CHAPTER 1

Introduction and Literature Review

1.1 Introduction

As we all know that water is the fundamental substance for the existence of all forms of the life on the earth surface i.e. there is no life without water. Although, almost 71% earth surface is covered by water but only 3% of this is fresh water. According to a report 1/3rd population of the world suffers from shortage of water and almost one billion people either have no direct access or they are denied to access to clean water (Romão, 2015).The problems of water scarcity is continuously increasing due to rapid industrialization, fast population growth, climate change and depletion of natural water sources (Qu et al., 2013; Schneider, 2015; Tollefson, 2011). However, various types of hazardous industrial and household discharges such as organic compounds from dyes, paints, resins, plasticizers, pharmaceuticals, personal care products, etc., contaminate the water bodies globally. The source of fresh water is limited and most part of this (1/3rd) is exploited for irrigation, industrial and domestic application (Schwarzenbach et al., 2006). All these factors compel us to not only look for alternative water resources but to also recycle the contaminated water streams to a quality which is able to meet the demands of the community/society.

1.2 Industrial pollution

The vast establishment of industries and uncontrolled population growth in recent decades are mainly responsible for environmental pollution, which is now a serious problem globally. According to recent estimates, per day almost 10 million cubic meter of industrial, sewage and agricultural waste water is globally discharged into water bodies and about 70-90% of this waste water is not treated even in developing countries. It is estimated that India has only 30% capacity of sewage treatment which is generated from its major cities. However, the amount of waste water generated differs from country to country. According to Han et al. all

the water utilized for industrial purposes generally released as waste water (Han et al., 2009). The main contribution in the generation of industrial waste water is made by water dependent industries such as textile, paper and pulp, thermal power plants, iron and steel industries etc. (Clark, 2011; Kookana and Rogers, 1995; Mehan et al., 2002). In highly developed and developing countries the amount of contaminated water generated from the similar type of industries are generally high.

1.3 Water pollution

Water pollution is simply the contamination of water by unwanted sources which makes it unfit for living beings. Water contamination can be natural as well as anthropogenic. Natural means of water pollution are as volcano eruptions, storms, earthquakes etc. that can change the quality of water. Various types of pollutants include chemicals (organic or inorganic), bacteria, parasites, trashes etc. Eventually all the other forms of pollution (air pollution, soil pollution) make their way to water. The sources of water contamination are mainly classified in two categories: point and non point contamination sources.

1.3.1 Point sources of contamination

In point source of contamination the contaminants entering into water bodies are from identifiable sources (i.e. source of water contaminations are known) such as effluents coming from industrial and municipal waste water, animal feedlots, sewage treatment plants, leachets from the sites of disposal of industrial wastes, ditches, runoff from metallurgical industries and coal mines etc. (Barilari et al., 2020). It can be easily distinguished from other sources of water pollution (Hogan, 2010).

1.3.2 Non-point sources of contamination

When contaminants entering into water are from non identifiable sources or sources of water

contamination is not known (i.e. contaminant does not comes from a single discrete sources) then contamination is known as non-point sources of contamination (Moss, 2008). Such type of contamination sources are difficult to control and they may come from industrial wastes, pesticides, fertilizers, urban and rural run offs, spills etc. (Duda, 1993). It is regarded that non-point sources of contamination are the prime source of water pollution (Xepapadeas, 2011) also it is very difficult to monitor and regulate such type of pollution.

According to a report, almost 90% of the generated waste water from all sources is directly discharged into water streams (river, lakes or oceans) without any prior treatment (Langergraber and Muellegger, 2005). This polluted water cause adverse impact on the environment as well as on the living beings which is a matter of great concern. Hence, it is required to develop effective techniques which not only conserve the water resources but also efficiently treats the waste water before discharging it in to larger water bodies. Moreover, these techniques should focus on the complete removal of the contaminants, so that further deterioration in the quality of water can be prevented.

Organic contaminants mainly come from synthetic dyes, pharmaceuticals, polymers, cosmetics surfactants, petrochemicals etc.; among these synthetic dyes and pharmaceuticals consist of some of very toxic and carcinogenic pollutants. In present time there are more than 10,000 types of commercially used dyes are available which produces, more than 0.7 million tons of organic waste annually (Rajeshwar et al., 2008). However, textile industries consume a large amount of water and about 1-20% of the dyes are lost during the dying process. So, it releases huge amount of waste water containing textile effluent. Organics from pharmaceuticals wastes and sewages may also be very hazardous and carcinogenic to the entire biota. Although, there are several methods available to treat the waste water but

photocatalysis is one of the efficient techniques among them because it is economic, non-toxic, safe and renewable process. Photocatalysis processes utilize solar light as a source of energy (renewable energy source). So, photocatalysis is the process of great importance, hence design and synthesis of artificial semiconductor photocatalysts having high activity attracts the attention of the researchers globally (Herrmann, 1999; Kudo and Miseki, 2009; Xiang et al., 2012).

From the different industrial workup adequate amount of organic effluents are generated. These effluents may come from textile printing, pharmaceutical, paper and pulp, sugar, tannery and food processing industries, among these particularly printing industry is quite diverse and has wide application such as printings of books, cartoons, containers, newspapers, textiles, sheeting's, brochures, metal foils, wallpapers etc. So, printing industry adversely affects the environment as it releases waste water containing hazardous materials. The wastes generated from printing industries mainly consists of dyestuffs, residual chemicals, solvent residues, photographic and residual chemicals, oil spills and wiping material containing dyes, pigments. These substances are very toxic for our ecosystem (Kiurski et al., 2012).

As time progresses new technologies are continuously being developed. In the modern period there is huge competition to synthesize and develop new chemicals (compounds) which can be applied for different purposes in industries and the synthetic dyes is one of the many class of chemicals which can be used in different industrial purposes. Due to the uncontrolled use of these dyes in various industries, they become a part of industrial effluents. It is estimated that annually about 4.5×10^5 tons of dyes are produced across the globe and out of this almost 11% of these dyes are released as effluents during industrial workup. Majority of these

organic dyes are potentially toxic, carcinogenic and mutagenic in nature, so, the complete removal of the dyes from industrial effluents is a matter of great challenge for us.

It is already discussed in the above sections that waste water released from various industrial, agricultural and household activities contains large number of organic effluents including dyes, pharmaceuticals, phenolic derivatives etc. However, dyes as an effluent released mainly from textile or printing industries are one of the potential contaminants of water and environment. These dyes effluents are further discharged into larger water bodies like ponds, river and lakes where they may undergo certain chemical and biological transformation by consuming dissolved oxygen (DO) present in water; most of the dyes are highly toxic, hazardous and lethal to aquatic biota (Mushtaq et al., 2020). So, the decolourization as well as complete removal of these effluents comes from various industries (textile, printing, finishing, food processing) is a matter of great importance; because they adversely affect our ecosystem. Moreover, it should be noted that among different category of environmental pollutions like noise, soil, water and air pollution; water pollution is the one which directly affect the living beings.

1.4 Techniques Used for Waste Water Treatment

From the past several decades treatment of waste water is the topic of immense importance for the researchers all over the globe. In order to remove pollutants from waste water various technologies were designed and developed from time to time to meet the economic constraints as well as environmental regulations. There are different conventional methods which has been currently used to remove organic pollutants from waste water, these conventional methods are as adsorption, biological treatment (aerobic and anaerobic), precipitation, coagulation, flocculation etc.; although all these techniques essentially can

reduce the organic pollutants and suspended solids from the polluted water to limit the pollution but the complete removal of organic recalcitrants (pollutants) are not possible by conventional methods because some of these methods generates secondary wastes while others may be very slow (selective) or rapid but not selective. These processes can also be limited by their high operating and energy cost, generation of harmful by-products. Here in upcoming sections we will discuss about some of the most commonly used conventional methods for the treatment of waste water.

1.4.1 Adsorption

Adsorption is classical, cleaner and efficient technique for treatment of organic or inorganic contaminated waste water. In adsorption process generally a solid substrate is used, on the surface of which the pollutant (organic/inorganic) molecules dissolved in water bind either by physical or by chemical interaction. So, in adsorption the concentration of the adsorbate (pollutants) molecules increases at the surface of substrate (adsorbent) than in the bulk. Activated carbon obtained from carbonaceous materials like woods, charcoals, burnt fuels, nutshells etc. is preferably used as an adsorbent. Moreover, activated alumina is also a good adsorbent and used for the removal of organic wastes (2,4-dichlorophenol, 2,4,6-Trichlorophenol, pesticides) from contaminated water (Chen et al., 1989). Zeolites are low cost natural or synthetic hydrated alumino silicates which show good adsorption properties and they can easily be regenerated. Zeolites are multifunctional as they can be used as adsorbents, ion-exchangers, molecular sieves as well as a catalyst. Zeolites provide great surface area for the adsorption of dyes, petrochemicals and inks etc.; peats were used as an adsorbent for the removal of polar organic compounds. Various other types of adsorbent are also there like activated rice husk is a low cost and effective in color removal from

contaminated water (Gupta et al., 2006) and various polymeric adsorbents were also developed for specific adsorption of organic pollutants from waste water. However the drawbacks of adsorption process are that it generates secondary waste (sludge) and the separation of organic waste from the surface of adsorbent is very tough and tedious.

1.4.2 Biological Method of Treatment

Biological method of treatment of waste water usually deals with organic impurities present in contaminated water, as these impurities are easily dissolved in water and potentially toxic at low concentration level so they can be biodegraded quite easily. However, there are some persistent organic pollutants (POPs), biopolymers, xenobiotics and bio-accumulated products; for the removal of these pollutants role of microorganism comes into play (Loidl et al., 1990). Biological treatment technique removes organic pollutants mainly by three ways i.e. aerobic, anaerobic and combined aerobic-anaerobic biological methods. Activated Sludge Process (ASP) is the most commonly used biological treatment process mainly to remove nitrogenous and phosphate based organic pollutants in the presence of oxygen environment (aerobic method). However, this technique suffers from the generation of unwanted sludge and other byproducts (Low et al., 2000). Membrane Bioreactor (MBR) also is a type of aerobic treatment which is used to remove organic pollutants and the membrane fouling is the main drawback of this technique (Iorhemen et al., 2016). Moreover, the treatment of organic pollutants through aerobic process mainly generates CO_2, H_2O, sludge and biomass. Anaerobic technique is used to degrade various Persistent Organic Pollutants (POPs) like organo-chlorine pesticides, dyes and phenolic derivatives by microbes in the absence of oxygen, this technique efficiently reduces the BOD and COD the end product obtained through this technique are methane (CH_4), CO_2, and sludge. However, it suffers from

blocking of filters due to high organic loads. Further, the treatment of organic pollutants through combined aerobic-anaerobic method has great potential; it requires low maintenance and most importantly least byproducts generated after completion of treatment (Peng et al., 2008).

There are some serious drawbacks of the conventional techniques as discussed previously that lead to the evolution of some advanced and efficient techniques by which complete removal of the pollutants (without generating harmful by-products) from the waste water can be obtained. In order to achieve this, advanced oxidation processes (AOPs) have been proved to become one of the promising technologies in present time.

1.4.3 Advanced Oxidation Processes (AOPs)

Advanced oxidation processes are highly efficient and are used for the removal of almost all type of organic pollutants, like pesticides, dyes, plasticizers, POPs, petrochemicals etc. from waste water, researchers focused on AOPs because this processes has ability to almost completely mineralize the organic pollutants present in surface and ground water. According to U. S. Environmental Protection Agency (USEPA); AOPs is the best available method to provide pollution control of industrial and contaminated sites. AOPs are typically a set of chemical treatment which ends with the complete oxidation of various organic pollutants by hydroxyl radical ($OH^{\bullet}$). Hydroxyl radical act as an intermediate for this process and it oxidizes almost all type of organic pollutants non-selectively, as it has strong oxidizing power ($E_{OH^-/OH^{\bullet}} = 2.40$ eV) (Li et al., 2021). Here, 2.4 eV is the oxidation potential of OH^-, it means that 2.4 eV or higher potential will be required to convert OH^- to $OH^{\bullet}$. During the photocatalytic reaction H_2O or OH^- will transfer its electron to the holes of the valence band (VB) of semiconductor to produce the $OH^{\bullet}$; this reaction will only be possible if the

energy of VB will be equal to or higher than 2.4 eV. $OH^{\bullet}$ is considered as 2nd most strong oxidizing agent after fluorine. Based on the phase of the pollutants and catalysts used, AOPs were classified into two major categories i.e. (1) Homogeneous processes, (2) Heterogeneous processes. Further sub-classification of AOPs was done depending upon the types of oxidizing agent (i.e. H_2O_2 or O_3) and source of irradiation used. AOPs can also be classified into photocatalysis, electrocatalysis, sonocatalysis, photo-Fenton process, sonolysis etc. depending on the ways of generation of hydroxyl radical ($OH^{\bullet}$), the generation of $OH^{\bullet}$ may be photochemical and non-photochemical. Figure 1.1 represents the general classification of AOPs.

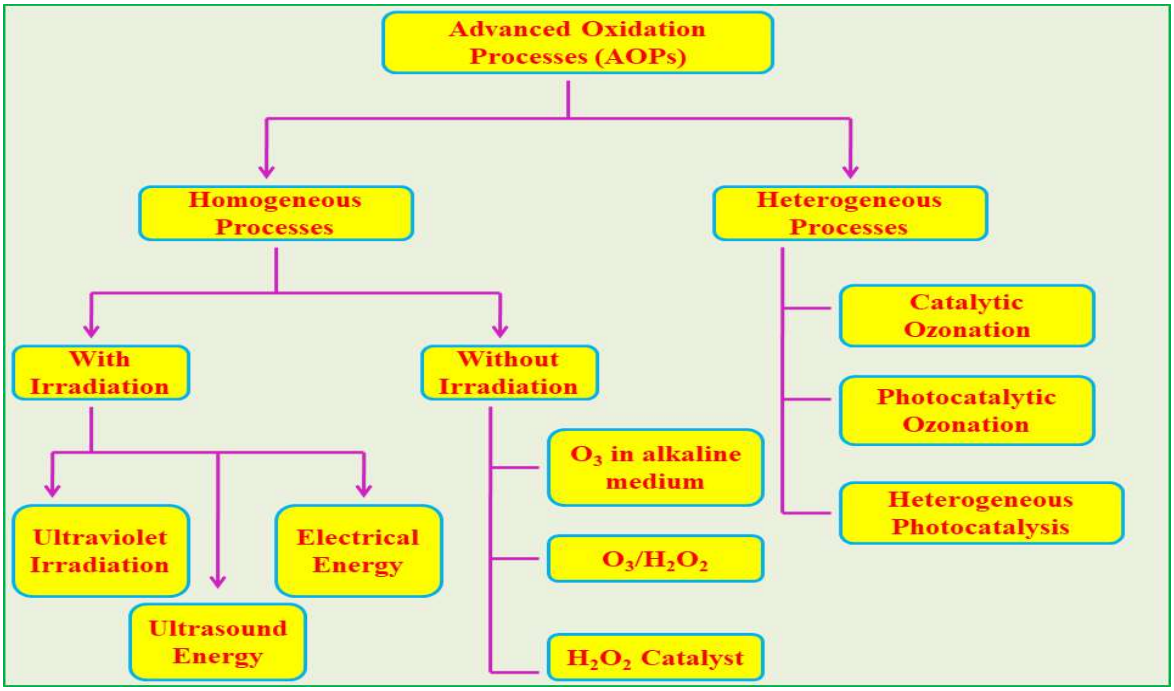


Fig. 1.1 Classification of AOPs

1.4.3.1 Homogeneous Processes

Homogeneous processes are a class of AOPs which are used to treat polluted waste water; it is a one phase system. This process uses an oxidant to generate hydroxyl radical which is responsible for the breakdown of organic contaminant. Some of the major oxidants used in

homogeneous process are Ozone (O_3), Hydrogen peroxide (H_2O_2), combination of Ozone and Hydrogen peroxide (O_3/H_2O_2) and Photo-Fenton system. Although the oxidizing power of these oxidants is relatively weak when they are used individually, but in the presence of some irradiating source of energy it gets increased due to the fast production of hydroxyl radicals ($OH^{\bullet}$).

Fenton process

Fenton reaction was first discovered by H. J. H. Fenton in 1894 when he observed a rapid formation of hydroxyl radical simply by a reaction in between Fe^{+2} and H_2O_2 under acidic condition (Equation 1.1). Equation 1.1 consists of simultaneous oxidation and reduction of Fe^{+2}/Fe^{+3} and $H_2O_2/^{\bullet}OH$ respectively (Benitez et al., 2007; Fenton, 1894), the next step involves the regeneration of the consumed Fe^{+2} ions, this process occurs slowly (Equation 1.2) because, the value of the rate constant is very low. So, the Fenton process requires regular addition of the Fe^{+2} salts to continue the reaction. The major drawback of this process is the accumulation of Fe^{+3} ions as sludge.

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + {}^{\bullet}OH + OH^{-}, \quad k = 40\text{-}80\ M^{-1}\ s^{-1} \qquad (1.1)$$

$$Fe^{+3} + H_2O_2 \rightarrow Fe^{+2} + {}^{\bullet}OOH + H^{+}, \quad k = 0.001\text{-}0.01\ M^{-1}\ s^{-1} \qquad (1.2)$$

Photo – Fenton process

The photo-Fenton process is just an advancement or enhancement of Fenton process (Giannakis et al., 2017; Hu et al., 2011), this process uses lights in the near UV or visible region to enhance the production of hydroxyl radical (Equation 1.3) and also to improve the rate of reduction of Fe^{+3} back into Fe^{+2} (Equation 1.4 and 1.5) (Chong et al., 2010; Kitsiou et al., 2009; Pignatello et al., 1999; Wu et al., 2014).

$$H_2O_2 + h\nu \rightarrow OH^{\bullet} + OH^{\bullet} \qquad (1.3)$$

$$Fe^{+3}(OH^{-}) + h\nu \rightarrow Fe^{+2} OH^{\bullet} \quad (1.4)$$

$$Fe^{+3} + H_2O + h\nu \rightarrow Fe^{+2} + OH^{\bullet} + H^{+} \quad (1.5)$$

Some other types of reactions involved in homogeneous processes under UV light irradiation are as follows:-

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \quad (1.6)$$

$$H_2O_2 + h\nu \rightarrow 2OH^{\bullet} \quad (1.7)$$

$$O_3 + H_2O_2 + h\nu \rightarrow OH^{\bullet} + {}^{\bullet}OOH + O_2 \quad (1.8)$$

Although these techniques is efficient in environmental treatment but they suffers from some serious drawbacks like facing technical difficulty in separation of catalysts and economically unfavorable process, moreover, some processes like Photo-Fenton works only at low pH range (2.8-3.5). So, in order to solve these problems, heterogeneous processes came into existence.

1.4.3.2 Heterogeneous Processes

Heterogeneous processes are also a class of AOPs used for the remediation of waste water; unlike homogeneous processes, it is a two phase system (i.e. reactants and substrates both are present in different phases). This process is further subdivided mainly into, (i) catalytic ozonation, (ii) photocatalytic ozonation, and (iii) heterogeneous photocatalysis; among these three processes we are going to focus only on the heterogeneous photocatalysis in the present thesis but before discussing about heterogeneous photocatalysis, we should familiarize ourselves with the term photocatalysis.

1.4.3.2.1 Photocatalysis

Photocatalysis composed of two parts, i.e. photo (light) and catalyst. So, photocatalysis can simply be defined as, “A process which enhances the rate of chemical conversion by a

substance without being consuming itself under the influence of suitable light source" and the substance which enhances the rate of chemical reaction in the presence of light is called as photocatalyst. Photocatalysis is a class of AOPs in which in-situ generation of reactive oxygen species (ROS) intermediate such as hydroxyl radical ($OH^{\bullet}$), anionic superoxide radical ($O_2^{\bullet-}$), peroxy radical ($ROO^{\bullet}$) and hydro-peroxy radicals ($HOO^{\bullet}$) takes place by using suitable source of energy. Photocatalytic process has the strong ability to oxidize almost all type of organic pollutants into CO_2, H_2O and inorganic ions which initially the part of organic pollutants or it converts them into some less harmful side products (Andreozzi et al., 1999; Bolton et al., 1996; Pignatello, 1992). Photocatalysis possesses several advantages over conventional waste water treatment techniques such as:-

(i) In photocatalytic process the formed end products are harmless in contrast to the conventional method.

(ii) Photocatalytic processes have great potential towards the complete mineralization of organic pollutants present in water.

(iii) This process can be operated in any medium; i.e. solid, liquid or gaseous.

(iv) It requires mild reaction condition for chemical transformation, and this process is easy to operate.

(v) In contrast to conventional methods photocatalytic processes produces almost minimal amount of secondary waste.

1.5 Heterogeneous Photocatalysis

Since long time heterogeneous photocatalysis is considered to be a sustainable technique to solve both the environmental and energy related problems. It is referred as heterogeneous photocatalysis because catalysts and reactants (organic wastes in our case) both are present in

different phases. This process usually requires a semiconductor photocatalyst which is able to absorb the light of suitable wavelength.

Heterogeneous photocalysis is an interesting topic of research for scientists. Initially it comes into attention when A. Fujishima and K. Honda reported their study on electrochemical photolysis of water by TiO_2 subjected to an electrical bias under UV-light illumination (Fujishima and Honda, 1972). So, the discovery of Fujishima & Honda is a landmark for the researchers. In recent years, the application of heterogeneous photocatalysis for environmental remediation and energy production is a very active area of research (Ahmad et al., 2016; Chen et al., 2008; Hoffmann et al., 1995). Heterogeneous photocatalysis includes a wide variety of reactions like, dehydrogenation, water detoxification, metal deposition, hydrogen transfer, removal of pollutants, mild or strong oxidation reactions. In heterogeneous photocatalysis semiconductor materials are mostly used as photocatalysts because of their unique property in between conductor and insulator. Semiconductor possess a marginal band gap of energy and continuum of energy levels where the highest occupied band energy is referred to as valence band (VB) while lowest unoccupied band of energy is known as conduction band (CB) (Fujishima et al., 2000). However, there is no separation between VB and CB of metals, and insulators have such a large band gap that it is not possible to excite the electrons from their VB to CB by using UV or visible light source of irradiation (figure 1.2).

The aim of using semiconductor meterials as a photocatalyst is meant for the efficient removal of organic pollutants from waste water. A good photocatalyst should be photoactive, chemically and biologically inert, nontoxic, inexpensive, capability to absorb near UV or visible light, photostable and recyclable or reusable.

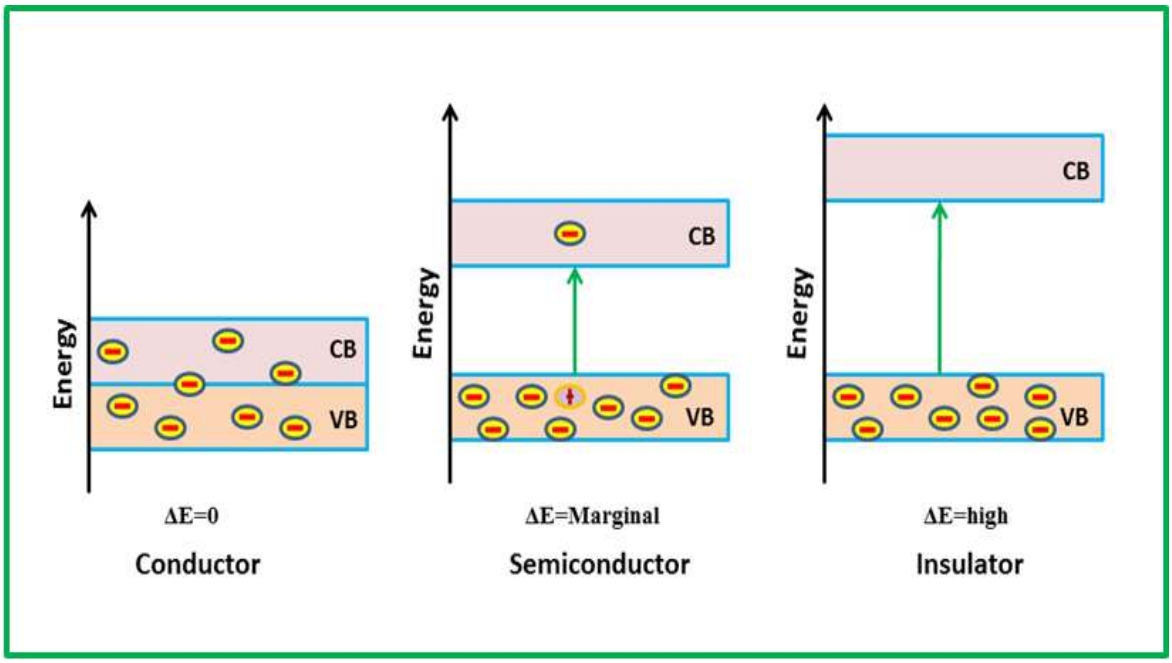


Fig. 1.2 Description of band gap in metal, semiconductor and insulator

Heterogeneous photocatalysis is highly efficient, cost effective and produces non-toxic side products; hence, it attracted the attention of researchers and ecologist globally.

1.5.1 Basic Principle and Mechanism of Heterogeneous Photocatalysis

As it is discussed in the above section that heterogeneous photocatalysis mainly involve semiconductor materials as photocatalyst, they have filled VB and empty CB energy levels which are separated by an energy gap known as band gap energy (Eg). This band gap of the semiconductor material is generally in the range of 0.3-3.8 eV. So, when semiconductor materials are irradiated by photons of light having energy equal to or exceed the band gap energy, excites electron (e^-) to jump from their VB to CB leaving holes (h^+) behind it. The combination of electrons and holes are commonly known as photogenerated excitons or photogenerated charge carriers, they further drive the photocatalytic reactions. There are mainly two possibilities of these photogenerated electron (e^-) and holes (h^+), either they may be recombine with each other to dissipate heat as energy or they travel to the surface of

semiconductor where they react with acceptor or donor species and may initiate the redox reactions (figure 1.3) to decompose the organic pollutants.

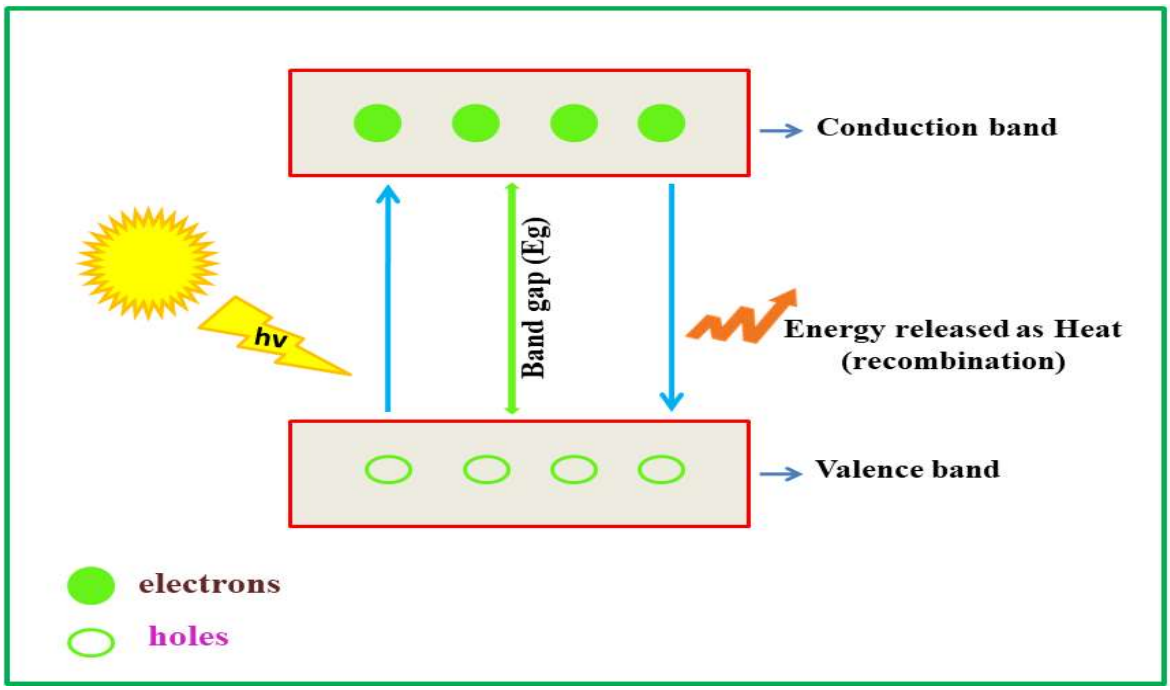
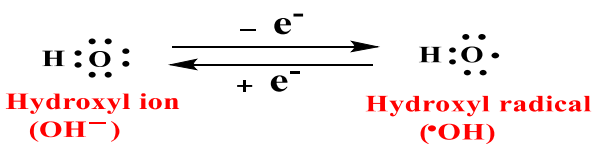


Fig. 1.3 General process of excitation and recombination of electrons

During the process of heterogeneous photocatalysis one or more reactive intermediate ($OH^{\bullet}$, $O_2^{\bullet-}$, $^{\bullet}OOH$, H_2O_2) species may generates which plays a very important role in the decomposition of organics (figure 1.4) (Bussi et al., 2002).

Note: Hydroxyl ion (OH^-) and hydroxyl radical ($OH^{\bullet}$) differs from each other just by one electron but they differ largely by their function, hydroxyl ion act as an antioxidant (suppress the oxidation or reduces the ability of a radical to oxidize the other particles) whereas hydroxyl radicals have a strong oxidizing power hence, it oxidizes a large variety of organic pollutant molecules, tissues, DNA etc.



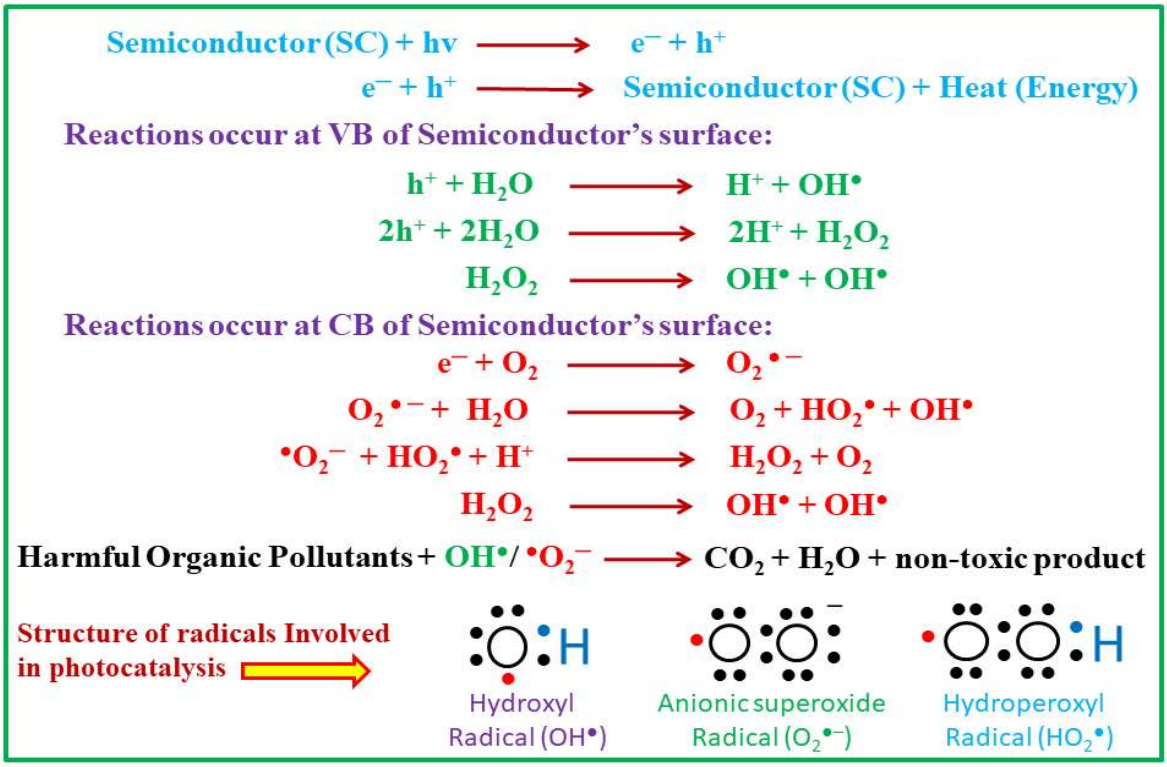


Fig. 1.4 Basic reactions involves in heterogeneous photocatalysis

In heterogeneous photocatalytic schemes the reactant molecules which are going to be reduced/oxidized do not need to directly interact with the photocatalysts.

The transfer of the charge between the targeted species and the semiconductor photocatalysts mainly depends on the redox potentials of that species and on the alignment of the band positions (position of VB and CB) of the semiconductor. The molecule which is going to oxidize during the photocatalysis should have lesser redox potentials than the VB position of the semiconductor. However, if the molecules are reduced then their redox potentials must be higher than the CB of the semiconductor photocatalyst. The significant difference between the respective band potentials of the semiconductors and redox potentials of the targeted species is known as overpotential and its value should be large enough for befitting reaction kinetics. The value of the overpotential may change by changing the photocatalysts.

As discussed above that photogenerated charge carriers (e^-/h^+) either recombine or they may

react with the acceptor or donor species. Both these process depend mainly on the relative kinetics of alternative processes. The process of recombination either may occur at bulk or on the surface of the semiconductors. Moreover, the energy dissipated during the recombination is either radiative or non-radiative. Overall, recombination is a very critical process in photocatalysis which determines the lifespan of the photogenerated excitons. If the photogenerated e^- and h^+ are separated for a long (i.e. slow recombination), then they get more time to react with the species adsorbed on the surface of the semiconductor.

So, ultimately our goal is to delay the rate of recombination of e^- and h^+ and increase their number which can easily reach to the surface of the semiconductors to create more possibility for the photocatalytic reactions with the targeted pollutants adsorbed on the surface of the photocatalyst. Restrained rate of charge recombination and increase in the number of charge carriers makes the photocatalysts more effective towards photocatalytic degradation process.

1.6 Basic strategies adopted for efficient charge separation

The efficiency of semiconductor photocatalysts depends mainly on their behavior of charge separation and transfer kinetics, which is very far from fulfilling the requirements of industrial application.

Speaking in general, the semiconductor based photocatalysis comprise of three crucial steps in favor of charge kinetics: (i) separation of charge under photoexcitation; (ii) transfer of charge to the surface of the semiconductor; (iii) direct participation of photogenerated excitons in redox reactions occurring at the surface of semiconductor. Among these three steps the first one i.e. separation of charge under photoexcitation is most critical and crucial step. Moreover, the more crystallinity of the materials also helps in improving the photocatalytic efficiency. The process of charge separation and transfer can be improved by

incorporating a co-catalyst with the individual photocatalyst, such as composites of two different semiconductors brings together to improve the charge separation, a combination of noble metal and semiconductor also helps to improve photocatalytic performance, the process of charge separation can also be enhanced by doping of metals into lattices of semiconductors.

1.6.1 Interface engineering at junctions

To avoid the charge recombination and facilitate the photocatalytic reactions occurring at the surface, addition of other photo-responsive semiconductor material as co-catalyst, to the surface is necessary. The perfect combination of composites of two or more component is essential to obtain a system with restrained recombination and high rate of charge transfer. Hence, proper engineering about band positions and interfaces/boundaries between different components of a composite is very important. In order to this heterojunction strategy has been applied and studied most in the recent.

Heterojunction generally refers to the formation of an interface between different semiconductors. Based on the alignment of band edges of the semiconductors, mainly three types of heterojunction can be form (figure 1.5); (i) straddling gap, (ii) staggered gap, and (iii) broken gap heterojunctions.

Figure 1.5a represents the heterojunction of two semiconductors having straddling band alignment, in such type of alignment, the VB and CB band positions of one semiconductor (SC-I) lies in between the bandgap of other semiconductor (SC-II). When composites with this type of arrangement is irradiated by suitable source of light the electrons gets excited to their CB leaving holes behind it (in VB), now exited electrons from the CB of SC-II transferred to the CB of SC-I and simultaneously holes will also migrate from VB of SC-II to

the VB of SC-I; so, electrons and holes are accumulated respectively in the CB and VB of only one semiconductor (i.e. SC-I). Therefore, in this case no efficient charge separation was observed but contrary to this there is increased rate of recombination was achieved.

Figure 1.5b shows the staggered type heterojunction. Here the CB of SC-II aligned at higher than the CB of SC-I and VB of SC-II also lies above the VB of SC-I. In such type of arrangement the photogenerated electrons will transfer from CB of SC-II to CB of SC-I whereas, holes will move from VB of SC-I to VB of SC-II. This type of band alignment is most common in heterojunction photocatalysis. Another one is broken gap heterojunction (figure 1.5c), which has highly mismatching band alignment. Hence, this type of combination is found rarely (Marschall, 2014).

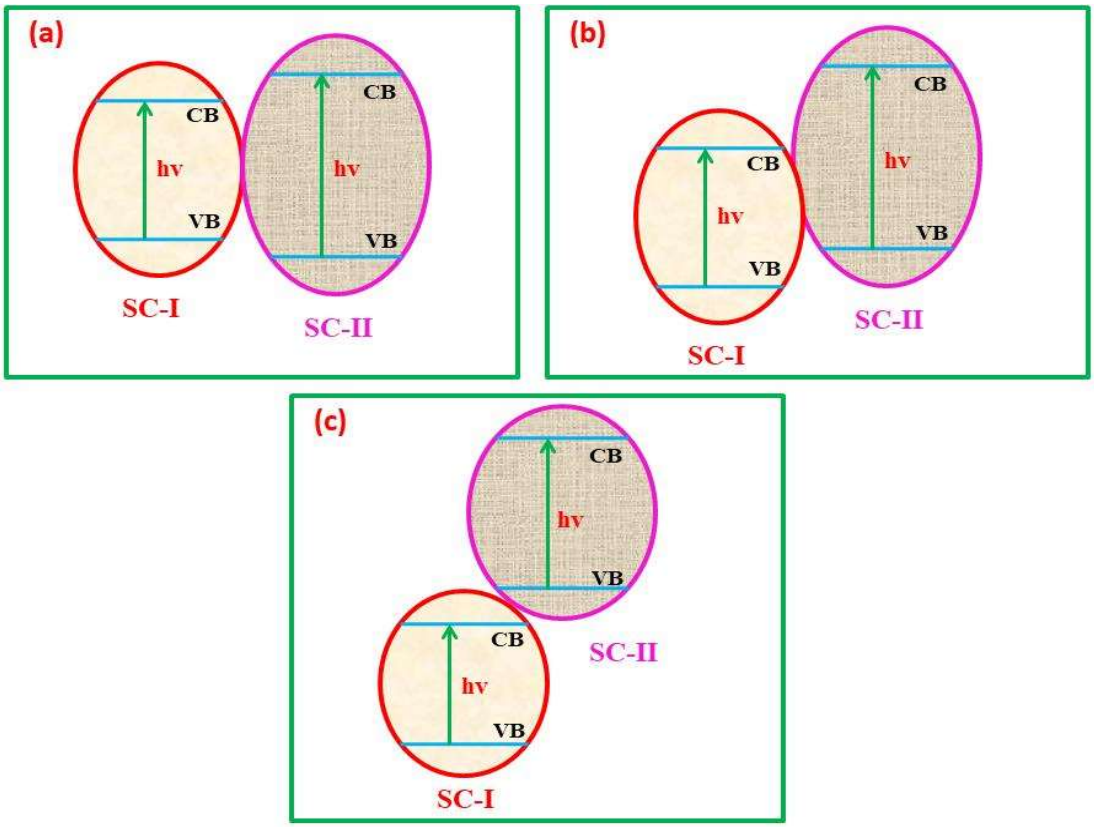


Fig. 1.5 Representing band alignment in heterojunctions (a) straddling type, (b) staggered type, and (c) broken type

Apart from heterojunction, homojunction is a term coined in photochemistry which refers to the interface between two similar types of semiconductors having equal band gaps but doped by a different element. For an example, interface between p-type (acceptor doped) and n-type (donor doped) silicon semiconductor is a homojunction, although this junction is also called as a p-n junction. Bending of band which is caused by different levels of doping generates the depletion region near the interface. The phase junction formed between different phases of polymorph semiconductor in photocatalysis is also a type of homojunction (Zhang et al., 2008).

The interface formed between p-type and n-type is referred as a p-n junction. In p-type semiconductors holes (h^+) are present in excess while, in n-type semiconductors electrons (e^-) are in excess. Figure 1.6 displays the schematics of p-n junction from which it can be illustrated that the Fermi energy level (E_F) of a p-type semiconductor is posited near to its VB, however in case of n-type it is near to the CB. So, when a junction (interface) is formed between p-type and n-type semiconductor then e^- moves from n-type to p-type semiconductor and hole travels toward n-type semiconductor due to diffusion. This movement continues until the establishment of equilibrium between e^- and h^+ and consequence to this there is creation of a depletion zone of free charge carriers at junction.

The composite which forms a p-n junction when irradiated by an appropriate source of light, generates e^- and h^+ in their CB and VB respectively. Now, e^- from more negative CB migrates to less negative CB while, h^+ moves from more positive to less positive. Overall, we can say that the photogenerated electrons get concentrated (accumulated) on less negative CB and holes are accumulated on less positive VB; by this way one can get efficient separation of charges (as e^- and h^+ are present on different semiconductor).

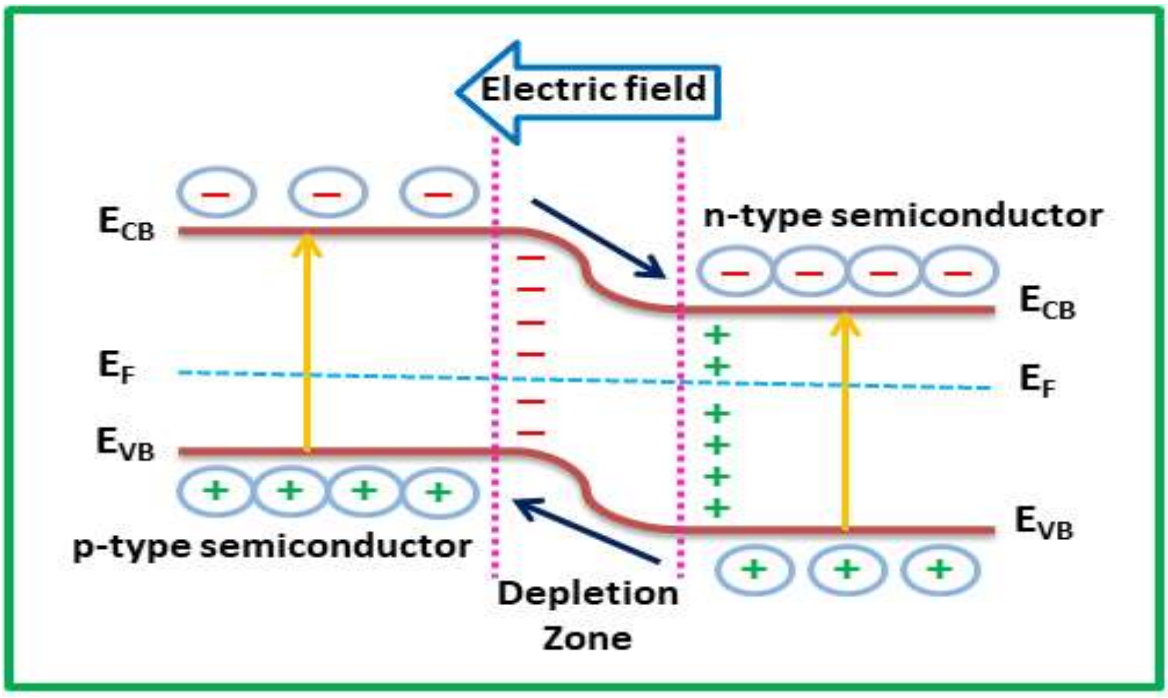


Fig. 1.6 Representation of a p-n junction

1.7 Chemical Methods used for the preparation of nanoparticles

Various techniques have been developed by the scientists to synthesize and fabricate the materials in nano-range (1-100 nm) size. Here we have discussed some chemical methods which have been used since past several decades.

1.7.1 Sol-gel method

Sol-gel method is a wet chemical method which is specially used to synthesize inorganic oxides and various oxides based composite materials at low temperature (less than 100 °C). By this technique; thin films, filaments, powders and colloidal dispersions can be easily produced (Gupta and Tripathi, 2012; Parashar et al., 2020). In this method inorganic precursor (usually metal nitrates) dissolved in water/alcohol, the hydrolyzed solution gets converted into gel by continuous heating and stirring process. The formed gel will be damp which is further dried by suitable method depending upon the desired application and properties of the gel, the as obtained dried powder is calcined in a furnace. It is a cost

effective method and low temperature favors the good control over the composition of the desired product (molecular homogeneity).

1.7.2 Hydrothermal Method

Hydrothermal method is the most commonly used method to synthesize the nanomaterial, this process requires high temperature (generally 120-200 °C) and pressure conditions, and for this the reactions are carried out in tightly sealed vessels (Teflon lined stainless steel autoclave) which withstand with the extreme conditions of temperature and pressures. Nanomaterials of different morphology (nanoparticles, nanotubes, nanowires, nanorods, porous nanospheres etc.) can be easily synthesized by this method. Hydrothermal method possess several advantages over other methods as by this method, minimum loss of material and high yield can be obtained, the nanomaterials which are not stable at high temperature can be prepared, materials with high porosity are also produced by this method (Gan et al., 2020). In hydrothermal methods the vessel should be partially filled by the mixed solution and reactions are mostly carried out at temperature higher than the boiling point (B.P.) of the solvents.

1.7.3 Electrochemical method

This is also an efficient method for the fabrication of nanomaterials with advantages of high purity, low cost and environmental friendliness. In this method the reactions are carried out in a solution of electrolyte by applying the voltage, the materials are deposited on the electrodes by varying various deposition parameters as number of coulomb passed, potential, deposition time, temperature etc. the morphology and size of the nanomaterials can be reduce by this method.

1.7.4 Co-precipitation method

This method generally uses inorganic salts as a precursor which dissolved in a suitable solvent (water or other solvent) to obtain a homogeneous clear solution of ions and when the optimum concentration of the species is achieved followed by the simultaneous nucleation and growth phases the dissolved salts start precipitating in the form of their hydroxides or oxalates. Furthermore, temperature, pH and concentration of the solution have great effect on the size and shape of the nanomaterial (Reddy, 2011). Once the precipitation is over then the precipitated solution gets filtered and washed repeatedly to remove unwanted impurities after that obtained sample is dried followed by calcination to get oxides from hydroxides.

1.8 Literature Review on Metal Oxides Based Semiconductors

Metal oxide based heterogeneous catalysis process is one of the promising advanced techniques for the removal of ambient concentration of organic and inorganic pollutants from aqueous systems. Generally, metal oxide (MO) of transition metals is one of the intensely used semiconductor materials to design various kind of photocatalyst, either by combining novel metal or by other semiconducting materials. In this regards a lot of metal oxides like NiO, ZnO, CuO, Cu_2O, TiO_2, WO_3, which are abundant in nature, have been extensively used as photocatalysts because of their biocompatibility, exceptional stability in a variety of conditions and capability to generate charge carriers when irradiated with required amount of light energy. As these metal oxides are eco-friendly and are free from toxic and hazardous materials they have proved their efficiency in degrading a wide range of distinct pollutants into biodegradable compounds and eventually mineralizing them to harmless end products (Altın and Sökmen, 2014; Malwal and Gopinath, 2015; Saravanan et al., 2013; Zhang et al., 2017). However, all these photocatalyst individually suffer from some serious limitations like

(i) fast recombination rate of photogenerated e^- and h^+ (ii) poor absorption of light (iii) poor charge transport to the surface of the photocatalyst (iv) low surface area. So, further modifications were required to improve their photocatalytic property.

1.8.1 NiO based semiconductor photocatalysts

Nickel oxide is a p-type semiconductor having a large band gap in the range of 3.3-3.6 eV. NiO is antiferromagnetic in nature and its crystal structure is similar to NaCl-type (cubic close packing); because of the interesting electronic configuration, unique optical property and great magnetic behavior of NiO, it has been under extensive investigation by researchers (Dong et al., 2014; Park and Kim, 2003). The scope of NiO nanoparticle is very wide and it is used in storage batteries, magnetic materials, sensing, catalysis etc. (Alagiri et al., 2012; Ramesan and Santhi, 2017; Wu et al., 2007; Xin et al., 2007).

According to El-Kemary et al. NiO exhibits good photocatalytic property because it has high absorptive affinity, strong photosensitivity, and durability (El-Kemary et al., 2013). Hameed et al. synthesized NiO/Bi_2O_3 nanocomposite and they chose methyl orange (MO) as a model pollutant to evaluate the photocatalytic activity of the nanocomposite, they found that the activity of the nanocomposite was significantly higher than its components in pure form which is due to inhibition of recombination of photogenerated charges in NiO/Bi_2O_3 composite (Hameed et al., 2009a). Further, Hameed et al. have also used NiO/ZnO nanocomposite for the removal of MO and methylene blue (MB) dyes, they proved that the formation of nanocomposite improves the photocatalytic performance of less active component (Hameed et al., 2009b). Faisal et al. made a combination of NiO/TiO_2 nanocomposite and got enhanced photocatalytic activity for the degradation of methylene blue (MB) (Faisal et al., 2018). Rosaline et al. have examined the photocatalytic activity of

NiO/WO_3 nanocomposite by the photocatalytic removal of eosin yellow (Rani Rosaline et al., 2020). Fu et al. have synthesized amorphous $NiO/g\text{-}C_3N_4$ and applied as a photocatalyst for the overall splitting of water, they found that NiO works as an efficient cocatalyst and it greately promote the charge separation of photogenerated e^- and h^+ and provides more active sites when combines with $g\text{-}C_3N_4$ and thus facilitate the water splitting (Fu et al., 2018).

The photocatalytic property of NiO can also be modified by forming its nanocomposites with noble metals. For this purpose, Fragua et al. have explored Au/NiOx nanocomposites, in their study they found that the nancomposite exhibited enhanced photocatalytic activity than pure NiOx (Fragua et al., 2020). The formation of heterojunction between Ag and NiO facilitates the photocatalytic evolution of H_2 (Bagtache et al., 2019). Copper doped NiO was used by Zaheer et al. for the enhanced photocatalytic degradation of Erichrome Black-T and MB dye (Ahmad et al., 2019).

1.8.2 ZnO based semiconductor photocatalysts

ZnO is the 2nd most efficient metal oxide as a photocatalyst after TiO_2. ZnO based photocatalysts are used to degrade a wide variety of organic pollutants such as synthetic dyes, petrochemical wastes etc. (phenolic derivatives, benzene, toluene, xylene, naphthalene, and hexane) (Barreca et al., 2007; Ferrari-Lima et al., 2015; Gondal and Sayeed, 2007). However, several factors regulate the efficiency of a photocatalyst, such as band gap of the material, charge separation, migration of charge to the surface of the catalyst and dispersibility. ZnO based hybrid materials have a great sensitivity towards light and a wide bandgap of ZnO (3.37 eV) makes it possible to absorb solar spectrum in a wider range than other semiconductor photocatalysts (Pardeshi and Patil, 2009). Moreover, the large bandgap of ZnO also helps to provide suitable band positions for oxidation and reduction reactions

occurring at the surface (Saucedo-Lucero and Arriaga, 2013). To improve the charge separation and so photocatalytic activity of ZnO, it was modified by introducing noble metals or by some other metal oxides/sulfides. Yu et al. have synthesized ZnO microcuboid and deposited different noble metals; they found that modified ZnO has enhanced photocatalytic performance mainly due to increased charge separation (Yu et al., 2013), Dermenci et al. have prepared Ag/ZnO nanocomposite, they evaluated the activity of the nanocomposite by the photocatalytic degradation of methylene blue (MB) and found that Ag/ZnO was more efficient than pure ZnO which is mainly due to restrained recombination of photogenerated charges (e^-/h^+) (Dermenci et al., 2014). Similarly, the photocatalytic activity of various other combinations of ZnO with metal oxides and metal sulfides such as Fe_2O_3/ZnO, CuO/ZnO, ZnO/SiO_2, ZnO/g-C3N4, rGO-ZnO, MoS_2/ZnO, CdS/ZnO etc. have also been investigated (Hassanpour et al., 2017; Henni et al., 2019; Jo and Clament Sagaya Selvam, 2015; Rohilla et al., 2021; Tian et al., 2016; Xie et al., 2015; H. Zhao et al., 2015); in all these combinations the photocatalytic activity of modified ZnO gets increased; from these findings we got motivated and developed almost a new combination of ZnO nanoparticles with NiS because before to our study there is only one report on NiS/ZnO by Perfecto et al. for sensing of butanone (Perfecto et al., 2021). Other different combinations of NiS have been widely studied; like, Zhang et al. have used NiS as a co-catalyst which improves the photocatalytic hydrogen production rate of TiO_2 (Zhang et al., 2012). He et al. reported that NiS forms a p-n junction with CdS pyramid which greatly enhance the photocatalytic hydrogen production rate of CdS (He and Guo, 2017). Majhi et al. employed NiS/Bi_2O_3 nanocomposite for the photocatalytic degradation of tramadol and they observed that nanocomposite exhibits excellent photocatalytic performance; the reasons for this enhanced performance are the

strong absorption of light and improved charge separation (Majhi et al., 2019).

1.9 Objectives of the present work

The objective of the work presented ahead in this thesis is mainly aimed to explore the photocatalytic behavior of NiO and ZnO based nanocomposite photocatalyst over different organic pollutants such as malachite green (MG), rhodamine B (RhB) and p-nitrophenol (PNP). As from literature survey it is clear that photocatalytic properties of the semiconductor can be improved by various ways. So, in present investigation we also focused on improving photocatalytic property by modifying the electronic structure of semiconductors. This thesis deals with the synthesis of g-C_3N_4/NiO, Ag/NiO and NiS/ZnO nanocomposite photocatalysts. The synthesized photocatalysts are analyzed by High Resolution X-ray diffraction (HR-XRD), UV-Visible diffuse reflectance spectroscopy (UV-Vis DRS), Fourier transform reflectance spectroscopy (FT-IR), High Resolution Transmission Electron Microscope (HR-TEM), Field-Emission Scanning Electron microscope (FE-SEM), X-ray Photoelectron Spectroscopy, fluorescence measurement and Brunauer-Emmett-Teller (BET) measurement.

Furthermore, the photocatalytic performance of synthesized catalysts was evaluated by degradation of MG, RhB and PNP pollutants under irradiation of UV light source in aerobic condition. The objective of works of this thesis is summarized in point wise as follows:-

(1) Synthesis and photocatalytic behavior of g-C_3N_4, NiO and g-C_3N_4/NiO nanoparticles.

(2) Synthesis and photocatalytic behavior of Ag, NiO and Ag/NiO nanoparticles.

(3) Synthesis and photocatalytic behavior of NiS, ZnO and NiS/ZnO nanoparticles.

1.10 Targeted organic pollutants

In the present thesis we have reported about the photocatalytic removal of some targeted

organic pollutants such as malachite green, rhodamine B and p-nitrophenol by different photocatalysts. These all are highly persistent and potentially toxic or carcinogenic in nature. A brief introduction about the pollutants used is discussed in the below sections..

1.10.1 Malachite green (MG)

Malachite green is an N-methylated diaminotriphenylmethane dye. It is widely used in textile, aquaculture, food processing and other industries for different purposes such as a coloring agent, antiparasitical, antifungal and antibacterial agent and as a food additive. MG is environmentally persistent and it is found that MG and leucomalachite green (reduced form of MG) can be carcinogenic, mutagenic and teratogenic. It can also be cytotoxic to mammalian cells and damage the nervous system, brain and liver when ingested. Because of, these serious health issues related to the extensive usage of MG, its complete removal from the environment is extremely important (Raval et al., 2017). Structure and the characteristic UV-Visible absorbance spectra of MG (617 nm) is shown in figure 1.7. The observed characteristic peak of MG is due to n-π* transitions (Mohammad et al., 2019); molar absorptivity (Ɛ) of MG was 37318 $mole^{-1}$ liter cm^{-1}.

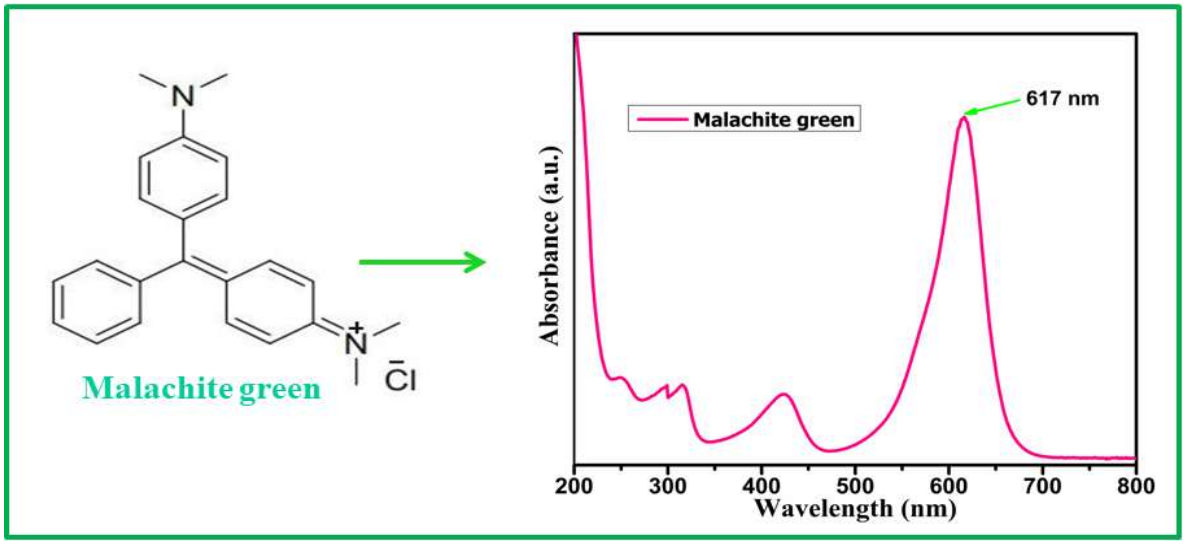


Fig. 1.7 Showing structure and UV-Visible absorbance spectra of MG

1.10.2 Rhodamine B dye

Rhodamine B is a dye of Xanthenes family, which is used to give color to cotton, silk, wool, papers, fibers, nylon, leather, wood stains and distempers on china clay. It is also used in cosmetic and pharmaceutical industries. However, RhB is frequently used as a tracer to determine the rate and direction of flow of liquid.

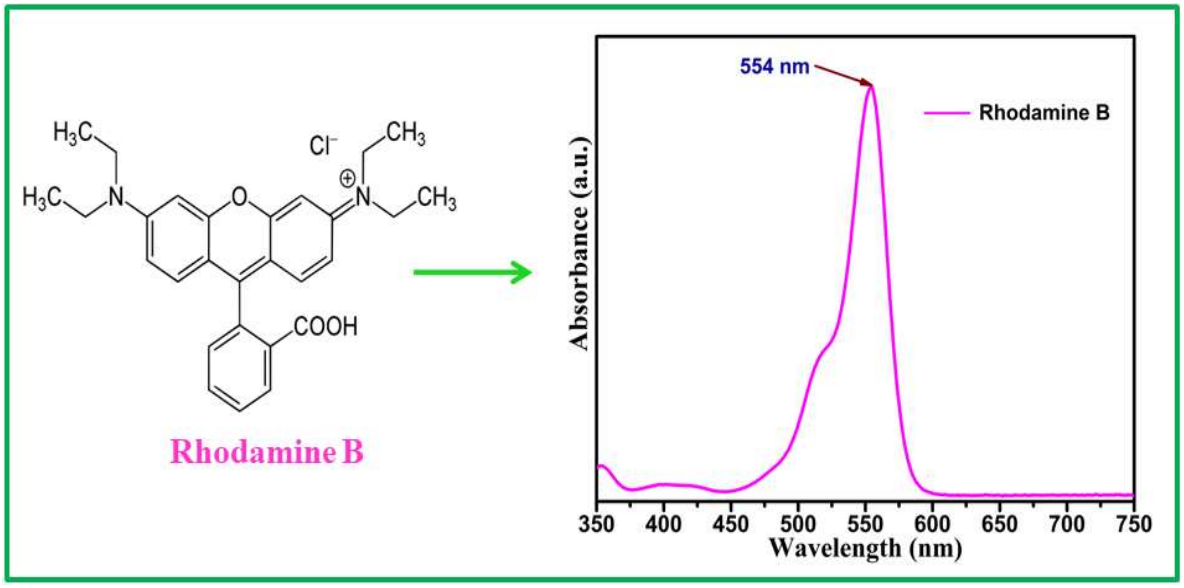


Fig. 1.8 Represents the structure and corresponding absorbance spectra of RhB

Discharge of RhB as an effluent from various industries in to water stream; seriously contaminate them (water stream), as RhB is potentially toxic and carcinogenic in nature; hence, removal of this dye from the environment and water stream is necessary. The characteristic absorption peak of RhB in UV-Vis spectrophotometer was recorded at 554 nm (figure 1.8); which is due to n-π* transitions (Prabakaran et al., 2022) and the calculated molar absorptivity (Ɛ) was 51255 $mole^{-1}$ liter cm^{-1}.

1.10.3 p-nitrophenol

p-nitrophenol is a conjugate acid of p-nitrophenolate. It is regarded as a persistent organic pollutant in the environment due to its stability, anthropogenic activity, and bioaccumulation

ability, which can severely contaminate the groundwater, soil, and air. It has been found that p-nitrophenol and other phenolic derivatives are highly toxic for the entire biota and they are categorized as high priority pollutants by the United State Environmental Protection Agency (U.S.E.P.A.) (Das and Dey, 2020).

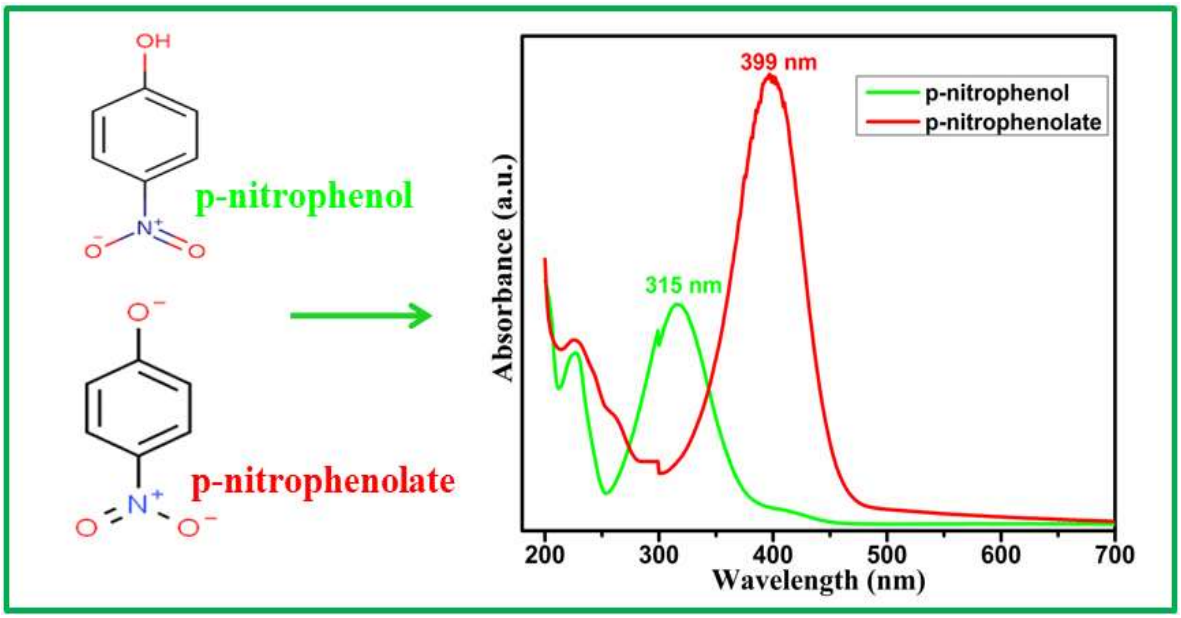


Fig. 1.9 Represents the structure and absorbance spectra of p-nitrophenol and p-nitrophenolate

The characteristic peak of p-nitrophenol comes at around 315 nm in UV-Visible absorbance spectra while in case of p-nitrophenolate this peak will shift towards higher wavelength and will appear at around 399 nm. Figure 1.9 presents the structure of p-nitrophenol and p-nitrophenolate and their corresponding absorbance spectra.