PREFACE

This thesis deals with the photocatalytic degradation of few selected organic pollutants in aqueous system of titanium dioxide under a variety of conditions with an aim to determine the optimal degradation condition and also to identify the intermediate products formed during the photooxidation process through GC/MS analysis technique.

The thesis entitled "Photocatalysed degradation of few selected organic systems in aqueous suspension of semiconductor" is divided into four chapters.

The Chapter 1 of the thesis deals with the photocatalysed degradation of three selected pesticide derivatives such as isoproturon (1), chlorotoluron (2) and chlorbromuron (3) in aqueous suspensions of titanium dioxide in the presence of light and oxygen. The degradation was studied under a variety of conditions such as type of photocatalyst, pH, substrate and catalyst concentration and in the presence of different electron acceptors in addition of molecular oxygen. The irradiation experiments were carried out using the "Pyrex" filtered out put of a 125 W medium pressure mercury lamp in an immersion well photochemical reaction vessel. The degradation was studied by monitoring the change in substrate concentration employing UV spectroscopic analysis technique and decrease in Total Organic Carbon (TOC) content as a function of
irradiation time. The degradation of the pesticide derivative 1 was also investigated under sunlight and efficiency of degradation was compared with that of the artificial light source.

The degradation rates for the decomposition (change in absorption intensity Vs irradiation time) and mineralization (depletion in TOC Vs irradiation time) of the pollutants was determined from the linear regression of plot of the natural logarithm of TOC and the model pollutant concentration as a function of irradiation time. i.e. first order kinetics. The rate was calculated in terms of mole L⁻¹ min⁻¹ employing the following equations;

\[ \frac{-d[TOC]}{dt} = kc^o \]
\[ \frac{-d[A]}{dt} = kc^n \]

TOC = Total Organic Carbon, A = absorbance, k = rate constant, c = concentration of pollutant, n = order of reaction.

The degradation rates were found to be strongly influenced by all the parameters studied.

An attempt was made to identify the intermediate products formed during the photooxidation process of the pesticide derivative under investigations through GC/MS analysis technique. The products were characterized based on their molecular ion and mass spectrometric
fragmentation pattern. Irradiation of an aqueous solution (250 mL) of isoproturon (1, 0.3 mM) in the presence of TiO₂ (1.5 g L⁻¹) for 2 h, followed by GC/MS analysis of the methylene chloride extract gave 4-isopropylphenylurea (10), 4-isopropylaniline (11) and 1,1-dimethyl-3-phenylurea (9) as the identified degradation product along with some unchanged starting material. The irradiation of an aqueous solution of chlorotoluron (2, 0.35 mM, 250 ml) under analogous conditions gave 3-(3-hydroxy-4-methylphenyl)-1,1-dimethyl-urea (17), (3-chloro-4-methyl-phenyl) urea (18) and 3-chloro-4-methyl-phenylamine (19) along with some unchanged starting material.

The Chapter 2 of the thesis deals with the photocatalysed degradation of four selected pesticide derivatives such as, thiram (1), carbaryl (2), zineb (3) and sodium diethyldithiocarbamate (4) in aqueous suspensions of titanium dioxide using different parameters. The decomposition and mineralization of the pesticides were monitored by measuring the change in substrate concentration and depletion in TOC content as a function of irradiation time. The degradation rate for the decomposition and mineralization of the pollutant was found to be strongly influenced by all the parameters studied such as type of photocatalyst, pH, catalyst and substrate concentration and in the presence of electron acceptors.
The photocatalyst, Degussa P25 was found to be more efficient for the degradation of the pollutant as compared with other commercially available TiO$_2$ samples from Milenium inorganic, Travancore Titanium Product and Hombikat UV100.

The GC/MS analysis of an irradiated mixture of pesticide derivative 1 in aqueous suspension of titanium dioxide showed the formation of several intermediate products of which three products such as 7, 8 and 11 were identified based on their molecular ion and mass fragmentation pattern. Irradiation of aqueous suspension of pesticide derivatives 2 and 3 under analogous condition and workup of the reaction in usual manner gave a residual mass. The GC/MS analysis of the irradiated residue showed the formation of several intermediate products. A probable pathways for the decomposition of compounds 2 and 3 have been proposed. The GC/MS analysis of the irradiated mixture of the pesticide derivative 4 showed diethylamino-dimercapto-methanol (28) and amino-dimercapto methanol (32) as the intermediate products. A probable pathways for the formation of different products involving electron transfer reaction and reaction with hydroxyl radical and superoxide radical anions have been proposed in Schemes 2.1 - 2.5.

The Chapter 3 of the thesis deals with the photocatalysed degradation of two selected surfactant, N,N-bis(2-hydroxyethyl)dodecanoyl
amide (1), cetyl trimethyl ammonium bromide (2) and a textile dye derivative, bromothymol blue (3) in aqueous suspensions of titanium dioxide under varying conditions. As usual the decomposition and mineralization was studied UV spectroscopically and using TOC analyzer. The photocatalyst, Degussa P25 was found to be more efficient for the degradation of these pollutants. The degradation product formed during the photooxidation process of the surfactant 1, in the presence of Degussa P25 was analyzed through GC/MS analysis technique. A probable pathway for the decomposition of surfactant 1 has been proposed.

The Chapter 4 of the thesis deals with the photocatalysed degradation of three selected antibiotics norfloxacin (1), ciprofloxacin (2) and amoxicillin (3) in aqueous suspensions of titanium dioxide using different parameters. The decomposition and mineralization of the compounds were monitored by measuring the change in substrate concentration and depletion in TOC content as a function of irradiation time with an aim to determine the optimum degradation condition. The degradation rate for the decomposition and mineralization of the pollutant was found to be strongly influenced by all the parameters studied such as type of photocatalyst, pH, catalyst and substrate concentration and in the presence of electron acceptors.
Reasonable mechanisms have been suggested to account for the formation of the various products in the reaction of different pollutants listed under Chapters 1-3.

**Note:** The numbers of the various compounds given in parentheses corresponds to those under the respective chapters.