



Green Chemistry Principles Vis-a-Vis Healthy Practices for College Chemistry Laboratories

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ABSTRACT

Social and economic behaviour of the ever increasing human population has become a major hurdle in accomplishing the goals of UNEP. Government of India has framed key policies for adoption in the management of environment and natural resources. Supreme court of India, on its part, has made environmental education mandatory from KG to PG fostering sensitisation on environmental issues and motivation towards cleaner environmental goals in Gen.next. Green chemistry forms an integral part of UGC model curriculum for undergraduate colleges offering chemistry.

Chemistry education involves theoretical as well as experiential learning. Students pursuing chemistry at UG level are expected to understand theoretical concepts in the class room and apply the same in the laboratory experimentation. Experimentation sometimes involves use and generation of hazardous chemicals. The 12 green chemistry principles propounded by Anastas & Warner in 1998 are taught with suitable illustrations in the theory classes but seldom practised in college laboratories. Whereas Green Chemistry principles are of recent origin, laboratory procedures adopted for experimentation are age old. The Greener experimental procedures developed by the DST task force committee are still in oblivion. We preach but we do not practice.

This paper aims to indentify and highlight adoptable economic, ergonomic and ecofriendly laboratory practices which are in compliance with the 12 green chemistry principles, fostering heightened efficacy in teaching and practicing green chemistry for accomplishing greener environmental goals.

KEYWORDS : Green Chemistry principles, economic, ergonomic, ecofriendly, laboratory practices.

Introduction

The Earth is the only planet known to be supporting life. It, therefore, is mandatory for all of us to live in harmony with Earth supporting systems and life forms. The Earth's supporting systems and life forms constitute its environment. Environment is the first victim of poorly conceptualized and haphazardly implemented devolvement initiatives. But conservation and protection of environment have been an inseparable part of Indian heritage and culture. Green Chemistry involves Design of chemical products and processes that reduce or eliminate the use or generation of substances hazardous to humans, animals, plants, and the environment.

The UNEP guidelines are relevant to present and future multilateral environmental agreements and cover a broad range of environmental issues such as (a) global environmental protection (b) management of hazardous substances and chemicals (c) prevention and control of pollution and desertification, (d) management and conservation of natural resources, biodiversity and wildlife and (e) environmental safety and health, in particular human health. But social and economic behaviour of the ever increasing human population has become a major impediment in achieving the goals of UNEP. The constitutional provisions in India insist on the importance of safeguarding and sustaining environment quality. Article 51A of Indian constitution states that "It shall be the duty of every citizen of India to protect and improve natural environment, including forests, lakes, rivers and wild life and to have compassion for living creatures". Supreme court of India, on its part, has made environmental education mandatory from KG to PG fostering sensitisation on environmental issues and motivation

towards cleaner environmental goals in posterity. Green chemistry is made an integral part of UGC model curriculum for undergraduate colleges (offering chemistry) with an objective to highlight the importance of green chemical procedures for sustainable growth from UG level itself.

Green Chemistry is defined as invention, design, development and application of chemical products and processes to reduce or to eliminate the use and generation of substances hazardous to human health and environment. The 12 green chemistry principles propounded by Anastas & Warner in 1998 are taught with suitable illustrations in the theory classes in many colleges across India. Whereas Green Chemistry principles are of recent origin, laboratory procedures adopted for experimentation are age old.

Scope of the paper

Our future challenges in resource, environmental, economical, and societal sustainability demand more efficient and benign scientific technologies for working with chemical processes and products. Green chemistry addresses such challenges by inventing novel reactions that can maximize the desired products and minimize by-products, designing new synthetic schemes that can simplify operations in chemical productions, and seeking greener solvents that are inherently environmentally and ecologically benign. Together, such fundamental innovations in chemical sciences will lead us to a new generation of chemical syntheses.

We preach green chemistry principles in classrooms but we do not

practice them in our college laboratories. Several Greener experimental procedures have been developed by the DST task force committee for college chemistry laboratories. But they are still in oblivion. Green chemistry experiments are introduced not to drastically replace the conventional ones, rather they can be considered complementary to the existing protocols. These principles not only provide a wider view of various ergonomic and ecofriendly laboratory techniques but also imbibe inquest in innovative minds for future development and growth which is both sustainable and eco friendly.

Experimentation is an integral part of teaching-learning chemistry. Chemistry laboratories, apart from contributing to experiential learning, are also sources of in house pollution at a formidable level. Chemistry laboratories should continue to exist in harmony with the environmental imperatives of the land and also endeavour to forge forward by adopting the traditional conservation ethos. College chemistry laboratories cater to the learning needs of large number of students which implies chemicals usage on a large scale. It is, therefore, very much essential to propagate as well as practice green laboratory procedures to minimise the pollution generated by chemistry laboratories. Including new greener experiments in syllabi or substituting the procedures for the existing experiments with greener ones promulgated by DST monograph can contribute a lot to minimising pollution caused by chemistry laboratories. Wherever possible and feasible, the conventional procedures should be replaced with the greener ones. An attempt is made in this paper to highlight greener practices applicable for college chemistry laboratories with an objective to promote ecofriendly experiential learning. The objective of this paper is to suggest simple, ecofriendly and adoptable amendments to the existing hazardous laboratory practices and procedures, with an aim to contribute to the accomplishment of the greener goals of UNEP.

The following is the list of the twelve Green Chemistry principles and green laboratory practices/procedures in compliance with those principles. These can be adopted at college level so as to make college chemistry laboratories less polluting and more ecofriendly.

Prevention

It is better to prevent waste than to treat or clean up waste after it is formed. Distillation and determination of melting and boiling points are experimental tasks for UG and PG students. These students while conducting their practical can simultaneously demonstrate the same to junior students. This 'Teach while you learn' practice involving demonstration by senior students to junior students can help in reducing fuel and chemical wastage. It is also advisable to demonstrate experiments to junior students with computer simulations where ever possible. Water used for cooling and condensation can be collected in large drums and re-circulated with the help of small motors. This reduces wastage of water.

Atom Economy

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product. Preparation of Acetanilide is a mandatory task for all students pursuing chemistry at UG level. Acetanilide is normally prepared in laboratories by treating aniline with acetic anhydride and dichloromethane in the presence of pyridine. But this method involves use of dichloromethane and pyridine which are not ecofriendly. The alternative greener procedure developed by DST task force advocates the use of Zinc dust and glacial acetic acid. This method is atom economic and more ecofriendly when compared to the traditional method. For the purpose of bromination, tetrabutylammonium tribromide can be used selectively in place of the hazardous bromine liquid.

Less hazardous Chemical synthesis

Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment. In qualitative organic analysis the preparation of a derivative of the identified organic compound is required for confirmation of its identity. For carboxylic acids the most common derivative is amide and acetanilide which are prepared through acid chlorides by treatment with phosphorus pentachloride or thionyl chloride which are highly toxic. Thus, an alternative method for preparation of a solid derivative of carboxylic acids avoiding these toxic chemicals is highly desirable. The N-benzyl benzamide can be a

good alternative and it can be prepared in a greener way as well. For methylation purpose dimethyl carbonate can be used as a substitute for hazardous dimethyl sulphate and methyl halides. Direct use of H_2S from Kipp's apparatus can be avoided by using saturated solutions of H_2S in water from an air tight dropping bottle.

Designing Safer Chemicals

Chemical products should be designed to preserve efficacy of the function while reducing toxicity. It is highly advisable to carry out spot tests for acidic and basic radicals of salts using spot plate/ filter paper/micro test tube by adopting the procedures suggested in the DST monograph. Tests involving Hg, As, Cd, Pb, Bi and Cr should be avoided at UG level. PG chemistry students can perform spot tests with them and demonstrate to UG students.

Safer solvents and Auxiliaries

The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous. For determination of distribution ratio between polar and non polar solvents carcinogenic organic solvents like benzene and CCl_4 should be avoided. Instead Toluene or acetic acid in butanol can be used. Liquid bromine is a highly toxic and hazardous laboratory reagent. It is commonly used as a brominating agent. It can be replaced by tetrabutylammonium tribromide which is a green brominating agent.

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. Burners should be regularly maintained to avoid fuel wastage. Water baths/oil baths and burners and heating mantles should be so designed as to facilitate usage by a group of students at a time. Using manual centrifuge machines in place of electrical ones can reduce the consumption of electricity.

For quantitative measurements lower concentrations and lesser volumes should be deployed. Micro burettes (10ml) and graduated pipettes along with 10ml and 5ml volumetric flasks can go a long way in reducing chemicals usage. Where ever possible instrumental and chromatographic methods of analysis should be adopted from the UG level itself, because these methods, apart from being error free, require chemicals in very low concentrations and have no negative influence on health or environment. Students could be grouped into batches of 4 to 6 and given a collective task (of analysis or synthesis) in minimised amounts. This would minimise chemical usage as well as promote cooperative learning among students.

Use of Renewable feed stocks

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical. Reusing reduces solid waste and production stage pollution. It reduces the demand for material as well as energy resources. It can also dissuade us from the 'use and throw' culture. Worn out rubber tubes of gas connections can be reused for water connection to condensers and suction pumps.

Organic and Inorganic compounds synthesized by students can be collected and utilised for analysis tasks. S - Benzylisothiuronium-chloride, Acetanilide, Methyl Orange, Benzoic acid and Nitrobenzene synthesized as part of the organic compound synthesis practical can be reused in Organic analysis as well as for derivatisation of functional groups. Residue generated during the preparation of sodium carbonate extract for the purpose of identification of anions can be reused for identification of cations. Also borax bead test and flame test should be practised extensively to identify the basic radicals. The acid wash obtained during preparation and solvent extraction of Nitrobenzene can be used for cleaning porcelain surfaces.

Reduce derivatives

Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible. Derivatization of functional groups is done to confirm the identity of the functional group. This can be avoided if students are trained to follow the TLC behaviour of compounds instead.

Catalysis

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents. In the synthesis of 2-Phenylbenzothiazoles from 2-Aminothiophenol and benzaldehyde ionic liquid, 1-Phenyl-3-methylimidazolium bromide can be used as catalyst as well as reaction medium thus avoiding the usage of other solvents. This ionic liquid, [pmlm]Br is benign and works here as catalyst as well as reaction medium and thus no other solvent is required in this reaction. The reaction is also atom efficient.

Design for degradation

Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products. The synthesis of biodiesel from vegetable oil- This experiment focuses on synthesis of diesel fuel from vegetable oil. The mechanism involves a transesterification reaction, the process of transforming one type of ester into another type of ester. In this transesterification reaction, vegetable oil is the renewable feedstock and the product is environment friendly biodiesel.

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. For qualitative analysis shifting from macro analysis to semi micro and micro analysis helps in minimising use as well as generation of toxic chemicals. Students should be encouraged to use lesser quantities of chemicals for analysis as well as synthesis tasks. Spot tests must be introduced for detection of acidic and basic radicals in salts because this brings down the usage of reagents and is cost effective as well. This also minimises the wastage due to spillage into water baths and burners. PCl_5 , PCl_3 , POCl_3 and SOCl_2 are proven toxic chemicals. They are used in the synthesis of acid chloride from acid. Instead the acid can be converted to anhydride and reacted with ethylchloroformate and thus the usage of PCl_5 , PCl_3 , POCl_3 and SOCl_2 can be avoided.

Inherently Safer Chemistry for Accident Prevention

Substances used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires. Extra elements (like N, S, Cl, Br, I) present in organic compounds can be detected by using an intimate mixture of Na_2CO_3 and Zn dust in place of Na metal. This procedure eliminates the risk of explosion due to Na metal. Sufficient number of exhaust fans and

fume hoods in good working condition should be made available in the laboratory. It is advisable to conduct experiments with fume hood reagents in the fume hood itself.

Laboratories need to be properly ventilated and well maintained to minimise accumulation of toxic fumes for longer periods of time. At least one or two windows, protected with a mesh, should be left open during vacation. Instructions pertaining to good laboratory practices and standard operating procedures (for instruments) along with do's and don'ts in the laboratory should be prominently displayed in the laboratory. Based on their levels of toxicity, laboratory reagents can be indexed and segregated into bench, rack and fume hood reagents and placed accordingly. It is important to sensitise and make students aware of their respective hazardous effects as well. Corrosion due to accumulation of acidic fumes can be minimised by replacing metal, plastic and rubber with wood, glass and porcelain to the extent possible. Unavoidable metal and rubber surfaces can be protected with suitable coatings. Gas taps, water taps and electrical gadgets should be put off, immediately after use. Laboratory fumes can be avoided reducing usage of concentrated mineral acids and storing liquor Ammonia in air tight bottles.

Conclusions

Green procedures highlighted in this paper can be readily adopted because they do not involve usage of sophisticated equipment or expensive chemicals or longer reaction times. These procedures and practices can be readily practiced. They can be popularised by conducting training workshops to chemistry teachers and laboratory support staff. This can prove to be an effective intervention strategy to address the problem of pollution from college chemistry laboratories. These training workshops can aim to inform teachers about green laboratory procedures and inspire them to adopt these in their practical teaching classes (in their own as well as others' interest). These teachers can in turn transmit this information to students and involve them in the implementation of these greener practices and thus impact their mind set and inculcate greener habits in them. Students can gain Knowledge on green laboratories procedures and then aim to solve the problem of non green laboratory procedures by applying the gained input for synthesizing new greener procedures as well. This will ultimately result in not only preaching but also practicing green chemistry principles

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