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RESEARCH ARTICLE

NANOMATERIAL FOR PHOTOCATALYSIS AND THEIR APPLICATION IN ENVIRONMENTAL CLEAN-UP

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ABSTRACT

In recent years, nano-based photocatalyst has shown a great potential as a low-cost, green chemical based and sustainable waste water treatment technology. Development of materials for photo oxidation and photocatalysis has followed an evolutionary pathway from usual bulk metals and semiconductors to colloidal materialsand, recently, to nanosized materials. Nanosized materials, whose electronic properties are size-tunable, enable the application of a larger range of semiconductors as a potential material for photocatalytic processes in the fieldof environmental remediation. The continuous worsening environmental pollution and energy shortages have raised awareness of a potential global crisis. For the sustainable development of the ecologicalsociety, the development of pollution-free and green chemistry based technologies for environmental remediation is an urgent need. Among the wide variety of green earth and renewable energy projects underway, nano-photocatalysis has emerged as one of the most promising new technology because it represents an easy way to utilize the energy of either natural sunlight or artificial internal illumination, and is available abundantly everywhere. Nano-photocatalysis is a rapidly expanding technology for the removal as well as the mineralization of toxicants from the waste in order to environmental clean-up and sustainable development. The ability of this advanced oxidation technology has been extensively demonstrated to remove persistent organic compounds, toxicants, pesticides and dye effluents from the waste water. This paper reviews the recent R&D progresses of semiconductor nano-photocatalyst, mechanism, affects, present and future prospectus of photo oxidation processes for waste water treatment.

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INTRODUCTION

Water resources are of critical importance to both natural ecosystem and living beings. This scarce natural resource is being contaminated every day by various anthropogenic activities such as rapid growth of population, extended droughts, urbanization and industrialization that ultimately make the environment polluted [1]. Environmental pollution from industrial wastewater particularly in developing countries like India is of major concern. A recent United Nations Educational, Scientific and Cultural Organization (UNESCO) report reveals that more than 6,000 people die every day from water-related disease, and the availability of drinking quality water, especially in the developing nations. These statistical figures are likely to grow in the near future, as increasing water contamination due to continuous discharge of micro-pollutants and contaminants into the natural water cycle. About 90% of all diseases occurring in developing countries are related to the consumption of impure water leading to nearly 4 billion reported cases of diseases contracted from water in the world. Industrial effluents discharged from various industries like textile, tannery, pharmaceuticals, pesticides, sugar processing, dye and distilleries contain higher amount of metals like chromium, copper, nickel, lead, mercury and cadmium and results in a series of well documented problems in living beings because the heavy metals cannot be completely degraded [2].

Present wastewater treatment technologies demand high capital investment, operation and maintenance cost, and large area. At present, many physiochemical methods like distillation, reverse osmosis, carbon adsorption, ion exchange resins and nano-filtration are used. Major drawbacks of these methods include disposal problems, membrane deformation, sludge formation, handling, and technical constraints [3]. Non-biodegradable Pollutants present in wastewater is a point of major concern in

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developing countries. Majority of these pollutants require a high priority of treatment for development of water quality criteria and effluent limitation guidelines because they are frequently found in wastewater such type of pollutants are denoted to as priority pollutants. This necessitates cost effective, innovative and most advantageous methods for treatment of waste water. These have led to the rapid R&D in the field of "Advanced Oxidation Processes (AOPs)" as the advanced water treatment technologies. The main aim of these AOPs are based on the *in-situ* generation of highly reactive species or generation of free radical charged particles for rapid degradation and mineralization of unmanageable organic compounds and pollutants, water pathogens, toxicants, pesticides and disinfection by-products [4, 5].Once ground water is polluted with toxic chemicals, it takes many years for the contamination to disintegrate or be cleaned up. Cleanup of these contaminants may also be very costly and complex.In recent years, photocatalytic oxidation processes have been successfully utilized for the elimination of contaminants from waste water. [6]

1.Nanotechnology for Waste water treatment

Nanomaterials have been gaining much interest in the area of environmental clean-up &remediation mostly due to their enhanced surface and also other specific changes in their physical, chemical and biological properties develop due to their size [4]. An emerging area of research is the development of novel nanomaterials with increased affinity, selectivity and capacity, for the removal of heavy metals and other contaminants. The benefit of using nanomaterials may derive from their enhanced surface reactivity, higher surface area and other important characteristics. Research is underway to use advance nanotechnology in water purification for safe drinking. Nanotechnology for water purification plays an important role in water purity and security of the world. The application of nanotechnology in the clean-up of contaminated water could be summarized as-

- Nanoscale filtration techniques (Nanofiltration using membranes),
- Nanoadsorbents (sorbents, nanoclays, zeolites),
- Nanocatalysis (nanosizedsemicondutor catalyst for environmental clean-up),
- Nanocomposties (Mixture of two or more nanoparticles to enhance the efficiency).

Nanotechnology offers lot of potential in the area of water purification due to large surface to volume ratios offered by nanostructures and the possibility of preparing photocatalytic membranes by growing semiconducting nanostructures on conventional membranes. Various methods such as Photocatalysis, Nanofiltration, Adsorption, and Electrochemical oxidation involve the use of Titanium dioxide (TiO_2), Zinc Oxide (ZnO), polymer membranes, ceramic membranes, carbon nanotubes, nanowire membranes, submicron nanopowder, metal (oxides), magnetic nanoparticles, are used to resolve or greatly diminish problems involving water quality in natural environment [7, 8, 9]. Nanoparticles, nanomembrane and nanopowder and other nanomaterials used for detection and removal of chemical and biological contaminants include heavy metals, nutrients, pesticides, cyanide, organics, algae, viruses, bacteria, parasites and antibiotics [9]. Membrane processes, nanobased materials and the combination of both offer a wide range of possibilities for water treatment by means of filtration and catalytic processes at the same time. The increased public concern with these environmental pollutants has prompted the need to develop novel treatment methods with photocatalysis gaining a lot of interest in the field of pollutant degradation. The photocatalytic detoxification of wastewater is a process that combines heterogeneous catalysis with solar technologies [10].Heterogeneous photocatalytic systems mainly involves the use of metal oxide semiconductors like TiO_2 and ZnO and are capable of operating effectively waste water treatment which has been discussed along with other nanotechnology routes [11, 13]. Photocatalytic membranes using ZnO nanostructures are considered beneficial over freely suspended nanoparticles due to the ease of its removal after treatment.Existing waste watertreatment technologies such as adsorption and coagulationsimply concentrate the pollutants present by transferring themfrom one phase to the other, but still remain and not being completely "eliminated" or "degraded" [12]. Otherconventionalwater treatmentmethods such as sedimentation, filtration, chemical and membrane technologies involve highoperating costs and could generate toxic secondary pollutants into the ecosystem. These have led to the rapid R&D in the field of "Advanced Oxidation Processes (AOPs)" as the innovative water treatment technologies [13]. All AOP's are identified by the same chemical feature: the production of hydroxyl radical's 'OH'. These radicals are extremely reactive species and attack mainly every organic molecule with rate constants usually in the order of 106-109 mol l-1 s^{-1}. Among these AOPs, heterogeneous photocatalysis employing semiconductor catalysts (TiO_2, ZnO, Fe_2O_3, CdS, GaP and ZnS) has demonstrated its efficiency in degrading a wide range oftoxic contaminants into biodegradable compounds, and finally mineralized them to carbon dioxide and water [14, 15, 16].An interesting class of AOP consists of the so-called Advanced Photochemical Oxidation (APO) processes (US EPA, 1998). APO processes are characterized by a free radical mechanism initiated by the interactions of photons of a proper energy level with the molecules of chemical species present in the solution or with a catalyst. The most used APO technologies can be divided into the following groups: (1) heterogeneous photocatalysis, (2) homogeneous photocatalysis, and (3) the photo-Fenton process [17].In favorable cases, APO, can cause total decomposition of the organic constituents of the pollutant, generally referred to as "total mineralization" (complete oxidation to carbon dioxide and water, inorganic salts of all heteroatom other than oxygen).Semiconductor-assisted photocatalyst is one of the most extensively investigated AOPs, because of its capacity to degrade a high number of recalcitrant chemicals in gaseous or aqueous systems, through comparatively inexpensive procedures [18].

2.Photocatalysis: A Green Chemistry Approach

Photocatalysis is defined as the "acceleration of a photoreaction by the action of a catalyst." It occupies a central place in ecological equilibrium. Mankind has received the gift of solar energy and had tried to explore the utilization of this vast and abundant source of energy [136]. Utilization of solar energy is a very interesting aspect of science. Solar photocatalysis has therefore become a very important area of research, wherein, sunlight is the source of illumination to perform different photocatalytic reactions. The application of photocatalytic water purification process has gained extensive attention due to its efficiency in degrading and mineralizing the recalcitrant organic compounds as well as the possibility of utilizing the solar, UV and visible light spectrum [18]. Nanotechnology is one of the most promising emerging technologies for efficient, economical and environmentally friendly water and waste water treatment offering great potential for the developing countries [19]. The major significance of this process is that, it can degrade or detoxify, various organic chemicals, which has not been degraded by several other methods of purification [20]. The two most significant applications of photocatalysis have been in solar water splitting and the purification of air and water containing low concentrations of pollutants. In photocatalysis, the catalyst is fully regenerated after the reaction. A good photocatalyst should absorb light efficiently preferably in the visible or near UV part of the electromagnetic spectrum [21]. Sufficient electron vacant states need to be present to inhibit recombination of electron hole pairs upon light exposure. Nanostructured photocatalysts offer large surface to volume ratios allowing higher adsorption of the target moleculesor contaminant over the surface and also provides large surface reactivity [22]. Intensive research over the past decade for its implementation in the purification of drinking water can be found in the literature.

In recent years interest has been focused on the use of semiconductor materials as photocatalysts for the removal of organic and inorganic contaminants from waste water. Heterogeneous photocatalysis is eco-friendly way to reduce the pollutants load of wastewater [21, 23]. The initial interest in the heterogeneous photocatalysis was started when Fujishima and Honda discovered the photochemical splitting of water into hydrogen and oxygen with TiO_2 in 1972. Heterogeneous photocatalysis is currently being considered as a promising technique for water purification in comparison to other conventional methods, as it can break up complex long chained organic molecules (normally toxic) into simpler fragments as well as distort cell walls of microbes thereby immobilizing them [23, 24]. Heterogeneous photocatalysis is a process in which two active phases solid and liquid are present. The solid phase is a catalyst, usually a semiconductor, based on the irradiation of a catalyst, usually a semiconductor, which may be photoexcited to form electron-donor sites (reducing sites) and electron-acceptor sites (oxidizing sites), providing great scope as redox reagents [25]. Ever from the time when the report of the use of illuminated TiO_2 particle to decay cyanide in water 1977, there has been increasing interest in the environmental applications of photocatalysis. TiO_2, the semiconductor most thoroughly investigated in the literature, seems to be the most promising for photocatalytic destruction of organic pollutants [26]. Several researchershave typically used TiO_2, which is a perfect photocatalyst, because it is highly stable chemically, and the photo generated holes are highly oxidizing. So, most of the investigations have focused on nanosized TiO_2 (specifically Degussa P-25 TiO_2) and Zinc oxide (ZnO) nanoparticles [27]. However, other materials such as CdS and ZnS, colloids were also investigated for their photochemical properties. A number of important features for the heterogeneous photocatalysis have extended their practical applications in water treatment;the ideal photocatalyst should possess the following properties [27, 28, 29]

(i) Photo activity,
(ii) Biological and chemical inertness,
(iii) Stability toward photo corrosion,
(iv) Suitability towards visible or near UV light,
(v) Low cost,
(vi) Lack of toxicity.
(vii) Ability to complete mineralization and photo oxidation,
(viii) Stable at low temperature and pressure.

Photocatalysis completely degrade the pollutant as well as complete mineralization is also achieved in case of pesticides and other toxicants [28]. The object of destructive oxidation processes is to mineralize organic contaminants, *i.e.*, convert them to carbon dioxide and water and other harmless products. Photocatalytic degradation is attractive for treatment of waste streams which are too dilute for incineration and too concentrated for biological treatment andcontain highly toxic organic compounds [29, 30]. Table 1 shows the various pollutant degraded by the use of nanostructured photocatalyst-

Nanoparticles of metal oxides are efficient photocatalysts and can degrade both chemical and biological contaminants [32, 33]. Higher the surface area available more will be the adsorption of the target molecules and higher will be the efficiency of the photocatalytic degradation. The biggest limitation in the use of nanoparticles for practical applications is the difficulty of removing the particles after treatment. To solve this problem, an additional process step would need to be entailed for post-separation of the catalysts. This separation process is crucial to avoid the loss of catalyst particles and introduction of the new pollutant of contamination of TiO_2 in the treated water [34].

The catalyst recovery can be achieved through process hybridization with conventional sedimentation, cross-flow filtration or various membrane filtrations. Research is going in the field of particle entrapment over the membrane to prevent the loss of the catalyst [35].

3. Semiconducting Nanoparticles as Prominent Photocatalyst

Semiconductors are defined by their exceptional electric conductive behavior, somewhere between that of a metal and an insulator. Semiconductors with dimensions in the nanometer realm are important because their electrical, optical and chemical properties can be tuned by changing the size of particles [36, 123]. Amongst the various types of nanomaterials, semiconductor nanoparticles have been widely investigated because of its wide applications in devices, solar cells and photocatalysis [37, 124]. Wide range of nanobasedsemiconductors may be used for photocatalysis, such as TiO_2 ZnO, WO_3, Fe_2O_3, MgO, CdS, ZnS, CdTe, and CdSe [38, 39, 125, 126].

Table 1. Examples of Pollutants degraded by Photocatalysis using different semiconductors

Contaminant	Nano-photocatalyst	References
1.Pesticides/Herbicides		
Azimsulfuron	UV/TiO_2 coated on glass	4,8, 31
Organophosphate & Phosphonoglycine	UV/TiO_2 immobilized on silica gel	16, 28
Pirimicarb	ZnO	8, 25, 40
Organochlorines	TiO2/ZnO/SiO_2	9, 12, 13
Sulfonylurea	TiO2/ZnO/SiO_2	22, 23, 24
Parathion-methyl	ZnS/TiO_2	28
Glyphosate	Ce-TiO_2	29
2.Dyes		
Acid Red	ZnO/SiO_2 CuO-ZnO Ag/TiO_2 TiO_2 Fe_2O_3/SnO_2	21, 32
Methyl orange	UV/TiO_2 on glass ZnO/ZnS N-TiO_2 SnO_2 CNTs/P-TiO_2 SnS_2 Fe^{+3}-TiO_2-Zeolite Fe_3O_4/ZnO	35, 40
Methylene Blue	LiFe/$(WO_4)_2$ SiOC/ZnO TiO_2/SiO_2 ZnO/Au BSA/CdS Co/ZnO Zn-Al-In(MMO) ZnO/TiO_2	35, 36, 37,42,45
Rhodamine B	$BiFeO_3$ Ag-TiO_2 P-TiO_2 ZnO/CuO TiO_2/ZrO_2 CeO_2-ZnO UV/TiO_2 bilayer $MgFe_2O_4$/TiO_2	15, 16, 20, 22, 25
Congo Red	TiO_2/SiO_2 TiO_2/Sulfanilic acid Chitosan/CdS	10, 12, 22, 23, 26, 32, 40
3.Phenol	Ag/TiO_2 CdS/TiO_2 TiO_2-$ZnFe_2O_4$ WOx/TiO_2 Fe-TiO_2	8, 36
4.Organic Pollutant	$InVO_4$ TiO_2 Ag/ZnO TiO_2/Ni	29, 46, 58
5.Benzylparaben	UV/TiO_2 (Degussa P25)	24, 49,52
6.β-naphthol	UV/TiO_2-SiO_2	33, 62, 68
7.Paper mill wastewater	Solar/TiO_2 ZnOFe_2O_3	65
8.Municipal waste water	Solar/sol-gel TiO_2& Degussa P25 Fe_2O_3 TiO_2/ZnO TiO_2-Ag ZnO-Ag	10, 15, 22, 32, 44, 46
9.Contaminated soil	Plasma/TiO_2 ((Degussa P25)	58, 61, 62

This is because of the fact that semiconductors are: (i) inexpensive, (ii) non-toxic, (iii) having high surface area, (iv) having broad absorption spectra with high absorption coefficients, (v) exhibiting tunable properties which can be modified by size reduction, doping and sensitizers (vi) affording facility for multi electron transfer process, and (vii) capable of extended use without substantial loss of photocatalytic activity [40, 41, 126, 127]. The various properties and application of nanomaterial as photocatalyst is shown in Figure 1.

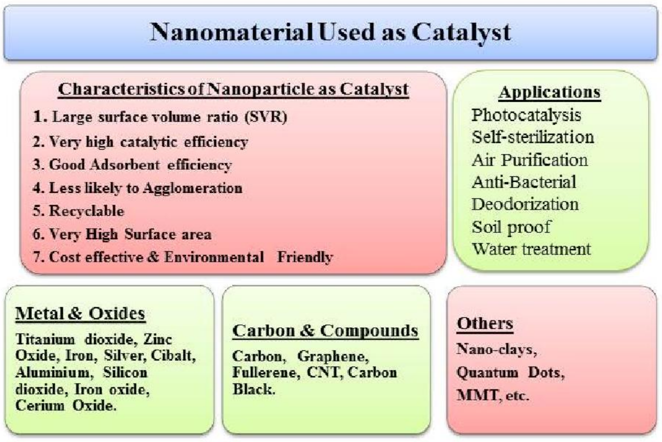

Fig.1. Various Nanomaterial used as Catalyst, Characteristics & Application

During the past decade, the photochemistry of nano semiconductor particles has been one of the fastest growing research areas in physical chemistry. The interest in these small semiconductor particles originates from their unique photo-physical and photo-catalytic properties [42]. Semiconductors are basically important as a photocatalyst because of unique combination of its electronic structures, light absorption properties, charge transport characteristics and life of excitation state. The application of illuminated semiconductors for degrading undesirable organics dissolved in air or water is well documented and has been successful for a wide variety of compounds. Nanosized particles, with diameters ranging between 1-10 nm, possess properties which fall into the region of transition between the molecular and the bulk phases. In solid state terminology this means that the bands split into discrete electronic states (quantized levels) in the valence and conduction bands and the nanoparticle behaves more and more like a giant atom [43].Catalytic behavior is strongly materials dependent, in the nanosize regime, a new class of materials has emerged where quantum confinement and surface phenomena based on particle size dominate the materials properties. Semiconductor nanoparticles exhibit size dependent properties, when their size is comparable to the size of Bohr diameter for exciton [44]. Some groups have showed, for II-VI and III-V semiconductors, the change in band gap with particle size. A semiconductor is characterized by an electronic band structure in which the highest occupied energy band, called valence band (VB), and the lowest-occupied energy band, called conduction band (CB), are separated by a band gap, *i.e.* a region of forbidden energies [45]. A Fermi level, EF, which represents the chemical potential of electrons in a semiconductor, is placed in the forbidden gap energetically. The energetic distance between them amounts to 0.7-3.5 eV for semiconductors and is called a forbidden band or a band gap, EG. The distance between the valence and conductivity bands determines electronic properties of the solid, e.g. electric conductivity [46]. Wei and coworkers reported the use of hybrid Fe_2O_3-Pd nanoparticle photocatalyst grown by epitaxial growth of Fe_2O_3 on Pd nanoparticles, showed improved photocatalytic efficiency, although this was limited by the presence of organic stabilizers which are difficult to remove. Other materials considered in recent work include ZnS, ZnO, CdSe, Fe_2O_3 and InP. Some of these materials were reported to show some photocatalytic promise, but with uncertainty over their efficiencies and spectral characteristics [47, 48, 49]. Fe_2O_3 is particularly interesting because of its stability against photo-chemical corrosion at neutral or basic pH and has band gap energy of around 2.0-2.2 eV corresponding to the absorption of 564 to 620 nm light [50]. Table-2 shows the energy band gap values of various semiconductors-

Table 2. Band gap Energy of various semiconductors

Semiconductor Photocatalyst	Band gap Energy (E_{bg})
Titanium dioxide (TiO_2)	3.23 eV
Zinc Oxide (ZnO)	3.2 eV
Magnesium Oxide (MgO)	7.8 eV
Cadmium Sulfide (CdS)	2.4 eV
Iron Oxide (Fe_2O_3)	2.2 eV
Tungsten trioxide (WO_3)	2.6-3.0 eV
Zinc Sulfide (ZnS)	3.7 eV
Gallium Arsenide (GaAs)	1.4 eV
Gallium Phosphate (GaP)	2.3 eV
Tin Oxide (SnO_2)	3.5 eV
Cadmium Selenide (CdSe)	1.7 eV

4.Mechanism of Semiconductor Photocatalysis

Among the new oxidation methods or advanced oxidation processes (AOP), heterogeneous photocatalysis appears as an emerging destructive technology leading to the complete mineralization of many organic pollutants by destruction of pollutants in aqueous solutions using catalyst [51]. During past few years, semiconductor mediated photo catalysis has been reported as a promising way to destroy toxic and hazardous organic substances in industrial wastewater and drinking water. Systematic studies of photocatalysed reactions are of prime importance both for a major understanding of the nature of heterogeneous photocatalysis and for optimizing its efficiency [52]. Photocatalytic degradation of organic compounds is based on semiconductor photochemistry [53]. When a semiconductor particle is irradiated by the light of energy higher or equal to the band gap energy, electron from the valance band is excited to the conduction band with simultaneous generation of a hole (h^+) in the VBand electron (el^-) in CB. [54] According to the band theory, each solid can be characterized by two energetic bands: a valence band, VB, which possesses lower energy, completely filled with electrons; and a conduction band, CB, with higher energy, empty at 0°K.The bands of interest in photocatalysis are the populated valence band (VB) and it's largely vacant conduction band (CB), which is commonly characterized by band gap energy (E_{bg}) [55, 56]. When the semiconductor is illuminated with light ($h\upsilon$) of greater energy than that of the band gap, an electron is promoted from the VB to the CB leaving a positive hole in the valence band and an electron in the conduction band. The holes facilitate the oxidation of organic compounds by the formation of hydroxyl radicals, and the electrons mediate reduction and oxidation reactions by the formation of superoxide radicals [57, 58, 59].

The mechanism of the photocatalytic degradation can be explained with following reaction steps taking TiO_2 as a model catalyst [60, 61]

1. Absorption of efficient photons ($h\nu \geq E$G=3.2 eV) by Titanium dioxide:

$(TiO_2)+ h\nu \rightarrow e^{-CB} + h^{+\,VB}$ ……………………………………………………(1)

2. Oxygen ionosorption (first step of oxygen reduction; oxygen's oxidation degree passes from 0 to −1/2):
$(O_2)_{ads} + e^{-CB} \rightarrow O_2$ ……………………………………… (2)

3. Neutralization of OH^-groups by photo-holes which produces OH°radicals:
$(H_2O \Leftrightarrow H^+ + OH^-)_{ads} + h^{+VB} \rightarrow H^+ + OH^{\bullet}$ ………………. (3)

4. Neutralization of $O_2^{\circ -}$by protons:
$O_2^{\circ -} + H^+ \rightarrow HO_2^{\circ}$ ………………………………………… (4)

5. Transient hydrogen peroxide formation and dismutation of oxygen:
$2HO_2^{\circ -} \rightarrow H_2O_2 + O_2$ ……………………………..…… (5)

6. Decomposition of H_2O_2 and second reduction of oxygen:
$H_2O_2 + e^- \rightarrow OH^{\circ} + OH^-$ ………………………………… (6)

7. Oxidation of the organic reactant via successive attacks by hydroxylradicals:
$R + OH^{\circ} \rightarrow R\bullet + H_2O$ …………………………………….. (7)

8. Direct oxidation by reaction with holes:
$R + h^+ \rightarrow R^{+\circ} \rightarrow$ Degraded Products …………………… (8)

As an example of the last process, holes can react directly with carboxylic acids generating CO_2:
$RCOO^- + h^+ \rightarrow R^{\bullet} + CO_2$ ……………………………….... (9)

To the outer surface, the excited electron and the hole takes part in redox reactions with adsorbed species such as water, hydroxide ion (OH^-), organic compounds, and oxygen. The charges react directly with adsorbed pollutants, but reaction with water is more likely as the water molecules are more populous compared to contaminant molecules [62]. Oxidation of water or OH^- by the hole produces the hydroxyl radical (•OH), an extremely dominant and indiscriminant oxidant [63]. Photoreduction, photooxidation and adsorption occur on or near the particle surface as shown from Figure 2.

Contaminant $\xrightarrow{TiO_2/O_2/Hv=Eg}$ Intermediate Products $\longrightarrow CO_2 + H_2O +$ Other environment friendly compounds.

5.Affecting Factors

Various studies on photo-catalysis of pesticides, organic pollutants, phenols and their derivatives indicated that the photo-catalytic degradation process is mainly affected by following factors [64]. They are-

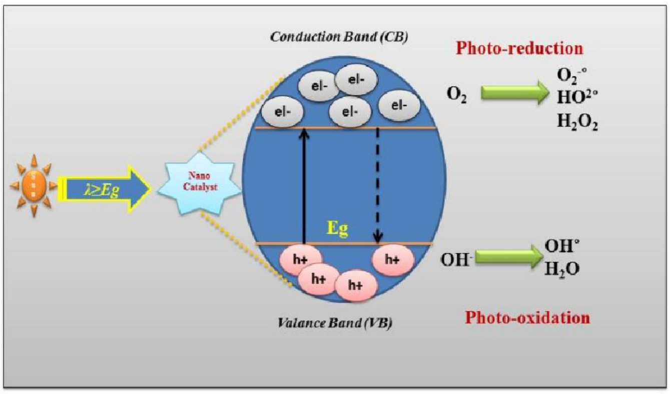

Figure 2. Representation of reactions taking place at the surface of catalyst

a)*Dependent on the solution pH*: pH plays an important role in photocatalytic oxidation processes because pH affects the production of hydroxyl radical which is powerful oxidizing agent [64].The pH is a complex parameter as it is related to the ionization state of the surface. pH changes can influence the adsorption of contaminant molecules onto the catalyst surfaces, an important step for the photocatalytic oxidation to take place. In photocatalytic water system, pH is one of the major governing parameters that affect thesize of catalyst aggregates, charge on the catalyst particles, and the positions of conductance and valence bands. The effect of pH on the photocatalytic reactions of organic compounds and adsorption on TiO_2 surface has been comprehensively studied. Change in pH can results improvement in the efficiency of photo removal of organic pollutants in presence of titanium dioxide without affecting the rate equation.

b)*Types of catalyst and concentration*: In various studies, it was perceived that the degradation rate was found to increase with the increase in catalyst concentration upto5 gL^{-1} and on subsequent addition of catalyst lead to the decrease in degradation rate [65]. The rate of photocatalytic reaction is strongly influenced by concentration of the photocatalyst. Heterogeneous photocatalytic reactions are known to show proportional increase in photodegradation with catalyst loading. Concentration of catalystin the photocatalytic water treatment system is directly proportional to the overall photocatalytic reaction rate [66].

c)*Effect of light intensity and wavelength*: The photochemical effects of light sources with different wavelength emitting ranges will have intense result on the photocatalytic reaction rate, depending on the types of photocatalysts used crystalline phase, *anatase,rutile* and *wurtzite [68]*. Light intensity is one of the few parameters that affect the degree of photocatalytic reaction on organic substrates. To achieve a high photocatalytic reaction rate, particularly in water treatment, a relatively high light intensity is required. It was also discovered that the dependency of the reaction rate on radiant intensity behaves in differently under different lighting conditions [69].

d)*Catalyst loading*: It is reported that in any reactor system, the initial rates are directly proportional to catalyst concentration, indicating the heterogeneous regime. It is observed that there is a limit of catalyst concentration that must be used for the photodegradation of a particular pollutant in wastewater, above which the rate of photocatalysis will even decrease [69]. Concentration of catalyst in the photocatalysis affects the overall photocatalytic reaction rate in a true catalytic regime, where the amount of catalyst is directly proportional to the overall catalytic reaction rate, as the amount of catalyst increase the rate of degradation is also increase [70]. The rise in degradation rate after increasing the catalyst loading can be ascribed to the point that a large amount of photons are adsorbed, thus accelerating the process. When all the compound solution molecules are adsorbed onto the catalyst surface, no further improvement is seen by the addition of more catalyst [71]. A studydocumented the effect of catalyst dose on two dyes acridine orange and ethidium bromide and observed that the degradation rate for the decomposition of both the dyes in the presence of TiO_2 Degussa P25 increases with the increase in catalyst concentration and a further increase in catalyst concentration leads to a decrease in degradation rate [72, 73].

e)*Effect of surface area and adsorption*: Surface area is one of the most important aspects of semiconductor photocatalysis. It is known fact that as the size goes down to nanometer regime there is gradual increase in surface area, with the increase in surface area, there is increase in percent degradation rate of pollutant [75]. More is the surface area available, more pollutant will adsorb over the surface means directly increase in the degradation rate [74].

f)*Composition and concentration of pollutant*: Previous investigations have reported the dependency of the photocatalytic reaction rate on the concentration of water contaminants. The pollutant concentration is very important parameter. It is observed that with the risein concentration of the compound solution, there is a decrease in the percentage degradation rate [76]. The reason behind this behavior may be due to the increase in the extent of adsorption on the catalytic surface at essential compound concentration which reduces the catalytic activity [77].

g)*Reaction temperature*: Numerous studies have been conducted on the dependence of Photocatalytic reaction on the reaction temperature. It is observed from various studies that there is reduce in the photocatalytic activity, when the reaction temperature rises [78].

h)*Effect of light irradiation:* It is observed from the results that the percentage degradation increases with increase in the light intensity [79]. The UV irradiation generates the photons required for the electron transfer from the valence to the conduction band of a semiconductor photo catalyst and the energy of a photon is related to its wavelength and the overall energy input to a photocatalytic process is dependent on light intensity. The rate of degradation increases when more radiations fall on the catalyst surface and hence more hydroxyl radicals are produced [80].

Understanding the impacts of various parameters on the photocatalytic degradation efficiency is of prime concern from the design and the operational points of view when choosing a sustainable and efficient technique for the treatment of waste water [81].

6. Photocatalytic Reactor System

Significant advances have been made in reactor design for various photocatalytic reactions. Published literature contains several types and designs of photocatalytic reactors [80].There are two types of reactors developed for photocatalysis namely- a) fixed bed, and b) slurry type. Heterogeneous photocatalytic reactions are carried out either in a slurry-type reactor where the catalyst particles are suspended in the contaminated water or in an immobilized-type or fixed bed reactor where the catalyst particles are immobilized onto the surface of various inert substrates of various types and configuration [79, 80, 152]. Photocatalytic reactors with suspended catalyst give much better contact between the photocatalyst and dissolved impurities comparing to reactors with immobilized catalyst [81, 137]. To achieve a successful implementation, numerousreactor design parameters must be optimized, such as the photo reactor geometry, the type of photo-catalyst and the utilization of radiation energy. A major issue regarding the successful implementation of photocatalytic reactors is the proper transmission of radiation in a highly scattering and absorbing medium composed of water and nanoparticles (catalyst) [135,138]. The successful scaling-up of photo-catalytic reactors involves increasing the number of photons absorbed per unit time and per unit volume [153]. For a high activity in the reactor, a large area has to be illuminated. Therefore, in immobilized systems the thickness of the catalyst layer shouldbe small enough to enable the light energy to reach all the catalyst [84, 85, 151]. Thus, one of the most importantparameters for the design of photocatalytic reactors is light intensity and how the reactor isdesigned to get maximum exposure to the radiation and to accommodate various light sources. Light intensity is an important reactor design factor when considering light sources because the major requirement of any photocatalytic process is that the catalyst, pollutant and source of illumination must be in close proximity [86, 150]. It has also been shown that an excess of light promotes a faster electron-hole recombination and the low activation energy of photocatalytic reactions, compared with ordinary thermal reactions [87].

The hybrid photocatalytic membrane reactor system is generally known as the “photocatalytic membrane reactors” (PMRs). This is owing to the nature of the hybrid system where the membrane filtration unit could be configured into different positioning with the photocatalytic reactor [88]. Fu *et al.*designed a submerged membrane reactor with two different reaction zones; UV slurry TiO_2 zone with a movable baffle that separates the submerged membrane module. These PMRs can be generalized by (1) irradiation of the membrane module and (2) irradiation of a feed tank containing photocatalyst in suspension [89].

7. Doping of nanoparticle

Usually doping involves the use of metals or non-metals and is intended to extend the photocatalytic activity of a semiconductor lower energy excitation. Doping of semiconductors is the process of locally manipulating their charge carrier density and conductivity [90, 83]. Technically, doping is the introduction of foreign elements into the parent photocatalyst without giving rise to new crystallographic forms, phases or structures and the aims are to enhance the net separation of photo generated charges [91, 92]. Depending on their number of valence electrons, the dopants (as donors) can either donate excess electrons as negative free charge carriers to the semiconductor conduction band at moderate temperature (*n-type doping*), or they (as acceptors) can accept additional electrons from surrounding atoms to complete the covalent chemical bonding, leaving positively charged holes as charge carriers in the semiconductor valence band (*p-type doping*).Doping of photocatalyst with metals and non-metals creates new energy levels between the valance and Conduction band of the catalyst, which in turn reduces its band gap and helps the doped catalyst to absorb in the visible light region [93].In doped semiconductors weather it is p-type or n-type, the Fermi level is shifted (blue shift & red shift) by the impurities, illustrated by their band gaps [94].

Higher photocatalytic activity, stability and nontoxicity of dopant ions are among the advantages of nonmetal over metal dopants and, in general, TiO_2 and several other materials have been studied including the effect of impurity levels in the dopant on photocatalytic efficiency [95]. In addition, results obtained using TiO_2 and oxides such as WO_3, Ta_2O_5 and $Ba_5Ta_4O_{15}$ have been published. The presence of metal dopants was found in some cases to enhance charge separation as well as interfacial charge transfer in many other cases, the metal dopants actually resulted in rapid charge recombination through their switchable redox states, for example, $Fe^{3+} \leftrightarrow Fe^{2+}$ and thereby reducing the electron diffusion length and lifetime [96, 97]. This is one of the reasons for the reduced quantum efficiency in many photo response-extended doped photocatalysts. Doping of TiO_2 with fine noble metals such as silver (Ag), gold (Au) and palladium (Pd) has been carried out widely as a means of improving charge separation [98]. Doping has been reported to establish a barrier through equilibration between the photocatalyst and metal deposits and is governed by the difference in work function of the deposits and the electron conduction band of the photocatalyst and does not influence the mechanism of the specific reaction [99].

8.Catalyst Surface Chemistry

Surfaces and interfaces are very important for nanomaterials [100, 148]. As particles become smaller, the amount ofatoms found at the surface increases relative to the proportion inside its volume;it means that nanoparticlescan be highly reactive. The higher surface energy can also make nanoparticles interact strongly and stick together. For nano particle, nearly 70–80% of all the atoms reside on the surface [101]. This has important implications for photocatalysis and especially for the issues of charge separation. With such a large number of atoms on the surface it is quite easy to understand how the surface chemistry could dominate the properties of the nanoparticle [102].The large surface area provided by nanosized materials provides immense possibilities in the fields of photocatalytic degradation of waste as well as photocatalytic production of H_2.Surface area is an extremely important parameter in photocatalytic destruction of toxic chemicals as it minimizes materials use. Surface area and surface defects plays very important role in the photocatalytic activity of metal-oxide nanostructures, contaminant molecules need to be adsorbed on to the catalyst surface for the redox reactions to occur [103]. The higher the reactive surface area, higher will be the adsorption of target molecules resulting better photocatalytic activity. Photocatalytic reactions mainly occur at or very close to the surface of an illuminated photocatalyst [104]. However, recent studies have shown that photocatalytic reactions can also occur at certain distances from the illuminated surface, through the diffusion of reactive species in air or solution phase, or through the diffusion of reactive species on the surface. These discoveries are important for the design of photocatalytic systems [105]. Doping of metal oxides with metals and or transition metals creates quasi-stable energy states within the band gap resulting surface defects which affects the optical and electronic properties. Increased electron trapping due to higher defect sites leads to enhancement in the photocatalytic efficiency. Modifications to semiconductor surfaces such as addition of metals, dopants, or combinations with other semiconductors are beneficial in decreasing the electron and holes recombination rate and thereby increasing the quantum yield of the photocatalytic process [106]. Zinc oxide (ZnO), with a high surface reactivity owing to a large number of native defect sites and exhibits comparatively higher reaction and mineralization rates and generate hydroxyl ions more efficiently than titania (TiO_2) [105, 106].

9.Quantum Confinement in Semiconductors

In the nano regime, one of the most direct effects of reducing the size of materials to the nanometer range is the appearance of quantization effects due to the confinement of the electrons [107]. Quantum-size (Q-size) effects occur when the size of the semiconductor particles become smaller than the Bohr radius of the first excitation state [108]. Quantum size effects (QSE) occur for semiconductor particles on the order of 10-100 A in size. More specifically, as the particle size decreases, and becomes comparable to either the *de Broglie* wavelength of the carriers or the Bohr exciton, spatial confinement of the charge carriers occurs. This confinement leads to quantization of energy levels (*i.e.,* quantum confinement), the formation of discrete states and an increase in the optical gap [109].

The quantum size effect was first discussed by Frohlich in 1937 in terms of the spacing of electron energy levels. The quantum confinement effect is observed by a blue shift in the optical absorption band of a semiconductor as its size is decreased from bulk to the nano regime [110]. There are different length scales defining confinement of an electron in a metal, an electron in a semiconductor, or a hole in the same semiconductor. This has been stated by other authors as when the particle size of the colloidal particle becomes comparable to the *De Broglie* wavelength of the charge carriers [111, 136]. Weller *et al.* (1995) has stated that size quantization effects for semiconductor particles typically occur in a diameter range between 2-50 nm. Quantization effects for an electron in an evacuated box were estimated to become significant at box dimensions of ~0.1 nm (using the ‘particle in a box’ model). Size quantization in semiconductor particles leads to drastic changes in numerous important properties of the material [112, 113]. Firstly, size quantization affects the electronic properties of the semiconductor particle, with the ultra-small crystallites composed of a few molecular units maintaining their discrete HOMOs (Highest Occupied Molecular Orbital) and LUMOs (Lowest Unoccupied Molecular Orbital). The electronic properties relate to the solid state physics aspects of the particles, that is, band structures and band gap, as well as the electrochemical positioning of the band gap edge potential with respect to the Nernst potential of the solution [114]. The band gap of the semiconductor becomes larger with decrease in particle size, and is indicated by an absorption shift to shorter wavelengths [115].

The conductivity of intrinsic semiconductors is basically dependent on the band gap. The band-gap energy of semiconductors tends to decrease with temperature. One of the main advantages of the application of Quantum sized particles is the increase in the band gap energy with decreasing particle size [116]. As the size of a semiconductor particle falls below the critical radius, the charge carriers begin to behave quantum mechanically and the charge confinement leads to a series of discrete electronic states. As a result there is an increase in the effective band gap and a shift of the band edges [117]. Thus by varying the size of the semiconductor particles, it is likely to enhance the redox potential of the valence-band holes and the conduction band electrons [118].

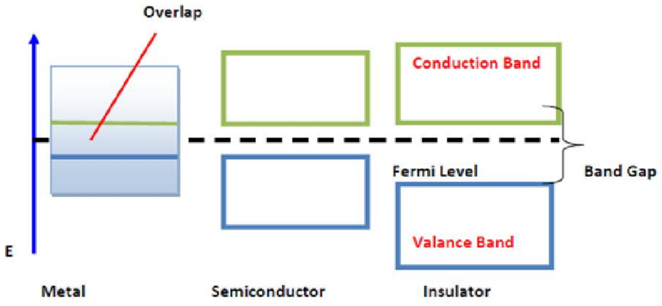

Figure 3. The Energy Band Model in Metal, Semiconductor and Insulator

Energy Band gap in metal, semiconductors and insulators is shown in figure-3, as the valance band and conduction band is overlapped in metals or conductors and there is no band gap between the valence and conduction band [119]. In metals, the valence band is not completely occupied with electrons and the filled valence band overlaps with the empty conduction band. In general, both states occur at the same time, the electrons can therefore move inside the partially filled valence band or inside the two overlapping bands [120]. In insulators, the valence band is fully occupied with electrons due to the covalent bonds, thus electrons cannot move because they are fixed between the atoms. While in Semiconductors, energy band gap lies between the conductors and insulators [121].

10.Different methods of synthesis of semiconducting nanoparticles

There are several methods used for the synthesis of nanoparticles, the synthesis of meso-structured porous materials represents a fascinating and intellectually challenging problem due to its potential for applications in catalysts, chromatography, and the controlled release of drugs, micro-electronics, and electro-optics [122, 82, 83]. High level of chemical purity is required as minute impurities can have large effects on the property of the nanoparticles [123]. Thus, keeping all these fact in mind, one canselect the appropriate method for the synthesis of desired nanoparticle-

a)Sol-gel technique: This method is one of the most common processes for producing nano-photocatalysts mentioned in several literatures. Over the years, solution precipitation and sol–gel processing have come to be the easiest method. Transition metal precursor is hydrolyzed with water and product is allowed to react to form precipitates, which are washed, dried and calcined at elevated temperatures to form nanocrystals of metal oxides. Smaller particles can be produced by slow and controlled hydrolysis and base catalyzed condensation reaction forms denser particles [136, 137].

b)*Calcination:* This is a high temperature technique. In this method volatile fraction is removed and phase transition as well as thermal decomposition takes place. This reaction is usually performed below the melting points of the reactants. Ores and other materials which need thermal decomposition are used in this method. Calcination can take place at different temperatures depending upon the material to be calcined [139].

c)*Chemical co-precipitation:* A simplistic and convenient method to prepare nanoparticles is chemical co-precipitation technique. Two or more soluble salts solutions are mixed in a definite ratio and co-precipitated with a base solution under inert atmosphere. Solutions of two or more water soluble salts of metals are dissolved in water, mixed and co-precipitated with alkali very slowly (in approximately 2 hours). Afterwards the resulting solution was stirred for 6 hours. The precipitate thus formed were filtered, washed, dried and sintered at about 400-600°C for 4-6 hours [140]. An increase in mixing rate decreased the size of nano-photocatalysts. It is a simple method which takes place at lower temperature than hydrothermal or thermal decomposition. Solvent used is environmental friendly and yield is high [39, 147].

d)Reverse Micelle technique: Micro emulsion of *oil-in-water* is used to prepare uniform sized nanoparticles. This emulsion contains three components oil, water and surfactant which form thermodynamically stable, single phase, isotropic transparent solution. The reacting reagents are present in nano water droplets surrounded by surfactant molecule. These water droplets containing reagents unite rapidly allowing mixing and precipitating the nanoparticles. Nano droplets of water solution are spherical and surrounded by surfactant molecular wall which act as a cage of growing particles [141]. The size of precipitated molecule changes with size of water pool in micelle. Mono dispersed nanoparticles of different sizes and morphology can be synthesized by this technique. This method is costly and have low yield.

e)*Hydrothermal technique:* Nanoparticles can also be synthesized by this technique which is also known as solvo-thermal technique. Hydrothermal synthesis defined as a method of synthesis of single crystals depends on the solubility of minerals in hot water under high pressure. The reactions are carried out in an autoclave at a pressure of 2000 pounds per square inch and a temperature of 200˚C or higher. Nanoparticles prepared by this method show better crystallinity and grain size [141, 142]. Nano photocatalyst with specific sizes and morphology can be synthesized by continuous hydrothermal technique. Reaction kinetics can be increased by microwave heating during hydrothermal technique. Microwave hydrothermal technique needs lower temperature as 150˚C and shorter time as 25 min as compare to conventional hydrothermal technique. It is also a single step, fast and easy technique for the preparation of nano-photocatalysts [143].

f)*Ball-milling or High Energy Ball-milling:* High energy ball milling of powder particles has been developed as an industrial process to successfully produce new alloys and phase mixtures. This powder metallurgical process allows the preparation of alloys and composites and nanomaterials, which cannot be synthesized via conventional routes. In nanomaterials research, this top down technique is well used to fine-tune the grain sizes of the materials in nanoscales.Transition metal oxides, borides, carbides and silicides can be synthesized by ball milling which is also known as mechano-chemical method [144].

g)*Micro emulsion:* Synthesis of nanoparticle in micro-emulsions is an area of considerable interest. Micro emulsions are colloidal 'nano-dispersions' of water in oil (or oil in water) stabilized by a surfactant film. The main idea behind this method is that by appropriate control of the synthesis parameters one can use these nanoreactors to produce tailor-made products down to a nanoscale level with new and special properties [145].Water-in-oil micro emulsions are used to prepare nanoparticles for more than two decades, and a wide variety of materials has been synthesized by these methods. Control parameters have been interpreted for influencing both nanoparticle concentration and morphology, allowing for controlled syntheses with various applications [145].

h)*Microwave (MW) assisted synthesis:* Microwave rapid heating has received considerable attention as a new method for the one-pot synthesis of metallic nanomaterial in solutions.The main advantages of MW irradiation are 1) uniform heating of the solution, so that a more homogeneous nucleation is obtained as well as a shorter crystallization time; 2) very short thermal induction period, which can lead to energy savings; 3) generation of localized high temperatures at the reaction sites which results in enhancement of reduction rates of metallic ions; 4) selective formation of specific morphology; and 5) superheating of solvents over the boiling points of solvent as a consequence of the microwave dissipation over the whole liquid volume. Further advantages are absence of convection processes, easy control, and low cost. Due to these advantages, monodispersed and better crystalline metallic nanostructures could be synthesized in a one-pot reaction within a few minutes [146].

i)*Sonochemical Synthesis:* This method involves the synthesis of nanoparticles when particles are exposed to ultrasonic irradiation. This method is best green chemistry based method. Sonochemical synthesis is found to be good for the synthesis of ZnO, TiO2 and other metal oxide nanoparticles [145, 147, 149].

11.Application of Photocatalysis

Heterogeneous photocatalysis has been demonstrated as a low cost and sustainable technology for the treatment of a mass of pollutants in air and water including organics and heavy metals. In recent years applications have been directed towards environmental clean-up andremediation of toxic waste, pollutants, and dye degradation [47, 154, 155]. Throughout most of this review various applications for nanosizedphotocatalysts have been discussed. The applications are derived essentially from bulk photocatalysis.

a)*Removal of heavy metals:* Heterogeneous photocatalysis has been widely used in the removal of heavy metals from waste water like Mercury (Hg), Chromium (Cr), lead (Pb), Cadmium (Cd) Arsenic (As), Nickel (Ni), Copper (Cu).The photoreducing ability of photocatalysis has been used to recover expensive metals from industrial effluent, such as Gold (Au), Platinum (Pt) and Silver(Ag) [48,49, 157].

b)*Destruction of organic pollutants:* Organic compounds such as alcohols, carboxylic acids, phenolic derivatives, or chlorinated aromatics, into harmless products *e.g,* carbon dioxide, water, and simple mineral acids, Herbicides and pesticides that may contaminate water such as 2,4,5 trichloro-phenoxyacetic acid, 2,4,5 trichlorophenol, S-triazine herbicides and DDT can be also completely mineralized into non-toxic byproducts [156, 160, 167, 168, 171, 172].

c)*Removal of inorganic Pollutants:* Inorganic species such as bromate, or chlorate, azide, halide ions, nitric oxide, palladium and rhodium species, and sulfur species can be decomposed. Metal salts like $AgNO_3$, HgCl and organometalic compound (*e.g* CH_3HgCl) can be removed from water, as well as cyanide, thiocyanate, ammonia, nitrates and nitrites [151, 158, 168].

d)Water disinfections: Used to decontaminate water from various microbes pollutant toxic for both human and environment *i.e. Streptococcus mutans, Streptococcus natuss, Streptococcus cricetus, Escherichia coli, Scaccharomycescerevisisas, Lactobacillus acidophilus,* poliovirus, *Microcystin toxins, Chlorella vulgaris, etc*[53, 54, 159, 162].

e)*Self-cleaning:* Exterior tiles, kitchen and bathroom components, interior furnishings, plastic surfaces, aluminum siding, building stone and curtains, window blinds [161].

f)*Air purification:* Room air cleaner, air conditioner, and interior air cleaner for factories, Air purification can also be obtained, at least up to a certain extent, at an illuminated surface coated with a semiconductor and this principle has been implemented for a variety of commercial applications, both indoor and outdoor [164, 169].

g)*Degradation of natural organic matter:* Humic substances have also been degradedphotochemically. Humic are naturally occurring biogenic heterogeneous organic substances characterized as being yellow brown and having high molecular weights. Advanced oxidation has been used to decrease the organic content in water including humic acid and it has the advantage of not leaving any toxic byproducts or sludge [163, 165]. Bekbolet and Ozkosemen investigated the photocatalytic degradation using humic acid as a model and observed that after 1 h irradiation and in the presence of 1.0 g/L TiO_2 (P25), 40% TOC and 75% of the color (400 nm) were removed. On the other hand, Eggins and coworkers found the suspension of TiO_2 (P25) irradiated by a mercury lamp showed a very efficient reduction of humic acid concentration of about 50% in 12 min. Heterogeneous photocatalysis has also been coupled with other physical methods in order to increase the degradation rate of organic molecules including humic substances [57, 170].

12.Recent advances and future challenges

Photocatalysis has progressed from explorative research to commercial development. A look to the recent literature reveals a steadily flux of more than 1300 international patents per year in this field for various applications from 2000 on most of which were concerned with pollution control and based on the use of TiO_2[58, 170].With further research and materials development, new applications for photocatalysts based on nanomaterials will emerge. One of the products of good research is new knowledge that enables new technologies. Our final review focus will emphasize the prospects and challenges of using photocatalysts for environmental clean-up and remediation. One of the major challenges for the scientific community involved in photocatalytic research is to increase the spectral sensitivity of photocatalysts to visible light, which composes the largest part of solar radiation. One must keep in mind the fact that photocatalytic environmental cleanup is only suitable for low-level pollutants, since the amount of ultraviolet photons is limited in both solar light and indoor illumination [59, 171]. In some fields, such as the outdoor self-cleaning application, the UV photons in solar light might be sufficient. However, for water purification, the level of UV photons in solar light is too low to perform effective photocatalytic cleanup, compared to the concentration of pollutants. This is the reason why photocatalysis is only considered as an auxiliary to biological remediation and other advanced oxidation process at the present stage [59, 171, 172]. The future of photocatalytic environmental cleanup is dependent on how efficiently the photocatalyst can use solar light.

Another major challenge is that nanoparticle TiO_2 does not only destroy all organic materials but also the organic matrix in which the nanoparticles are embedded. This limits its application to inorganic environments. Nanoparticle TiO_2 is expected to have minimal negative effect both on human health and the environment as it is usually immobilized in/on a substrate material [60,173]. However, nanoparticle TiO_2 can accumulate if its use is widespread and could potentially have health impacts for workers exposed to nanoparticle TiO_2 dust. There are currently no regulations related to the use of nanoparticle for water treatment, but standards on test methods for photocatalytic water purification are under development. Stricter water treatments standards would require new treatment methods and could thus further the application of photocatalytic systems with nanomaterials [174].

13.Conclusion

With developing different aspects of nanotechnology, the broaderenvironmental impacts of that will also need to be considered. Suchconsiderations might include models to determine potential benefits ofreduction or prevention of pollutants from industrial sources.Nanoscience technology holds great potential for the continuedimprovement of technologies regarding environmental protection. Thepresent review has given further evidence to this issue and it has tried toaddress what all the potential environmental impacts of the technologymight be. Therefore, the discussion in the review suggests that, a cleaner and greener environment, and renewable and sustainable energy economy can be achieved through photocatalysis.In order to promote the feasibility of photocatalysis in the near future, several key technicalconstraints ranging from catalyst development to reactordesign and process optimization have to be addressed**.**

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REFERENCES

[1] Ni, M., & Leung, M. K. H. 2007. A review and recent developments in photo-catalyticwater-splitting using TiO_2 for hydrogen production. *Renewable and Sustainable Energy Reviews*, 11:401–425.

[2] Turchi, C. S., & Ollis, D. F. 1990. Photo-catalytic Degradation of organic water contaminants: mechanisms involving hydroxyl radical attack, *Journal of Catalysis,* 122:178-192.

[3] Qamar, M. & Muneer, M. 2009. A comparative photo-catalytic activity of titanium dioxide and zinc oxide byinvestigating the degradation of vanillin.*Desalination,* 249:535–540.

[4] Qu, X., Pedro, J. J., & Li, Q. 2013. Applications of nanotechnology in water and wastewater treatment.*Water research,* 47:3931-3946.

[5] Devipriya, S. &Yesodharan, S. 2005. Photocatalytic degradation of pesticide contaminants in water.*Solar Energy Materials & Solar Cells,* 86:309–348.

[6] Herrmann, J. M. 1999. Heterogeneous photo-catalysis: fundamentals and applications to the removal of various types of aqueous pollutants. *Catalysis Today,* 5:115–129.

[7] Herrmann, J. M. 2010. Fundamentals and misconceptions in photo-catalysis. *Journal of Photochemistry and Photobiology A: Chemistry,* 216:85–93.

[8] Herrmann, J. M., & Guillard, C. 2000. Photo-catalytic degradation of pesticides in agricultural used waters.*Surface chemistry and catalysisChemistry*, 3(23):417–422.

[9] Anandan, S. & Yoon, M. 2003. Photo-catalytic activities of the nano-sized TiO_2-supported Y-zeolites*, Journal of Photochemistry and Photobiology C*: *Photochemistry Reviews*, 4:5–18.

[10] Gayaa, U. I., & Abdullaha, A. H. 2008. Heterogeneous photo-catalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews,* 9:1–12.

[11] Milenova, K. *et al*. 2013) The effect of introducing copper dopant on the photo-catalytic activity of ZnO nanoparticles.*Journal of chemical technology and metallurgy,* 48:259-264.

[12] Ying, Y., Song, T., & Huang, H. 2013. Nanoporous ZnO nanostructures for photocatalytic degradation of organic pollutants.*ApplPhys A*, 110:351–359.

[13] Barnes, R. J., & Molina, J. R. 2013. Comparison of TiO_2 and ZnO nanoparticles for photo-catalytic degradation of methylene blue and the correlated inactivation of gram-positive and gram-negative bacteria, *Nanopart Res*, 15:1432.

[14] Tiwari, D. K., Behari, J., & Sen, P. 2008. Application of nanoparticles in waste water treatment. *World Applied Sciences Journal,* 3(3):417-433.

[15] Sathiyanarayanan, S., Ravi, P.E., & Ramesh, A. 2009. Applications of Zinc Oxide nanorods as photo-catalyst for the decontamination of imidacloprid and spirotetramat residues in water. *The Open Catalysis Journal,* 2:24-32.

[16] Ali, A., & Muhammad, A. 2012. Doped metal oxide (ZnO) and photocatalysis: A Review. *JPIChE,* 40(1):11-19.

[17] Sobczyński, Dobosz, A. 2001. Water purification by photocatalysis on semiconductors.*Polish Journal of Environmental Studies,* 10(4):195-205.

[18] Twardowska, I. *et al*. 2006. UV/Vis light-enhanced photocatalysisfor water treatment and protection, *Soil and Water Pollution Monitoring, Protection and Remediation*, 3–23.

[19] Nohavica, D. & Gladkov, P. 2010. Zno nanoparticles and their applications – new achievements. *Nanocon,* 12-14:10.

[20] Muszkat, L. *et al.* 2002. Photocatalytic degradation of pesticides and bio-molecules in water.*Pest ManagSci*, 58:1143–1148.

[21] Angew, H. K. 2012. Semiconductor photocatalysis-mechanistic andsynthetic aspects. *Reviews,* DOI: 10.1002/anie.201201200.

[22] Kansal, S. K. 2009. Photocatalytic degradation of two commercial reactive dyes in aqueous phase using nanophotocatalysts. *Nanoscale Res Lett*, 4:709–716.

[23] Kanhere, P. & Zheng, J. 2012. Visible light driven photocatalytic hydrogen evolution and photophysical properties of Bi_3D doped $NaTaO_3$. *Intr. Journal of Hydrogen Energy,* 37:4889-4896.

[24] Farag, L. Y. *et al.* 2012. Nanomaterials as sorbents to remove heavy metal ions in wastewater treatment*. J Environ Anal Toxicol.*, 2:7.

[25] Baruah, S. & Mahmood, M. A. 2010. Enhanced visible light photocatalysis through fast crystallization of zinc oxide nanorods.*Beilstein J. Nanotechnol.,*1:14–20.

[26] McCullagh, C. *et al.* 2011. Photocatalytic reactors for environmental remediation: a review. *J ChemTechnolBiotechnol*, 86:1002–1017.

[27] Savage, N., & Diallo, M. S. 2005. Nanomaterials and water purification: Opportunities and challenges. *Journal of Nanoparticle Research*, 7:331–342.

[28] Saber, A. *et al.* 2010. Recent developments in photocatalytic degradation ofpesticides and phenols in storm and wastewater effluent.*In Proceedingsof the ERE 2010 Conference: Transitions to a Sustainable Future,* CSIRO, 1-5.

[29] Tyagi, P. K. *et al.* 2012. Nanomaterials Use in Wastewater Treatment; International Conference on Nanotechnology and Chemical Engineering *(ICNCS'2012)* December 21-22, 2012 Bangkok (Thailand).

[30] Ahmed *et al.* 2011. Influence of parameters on the heterogeneous photo-catalytic degradation of pesticides and phenolic contaminants in wastewater: a short review. *Journal of Environmental Management*, 92(3):311-330.

[31] Navarro, S. & Fenoll, J. 2009. Photo-catalytic degradation of eight pesticides in leaching water by use of ZnO under natural sunlight.*Journal of Hazardous Materials,* 172:1303–1310.

[32] Houas, A. & Lachhe, H. 2001. Photo-catalytic degradation pathway of methylene blue in water.*Applied Catalysis B: Environmental*, 31:145–157.

[33] Musee, N., Thwalaa, & Nota, N. 2011. The antibacterial effects of engineered nanomaterials: implications for wastewater treatment plants. *J.Environ. Monit.*, 13:164.

[34] Lazar, M. A., Varghese, S., & Nair, S. S. 2012. Photocatalytic water treatment by titanium dioxide: recent updates. *Catalysts, 2*:572-601.

[35] Ibhado, A. O., & Fitzpatrick, P. 2013. Heterogeneous Photocatalysis: recent advances and applications, *Catalysts*, *3*:189-218.

[36] Vinodgopal, K., Bedja, I., & Kamat, P. V. 1996. Nanostructured semiconductor films for photocatalysis. photoelectrochemical behavior of SnO_2/TiO_2 composite systems and its role in photocatalytic degradation of a textile azo dye. *Chem. Mater., 8:*2180-2187.

[37] Fox, M. A., & Dulay, M. 1995. Heterogeneous Photocatalysis*. Catalysis Rev.,* 83:341-357.

[38] Hoffmann*,* M. R. *et al.* 1995. Environmental applications of semiconductor photocatalysis.*Chem. Rev.,* 95:69-96.

[39] Tehrani-Bagha, A. R., & Amin, F. L. 2010. Decolorization of a reactive dye by uv-enhanced ozonation*. Prog. Color Colorants Coat*., 3:1-8.

[40] Evgenidou, E., Fytianos, K. & Poulios, I. 2005. Semiconductor-sensitized photo-degradation of Dichlorvos in water using TiO_2 and ZnO as catalysts. *Applied Catalysis B: Environmental* 59:81–89.

[41] Baruah, S., Pal, S. K. & Dutta, J. 2012. Nanostructured Zinc Oxide for Water Treatment.*Nanoscience & Nanotechnology-Asia,* 2:90-102.

[42] Dobbs, R. A., Wang, L., & Govind, R. 1989. Sorption of toxic organic compounds on wastewater solids: correlation with fundamental properties. *fnviron. Sci. Techno.,* 23:1092-1097.

[43] Vinu, R., & Madras, G. 2010. Environmental remediation by photocatalysis. *Journal of the Indian Institute of Science, 90:2.*

[44] Harrelkas, F., Paulo, A., & Alves, M. M. 2008. Photocatalytic and combined anaerobic photocatalytic treatment of textile dyes. *Chemosphere*; 72:1816–1822.

[45] Ibhadon, A., & Fitzpatrick, P. 2013. Heterogeneous Photocatalysis: Recent Advances and Applications. *Catalysts*, *3*:1-x.

[46] Ba-Abbada, M. M. *et al.* 2010. Solar photocatalytic degradation of environmental pollutants using ZnO prepared by Sol-Gel: 2, 4-Dichlorophenol as Case Study, *Int. J. of Thermal & Environmental Engineering,* 1(1):37-42.

[47] Haque, M. M., Bahnemann, D., & Muneer, M. 2011. Photocatalytic degradation of organic pollutants: mechanisms and kinetics, organic pollutants ten years afterthe stockholm convention – *Environmental and Analytical Update.*

[48] Oliveira, A. S., & Saggioro, E. N., Photochemistry for Environmental Remediation-Advanced Oxidation Processes for Industrial Wastewater Treatment. *Molecular Photochemistry* - Various Aspects Solar Photochemistry for Environmental Remediation.

[49] Carmen, Z., & Daniela, S., Textile organic dyes-characteristics, polluting effects and separation/elimination procedures from industrial effluents – A critical overview. *Organic Pollutants Ten Years afterthe Stockholm Convention – Environmental and Analytical Update.*

[50] Oliveros, L. E. & Braun, A. M. 2010. Photochemical Processes for Water Treatment. *Chem. Rev.,* 1093(93):671-698.

[51] Chen, L. I., Kuo, L. & Tseng, M. 2013. ZnO nanorod optical disk photocatalytic reactor for photodegradation of Methyl Orange. *Optics express*, 21(6):7240.

[52] Fujishima, A. & Honda, K. 1972. Electrochemical photolysis of water at a semiconductor electrode. *Nature,* 238(5358):37–38.

[53] Hoffmann, M. R. 1995. Environmental applications of semiconductor photocatalysis.*Chem.Rev.,* 95(1):69–96.

[54] Barber, J. 2009. Photosynthetic energy conversion: natural and artificial. *Chem. Soc. Rev.*38(1):185–196.

[55] Al-Qaradawi, S. & Salman, S. R. 2002. Photo-catalytic degradation of methyl orange as a model compound. *J. Photochem. Photobiol.Chem.*, 148(1-3):161–168.

[56] Yoon, M. & Negi, D. P. 2002. Photoinduced electron transfer in some photosensitive molecules-incorporated semiconductor/zeolites: New photocatalytic systems. *Proc. Indian Acad. Sci. Chem. Sci.*, 114(6):593–602.

[57] Tan, T. K. *et al.* 2011. Photodegradation of phenol red in the presence of ZnO Nanoparticles.World Academy of Science, *Engineering and Technology,* 55.

[58] Baruah, S. & Dutta, J. 2009. Nanotechnology applications in pollution sensing and degradation in agriculture: a review. *Environ ChemLett*, 7:191–204.

[59] Giahi, M. & Ghanbar, F. 2010. Photocatalytic degradation of Triton X-100 by Zinc oxide Nanoparticles.*Journal of Physical and Theoretical Chemistry*, 7 (3):189-193.

[60] Zhu, C. & Wang, L. 2000. Photocatalytic degradation of AZO dyes by supported TiO_2 + UV in aqueous solution. *Chemosphere,* 41:30-309.

[61] Akpan, U.G. & Hameed, B.H. 2009. Parameters affecting the photocatalytic degradation of dyes using TiO_2-based

photocatalysts: A review. *Journal of Hazardous Materials,* 170:520–529.

[62] Konstantinou, I. K. & Albanis, T. A. 2002. Review Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: intermediates and degradation pathways. *Applied Catalysis B: Environmental,* 1310:1–17.

[63] Prabha, I. 2013. Photocatalytic performance of nanocatalyst for the effective removal of dye in the wastewater. *ChemSci Trans.*, 2(1):220-224.

[64] Chong, M. N. 2010. Recent developments in photocatalytic water treatment technology: A review. *Water Reseach*, 44:2997-3027.

[65] Malato, S. *et al.* 2000. Solar photocatalytic mineralization of commercial pesticides: Oxamyl. *Solar Energy Materials & Solar Cells*, 64:1-14.

[66] Neppolian, B. *et al*. 2002. Solar/UV-induced photocatalytic degradation of three commercial textile dyes.*Journal of Hazardous Materials,* 89:303–317.

[67] Keun, L. S. & Mills, A. 2004. Detoxification of water by semiconductor photocatalysis.*Journal of Industrial and Engineering Chemistry*, 10:173-187.

[68] Cataño, F. A. *et al.* 2012. A Comparative study between TiO_2 and ZnO Photocatalysis: photocatalytic degradation of Cibacron Yellow Fn-2r Dye. *Latin American Applied Research,* 42:33-38.

[69] Al-Rasheed, R. A. 2005. Water treatment by heterogeneous photocatalysis:an overview. presented at *4th SWCC Acquired Experience Symposium,* Held In Jeddah, 2005.

[70] Ghule, L. A. *et al.* 2011. Photocatalytic degradation of methyl orange using ZnO nanorods.*Toxicological & Environmental Chemistry*, 93:4, 623-634.

[71] W. X. Li 2013. Photocatalysis of Oxide Semiconductors, *Journal of the Australian Ceramic Society,* Volume, 49(2), 2013, 41-46.

[72] Hupka, J., Zaleska, A., Janczarek, M., Kowalska, E., Górska, P. and Aranowski, R. 2006. Uv/Vis Light-Enhanced Photocatalysis for Water Treatment and Protection. Soil and Water Pollution Monitoring, Protection and Remediation, 3–23.

[73] Xiong, H.M., Shchukin, D.G., Mhwald, H., Xu, Y. and Xia, Y. 2009. Sonochemical Synthesis of Highly Luminescent Zinc Oxide Nanoparticles Doped with Magnesium (II). Angew. Chem. Int. Ed., 48, 2727 –2731.

[74] Gogate, P.R. and Pandit, A.B. 2004. Sonophotocatalytic Reactors for Wastewater Treatment: A Critical Review, *AIChE Journal*, 50(5), 1051.

[75] Barhon, Z. *et al*. 2012. Photocatalysis–Membrane Separation Coupling Reactor: Removal of Organic Pollutants from Water, S*cientific Study & Research Chemistry & Chemical Engineering, Biotechnology, Food Industry,* 13 (1), pp. 105 – 108.

[76] Shah, I., Huang, C.P., Chen, J. G., Doren, D. and Barteau, M. 2003. Semiconductor Metal Oxide Nanoparticles for Visible Light Photocatalysis.*NSF NIRT Grant No. 0210284* S. NSF Nanoscale Science and Engineering Grantees Conference, Dec16-18, 2003 Grant No. 0210284.

[77] Islam, N.M, Chatterjee, M., Ikushima, Y., Yokoyama, T., and Kawanami, T. 2010. Development of a Novel Catalytic Membrane Reactor for Heterogeneous Catalysis in Supercritical CO2, *Int. J. Mol. Sci.,* 11, 164-172; doi:10.3390/ijms11010164.

[78] Warszyński, P. 2010. Removal of natural organic matter from potable water using photo-catalytic membrane reactor. *Physicochem.Probl.Miner.Process,* 4573-84.

[79] Gallucci, F., Basile, A. and Hai, F. I. "Introduction—A review of Membrane reactors" in Membranes for membrane reactors:Preparation, Optimization and Selection (eds. Basile, A., Gallucci, F.), page 1-62, Wiley InterScience, USA, 2011.

[80] Diban, N., Aguayo, A.T., Bilbao, J., Urtiaga, A. and Orti, I. 2013. Membrane Reactors for in Situ Water Removal: A Review of Applications. *Ind. Eng. Chem. Res*., 52, 10342 −10354.

[81] Lee, W., Kang, J. and Chang, K. J. 2008. p-Type Doping and Compensation in ZnO, *Journal of the Korean Physical Society*, 53, 1; 196-201.

[82] Panigrahi, S., Kundu, S., Ghosh, S.K., Nath, S. and Pal, T.S. 2004. General method of synthesis for metal nanoparticles, *Journal of Nanoparticle Research*, 6: 411–414.

[83] Singh, A., Dutta, D.P., Roy, M., Tyagi, A. K. & Fulekar, M. H. 2013. Sonochemical synthesis, characterization, and photocatalytic properties of Bi22xSbxWO6 nanorods, *J Mater Sci.,* DOI 10.1007/s10853-013-7900-x.

[84]Pouretedal, H.R. & Hasanali, M.A. 2013. Photocatalytic degradation of some β-lactam antibiotics in aqueous suspension of ZnS nanoparticles, *Desalination and Water Treatment*, 51:13-15, 2617-2623, DOI:10.1080/19443994.2012.749197.

[85] Mountacer, H., Nemmaoui, S. M., Rafqah, S., Voyard, G. and Sarakha, M. 2013. TiO2 Photocatalysis of the OrganophosphorusFenamiphos: Insight into the Degradation Mechanism, ISRN Environmental Chemistry. Article ID 319178, 8 pages.

[86] Andreozzi, R., Caprio, V., Insola, A. andMarotta, R. 1999. Advanced oxidation processes (AOP) for water purification and recovery, *Catalysis today*, 53:1, 51–59.

[87] Qamar, M., Muneer, M. and Bahnemann, D. 2006. Heterogeneous photocatalysed degradation of two selected pesticide derivatives, triclopyr and daminozid in aqueous suspensions of titanium dioxide, *Journal of Environmental Management*, 80:2, 99–106.

[88] Kajiebaf, V.T, Sarpoolaky, H., and Mohammadi, T., 2013. Synthesis of Nanostructured AnataseMesoporous Membranes with Photocatalytic and Separation Capabilities for Water Ultrafiltration Process, *International Journal of Photo-energy*, Volume 2013, Article ID 509023, 11 pages.

[89] Abhang, R. M., Kumar, D. and Taralkar, S. V. 2011. Design of Photocatalytic Reactor for Degradation of Phenol in Wastewater, *International Journal of Chemical Engineering and Applications, 2: 5.*

[90] Centi, G. & Perathoner, S. 2003. Catalysis and sustainable (green) chemistry, *Catalysis Today*, 77; 287–297.

[91] Mohamed,V., McKinney, D.L. & Sigmund, W.M. 2012. Enhanced nanocatalysts, *Material Science & Engineering,* 73;1-13.

[92] Wang, D., Xie, T., and Li, Y. 2009. Nanocrystals: Solution-Based Synthesis and Applications as Nanocatalysts, *Nano Res*, 2: 30 46.

[93] Izadifard, M., Achari, G. and Langford, C.H. 2013. Application of Photocatalysts and LED Light Sources in Drinking Water Treatment, *Catalysts*, *3*, 726-743; doi:10.3390/catal3030726.

[94] Polshettiwar, V., Luque, R., Fihri, A., Zhu, H., Bouhrara, M. and Basset, J.M. 2011. Magnetically Recoverable Nanocatalysts, *Hem. Rev,* 111, 3036–3075.

[95] Grcicˇ, I. and Puma, L.G. 2013. Photocatalytic Degradation of Water Contaminants in Multiple Photoreactors and Evaluation of Reaction Kinetic Constants Independent of Photon Absorption, Irradiance, Reactor Geometry and Hydrodynamics, *Environ. Sci. Technol*. 47, 13702 −13711.

[96] Chen, R., Du, Y., Wang, Q., Xing, W., Jin, W., and Xu, N. 2009. Effect of Catalyst Morphology on the Performance of Submerged Nanocatalysis/ Membrane Filtration System, *Ind. Eng. Chem. Res.,* 48, 6600–6607.

[97] Colmenares, J.C., Luque, R., Campelo, J.M., Colmenares, F., Karpiński, Z. and Romero, A.A. 2009. Nanostructured Photocatalysts and Their Applications in the Photocatalytic Transformation of Lignocellulosic Biomass: An Overview, *Materials, 2*, 2228-2258; doi:10.3390/ma2042228.

[98] Tayade, R.J., Natarajan, T.S. and Bajaj, H.C. 2009. Photocatalytic Degradation of Methylene Blue Dye Using Ultraviolet Light Emitting Diodes, *Ind. Eng. Chem. Res*, 48, 10262–10267.

[99] Tayade, R. J., Kulkarni, R. G., and Jasra, R. V. 2007. Enhanced Photocatalytic Activity of TiO2-Coated NaY and HY Zeolites for the Degradation of Methylene Blue in Water. *Ind. Eng. Chem. Res*., 46, 369–376.

[100] Akyol, A., Yatmaz, H. C., and Bayramoglu, M. 2004. Photocatalytic decolorization of Remazol Red RR in aqueous ZnO suspensions. *Appl. Catal., B* 2004, 54, 19–24.

[101] Konstantinou, I. K. and Albanis, T. A. 2004. TiO2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: A review. *Appl. Catal., B,* 49, 1–14.

[102] Sud, D. & Kaur, P. 2012. Heterogeneous Photocatalytic Degradationof Selected Organophosphate Pesticides: A Review, *Critical Reviews in Environmental Science and Technology,* 42:22, 2365-2407, DOI: 10.1080/10643389. 2011.574184.

[103] Chong, M.N., Bo, J. Christopher, W.K. and Saint, C. 2010. Recent developments in photocatalytic water treatment technology: A review. *Water Research,* 44; 2997-3027.

[104] Fujishima, A., Zhang, X., and Trykm D.A. 2007. Heterogeneous photocatalysis: From water photolysis to applications in environmental cleanup, *International Journal of Hydrogen Energy,* 32,2664–2672

[105] Baruah,S., Pal, S.K. and Dutta, J, 2012. Nanostructured Zinc Oxide for Water Treatment, *Nanoscience & Nanotechnology-Asia*, 2.

[106] Ravelli, D., Dondi, D., Fagnoni, M. and Albini, A. 2009. Photocatalysis. A multi-faceted concept for green chemistry, *ChemSoc Rev.,* 38, 1999–201.

[107] Gautam, P., Madathil, D., & Nair, A N. B. 2012. Nanotechnology in Waste Water Treatment : A Review, 5(5), 2303–2309.

[108] Hildebrand, H., Mackenzie, K., &Kopinke, F. D. 2008. Novel nano-catalysts for wastewater treatment. *Global Nest Journal*, 10(1), 47–53. Retrieved from <Go to ISI>://000254825700007

[109] Jain, K. K. 2012a. Nanotechnology and Water. Contemporary Materials, 1(3), 26–30. http://doi.org/10.7251/COM1201026J

[110] Mansoori, G. a, Bastami, T. R., Ahmadpour, a, & Eshaghi, Z. 2008. Chapter 2 Environmental Application of Nanotechnology. *Annual Review of Nano Research*, 2, 1–73. http://doi.org/10.1142/9789812790248_0010

[111] Mohammadi, M., & Sabbaghi, S. 2014. Photo-catalytic degradation of 2,4-DCP wastewater using MWCNT/TiO2 nano-composite activated by UV and solar light. Environmental Nanotechnology, Monitoring & Management, 1-2, 24–29. http://doi.org/10.1016/j.enmm. 2014.09.002

[112] Oseghe, E. O., Ndungu, P. G., & Jonnalagadda, S. B. 2014. Synthesis of mesoporousMn/TiO2 nanocomposites and investigating the photocatalytic properties in aqueous systems. Environmental Science and Pollution Research, 22(1), 211–222. http://doi.org/10.1007/s11356-014-3356-z

[113] Pandey, B., & Fulekar, M. H. 2012. Nanotechnology: Remediation Technologies to Clean Up the Environmental Pollutants. *Res. J. Chem. Sci*., 2(2), 90–96. Retrieved from http://www.isca.in/rjcs/Archives/vol2/i2/15.pdf

[114] Qu, X., Alvarez, P. J. J., & Li, Q. 2013. Applications of nanotechnology in water and wastewater treatment. Water Research, 47(12), 3931–3946. http://doi.org/10.1016/j.watres.2012.09.058

[115] Răileanu, M., Crişan, M., Niţoi, I., Ianculescu, A., Oancea, P., Crişan, D., & Todan, L. 2013. TiO2-based nanomaterials with photocatalytic properties for the advanced degradation of xenobiotic compounds from water.A literature survey. Water, Air, and Soil Pollution, 224(6).http://doi.org/10.1007/s11270-013-1548-7

[116] Savage, N., & Diallo, M. S. 2005. Nanomaterials and water purification: Opportunities and challenges. *Journal of Nanoparticle Research*, 7(4-5), 331–342. http://doi.org/10.1007/s11051-005-7523-5

[117] Shan, G., Surampalli, R. Y., Tyagi, R. D., & Zhang, T. C. 2009. Nanomaterials for environmental burden reduction, waste treatment, and nonpoint source pollution control: A review. *Frontiers of Environmental Science and Engineering in China*, 3(3), 249–264. http://doi.org/10.1007/s11783-009-0029-0

[118] Tiwari, D. K., Behari, J. & Sen, P. 2008. Application of Nanoparticles in Waste Water Treatment. Carbon Nanotubes, 3(3), 417–433. Retrieved from http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:Application+of+Nanoparticles+in+Waste+Water+Treatment#7

[119] Tyagi, P. K., Singh, R., Vats, S. & Kumar, D. 2012a. Nanomaterials Use in Wastewater Treatment. International Conference on Nanotechnology and Chemical Engineering, 5.

[120] Wang, X., Guo, Y., Yang, L., Han, M., Zhao, J., & Cheng, X. 2012. Nanomaterials as Sorbents to Remove Heavy Metal Ions in Wastewater Treatment. *Journal of Environmental & Analytical Toxicology*, 2(7). http://doi.org/10.4172/2161-0525.1000154

[121] Abe, R. 2010. Recent progress on photocatalytic and photoelectrochemical water splitting under visible light irradiation. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, *11*(4), 179–209. http://doi.org/10.1016/j.jphotochemrev.2011.02.003

[122] Ashokkumar, M. 1998. An overview on semiconductor particulate systems for photo production of hydrogen. *International Journal of Hydrogen Energy*, *23*(6), 427–438. http://doi.org/10.1016/S0360-3199(97)00103-1

[123] Bangal, M., Ashtaputre, S., Marathe, S., Ethiraj, a., Hebalkar, N., Gosavi, S. W., …Kulkarni, S. K. 2005. Semiconductor nanoparticles.*Hyperfine Interactions*, *160*(1-4), 81–94. http://doi.org/10.1007/s10751-005-9151-y

[124] Bhatkhande, D. S., Pangarkar, V. G., &Beenackers, a. a. C. M. 2002. Photocatalytic degradation for environmental applications – a review. *Journal of Chemical Technology & Biotechnology*, *77*(1), 15. http://doi.org/10.1002/jctb.532

[125] Chatterjee, D. & Dasgupta, S. 2005. Visible light induced photocatalytic degradation of organic pollutants. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, *6*(2-3), 186–205. http://doi.org/10.1016/j.jphotochemrev.2005.09.001

[126]Chong, M. N., Jin, B., Chow, C. W. K., & Saint, C. 2010. Recent developments in photocatalytic water treatment technology: A review. *Water Research*, *44*(10), 2997–3027. http://doi.org/10.1016/j.watres.2010.02.039

[127] Fujishima, A., Zhang, X. & Tryk, D. A. 2007. Heterogeneous photocatalysis: From water photolysis to applications in environmental cleanup. *International Journal of Hydrogen Energy*, *32*(14), 2664–2672. http://doi.org/10.1016/j.ijhydene.2006.09.009

[128] Haque, M. M., Bahnemann, D., & Muneer, M. 2003. Photocatalytic Degradation of Organic Pollutants : Mechanisms and Kinetics, 3.

[129] Kudo, A. 2006. Development of photocatalyst materials for water splitting.*International Journal of Hydrogen Energy*, *31*(2), 197–202. http://doi.org/10.1016/j.ijhydene.2005.04.050

[130] Lin, Y., Yuan, G., Liu, R., Zhou, S., Sheehan, S. W., & Wang, D. 2011. Semiconductor nanostructure-based photoelectrochemical water splitting: A brief review. *Chemical Physics Letters*, *507*(4-6), 209–215. http://doi.org/10.1016/j.cplett.2011.03.074

[131] Liqiang, J., Yichun, Q., Baiqi, W., Shudan, L., Baojiang, J., Libin, Y., …Jiazhong, S. 2006. Review of photoluminescence performance of nano-sized semiconductor materials and its relationships with photocatalytic activity. *Solar Energy Materials and Solar Cells*, *90*(12), 1773–1787. http://doi.org/10.1016/j.solmat.2005.11.007

[132] Maeda, K. 2011. Photocatalytic water splitting using semiconductor particles: History and recent developments. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, *12*(4), 237–268. http://doi.org/10.1016/j.jphotochemrev.2011.07.001

[133] Mills, A. & Le Hunte, S. 1997. An overview of semiconductor photocatalysis.*Journal of Photochemistry and Photobiology A: Chemistry*, *108*(1), 1–35. http://doi.org/10.1016/S1010-6030(97)00118-4

[134] Ozdemir, S. S., Buonomenna, M. G. & Drioli, E. 2006. Catalytic polymeric membranes: Preparation and application. *Applied Catalysis A: General*, *307*(2), 167–183. http://doi.org/10.1016/j.apcata.2006.03.058

[135] Pilutti, A. M., Nemeth, J. E. & Nemeth, P. J. E. 2011. Technical and Cost Review of Commercially Available Mf / Uf Membrane Products. *Aquatech Amsterdam,* 2011, 1–15.

[136] Ravelli, D., Dondi, D., Fagnoni, M. & Albini, A. 2009.Photocatalysis.A multi-faceted concept for green chemistry.*Chemical Society Reviews*, *38*(7), 1999–2011. http://doi.org/10.1039/b714786b

[137] Shannon, M. a, Bohn, P. W., Elimelech, M., Georgiadis, J. G., Mariñas, B. J. & Mayes, A. M. 2008. Science and technology for water purification in the coming decades. *Nature*, 452(7185), 301–310. http://doi.org/10.1038/nature06599

[138] Shchukin, D. G., & Sviridov, D. V. 2006. Photocatalytic processes in spatially confined micro- and nanoreactors. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, *7*(1), 23–39. http://doi.org/10.1016/j.jphotochemrev.2006.03.002

[139] Steinfeld, A. 2002. Solar hydrogen production via a two-step water-splitting thermochemical cycle based on Zn/ZnO redox reactions. *International Journal of Hydrogen Energy*, *27*(6), 611–619. http://doi.org/10.1016/S0360-3199(01)00177-X

[140] Tiwari, D. K., Behari, J., & Sen, P. 2008. Application of Nanoparticles in Waste Water Treatment. *Carbon Nanotubes*, 3(3), 417–433. Retrieved from http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:Application+of+Nanoparticles+in+Waste+Water+Treatment#7

[141] Valencia, S., Marin, J. M., & Restrepo, G. 2010. Study of the Bandgap of Synthesized Titanium Dioxide Nanoparticules Using the Sol-Gel Method and a Hydrothermal Treatment~!2009-10-14~!2009-10-30~!2010-01-27~! *The Open Materials Science Journal*, *4*(2), 9–14. http://doi.org/10.2174/1874088X01004020009

[142] Zhu, J. & Zäch, M. 2009.Nanostructured materials for photocatalytic hydrogen production.*Current Opinion in Colloid & Interface Science*, *14*(4), 260–269. http://doi.org/10.1016/j.cocis.2009.05.003

[143] Aliabadi, M., & Sagharigar, T. 2011. Photocatalytic Removal of Rhodamine B from Aqueous Solutions Using TiO 2 Nanocatalyst, *1*(12), 620–626.

[144] Aysin, B., Park, J., & Ozturk, A. 2011. Production of silver loaded photocatalytic tio 2 powders by ball milling, 1–6.

[145] Bansal, P., Dhir, A., Prakash, N. T., & Sud, D. 2011. Environmental remediation of wastewater containing azo dyes with a heterostructurednano photocatalyst, 50(July), 991–995.

[146] Beydoun, D., Amal, R., Low, G. & Mcevoy, S. 2000. Role of nanoparticles in photocatalysis, 439–458.

[147] Chauhan, R. & Kumar, A. 2012. Photocatalytic studies of silver doped ZnO nanoparticles synthesized by chemical precipitation method, 546–553. http://doi.org/10.1007/s10971-012-2818-3

[148] Chen, W., Qi, D., Gao, X., Thye, A. & Wee, S. 2009. Progress in Surface Science Surface transfer doping of semiconductors.*Progress in Surface Science*, *84*(9-10), 279–321. http://doi.org/10.1016/j.progsurf.2009.06.002

[149] Crdl, T. (N.D.).Visible-light Photocatalyst - Nitrogen-doped Titanium Dioxide -, 40(3), 45–50.

[151] Diban, N., Aguayo, A. T. & Bilbao, J. 2013. Membrane Reactors for in Situ Water Removal : A Review of Applications.

[152] Gallucci, F. & Basile, A. 2011. Introduction - A review of membrane reactors, 1–61.

[153] Kimura, S., Kodama, S., &Sekiguchi, H. 2013. Development of photocatalytic reactor having light source inside by electrical discharge, (August), 4–7.

[154] Madhusudhana, N., Yogendra, K. & Mahadevan, K. M. 2012. Photocatalytic Degradation of Violet GL2B Azo dye by using Calcium Aluminate Nanoparticle in presence of Solar light, *2*(3), 72–77.

[155] Madhusudhana, N., Yogendra, K., Mahadevan, K. M., &Naik, S. 2011. Photocatalytic Degradation of Coralene Dark Red 2B Azo Dye Using Calcium Zincate Nanoparticle in Presence of Natural Sunlight : An Aid to Environmental Remediation, *2*(4), 294–298.

[156] Meng, J., Yang, B., Zhang, Y., Dong, X. & Shu, J. 2010. Chemosphere Heterogeneous ozonation of suspended malathion and chlorpyrifos particles. *Chemosphere*, 79(4), 394–400. http://doi.org/10.1016/j.chemosphere.2010.02.008

[157] Mohanraj, V. J., & Chen, Y. 2006. Nanoparticles – A Review, *5*(June), 561–573.

[158] Neppolian, B., Choi, H. C., Sakthivel, S., Arabindoo, B., & Murugesan, V. 2002. Solar / UV-induced photocatalytic degradation of three commercial textile dyes, 89, 303–317.

[159] Ni, M., Ã, M. K. H. L., Leung, D. Y. C., &Sumathy, K. 2007. A review and recent developments in photocatalytic water-splitting using TiO 2 for hydrogen production, *11*, 401–425. http://doi.org/10.1016/j.rser.2005.01.009

[160] Notice, E. 2011. Influence of Parameters on the Heterogeneous Photocatalytic Degradation of Pesticides and Phenolic Contaminants in Wastewater : A Short Review, 92, 311–330.

[161] Okuyama, K., Lenggoro, W., & Project, N. 2005. Nanoparticle Preparation and Its Application - A Nanotechnology Particle Project in Japan, 1–4.

[162] Rao, P., Patel, G., Sharma, S. L., & Suresh, C. (n.d.). Toxicological & Environmental Chemistry Photocatalytic degradation of crystal violet over semiconductor zinc oxide powder suspended in aqueous solution, (April 2015), 37–41. http://doi.org/10.1080/02772249709358460

[163] Ray, A. K., &Beenackers, A. A. C. M. 1998. Development of a new photocatalytic reactor for water puri ® cation, 40, 73–83.

[164] Rodríguez, S. M. 2007. Waste water treatment by advanced oxidation processes (solar photocatalysis in degradation of industrial contaminants) Photoreactors Introduction Biodegradable substances : Non-viable Air stripping Bio-treatment Ozone, (October), 1–40.

[165] Shah, S. I., Huang, C. P., Chen, J. G., Doren, D., &Barteau, M. 2003. Semiconductor Metal Oxide Nanoparticles for Visible Light Photocatalysis, (0210284), 16–18.

[166] Tayade, R. J., Surolia, P. K., Kulkarni, R. G., & Jasra, R. V. (n.d.). Photocatalytic degradation of dyes and organic contaminants in water using nanocrystallineanatase and rutile TiO 2, 455. http://doi.org/10.1016/j.stam.2007.05.006

[167] Sud, D., & Kaur, P. 2011. Critical Reviews in Environmental Science and Technology Heterogeneous Photocatalytic Degradation of Selected Organophosphate Pesticides : A Review Heterogeneous Photocatalytic Degradation of Selected Organophosphate Pesticides : A Review, (December 2014), 37–41. http://doi.org/10.1080/10643389.2011.574184

[168] Turchi, C. S. 1990. Photocatalytic Degradation of Organic Water Contaminants : Mechanisms Involving Hydroxyl Radical Attack, 192, 178–192.

[169] Ullah, I., Ali, S., Hanif, M. A., & Shahid, S. A. 2012. Nanoscience for environmental remediation : A Review, *2*, 60–77.

[170] Umar, M., & Aziz, H. A. 2013. Photocatalytic Degradation of Organic Pollutants in Water.

[171] Verma, A., & Dixit, D. 2012. Photocatalytic degradability of insecticide Chlorpyrifos over UV irradiated Titanium dioxide in aqueous phase, *3*(2), 743–755. http://doi.org/10.6088/ijes.2012030132001

[172] Verma, A., Sheoran, M., & Toor, A. P. 2013. Titanium dioxide mediated photocatalytic degradation of malathion in aqueous phase, 20(January), 46–51.

[173] Yogendra, K., Naik, S., Mahadevan, K. M., &Madhusudhana, N. 2011. A comparative study of photocatalytic activities of two different synthesized ZnO composites against Coralene Red F3BS dye in presence of natural solar light, 1(1), 11–15.

[174] Zhang, Y., Ram, M. K., Stefanakos, E. K., &Goswami, D. Y. 2013. Surface & Coatings Technology Enhanced photocatalytic activity of iron doped zinc oxide nanowires for water decontamination. *Surface & Coatings Technology*, 217, 119–123. http://doi.org/10.1016/j.surfcoat.2012.12.001

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