



## Sustainable Green Chemistry for Better Living: A Challenge of 21<sup>st</sup> Century

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### ABSTRACT

*Prevention is better than cure is the principle to introduce the term Green Chemistry. In the period of 1980s and 1990s, several environmentally conscious terms entered the chemical arena, e.g., clean chemistry, environmental chemistry, green chemistry, benign chemistry and sustainable chemistry. United state environmental agency (US-EPA) coined the term green chemistry which is an environmentally benign chemistry. It involved the philosophy of chemical research and engineering that encourages the design of products and processes that minimized the use and generation of hazardous substances. Click chemistry is often cited as a style of chemical synthesis that is consistent with the goals of green chemistry. The focus is on minimizing the hazard and maximizing the efficiency of any chemical choice. It is distinct from environmental chemistry which focuses on chemical phenomena in the environment. Over the past decades there has been a growing awareness on the adverse impact of chemical processes on the environment. According to Manley et.al. (2008), this is the joint responsibility of every human being to understand how to foster innovation to proliferate green chemistry and to design sustainability.*

**Key Words:** Green chemistry; Environment: Sustainability; Benign solvents; Future perspectives

### INTRODUCTION

As the natural resources are used up in the world, chemists and biotechnologists are being asked to come up with innovative ways in which renewable resources can be used to replace non-renewable ones. But there will continue to be a demand for some non-renewable resources. If we wish to make materials that use less resources today, we should try to minimize the amount of raw material that is incorporated in the object. As new materials are developed, new standards must be made to ensure fitness for the purpose of these materials. Analytical chemistry provides the means for ensuring that the material should meet the purpose for which it is designed. For this, green chemistry principles must be applied to the resources industry and raw material use. The concept of green chemistry though widespread in developed countries like US, needs to be implemented in India with a wider vision.

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<sup>1-3</sup> 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:

(a) An increasing awareness in industry of the importance of concepts such as waste minimization<sup>4</sup> and atom utilization<sup>5</sup>.

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(b) Greater involvement by governments in controlling the use of resources and the productive disposal of waste.

(c) Emergence of other underpinning concepts as general principles which can be used in the conception and execution of synthetic chemistry and in the usage of chemicals produced.

The term green chemistry<sup>6,7</sup> describes an area of research arising from scientific discoveries about pollution and from public perception, in much the same way as the identification and understanding of a deadly disease stimulating the call for a cure. This term, which was coined at the Environmental Protection Agency (EPA) by Paul Anastas, represents the assumption that chemical processes that carry environmental negatives can be replaced with less polluting or non-polluting alternatives. Green chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products, associated with a particular synthesis or process. Thus chemists can greatly reduce risk to human health and the environment. History of green Chemistry:

Before 1998, alternative terms like clean chemistry, benign chemistry, environmental chemistry were frequently used for these studies. But after 1998, the use of green chemistry has clearly been growing rapidly in a linear fashion. Catechart (1990) was probably the first chemist who used the term in the title of his article. Catechart discussed the advantages and disadvantages of the significant growth of the Irish Chemical Industry. In 1996 other pioneer workers like Anastas, Wulliams and Warners had published articles on Green Chemistry., An overview in Green Chemistry: Designing Chemistry for the Environment. This publication presented a green chemistry philosophy. They commented that " Knowledge" is a driver for the growth of green chemistry.

But still there are many viewpoint. Leitner (1999) argued that clean chemistry, green chemistry and sustainable chemistry are the same. Recently a comparable opinion was put forward during the 1<sup>st</sup> meeting of the working party on green and sustainable chemistry (European Association for Chemical and Molecular Sciences) on 28<sup>th</sup> February 2008 about the prefixes sustainable and green. As far as prefixes are concerned, members of the working party on green and sustainable chemistry commented that " No consensus in scientific community" ( Tundo 2008).

Moreover Winterton (2001) mentioned that he is not certain that all "*Chemistry that calls itself green is necessarily going to lead to pollution prevention*"

If we look on the historical development on this issue, we can divide the development into 3 periods.

1. First period: No formal starting point, but roughly ends in 1993.
2. Second period: From 1993-1998.
3. Third period: From 1999- till date.

Rachel Carson (1962) introduce her agenda for protection of the environment with her article "Silent Spring". From then gradually, politics got involved. US President Mr. Nixon in 1970 introduced US Environmental Protection Agency (US-EPA). US-EPA adopted a command and control policy on the execution of environmental regulation. In 1990, US Congress passed the "Pollution Prevention Act of 1990 under the administration of US President George H W Bush. The findings of the US-congress outline that there was a shared interest of US-EPA and chemical industries to cooperate and meet environmental and economic goals.

### **PRINCIPLES OF GREEN CHEMISTRY**

Anatas and Warner in their book, Green Chemistry: The Theory and practice, Oxford University Press Inc., New York (1998), p-30 (1998) present a green chemistry philosophy which is commented that it "has been driven by new knowledge".

There are 12 principles of green chemistry toward ideal synthetic methods to save natural resources.

1. Prevention: It is better to prevent waste than to treat or clean up waster after it has been created.  
It refers to "zero" waste technology, i.e., the waste product from one process may be used as raw materials from other process, so that waste production may be minimized or eliminated.
2. Atom Economy: Synthetic methods should be designed to maximize the incorporation of all materials used in the process in the final product.

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The objective behind this principle is to minimize by products in chemical transformation and reaction sequence. In other words it deals with the maximum incorporation of the reactant molecules into the final product which gives rise to the concept of atom economy.

Atom economy may be defined as % atom economy =

$$\frac{\text{(Formulation wt of the product)}}{\text{(Sum of formula wt of all the reactants)}} \times 100$$

Thus atom economy is a very useful tool to minimize the environmental pollution level for the welfare of human and other living organisms.

3. Less hazardous chemical syntheses: Wherever practicable, synthetic methods should be designed to use and generate substances that process little or no toxicity to human health and environment.

It emphasizes 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 technologies tools. If any hazardous waste is produced, the chemistry should be designed to nullify the effect of the same on living organisms including human beings.

4. Designing safer chemicals: Chemical products should be designed to effect their desired function while minimizing their toxicity.

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

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

In many processing and manufacturing units use of auxiliary substances in different steps can be avoided by exploring alternative methods of manipulation of auxiliary substances with water, so that the waste products will be less or non-toxic. If there is no option for using water as solvent, alternative methods may be developed for solventless reactions.

6. Design for energy efficiency: Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

This principle gives rise the concept of "green energy". It looks for the alternative ways to save energy or increase energy efficiency of the system or produce energy from the waste products and use of the same for synthetic processes. The energy demand for a synthetic process depends on various factors such as starting materials, solvent used and the reaction pathways and manipulation of these factors may requires lesser energy than usual. For this purpose microwave assisted reactions increased the yield, purity and decrease the reaction time.

7. Use of renewable feed stocks: A raw material of feedstock should be renewable rather than depleting whenever technically and economically practicable.

Over exploitation of non-renewable resources causes the depletion of natural resources drastically giving rise to non-sustainability of resources. Sustainability means to ensure that future generation will have the opportunity to use their fair share of resources and will inherit a quality environment. Thus more importance should be given on use of renewable resources rather than non-renewable. Use of renewable resources such as agricultural or biotechnology products are advantage able as it gives biodegradable process waste which generally not create any environmental problems.

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 wastes.

Especially in organic chemical synthesis, various blocking agents are used to get desired product which ultimately causes less atom economy and generation of more waste products which may be toxic. In some cases salts or their derivatives are used to alter the physical properties like viscosity, surface tension, water solubility etc. of the reactants to carry out desired processing. After completion of the reaction, these salts or their derivatives are obtained as waste product which would be a threat to the environment.

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

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Catalysts provide alternative pathway to a reaction which makes the reaction faster and less energy consuming. It results 100% atom economy as catalysts are recoverable after completion of reaction without alteration in its physical and chemical properties. Catalytic reaction also give better results than normal synthetic reaction. Thus catalytic reactions are more preferable.

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.

This principle broadly suggests that the waste product or by product from any chemical synthesis process should be biodegradable. Non-biodegradable or calcitrant chemicals remain in environment for a longer period of time and they may have detrimental effects on ecological systems. Sometimes, the degradation product from biodegradable substances also possesses toxicity potential. So proper investigations should also be carried out on toxicity of degradation products.

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.

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

12. Inherently safer chemistry for accident prevention: Substances and the form of a substances used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases of poisonous gases, explosions and fires.

Sometimes the gaseous reactant materials may become responsible for accidents in manufacturing/processing plants as they are susceptible to explosion. Thus the processing units must be designed to replace the gaseous feed materials with liquid or

### **CHEMISTRY IN DAY TO DAY LIFE**

#### **ZINC REMOVAL WITH OLD NEWSPAPERS**

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  $\text{NaHCO}_3$  (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

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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 flocculants with performance close more established flocculants such as  $K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$  (potash alum). The findings of the study were published in December (2007) issue of *Bioresource Technology*.

### **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 method uses  $H_2O_2$  (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 a cheap, abundantly available seaweed, *Sargassum wrightii*. The seaweed added to a chrome tanning solution fully removed the heavy metal in 6hours. A maximum uptake of 35 mg of Cr/gm of seaweed was reported. Later, the chrome-loaded seaweed were used to make  $Cr_2(SO_4)_6$  (chromium sulphate), which is a major tanning agent as reported in journal *Environmental Science and Technology vol.38, No.1,2004*. These methods are of special significance to the small and medium leather enterprises due to the cost effectiveness and environmental sustainability.

### **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 per cent 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, Vol.31, No.1&2, 2008*. Some other plants and plant products too have been used to clean wastewater. *Erythrodontium barteri*. a moss, removes 97 per cent of Cu from wastewater, says study done at OOU in Nigeria, published in the *International Journal of Physical Sciences, Vol.2, No. 11, 2008*. The biomass waste traps all the positively charged heavy metal ions, the study explains.

### **NEW CARBON-BASED NANOTUBE FILTER CLEANS DRINKING WATER, PETROLEUM TOO**

A team of Indian and US researchers has created a tiny filter, which is entirely made of C-atoms and has several applications ranging from sieving out the minutest germs in drinking water to filtering unwanted HCs in petroleum products. The cylindrical filter that has been prepared by the NY-based RPI and India's BHU is made of C-nanotubes strong enough withstanding high temperatures. [SMALL WONDER: these nanotubes belong to the third crystalline form i.e. fullerene of carbon, unknown till the mid-1980s. Till then, graphite and diamond were the only know crystalline forms of carbon. These nanotubes, which are only a few nanometers wide (1/10,000<sup>th</sup> the width of human hair), and bearing length millionx greater than their width, are a 1000x stronger than metals like Ag and Cu and 6x lighter than steel. They can also withstand very high temperatures. It was unknown C-fibres were hollow untill Japanese researcher Sumio Lijima's invention in 1991. Since then, scientists all over the world have been trying to develop products employing this wonder material.] Scientists led by Pulickel M Ajayan of RPI and P N Srivastava of BHU found a solution to the problem of the size of the carbon tubes by devising a method to make large-scale structures. A solution of  $C_6H_6$  ferrocene – materials needed to assemble C- nanotubes – into a stream of Ar gas and then sprayed the entire mixture into a quartz tube located inside a furnace maintained at 900°C. As a result of the spray, dense forest of C-nanotubes formed on the inner walls of the quartz tube, yielding a hollow black cylinder several centimeters long and up to 1cm in

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diameter. The cylinder had been carefully removed which now consists of trillions of nanotubes. Each nanotube was only a few hundred  $\mu\text{s}$  long, essentially the thickness of C-cylinder's wall.

In the article Carbon Nanotube Filters authored by Ajayan (September 2004 issue of the Journal *Nature Materials*), manufacture and application of such filters and the way to spray well-ordered nanotube structures directly onto a substrate had been well discussed. Practicability: one end of the cylinder was sealed and flowed petroleum through the other. Separation of heavier and complex HCs from crude oil, which is an important step in purifying gasoline, was achieved. Also, the filter was found to separate E Coli- a bacterium responsible for intestinal ailments and poliovirus, which is at least  $100\times < \text{E Coli}$  present in contaminated water, effectively. The high surface area of nanotube membranes, the cheaper cost of manufacturing them and the fact they can be cleaned by easy means may make them competitive with ceramic-and polymer-based membranes used commercially. There is utmost need of a cost effective and robust nanotube assembly for filtration, most simple problem that nanotube can solve. By adjusting the size and flow of the nozzle, it's possible to define the geometric structure of the nanotube form.

#### **CHEAPER METHOD EMPLOYING GLUCOSE AND ENZYMES TO FILTER WATER**

Removal of organic toxins from groundwater requires chemical additives, which are expensive and environmentally hazardous. Now researchers at the University Kentucky in UK have developed a novel technique to breakdown such contaminants. The new purification system uses two highly porous membranes to generate purifying hydroxyl radicals. Till now organic compounds were degraded using Fenton reactions – a method based on the concept that some metals like iron have a strong catalytic power to generated highly reactive hydroxyl radicals. The radicals react with, and ultimately degrade, the organic impurities. Other than the use of chemicals the process also requires acidic conditions. This approach immobilizes the iron in a membrane pore and thus reaction can be carried out at near neutral pH conditions. The new device has two porous, micro-filtration membranes. To purify water, glucose is added to it and then passed through the first membrane. Here an enzyme – glucose oxidase – converts the glucose to hydrogen peroxide. In the second membrane hydrogen peroxide reacts with the iron, and thus purifies the water.

The details of this remediation system were published in the April issue of *Proceedings of the National Academy of Sciences*. "The concept has been developed for organic detoxification, but can be extended for disinfection and virus inactivation", says Dibakar Bhattacharya, one of the authors of the study. The researchers say as the level of hydrogen peroxide in the filter can be controlled, and because iron is trapped in the membranes, no additional chemicals need to be supplied. The operating cost of purification is estimated to be about seven cents per 1,000 litres. The energy cost is also low since highly porous microfiltration membranes; the materials are commercially available. In contrast to commercial membranes that reject impurities, in this purification system pollutants are allowed the reactants to convert contaminants to non-toxic end products. Reviewing the purification system, Pawan Labhasetwar, researcher at the NEERI, says the technology can be used in India. But several factors such as membrane fouling (accumulation of unwanted materials), filtration efficacy, inlet water characteristics and their impacts on the system must be studied in detail.

#### **GREEN DRY CLEANING OF CLOTHES**

Perchloroethylene (PERC)  $\text{Cl}_2\text{C}=\text{CCl}_2$ , 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, Timonthy Romack, and James Clain made use of liquid  $\text{CO}_2$  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  $\text{CO}_2$  and a surfactant, thereby eliminating the need of halogenated solvents [2].

#### **VERSATILE BLEACHING AGENT**

It is common knowledge that paper is manufactured from wood (which contains about 70% polyssacharides 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  $\text{Na}_2\text{S}$  (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  $\text{Cl}_2$  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

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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 [3] 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 water [3].

### **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 copolymers 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.

### **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 upcycling – 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, Illinois, USA, this method is called "re-mediation". gram pieces of high density or low density polyethylene are heated at  $700^{\circ}C$  for two hours in the presence of a catalyst, cobalt acetate [ $(CH_3COO)_2Co$ ] 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 nano tubes 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 cellphone 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  $\mu m$  carbon bodies, which have applications in printers, toners, filtration technology and the pain and tyre technology.

### **BACTERIUM DECONTAMINATING SOILS AND GENERATING ELECTRICITY FROM MUD AND WASTE**

Fuel cells which use microorganisms to convert chemical energy to electrical energy are seen as one of the future source of clean power. Microbes' capacity to extract electricity from mud and wastewater, have been known by various researchers. Dereck Lovley and teammates from the UM, USA, found the microbe, Geobacter, which absorbs metals from the soil (bioremediation) for its metabolism, in the sediments of Potomac River, in the US in 1987. In 2002, another ability of Geobacter was stumbled, having the potential to generate electricity. After some thorough studies, the reason has been traced in 2005. The conductive pili or hair-like filaments located on the surface of the cell were found to transfer electrons from the metals absorbed. The geobacter was grown on a graphite electrode; provided an organic substrate (-acetate) as food allowing a biofilm to develop. Then a 400mv current was passed through the electrode. This induced Geobacter to transfer electrons and generate power. Gradually Lovley's team witnessed the growth of a new strain of the microbe that dramatically increased the transfer of electrons and the power output up to 8 times.

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The findings reported in the August issue of *Biosensors and Bioelectronics*, open the door to improved microbial fuel cell architecture. As a conservative estimate, the output was increased 8-fold, breaking through the plateau in power generation that has been holding back in recent years. Now there is a whole range of applications that microbial fuel cells can be put to: converting waste water and renewable biomass to electricity, treating a single household's waste for producing electricity powering the house, mobile electronics, vehicles and bioremediating contaminated environments. In 2007, the UC, in Australia, designed a microbial cell in collaboration with FBC, with a 10L capacity, converting the brewery's waste into clean water and electricity.

### **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 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.

### **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.

Sheela Berchmans of CERl 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 *Bluconobacter roseus* – can spoil wine. These researchers at CERl 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.

### **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. The findings were released in the February (2009) 5 issue of *Nature*.

### **PLATINUM FREE FUEL CELL**

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.



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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/cm<sup>2</sup> 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 colourless 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. Geradine Botte of Ohio University uses an electrolyte approach 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 urea (NH<sub>2</sub>CONH<sub>2</sub>), 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," Botte added Chemistry World Journal. 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 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 bio-degradable 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.

### **INSTANT 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 per cent 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, 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 per cent as compared to 25 per cent 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 Al<sub>2</sub>O<sub>3</sub>. 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

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pressurised 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 byproducts solid aluminium with a liquid Ga core remain with water. By recycling this byproduct, 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.

### **CLEAN FUEL FROM SEWAGE**

Biofuels extracted from human waste will now replace petrol and diesel in buses across Oslo (Norway). The city's two sewage plants will crank out the bio-CH<sub>4</sub> (an environment-friendly, C-neutral renewable source of energy) from Bekkelaget sewage treatment plant. The new buses to be introduced by 2010 in the Norwegian capital will run on this biofuel, which is generated by fermenting sludge. Bio-CH<sub>4</sub> has been found to emit 78% less NO<sub>x</sub> and 98% fewer fine particles and is 92% less noisy. It's observed that by going to the wash room, a person produces the equivalent of 8L of diesel/year. Hence, the sewage from large number of houses, when converted to bio-CH<sub>4</sub>, can be used to operate as many as 80 buses for 100,000km each.

### **DIESEL FROM FUNGUS**

A reddish microbe found on the inside of a tree at a secret location in the rain forests of northern Patagonia could unlock the biofuel of the future. Its potential is so startling that the researchers have coined the term "mycodiesel" – a derivation of the word for fungus – to describe the bouquet of hydrocarbons that it breathes. "This is the only organism that has ever been shown to produce such an important combination of fuel substances," stated Gary Strobel (70 year-old veteran of the world's rainforests), a professor of biology at MSU. "The fungus can even make these diesel compounds from cellulose, which would make it a better source of biofuel than anything we use at the moment." The study appeared in a peer-reviewed British journal, *Microbiology*. It's established to come across *G roseum* thanks to "two cases of serendipity". The first was in the late 1990s, a previously unidentified fungus called *M albus* came across. By sheer accident, it was found that *M albus* releases a powerful VOC – meaning gassy- antibiotic. Intrigued by this, the team tested *M albus* on the ulmo tree, whose fibres are a known habitat for fungi, in the hope that this would show up a new fungus. Quite unexpectedly, *G roseum* grew in the presence of these gases when almost all other fungi were killed. It was totally surprised to learn about making a plethora of HCs and HCs derivatives, when gas composition of *G roseum* was examined. Biofuels have been promoted as good alternatives to oil, which is sourced from politically volatile regions and is a major contributor to the GHE.

### **UNCONVENTIONAL WASTEWATER TREATMENT STRATEGIES**

#### **ZINC REMOVAL WITH OLD NEWSPAPERS**

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 NaHCO<sub>3</sub> (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 flocculants with performance close more established flocculants such as  $K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$  (potash alum). The findings of the study were published in December (2007) issue of *Bioresource Technology*.

### **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 method uses  $H_2O_2$  (Hydrogen peroxide) with a zeolite (a porous substance) and organic Cu-complex based catalyst to remove Cr (VI). This process removes Cr  $\sim 5x$  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  $60^\circ C$ . Studies on commercial tannery wastewater, indicates that the catalyst can be recycled without any large change in its efficiency. The second method uses a cheap, abundantly available seaweed, *Sargassum wrightii*. The seaweed added to a chrome tanning solution fully removed the heavy metal in 6hours. A maximum uptake of 35 mg of Cr/gm of seaweed was reported. Later, the chrome-loaded seaweed were used to make  $Cr_2(SO_4)_6$  (chromium sulphate), which is a major tanning agent as reported in journal *Environmental Science and Technology vol.38, No.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 carryout 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 per cent. P removal increased from 55.6 to 63.3 per cent and up to 80.4 per cent 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 shells 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 per cent 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*, Vol.31, No.1&2, 2008. Some other plants and plant products too have been used to clean wastewater. *Erythrodontium barteri*, a moss, removes 97 per cent of Cu from wastewater, says astudu done at OOU in Nigeria, published in the *International Journal of Physical Sciences*, Vol.2, No. 11, 2008. The biomass waste traps all the positively charged heavy metal ions, the study explains.

### **BRAND NEW FRIENDLY BUGS TO TREAT EFFLUENT**

Researchers from NEERI have discovered hundreds of hitherto untapped friendly bacteria from CEPS. This could completely revolutionise the way industries currently treat their wastewater. It would also help create a valuable metagenomic library of 'good bacteria' for everyone to use. CETPs, the biological wastewater treatment facilities, receive inputs from variety of industry. About 25 to 30 different kinds of bacteria work as a community and biodegrade the thousands of harmful chemicals in this wastewater. While genomics experts have extensively explored soil microbes, a very few studies have been carried out to map microbes responsible for converting harmful compounds into harmless ones. Such studies assume importance because CETP sludge receives wastewater from different industries with individual market-driven demands. Exploiting the 'over-looked' genetic resources might revolutionise methods used to degrade recalcitrant and xenobiotic pollutants that do not get degraded by known culturable bacteria. The team detected a total of 76 culturable and over 200 unidentified strains. Strains to identify antibiotics that could kill certain bacteria in microbial ecosystem will also be studied.

### **GREEN CHEMISTRY IN INDIA**

The green chemistry wave has reached our country too. We need to work for its betterment by encouraging the practices of green chemistry. Collaborations between industrial and academic partners are important to expedite the transfer of significant green products to the Market place. For such collaborations to be successful, individuals in these two differently motivated cultures need to work together to advance green science. Governments could undoubtedly facilitate formation of more effective industrial/academic partnerships. Under an agreement with the Green Chemical Institute, University of Delhi has been accepted as an international chapter. The Indian chapter will promote green chemistry through education, information collection and dissemination, research and international collaboration via conferences, workshops, meetings and symposia.

### **PERSPECTIVE AND FATE OF GREEN CHEMISTRY**

For the promotion of green chemistry, it's imperative to create a brand of green thinkers. Green chemistry should be of upfront consideration. Scholars of all levels must be made aware of the introductory ethics and philosophy of green chemistry. Educators should possess procedures and methodologies and need to equip themselves with training material, tools and similar infrastructures besides collaborations. For a successful implementation more and more green-school programmes as is run by CSE, New Delhi, must be created. Support in terms of tax incentives and awards for promoting green ideas. Information, technologies transfer and approaching beyond sustainability would be welcome step in promoting the green chemistry.

Green Chemistry has the potential of wiping out the possible occurrence of tragedies like Bhopal Gas by paving way for safe eco-friendly environment. There is utmost need to emphasize on

creating awareness about green chemistry not only amongst the chemists and scientific community but also industries and commercial institutions. Leading countries like USA, UK, Japan, Italy, Australia and other developed nations have given green chemistry top priority with a view to safeguarding their environment and economic interests. In India, it's in the inception stage and has assumed rapid strides embracing catalysis, benign solvents, renewable feedstock, green nanomaterials, biodegradable polymers and others. Educating the next generation of researchers and training in green techniques occupies a central theme in the outreach activities.

#### ABBREVIATIONS

HTP: Highthroughput; FG: Flue Gas; CFP: Carbon Foot Print; UT: University of Tokyo; UM: University of Massachusetts; UC: University of Queensland; FBC: Fosters Brewing Company; MCD: Municipal Corporation of Delhi ; UE: University of Edinburgh; IPMA: Indian Paper Manufactures Association; KAISTU: KAIST University; PLA: Polylactic Acid; MSU: Montana State University; ANL: Argonne National Laboratory; PSU: Penn State University; CERI: Central Electrochemical Research Institute; SECEPU: School of Electrical and Computer Engineering of Purdue University; CLRI: Central Leather Research Institute; LU: Lehigh University; TU: Tongji University; OOU: Olabisi Onabanjo University; NEERI: National Environment Engineering

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