

Program/Semester:	M.Sc. Renewable Energy (Semester IV)
Module:	REC-401: Hydrogen Energy and Fuel Cells
Unit:	IV
Topic:	Solar Photo-catalytic Detoxification
Course Incharge:	Neelam P. Mishra, Ph.D.

Introduction

- The use of solar radiation for photo-catalytic removal of contaminants or pollutants from the environment is described as solar photo-catalytic detoxification. Solar photo-catalytic detoxification is a promising technology used in solar energy conversion and for environmental purification. These methods, based on catalysis and photochemistry are usually known as advanced oxidation processes (AOPs). Advanced oxidation processes are widely used for oxidation of a wide range of organic compounds and thus have enormous potential for water treatment technologies to remove bio-reclacitrant organic pollutants, which are not treatable by conventional technologies due to high chemical stability and/or low biodegradability of such pollutants. The type of compounds that are degraded using this mechanism include alkanes, haloalkanes, aliphatic alcohols, carboxylic acids, alkenes, aromatics, haloaromatics, polymers, surfactants, herbicides, pesticides and dyes.
- AOPs are characterized by the generation and subsequent reaction of hydroxyl radicals in driving oxidation processes. Hydroxyl attack is not very selective, which is a useful attribute for achieving complete abatement of even less reactive pollutants and thus important in air and water pollution mitigation. Hydroxyl radicals can be produced by different oxidation processes usually requiring the presence of ultraviolet light or ozone which make these processes expensive. Therefore, solar photo-catalytic

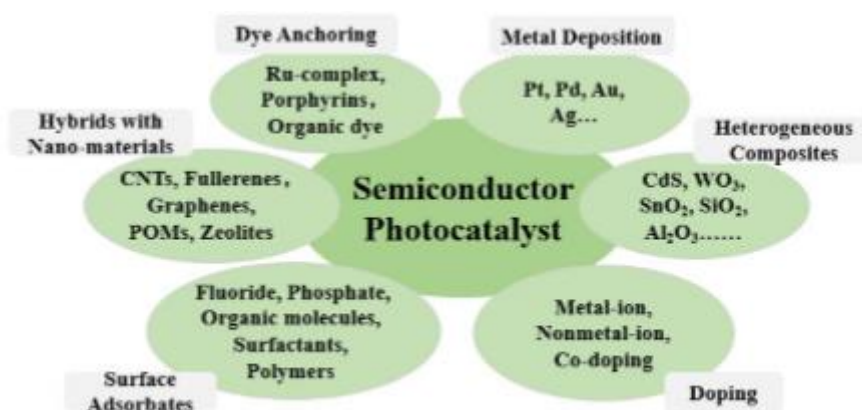
oxidation processes driven by solar irradiation (>300 nm wavelength) provide more effective low cost mechanisms for detoxification of pollutants.

- Another important application related to solar photo-catalysis is disinfection of water and wastewater, which involves the killing of microbial cells through the use of photo-excited semiconductor materials.

Types of Photo-catalysts and their Properties

- A photo-catalyst is defined as a substance which is activated by adsorbing a photon and is capable of accelerating a reaction without being consumed. These substances are invariably semiconducting oxides.
- An ideal photo-catalyst for photo-catalytic oxidation is characterized by the following attributes:
 1. Photostability
 2. Chemically and biologically inert nature
 3. Availability and low cost
 4. Capability to adsorb reactants under efficient photonic activation
- Several semiconductors (TiO_2 , ZnO , Fe_2O_3 , CdS and ZnS) can act as photo-catalyst but TiO_2 has been the most widely used nanomaterial in photo-catalytic processes due to its ability to breakdown organic pollutants to achieve complete mineralization. Photo-catalytic and hydrophilic properties of TiO_2 make it an ideal catalyst due to its high reactivity, reduced toxicity, chemical stability and lower costs. Fujishima and Honda pioneered the concept of titania photo-catalysis, also known as “Honda-Fujishima effect”.
- Titania has three crystal forms-rutile, brookite and anatase. Out of these, anatase and rutile types are commonly used as photo-catalyst. These are used in air purification, water pollutants degradation, antibacterial disinfection, deodorant and antifog substances.
- The use of advanced and modified catalyst structure and composition and addition of electron acceptors can lead to increase in the photo-catalytic rate. Impurity doping is

done to extend the spectral response of TiO₂ into the visible region and enhance its photo-catalytic activity. Doping with various transition metal cations such as Cr, V, Pb and Cu have shown both positive and negative effects on the photo-catalytic activity of titania. Anionic non-metal dopants such as carbon, nitrogen and sulphur may be more appropriate for the extension of photocatalytic activity into the visible light region because the related impurity states are near the valence band edge but do not act as charge carriers.

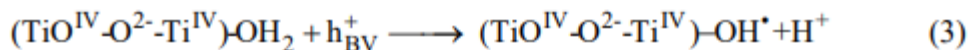
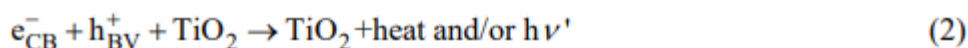


Mechanism and Fundamentals of Photo-catalytic Reactions

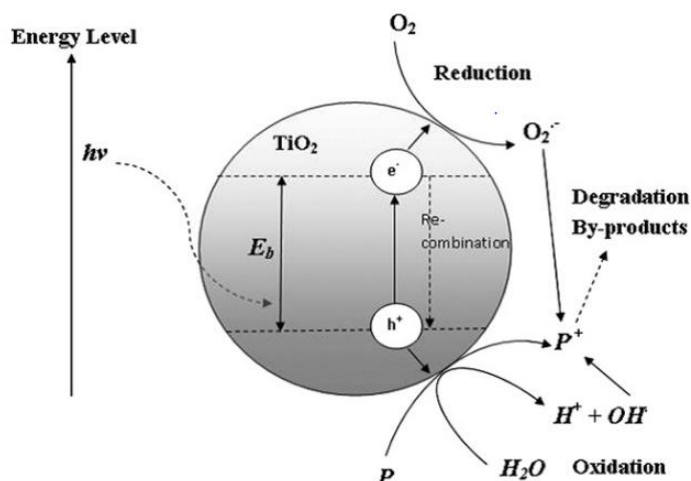
- Photo-catalytic detoxification involves the degradation of recalcitrant and non-biodegradable contaminants into carbon dioxide, water and inorganic molecule. Detoxification is carried out intensively either through heterogeneous TiO₂/UV light photo-catalysis or homogenous photo-Fenton method (addition of H₂O₂ to Fe²⁺ in the presence of UV-VIS light).
- Solar heterogeneous photo-catalysis consists of utilizing the near UV part of the solar spectrum (wavelength <380 nm) to photoexcite a semiconductor catalyst in the presence of oxygen. This photo-catalytic process, using UV/TiO₂ is based on the adsorption of photons with energy higher than 3.2eV (wavelength <390nm) resulting in initiating excitation related to charge separation event (gap band), Generation of excited high-energy states of electron and hole-pairs occurs when band gap

Prepared by:
Neelam P. Mishra, Ph.D.
 CoE in Renewable Energy Education & Research
 University of Lucknow, Lucknow - 226021

semiconductors are irradiated higher than their band gap energy. It results in the promotion of an electron in the conduction band (${}^{\ominus}\text{CB}^-$) and formation of a positive hole in the valence band (${}^{\oplus}\text{VB}^+$). The ${}^{\oplus}\text{VB}^+$ and ${}^{\ominus}\text{CB}^-$ are powerful oxidizing and reducing agents, respectively. The ${}^{\oplus}\text{VB}^+$ reacts with organic compounds resulting in their oxidation producing CO_2 and H_2O as end products. The ${}^{\oplus}\text{VB}^+$ can also oxidize organic compounds by reacting with water to generate $\cdot\text{OH}$ radical. Hydroxyl radicals ($\cdot\text{OH}$) produced in the reaction has the second highest oxidation potential (2.80 V) which is only slightly lower than the strongest oxidant, fluorine. Due to its electrophilic nature $\cdot\text{OH}$ can non-selectively oxidize almost all electron rich organic molecules eventually converting them to CO_2 and water.



- The conductive band can react with O_2 forming an anion superoxide radical $\text{O}_2^{\bullet-}$. Further reaction can lead to the formation of hydrogen peroxide which results in the formation of hydroxyl radicals.
- The presence of dissolved oxygen is extremely important during photocatalytic degradation as it can make the recombination process on TiO_2 ($({}^{\ominus}\text{CB}^-/{}^{\oplus}\text{VB}^+)$) difficult which results in maintaining the electroneutrality of the TiO_2 particles. Thus, it is essential for effective photo-catalytic degradation of organic pollutants that the reduction process of oxygen and the oxidation of pollutants process simultaneously to avoid the accumulation of electron in the conduction band and thus reduce the rate of recombination of ${}^{\ominus}\text{CB}^-$ and ${}^{\oplus}\text{VB}^+$.



- The solar homogenous photo-catalytic detoxification process (photo-Fenton) is based on the production of hydroxyl radicals by Fenton reagent (H_2O_2 in the presence of Fe^{2+}). The rate of degradation of organic pollutants with Fenton reagents is strongly accelerated by irradiation with UV-VIS light irradiation at wavelength higher than 300nm. In these conditions the photolysis of Fe^{3+} complexes allows Fe^{2+} regeneration and the occurrence of Fenton reactions due to the presence of H_2O_2 . Photo-Fenton reactions use solar radiation of wavelength approximately 580nm.

Radiation Sources and System Design

- Both artificial ultraviolet lamps and sunlight can be used as the radiation source for photo-catalytic process. Harnessing solar energy for photo-catalytic degradation is expected to increase in future as nearly 4-5% of the sunlight that reaches the earth's surface is in the range of 300-400 nm near UV light. However, solar energy has limitations due to the geographical variations when compared with the artificial UV lamps.
- Contrary to solar-thermal processes, which collect large amounts of photons at any wavelength to reach a specific range, solar photo-catalytic processes use only the high-energy short wavelengths photons to promote photochemical reactions (<600 nm).

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Neelam P. Mishra, Ph.D.
 CoE in Renewable Energy Education & Research
 University of Lucknow, Lucknow - 226021

- The specific hardware needed for solar photochemical applications is very much like that of solar thermal applications. As a result, both photochemical systems and reactors have followed conventional solar thermal collector designs such as concentrating parabolic troughs and non-concentrating collectors. However, in photochemical processes, the fluid must be directly exposed to the solar radiations and therefore the absorber must be transparent to the photons and the temperature usually does not play a significant role, so no insulation is required.
- The first photoreactor for solar photo-catalytic applications was based on parabolic trough collectors (PTCs) because of two reasons: (i) technology was relatively mature and standardized and (ii) it was easily adaptable. However, it became evident that PTCs are unsuitable for photo-catalytic applications for various reasons:
 1. Water is heated
 2. Radiation flux is too high
 3. Most of the photons are not used efficiently and
 4. Their cost is too high

On the other hand, non-concentrating solar collectors are static systems with no solar tracking mechanism and in principle, more economical than PTCs, their beam sunlight collection is less energy efficient, given their fixed orientation to the incoming radiation. Non-concentrating flat reactors are also not suitable for the photo-catalysis because of the requirements for chemical inertness and resistance to both weather and ultraviolet light.

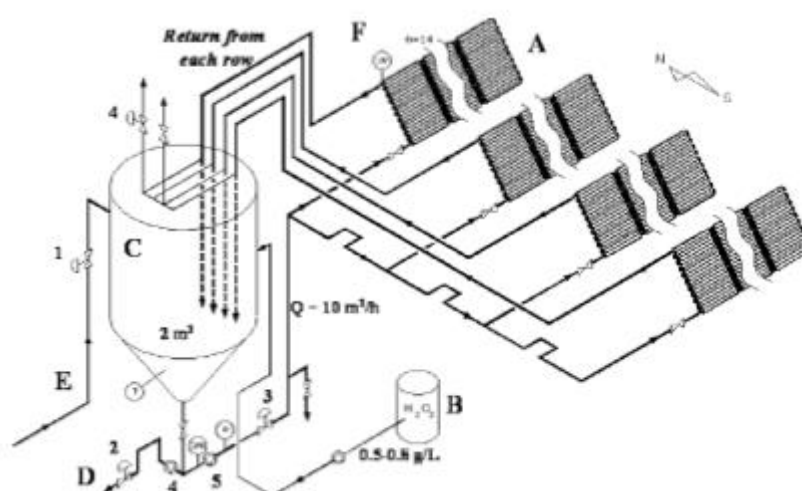
Table 1 Comparison between nonconcentrating and concentrating systems used in photocatalytic applications

Advantages of nonconcentrating systems	Disadvantages of nonconcentrating systems	Advantages of concentrating systems	Disadvantages of concentrating systems
Can make use of both direct and diffuse solar radiation	Construction materials problematic due to weather resistance, chemical inertness, and ultraviolet transmission	Noticeably smaller reactor tube area (shorter loop in which to confine, control, and handle the water)	They can only make use of direct solar radiation
Are simpler systems, with lower investment cost and fewer maintenance requirements	Are usually laminar flow, which can cause mass transfer problems in photocatalysis	More efficient use of a supported catalyst, as less is needed per unit collector surface	Usually expensive
Water may not heat up significantly even if no special measures are taken to that effect	Reactant vaporization	Turbulent flow (favors mass transfer and avoids possible catalyst sedimentation problems)	Lower optical efficiency and quantum efficiency also due to higher recombination of e^-/h^+ than in nonconcentrating systems
Since recombination of e^-/h^+ is lower than in a concentrating system because the photonic density is lower, they have both high optical efficiency and high quantum efficiency	Reactant contamination	There is no evaporation of volatile compounds	Possible water overheating

- Compound parabolic concentrators (CPCs) are the most suitable engineering design for solar photochemical detoxification applications. CPCs combine both the characteristics and advantages of both parabolic concentrators and static flat plate collector systems. CPCs are static collectors with an involute reflective surface around a cylindrical reactor tube, which can capture both direct and diffuse UV-sunlight. It is also cost effective, easy to use and requiring low capital investment. The reflector design enables almost all UV-radiations arriving at the CPC aperture to be collected and available to the process in the reactor. The light reflected by CPC is distributed around the back of the tubular photoreactors so that most of the reactor tube circumference is illuminated. Most of the components of the solar photoreactors are made up of standard materials with no special requirement except for the reactor, the reflective surface and the catalyst since almost all the solar photochemical processes require a catalyst or a sensitizer.
- The main advantages of CPCs are:
 1. Their turbulent flow conditions

Prepared by:
Neelam P. Mishra, Ph.D.
 CoE in Renewable Energy Education & Research
 University of Lucknow, Lucknow - 226021

2. Absence of vaporization of volatile compounds
3. Absence of tracking
4. Absence of overheating
5. Potential to use both direct and different solar radiation
6. Low cost
7. Weatherproof properties
8. Absence of reactant contamination and
9. High optical and quantum efficiency



Solar Photo-catalytic Detoxification Plant

Performance Parameters/Influencing Factors

- The performance of photo-catalytic reaction processes can be influenced by many factors. The effects of each factor on photo-catalytic reaction are summarized in the following table:

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 CoE in Renewable Energy Education & Research
 University of Lucknow, Lucknow - 226021

Table 1. Effects of influencing factors on photocatalytic reaction.

Influencing Factors		Effect on Photocatalysis
Catalyst concentration		- The reaction rate increases with the increase of the catalyst concentration.
		- Above a certain dose, the reaction rate decreases as the catalyst concentration increases.
Light source and light intensity	Light source	- Provide light of different wavelengths.
	Light intensity	- Improve light intensity and promote photocatalytic reaction.
PH value		- Related to target degradation products.
Plus oxidants		- Reducing the recombination of photogenerated electrons and holes to improve photocatalytic efficiency.
Inorganic ion	Anion	- Improve the separation speed of photogenerated electrons and holes and promote photocatalytic reaction.
	Cation	- Becomes a scavenger of hydroxyl radicals, forming anion radicals. - The competitive adsorption of active sites on the surface of the catalyst may affect the photocatalytic degradation of organics.
Temperature		- Has little effect.

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