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WATER – ENERGY NEXUS: ROLE OF SOLAR ENERGY

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Abstract

To address the interrelated crises of the energy and the environment, solar energy should be used for wastewater treatment. This review summarizes the various techniques of using solar energy for getting usable water from sea water and wastewater. A part of the contents of this paper was presented in a lecture delivered at a programme of FOSET on June 21, 2013.

Introduction

The other name of water is 'life'. Life in this planet would not have been possible if there was no water. From the very outbreak, human civilization had grown and developed around a source of clean and usable water. Indus-valley, Egyptian and Mesopotamian civilization were built around the rivers Indus, Nile and Tigris-Euphratis respectively. With the advancement of civilization, the natural supply of water has become inadequate in terms of both quantity and quality because of the increase in population and the anthropogenic activities accompanying the advancement. Water has become scarce day by day as civilization progressed.

Among the total world population of 6700 million, approximately 600 million people are suffering from chronic water scarcity and nearly 1 billion people do not get safe drinking water. In developing countries, 80% of the diseases are caused by poor sanitation and unsafe drinking water. 15% of urban and 25% of rural population does not have access to safe drinking water in India. Groundwater is available to one-third of the world's population and its use is likely to increase in future. Due to developmental activities, the level of groundwater table is falling by 1-3 m per year. If the current trend continues, two out of three people on Earth will be living in water-stressed areas by 2025. Water supply is therefore a major challenge in the coming years.

To address the present problem of water scarcity, we have to re-use wastewater. Wastewater treatment has become mandatory, not only by the law, but also by the absolute necessity of clean water for survival of mankind. Here, we find a circular relationship between water and energy. Treatment of water/ wastewater needs energy. Bottled drinking water requires 1.5 – 3 kWh energy per litre and tap water needs 1.4×10^{-3} kWh energy per litre. On the other hand, 95 litre water is required for generation of 1kWh of conventional energy from fossil fuel. To break this cycle, there is no other way than to use a renewable source of energy for the treatment of water and wastewater. Among the various renewable energy sources like solar, wind, tidal and biological, solar energy may be considered as a 'smart choice' especially for a tropical country like India. In addition to be huge in magnitude, environmentally clean solar energy is available at free of cost.

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. The annual average daily global radiation received in India is approximately 450 langleys[1] per day. Peak values are in Rajasthan or Gujarat measured in April or May as 600 langleys per day whereas the value at the lower side during monsoon or winter is about 300 langleys/day. A strange coincidence is noticed all over the world; where water is scarce, there is abundance of sunlight. Countries like Mexico, Spain, Brazil and India may be the examples. Hence it may be considered as a natural destiny that sunlight should be used for water treatment. 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.

For treatment of water, we can use both heat and light components of sunlight. We can divide the usage of sunlight for water treatment as follows:

- Solar distillation or desalination
- Solar disinfection
- Solar detoxification
  - Photocatalytic oxidation and reduction of pollutants
    - Homogeneous – photo-Fenton
    - Heterogeneous – semiconductor photocatalysis

In the present paper, a brief overview on the abovementioned topics will be covered.

[1] 1 langley is equal to 1 cal/cm^2 or 1.163×10^{-2}kWh/m^2. This unit has been adopted after the name of Samuel Langley who made the first measurement of spectral distribution of the Sun.

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Solar distillation or desalination

Though water is one of the most abundant natural resources, 97% of the earth's water is saltwater. From ancient times people try to use sea water for their use after suitable treatment. Among the first attempts to harness solar energy was the development of the equipment suitable for distillation and desalination. Basically it was an attempt to mimic the nature's water cycle where saline water is converted into sweet water using solar heat. Aristotle (384-322 BC) also described the natural water cycle which is nothing but a huge solar energy driven open distiller in a perpetual operating cycle.

There may be two main types of systems for solar distillation or desalination. If there are two separate devices for distillation and collection, the system is said to be indirect collection system whereas if a system has a single device for distillation and collection, it is called a direct collection system.

Direct collection system uses greenhouse effect for evaporation of salty water. A typical schematic is given below:

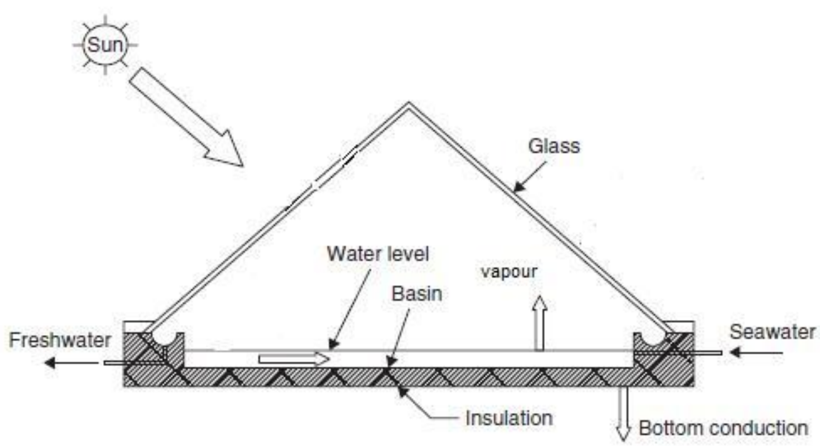

Figure -1: Schematic diagram of a direct collection-type solar still [1]

The still consists of an airtight basin, usually constructed out of concrete, galvanized iron sheet (GI), or fiber-reinforced plastic (FRP), with an inverted V-shaped top cover of transparent material such as glass or plastic. The inner surface of the base, known as the *basin liner*, is painted black to absorb the solar radiation incident on it. There is also a provision to collect distillate output at the lower ends of the top cover. The brackish or saline water is fed inside the basin. The sun's rays pass though the transparent roof and are absorbed by the blackened bottom of the basin. As the water is heated, its vapor pressure is increased. The resultant water vapor is condensed on the underside of the roof and runs down into the troughs, which carry the distilled water to the reservoir. The still acts as a heat trap because the roof is transparent to the incoming sunlight but opaque to the infrared radiation emitted by the hot water (greenhouse effect). The roof encloses the vapor, prevents losses, and keeps the wind from reaching and cooling the salty water.

The stills require frequent flushing to prevent precipitation of salt, which is usually done during the night. Design problems encountered are brine depth, vapor tightness of the enclosure, distillate leakage, methods of thermal insulation, and cover slope, shape, and material. A typical still efficiency, defined as the ratio of the energy utilized in vaporizing the water in the still to the solar energy incident on the glass cover, is 35% (maximum) and daily production of sweet water is about 3 – 4 L/m^2. Salt is a by-product of this process and we can also utilize this process for production of salt from sea-water.

Disinfection using both light and heat of the sun – SODIS technology

Till 2000 one-sixth of the world's population did not have access to safe drinking water. No access to safe drinking water leads to several water-borne diseases including diarrhoea, cholera, typhoid, hepatitis, amoebic and bacillary dysentery. Each year 4 billion cases of diarrhoea cause 2.2 million deaths, mostly among children below 5 years of age. Deaths due to diarrhoea, therefore, represent approximately 15% of the child-deaths under the age of five in all the developing countries.

Only 4.5% of the solar irradiance reaching the earth's surface is UV radiation, about 43% is visible and 53% is infra-red. The wavelength ranges of UV are: 400–315 nm for UV-A; 315–280 nm for UV-B; and 280–100 nm for UV-C of which UVA fraction is present in larger proportion. Solar water disinfection (SODIS) is a simple water treatment method using solar radiation (UV light and heat) to destroy pathogenic bacteria and viruses present in water. Its efficiency to kill protozoa is dependent on the temperature reached during solar exposure and on the climatic and weather conditions.

Research on solar water disinfection was initiated by Professor Aftim Acra at the American Institute at Beirut in 1984. Later on INRESA (Integrated Rural Energy Systems Association) launched a network project in 1985 and a workshop was organized by Brace Institute of Montreal to review the results in 1988.

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The salient features of this technology are as follows:

- SODIS is a simple technology and can be accomplished by illiterate and underprivileged population.
- It is a cheap technology that does not need any costly resource like fossil fuel to boil the water for disinfection.
- It improves overall health of the family at a minimal cost.
- It is an eco-friendly technology since no greenhouse or toxic gas is generated.
- It destroys micro-organisms but cannot destroy chemical pollution.
- There is a synergy between UV and infra-red components of the sunlight for destruction of the micro-organisms.

Till date it is a small scale household technology and could not be scaled up. It is not effective if the water is too turbid. The success of SODIS technology is dependent on the seasonal and daily variation of the intensity of sunlight.

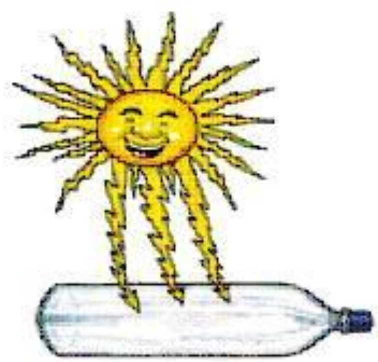

Figure 2: Solar disinfection of drinking water (SODIS technology) [3]

The basic SODIS technique is very simple. Transparent containers are filled with contaminated water and placed in direct sunlight for at least 6 h, after which time it is safe to drink. The transparent containers (reactors) can be glass or plastic (usually polyethylene-terephthalate – P.E.T.) – even plastic bags can be used. Plastic bottles are more robust than glass bottles since there is a risk of a fall from a roof. Very turbid water with a turbidity more than 30 NTU cannot be used for SODIS. Chemical pollutants cannot be removed by using SODIS, either.

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It is recommended that solar disinfected water should be consumed within 24 h to avoid the possibility of post-exposure re-growth. The efficiency of the basic protocol can be enhanced by adding a number of additional steps such as:

- Placing filled bottles on reflective surfaces to boost the amount of sunlight absorbed by the reactor.
- Painting the underside of the SODIS reactor black to enhance solar heating.
- Shaking a two-thirds filled bottle vigorously for 30 s before topping up and sealing, to increase initial levels of dissolved oxygen for solar induced oxidative inactivation processes.
- Filtering the water before filling the bottle, since turbidity may inhibit the penetration of sunlight.

When DNA is irradiated with UV light, some of that light is absorbed by the pyrimidine rings of thymine and cytosine bases in the DNA. Although the UV-A wavelengths are not sufficiently energetic to modify DNA bases directly, they facilitate formation of reactive oxygen species (ROS) in water such as singlet oxygen, superoxide, hydrogen peroxide, and hydroxyl radical. Excitation of endogenous photo-sensitizers within cells such as porphyrins, flavins, and quinones, NADH/NADPH, and others are believed to contribute to the formation of intracellular ROS. Once formed, these ROS can cause damage to DNA; oxidations of amino acids in proteins; oxidations of polyunsaturated fatty acids in lipids. Additionally, sunlight can be absorbed by natural exogenous photo-sensitizers present in surface waters, which in turn can react with oxygen to produce ROS , that can exert a disinfecting effect. A strong synergistic effect has been observed between optical and thermal inactivation processes for water temperatures exceeding 45 °C. One explanation suggested by McGuigan et al. (1988) for this synergistic response is that in addition to a slow pasteurizing effect, elevated water temperatures inhibit the DNA repair mechanisms.

Detoxification using the light of the sun: Homogeneous and Heterogeneous Photocatalysis

The non-biodegradable organic pollutants present in various industrial wastewater can be treated efficiently using photo-assisted advanced oxidation processes (AOP) such as photo-Fenton and photocatalytic reactions, the excitation- energy being supplied by the sunlight. UV and visible light can catalyze redox reactions in homogenous and heterogeneous media. In presence of soluble ferrous salts and hydrogen peroxide, light enhances the rate of reaction in a so-called homogeneous 'photo-Fenton reaction' which oxidizes organic pollutants ultimately into carbon dioxide and water.

In case of heterogeneous photocatalysis, a semiconductor is used for a heterogeneous surface. In aqueous medium, a semiconductor photocatalyst is suspended and the slurry is exposed to light for enhancement of photo-induced reaction.

In both cases, the active oxidant is hydroxyl radical, which has a very high oxidation potential that attacks organic pollutants to decompose into carbon dioxide and water. The counterpart of such oxidation reaction is sometimes used for reduction of toxic heavy metal ions at higher oxidation state to the less toxic lower oxidation state.

Homogeneous Photo-catalysis or Photo-Fenton reactions

Fenton and photo-Fenton processes are among the oldest and the most applied AOP. The first study was reported in 1960s but the actual chemistry of Fenton and photo-Fenton process is still under exploration and discussions. However the decomposition of H2O2 in presence of Fe^{2+} was reported by Fenton in 1894.

Even in absence of a light source H2O2 decomposes by Fe^{2+} ion that are present in the aqueous phase resulting the formation of hydroxyl radical. When a light source is present, the rate of photo-Fenton was reported to be positively enhanced compared to the dark condition.

The most accepted mechanism for photo-Fenton reaction is given below:

$$Fe_{aq}^{2+} + H_2O_2 \rightarrow Fe_{aq}^{3+} + HO^{\bullet} + OH^{-} \quad (1)$$

$$Fe_{aq}^{3+} + H_2O_2 \xrightarrow{h\nu} Fe_{aq}^{2+} + HO^{\bullet} + H^{+} \quad (2)$$

If the reaction is carried out in absence of light, then the regeneration of Fe^{2+} needs one more molecule of H_2O_2 as follows:

$$Fe_{aq}^{3+} + H_2O_2 + H_2O \rightarrow Fe_{aq}^{2+} + H_3O^{+} + HO_2^{\bullet} \quad (3)$$

Hence photo-Fenton reaction not only generates one more unit of HO• radical, but also it minimizes the requirement of H_2O_2 by one unit.

Fenton and photo-Fenton reactions are found to be the most effective at acidic pH (generally pH=3). This is owing to the fact that at such low pH, the precipitation does not take place and further promotes the presence of dominant iron species of $[Fe(OH)]^{2+}$ in water. However after treatment the treated wastewater has to be neutralized before discharging it to the public sewerage. This is not cost effective for operation as it requires high chemical costs for pH rectification. This neutralization process would also increase the total dissolved solid (TDS) load. So sometimes Fenton and photo-Fenton oxidation has to be carried out in near-neutral pH, for which the reaction mechanism is controversially different from that at acidic pH.

The basic process parameters influencing the rate of solar energy assisted photo-Fenton reaction are pH, initial concentration of the substrate, molar ratio of Fe^{2+}: H_2O_2. Temperature is not a very significant parameter affecting the rate of photo-Fenton reaction especially when solar energy is used.

Heterogeneous photocatalysis using semiconductors

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 to the higher energy level of the conduction band leaving a 'hole' behind. 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 or a superoxide radical 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. Among the common semi-conductor catalysts, TiO_2 in the anatase form has been used for many waste degradation applications. But ZnO has a few advantages over its formidable counterpart in terms of a higher quantum efficiency as well as catalytic efficiency.

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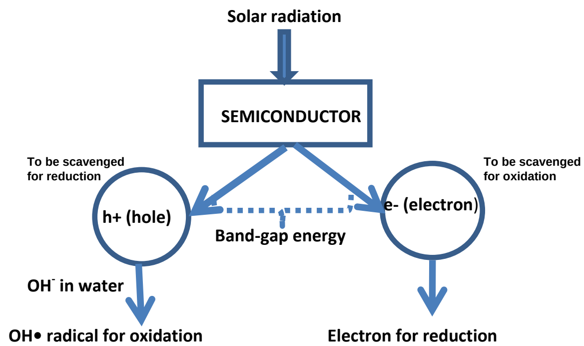

Figure -3: Scheme of the mechanism for semiconductor photocatalysis

A simplified mechanism for semiconductor photocatalysis is presented in Figure-3 whereas the stepwise oxidation reactions with TiO_2 may be summarized as follows:

Excitation	$TiO_2 \xrightarrow{h\nu} e^- + h^+$	(4)
Adsorption	$\text{site} + R_1 \Leftrightarrow R_{1,ads}$	(5)
	$OH\cdot + Ti^{IV} \Leftrightarrow Ti^{IV}\text{---}OH\cdot$	(6)
Recombination	$e^- + h^+ \rightarrow \text{heat}$	(7)
Trapping	$Ti^{IV} - OH^- + h^+ \Leftrightarrow Ti^{IV}\text{---} OH\cdot$	(8)
	$Ti^{IV} - H_2O + h^+ \Leftrightarrow Ti^{IV}\text{---}OH\cdot + H^+$	(9)
	$R_{i,ads} + h^+ \Leftrightarrow R^{\cdot+}_{i,ads}$	(10)
Hydroxyl Attack		
Case I	$Ti^{IV}\text{---}OH\cdot + R_{1,ads} \rightarrow Ti^{IV} + R_{2,ads}$	(11)
Case II	$OH\cdot + R_{1,ads} \rightarrow R_{2,ads}$	(12)

For photo-reduction, however, the electron generated in the first step is utilized after scavenging the hole.

Research group of the present author is engaged in studying sunlight-assisted homogeneous and heterogeneous photocatalytic degradation of organic and heavy metal pollutants in wastewater for last ten years. For heterogeneous photocatalysis, the semiconductors used were bulk and nanosized zinc oxide particles. Among the common semi-conductor catalysts, TiO_2 in the anatase form has been used for many waste degradation applications. But ZnO has a few advantages over its formidable counterpart in terms of a higher quantum efficiency as well as catalytic efficiency. Experiments were conducted in novel batch reactors. Reduction of hexavalent chromium was also accomplished by solar photocatalysis. Studies of the solar photo-Fenton degradation of dye and pesticides in simulated wastewater using a novel continuous reactor are under progress.

Pilot Plants

Plataforma Solar de Almeria is a R&D centre of the Centre for Energy, Environment and Technology under the Government of Spain. One of their objectives is education and formation of scientists and engineers of all over the world in solar thermal technologies, solar thermochemical processes and solar water treatment. They have facilities to install and study various solar water treatment plants in pilot scale. For homogeneous and heterogeneous photocatalysis they have successfully tested different types of reactors like Concentric Parabolic Reactor (CPR), Compound Parabolic Collecting Reactor (CPCR) and Thin Film Fixed Bed Reactor (TFFBR). Parabolic reflectors were used for concentrating sunlight. Wash water from a pesticide bottle washing facility has been treated using sunlight assisted photo-Fenton reactor. In TFFBR, TiO2 particles were immobilized on a surface over which polluted water was allowed to flow as a thin film under sunlight. Clean treated water was obtained at the bottom of the plate. Textile effluent from Tunisia was treated with such a TFFBR.

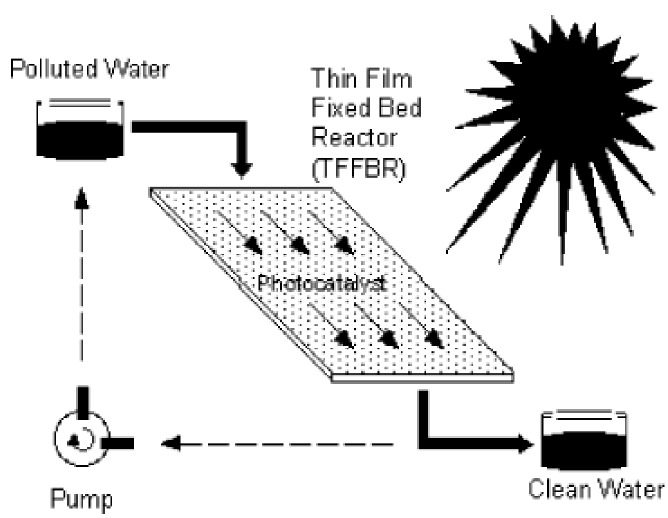

Figure-4: Schematics of water treatment using a TFFBR [2]

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In the meantime, nanomaterials and nanotechnology has entered the arena of science and technology. Nanosized semiconductors are being used as photocatalysts and in laboratory scale experiments, it has already been proved that nano-photo-catalysts are more efficient than the ordinary photocatalysts. Research group of the present author has also accomplished synthesis of ZnO nanoparticles and treatment of simulated wastewater using synthesized nanoparticles under sunlight. Pilot scale study has not yet been reported widely. Various innovations are under progress in this field.

Conclusions

In the present paper, an overview of the processes, by which sunlight can be used for purification of water, has been presented. Besides, a lot of research is going on in various research laboratories to utilize solar energy for the welfare of mankind. It is not possible to review all those studies here for obvious reasons. There are a few disadvantages of using solar energy in a large scale. 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. Hence 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. These problems should be overcome before we use solar energy in technological scale.

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