INTERNATIONAL RESEARCH JOURNAL OF PHARMACY
www.irjponline.com ISSN 2230 – 8407
Review Article

GREEN CHEMISTRY POTENTIAL FOR PAST, PRESENT AND FUTURE PERSPECTIVES

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Article Received on: 02/03/12 Revised on: 25/03/12 Approved for publication: 18/04/12

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ABSTRACT
Chemistry brought about medical revolution till about the middle of twentieth century in which drugs and antibiotics were discovered. The world's food supply also increased enormously due to the discovery of hybrid varieties, improved methods of farming, better seeds, and use of insecticides, herbicides and fertilizers. The quality of life on earth became much better due to the discovery of dyes, plastics, cosmetics and other materials. Soon, the ill effects of chemistry also became pronounced, main among them being the pollution of land, water and atmosphere. This is caused mainly due to the effects of by-products of chemical industries, which are being discharged into the air, rivers/ oceans and the land. The use of toxic reactants and reagents also make the situation worse. The pollution reached such levels that different governments made laws to minimize it. This marked the beginning of *Green Chemistry* by the middle of 29th century. Green Chemistry is defined as environmentally benign chemistry. As on today, maximum pollution to the environment is caused by numerous chemical industries. Therefore, attempts have been made to design synthesis for manufacturing processes in such a way that the waste products are minimum, they have no effect on the environment and their disposal is convenient. For carrying out reactions it is necessary that the starting materials, solvents and catalysts should be carefully chosen. For example Benzene (C_6H_6) as a solvent must be avoided at any cost since it is carcinogenic in nature. If possible, it is best to carry out reactions in the aqueous phase. With this view in mind, synthesis methods should be designed in such a way that the starting materials are consumed to the maximum extent in the final product. The reaction should also not generate any toxic by-products.
KEYWORDS: Safer chemicals, Hazardous wastes, Chemical education, Environmental objectives, etc.

INTRODUCTION

The Green Chemistry revolution provides an enormous number of opportunity to discover and apply new synthetic approaches using alternative feedstock; Eco friendly reaction conditions, energy minimization and the design of less toxic and inherently safer chemicals. The origin and basis of Green Chemistry for achieving environmental and economic prosperity is inherent in a sustainable world. One important element of sustainable chemistry is commonly defined as the chemical research aiming at the optimization of chemical processes and products with respect to energy and material consumption, inherent safety, toxicity, environmental degradability, and so on[23]. While considering progress has been made in environmental chemistry, Green Chemistry, and the environmental assessment of chemical products, however, the societal aspect of sustainable chemistry remains to be fully recognized in all branches of chemical research. One prerequisite for this is the inclusion of sustainable chemistry into chemical education from the very beginning.

Green Chemistry is the utilization of set of principles that reduces or eliminates the use or generation of hazardous substances in design, manufacture and application of chemical products. In practice, Green Chemistry is taken to cover a much broader range of issues than the definition covers[14]. As well as using and producing better chemicals with less waste, Green Chemistry also involves reducing other associated environmental impacts[14], including reduction in the amount of energy used in chemical processes. Consequently, there have been efforts to achieve environmentally benign synthesis and various acts have been passed to control and treat pollution, in an endeavor to encourage industries and academics to devise novel technologies, processes and educational materials, discouraging the formation or use of hazardous substances. Green Chemistry is not different from traditional chemistry in as much as it embraces the same creativity and innovation than has always been central to classical chemistry. However, there lies a difference in that historically synthetic chemists have not been seen to rank the environment very high in their priorities. But with the increase in environmental consciousness throughout the world, there is a challenge for chemists to develop new products, processes and services that achieve necessary social, economical and environmental objectives[24]. Since the types of chemicals and the types of transformations are much varied, so are the Green Chemistry solutions that have been proposed. Developed 'The twelve Principles of Green Chemistry' that serve as guidelines for practicing chemists in developing and assessing how green a synthesis, compound, process or technology is[3].

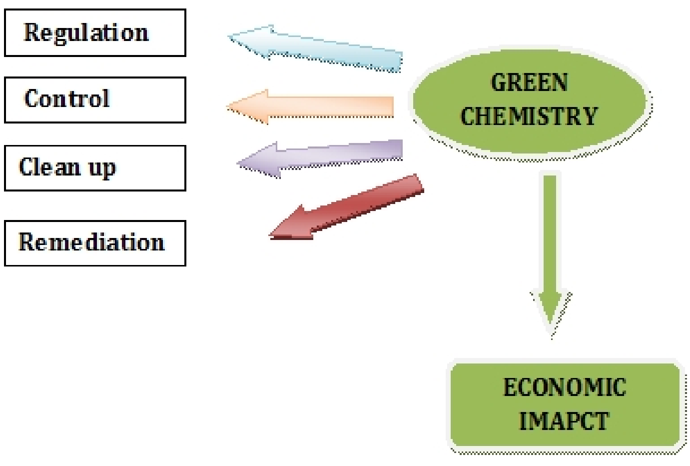


Figure 1. Green chemistry scenario[3]

Basic Principles of Green Chemistry

- Prevention of waste/ by-products
- Application of innovative technology to established industrial processes
- Maximum incorporation of the reactants (starting materials and reagents) into the final product
- Development of environmentally improved routes to important products
- Prevention or minimization of hazardous products
- Use of biotechnology alternatives
- Designing of safer chemicals
- Use of sustainable resources
- Minimum energy requirement for any synthesis
- Selecting the appropriate starting Solvents
- Selecting the most appropriate solvent
- Whenever possible avoid the use of protecting group
- Whenever possible prefer use of catalysts
- Biodegradable products
- Design manufacturing plants so as to eliminate the possibility of accidents during operations
- Strengthening of analytical techniques to control hazardous compounds

An evaluation of how green a chemical reaction or a chemical process is seems to be best done in terms of the 12 principles that have been advocated by Anastas and Warner. These tenets deal with fundamental issues such as pollution prevention, atom economization and toxicity reduction. The essence of the 12 principles may be summarized as follows:

Waste prevention instead of waste clean-up, atom economy as an important concern, design of environmentally friendly synthetic methodologies, design of safer chemicals, redundancy of auxiliary substances, conservation of energy, use of renewable feedstock, reduction of unnecessary derivatization, catalytic reactions instead of stoichiometric ones, debasement of final products after the end of their function, real-time analysis for pollution prevention and strategies for chemical accident prevention.

The society is dependent in many ways on the chemical industry to maintain the current standards of living and improve the quality of our lives – 'better living through chemistry'. The past few decades have been an era of successful chemistry. Developments in water treatment, waste disposal methods, agricultural pesticides and fungicides, polymers, materials sciences, detergents, petroleum additives and so forth, have all contributed to the improvement in our quality of life. But unfortunately all these advances come with a price tag of 'pollution'. Today, with 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 greener alternatives. Scientists and engineers from both the chemical industry and the academic world have made efforts to correct pollution problems by the more 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 humanity's approach to chemicals, especially synthetic organic chemicals, environmentally 'benign' or 'sustainable'. 'Organic chemistry textbooks, a generation from now will be unrecognizable compared with today's standard texts', predicts one of the progenitors of what is coming to be called green chemistry. For better living, what is needed is:

- An increasing awareness in industry of the importance of concepts such as waste minimization and atom utilization.
- Greater involvement by governments in controlling the use of resources and the productive disposal of waste.
- Emergence of other underpinning concepts as general principles which can be used the conception and execution of synthetic chemistry and in the usage of chemicals produced.

INDUSTRIAL INTEREST IN GREEN CHEMISTRY

Many forward-looking companies are embracing Green Chemistry, not only to protect the environment and to create good public relations, but also because it is often beneficial to the bottom line it is also estimated to cost US industries between $ 100 and $ 150 billion per year to comply with environmental regulations. In addition, cleaning up hazardous waste sites will cost hundreds of billions of dollars. In many companies, the cost of dealing with environmental regulations often exceeds their expenditure for research. Larger companies budget close to $ 1 billion per year for environmental compliance. If a company can significantly reduce this expenditure, then these funds can be spent in more productive areas and result in an improved bottom line. Thus, Green Chemistry (pollution prevention) is not only good for the environment but also for industry[20].

GREEN CHEMISTRY IN EDUCATION

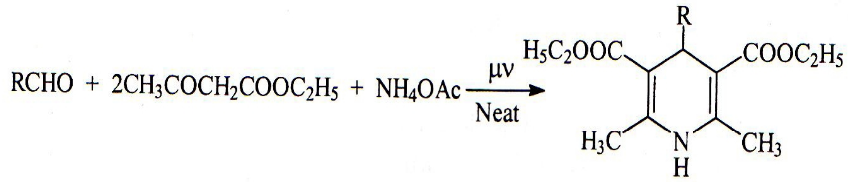
Convincing chemists to think in an environmentally friendly manner begins with education. The idea of including Green Chemistry in chemistry education was first put forward in 1994. Few Green chemistry textbooks have also been published[2]. Graduates, post graduates, teachers and researchers will find these books of immense use. Both Environmental Protection Agency (EPA) and American Chemical Agency (ACS) have recognized the importance of bringing Green Chemistry to the class room and the laboratory. Together they have launched a significant campaign to develop Green Chemistry educational materials and to encourage the 'greening' of the chemistry curriculum[1]. Student involvement in Green Chemistry principles and practices is essential to the integration the environmentally benign technologies in academia and industry. ACS Student Affiliate Chapters may be recognized as "green" chapters by engaging in at least three Green Chemistry activities during the academic year. Suggestions for these activities include:

Hosting a Green Chemistry speaker

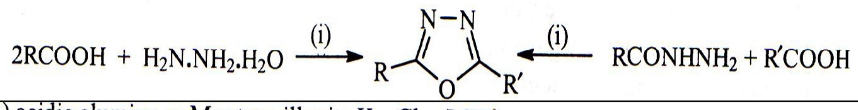
- Organizing an interdisciplinary Green Chemistry workshop on campus
- Working with a local company on a Green Chemistry project
- Developing a Green Chemistry activity with a local school
- Converting a current laboratory experiment into a greener one
- Organizing a Green Chemistry poster sessions on campus
- Distributing a Green Chemistry Newsletter to the local community
- Designing a green Chemistry web page

ENERGY CONSERVATION

Energy conservation and consumption has long been known to produce a major environmental effect. Chemistry and chemical transformations has long been known to produce a major role in capturing and converting substances into energy as well as converting existing sources of energy into a form that is usable to society. Microwave irradiation in the solid state[19] is a technique that is being utilized to affect chemical transformations rapidly, in contrast to those that have classically been conducted in liquid solutions. Solvent-free microwave assisted reactions[11] provide an opportunity to work with open vessels, thus, avoiding the risk of high pressure and increasing the potential for scale up of such reactions. The practical feasibility of microwave assisted solvent free synthesis has been demonstrated in various useful transformations[5] and in the synthesis of heterocyclic systems[12] **[Scheme 1-3]** .

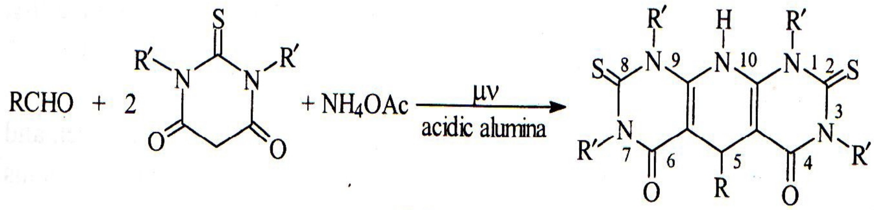


Scheme 1

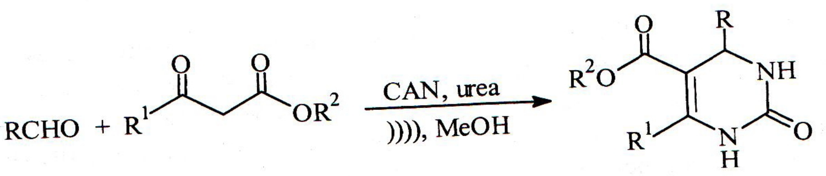


(i) acidic alumina or Montmorillonite K_{10} Clay/MWI

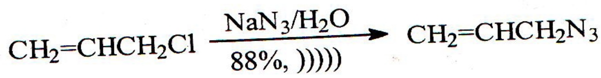
Scheme 2



Scheme 3



Scheme 4



Scheme 5

The microwave technique has shown distinct advantages in not requiring prolonged heating to carry out a reaction. Ultra sound is a relatively new way of introducing energy into chemical systems[10]. It has been used to enhance reaction rates[21] in a large number of classical reactions [**Scheme 4**]. Though the use of phase transfer catalysis in organic aqueous biphasic systems is well known to catalyse heterogeneous liquid-liquid reactions, ultra sound is much more effective in these reactions because ultrasonic waves generate extremely fine emulsions which results in very large interfacial contact areas between the liquids and a corresponding dramatic increase in the reactivity between dissolved species [**Scheme 5**].

The problems associated with waste disposal of solvents and excess chemicals have been overcome by performing reactions without solvent under microwave irradiation or ultrasound. Heterogeneous organic reactions have also proven useful to chemists. These reactions are affected by the reagent immobilized on the porous solid supports and have advantages over the conventional solution phase reactions because of good dispersion of active reagent sites, associated selectivity and easier work up.

SUSTAINABLE CHEMISTRY: STARTING POINTS AND PROSPECTS

Sustainability is significantly determined by how we manipulate matter within the economy, the inventive leadership of chemists is vital to its future. Sustainable chemistry should also address the societal aspect of sustainability, with respect to scientific research; the societal aspect is designed by two requirements:

(a) The assumptions, objectives and implication of chemical research and its technical application should be made more transparent to various societal actors.

(b) Uncertainty and ignorance should be treated explicitly in the course of scientific research.

CURRENT STATUS

Since 1991, Green Chemistry has grown into a significantly internationally engaged focus area within chemistry. Research programs and centers located in America, Europe, Asia/Pacific and Africa are focusing efforts around the principles of Green Chemistry; the breadth of this research is very wide and incorporates area such as:

I Bio-based Renewable

The utilization of benign, renewable feedstock is needed for addressing the global depletion of resources. Bio-based products hold great promise for achieving the goals of sustainable development and implementing the principles of industrial, ecological and Green Chemistry Achieving a sustainable chemical industry dictates switching from depleting finite sources to renewable feed stock. Research has focused on both, the micro and molecular levels

(i) The carbohydrate economy provides a rich source of feedstock for synthesizing commodity[15].

(ii) A continuous process and apparatus converts waste biomass into industrial chemicals, fuels and animal feed. Another process converts waste biomass such as municipal solid waste, sewage sludge, plastic, tires and agricultural residues to useful products, including hydrogen, ethanol and acetic acid.

(iii) A fermentation method for the production of carboxylic acids.

(iv) Shells from crabs and other sea life serve as a valuable and plentiful source of chitin, which can be processed into chitosan a biopolymer with a wide range of potential applications that are being currently explored for use in the oil-drilling industry[13].

(v) A method for mass producing taxol by semi continuous culture of Taxus genus plant.

(vi) The first bio-pesticide for sugarcane, called Bio Cane, has recently been launched in Australia. The product is based on a naturally-occurring fungus that has been cultured on broken rice grains to provide a medium for distribution. Biocane granules are claimed to be particularly effective against grey back cane grub.

(vii) Genetic engineering produces valuable chemical products via non-traditional pathways.

(viii) Glucose Yields Catechol and adipic acid[6].

(ix) Saccharomyces yeasts convert both glucose and xylose, present in cellulogic biomass, into ethanol[8].

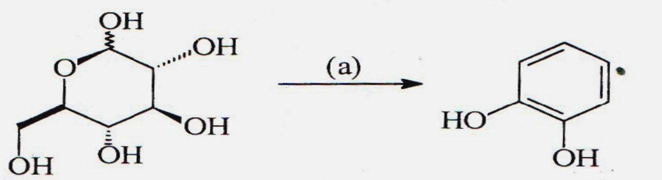
(x) A new environmentally friendly technology in mixed metals recovery from spent acid wastes has been used to recover zinc and ferrous chloride from pickle liquor.

(xi) CO_2 is also a renewable feedstock that has been incorporated into polymers[4].

(xii) A method of partially oxidizing alcohol such as methanol to ethers, aldehydes, esters or acids, by using a supercritical fluid mobile.

(xiii) The demand for non-ionic surfactants is growing and a new example of this is alkly glycoside, which is made from saccharide. This product can be used as a replacement for alkylaryl sulphonate anionic surfactants in shampoos. Sodium silicate can be used as a more environmentally benign replacement for phosphorus-containing additives in washing powder. Three coconut oil soap bases for liquid cleansing applications have been developed. One of these products has very light color and low odor, making it suitable for introducing dyes and fragrances.

Glucose $\xrightarrow{\text{Yields}}$ Catechol and adipic acid.[27]



(a) E. coli AB 2834 / pKD 136 / pKD 9.069 A, 37°C

GREEN ENGINEERING EDUCATION FOR SUSTAINABILITY FOR DEVELOPING COUNTRIES

In developing countries, the introduction of green chemistry is still in a stage of infancy, despite the significant need and the significant role green chemistry can play. Many of the practices in developing countries are still far from the concepts of safety, pollution prevention and design of energy efficiency. Environmental pollution and waste generation are some of the aching problems many developing countries are suffering from. Many of the reasons behind these problems lie in policies and strategies adopted that are based on end-of pipe treatment, rather than pollution prevention at source or implementing life cycle thinking in handling waste problems. Most frequently, income generation activities are dependent on an efficient use of energy and other resources such as water, which may pose some serious problems to future generations.

The United Nations reporting on the millennium development goals at a country level indicated a high level of energy consumption and limited energy resources in most of the developing countries. The report strongly recommends the imperative need to ration the use of energy resources in these countries and to implement energy conservation policies. The same trend of difficulties developing countries face has been illustrated in the series of country reports produced by the rural development at the water and environment department of the World Bank.

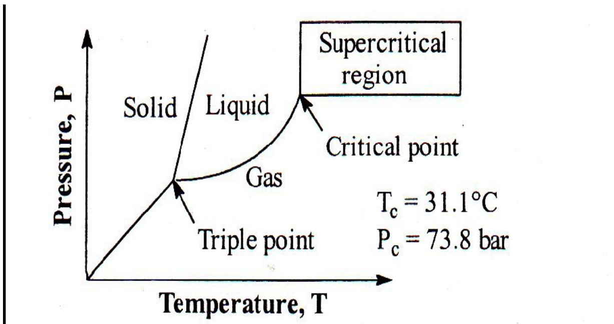
Sustainable chemistry could play a pivotal role in salvaging many of the ailing conditions that many of the developing countries are subjected to. The use of solar energy, introduction of sustainable farming, recycling, and the implementation of life cycle thinking and life cycle analysis as a management tool for some of the chronic issues such as municipal waste management, are some few examples of how green chemistry can benefit developing communities.

Green chemistry can also have a very strong impact on water sufficiency issues in that part of the developing world where water resources is the most vital issue. It is through the implementation of cleaner production and use of safe and biodegradable chemicals that a huge volume of wastewater could be reused to quench the emerging, critical need of water in many of these countries.

Zujang[22], presented a paper of existing philosophy, approach, criteria and delivery of Environmental Engineering (EE) Education (E3) for developing countries.

- In general EE is being taught in almost all major university major universities in developing countries, mostly under civil engineering degree programmes. The main component of E3 in near future will remain on basic sanitation in most developing countries, with special emphases on the consumer-demand approach.
- The concept, principles and methodologies of Green Chemistry and green engineering are fundamental in integrating sustainability throughout the system of our chemical enterprise. By incorporating these Green Chemistry approaches in the research and Development, scale up and commercialization stages in industry and by insuring that training of both established and next generation chemists and engineers includes Green Chemistry and engineering , large strides can and are being made sustainability in the chemical industry.
- In order to overcome environmental problems in developing countries, E3 include integrated urban water management, sustainable sanitation, appropriate technology, cleaner production, waste water minimization and financial framework.

COMPRESSED CO_2: AN ENVIRONMENT FRIENDLY SOLVENT



Phase diagram for CO_2

Many solvents are unpleasant but essential industrial chemicals. Supercritical CO_2 would be viable alternative but its use has been restricted by its limited solvent power. This is about to change. Beyond a specific temperature and pressure CO_2 becomes a supercritical fluid, a state that is neither a gas nor a liquid, but has properties of both, known as critical point.

A. The specific properties of Supercritical CO_2 make it an interesting "green" replacement for organic solvents, which are often less than ideal owing to their acute toxicity, ecological hazards or difficulty with disposal and recycling.

B. Supercritical CO_2 find applications in areas as diverse as the dyeing and cleaning of fibers and textiles. Polymerization and polymer processing, purification and crystallization of pharmaceuticals, and last but not the least as a reaction medium for chemical synthesis.

C. Most widely used CO_2 philic solubilizers have been polysiloxanes and fluorocarbons. The Beckman group[18] has now synthesized a nonfluorous but still highly CO_2 philic polymer, whose solubility in Supercritical CO_2, whose solubility in Supercritical CO_2 results from a judicious design. The target compound of the Beckman group was copolymer (Polyether polycarbonate group) with copolymers can be easily generated using an Al-catalyst to react propylene oxide (C_3H_6O) with CO_2 itself.

D. Polyether skeleton is highly flexible and has only weak polymer-2 interactions, when carbonate group is introduced. It enhances this flexibility, and therefore the entropy of mixing. At the same time a favorable interaction of the carbonyl group with CO_2 may increase the enthalpy of mining, thereby also improving the solubility of these compounds in CO_2.

GREEN CHEMISTRY IN DAY-TO-DAY LIFE

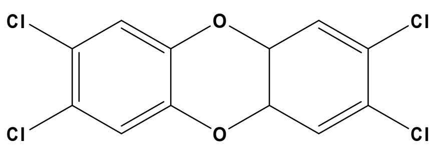
1. Dry Cleaning of Clothes

Perchloroethylene (PERC), $Cl_2C{=}CCl_2$ is commonly being used as a solvent for dry cleaning. It is now known that PERC contaminates groundwater and is a suspected carcinogen. A technology,

Known as Micell Technology developed by Joseph De Simons, Timothy Romark, and James McClain made use of liquid CO_2 and a surfactant for dry cleaning clothes, thereby replacing PERC. Dry cleaning machines have now 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 solvents[16].

2. Versatile Bleaching Agents

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 sodium hydroxide (NaOH) and sodium sulphide (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 chlorine gas (Cl_2). 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 (by aromatic substitution) to produce dioxins, such as 2,3,4-tetrachloro-pdioxin and chlorinated furans. These compounds are potential carcinogens and cause other health problems.



2,3,7,8-tetrachloro-4a,10a-dihydrodibenzo[b,e][1,4]dioxine

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 hydrogen per oxide (H_2O_2), ozone (O_3) or oxygen (O_2) also did not give this the desired results. A versatile agent has been developed by Terrence Collins of Camegie Mellon University. It involves the use of hydrogen peroxide as a bleaching agent in the presence of some activators known as TAML activators[7] that as catalysts which promote the conversion of hydrogen peroxide into hydroxyl radicals that are involved in oxidation/ bleaching. The catalytic of TAML activators allows hydrogen per oxide to break down more lignin in a shorter time and at much lower temperature. These bleaching agents find use in laundry and result in lesser use of water.

CONCLUSION

The expansion of Green Chemistry over the course of the past decade needs to increase at an accelerated pace if molecular science is to meet challenges of sustainability. It has been said that the revolution of one day becomes the new orthodoxy of the next Green Chemistry is applied and must involve the successful implementation of more environmentally friendly chemical processes and product design. Most importantly we need the relevant scientific, engineering, educational and other communities to work together for sustainable future through Green Chemistry.

ACKNOWLEDGMENT

The authors are thankful to Institute of Pharmaceutical Science and Research Centre, Ajmer, Rajasthan.

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