Researchers at SU Stanford University in California reported successful turning paper coated with ink made of Ag and C-nanomaterials into a "paper battery" that holds promise for new types of lightweight, high performance energy storage. The same feature that helps ink adhere to paper allows it to hold onto the single-walled C-nanotubes and Ag-nanowire films. Earlier research found that Si-nanowires could be used to make batteries 10x as powerful as Li-ion batteries now used

to power devices such as laptops. This type of battery could be useful in powering electric or hybrid vehicles, would make electronics lightweight and long lasting, and might even lead someday to paper electronics, the researcher added. Battery weight and life has been an obstacle to commercial viability of electric-powered cars and trucks.

• **Removal of As using Ag Nanoparticles Caged in Al**

A filter, described in *PNAS* May 6, 2013, which meets in achieving United Nations millennium development goal of sustainable access to safe drinking water, uses nanomaterial to remove disease causing microorganisms and toxic heavy metals and metalloid As from water. It works by constantly releasing Ag ions, which are an effective disinfectant, into the water. Several Ag-based anti-microbial devices have been designed in the past but haven't been viable. One of the reasons being presence of organic and inorganic impurities in water that cling onto nanoparticle surface and hamper sustained release of Ag, states researchers. To find a way around this technical constraint, the researchers from IIT Chennai, formulated a cage-like nano-composite of Al-oxyhydroxide – chitosan with Ag particle embedded in it. This composite ensures sustained release of Ag ions into the water in an amount significantly less than the permissible limit set by USEPA (US-Environmental Agency). This eliminates a need for secondary filtrations to remove excess Ag ions. Ag nanoparticles remain intact as the Al cage reduces their contact with chemicals that might anchor on them.

▪ **Cooked by Sun**

Methane, an important constituent of cooking fuel, can now be manufactured in large quantities. All we need is a nanotube catalyst, carbon dioxide, water and lots of sun. Researchers used titanium dioxide to create nanotubes ~135nm wide and 0.1mm long. Steel tubes were filled with carbon dioxide and water vapour covering the ends of the containers with a film of nanotubes. When sunlight fell onto the nanotubes, water and carbon dioxide combined to form methane. The devices generated ~160 micro litres of methane/hour/gram of the nanotubes. This method can not only be an important generator of fuel but it might also help control emissions by using carbon dioxide from sources like a coal plant.

▪ **Pt-free Fuel Cells**

Fuel cells are, in principle, the most efficient way to convert hydrogen fuel into electricity. Conventional fuel cells consist of two electrodes coated with a Pt catalyst that splits hydrogen fuel into acidic hydrogen ions from one side to the other, creating an external electrical current. The use of Pt makes conventional fuel cells very expensive, but cheaper metals simply can't withstand the harsh acidic environment of the fuel cell. Now researchers in China have come out with a fuel cell that uses a new membrane material and eliminates the need for an expensive catalyst. The polymer used as membrane in the new fuel cell is comparable in structure to the highly conductive polymer Nafion (a sulphonated tetrafluoroethylene copolymer) that is used in conventional acidic fuel cells, but is less expensive than Nafion. The new fuel cell uses a Ag cathode and an anode coated with Ni nanoparticles decorated with Cr as the catalyst. The fuel cell

works by reacting hydrogen and oxygen to create hydroxyl ions and water, catalysed by the Ni anode. The hydroxyl ions are conducted across the polymer membrane, generating an external electrical current. At present the power output of the new fuel cell is modest-about 50milliwatts/cm² at 60°C. But the first demonstration of an alkaline fuel cell that does not require expensive metal catalyst, it is an important proof of principle, researchers state.

▪ **Vitamin C Finds Use in Unfamiliar Terrain**

In a new application for disease-fighting vitamin C, researchers have used it to assemble fibre bundles of Au, Ag and Pt nanoparticles. Such bundles are used in new-age medicine to produce sensors for disease detection, enhancement of optical imaging and even manufacture of cheaper and pollution-checking catalytic converters. According to the report published in Journal of Colloid and Interface Science Vol. 311 No.1, two methods are developed to produce fibre bundles of metallic nanoparticles with vitamin C. In the first method, ascorbic acid was allowed to degrade in acidic condition to form colorless fibres. Then, separately, made nanoparticles of Au, Ag and Pt were deposited on those fibres. In the second method, ascorbic acid was used as a reducing agent on salts of Au (hydrogen tetrachloroaurate) to form Au nanoparticles and subsequently grown into fibres. Using sophisticated imaging techniques like transmission and scanning electron microscopy, the assembly of nanoparticles forming composite fibre bundles were studied.

▪ **Hydrogen from Pee to fuel Cars**

Researchers have combined refuelling our car and relieving ourselves by creating a new catalyst that can extract hydrogen from urine. The catalyst couldn't only fuel the hydrogen-powered cars of the future, but could also help clean up municipal wastewater as reported by physorg.com. In OU (Ohio University) an electrolyte was used approaching to produce hydrogen from urine – the most abundant waste on the earth – at a fraction of the cost of producing hydrogen from water. Urine's major constituent is NH₂CONH₂ (urea) which incorporates four hydrogen per molecule – importantly less tightly bonded than the hydrogen atoms in water molecules. Electrolysis was used to break the molecule apart, developing an inexpensive nickel based electrode to efficiently oxidise the urea. To break the molecule down, a voltage of 0.37V needs to be applied across the cell, which is much less than the 1.23V needed to split water. "During the electrochemical process the urea gets adsorbed on to the nickel surface, which passes the electrons needed to break up the molecule. Storing pure hydrogen gas requires high pressure and low temperature. New nanomaterials with high surface areas can adsorb hydrogen, but have yet to be produced on commercial scale. MCD (Municipal Corporation of Delhi) is working on a project to generate electricity from urine. For this, it will install around 1000 waterless urinal kiosks around the city. Process involved: Waste is collected from waterless urinals and transported to portable power plants. Water, hydrogen are produced from the decomposition of biodegradable components of urine. Water is cleaned by reverse osmosis and can be used for industrial purposes, power is

generated from hydrogen. 1 litre of urine makes 1kw of power, enough to light a 50W bulb for 20 hours.

▪ **Don't Recycle, Upcycle Plastic**

A marvel of modernity, plastic has become an indispensable part of our daily lives. But repeated reprocessing disposal of plastic waste is environmentally unfriendly, polluting and a potential health risk. A new method proposes up cycling – taking waste and turning it into something of value – the ubiquitous plastic bag and converting it into useful nanotubes. According to V G Pol, a scientist at ANL (Argonne National Laboratory), Illinois, USA, this method is called "remediation". Gram pieces of high density or low density polyethylene are heated at 700°C for two hours in the presence of a catalyst, cobalt acetate [(CH₃COO)₂Co] the mixture is allowed to cool. Multi-walled nanotubes grow on the surface on the surface of catalyst surface. Carbon nanotubes are extremely thin with a diameter 10,000x less than a strand of human hair. These hollow cylinders made of C-atoms are extremely strong, have good thermal conductivity and are used in electronics, optics etc. These nanotubes were used as anode for Li-ion batteries. 1 Upcycled plastic from a grocery bag (3-6gram) can produce nanotubes (1-3gram) enough for one cell phone battery, which could suffice as an anode for one Li-ion rechargeable battery. It's thought that the same technology sans a catalyst could be used to grow spherical 2-10 μm carbon bodies, which have applications in printers, toners, filtration technology and the pain and tyre technology.

CONCLUSION

Green chemistry focuses on the reduction, recycling, and/or elimination of the use of toxic and hazardous chemicals in production processes by finding creative, alternative routes for making the desired products that minimize the impact on the environment. Green chemistry is a more eco-friendly green alternative to conventional chemistry practices. The green chemistry movement is part of a larger movement ultimately leading to a green economy- namely sustainable development, sustainable business and sustainable living practices. Green chemistry can contribute to achieving sustainability in three key areas. First, renewable energy technologies will be the central pillar of a sustainable high-technology civilization. Second, the reagents used by the chemical industry. Third, polluting technologies must be replaced by benign alternatives. The aim of the article is to acquaint the academicians, researchers, scientists and engineers with values and positive impact of green chemistry innovation, application and Technology. While Green chemistry offers principles for the development of 'greener' reagents and alternatives and more benign routes to synthetic methodologies, it does not have the capacity to bring about a radical change. An agreement has to be arrived at between the policy makers and the chemical practitioners in order to give Green chemistry the power it rightly deserves. And a policy needs to be frame to guide the practitioners so that overall efficiency as well as environmental cleanliness is achieved. It is reiterate that the espouse for Green chemistry must involve not only the academia or academic intelligentsia but also the science and technology agencies and the S&T administrators, since it is

only a synchronized movement of these apparently segregated entities that can bring about a reform movement in chemistry and chemical technology.

The research and development and the science and technology agencies that are responsible for the funding of scientific activities in the country must encourage and give preference to the development of greener science and technology. In order to ensure global environmental protection while keeping scientific and economic development on the forefront, the policy makers should understand the role of 'green' science and technology and make pollution prevention, rather than pollution control, their slogan. Though it is true that many industries and research organizations are yet to implement the principles of Green chemistry, nevertheless some of them have begun to realize that the 'think green' culture is more than just a fashion. In fact, the winds of changes have already started blowing and the more successful chemistry researchers and chemical technologists will like to appreciate and apply the values of green chemistry in innovation, application and teaching. Conclusively, green chemistry can be considered a bench level practice that also leads to cost reductions and product orientation besides all its other benefits discussed. In the future it will become a strategic tool for companies to rationalize their operations and create value. The firms pioneering innovations in feedstock process and product redesign built around sustainability protocols will lead way in the time ahead. Those firms which can demonstrate that a non-regulatory green chemistry approach be a viable strategy will bring about the much needed mind shifts.

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