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HETEROGENEOUS PHOTOCATALYSIS-A REVIEW

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ABSTRACT
A variety of conventional methods are available to meet our present energy demands. But as the world is witnessing tremendous developments in all areas of life, as such the conventional methods are no longer sufficient to meet our ever growing demands. Advanced oxidation processes (AOP) render great future for energy conversion and environmental issues like fuel generation, air and water detoxification, environmental cleanup etc. In view of the utilization of solar energy and AOPs, many applications like photovoltaic cells, solar cells, fuel production, organic synthesis, photo catalysis and many more has been studied in the last few decades. Out of these many applications of solar energy, this review paper focuses on Heterogeneous Photo catalysis. In this review, draw backs of conventional treatment methods, Advantages of AOPs in contrast to conventional methods, basic principle, working mechanism and applications of photocatalysis are discussed.

INTRODUCTION
With industrialization and population growth, the environmental contamination caused by organic pollutants, along with the rapid increase in greenhouse gas emissions, is becoming a burning issue all round the world [1]. The oil crisis also gave urgency to the innovation of alternate energy source and the increased pollution has alarmed the need for solar energy utilization. Further, as rapidly increasing population requires energy and resources to lead a comfortable standard of living, protection of natural water resources and development of new technologies for water and wastewater treatment has become increasingly important in the past decades. The organic pollutants in waste water sewage from industrial and domestic sources should be removed before discharge to the environment. Therefore, the development of novel and efficient processes to treat waste water is of utmost importance [2].

CONVENTIONAL WASTEWATER TREATMENT METHODS AND THEIR DRAWBACKS
Conventional water and waste water treatment methods have been entrenched for the removal of chemical, biological and organic contaminants which are of serious concern to the environment and public health. Many Physical, chemical and biological methods like coagulation, flocculation, ion exchange, ultra filtration, reverse osmosis, chemical precipitation, electrochemical technologies, activated sludge process are available for the putrefaction of these pollutants which include health hazardous trace metals like, chromium (Cr), Cadmium (Cd), mercury (Hg), Copper (Cu), lead (Pb), nickel (Ni), Arsenic (As) etc.

The conventional (Physical and Chemical) methods mainly concentrate on the removal of colloids and bacteria rather than the organic pollutants. They require long time for such treatments and high cost. The drawback of such treatments is that they either fail to achieve complete mineralization or are ineffective on pollutants that are non-adsorbable or non-volatile. Moreover, the major concern is that the pollutants are removed from one source only to be disposed to another source. Biological method needs more area, not very responsive to diurnal variation and toxicity of some chemicals, and is less adaptable in design and operation [4]. Although many organic pollutants can be degraded by conventional methods, some are really tough due to their hard chemical assembly and simulated organic origin. On the other hand they produce huge amount of sludge as they utilize more of chemicals necessitating further treatment. Several physical methods like membrane filtration, adsorption techniques etc., are readily available for the waste water purification, but there again the disadvantage is that they need periodic replacement and thus expensive.

ADVANCED OXIDATION PROCESSES (AOPS)
In the above circumstances, when the use of conventional methods is limited and not economical, it is necessary to uplift systems which are much more effective than the conventional purification methods. As a solution, the

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evolution of modern eco friendly methods which equally destroy the organic pollutants has become the challenging task in research field. Thus, over the past three decades, many research efforts have been focussed around the world to develop a newer, more powerful, and very promising technique called Advanced Oxidation Processes (AOPs) to treat the contaminants of drinking water and industrial effluents. AOPs are defined as near moderate temperature and pressure water treatment processes which involve the in situ generation of highly reactive hydroxyl radicals (OH•) along with superoxide radical (O2-•), peroxide (H2O2) etc in sufficient quantity to effect water purification [5]. Hence, in the near future, Advanced Oxidation processes (AOP) may probably replace the conventional methods for the treatment of organic pollutants during water treatment. The hydroxyl radical is highly reactive, less selective chemical oxidant and reacts in a faster rate with a wide range of organic compounds [6].

HETEROGENEOUS PHOTOCATALYSIS

Among AOPs Heterogeneous photocatalysis is becoming more popular in recent years because of its feature like solar energy utilization, transformation and environment issues [7].This process involves the acceleration of photoreaction in the presence of semiconductor photocatalysts. As there are two active phases, solid and liquid/gas are involved the process is known as heterogeneous. A Semiconductor can be defined as a material which is non conductive in its ground state due to wide energy gap or Band gap (Eg) between the top of the filled valence band (VB) and bottom of the vacant conduction band (CB).Semiconductors are used as photocatalysts because of their favourable properties like electronic structure, light absorption capability and charge transport characteristics. The band gap is one of the most key parameters to elucidate the optical properties of semiconductors [8].

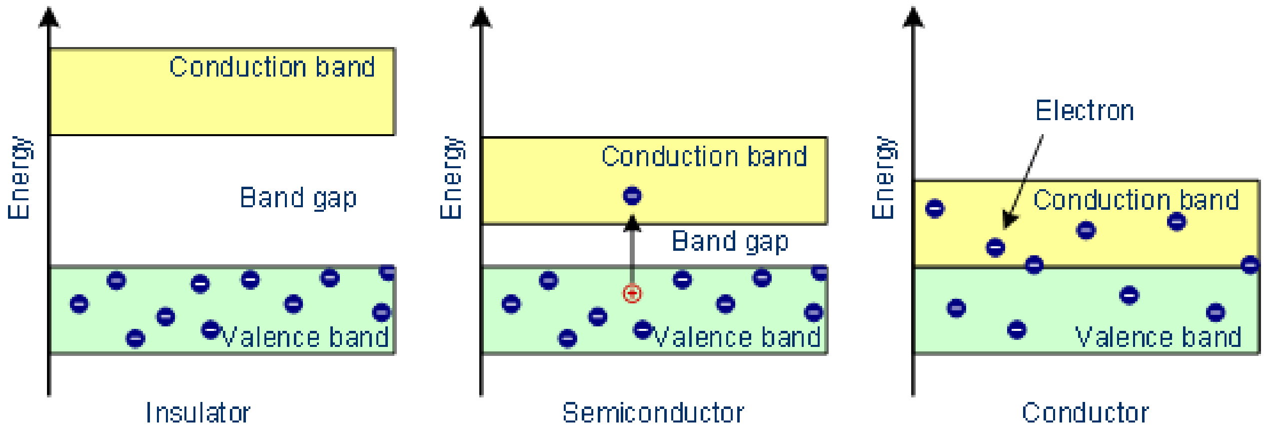

Figure 1.1: Schematic diagram of Band gap in Conductors, Semiconductors and Insulators

Photocatalysis is an interesting science in the field of green Chemistry. Photocatalysis is a catalytic process occurring at the surface of semiconductor materials under the irradiation of photons. It is a principal chemical process that incorporates the growth of renewable energy and environmental science like photocatalytic water/air treatment, hydrogen generation from water splitting, and high performance/less price solar cells. At present, the actual applications of photocatalysis are however, limited because of low separation chances of the photo induced electron-hole pairs in the photocatalysts. Therefore, this has been a challenge for the researchers to develop the photocatalysts that not only enhance the charge carrier separation but also is seen as a solution to address the key environmental issues.
Semiconductor Photocatalysis is being considered as a more advanced oxidation process to resolve environmental problems such as air pollution and industrial wastewater. One of the major advantages of Photocatalysis is that it does not have any further sludge disposal problems. Also Photocatalysts can be reused or recycled. Also in contrast to thermal catalysis which usually occurs at high temperatures, Photocatalysis occurs at ambient or room temperature and hence known as 'green method' for environmental remediation.

The merits of heterogeneous photocatalytic process over the conventional used treatment methods are:

(i) These processes can be carried out under ambient condition (moderate temperature and pressure) and the process uses atmospheric oxygen as oxidant and no other expensive oxidizing chemical is required.

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(ii) The oxidant is strong and less selective which completes the mineralization of almost all organic pollutants in wastewater.

(iii) This process is known as green method since the degraded bi-products (mineral acids, water and carbon dioxide) are non toxic or show moderate toxicity.

(iv) No residue remains at the end and hence no sludge disposal or landfill problem is generated in this process.\

(v) This method can be used at extremely low concentrations as the pollutants are firmly adsorbed to the catalyst surface.

(vi) These photocatalysts are cheap, non hazardous, stable, chemically and biologically inert, usually insoluble, reusable and regenerated.

PRINCIPLE OF PHOTOCATALYSIS

Photocatalysis is a chemical process where the light is used to activate a material, a photocatalyst, which accelerates the rate of the reaction without consuming itself. In this process, the reaction is originated by the generation of electron–hole pairs of the catalyst, normally a semiconductor. The different methods to utilise the solar irradiation through photocatalysis are ;

(1) Water splitting for the generation of fuel hydrogen (2) Organic transformations (3) Detoxification of the environment, (4) Counterfeit photosynthesis, (5) Photoelectrochemical transformations [13].

When a light energy which is equal to or greater than the band gap energy (Eg), is illuminated on the semiconductor the valence band (VB) electrons are excited to the conduction band (CB), leaving a positive hole in the valence band.

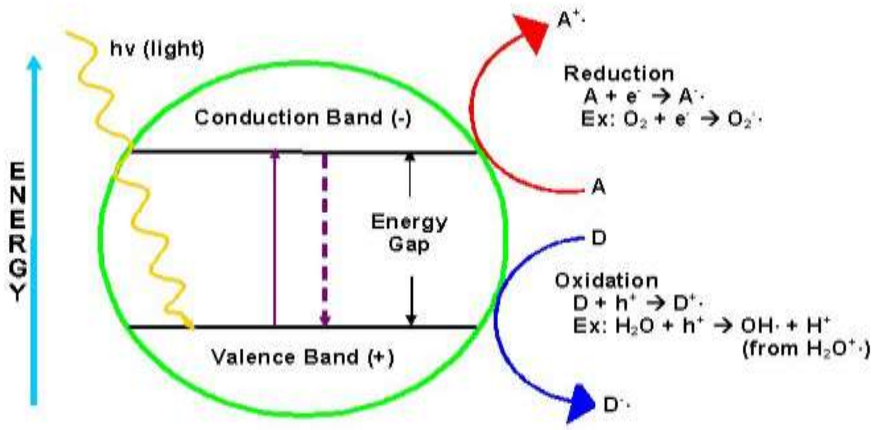

Figure 1.2: Schematic diagram for the mechanism of Photocatalysis

The excited electrons in the conduction band and holes in the valence band then find one or more routes of the degradation reactions as shown below (equations 1.1 to 1.12). Such photo induced electrons and holes migrate to the semiconductor surface and undergo adsorption reactions. The transfer of electrons is more productive when species are pre-adsorbed on the surface. There, the semiconductor may give electrons to reduce an electron acceptor and an electron from a donor species can react with the surface hole which oxidizes the donor species. The feasibility of the charge transfer processes of electrons and holes confide on the band gap of the semiconductor and the redox potential that the adsorbed species comprise.

During this phenomenon, the reaction of recombination of electrons and holes can occur as competition with the charge transfer to the semiconductor surface. Recombination can occur inside the semiconductor particle or at the surface with the simultaneous release of heat [14]. Atmosphere Oxygen which is available in the reaction media generally acts as an electron acceptor in most of the heterogeneous photocatalysis. The photo generated electrons can reduce molecular oxygen to O2•- which can be subsequently transformed into other chemical species, such as HO2•, HO2−, H2O2, and possibly HO• radicals. These activated oxygen species may undergo the oxidation of organic electron contributor. Also, photo generated holes can convert the electron donor by forming reactive species like surface-bound HO• radicals or by straight reaction with adsorbed organic species.

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Altogether, these reactions completely mineralize the organic pollutants to mineral acids, water and carbon dioxide [15].

The holes of the valence band reacts with OH- from the water molecule and generates OH• radicals which are the primary oxidants for the degradation of organic pollutants. Through a series of redox reactions, the organic pollutants mineralize to final products such as CO2, H2O and inorganic salts and ions. It is always necessary that redox reactions occur simultaneously, failing which electrons starts accumulating in the conduction band which results in the recombination of e-CB and h+VB [16][17].

$PC + hv \longrightarrow PC\ (e^-_{CB} + h^+_{VB})$ 1.1

$PC\ (h^+_{VB}) + H_2O \longrightarrow PC + HO^-_{ads} + H^+$ 1.2

$PC\ (h^+_{VB}) + OH^-_{ads} \longrightarrow PC + HO^{\bullet}_{ads}$ 1.3

$PC\ (e^-_{CB}) + O_{2ads} \longrightarrow PC + O_2^{\bullet -}$ 1.4

$O_2^{\bullet -} + H^+ \longrightarrow HO_2^{\bullet}$ 1.5

H_2O_2 could also be formed from $HO_2^{\bullet}$ species as

$PC\ (e^-_{CB}) + O_2^{-\bullet} + H^+ \longrightarrow H_2O_2$ 1.6

$^{\cdot}HO_2 + {}^{\cdot}HO_2 \longrightarrow H_2O_2 + O_2$ 1.7

$h^+_{VB} + OH^- \longrightarrow {}^{\cdot}HO$ 1.8

$Dye^*/\ Dye^{*+} + ({}^{\cdot}HO,\ O_2^{*-}) \longrightarrow$ degradation Product 1.9

The photo generated hydrogen peroxide undergoes further decomposition to yield hydroxyl radicals.

$H_2O_2 + hv \longrightarrow 2HO^{\bullet}$ 1.10

$H_2O_2 + O_2^{\bullet}- \longrightarrow HO^{\bullet} + O_2 + HO^-$ 1.11

$H_2O_2 + PC\ (e^-_{CB}) \longrightarrow HO^{\bullet} + HO^- + PC$ 1.12

For the reduction of recombination of electron-hole pairs and successful functioning of the photo catalyst and the adsorbed oxygen plays an important role. The recombination is reduced by the generation of superoxide radicals. On the other hand without the presence of water, hydroxyl radicals will not be generated and hence reaction media is mandatory for the process of photo catalysis to occur.

MECHANISM OF GENERATING OXIDIZING SPECIES

1. Mass transfer of the reactants from the liquid media to the surface of the catalyst.
2. Adsorption of the reactants to the photoactivated surface of the catalyst(Where electron-hole pairs are generated).
3. Reaction of photocatalysis for the adsorbed molecules on the catalyst Surface.
4. Desorption of the products from the catalyst surface.
5. Diffusion of these products to the reaction media.

BASIC REQUIREMENTS FOR AN IDEAL PHOTOCATALYST

Considering the above reactions and reaction environment, the basic characteristics of a photocatalyst to be considered as an ideal can be summarized as:

1. Possess suitable band width 2. Efficient conversion of visible light to electron-hole pairs 3. Smaller particle size 4. Large surface area and more active sites 5. Surface trapping of electrons and holes before recombination 6. Biological and Chemical inertness 7. Non toxic 8. Highly Photoactive.

PHOTOCATALYTIC MATERIALS

Many research reviews conclude that more or less any pollutant that includes aliphatic, aromatics, dyes, surfactants, pesticides, and herbicides can be completely decomposed by photocatalytic oxidation into harmless substances like CO_2 and H_2O. CdS, ZnO and NiO are some metal oxide semiconductors that were found as photocatalysts at the beginning. The actual development of this heterogeneous photocatalysis started during 1970's when A. Fujishima and K. Honda put forth TiO_2 as a photocatalyst (19). Titanium dioxide or titania, is the very familiar as an oxide of titanium with chemical formula TiO_2 as a photocatalyst has found diverse applications in number of processes like hydrogen production, effluent detoxification and disinfection, and organic synthesis because of its high stability and comparatively high quantum yield. Photocatalytic coatings deposited on windows, walls along with air purifiers are the main commercial uses but many other have been proposed and some experimental devices are already on the market. Because of the above reasons, TiO_2 became

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a synonm for photocatalyst in a short span of time (19). Even though it has been referred as a bench mark photo catalyst for the redox mineralization, it failed to work as a visible light responsive photo catalyst because of its wide band gap. Hence, in the last few years, many number of new materials have been synthesized as efficient alternative to TiO_2. In this scenario, ZnO and CdS are well known as an advanced research nano materials. Many other new semiconductor materials has also been inverstigated in order to develop visible light sensitive photocatalysts. These include coupled hetero structures of TiO_2 like TiO_2/WO_3, TiO_2/SnO_2, TiO_2/CdS etc., metal semiconductor composites like Ag/TiO_2, Au/TiO_2, Pt/TiO_2 etc [23]. Interestingly, in the last few years mixed oxides with main group elements like In, Bi, Sb, Ga or mixed oxides of transition metal like Ta, Nb or V have been synthesized as a novel photocatalysts. Also nitrides and sulphides of various metals are chosen to get materials of visible light sensitivity. Metal oxide based semiconductor materials have taken an exceptionally significant role due to their wide range of properties and corresponding application [9]. Inertness to chemical environment, long-term photo stability and thermal stability has made these materials supreme in many industrial and commercial applications, ranging from medicines, foods, cosmetics, catalysts, paints, pharmaceuticals, sunscreens and solar cells[10].

Work has been done on many other semiconductor materials like WO3, CdS, ZnO, Fe_2O_3 and SnO_2 also have been intensively investigated for their performance of photocatalytic activity. A real challenge of any photocatalytic process is to reduce the recombination of the photogenerated charge carriers, i.e., of electrons and holes, the band gap [23].

The nanostructure of such advanced functional materials affects almost all material characteristics such as material strength, surface properties, electrical, electronic and optical properties and hence much attention is directed towards the synthesis and characterization of new nanomaterials [11]. A nano crystal or a nano particle is a crystalline structure whose dimension is smaller than 100nm at least in one direction of its crystal structure. The utilization of light to activate such nano particles shows new ways to design green oxidation technologies for environmental remediation [12].
The traditional technologies like oxidation, activated carbon, nanofiltration (NF), activated sludge, and reverse osmosis (RO) membranes are not effective to decompose complex and complicated polluted waters containing pharmaceuticals, various industrial additives, and numerous chemicals. With such methods it is not possible to remove wide range of toxic chemicals and pathogenic microorganisms in raw water.

Biological methods like biological trickling filters and activated sludge are unable to remove a wide range of emerging contaminants and also most of these compounds remain soluble in the effluent Chlorination, though it provides residual protection against the regrowth of bacteria and pathogens renders undesirable tastes and odors. Nanotechnology can been considered effective to solve water problems related to quality and quantity. There are many features of nanotechnology to resolve the multiple problems of water quality in order to ensure the environmental stability.

Nanotechnology uses materials of sizes smaller than 100nm in at least one dimension meaning at the level of atoms and molecules as compared with other disciplines such as chemistry, engineering, and materials science. At this scale, materials possess novel and significantly changed physical, chemical, and biological properties because of their structure, higher surface area-to-volume ratio offering treatment and remediation, sensing and detection, and pollution prevention. Nanoparticles can penetrate deeper and thus can treat water/wastewater which is generally not possible by conventional technologies. The higher surface area-to volume ratio of nanomaterials enhances the reactivity with environmental contaminants [24].

CONCLUDING REMARKS

The environmental remedies like fuel production, effluent disinfection, air detoxification etc., by photocatalysis as an advanced oxidation process is becoming a novel method as clean energy. In the near past, many semiconductor based materials have been originated as effective photocatalysts.
TiO_2 is an efficient Photocatalyst among them but is active under UV light irradiation. Much work has been done for the generation of visible-active materials to achieve maximum utilization of solar spectrum. Research in this area has brought great grip to material science which contributes to the development of newer visible light sensitive materials continuously.

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- **FUTURE SCOPE**

Along with the revolution of nanoscience and technology, there is a huge scope for advanced nano semiconductor materials as photocatalysts in the near future. Photocatalysis is becoming a powerful and versatile tool for many applications in fuel production and chemical synthesis on the far side what we have realised today.

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