

THE BIOSPHERE: HOW THE REVOLUTION IN BIOLOGY RELATES TO GREEN CHEMISTRY

Dr. Sunil Chachere

Associat Professor

Head of Chemistry Department

Dnyanesh mahavidhyalaya, Navargaon

Tah. Sindhewahi Dist. Chandrapur

Abstract :

GREEN CHEMISTRY AND THE BIOSPHERE :

The biosphere consists of all living organisms and the materials and structures produced by living organisms. There is a very close connection between the biosphere and green chemistry including the following:

- Living organisms produce a wide range of materials that are used by humans for a variety of purposes.
- Large quantities of substances including pesticides and fertilizers are generated in the anthrosphere for use to control pests and enhance the growth and health of organisms in the biosphere.
- Reduction of the use and generation of toxic substances in the anthrosphere is designed to prevent harm to humans and other organisms in the biosphere.
- Environmental conditions largely determined by anthrospheric activities strongly affect organisms in the biosphere.

Individual organisms in the biosphere and organisms interacting in ecosystems can teach humans a lot about how to apply green chemistry. One important respect in which this is done is by the mild conditions under which organisms carry out complex chemical syntheses. Living things can function only within narrow temperature ranges that are close to those that humans find comfortable. (Even the 90-100°C temperatures under which thermophilic bacteria function in hot springs and similar locations are not very far from room conditions.) Therefore, the enzyme-catalyzed reactions that organisms carry out occur under much milder conditions than

the often high-temperature, high-pressure conditions of conventional chemical synthesis. Furthermore, organisms cannot tolerate

Hierarchical organization applies to living organisms from the level of atoms all the way to the biosphere as a whole. Proteins, carbohydrates, lipids, and nucleic acids in living organisms are organized into distinct microscopic bodies contained in cells and called organelles. Cells are bodies of several micrometers (μm) in size that are the basic building blocks of organisms in that they are the smallest bodies of organisms that can exist independently (even cells of humans can be grown in cell cultures outside the body, given the appropriate nutrients and conditions). Bacteria, protozoa, and some other kinds of organisms are single-celled, but higher organisms are composed of many cells which have specialized functions. Cells with similar functions comprise tissues and tissues in turn make up organs, which may be organized into whole systems of organs. An organism is a collection of organs and organ systems. A group of organisms from the same species comprise a population and a group of populations existing in the same place make up a community. Numerous communities living in a particular environmental area, interacting with each other and with their environment, make up an ecosystem. Finally, all Earth's ecosystems comprise the entire biosphere.

The process of metabolism is what occurs when organisms mediate chemical (biochemical) processes to get energy, make raw materials required for tissues in organisms or modify raw materials for this purpose, and reproduce. Although there are thousands of different metabolic reactions, two stand out. The first of these is photosynthesis shown in Reaction 9.3.1 in which plants use light energy to convert inorganic CO_2 and H_2O to glucose sugar, $\text{C}_6\text{H}_{12}\text{O}_6$. The second major type of metabolic reaction is the mirror image of photosynthesis, cellular respiration in which glucose is oxidized to CO_2 and H_2O , yielding energy that is used by the organism. An interesting aspect of the conversion and utilization of energy in metabolism is that all organisms use the high-energy chemical species adenosine triphosphate, ATP to transfer, convert, and store energy. Metabolism is addressed in more detail in Section

Genome Sequencing and Green Chemistry :

The Human Genome Project and related genome sequencing of other organisms have a number of implications for green chemistry. One of the key goals of green chemistry is to use chemicals that have maximum effectiveness for their stated purpose with minimum side effects. This certainly applies to pharmaceuticals in which a knowledge of the human genome may enable development of drugs that do exactly what they are supposed to do without affecting nontarget systems. This means that drugs can be made very efficiently with little waste material.

Some of the most important effects of DNA sequencing as it relates to green chemistry has to do with a wide variety of organisms other than humans. With an exact knowledge of DNA and the genes that it contains, it is possible to deal with organisms on a highly scientific basis in areas such as pest control and the biosynthesis of raw materials. An accurate map of the genetic makeup of insects, for example, should result in the synthesis of precisely targeted insecticides which kill target pests without affecting other organisms. Such insecticides should be effective at very low doses, thus minimizing the amount of insecticide that has to be synthesized and applied, consistent with the goals of green chemistry.

An exact knowledge of the genomes of organisms is extremely helpful in the practice of genetic engineering in which genes are transferred between species to enable production of desired proteins and to give organisms desirable characteristics, such as pest resistance. A number of medically useful proteins and polypeptides are now produced by genetically engineered microorganisms, most commonly genetically modified *Escherichia coli* bacteria. Perhaps the greatest success with this technology has been the biosynthesis of human insulin, a lack of which causes diabetes in humans. Two genes are required to make this relatively short polypeptide which consists of only 51 amino acids. Other medically useful substances produced by genetically engineered organisms include human growth hormone, tissue plasminogen activator that dissolves blood clots formed in heart attacks and strokes, and various vaccine proteins to inoculate against diseases such as meningitis, hepatitis B, and influenza.

GENETIC ENGINEERING :

Ever since humans started raising crops (and later animals) for food and fiber they have modified the genetic makeup of the organisms that they use. This is particularly evident in the cultivation of domestic corn which is physically not at all like its wild ancestors. Until now, breeding has been a slow process. Starting with domestication of wild species, selection and controlled breeding have been used to provide desired properties, such as higher yield, heat and drought tolerance, cold resistance, and resistance to microbial or insect pests. For some domesticated species these changes have occurred over thousands of years. During the 1900s, increased understanding of genetics greatly accelerated the process of breeding different varieties. The development of high-yielding varieties of wheat and rice during the “green revolution” of the 1950s has prevented (or at least postponed) starvation of millions of people. A technology that enabled a quantum leap in productivity of domestic crops was the development of hybrids from crossing of two distinct lines of the same crop, dating in a practical sense from the mid-1900s.

This section discusses the genetic modification of organisms to enhance their value. It addresses plants primarily because more effort has been made and more things have been accomplished in plant breeding than with other kinds of organisms. However, the general principles discussed apply to animals and other kinds of organisms as well.

Traditional breeding normally takes a long time and depends largely upon random mutations to generate desirable characteristics. One of its greatest limitations has been that it is essentially confined to the same species, whereas more often than not, desired characteristics occur in species other than those being bred. Since about the 1970s, however, the possibility has arisen of using transgenic technology to transfer genes from one organism to an entirely different kind. This has raised a vast array of possibilities for greatly modified species that could be applied to many different purposes. And it has led as well to a number of concerns regarding unintended consequences of the technology. Ideally, transgenic technology can be used beneficially in plant breeding to increase tolerance to stress, increase yield, enhance the value of the end product by enriching it in desired biochemicals such as essential amino acids, and

otherwise make plants more useful. Transgenic technology is possible because of the existence within cells of deoxyribonucleic acid, DNA. This long-chain biological polymer directs cell reproduction and metabolism as discussed in Section 9.7.

Transgenic technology is possible because a gene in DNA will make the protein for which it is designed in an organism that is quite different from the one in which the gene originated. So a gene transferred from one organism to another as a segment of DNA will often perform the function for which it was developed in the recipient organism. The details of how segments of DNA are transferred between organisms are beyond the scope of this work. Enzymes are used in the process, with restriction enzymes cutting out desired regions of DNA and ligase enzymes joining the ends of DNA together. Enzymes are used to further manipulate and amplify the DNA.

Perhaps the most difficult aspect of transgenic technology is identifying the genes responsible for desired characteristics and locating them among the millions of repeating units comprising the DNA strand. In addition to identifying specific genes, it is necessary to learn how they interact with other genes and the mechanisms by which they are regulated and expressed, the process by which a gene generates a specific protein.

After a specific gene is isolated, it is cloned by insertion into a bacterium, which reproduces the gene many times. In order for a gene to generate a desired protein at the appropriate time and location in a plant, a promoter must be added that functions as a switch. The easiest promoter to use is a constitutive promoter that causes the gene to be expressed in most of the plant's tissues and throughout its lifetime. The most successful promoter for this purpose is designated CaMV35S, which is isolated from the cauliflower mosaic virus. Other more specific promoters have also been used, such as those that are induced by light and function during photosynthetic processes. Much of the current effort in transgenic technology is devoted to the use of specific promoters that cause the gene to be expressed only where and when its protein product is needed.

So far, two major methods have been used to insert genes into a plant cell. The gene gun uses a very small projectile to literally shoot genetic information into cells. This method has been

used with monocot (“grassy”) species including corn and wheat. It suffers from a low percentage of “hits.”

The most widely employed method of gene insertion is the Agrobacterium method widely used on dicot (broadleafed) species, such as potatoes and soybeans, and more recently adapted to monocots as well. This method uses a bacterium that thrives in soil called Agrobacterium tumefaciens (the cause of crown gall disease in plants), which infects plants, using the plants’ metabolic processes for its own reproduction. The mechanism by which Agrobacterium is used to insert genetic information into plant cells is complicated and not completely understood. The bacterium enters a plant through a wound in the plant stem or leaves. Somehow the DNA incorporated into the bacterium is transferred through plant cell protoplasm to the plant DNA. This process may occur when the plant DNA becomes uncoiled during cell reproduction.

Only a few percent of plant cells targeted for gene insertion actually incorporate and express the gene. Therefore, it is necessary to have some means of knowing if the gene insertion has been successful. This is accomplished by the insertion of marker genes that make plant cells resistant to herbicidal compounds or antibiotics that kill normal plant cells. Plant cells are placed in media containing the toxic materials, and those cells that reproduce are the ones into which the desired genes have been successfully inserted. Following selection of the viable cells that presumably contain the desired transplanted genes, the cells are grown in tissue cultures in the presence of growthpromoting hormones and nutrients required for growth. This leads to the production of whole plants that produce seeds. Additional plants are grown from these seeds and evaluated for the desired characteristics.

Once plants containing desired transgenes have been produced, an exhaustive evaluation process occurs. This process has several objectives. The most obvious of these is an evaluation of the transplanted gene’s activity to see if it produces adequate quantities of the protein for which it is designed. Another important characteristic is

BIOLOGICAL INTERACTION WITH ENVIRONMENTAL CHEMICALS :

Organisms in the environment interact significantly with xenobiotic materials (those foreign to living systems) in their surroundings. The uptake of such materials by organisms is discussed in this section. The biodegradation of xenobiotic substances, primarily through the action of bacteria, is discussed in Section 9.10. Bioaccumulation is the term given to the uptake and concentration of xenobiotic materials by living organisms. The materials may be present in water in streams or bodies of water, sediments in bodies of water, drinking water, soil, food, or even the atmosphere. Bioaccumulation can lead to biomagnification in which xenobiotic substances become successively more concentrated in the tissues of organisms higher in the food chain. This usually occurs with poorly degradable, lipid-soluble organic compounds. Suppose, for example, that such a compound contacts lake water, accumulates in solid detritus in the water, sinks to the sediment, is eaten by small burrowing creatures in the sediment, which are eaten by small fish. The small fish may be eaten by larger fish, which in turn are consumed as food by birds. At each step, the xenobiotic substance may become more concentrated in the organism and may reach harmful concentrations in the birds at the top of the food chain. This is basically what happened with DDT, which almost caused the extinction of eagles and hawks.

Fish that bioaccumulate poorly degradable, lipid-soluble organic compounds from water will lose them back to water if they are placed in an unpolluted environment. The process by which this occurs is called depuration. The time required to lose half of the bioaccumulated xenobiotic material is called the half-life of the substance.

The most straightforward case of bioaccumulation is bioconcentration, which occurs when a substance dissolved in water enters the body of a fish or other aquatic organism by passive processes (basically, just “dissolves” in the organism), and is carried to bodies of lipid in the organism in the blood flow. The model of bioconcentration assumes that the organism taking up the compound does not metabolize the compound, a good assumption for refractory organic compounds such as DDT or PCBs. It also assumes that uptake is by nondietary routes, including diffusion through the skin and

BIODEGRADATION :

Bacteria, fungi, and protozoa in the environment play an important role in biodegrading both natural materials and synthetic substances. These processes occur predominantly in water, in sediments in bodies of water, and in soil. Biodegradation is the process by which biomass from deceased organisms is broken down to simple inorganic constituents, thus completing the cycle in which biomass is produced from atmospheric carbon dioxide and from water by photosynthesis.

The biodegradation of substances in the environment by the action of enzymes in microorganisms can be divided metabolically into two categories. The first of these is the utilization by microorganisms of organic matter that can be metabolized for energy and as material to synthesize additional biomass. This is the route taken by microorganisms degrading biomass from other organisms, and to a lesser extent in the biodegradation of some xenobiotic materials. The second way in which microorganisms metabolize environmental chemicals is through cometabolism in which the organism's enzymes act upon the substances as a "side-line" of their normal metabolic processes. The substances that are cometabolized are called secondary substrates because they are not the main compounds for which the enzymatic processes are designed.

A commonly cited example of cometabolism occurs with the action of *Phanerochaete chrysosporium* on organochlorine compounds, including PCBs and dioxins. Commonly known as the white rot fungus, this organism has an enzyme system that normally breaks down lignin, the degradation-resistant "glue" that holds cellulose together in wood and woody plants. Under certain stressed conditions, however, the enzyme will act to cometabolize synthetic organochlorine compounds and was once widely promoted as a means of remediating hazardous waste sites contaminated with such compounds.

The degree of biodegradation varies over a wide range. In the simplest case, the change to the substrate molecule is relatively minor, such as addition, deletion, or modification of a functional group. Complete biodegradation to simple inorganic species — CO₂ for carbon, NH₄

+ or NO_3^- for nitrogen, HPO_4^{2-} for phosphorus, SO_4^{2-} for sulfur — is the process of mineralization, which is crucial in completing elemental cycles in the environment.

An important step in biodegradation is the modification of a substance to reduce its toxicity. This process is called detoxication. An example of detoxication is given in Reaction 9.10.2, O₂ + OC₂H₅OC₂H₅ + O₂N⁻ → O₂N⁻OC₂H₅OC₂H₅ + HPO₄²⁻ (9.10.2) 4, other products 2- O₂N⁻OH for the conversion of insecticidal paraoxon, a potent nerve poison, to p-nitrophenol, which is only about 0.005 × as toxic. In some cases, however, action of microorganisms in the environment may produce a much more toxic material. An example of this is the generation of highly toxic, mobile methylmercury species, Hg(CH₃)₂ and HgCH₃⁺ from insoluble, relatively harmless inorganic mercury species.

A number of factors are involved in determining the effectiveness and rate of biodegradation. The compound in question has to be biodegradable. Biodegradability is influenced by both physical properties, such as water solubility, and chemical characteristics including the presence of functional groups amenable to microbial attack.

SUPPLEMENTARY REFERENCES :

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RECOMMENDED READING BOOKS :

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WEB LINKS FOR REFERENCE

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