Chapter 2

OVERVIEW OF PHOTOCATALYSIS

1.1. Introduction

There is generally a conception that Photo-catalysis originated with the discovery of Photo-electrochemical decomposition of water by Fujishima and Honda [2] in the 70s. Photo-catalysis which is a phenomenon wherein an acceleration of a chemical reaction in the presence of photons and catalyst has been reported in the literature in 50s (possibly even earlier to this) by Markham and Laidler [20]. Sister Markham followed this with a publication in chemical education [19] wherein she reported the photo-catalytic properties of oxides. In fact, Sister Markham reported that the absorption of photons by the solid generates electron hole pair which are utilized in the generation free radicals (hydroxyl radicals (.OH)). The chemical consequence of this process today goes with the name of Advanced Oxidation Process (AOP; which may or may not involve TiO2 and Photons). Markham had a number of subsequent publications on the photo-catalytic transformations on irradiated zinc oxide [12]. Photo-catalysis deals with the Photochemistry has been an integral part of life on earth. One often associates photo-catalysis with photosynthesis. However, the term photo-catalysis found mention in an earlier work by Plotnikov in the 1930's in his book entitled Allaemeine photochemie. The next major systematic development as stated earlier was in the 1950's when Markham and Laidler performed a kinetic study of photo-oxidation on the surface of zinc oxide in an aqueous suspension. By the 1970's researchers started to perform surface studies on photo-catalysts like Zinc Oxide and Titanium dioxide. The most commonly employed photo-catalyst is Titanium dioxide. TiO$_2$ exists mainly in three crystallographic forms, namely Brookite Anatase and Rutile. There have been a number of studies on the three modifications of titania. The energetics of the titania polymorphs were studied by high temperature oxide melt drop solution calorimetry. It has been shown that relative to bulk rutile, bulk brookite is 0.71±0.38 kJ/mol and bulk anatase is 2.61±0.41 kJ/mol higher in enthalpy. [21]. The effect of particle size on phase stability and phase transformation during growth of nanocrystalline aggregates and has been shown that mixed phases transform to brookite and/or rutile before brookite transforms to rutile. [13] Among these three forms, the most often used photo-catalyst is the anatase phase either in pure form or in combination with rutile form. There are various reasons for this preference of TiO$_2$ as photo-catalyst. These reasons include that it was the first system studied by Fujishima and Honda and TiO$_2$ exhibits possibly maximum photon absorption cross section (i.e., it

absorbs maximum number of photons of correct wavelength). This preference over TiO_2 is seen from the data given in Table 1.

Table 1 Statistical distribution of scientific publications focused on nanomaterials for PEC/Photo-catalysis hydrogen production [15]

Materials	percentage of study
TiO_2	36.2
Non-TiO_2Oxides	10.9
Oxy-sulphides	18.8
Oxy-nitrides	5.1
Other semiconductors	5.8
Composites and Mixtures	17.4
Non-semiconductors	5.8
Total	100

Degussa P25 Titanium dioxide generally employed as catalyst in many of the studies reported in literature and hence, considered as standard for photocatalytic activity comparison, contains both anatase (about 80 percent) and rutile (about 20 percent). It is in general impossible to completely trace the history of Photo-catalysis. Even Fujishima and his coworkers [3] have expressed concern on completely outlining the history of photo-catalysis. The main difficulty appears to be that photo-catalysis unlike other chemical reactions involves simultaneously both oxidation and reduction reactions on a surface possibly assisted by photons of appropriate wavelength corresponding to the band gap of the semiconductor employed as catalyst. In 1921 Renz reported that titania was partially reduced when it was illuminated with sunlight in the presence of organic substrates like glycerol [24]. In 1924, Baur and Perret [E. Baur, A. Perret. Helv. Chim. Acta, 7 (1924), p. 910] probably were the first to report the photodecomposition of silver salt on ZnO to produce metallic silver. Probably Baur and Neuweiler [5] were the first to recognize that both oxidation and reduction are taking place simultaneously on the production of hydrogen peroxide on ZnO. This was followed by the work of Renz in 1932 [25] who reported the photocatalytic reduction of silver nitrate and gold chloride on TiO_2. Goodeve and Kitchener [6] studied the photo-catalytic decomposition of dye on titania surfaces and even reported the quantum yields. In 1953, it has been recognized that the organic substrate was oxidized and oxygen was reduced. Unfortunately, these studies have been carried out on ZnO surfaces and hence could have been hampered because of the inevitable problem of photo-corrosion of ZnO [20]. There were few attempts in between for the production of

hydrogen peroxide and decomposition of dyes on illuminated semiconductor surfaces. There were attempts to study the photo-catalytic oxidation of organic substrates on a variety of oxide surfaces from other parts of the world in and around this period. In the 1960s photo-electrochemical studies on ZnO with various redox couples were started. All these studies culminated in the photo-electrochemical decomposition of water by Fujishima and Honda which opened up means for solar energy conversion and also for the generation of hydrogen fuel. Subsequently Bard and his coworkers [16] have demonstrated that illuminated TiO_2 could be used for the decontamination of water by photo-catalytic decomposition. This has led to new photo-catalytic routes for environmental clean-up and also for organic synthesis. These aspects will be dealt with separately. Fujishima et al., have provided a more detailed and authentic write-up on the history of photo-catalysis [3].

1.2. Basic Principle of Photocatalysis

According to the glossary of terms used in photochemistry [IUPAC 2006 page 384] photo-catalysis is defined as the change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible or infra-red radiation in the presence of a substance the photo-catalyst that absorbs light and is involved in the chemical transformation of the reaction partners. When a semiconductor (or an insulator) is irradiated with light of suitable wavelength corresponding to the energy of the band gap, electrons occupying the usually or mostly filled energy levels in the valence band will be transferred to an allowed energy states in the normally empty conduction band thus creating holes in the valence band. This electron-hole pair is known as exciton. These photo-generated electron-hole pairs promote the so-called redox reaction through the adsorbed species on the semiconductor or insulator surface. However, the band gap of the insulators will be usually high and as such generating of such high energy photons will not be comparatively easy and hence insulators are not considered as possible candidates for Photo-catalysis. Generally, metals cannot be employed as photo-catalysts since their occupied and unoccupied energy states are overlapping with respect to energy and hence the recombination of electron-hole pair will be the most preferred process and hence the conversion of photon energy to chemical energy using metals will not be advantageous. The choice of semiconductors for photocatalysis is clear from Fig.2.1. It is generally considered that the energy position of the top of the valence band of a semiconductor is a measure of its oxidizing power and the bottom of the conduction band is a measure of its reducing capacity. It is therefore necessary one has to know with certain level of accuracy the energy positions of the top of the valence band and bottom of the conduction band so that the reactions that these excitons can promote can be understood. One such compilation is given later in this chapter in Table 3.

Photo-catalytic destruction of organic pollutants in water is based on photochemical process involving semiconductors. When a semiconductor is irradiated with UV
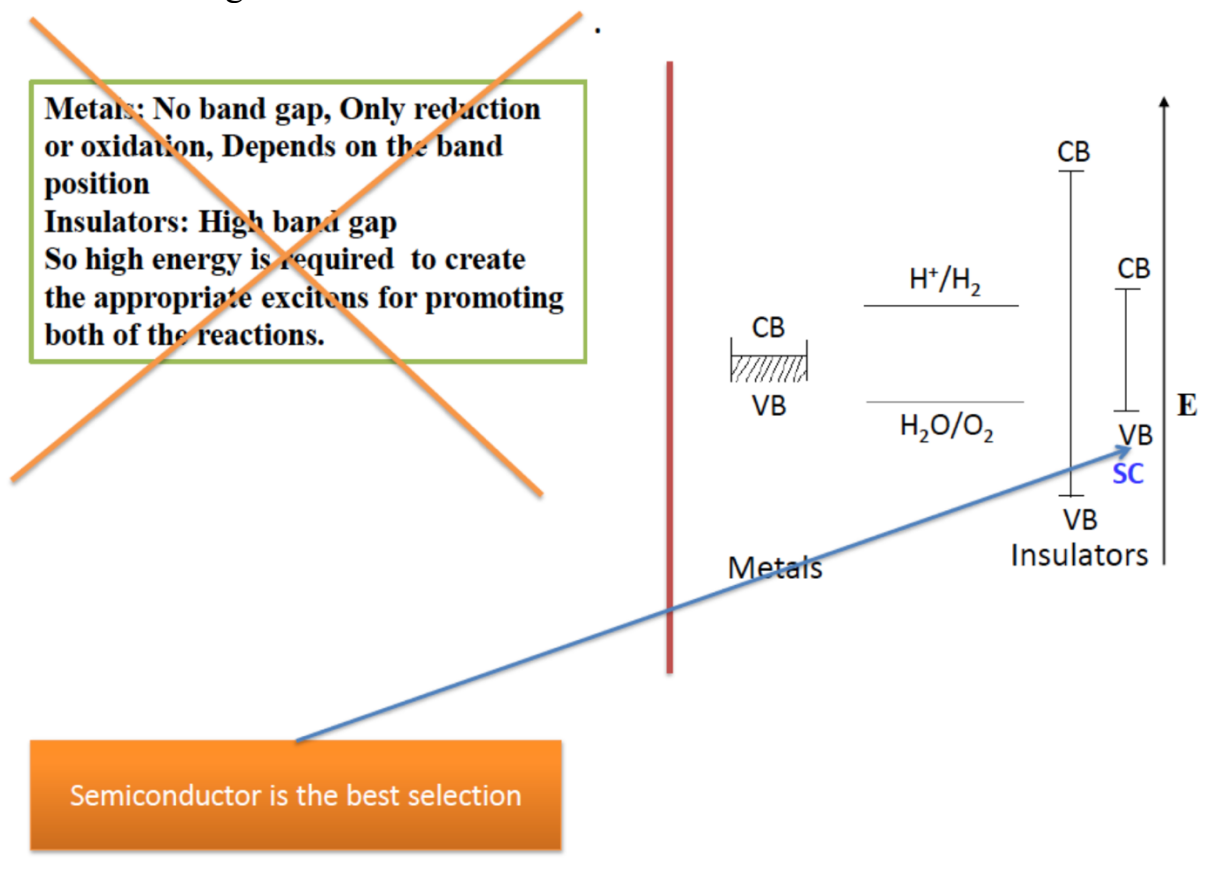

Fig 2.1. The choice of semiconductors for photo-catalysis is pictorially represented.

light (usually but it can be any other radiation as well) light of wavelength appropriate for excitation from valence band to the conduction band of the chosen semiconductor, an exciton is created. The photochemical oxidation of the organic substrate normally proceeds by the adsorption of the substrate on the surface of the semiconductor with transfer of electrons with the hole generated. However other possible oxidation processes can also take place with radicals generated (OH radical if the solvent is water) at the surface of the semiconductor surface. Thus, a variety of surface reactions will take place on the photo-excited semiconductor surface, the preferred reaction depends on the nature of the substrate under consideration and its nature of adsorption and activation on the semiconductor surface. In Fig 2.2 a simple representation of these possible processes is shown by considering simple general reactions water giving hydroxyl radicals and organic substrate being oxidized all the way to carbon dioxide and water in order to get an idea of what can takes place on the surface of semiconductor as a result of photoexcitation and catalysis. Since it is possible that the organic substrate can be completely degraded to carbon dioxide

and water, this process has been considered to be a viable method for the decontamination of water. In addition, it should be kept in mind that hydroxyl radical is a powerful oxidizing agent as compared to other common oxidizing agents as can be seem from the data given in Table.2. It is clear from the data given in Table.2 that the aqueous phase reactions will still be preferred in Photo-catalyst
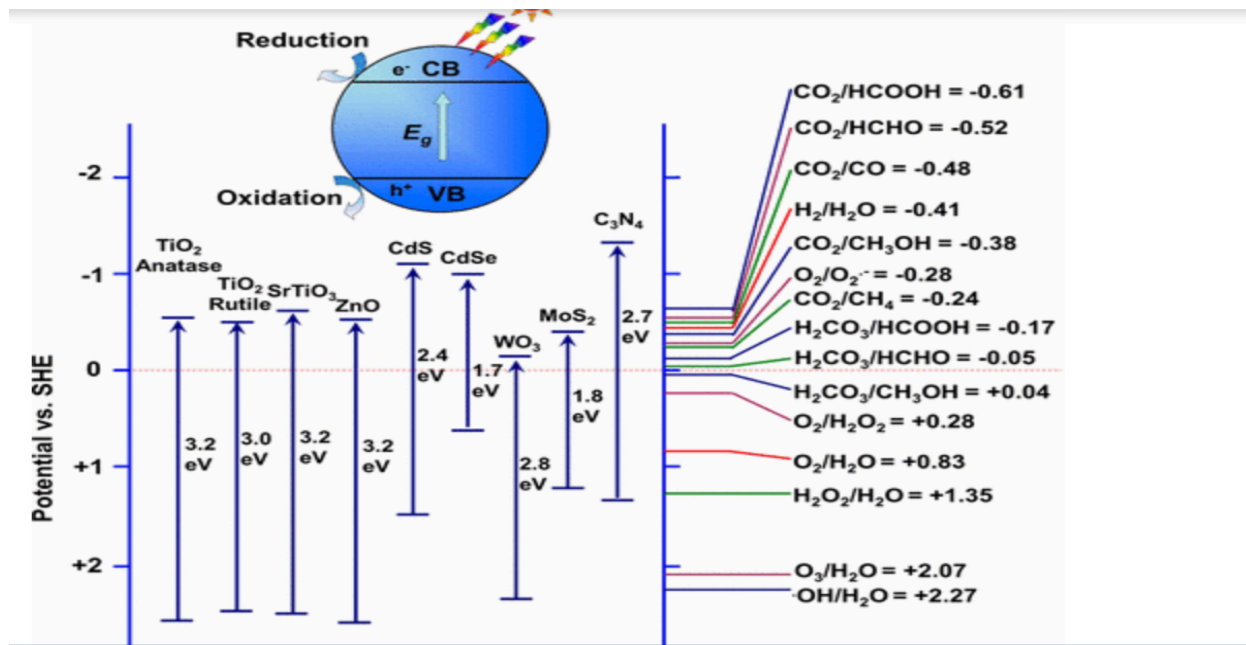

Figure 2.2.: Schematic representation of the principle of photocatalysis showing the energy band gap of a semiconductor particle. Typical reactions considered water → hydroxyl radical; organic substrate + hydroxy radical→ carbon dioxide + water + mineral acid

Table 2 Oxidizing power of some of the commonly employed oxidizing agents.

Oxidant	Oxidation Potential(V)
Hydroxy Radical	2.80
Ozone	2.07
Hydrogen Peroxide	1.77
ClO_2	1.49
Chlorine (Cl_2)	1.35

1.3. **Limitations of photo-catalysis**

Though Photo-catalytic technology has been emerging as a viable technology for the remediation of pollutants from water, it can be applied to a variety of

compounds. One of the factors to be considered is the possibility of mass transfer limitations due to the characteristics imposed in the reaction chamber by the existence of the catalyst in various forms in dispersed state. In fact, the construction of an appropriate photo-chemical reactor itself has been a major issue and various designs have been proposed in literature. A simple reactor design conventionally employed is shown in Fig.2.3. Sclafani et al. [4] postulated external mass transfer limitations to interpret their results in a packed bed reactor filled with spheres of semiconductor catalyst (in this case pure titanium dioxide (ca. 0.12 cm in diameter)). Chen and Ray [8] studied internal and external mass transfer limitations in catalytic particles of photo-catalytic reactors and concluded only mild mass transfer restrictions since the effectiveness factor observed was near 0.9 and hence rotating disc photo reactor when the spherical particles of the semiconductor fixed on a solid support. The specific role of mass transfer was analyzed in terms of one of the dimensionless Damkhler numbers. In other reactor configurations, particularly films and membrane reactors other quantitative observations of internal mass transfer limitations have been published. [9], [7] and many others (see for example one of the reviews on this topic in Legrini et al. [22]). Unfortunately, these limitations have not been examined with other type of reactors like slurry reactors. In addition, since photons are coupling with a heterogenous system, this can result in gradients in concentration or the coupling of the photon field with the scattering particles. The points that emerge from the data presented in these two tables are that the top of the valence band is nearly the same for the oxide semiconductors and the bottom of the conduction band depends on the cation involved and hence the oxide semiconductors will be more or less behaving in a similar manner. The other chemical limitations involved in the photo-catalytic degradation of pollutants from water are: The adsorption of the pollutant species on the surface of the semiconductor. This fact has been recognized in the literature but still not many quantitative relationships have emerged indicating the importance of this step in the photo-degradation processes. However, the importance of this step is apparent since the charge transfer from the semiconductor to the substrate and hence cause their degradation is possible only in the adsorbed state of the substrate since charge transfer has restrictions with respect to distances involved. In addition, the adsorption is directly related to the surface area of the photo-catalyst and hence it is conventional to optimize the surface area of the photo-catalyst. The pH may also have an effect on the photo-degradation of organic pollutants since the nature of the species involved can change with respect to pH. In addition, in aqueous medium the potential changes by 59 milli-volts per pH unit and this also can affect the process of degradation. In solution phase, the presence of both type of counter ions namely, anions and cations can affect the photo-degradation process due to reasons like photon absorption by the ions and also the type of species that will be generated as

a result of photon absorption. When the composite solar radiation is employed for photo-degradation process, the temperature of the system can affect all the reactions (normally increase is noticed) except for the electron hole creation step. However, the solubility of oxygen will decrease with increase in temperature and this can also affect the rate of photo-degradation reaction. In a subsequent chapter, the studies reported on the application of photo-catalysis for the decontamination of water will be considered. This field seems to assume importance in these days due to various reasons. However, the studies reported in this area have to be considered with care since the products of oxidation and their effects have not yet been established though it is generally assumed to be carbon dioxide. As seen earlier that one of the areas in which photocatalysis has been extensively employed is the decontamination of water. Water covers over two thirds of earth's surface and less than a third is the land area. Oceans, rivers and other inland waters are continuously polluted by human activities leading to a gradual decrease in the quality of water. There are specified limits of concentration beyond which the presence of some substances is considered as polluting water. In Table 5, the recommended tolerance limits of pollutants are given. The common pollutants in water are classified as inorganic contaminants and organic pollutants. The main inorganic contaminants are the metal ions, nitrates, nitrites, nitrogen dioxide, ozone, ammonia, azide and halide ions. There are various studies reported in literature that deal with the photocatalytic decomposition or transformation of these inorganic contaminants. Photocatalytic decomposition (mostly oxidation) of organic pollutants has been of great interest. In these studies, the reaction is carried out in presence of molecular oxygen or air for complete oxidation to carbon dioxide and water and possibly inorganic mineral acids as the final products. It has been shown that many of the organo-chlorides, pesticides, herbicides and surfactants are completely oxidized to carbon dioxide, water and hydrochloric acid. It may be worthwhile to realize the effect of some of the pollutants on human health. The data collected from literature are given in Table.6. It is to be remarked the effects of pollutants generally affect the human health in a variety of ways basically affecting the nervous system.
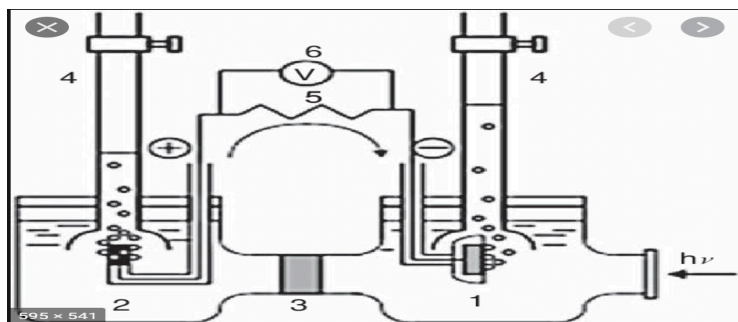
Figure 2.3. Typical reactor design conventionally employed for the photo-splitting of water. This is termed as Fujishima Honda cell.

Table.3. Electro-negativity, [χ], Band gap, (Eg) energy levels of the conduction band bottom (ECB) and energy position of the top of valence band (E V B) [data extracted from Y. Xu and M.A.A. Schoonen, American Mineralogist, 85, 543-556 (2000)]

Substance oxide	Electronegativity (χ)	Band gap (E_g)	Conduction band E_{CB}	Valence Band E_{VB}
$BaTiO_3$	5.12	3.30	-4.58	-7.88
Bi_2O_3	6.23	2.80	-4.83	-7.63
$CoTiO_3$	5.76	2.25	-4.64	-6.89
CuO	5.81	1.70	-4.96	-6.66
Fe_2O_3	5.88	2.20	-4.78	-6.98
Ga_2O_3	5.35	4.80	-2.95	-7.75
$KNbO_3$	5.29	3.30	-3.64	-6.94
$KTaO_3$	5.32	3.50	-3.57	-7.07
$MnTiO_3$	5.59	3.10	-4.04	-7.14
Nb_2O_5	6.29	3.40	-4.59	-7.99
NiO	5.75	3.50	-4.00	-7.50
$NiTiO_3$	5.79	2.18	-4.70	-6.88
PbO	5.42	2.80	-4.02	-6.82
SnO_2	6.25	3.50	--4/50	-8.00
$SrTiO_3$	4.94	3.40	-3.24	-6.64
TuO_2	5.81	3.20	-4.21	-7.41
V_2O_5	6.10	2.80	-4.70	-7.50
WO_3	6.59	2.70	-5.24	-7.94
ZnO	5.79	3.20	-4.19	-7.39
ZrO_2	5.91	5.00	-3.41	-8.41

Table.4. Band positions of some semiconductor photo-catalysts in aqueous solution at pH =1 and positions are given in volts versus NHE.

Semiconductor material	Valence Band V vs NHE	Conduction band V vs NHE	Band Gap (eV)	Band gap (wavelength)
TiO_2	+3.1	-0.1	3.2	387
SnO_2	+4.1	+0.3	3.9	318
ZnO	+3.0	-0.2	3.2	387

ZnS	+1.4	-2.3	3.7	337
WO$_3$	+3.0	+0.2	2.8	443
CdS	+2.1	-0.4	2.5	490
CdSe	+1.6	-0.1	1.7	729

In addition, there are some Persistent Organic Pollutants (POP) like aldrin, chlordane DDT, hexachlorobenzene, furans, polychlorinated biphenyls, Polycyclic aromatic hydrocarbons (PAHs) and so on. These substances some of which are called the dirty dozen cause many disorders including cancer breast cancer, damage to reproductive system, neuro-behavioural disorders and health related concerns.

Table 5 Recommended tolerance limits of pollutants in water [Data collected from K.C. Agarwal, Industrial power engineering and Applications, Butterworth-Heinemann, pp.565 (2001)

S. No	Parameter	Recommended Tolerance level
1	Biological Oxygen Demand (BOD)	30 mg/l
2	Chemical Oxygen Demand (COD)	250 mg/l
3	Alkali traces	maximum upto pH 9
4	Acid	Not less than pH 5.5
5	Total suspended solids	100 mg/l
6	Oil and Grease	10 mg/l
7	Dissolved phosphates as P	5 mg/l
8	Chlorides as Cl	600 mg/l
9	Sulphates (as SO$_4$)	1000 mg/l
10	Cyanides as (CN)	0.2 mg/l
11	Total Chromium	2 mg/l
12	Hexavalent chromium	0.1 mg/l
13	Zinc as Zn	0.25 mg/l
14	Iron	3 mg/l
15	Total heavy metals	7 mg/l
16	Total Phenolic compounds	1 mg/l
17	Lead (Pb)	0.1 mg/l
18	Copper as Cu	2 mg/l
19	Nickel as Ni	2 mg/l
20	Bioassay test	89% survival after 96 hours

1.4. Advanced Oxidation Processes

Irrespective of the method of generation of hydroxyl radicals, the methods which utilize hydroxyl radicals for carrying out the oxidation of the pollutants are grouped as Advanced Oxidation Processes. Hydroxyl radicals are extraordinarily reactive species and have one of the highest oxidation potential (2.8 V). The values of rate constants in reactions with organic substrates are in the range of $10^6 – 10^9$ M^{-1} s^{-1} [23,1,14] (Table 7). In addition, hydroxyl radicals do not show any selectivity with respect to the position of attack on the organic substrates which is useful aspect for the treatment of water. The fact that the production of hydroxyl radicals can be made by a variety of methods adds to the versality of Advanced Oxidation Processes thus allowing a better compliance with the specific treatment requirements. An important consideration to be made in the application of AOP to waste water treatments is the requirement of expensive reactants like hydrogen peroxide and /or ozone. Hence, AOP cannot replace the application of more economical treatment methods such as biological degradation whenever possible. A list of the different possibilities offered by AOP are briefly given in Table 8.

Table 6 Possible pollutants in water and their effect on human health

Pollutant	Adverse effect on human health
Atrazine	Cancer, damage to nervous system
Benzene	Cancer anemia
Pentachlorophenol	Liver and Kidney damage and Cancer
Trichloroethylene	Cancer
Trichloroethane	Damage to Kidney, liver and nervous system
Bromoform	Damage to nervous system and muscle
Carbofuran	Damage to nervous system, kidney reproductive system
Carbon tetrachloride	Cancer
Chlorobenzene	Damage to nervous system, kidney and liver
Dichloroethane	Damage t0 nervous system muscle and cancer
Eridriin	Damage to nervous system, kidney, liver anemia and cancer
Ethylbenzene	Damage to nervous system, liver and Kidney
Heptachlor	Cancer
Heptachlor epoxide	Cancer
Hexa-chloro-cyclopentadiene	Damage to Kidney and stomach

Lindane	Damage to nervous system liver and kidney
Simazine	Damage to nervous system, Cancer
Styrene	Damage to nervous system, liver
Tetrachloroethylene	Damage to nervous system, Cancer
1,2,4-trichlorobenzene	Damage to liver and Kidney
Xylene pesticides	Damage to nervous system kidney lungs and membranes
Toluene	Damage to nervous system, liver and kidney

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Table.7. Values of second order rate constants for the oxidation by ozone and hydroxyl radical for a variety of compounds [data from [23]]

Organic compound	value of rate constant $M^{-1} s^{-1}$	
	Ozone[a]	OH radical[b]
Benzene	2	7.8×10^9
n-butanol	0.6	4.6×10^9
t-butanol	0.3	0.4×10^9
Chlorobenzene	0.75	4×10^9
Tetracholoroethylene	<0.1	1.7×10^9
Toluene	14	7.8×10^9
Tricholorethylene	17	4.0×10^9
		[a.]

a- from Hoigne and Bader, 1983; b- from Farhataziz and Ross, 1977.

Table 8 Sources involved in the various Advanced Oxidation Processes

Source of Oxidants	Name of the processes
H_2O_2/Fe^{2+}	Fenton
H_2O_2/Fe^{3+}	Fenton like
$H_2O_2/Fe^{2+}, Fe^{3+}/UV$	photo-assisted Fenton
$TiO_2 h\nu/O_2$	Photocatalysis
O_3 or H_2O_2/UV	Photo-assisted oxidation

Heterogeneous Photo-catalysis

Among the AOPs mentioned, photo-catalysis is the promising method. This is attributed to its potential to utilize energy from the sun without the addition of others forms of energy or reagents. The reactions carried out by the photo-catalysts are classified into two categories namely homogeneous or heterogeneous photo-catalysis. Heterogeneous photo-catalysis is based on the semiconductors which are employed for carrying out various desired reactions in both liquid and vapour phases. Photo-catalysis involve the formation of highly reactive electrons and holes in the conduction and valence bands respectively. The electrons are capable of carrying out reduction reactions and holes can carry out oxidation reactions. There are also other processes that take place in the semiconductor. The electron and hole can react with acceptor or donor molecules respectively or recombine at surface trapping sites. They can also be trapped at bulk trapping sites and recombine with the release of heat. The electron hole can be exploited in a number of ways: (i) For producing electricity(solar cells)-Photo-voltaic; (ii) For decomposing or removing pollutants-Photo-oxidation; (iii) For the synthesis and production of useful chemicals-Photo-catalysis; (iv) For the photo-electrolysis of water-photo-electro-chemistry. As the recombination of the photogenerated electron and hole occurs on a pico-second time scale, electron transfer at the interface can kinetically compete with recombination only when the donor or acceptor is adsorbed on the surface of the semiconductor before irradiation. Hence adsorption of the substrate prior to irradiation is important for efficiency of the heterogeneous photo-catalytic process. [18]. Hydroxyl groups or water molecules adsorbed on the surface can serve as traps for the photogenerated hole, leading to the formation of hydroxyl radicals in the case of metal oxide suspensions. Strong adsorption of acetone and 2-propanol on ZnO has been observed during temperature programmed desorption [17]. Metal oxide surfaces have a surface density of about 4-5 hydroxy groups $/nm^2$ as has been shown by the continuous distribution of adsorption energies in the Freundlich isotherm. Many organic substrates were found to play the role of adsorbed traps for the photo-generated holes. For example, in a colloidal suspension of TiO_2 in acetonitrile, radical ions are detected directly during flash excitation [17]. Apart from materials derived from TiO_2 by modifications like doping, coupling with an additional phase or morphological changes different compounds with distinct composition and structure have also been examined. Various tantalates, [10] [11], niobates [26], Oxides of bismuth like $Bi_2W_2O_9$, Bi_2MoO_6, $Bi_2MO_3O_{12}$ and oxides of Indium as In_2O_3, $Ba_2In_2O_5$ MIn_2O_4, (M=Ca, Sr) were found to be capable of photo-splitting water. Tantalum nitride and tantalum oxynitride were also found to be effective catalysts for water splitting.

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