ABSTRACT

Comprising over 70% of the Earth's surface, water is undoubtedly the most precious natural resource that exists on our planet. Without the seemingly invaluable compound comprised of hydrogen and oxygen, life on Earth would be non-existent: it is essential for everything on our planet to grow and prosper. Although we as humans recognize this fact, we disregard it by polluting our rivers, lakes, and oceans. Subsequently, we are slowly but surely harming our planet to the point where organisms are dying at a very alarming rate. In addition to innocent organisms dying off, our drinking water has become greatly affected, as is our ability to use water for recreational purposes.

Currently, the pollution of rivers and streams with chemical contaminants has become one of the most crucial environmental problems. Water borne chemical pollution entering rivers and streams cause tremendous amounts of destruction. Eutrophication of surface waters from human and agricultural wastes and nitrification of groundwater from agricultural practices has greatly affected large parts of the world. Acidification of surface waters by air pollution is a recent phenomenon and threatens aquatic life in many area of the world. Of the two types of water pollution, point source and nonpoint source, pollution arising from nonpoint sources accounts for a majority of the contaminants in streams and lakes and are much more difficult to control. An example of this type of water pollution (nonpoint source) is when fertilizer from a field is carried into a stream by rain, in the form of run-off, which in turn effects aquatic life. Besides this, with over 70 percent of the planet covered by oceans, people have long acted as if these very bodies of water
could serve as a limitless dumping ground for wastes. Raw sewage, garbage, and oil spills have begun to overwhelm the diluting capabilities of the oceans, and most coastal waters are now polluted. Beaches around the world are closed regularly, often because of high amounts of bacteria from sewage disposal, and marine wildlife is beginning to suffer.

More importantly, ninety-five percent of all fresh water on earth is ground water. Ground water is found in natural rock formations. These formations, called aquifers, are a vital natural resource with many uses. Estimates suggest that nearly 1.5 billion people lack safe drinking water and that at least 5 million deaths per year can be attributed to waterborne diseases.

Clearly, the problems associated with water pollution have the capabilities to disrupt life on our planet to a great extent thus acknowledging the fact that water pollution is, indeed, a serious issue. In developed countries, these general types of pollution have occurred sequentially with the result that most developed countries have successfully dealt with major surface water pollution. In contrast, however, newly industrialized countries such as China, India, Thailand, Brazil, and Mexico are now facing all these issues simultaneously.

In order to combat water pollution, a number of scientific groups are working all over the world to develop an efficient physicochemical method for wastewater treatment. Physical methods, such as adsorption, biological methods (biodegradation) and chemical methods (chlorination, ozonation) are the most frequently used for the treatment of wastewater. Among many processes proposed and/or being developed for the destruction of the organic contaminants,
biodegradation has received the greatest attention. However, many organic chemicals, especially those that are highly toxic or refractory, are not amendable to microbial degradation.

Recently, there has been considerable interest in the utilization of heterogeneous photocatalysis involving TiO₂ for the destruction of organic compounds in contaminated water. The mechanism constituting heterogeneous photocatalytic oxidation processes has been discussed extensively in the literature. Briefly, when a semiconductor such as TiO₂ absorbs a photon of energy equal to or greater than its band gap width, an electron may be promoted from the valence band to the conduction band (e⁺cb) leaving behind an electron vacancy or “hole” in the valence band (h⁻vb). If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with absorbed species. Specially, h⁺vb may react with surface-bound H₂O or OH⁻ to produce hydroxyl radical (OH⁺) and e⁻cb is picked up by oxygen to generate superoxide radical anion (O₂⁻·). These reactive species are primarily responsible for the photodegradation of organic pollutants.

The present work entitled “Semiconductor mediated photocatalysed degradation of few selected organic pollutants” deals with photocatalytic degradation of few selected organic pollutants in aqueous suspensions of titanium dioxide under a variety of conditions with an aim to determine the optimal degradation conditions. An attempt has also been made to identify the intermediate products formed during the photooxidation process through GC/MS analysis
technique in order to have a better understanding of the mechanism involved in these processes. This thesis is divided into four chapters.

The Chapter 1 deals with photocatalysed degradation of four selected herbicide derivatives, such as picloram (1), dicamba (2), floumeturon (3) and diphenamid (4) in aqueous suspensions of titanium dioxide (TiO$_2$) under a variety of conditions. The degradation was studied by monitoring the change in substrate concentration employing UV spectroscopic analysis technique and depletion in Total Organic Carbon (TOC) content as a function of irradiation time. The degradation was studied using various parameters, such as types of TiO$_2$ powders, solution pH, substrate concentration, catalyst concentration and in the presence of different electron acceptors. The degradation of herbicide derivative 4 was also investigated under sunlight and efficiency of degradation was compared with that of artificial light source. The degradation for the decomposition (decrease in absorption intensity vs. irradiation time) and mineralization (depletion in TOC vs. irradiation time) of all the herbicide derivatives under investigation has been found to follow first order kinetics (i.e. linear regression of plot of natural logarithm of absorption intensity and TOC content vs. irradiation time).

The degradation rate for the decomposition and mineralization were calculated in terms of mole L$^{-1}$ min$^{-1}$ using the following equations,

$$-\frac{d[TOC]}{dt} = k \ c^n$$

$$-\frac{d[A]}{dt} = k \ c^n$$

TOC = Total Organic Carbon, A = absorbance, k = rate constant, c = concentration of the pollutant, n = order of reaction
The degradation rate for the decomposition and mineralization of compounds were found to be influenced by all the parameters studied. The photocatalyst, TiO$_2$ Hombikat UV100 was found to be slightly better for the degradation of 1, whereas, TiO$_2$ Degussa P25 was found to be more efficient for the degradation of 2-4 as compared with other TiO$_2$ samples. The degradation rates were found to be higher in acidic pH range. The different electron acceptors employed have been found to accelerate the reaction rate. The mechanistic detail and discussion regarding the effect of various parameters on the photocatalytic degradation of different compounds under investigation has been discussed in detail.

The GC/MS analysis of the irradiated sample of picloram (1) in the presence of Hombikat UV100 (1 gL$^{-1}$) showed the formation of three intermediate products such as 4-amino-dichloro-hydroxypicolinic acid (8), 2,3,5-trichloro-pyridin-4-ylamine (9) and 3,5,6-trichloro-pyridine-2-carboxylic acid (10). The GC/MS analysis of the irradiated sample of dicamba (2) in the presence of Degussa P25 (1 gL$^{-1}$) showed the formation of six products such as 3,6-dichloro-2-methoxyphenol (12), hydroxy added product (13), 3,6-dichlorosalicylic acid (14), chloro-hydroxy derivative (15), dihydroxy added product (16) and dichlorodihydroxy benzoic acid derivative (18). The GC/MS analysis of the irradiated sample of floumeturon (3) in the presence of Degussa P25 (1 gL$^{-1}$) showed the formation of several intermediate products. The probable degradation pathways for the photocatalytic reaction of floumeturon (3) have been proposed. The GC/MS analysis of the irradiated sample of diphenamid (4) in the presence of Degussa P25 (1 gL$^{-1}$) showed the formation of five products such as $\alpha$-phenylbenzeneacetic acid (26), 2,2-diphenyl-2-hydroxyacetic acid (28),
benzoyl formic acid (30), nordiphenamid (32) and N,N-dimethyl-α-hydroxyphenylbenzene acetamide (34). A probable pathway for the formation of different products from 1-4 involving electron transfer reactions and reaction with hydroxyl radicals and superoxide radical anions formed in the photocatalytic system have been proposed in Schemes 1.1-1.5. The above-mentioned products were characterized either on the basis of molecular ion peak and mass spectrometric fragmentation pattern or by comparing them with GC/MS library.

The Chapter 2 of the thesis deals with the photocatalysed degradation of three selected organophosphorus insecticide derivatives, namely phosphamidon (1), dichlorvos (2) and acephate (3) in the presence of titanium dioxide. The degradation of 1 and 2 was studied by monitoring the change in substrate concentration employing UV spectroscopic analysis technique whereas the degradation of 3 was studied by measuring the depletion in Total Organic Carbon (TOC) content as a function of irradiation time using different parameters. The photocatalyst, Degussa P25 showed highest photocatalytic activity as compared with other TiO₂ powders for all the insecticides under investigation. The model compound 2 and 3 was found to degrade faster at lower pH, whereas degradation of 1 was more or less same in the pH range studied.

The GC/MS analysis of the irradiated sample of dichlorvos (2) in the presence of Degussa P25 (1 gL⁻¹) showed the formation of several intermediate products. The probable degradation pathways for the photocatalytic reaction of dichlorvos (2) have been proposed in Scheme 2.1. The GC/MS analysis of the irradiated mixture of acephate (3) in the presence of Degussa P25 (1 gL⁻¹) showed the formation of three
photoproducts such as (1-Hydroxy-ethyl)-thiophosphoramidic acid, O,S-dimethyl ester (15), (1-Hydroxy-ethyl)-phosphoramidic acid, monomethyl ester (17) and (1-Hydroxy-ethyl)-thiophosphoramidic acid, S-methyl ester (18). These products were identified based on their molecular ion and mass spectrometric fragmentation pattern with those reported in the GC/MS library and probable pathway for their formation is shown in Scheme 2.2.

The Chapter 3 of the thesis deals with the photocatalysed degradation of three selected organic systems such as dimethyl terephthalate (1), 2,4-dichlorobenzoic acid (2) and 3,5-dinitrobenzoic acid (3) in aqueous suspensions of titanium dioxide. The degradation of all the compounds was investigated by monitoring the depletion in Total Organic Carbon (TOC) content as a function of irradiation time. The degradation kinetics have been studied under different conditions such pH, catalyst concentration, substrate concentration, different types of TiO₂ and in the presence of electron acceptor such as hydrogen peroxide besides molecular oxygen. The degradation rates were found to be strongly influenced by the above parameters. Different degradation behaviors of the compounds have been observed on the variation of solution pH. The two intermediate products such as dihydroxy added product (11) and 2-(acetyloxy)-1,4-benzenedicarboxylic acid, dimethyl ester (19) were identified through GC/MS analysis technique by comparing the molecular ion and mass spectrometric fragmentation pattern with those reported in the library in the photocatalytic reaction of dimethyl terephthalate (1). The GC/MS analysis of irradiated mixture of 2,4-dichlorobenzoic acid (2) gave mono-chlorobenzoic acid (21) and monochloro-monohydroxy benzoic acid derivative (24) as the identified
degradation products. The compound (21) has been identified by comparing the molecular ion peak and mass spectrometric fragmentation pattern with those reported in the library whereas compound (24) has been characterized on the basis of molecular ion peak and mass spectrometric fragmentation pattern. The GC/MS analysis of irradiated mixture of 3,5-dinitrobenzoic acid (3) led to the formation of dihydroxy added product (27) and 3,5-dinitrophenol (30). Both the product has been characterized based on their molecular ion and mass spectrometric fragmentation pattern.

The chapter 4 includes the photocatalysed degradation of three selected dye derivatives, acid red 17 (1), acid orange 10 (2) and acid yellow 36 (3) in aqueous suspensions of titanium dioxide under a variety of conditions. The degradation was studied by monitoring the change in substrate concentration employing UV spectroscopic analysis technique as a function of irradiation time. The degradation rate for the decomposition of compounds 1-3 was studied using various parameters in order to determine the optimal degradation condition. The photocatalyst, Hombikat UV100 was found to be better for the degradation of 1, whereas the degradation of 2 and 3 was more efficient in the presence of Degussa P25 as compared with other TiO₂ samples.

Reasonable mechanisms have been suggested to account for the formation of various products in the reaction of different compounds listed under Chapters 1-3. Note: The numbers of various compounds given in the parentheses corresponds to those under the respective chapters.