Review Article

Green Chemistry- Past Present and Future

Jayati Mal

Department of Chemistry, Vidyasagar College, Kolkata, West Bengal, India.

ABSTRACT

The worldwide environmental crisis due to the adverse effect of the chemicals and pollutants lead the chemical community to coin the term "Green Chemistry" in early nineties. From then politicians, industrialists, researchers, academicians from one corner raised their voice to implement green chemistry in industries, research institutes, and education and in daily lives. Though USA was a forerunner in the advancement of Green Chemistry, other countries like Italy, France, Greece, Japan, U.K. and India played a major role in advancing green chemistry. Green Chemistry from the late nineties became course syllabi in many universities throughout the world.

Keywords: Green Chemistry, Green Education, Sustainability.

INTRODUCTION

The United Nations has proclaimed the year 2011 as the 'International Year Of Chemistry.' Under this banner the worldwide chemical community is more aware of our ecological misbalance and environmental disasters. But these were not the scenario half a century ago when Rachel Carson, in 1962 a famous Historian raised his voice against reckless use of chemicals like DDT, an insecticide effective in controlling insect pests, was responsible for causing a precious decline in the bald eagle population and is a suspected carcinogen. The book "Silent Spring"[1]written by her opened the eyes of the whole world where she rendered agendas for protection of environment. From then on politics got involved, resulting in the foundation of US Environmental Protection Agency (EPA) in 1970 by President Nixon. US EPA commanded and controlled policy in the execution of environmental regulations. As a result in 1985, the Environmental ministers of the OECD (Organization for Economic Cooperation and Development) countries focused on three themes. 1. Economic development and environment, 2. Pollution Prevention and Control, 3.Environmental Information and National Reviews. The USA EPA established the office of Pollution Prevention and Toxics in1988. In 1990 US Congress passed the 'Pollution Prevention Act' which found that there was a shared interest of government (US EPA) and chemical industry to cooperate and meet environmental needs. Though the United States were forerunner, many developed countries like Japan, UK, Italy, and Germany along with India had the urge of environmental consciousness. In mid eighties chemical technology has been rather malevolent in number of cases. Some infamous examples were the Cuyahoga river in Ohio was polluted that it actually caught fire.b) Bhopal gas tragedy in 1984 that killed at least 3000 people by toxic methyl isocyanate gas leak at a Union Carbide Pesticide plant c) Another was Chernobyl nuclear reactor explosion in 1986 which entitled huge radioactive cloud all over Europe. The reason for this malevolence can be attributed to the fact that a number of commonly used chemicals have high level of toxicity, so an enormous environmental damage caused the chemists and chemical technologists in the twentieth century to wake up to the realization that the time has come to clean up the bad reputations of chemicals, to reduce hazardous waste of chemical industries which typically include volatile organic solvents.

Green Chemistry at a glance

Green Chemistry gained its current standing as a scientific discipline as well as practical means to pollution prevention as the result of collaboration between the government, Industry and academia in early 1990's.In 1991 the phrase 'Green Chemistry' [2]invented by the chemist Paul Anastas , who was then the chief of Industrial chemistry branch at the US EPA. Agenda 21, the Rio Declaration on Environment and Development and the statement of principles for the sustainable management of

forests were adopted by more than 178 governments at the United Nations Conference on Environment and Development (UNCED) held in Rio de Janerio, Brazil, on 3rd to 4th June 1992. Agenda 21 addresses to the pressing problems of today. It reflects a global consensus and political commitment at the highest level of development and environmental cooperation. Agenda 21 acts as a guide for green chemistry research and a sustainable future. In June 1993, a white paper entitled "Chemistry for a clean world'' published by the European Community's chemistry council attracted a great deal of attention in Europe. The first symposium "Benign by Design: Alternative Synthetic Design for Pollution Prevention was held in Chicago. In 1995 EPA started to grant the U.S.Presidential green chemistry challenge award annually to encourage academicians, researchers, technologists to work together in the design and implementation of green chemistry principles. Five awards are distributed each year with the categories 1) Academic 2) Greener Synthetic pathways3) Designing greener chemicals 4) Small business 5) greener reaction conditions. There are similar awards in Great Britain, Australia, Italy, Germany and Japan. In 1997 Green Chemistry Institute was formed by Joe Breen and it became a part of ACS in 2001. The institute works to advance the growth of green chemistry and green engineering, a movement to develop and implement manufacturing processes that are both economically sound and environmentally sustainable. The 12 principles of green chemistry originally published by Paul Anastas and John Warner in ''Green Chemistry, Theory and Practice (Oxford University Press, New York, 1998) provide guidance for chemists to implement green chemistry. Economic, environmental and societal drivers are forcing a change in the chemical and related industries across the world and these drivers will eventually influence all the countries. They include increasing energy and petrochemical costs, increasing costs of waste disposal and storage of hazardous substances, increasing fines for pollution, new legislation causing testing of all chemicals, increasing demand of emerging nations and supply chain pressure.[3] The Royal Society of London formed "The Green Chemistry Network and started to publish the paper "Green Chemistry "in 1999. The Green Chemistry theme of CHEM RAWN XIV founded in 1997 in Geneva builds on the efforts of IUPAC working party on "Synthetic Pathways and Processes in Green Chemistry". In Japan a green organization called 'Green and sustainable Chemistry Network' was established in 1999 to propagate the principles of Green Chemistry.

Green Chemistry towards twenty first century

During the early twentieth century chemists were very much concerned to synthesize all possible chemicals found in nature. While this has been a dazzling accomplishment by the mankind, the toxicity of chemicals has been completely neglected. The lack of awareness and safety of the surrounding environment of twentieth century scientists were replaced by the enormous consciousness of the twenty first century. In both developed and developing countries green chemistry provides a preventive medicine for the environment.

In the year of 2002, Handbook of Green Chemistry and Technology was published in Greece. MISTRA's green chemistry program[4] was started in 2003. In 2005, Professor Ryoji Noyori, Noble Prize winner in Chemistry identified 3 key developments in green chemistry 1)use of supercritical CO_2 as green solvent 2)Aqueous $H_2O_2$for clean oxidations c) Use of hydrogen in asymmetric synthesis.[5] The Warner Babcock Institute for Green Chemistry dedicated to the development of non-toxic, environmentally benign, and sustainable technological solutions for society.was established in 2007 by John Warner where he served as a president and chief technical officer.In 2007, Europe put into place the Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) program, which requires companies to provide data showing that their products are safe. This regulation ensures not only the assessment of the chemicals' hazards as well as risks during their uses but also includes measures for banning or restricting/authorizing uses of specific substances..

Some states in United States have concluded that advancing Green Chemistry is a key component in stimulating economic development, in advancing a clean technology economy, in creating educational opportunities, and in achieving a safe and healthy environment for its people. They consider Green Chemistry a powerful mechanism that enables consumers, businesses and manufacturers to minimize exposure to toxic chemicals without stifling economic or scientific progress. The Environmental Council of the States passed

a resolution on the promotion of green chemistry for sustainable economic development and protection of public health and the environment.

Green Chemistry in Education

Many institutions have courses [and degrees on Green Chemistry. Examples from across the globe are Denmark's Technical University, and several in the US, e.g. at the Universities of Massachusetts-Boston, Michigan, and Oregon[6]. A master's level course in Green Technology has been introduced by the Institute of Chemical Technology, India,in the UK at the University of YorkUniversity of Leicester, Department of Chemistry and MRes in Green Chemistry at Imperial College London.

For propagation of green chemistry education, 'Beyond Benign' was created by Dr. John Warner, a founder of the field of Green Chemistry, to provide an approach and means for scientists, particularly those involved in green chemistry and sustainable science, to reach out to the public. Guided by the belief that all scientists should be able to explain their research in a simple and meaningful manner to people from all backgrounds and of all ages, in 1999 Dr. Warner incorporated community outreach into his students' academic experience as a requirement. His vision is to increase public awareness and understanding of science in general and specifically of the relationships between chemistry, human health and the environment. Over the eight academic years between 1999 and 2007, the basic concepts of Green Chemistry were brought to an estimated 16,000 K-12 students through outreach program.

Beyond Benign has three main focuses

- **K-12 Curriculum and Training** – The concepts of Green Chemistry and Sustainability will be integral knowledge for all future scientists and educated citizens. We believe that education of these topics must begin at the K-12 level. Through Beyond Benign's K-12 Curriculum and Training programs, a number of lesson plans, curriculum materials and training opportunities are presented to the K-12 educational community to aid in the implementation of science driven by the principles of Green Chemistry throughout the K-12 educational system.
- **Community Outreach and Communications** – Community education is an essential piece to an environmentally, socially and economically prosperous world. 'Beyond Benign' seeks to educate the community to inspire future scientists and to create more informed consumers and voters who are able to support a growing industrial market based in concepts of Green Chemistry and sustainability.
- **Workforce Development** – Green Chemistry in practice implies designing safer, economical, efficacious and efficient processes and products. All of these aspects are symptoms of good product design and good manufacturing processes in industry and can result in economic benefit for industries that implement these practices. Green Chemistry can be a tool for regional economic development and jobs creation. Education and training at the academic and professional level are required to support a workforce that can sustain industries driven by the principles of Green Chemistry.

  Green School throughout the world is also an amazing project, pioneering sustainability within education, where sustainability for the future is taught. Green School in Bali, Indonesia is giving its students a natural, holistic and student-centered education in one of the most amazing environments on the planet. The U.S. Green Building Council's Center for Green Schools awarded Green School the "2012 Greenest School on Earth".

Green Chemistry in Indian Scenario

The prospects of green chemistry in India are not so miserable[7,8]compared to the other developing countries. The first National Symposium on green chemistry in 1999 at the University Of Delhi shows the green awareness of the country. In 2001, the first IUPAC International Symposium on Green Chemistry was conducted in New Delhi, in which many excellent presentations illustrated the interdisciplinary nature of green chemistry.

Green ChemisTree Foundation and Newreka Green Synth Technologies' Pvt. Ltd. have been organizing the conference "Industrial Green Chemistry World" since 2009 and are doing incredible ground breaking work in India. **IGCW** is the first International platform created to bring individuals and organizations committed

and focused towards expanding implementation and commercialization of Green Chemistry based technologies and products by the chemical industry in a way that nothing exist as 'green' chemistry, but that becomes just the way of doing chemistry.Green ChemisTree Foundation is a non-profit arm of Newreka, created to bring forth technical know-how to the chemical industry and update them on global trends of green chemistry and engineering (GC&E) applications. Green ChemisTree Foundation has the vision to bring forth technical know-how regarding green chemistry and engineering applications amongst the Chemical community including Industry, Academia, Research Institutes, Govt. bodies, and Students. Newreka Green Synth Technologies' Pvt. Ltd. is an Enviropreneur venture, initiated by Chemical Engineers from IIT- Bombay, with the objective to address environmental concerns by reducing the E-factor. Beyond Benign, Boston and Warner Babcock Institute for Green Chemistry were invited to participate in the Industrial Green Chemistry World Conference in Mumbai, India over December 4-6, 2011. The conference was truly international with representatives from across the globe. Over the three days hundreds of participants attended the symposium, seminar series, exhibition and Green Innovation Award ceremony. The Industrial green chemistry world will organize conference in Mumbai on December 2013 where the speakers will be Paul Anastas, John Warner fathers of green chemistry and Professor Roger Sheldon.

Dr.Reddy's Lab. is also a pioneer in applying green principles in pharmaceutical industry. Its goal towards "Green Chemistry & Engineering" is fundamentally based on the very first principle involving pollution prevention or promotion of innovative Science and Technology that reduce or eliminate the use of hazardous substances by design rather than pollution management.

Real world examples of Green Chemistry Practices in Indian Industry

In the process of manufacturing of Ranitidine, an anti ulcer drug, dimethylsiulfide is generated that is detrimental to the health and environment. Several works of Professor Mihir K. Chaudhuri of IIT Guwahati,[9] Dr. M. Lakshmi Kantam of IICT, Hyderabad, newer catalysts have been designed to achieve a green process for production of the Ranitidine HCl.The functional catalysts have been designed jointly by RCHEM Pvt. Ltd. Hyderabad and Professor MihirK. Chaudhuri of IIT Guwahati. The heterogeneous catalysts that have been put on to use for the commercial production of the drug are based on Vanadium- Titanium or Titanium- Phosphorous compounds. With hydrogen peroxide as an oxidant the catalyst convert dimethylsulphide with bad odour to dimethyl sulphoxide, a colourless and odourless liquid.DMSO That is generated is used in the manufacturing process of the drug, thereby reducing the cost production by 20%.

Some example of Green innovations in daily life

1. Shaw Industries innovated novel EcoWorx™ carpet tiles which replaced conventional backings for carpet tiles which contain bitumen, polyvinyl chloride (PVC) or polyurethane. Shaw Industries selected a combination of polyolefin resins from Dow Chemicals as the base polymer of choice of Ecoworx™ due to low toxicity of its feed stocks, superior adhesion property, dimensional stability and its ability to be recycled.
2. BASF Corporation developed environmental friendly Rightfit ™ azo pigments which replaced conventional pigments based on lead, chromium and cadmium heavy metals. Rightfit ™azo pigments contain calcium, barium, strontium instead of heavy metals. It has the right environmental impact, right colour space, right pergormane characteristics and right cost-to performance value.
3. Jeneil Biosurfactant Company has launched a series of rhamnolipid biosurfactant products making them commercially available and economical for the first time replacing petroleum derived surfactants.These biosurfactant products provide good emulsification, wetting, detergency and foaming properties along with very low toxicity. They are readily biodegradable and leave no harmful or persistent degradation products.
4. Metabolix Incorporation has used new biotechnology methods to develop microorganisms that produce polyhydroxy alkanoates directly. These natural plastics have arrange of environmental benefit s including reduced reliance on fossil carbon, reduced solid waste, reduced

greenhouse gas emissions. PHAs biodegrade to harmless products in the environment reducing the burden of plastic waste on the landfills and the environment.

5. Sernade® is an effective environmentally friendly biofungicide developed by Agra quest Incorporation. Sernade® has been applied on 30 crops in 20 countries and is registered for use on blueberries, grape vines, green beans, leafy vegetables. It has been registered for home and garden use. It is used in integrated pest management. (IPM).
6. In 2011, Professor Bruce H. Lipshutz of University Of Calofornia, Santa Barbara was selected as the 2011 winner of EPA's Presidential Green Chemistry Challenge Award for his project "Towards Ending our Dependence on Organic Solvents". Most chemical reactions rely on organic solvents, which seem to be volatile, toxic and inflammable and generates a lot of waste. Professor Lipshutz has designed a novel second generation surfactant called TPGS-750-M, that forms tiny droplets in water. Organic reactants dissolve in these droplets and reacts efficiently allowing water replace organic solvent.

GREEN INNOVATIONS IN PHARMACEUTICALS

1. Synthesis of Cytovene™ - Cytovene is a potent antiviral drug synthesized by Roche Colorado Corporation. They have successfully applied green principles for production of ganciclovir, the active ingredient of Cytovene. It is used in treatment of cytomegalovirus (CMV) retinitis infections in immunocompromised patients including patients with AIDS.
2. Green designing of Sertraline Process- Pfizer Incorporation applied green chemistry for synthesis of Sertraline, the active ingredient in Zoloft® which is used for treatment of depression in adults. The new process consists of imine formation of mono methyl amine with a tetralone, followed by reduction of imine function and in situ resolution of diastereomeric salts of mandelic acid to provide chirally pure sertraline in much higher yield and with greater selectivity.
3. Merck & Co. Inc. redesigned the synthesis of Aprepitant , the active ingredient in Emend®- Anew therapy for Chemotherapy induced Emesis. Aprepitant which has two heterocyclic rings and three stereogenic centres is a challenging synthetic target. Merk's new route to Aprepitant applies green chemistry principles and involves three atom economical steps. It involves incorporation of a chiral alcohol as a feed stock, which is itself synthesized in a catalytic asymmetric reaction.
4. **General Preparation of Paracetamol**: It is generall prepared from p-nitrophenol by reduction (Sn+HCl) followed by reaction with acetic acid – acetic anhydride mixture. Alternatively it is obtained by Beckmann rearrangement of oxime of p-hydroxyacetophenone. **Greener Preparation of Paracetamol: In** the green synthesis of paracetamol,p-hydroxyacetophenone is reacted with ammonia and hydrogen peroxide in presence of titanium (IV)-silicate catalyst [9] to give oxime of p-hydroxy acetophenone. The oxime of p-hydroxy acetophenone on Beckmann rearrangement gives paracetamol.
5. Ibuprofen, a very important analgesic were manufactured by the Boots company of England in 1960s which is a six step process and results in large quantities of unwanted waste chemical byproducts that must be disposed of. Atom Economy of the synthesis is 40% only.

The BHC Company developed a new greener commercial synthesis of ibuprofen which involves only three steps, small unwanted products and very good atom economy (80%) Figure 1

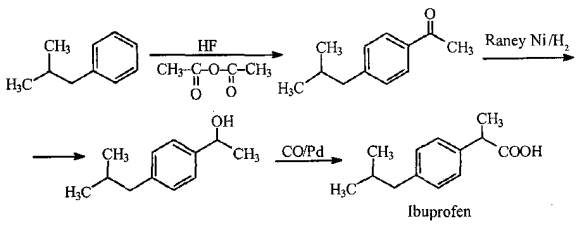

Fig. 1

CONCLUSION

If we lean back from 2013 towards the embryo stage of green chemistry, we can feel that green chemistry has been disseminated throughout the world by researchers, educationalist, students and common people at different level, Green chemistry shows the academician a path to implement research for the benevolence of society and environment and not for themselves.[10]Many challenges still lie ahead, and the solutions will be found not only in the discipline of chemistry but at its interfaces with engineering, physics, and biology. Green Chemistry must establish a comprehensive set of design principles and interdisciplinary cooperation to move toward routine consideration of hazards as molecular properties just as malleable to chemists as solubility, melting point, or colour. So let us hope for a clean world free from toxic and carcinogenic materials.

REFERENCES

1. Rachel Carson, Silent spring, 1962.
2. Anastas PT and Williamson TC. Green Chemistry, Oxford University Press, New York. 1998.
3. Anastas PT. Green Chemistry: Challenging perspectives, Oxford University Press, New York. 2000.
4. www.mistra.org/en/mistra.html
5. Ryoji Noyori. Chemical Communications. 2005:1807
6. www.greenchem.uoregon.edu/gems.html
7. Kidwai M. Pure Appl Chem. 2001:1261-1263.
8. Chaudhuri, Mihir K. et al. Current Science. 2002:1427
9. de Bars J, J Dakkka and Sheldon RA. Appl Catal A General. 1966;136:69.
10. Ryoji Noyori, Key Note Address at the Second International Conference on Green and Sustainable Chemistry, Washigton DC, June. 2005.