https://doi.org/10.36375/prepare_u.a35

SUNLIGHT FOR REMEDIATION OF POLLUTED ENVIRONMENT

Prof. (Dr.) Sampa Chakrabarti

The day when the prehistoric man invented fire, the demand of energy started; at the same time environmental pollution also started from that day since combustion of fuel generates undesirable greenhouse gas. With the advent of civilization, both energy-crisis and anthropogenic pollution increased. Meanwhile the definition of civilization started changing during the industrial revolution. Life of people changed after industrial revolution and civilization demanded more and more energy every day. To generate such energy from conventional sources, we still have no other alternative than to pollute the environment. Other developmental activities also resulted in pollution of the environment. Consequently the conventional resources for energy generation are depleted and at the same time environment deteriorates. People started getting aware about the environment since 1980s. There are several remedial solutions for environmental problems using advanced technologies, but most of them, once again, need huge energy. For example, we have to boil water to get rid of the pathogens, we have to switch on UV lamps for detoxification of water. In an effluent-treatment plant there are pumps and other equipment that need energy. This is therefore a vicious cycle and to break the cycle, we must use renewable energy for environmental remediation.

In a tropical country like India, solar energy is the best possible choice among the other renewable sources of energy. The sun is a sphere of diameter 1.39×10^9 m and is 1.5×10^8 km away from the earth. Its mass is 2×10^{30} kg and volume is 1.4×10^{18} km^3. The effective black-body temperature in the sun is 5760 K that is 5487 deg C. The total energy output of the sun is 3.8×10^{20} MW, which is equal to 63 MW/m^2 of the sun's surface. This energy radiates outward in all directions and the earth receives only a tiny fraction of the huge amount of radiation. Nevertheless this small fraction amounts to 1.7×10^{14} kW and with this radiation falling on the earth's surface for 84 minutes only is equal to the world energy demand for one year. Light energy from the sun is approximately 100,000 lux or lumen per square meter at the earth's surface. Solar radiation is received at the earth's surface in an attenuated form because it is subjected to the mechanisms of absorption and scattering as it passes through the earth's atmosphere. Absorption occurs mainly due to the presence of ozone, water vapour and particulate matter in the atmosphere whereas scattering occurs by all the gases and particles. It goes without saying that less attenuation occurs with a cloudless sky. India is a tropical country and the daily average solar energy incident over India varies from 4 to 7 kWh/m^2 with about 2300 - 3200 sunshine hours per year, depending upon location. It is thus especially desirable that environmental remediation problems in India may be addressed economically with the help of solar energy rather than employing a relatively costly power generated from fossil fuel.

We need energy for the treatment of solid, liquid or gaseous wastes. Advanced oxidation techniques, nowadays used for treatment of polluted environment require energy for exciting electrons to generate reacting species. If we can use solar energy for the mentioned purposes, we shall be able to improve the quality of environment without polluting it in some other way. However there are a few problems with sunlight:

There are some problems also for the use of sunlight:

- It is a dilute source of energy. The radiation flux is approximately $1kW/m^2$ and over a day, it is approximately $7kWh/m^2$. These are low values for potential technological utilization.

- A large area is required for collection of solar energy and with the increasing scarcity of land, it is difficult to capture sunlight.

- Though freely available, the availability varies widely with time and location. It also varies with day-night cycle and local weather conditions.

Advanced oxidation Processes (AOP) are characterized by generation of hydroxyl radical (OH•) that attacks organic pollutants. It may be produced by several means like catalytic dissociation of hydrogen peroxide or excitation of semiconductors. In all cases sunlight enhances the rate of generation of the oxidizing species and facilitates remediation of the polluted environment.

We are familiar with the hymn or stotra:

Om javakusumsankasam kashyapeyam mahadyutim

Dhantarim sarbapapaghnam pronotohsmi dibakaram

It means *I salute the hibiscus-red, bright, king of the day, Sun-God, who is the son of Kashyap and who destroys all our sins*. From the environmental point of view let us note the word '*sarbapapaghna*' that is *destroyer of all sins*. In the Vedic age, we used to worship natural forces as Gods. Therefore, *sin* can be defined as the harm caused to the Nature and from the ancient days there is a belief that the solar energy can destroy all environmental pollutions caused by wrong human activity. Afterwards it was supported by scientific evidences that the ultraviolet ray present in the sunlight destroys the pathogens present in water and till today, we use UV radiation for getting safe drinking water.

It is a common practice in India to expose anything stale to the sunlight, starting from old garments to long-stored food-grains, for making it further usable destroying the harmful bacteria, fungi and other microbes. The heat and light of solar energy had been used for healing and cure of several diseases from ancient days. As per Indian mythology, *Shambo*, one of the sons of *Lord Krishna*, worshipped the Sun-God for the cure of Leprosy he was suffering from. Till today direct sunlight is one of the accepted remedies of Leprosy and other skin problems.

https://doi.org/10.36375/prepare_u.a35

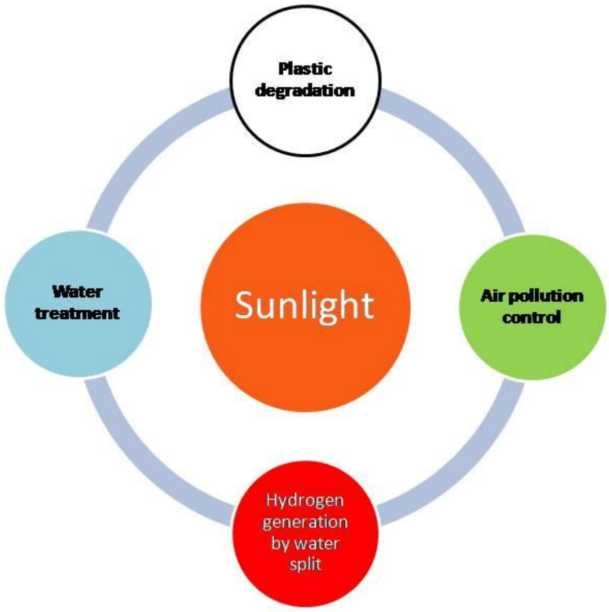

Figure-1: Sunlight can help abating all phases of pollution

Now let us see how sunlight can help to abate the pollution due to plastic waste (solid), industrial wastewater and biologically contaminated water (liquid) and toxic gases in air (gas). We will also see how hydrogen, the next generation fuel, can be obtained from water split using sunlight. Solar photovoltaic, on the other hand, is a widely-researched discipline and is out of scope of this article though the direct current (DC) generated by solar photovoltaic can indirectly protect the environment by decreasing the use of fossil fuel and generation of green house gas.

Basic principles of photocatalysis should be made clear before discussion sunlight assisted degradation of pollutants.

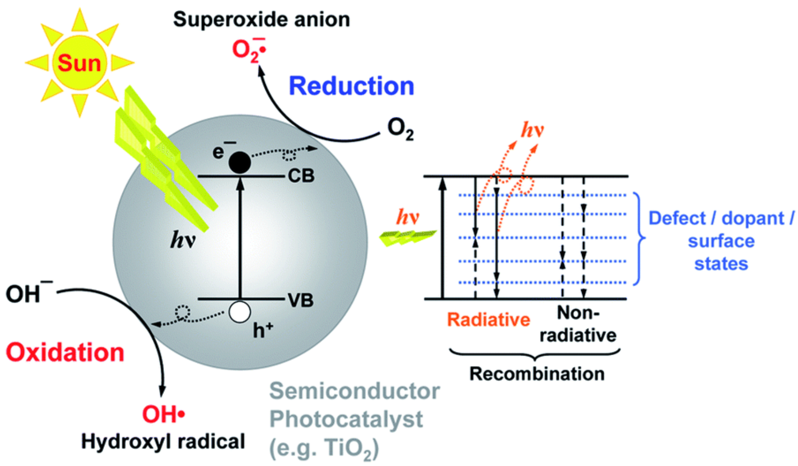

Fig-2: Scheme of heterogeneous photocatalysis using sunlight

The electronic structure of a semi-conductor catalyst is characterized by a filled valence band and an empty conduction band. A high energy radiation in the visible or UV range excites the atom to eject a valence band electron (e^-) to the higher energy level of the conduction band leaving a 'hole' (h^+) behind. The valence band holes are powerful oxidants (+1.0 to +3.5V vs NHE depending on the semiconductor and pH), while the conduction band electrons are good reductants (+0.5 to -1.5V vs. NHE). Most organic photodegradation reactions utilize the oxidizing power of the holes either directly or indirectly; however, to prevent a build up of charge one must also provide a reducible species to react with the electrons. In an appropriate environment, a 'hole' may 'react' with a hydroxyl ion in an aqueous solution to yield a hydroxyl radical (•OH) or a superoxide radical(O_2•) having a high oxidation potential that can attack an organic compound and decompose the same to carbon dioxide and water. Similarly the photogenerated electrons react with the reducible molecules to generate respective products. For this, the electron and the hole should respectively be scavenged by suitable reagents as required. In fact nature is a big photo reactor with sun as its source of energy.

Fenton and photo-Fenton processes can be the examples of the homogeneous photocatalysis that can be used for wastewater treatment. It is the decomposition of H_2O_2 into hydroxyl radicals by the catalysis of Fe^{2+} ion in water. The rate of generation of •OH radical can be further increased by sunlight.

The equation for photo Fenton reaction can be written as follows:

$$Fe^{3+}{}_{aq+} + H_2O \xrightarrow{h\nu} Fe^{2+}{}_{aq} + HO\bullet + H^+ \quad (1)$$

For treatment of wastewater, both heat and light of the sun can be used. Solar heat helps in treatment of sea water by solar desalination and distillation. It basically mimics the natural water cycle. Heat and light of sun disinfect water contaminated with pathogens by SODIS technology. Sunlight detoxifies industrial wastewater by photocatalysis described above. Solar water treatment has been described in detail in my previous article published in *Thought* in 2013.

With globalization and industrialization, quality and quantity of solid waste generated are rapidly changing. Research and development on material science and packaging industries deliver various polymers used for improved packaging materials. Plastics and polymers were once hailed as wonder materials due to their water repellence, light weight and low cost. Afterwards it had become the worst of the solid wastes that clogs the sewerage channels, cannot be disposed as landfills since they are non-biodegradable and cannot be incinerated since they release toxic gases.

The need of invention of an easily degradable plastic material is a demand of the day. On view of the discarded plastics thrown away in water-bodies in presence of sunlight and air, it is highly desirable that a plastic that is degraded with the help of sunlight in presence of air and water that is under a natural condition should be used. The process of natural degradation is too slow, so we need a photocatalyst for enhancing degradation reaction utilizing sunlight. Doped and undoped semiconductors like TiO_2, ZnO, ZnS, CdS are the

https://doi.org/10.36375/prepare_u.a35

common photocatalysts. Polymers studied for degradation are Polyvinyl Chloride(PVC), Polyethylene (PE) and Poly styrene (PS).

Researchers degrade plastic with sunlight by preparing a plastic-catalyst composite film and expose it to the sunlight. Photocatalysts are dispersed in the polymer matrix and the film of the composite polymer is exposed to sun light in presence of air and water. The photogenerated •OH radical attacks the polymer chain to break the same. The degradation is generally monitored by reduction in weight. Surface morphology of the composite film is studied by SEM. The intermediates and products generated by degradation are analyzed by FTIR-ATR. A few reports are available on the photocatalytic degradation of polymer in presence of UV/solar irradiation. Some obtained about 15% weight loss in 3 hours. However this technology is still in the laboratory.

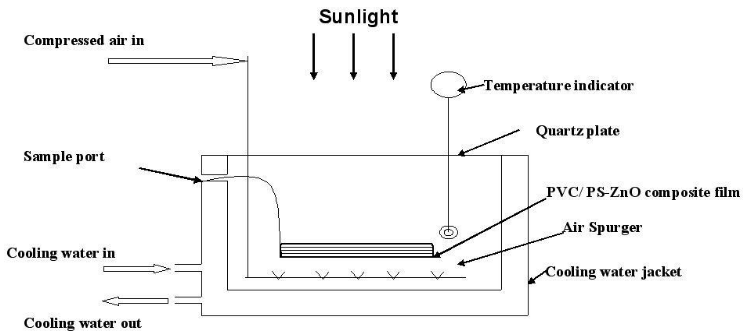

Fig-3: Experimental Set-up for solar photodegradation of plastic (Chakrabarti et al 2012)

According to the definition of the World Health Organization (WHO), *Air Pollution* is the contamination of the indoor or outdoor environment by any chemical, physical or biological agents that modifies the natural characteristics of the atmosphere. Pollutants can be in the form of solid particles, liquid droplets or mists and vapours or gases. They may be natural or anthropogenic. Common examples of natural causes of air pollutions are volcanic eruptions and forest fires. Volcanic eruptions result emission of sulphur dioxide, carbon dioxide and hydrogen fluoride. All forest fires emit toxic carbon monoxide, sulphur dioxide (small amount), nitrogen dioxide, ozone (at a very high temperature) and particulate matters. Particulates comprising soot, tar and organic compounds are emitted in very large quantities. Nevertheless the natural causes are usually not frequent whereas the significant extent of air-pollution is caused by anthropogenic activities. Unplanned growth of the cities, increasing traffic, high influx of population in urban area, increase in energy consumption and change of its pattern as well as unplanned industrial development has resulted in increase in air pollution especially in urban areas.

Air pollutants can be classified into *Primary* and *Secondary* pollutants. *Primary* pollutants are directly emitted or generated from a process such as carbon monoxide CO or carbon dioxide CO_2 gas from the combustion in an engine. *Secondary* pollutants are not emitted directly – they are formed by reactions of primary pollutants in air. The various sources of air-pollution contribute to the total load of air-pollution as described in the following figure. Among them, transportation is the major contributor. In developing countries still a significant number of households are ran with coal and biomass as fuel for heating, cooking and lighting. Hence indoor air quality is influenced by the quality of domestic fuel used. Another source of VOC in the indoor air is paints, varnishes and chemicals used for decoration, surface-protection, deodorization and disinfection. The mechanical or physico-chemical means like centrifuge, electrostatic precipitators, absorbers and scrubbers are out of scope of this article.

As already described semiconductor photocatalysts are often used for the treatment of polluted water using solar energy. Use of photocatalysis for the remediation of polluted air is relatively new and started only in the nineties. For the purpose of air pollution control, the catalyst should be suitably immobilized. For indoor air, window pane or the paint on the wall is among the popular choices whereas for treatment of outdoor air, the preferred option is to use semiconductor materials with construction materials like building blocks, panels or paving.

Mechanism for degradation of volatile organic compounds is the same as described above, organic compounds are ultimately oxidized to CO_2. NO was oxidized to HNO_2 and HNO_3.

TiO_2-based tiles had been used in over 5000 buildings in Japan where the sales of photocatalytic construction materials made up to 60% of the whole photocatalytic market share. In Italy, Italcementi S.p.A developed different types of cement with a TiO_2 surface – TX Aria™, TX Active™ and TX Millenium™. TioCem®, manufactured by Hiedelberg Cement Technology Centre GmbH is another photocatalytically active concrete product containing TiO_2 that promotes catalytic conversion of NO_x and other air-pollutants. These photocatalytic cements were among Time magazine's top 50 inventions in 2008. TiO_2-cement composites show a synergy between the cementitious material and TiO_2 that makes cement an ideal substrate for environmental photocatalysis. Mitsubishi Materials Corporation of Japan developed a paving stone NO_xer™ that oxidizes NO_x into nitric acid that was neutralized by the concrete or washed away by rain. The test areas of Belt Highway No.7, Tokyo International Airport or Ishigaki Domestic Airport showed lowering of NO_x by 10-30%. Some estimates showed that removal of NO_x by such surfaces were 50000t per year. Large scale photocatalytic removal of NO_x was carried out by European Photoreactor (EUROPHORE) in Spain. The photoreactor consisted of two hemispherical Teflon chambers of $200m^3$ volume placed outdoor. The chambers were equipped with on-line sensors and analytical devices.

With advancement of civilization, we need more and more energy so that we can live with a better standard of living. Conventional energy sources are rapidly depleting and search for an alternative pollution- free, storable and economical fuel is the demand of the day. In one hand, the fossil fuels are scarce and on the other hand greenhouse gases generated by burning fossil fuels are polluting the environment. In this backdrop, the alternative fuel should be cheap and clean.

Hydrogen has been identified as one of the promising alternatives among the next-generation fuels. As a fuel it is a clean one since on burning it does not produce CO_2 like the carbonaceous fuels. Electrolysis is a method of obtaining hydrogen from water, an abundantly available raw material. But for electrolysis, we have to use huge amount of conventional fuel for generating electricity and will eventually end up in a catch-22 situation. Hence we should use a renewable energy for splitting water so that a clean fuel can be generated using a green energy. Honda and Fujishima first reported water-splitting with TiO_2 photoctalyst in 1972. If an external potential is applied after the generation of photocatalytic hole and electron (Fig-1), these photogenerated electrons migrate through the bulk to reach the Pt counter electrode, thereby reducing H^+ into H_2. Meanwhile, the holes that were left behind on the surface of the semiconductor, oxidize water, forming O_2.

The basic chemical reactions are as follows:

$$Catalyst + h\nu \longrightarrow h^+ + e^- \quad (2)$$

$$H_2O + 2h^+ \longrightarrow 2H^+ + \frac{1}{2}O_2 \quad (3)$$

$$2H^+ + 2e^- \longrightarrow H_2 \quad (4)$$

A schematic diagram can be represented as follows:

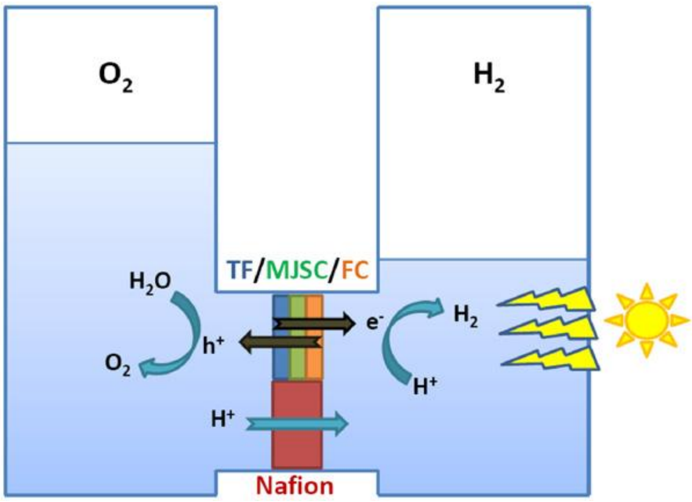

Fig-4: Sunlight assisted water splitting with Nafion membrane (Huang et al, 2012)

Basically the discovery of photo-splitting of water using semiconductor photocatalysis by Honda and Fujishima in 1972 laid the foundation stone of using photocatalysis for the cleaning of the environment. Early reports of photocatalytic water treatment were published during 1969-1977 that demonstrated that toxic and hazardous pollutants like phenols, cyanides or polychlorinated biphenyls could be broken down to less hazardous products by semiconductor photocatalysts.

The objective of providing a solar collection device is to expose a dark region to solar radiation so that the radiations are collected and the energy is transmitted to achieve a specific purpose. For thermal applications, the heat energy is collected and the medium is heated with the heat energy of the sun. For photochemical applications, the photons are collected to promote specific chemical reactions. The equipment that performs this function is called solar collector. Though mainly used for thermal applications, concentrating collectors and reactors are also used for photochemical applications. For control of water pollution, the most popular reactor so far is CPC reactor. Another useful configuration is TFFBR. However non-concentrating reactors are optically more efficient since they collect both direct and diffused solar radiations. For solar degradation of plastics, normally used reactors are simple box-type. Window-panes, concrete slabs, corrugated roofs and panels are often treated with semiconductors and used for treatment of polluted air in presence of moisture and solar radiation. All these reactors should be further modified for efficient use of sunlight for environmental remediation.

There are several challenges that should be addressed before we widely use solar photoreactors.

- Photoreactors should be specifically designed for a particular light source
- Scale-up is difficult and during scale up, it is very difficult to maintain the optimum ratio of irradiated surface to total volume.
- Quantum yields are generally less than 1 indicating necessity of efficient catalysts
- Suppression of charge recombination.
- For water splitting, the sites for generation of H_2 and O_2 cannot be physically separated and there may be a chance for explosion.
- No electrical bias can be applied to prevent electron hole recombination.
- In case of water treatment, separation of the suspended particles after treatment process is difficult and costly especially when nanoparticles are used.

During the nineties, evolution or revolution of nanotechnology brought a sea-change in the field of photocatalysis. Reduction of size of the conventional bulk semiconductors not only drastically increased the catalytic surface area but also manifested unexpected properties. It could in turn overcome the disadvantages of the photocatalyst-films. On the other hand, size quantization of nanoparticles caused significant change in the optical band gaps of semiconductor nanoparticles. The band gap of semiconductor quantum dots increased than that of their bulk counterparts due to quantum confinement. This 'blue shift' in some cases increased the photocatalytic activity by preventing recombination of photogenerated holes and electrons, but for visible or solar photocatalytic applications it is generally undesirable.

In my opinion the main challenge for application of sunlight for environmental remediation is its confinement in the laboratory. Most of the studies reviewed in the previous chapters are on the laboratory scale works. More pilot scale studies are necessary for its industrial application. But scaling up a laboratory scale experimental set-up is not an easy job especially where sunlight is used. Different configurations of solar concentrators and reactors are to be tried before selecting the best option. Even in the laboratory scale exploring different types of reactor other than the conventional ones is surprisingly less. Therefore extensive research is required on solar photoreactors.

This, in turn, requires public awareness and government funding. In general, in developing countries like India, owners of the small and medium scale industries are not yet aware about the environmental pollution they are causing. If such owners of small and medium scale industries would be aware that they can run effluent treatment plants (ETP) without much running cost using sunlight, they could become interested. It may be noted that competitive technologies like coagulation, adsorption and bioremediation are sufficiently mature and cost effective. The small industry sector has to be educated about the limitations of the conventional technologies compared to solar photocatalytic process. They must be convinced that for non-biodegradable pollutants solar photocatalytic process is the best and the cheapest option. Otherwise commercialization of a new entrant may not be that easy. Combined ETP can also be installed for industrial complexes and participating industries may be provided with incentives to encourage. State and central pollution control boards have significant roles in popularization of sunlight-assisted environmental remediation techniques.

References:

Sukhatme SP and Nayak JK, Solar Energy: Principles of Thermal Collection and Storage; Third Edition, Tata-Mcgrew-Hill Publishing Company Limited (2008).

Kalogirou S, Solar energy engineering: Processes and systems, First Edition, Academic Press- Elsevier (2009).

Chakrabarti S, Sil D, B Chaudhuri and Bhattacharjee S, Comparison of the photocatalytic degradation of polyvinyl chloride and polystyrene with zinc oxide semiconductor catalyst under tropical sunlight, *Chemical Technology* – an Indian Journal published by Trade Science Inc, India (ISSN 0974-7443) **6:** 58-64 (2012).

Mo J, Zhang Y, Xu Q, Lamson JJ, Zhao R, Photocatalytic purification of volatile organic compounds in indoor air: A literature review, *Atmos Environ* **43**: 2229–2246 (2009)

Spasiano D, Marotta R, Malato S, Fernandez-Iba˜nez P, Di Somma I, Solar photocatalysis: Materials, reactors, some commercial, and pre-industrialized applications. A comprehensive approach *Appl Catal B* **170**: 90–123 (2015)

Chakrabarti S, Water-Energy Nexus: Role of Solar Energy, Thought, Vol: XVIII, Issue 3&4, July-December 2013

Maeda K, Photocatalytic water splitting using semiconductor particles: History and recent developments; *J Photochem Photobiol C-Photochem Rev* 12: 237– 268 (2011)

Huang C-W, Liao C-H, Wub C-H, Wu JCS, Photocatalytic water splitting to produce hydrogen using multi-junction solar cell with different deposited thin films; *Sol Energ Mater Sol Cell* 107: 322–328 (2012)