Photolytic Degradation of Acephate, Glyphosate and Malathion

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By

Nik Raihan Nik Yusoff

Brunel University

Institute for the Environment

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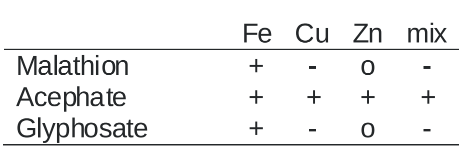
ABSTRACT

A photolytic cell system suitable for the treatment of wastewater streams containing three pesticides, i) acephate, ii) glyphosate and iii) malathion is reported. The system is capable of destroying these three organic compounds, commonly present in wastewater streams originating from agrochemical industries in Malaysia, and can lead to complete mineralisation under the optimum conditions. The system is based on an advanced oxidation process and involves the production of hydroxyl free radicals in the presence of a UV source. The performance of the system, for the three pesticides, was optimised by investigating the effects of i) UV source, ii) pH of the solution, iii) initial concentration of the substrate, iv) addition of oxidants, v) hydrogen peroxide (H_2O_2) in the presence and absence of single and mixed metal ions. To monitor the degradation efficiency of the system, the residual concentrations of these organic compounds and metal ions were analysed using five analytical techniques i) total organic carbon (TOC), ii) high performance liquid chromatography (HPLC), iii) ion chromatography (IC), iv) UV/Visible spectroscopy (UV/Vis), and v) atomic absorption spectroscopy (AAS).

The data show that the developed photolytic cell system is capable of achieving complete mineralisation of the three pesticides with the use of both 400 W and 600 W UV lamps. However, the 400W UV lamp was used, for economic reasons, to optimise the system for the remaining factors. Changes in the pH of aqueous solutions influenced the degradation efficiency and a complete degradation of the three pesticides was achieved at their self-pH values ranging from 5.0-5.5. The degradation of acephate increased and malathion decreased at their higher initial concentrations whereas no significant effect related to concentration was observed for glyphosate. Results show that the degradation followed a first order kinetics and the degradation rates were: malathion > acephate > glyphosate. The addition of 30 mg/L of H_2O_2 enhanced the degradation of the pesticides and after 5 hours irradiation these were 95.7%, 91.5% and 81.3% for malathion, acephate and glyphosate respectively.

The presence of metal ions was observed to affect degradation (Table 1). With 5.0 mg/L of Fe(II) the degradation of all three pesticides increased, and in all cases acephate removal was improved. Removal of both malathion and glyphosate was negatively affected by copper, an effect that work with mixtures indicated was stronger than the positive effect of iron.

Table 1. Effect of metals on removal



	Fe	Cu	Zn	mix
Malathion	+	-	o	-
Acephate	+	+	+	+
Glyphosate	+	-	o	-

The addition of H_2O_2, in the presence of single metal ions, increases the degradation. However, the addition of H_2O_2, in the presence of mixed metal ions, has no significant effect on the degradation of glyphosate and malathion. The effect of mixed metal ions on the three pesticides and the effect of Zn(II) ions on acephate and malathion are reported for the first time in this thesis.

The developed photolytic cell system can be used for the treatment of wastewater streams originating from point sources, for example, agrochemical industries, under the optimum conditions. The synergistic combination of the developed system with the existing standard technologies is also proposed for the treatment of surface water at water treatment facilities in Malaysia. The application of the developed system can also be extended, with minimum modifications, for the treatment of wastewater streams originating from different manufacturing industries in Malaysia, for example, textile, paper/pulp, printing, coke, petroleum, paint, solvent, pharmaceuticals and wood-preserving chemicals. All these industries produce wastewater streams containing low concentrations of organic pollutants and heavy metal ions.

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Glossary of Abbreviations

λ_{max}	Maximum emission wavelength
ε	Absorption coefficient
A	Absorbance
AAW	American Air and Water
AMPA	Aminomethylphosphonic acid
AOP	Advanced oxidation process
ASRS	Anion self regenerating supressor
c	Concentration
Cal/EPA	California Environmental Protection Agency
CIA	Central Intelligence Agency
cb	Conduction band
DOA	Department of Agriculture
DOE	Department of Environment
DOSM	Department of Statistic Malaysia
EFSA	European Food Safety Authority
EGDF	Ethylene glycol diformate
ELCFED	European Lamp Companies Federation
EQA	Environmental Quality Act
EQS	Environmental Quality Standards
ESR	Electron spins resonance

FAO	Food and Agriculture Organization of the United Nations
FAAS	Flame atomic absorption spectrometer
GDP	Gross domestic product
HPLC	High performance liquid chromatography
HP	High pressure
I_0	Intensity of the incident light
I	Intensity of light after passing through the solution
IC	Inorganic carbon
IC	Ion chromatography
IFA	International Fertiliser Industry Association
K	Equilibrium constant
k	Rate constant
l	Path length of sample cell
LMCT	Ligand to metal charge transfer
LP	Low pressure
M	Molar
MIDA	Malaysian Investment Development Authority
MOF	Ministry of Finance
MoHE	Ministry of Higher Education
MPOB	Malaysian Palm Oil Board
NDIR	Non-dispersive infrared

NHS	National Health Service
NPS	Non point source
NRE	Natural Resources and Environment
NS	Not studied
O_3	Ozone
OC	Organochlorine
OP	Organophosphate
PAN-UK	Pesticide Action Network-United Kingdom
PMEP	Pesticide Management Education Program
PS	Point source
R^2	Regression coefficient
SDWF	Safe Drinking Water Foundation
TC	Total carbon
TOC	Total organic carbon
USEPA	United Stated Environmental Protection Agency
UV	Ultraviolet
UV/Vis	Ultraviolet/Visible
vb	Valence band
W	Watt
WEPA	Water Environment Partnership Asia

CHAPTER 1: Introduction

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1.1. Environmental Pollution

When we talk about environmental pollution we are basically talking about the three main environmental compartments namely water, soil and air. Environmental pollution is any discharge of material or energy into water, soil, or air that causes or may cause acute (short-term) or chronic (long-term) harm to the ecosystem or that lowers the quality of life. Pollutants may have an adverse effect, directly or indirectly, on life or on quality of life. If it does not affect life in any way then it should be described as contamination, not pollution. Since the biosphere interacts with all other quarters of the globe (Figure 1.1), environmental pollution may be anything which affects the hydrosphere, the lithosphere and the atmosphere – or water, soil and air, i.e., environmental pollution acts predominantly upon an ecosystem (Javaid, 2006).

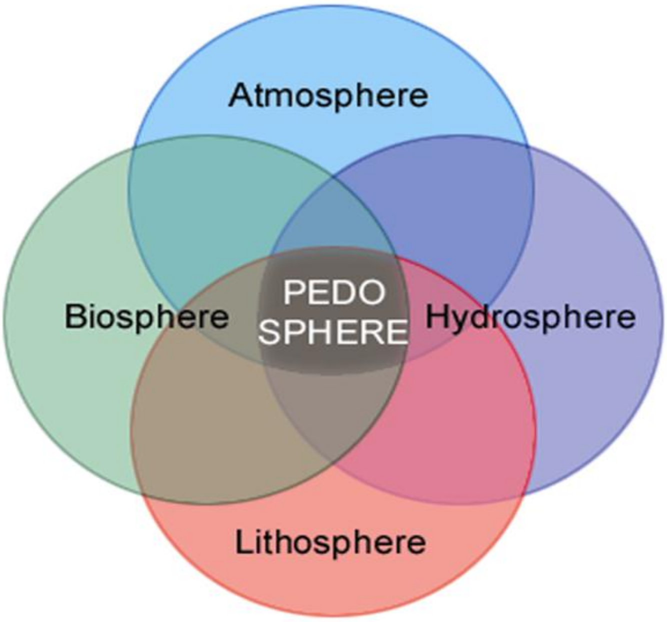

Figure 1.1: Global environmental system.

Pollutants are materials that affect the global environment, with a detrimental effect on the biosphere. They may be chemical in nature but results could also be harmful physical phenomena, e.g. greenhouse gases leading to global warming (Javaid, 2006). Those pollutants of a chemical nature, e.g. synthetic organic compounds, mainly pesticides, and heavy metal ions (Fe(II), Cu(II) and Zn(II)) are the major concern of this thesis. The main aim of the work described in this thesis is to develop a photolytic cell system, based on an advanced oxidation process (AOP), to combat the problems associated with the management of three pesticides namely acephate, glyphosate and malathion in Malaysia. In addition, the use of these three pesticides all over the world, including Malaysia, and the environmental problems associated with their usage are described in detail in later chapters.

1.2. Sources of Environmental Pollution

In pollution science, the source refers to the site that has the potential to introduce pollutants into one of the three main environmental sectors, namely water, soil and air (Petts, Cairney and Smith, 1997; Javaid, 2006). The sources of pollutants in the environment can be divided into point sources (PS) and nonpoint sources (NPS). Environmental pollution originating from a single, identifiable source, such as a discharge pipe from a factory or sewage plant, is called point source (PS) pollution. Pollution that does not originate from a single source, or point, is called nonpoint source (NPS) pollution. The concentrations of potentially harmful substances in water, soil, and air may arise from both point and nonpoint sources. A significant proportion of pollutants in the environment arise as a result of man's activities. These include emissions from textile, leather, electroplating, metal mining, smelting and refining, power generation, manufacturing and transport, urban and household activities, waste disposal to landfill, combustion processes, use of agricultural materials including pesticides and fertilizers, and the utilisation/disposal of sewage sludge on farmland (Thornton, 1995; Javaid, 2006).

Environmental pollution originating from point sources has largely been controlled by both national and international legislations. A large number of technologies have been developed to combat the environmental pollution problems associated with water pollution originating from point sources. However, a large amount of water pollution does not come from a single point and the effects of nonpoint source pollutants on specific waters vary and may not always be fully assessed. However, we know that these pollutants have harmful effects on drinking water supplies, recreation, fisheries and wildlife.

In both developed and developing countries, regulations have been introduced to regulate various types of water pollution and to mitigate the adverse effects of pollution. In Malaysia, for example, the regulation related to water pollution has been set by Department of Environment (DOE) under the Ministry of Natural Resources and Environment (NRE) (DOE, 2013). The Environmental Quality Act 1974 ordains restrictions on the discharge or deposit of any environmentally hazardous substances, pollutants or wastes into any inland waters (WEPA, 2013).

Environmental pollution levels must be controlled at all the time if we want to keep our environment safe and healthy. Without proper pollution control, the environment will become unhealthy and nothing will be able to live in it. It is relatively easy to control emissions of pollutants from a point source compared to a nonpoint source because nonpoint source pollutants (i) are difficult or impossible to trace to a source, (ii) enter the environment over an extensive area and sporadic timeframe, (iii) have the potential for maintaining a relatively long active presence on the global ecosystem, and (v) impossible to use a treatment system to remove both inorganic and organic pollutants from water systems at large scales.

Figure 1.2 shows the outline waste streams originating from both point and nonpoint sources for which the treatment technologies need to be developed and optimised to control environmental pollution problems associated with both of these sources. The research work described in this thesis has been focussed on the development and optimisation of advanced oxidation technology suitable for the treatment of wastewater streams containing organic pollutants, mainly pesticides.

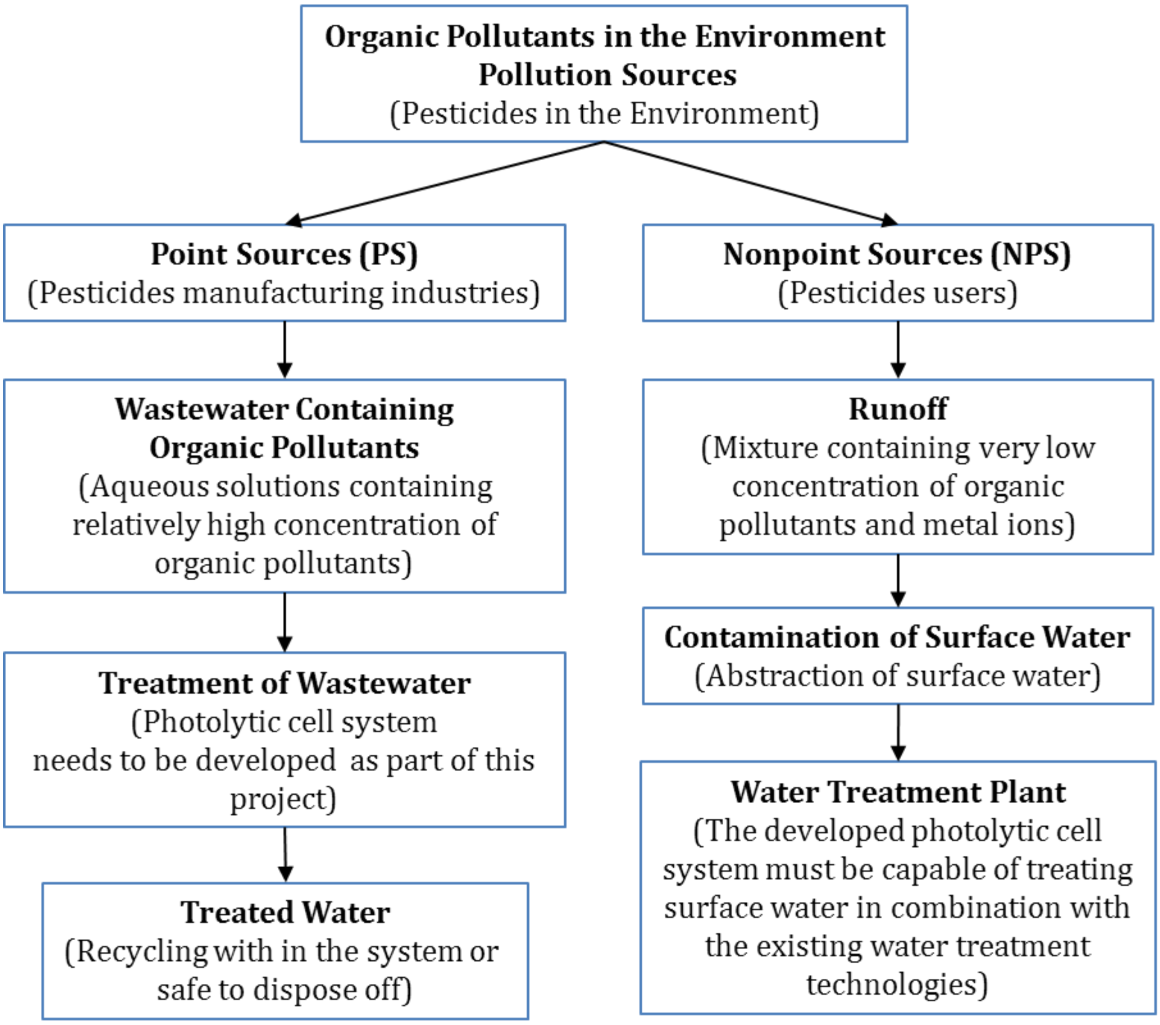

Figure 1.2: Treatment of wastewater streams containing organic pollutants.

1.3. Organic Pollutants in the Environment

A number of organic pollutants are described in this section as examples of the problems associated with organic chemicals in the environment. A large number of industries such as textile, paper/pulp, printing, coke, petroleum, pesticide, paint, solvent, pharmaceuticals and wood-preserving chemicals, consume large volumes of water and organic based chemicals. These organic chemicals have large differences in chemical composition, molecular weight, toxicity etc. Many persist in the environment for long periods of time and hence are known as persistent organic pollutants that can cause serious health and environmental problems. There is a growing concern about organic pollutants that have a potential for causing neurological disorders, suppressing the immune system, increasing the risk of cancer and causing endocrine disruption etc. Organic pollutants can be transported by air and water and many move through the soil. Effluents of many industries may also contain undesired quantities of organic pollutants and therefore need to be treated before their discharge into any medium.

Many persistent organic pollutants were widely used during the boom in industrial production after World War II, when thousands of synthetic chemicals were introduced into commercial use. Many of these chemicals proved beneficial for pest control, crop production and industry. These chemicals, however, can also produce unforeseen effects on human health and the environment especially when they are stable molecules and can accumulate and pass from one species to another through the food chain (Baird, 1999). To address this concern, a conference was held in Stockholm, Sweden, in May 2001 where the treaty known as the Stockholm Convention was signed by more than 90 countries who promised to reduce or eliminate the production, use and release of twelve key persistent organic pollutants (Table 1.1), which are known as "the dirty dozen'' (USEPA, 2013).

Table 1.1: The key persistent organic pollutants – the dirty dozen

Pesticides organic pollutants	Uses
Aldrin	Crop insecticide (corn, cotton)
Chlordane	Crop insecticide (cotton, citrus, vegetable potatoes
DDT	Crop insecticide (cotton)
Dieldrin	Crop insecticide (corn, cotton)
Endrin	Crop insecticide (grains, cotton)
Heptachlor	Crop insecticide (termites and soil insects)
Hexachlorobenzene	Fungicide for seed treatment
Mirex	Insecticide (termites, fire ants)
Toxaphene	Insecticide (livestock and crop)
PCBs e.g. 2,4-D and 2,4,5-T	Industrial chemical (heat exchange fluid for electrical transformers, paint and plastic additive)
Dioxins	Unintentionally produced during combustion
Furans	Unintentionally produced during combustion

Phenol and its derivatives are another group of organic pollutants which are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential to harm human health. It should be noted that the contamination of drinking water by phenolic compounds even at concentration of 0.005 mg/L could bring about significant taste and odour problems making it unfit for use. Human consumption of phenol-contaminated water can cause severe pain leading to damage of the capillaries ultimately causing death. Phenol-containing water when chlorinated during disinfection of water also results in the formation of chlorophenols. The most important pollution sources containing phenols and phenolic compounds such as nitrophenols, chlorophenols, are the wastewaters from the iron-steel, coke, petroleum, pesticide, paint, solvent, pharmaceutical, wood preserving chemicals and paper and pulp industries (Calace *et al.*, 2002).

1.3.1. Pesticides pollution

Every day the world's population increases by more than 200,000 people. One billion people were added in the last 10 years (US Bureau of the Census, 2013). By 2050 the population is projected to grow by 40 to 50% (Figure 1.3).

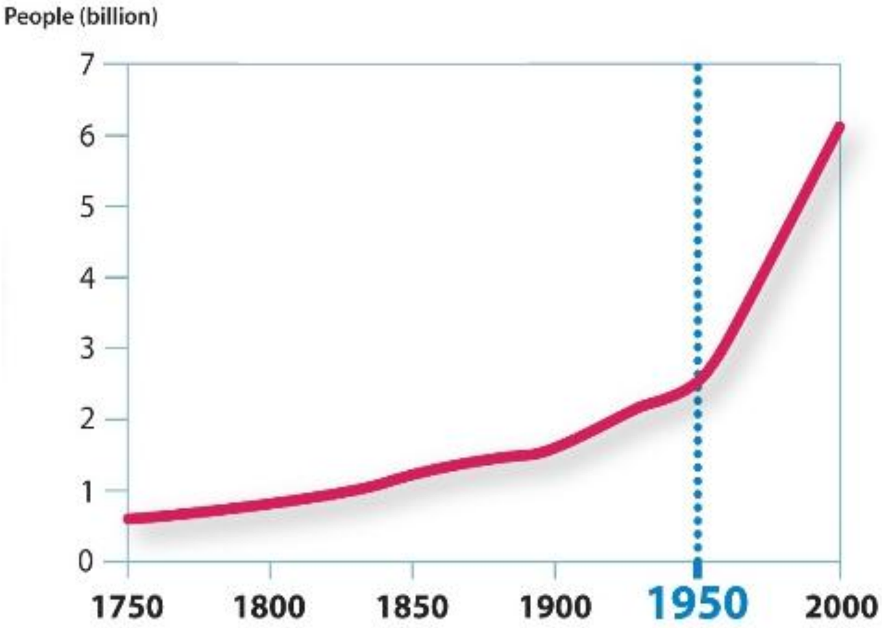

Figure 1.3: Total world population (US Bureau of the Census, 2013).

The need to increase the world food production for the rapidly growing population is well recognise (Schreinemachers and Tipraqsa, 2012; Abhilash and Singh, 2009). Thus, increasing the global food supply requires the intensification of agriculture and this has led to a dramatic increase in the consumption of both fertilisers and pesticides (Figure 1.4 and 1.5). Unlike fertiliser, the intensive use of pesticides do not directly contribute to better crop yields but simply help to control the potential losses caused by animal pest (such as insects, mites, nematodes and rodents), plant pathogens (such as fungi, viruses and bacteria) and weeds (Schreinemachers and Tipraqsa, 2012; Oerke, 2006). Although there are important benefits from the proper use of pesticides there are also risks. One of the major risks associated with the increased usage of pesticides is the contamination of groundwater and surface water resources. Data collected during 1992–2001 from 51 major hydrologic systems across the United States indicate that one or more pesticide or pesticide breakdown product was detected in more than 50% of 5,057 shallow wells and in all of the 186 stream sites that were sampled in agricultural and urban areas (Gilliom *et al.*, 2006).

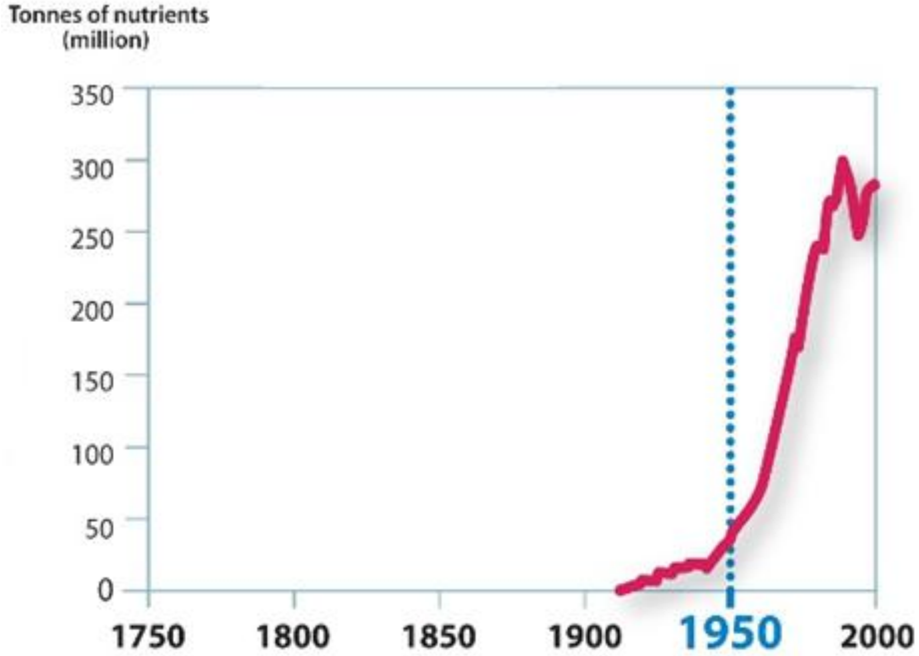

Figure 1.4: Total consumption of fertilisers (IFA, 2013).

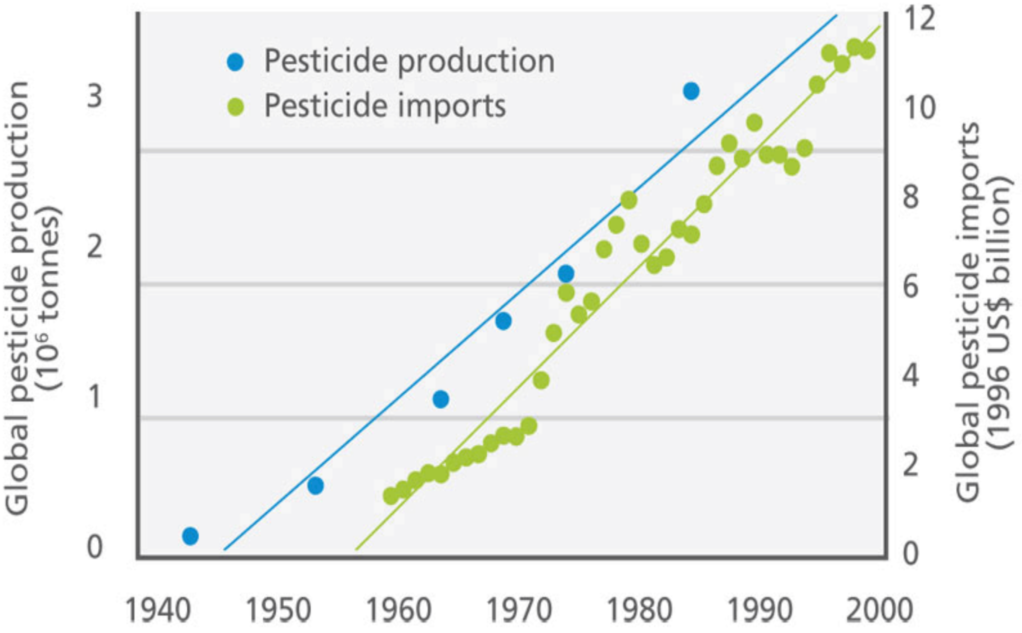

Figure 1.5: Global Pesticides production (Land Commodities Research, 2013).

Although there are various definitions of pesticides (Baird, 1999; Planas *et al.*, 1997), mainly pesticides are the synthetic compounds or mixtures intended for preventing, destroying, or controlling pests including vectors of human or animal disease, unwanted species of plants, and pests causing harm during or otherwise interfering with the production, storage, processing and transportation, or marketing of food or agricultural commodities (Sud and Kaur, 2012).

The worldwide consumption of pesticide is about two million tons per year. Of which 24% is consumed in the USA alone, 45% in Europe and the rest is in other countries (Abhilash and Singh, 2009). The pesticide consumption in the agriculture sector showed that herbicides are the leading category followed by insecticide and fungicide (Abhilash and Singh, 2009) as the weeds produced the highest potential crop loss (34%), with animal pests (18%) and pathogens (16%) being less important (Oerke, 2006). However, warm, humid and tropical climate countries, such as India, Malaysia and Indonesia, are required to use more insecticides than herbicides for crop protection. For example, the pesticide usage in oil palm plantation which are the top crop production in Malaysia and Indonesia (FAO, 2013); needs more insecticide as the crops required more intensive care from pests since crop loss is even more severe in tropical countries because the prevailing high temperature and humidity provides highly conducive and favourable breeding environment for insects (Abhilash and Singh, 2009).

There are various groups of pesticides such as carbamate, pyrethroid, organochlorine and organophosphate. Organophosphate pesticides (OPs) are widely used in modern agriculture as an alternative and effort to substitute the organochlorines (OCs) for pest control because of the longevity and toxicity of the organochlorines pesticides (Sud and Kaur, 2012; Malhat and Nasr, 2011). The longevity of organochlorine has been proved where the occurrence of OCs have been detected in Malaysia where their consumption (such as DDT, heptachlor, dieldrin and endosulfan) have been detected (exceeded the maximum residue level) in the 7 out of 25 rivers flowing through rice-growing areas in Malaysia rivers (Tan and Vijayaletchumy, 1994). Since OPs meet the suitable environmental conditions to replace OCs, thus, it is possible that OPs can persist in many environmental sites for a long period of time (Sud and Kaur, 2012) and can pose a special threat to the environment and human health as occurred on the organochlorine consumption. In fact, the occurrence of OPs have been already detected recently in three tributaries of Kedah State, where orthophosphate attributed from agricultural site run off has been recorded at higher concentration (Haris and Omar, 2007). Regardless of the pesticides' group, it has been reported that pesticides manufacturing industries and specifically their use over a long period in agricultural and non-agricultural area can reach the water resources which then influences the quality of groundwater and surface water (Chowdhury *et al.*, 2013; Bao *et al.*, 2012; Malhat and Nasr, 2011; Shayeghi, Khoobdel and Vatandoost, 2007; Lapworth *et al.*, 2006; Ramachandran and Mourin, 2006; Skark *et al.*, 2004; Kolpin, Barbash and Gilliom, 1998; Skark *et al.*, 1998; Spliid and Køppen, 1998; Kolpin *et al.*, 1997; Planas *et al.*, 1997).

Globally, an alarming level of pesticides has been reported in air, water and soil as well as in foods and biological materials. Some of these pesticides have been reported to be persistent, toxic, mutagenic and carcinogenic. Pesticide contamination of water systems is also a major concern as residues reach the aquatic environment through manufacturing plants, direct surface run-off, leaching, careless disposal of empty containers, equipment washings, etc (Javaid, 2006). Apart from surface water, pesticides can also contaminate groundwater from both point sources and non-point sources. From nonpoint sources, pesticides typically enter surface water when rainfall or irrigation exceeds the infiltration capacity of soil and resulting runoff then transports pesticides to streams, rivers, and other surface-water bodies. Contamination of groundwater may result directly from spills and from pesticide applications (Thodal, Carpenter and Moses, 2013). Groundwater contamination also may come indirectly by the percolation of agricultural and urban irrigation water through soil layers and into groundwater (Figure 1.6).

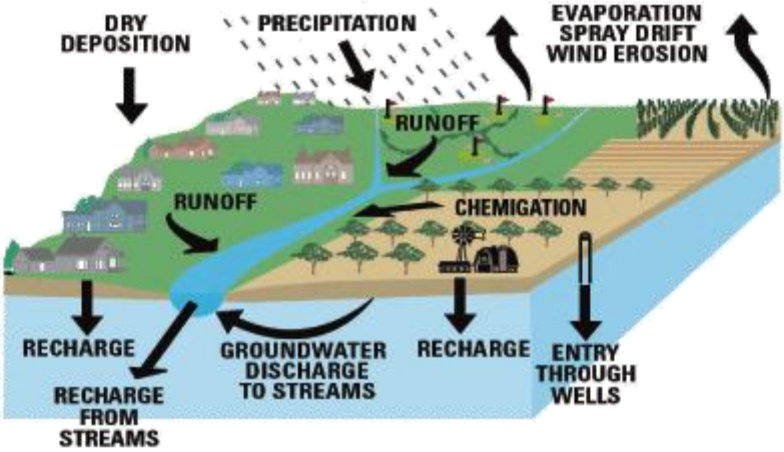

Figure 1.6: Schematic diagram illustrating routes of pesticides into streams and groundwater (Gilliom *et al.*, 2006).

To protect surface water and groundwater from pesticide contamination, the USEPA developed a pesticide management of education (Hefner and Donaldson, 2013), regulation (Johnson *et al.*, 2013) and monitoring (Nyle *et al.*, 2013) to protect water resources from pesticide contaminants. Monitoring of streams, rivers and other surface-water bodies show the presence of low levels of various types of pesticides along with different types of heavy metals (Ghanem *et al.*, 2011). The main objectives of sampling and monitoring are to assess the occurrence of pesticides in both surface water and groundwater to provide decision makers with information needed to evaluate and manage pesticide application practices designed to protect drinking water resources, especially the deeper, potable groundwater as well as aquatic species (Thodal, Carpenter and Moses, 2013). The protective measures may include the use of alternative products or application restrictions for pesticides that cause contamination (Hefner and Donaldson, 2013).

1.4. Treatment of Water Stream Containing Organic Pollutants

There are many possible methods which can be used to remove or destroy organophosphate compounds including biological degradation (Chai *et al.*, 2010; Chai, Tahir and Hansen, 2009), adsorption (Hu, Zhao and Sorohan, 2011; Pal and Vanjara, 2001), solar radiation (Xu *et al.*, 2011), ozonation (Beduk, Aydin and Ozcan, 2012; Cernigoj, Stangar and Jirkovsky, 2010) and treatment with ultraviolet radiation (Chen, Hu and Wang, 2012; Shayeghi *et al.*, 2012; Han *et al.*, 2009; Rahman *et al.*, 2006). These methods are able to destroy the organic compounds however, the efficiency of many of these methods is reduced in the presence of heavy metal ions. This observation is particularly true if the organic species form strong complexes with the metal ions in the solution. Due to this, heavy metal pollution has become one of the most serious environmental problems today (Fu and Wang, 2011) beside the water pollution affected from organic pollutants. In mixed industrial effluent for example, the presence of metal ions such as copper can retard the destruction of organic contaminant (Chaudhary, Hassan and Grimes, 2009; Chaudhary and Grimes, 2008; Chaudhary, Grimes and Hassan, 2001; Chaudhary *et al.*, 2000). Thus, in order to complete the degradation, heavy metals should be removed from the wastewater first in order to protect people and the environment. Many methods have been used to remove heavy metal ion include chemical precipitation, ion-exchange, adsorption, membrane filtration and electrochemical treatment technologies (Fu and Wang, 2011). The mentioned methods for the heavy metal removal in the wastewater are not reliable when the wastewater also contained other organic pollutant such as pesticide. The development of advanced oxidation process (AOPs) either homogeneous such as photodecomposition of organic matter in the presence of hydrogen peroxide (H_2O_2/UV) and ozone photolysis (O_3/UV), or heterogeneous such as photocatalysis by semiconductor (TiO_2, ZnO, ZrO_2 or WO_3/UV) are the most effective technologies for the degradation of organic pollutants where the powerful oxidising agent, especially •OH or another radical is generated (Sud and Kaur, 2012; Ciesla *et al.*, 2004). Among AOPs, heterogeneous photocatalysis using TiO_2 as photocatalyst and the presence of dissolved transition metal ions such as Cu(II), Fe(II) and Fe(III) ions appeared as the most studied area where the presence of heavy metal ions can be profoundly influence the rate of TiO_2 photocatalytic oxidation, either enhancing or retarding the photoactivity of the catalyst depending on parameters such as the concentration of metal ions, the pH solution and the organic being degraded (Chaudhary, Hassan and Grimes, 2009; Chaudhary and Grimes, 2008; Lam *et al.*, 2007; Lopez-Munoz, Aguado and Ruperez, 2007; Shifu and Yunzhang, 2007; Wahyuni, Mudasir and Hadipranoto, 2006; Beydoun *et al.*, 2002; San *et al.*, 2002; Chaudhary, Grimes and Hassan, 2001; Hua *et al.*, 1995).

Although much has been published, there still remain gaps in understanding the photoredox reactions of transition metal complexes. This reaction is one of the growing interests in the development of new methodologies of AOPs for the degradation of organic pollutants such as organophosphate pesticides. The reaction is without using TiO_2 as a photocatalyst, however, the presence of dissolved metal ions can influence the photodegradation process for the removal or destruction of organophosphate pesticides in the wastewater since the dissolved metal ions can act as a catalyst as well, and thus may become relevance to the environmental metal cycling and self-cleaning processes (Ciesla *et al.*, 2004). To study this, acephate, glyphosate and malathion have been selected for the study since they are being produced and widely used in Malaysia. Furthermore, the occurrence of these pesticides in rivers, surface water and groundwater has been detected in Malaysia (Somchit *et al.*, 2009; Haris and Omar, 2007; Tan and Vijayaletchumy, 1994). Thus, a list of objectives has been set in the next section where the focus was to optimise the photodegradation conditions of three organophosphate pesticides. The optimised conditions will then be used for a technology development suitable for the treatment of wastewater streams containing pesticides.

1.5. Aims and Objectives

The research work described in this thesis is fully funded by Ministry of Higher Education (MoHE), Malaysia. The main aim of this work is to investigate the effects of various operating parameters on the photodegradation of three pesticides i) acephate, ii) glyphosate and iii) malathion. The developed photolytic system must be able to treat wastewater streams originating from pesticide manufacturing industries in Malaysia. The specific objectives of this project are:

1. To highlight the problems associated with the treatment of wastewater streams containing organic pollutants, especially pesticides, in the presence of heavy metal ions.
2. To develop analytical methods for the analyses of three selected pesticides; acephate, glyphosate and malathion in the presence and absence of three selected heavy metal ions ((Fe(II), Cu(II) and Zn(II)) using an HPLC system.
3. To investigate the effect of various UV sources on the photodegradation of the three pesticides; acephate, glyphosate and malathion in aqueous solution.
4. To study the effect of pH values on the degradation of each of the three pesticides.
5. To investigate the effect of varying the concentration of the selected pesticides (15 – 100 mg/L) on the photodegradation rate.
6. To study the effect of hydrogen peroxide (H_2O_2) on the photodegradation of the three pesticides.
7. To determine the effect of varying the concentration (5.0 – 15.0 mg/L) of single metal (Fe(II), Cu(II) and Zn(II)) ions on the photodegradation of the three pesticides.
8. To determine the effect of mixed metal ions ((Fe(II), Cu(II) and Zn(II)) on the photodegradation of the three pesticides.
9. To study the effect of single and mixed metal ions in the presence of H_2O_2 on the photodegradation of the three pesticides.

1.6. Thesis Outline

This thesis is divided into five chapters. Chapter one reports on the background information on environmental pollution problems associated with organic pollutants, especially pesticides, and information on the existing treatment methods commonly used for the treatment of wastewater streams containing organic pollutants. The aims and objectives of this work are also given in this chapter. Chapter two presents an overview of the current state of knowledge and the findings of research into the pesticides and also provides detailed information about advanced oxidation processes (AOPs) which are normally used for the treatment of wastewater containing organic pollutants. In addition, an overview of the three pesticides, the oxidants and the heavy metal ions used in this study are also discussed in this chapter. Chapter three is concerned with the materials, methods and experimental procedures that are used in this study. Descriptions of all the analytical techniques used throughout this work are also outlined in this chapter. Chapter four includes the discussion of the optimisation results obtained from the conducted experiments. Finally, chapter five provides a summary of the main findings of this work. The applications of the developed system, in Malaysia, to solve the environmental pollution problems associated with the management of wastewater streams contain both organic and heavy metal ions are also proposed in chapter 5. Recommendations for future work are also stated in chapter 5.

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CHAPTER 2: Literature Review

CHAPTER 2: Literature Review

2.1. Summary

An overview of the current research knowledge into the study of the three pesticide compounds, their use and photodegradation studies are presented in this chapter. A comprehensive literature review was done on water pollution and the treatment methods which are commonly used to remove toxic hazardous materials from wastewater streams at various treatment plants. This chapter also discussed the use of advanced oxidation processes (AOPs) to remove organic pollutants from water streams. Finally, the role of adding materials such as oxidants and dissolved metal ions will be covered in order to understand the removal rate of organic pollutant using AOPs.

2.2. Water Pollution

Humans need to consume several litres of fresh water daily to sustain their lives, however, the sources of water suitable for human consumption are very limited as over 97% of the world's water is seawater and thus unsuitable for drinking or agricultural purposes whereas three quarters of the fresh water is trapped in glaciers and ice caps whilst only 0.01% of the total water supply come from lakes and rivers (Baird, 1999). So it is important to keep this source clean and non-polluted. Apart from anthropogenic sources, water pollution can be the result from natural phenomena such as volcanoes eruption, storm and earthquake (Mezughi, 2010).

Fresh water resources such as lakes and rivers are called surface water and the great contribution (0.6% of the world's total water supply) to the fresh water is groundwater (Baird, 1999). Ordinarily, surface water is easily polluted however, groundwater resources also can be affected by pollution for instance, when pesticides in particular weed killers are applied in the garden and drain into the ground. Well sampling data collected in 2010 found that more than 21 pesticides and their degradates were detected in 286 wells located in 18 counties out of 51 counties sampled in Sacramento, California (Cal/EPA, 2012). Samples from several creeks in urban areas which are located in the residential neighbourhoods, commercial industries and construction areas also detected pesticides such as malathion, diazinon, carbaryl, simazine and diuron (Cal/EPA, 2013). The massive use of agrochemicals in large scale farming areas including rice, soya and wheat in Uruguay, has proved that its usage affecting the freshwater fishes. This happened by accumulation of pesticide in the organs and tissues of the fish when the pesticide-loaded soil or field run-off reaches watercourses (Carcamo, 2010).

There are mainly two sources of water pollution commonly called point sources and non-point sources (Figure 2.1). If the pollution comes from a discharge pipe attached to a factory, it is known as point source pollution whilst non-point sources happen from many scattered sources. Ordinarily, the place where point source pollution happens will be the most affected area with high concentration of pollutant and this situation is less likely to happen with non-point source pollution. However, the non-point sources cause quite a lot of pollution to surface or groundwater. The use of drugs (painkillers), personal care products (sun screening agents and fragrances), pharmaceuticals and pesticide products in agricultural sector, residential area or for the public health contribute to the pollution. Virtually, those substances were being flush out from toilet or pour down into the drain thus contribute to the sewage waste for the wastewater treatment. The treated wastewater effluent was then released back to the water bodies. However, not all contaminants were able to be treated as they still frequently detect in the wastewater treatment plant (Cabeza *et al.*, 2012).

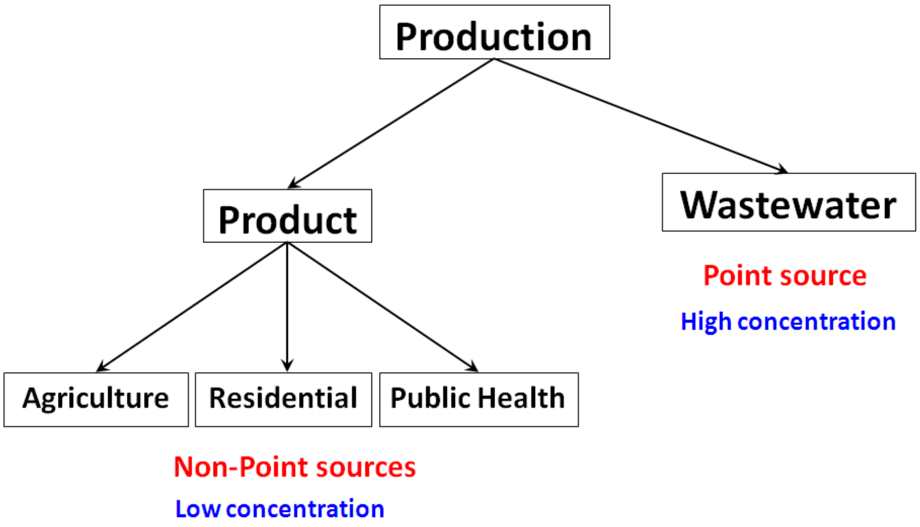


Figure 2.1: Point sources and non-point sources of pollution.

2.3. Malaysia's Legislation on Water Quality

About 27 million Malaysians generate 6 million tons of sewage every year and to combat this, around 8,000 public sewage treatment plants were set up in order to treat the sewage and release back into the rivers (Liew, 2013). Data revealed that the number of river basin monitored was 143 with 1,064 monitoring stations and out of these, 638 were found to be clean, 376 slightly polluted and 50 highly polluted (DOE, 2013). These data show that river pollution exists in Malaysia, thus proper treatment of sewerage is paramount since 98% of Malaysia's fresh water supply comes from surface water (Liew, 2013). Therefore, there is a need to control and maintain the quality of water in the rivers to ensure the safe quality of available water because the deterioration of water quality reduces the usability of the resources (Fulazzaky, Seong and Masirin, 2010).

In Malaysia, the Department of Environment (DOE) under Ministry of Natural Resources and Environment (NRE) is the responsible body which regulates laws related to water pollution issues. Among the laws relevant to water quality management include: 1) 1929 Mining Enactment, 2) 1930 Water Enactment, 3) 1954 Drainage Work Ordinance, and 4)1974 Street, Drainage and Building Act. However, these laws were more focused on the specific areas of activity (Daud, 2013).

Due to the complex environmental problems, a comprehensive legislation which is the Environmental Quality Act 1974 (EQA 1974) has came into force on 1 April 1974 for the abatement, pollution control and enhancement of the environment.

Under EQA 1974, three legislations were formed as an initial legislative approach to water quality management and these were (Daud, 2013):

1. Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulations 1977
2. Environmental Quality (Prescribed Premises) (Raw Natural Rubber) Regulations 1978
3. Environmental Quality (Sewage and Industrial Effluents) Regulations 1979

In 2009, Environmental Quality (Sewage and Industrial Effluents) Regulations 1979 was replaced by new three laws, which are (WEPA, 2013):

1. Environmental Quality (Sewage) Regulations
2. Environmental Quality (Industrial Effluent) Regulations
3. Environmental Quality (Control of pollution from Solid Waste Transfer Stations and Landfills) Regulations

A number of regulation laws have been legislated relating to water quality in Malaysia and these show that, the government is really concerned on the sustainable use of water resources, conservations of river's vitality and diversity also continuous improvement on water quality.

Under Environmental Quality (Industrial Effluent) Regulations, the pollution control from agro based industries such as raw natural rubber and palm oil mills has proven to be very successful since these industries have made great effort to comply as rapidly as possible with the stipulated effluent discharge standard regulation. They invested in the pollution control research and also were induced to install effective wastewater treatment systems instead of paying the pollution fees (Daud, 2013). However, it has been reported as well that the new environmental problems have been emerged consequently from chemical and manufacturing industries. These industries have generated organic pollutants, toxic wastes, metal ions and persistent organic pollutants into the water resources. Although all industries are required by laws to install wastewater treatment system to treat their effluent discharges before being release to the river, however, they (mostly small and medium size industries) do not comply with the regulations due to the financial problems and the lack of space for the construction of wastewater treatment facilities (Daud, 2013).

2.4. Water Treatment Process

Generally wastewater effluent streams originating from various sources are treated using different methods in order to produce suitable and safe treated effluent streams which can be discharged into the environment. Conventional wastewater treatment is a combination of physical and biological processes to remove organic matter. Gray (1989) classified the treatment into several stages where the wastewaters need to go to the preliminary, primary, secondary and tertiary treatments, however, not all the stages may be utilised as it depend on the quality of the final effluent required.

In the preliminary treatment, the flow measurement, screening, shredding and grit removal are normal steps as these steps can protect the equipment at the wastewater treatment plant, for example screening prevents large solids from fouling. Whereas grit, sand and dense material solids are removed by grit removal otherwise they will cause clogging in the primary treatment stage (Hammer, 2004). Following preliminary treatment, the raw sewage enters the primary treatment or sedimentation process which usually involves the removal of settleable solids where the removal efficiency can be as high as 70%, since a number of processes such as flocculation and adsorption occur simultaneously (Gray, 1989). The flow from primary stage is now known as settled sewage and this settled sewage then proceeds to the secondary treatment. Mostly aerobic microorganisms (bacteria, algae, viruses, protozoa and fungi) are found in wastewater treatment (Hammer, 2004) thus, the secondary treatment involves the biological treatment for example using activated sludge. The settled sewage is aerated in the tank or reactor and leads to the removal of organic matter and it is returned continuously to the aeration area to mix with new entering sewage in order to maintain microbial breakdown of the wastewater for the final effluent (Malato *et al.*, 2009; Hammer, 2004; Gray, 1989). Ordinarily, most effluents discharge to rivers receive secondary treatment, however, tertiary treatment will be necessary if more pollutant need to be remove (Gray, 1989).

2.5. Advanced Oxidation Processes (AOPs)

Generally, conventional biodegradation by activated sludge is very effective in the treatment of most domestic sewage waters. However, many toxic compounds and heavy metal ions that are resistant to bacterial biodegradation are contained in industrial effluents (Halmann, 1996). However, the extensive use of large amount of pesticides and other agrochemicals in modern intensive agriculture results in their accumulation in surface and groundwater (Devipriya and Yesodharan, 2005; Malato *et al.*, 1999). Furthermore, many of these compounds are recalcitrant to biotreatment due to their toxicity at higher concentration and will eventually end up ultimately polluting water bodies (Zhang and Pagilla, 2010; Esplugas *et al.*, 2002; Halmann, 1996). Among the advanced treatment technologies for the removal of such xenobiotic substances, advanced oxidation processes (AOPs), which include irradiation with UV or visible light, with or without additional oxidants (oxygen, ozone and hydrogen peroxide) and with heterogeneous photocatalyst such as dispersed or immobilised semiconductors have present a particularly attractive option (Halmann, 1996).

AOPs which involve the generation of hydroxyl radicals, •OH (De Laat, Le and Legube, 2004; De Laat *et al.*, 1999) are able to degrade almost any organic molecule, yielding short chain or smaller organic acids, inorganic ions and carbon dioxide as final products (Klamerth *et al.*, 2013; Malato *et al.*, 2009). The processes are: UV alone (Shayeghi *et al.*, 2012; Lundhoie and Friestad, 1986), UV/H_2O_2 (Manassero *et al.*, 2010; De Laat *et al.*, 1999), UV/H_2O_2/with Fe^{3+} or Fe^{2+} (Klamerth *et al.*, 2013; Zhang and Pagilla, 2010; De Laat *et al.*, 1999; Huston and Pignatello, 1999) and UV/TiO_2 or TiO_2 doped with other transition metals (Fouad and Mohamed, 2011; Yu *et al.*, 2010; Echavia, Matzusawa and Negishi, 2009; Han *et al.*, 2009; Ali and Hassan, 2008; Bavcon Kralj *et al.*, 2007; Singh and Muneer, 2004).

Ultraviolet (UV) photolysis was efficiently used for various pesticides degradation during last decade which revealed diverse mechanisms and the formation of by-products (Zabar *et al.*, 2011; Burrows *et al.*, 2002). Photolysis or direct irradiation will lead to the promotion of the pesticides to their excited states which can then undergo other processes such as homolysis, heterolysis or photoionisation as depicted in Figure 2.2 which adapted from (Burrows *et al.*, 2002).

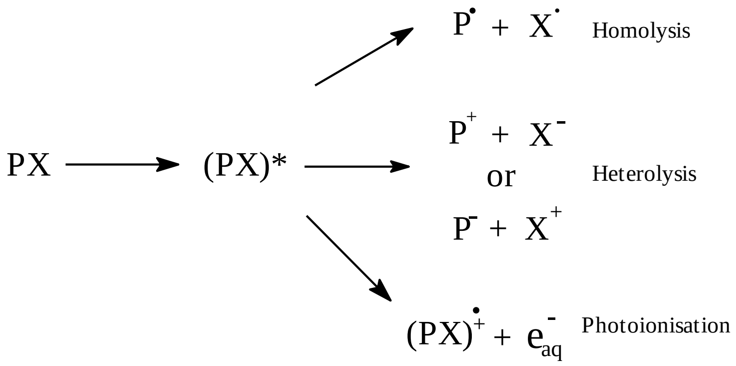


Figure 2.2: Possible chemical events taking place upon direct photolysis.

Furthermore, this system is better than others as (1) no added chemical materials needed, (2) most pesticide materials can be degraded in the reactor and (3) there is no need to use any absorbent media to act as the final polishing step (Shayeghi *et al.*, 2012).

However, the possibility of using photocatalytic reactions for the degradation of trace pesticides in water has been receiving much attention in recent years (Devipriya and Yesodharan, 2005). By far, the most investigated photocatalyst for the removal of organic pollutants from water is titanium dioxide, TiO_2. TiO_2 has proven to be the most suitable for widespread environmental applications due to its biological and chemical inertness, strong oxidising power, lower cost, and long-term stability against photocorrosion and chemical corrosion (Shifu and Yunzhang, 2007).

TiO_2 is insoluble in water and dilute acids. The catalyst is cheap and can also be activated with sunlight (Mehrotra, Yablonsky and Ray, 2005). It is found in nature in three forms: rutile, anatase and brookite. Rutile is the most common and the other two are comparatively rare. However, the pure anatase was revealed to have the best catalytic efficiency while pure rutile has the least (Devipriya and Yesodharan, 2005). Most of the literature describes the use of anatase (Chaudhary, Hassan and Grimes, 2009; Echavia, Matzusawa and Negishi, 2009; Han *et al.*, 2009; Chaudhary and Grimes, 2008; Lhomme, Brosillon and Wolbert, 2008).

It is believed that the photocatalytic degradation reaction of organic pollutants occurs on the surface of TiO_2, (Shifu and Yunzhang, 2007). When a semiconductor oxide for example, TiO_2 is irradiated with light (*hv*), electrons are promoted from the valence band (vb) to the conduction band (cb) thus, electron-hole is generated which shown in equation (2.1).

$$TiO_2 \xrightarrow{hv} TiO_2(e^- + h^+) \tag{2.1}$$

The electron-hole pair will initiate oxidation and reduction processes of adsorbed substrates. In aqueous solution, the electron then reduces the dissolve oxygen. Superoxide radical ions ($O_2^{\bullet-}$) are thus formed in equation (2.2), whilst, the •OH radicals are formed from the holes reacting with either H_2O or OH^- adsorbed on the TiO_2 surface (equations 2.3 and 2.4) (Shifu and Yunzhang, 2007; Rahman *et al.*, 2006; Devipriya and Yesodharan, 2005).

$$O_2 + e^-_{cb} \rightarrow O_2^{\bullet-} \tag{2.2}$$

$$H_2O + h^+_{vb} \rightarrow \bullet OH + H^+ \tag{2.3}$$

$$OH^- + h^+_{vb} \rightarrow \bullet OH \tag{2.4}$$

The formation of superoxide anion radicals, $O_2^{\bullet-}$ and hydroxyl radicals, •OH in aqueous medium thus accelerate the oxidation of pollutants to produce harmless species. Nevertheless, in order to remain these circumstances, the recombination of electron-hole pairs must be avoided by availability of enough electron acceptors in water. The most easily and available electron acceptor is molecular oxygen (Halmann, 1996).

Photocatalytic processes to degrade organic pollutants in water by utilising TiO_2 as a catalyst either in the form of unsupported suspended TiO_2 powder or in the form of TiO_2 immobilised on a substrate have been subject of extensive research recently

(Balasubramanian *et al.*, 2004). Although the illuminated aqueous dispersion of TiO_2 shows high photocatalytic activity due to the large surface area, the major drawback was the difficulty in the recovery of the photocatalyst after treatment (Gunlazuardi and Lindu, 2005). In response to the retrieving of TiO_2 after treatment, many researchers have introduced an immobilised catalyst such as using glass slide and silica gel as a support (Zabar *et al.*, 2012; Wong, Tan and Mohamed, 2011; Echavia, Matzusawa and Negishi, 2009; Ali and Hassan, 2008). Most of them reported that immobilised TiO_2 showed higher photocatalytic degradation compared with the suspension TiO_2. Another modification of immobilised TiO_2 was using ion doping which aimed at extending the photosensitivity of TiO_2 into the visible region in order to increase the efficiency of the catalyst toward the degradation of acephate and malathion particularly (Fouad and Mohamed, 2012; Fu *et al.*, 2012; Fouad and Mohamed, 2011). This new approach will be particularly relevant from the solar energy point of view (Devipriya and Yesodharan, 2005). In spite of these developments, the major key in the removal efficiency of organic pollutants are the variations in molecular structure as it induced variations in removal rates of AOPs (Wols and Hofman-Caris, 2012).

The Fenton process has been extensively studied well for its prospective application in unmanageable wastewater treatment (He and Lei, 2004). Furthermore, this system does not involve any TiO_2 catalysts, however the generation of hydroxyl radicals was between hydrogen peroxide and iron(II) salts as shown in the equation (2.5) (Esplugas *et al.*, 2002),

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + \bullet OH + OH^- \qquad (2.5)$$

however this process was sensitive to pH (Pignatello, 1992). The best condition was in acidic medium around pH 3 as iron precipitates at higher pH (Klamerth *et al.*, 2013; He and Lei, 2004). If the precipitation occurred, the salt content increased in the treated water. Due to this, it needs to be neutralised first, as it would give negative effect for certain purposes such as irrigation. Table 2.1 provides information to differentiate between different types of Fenton processes. The main difference lies in the use of both ferrous or ferric ions and whether the process is carried out in the presence or absence of energy sources (Ikehata and El-Din, 2006).

Table 2.1: Fenton processes.

Process	Oxidant(s)	Other chemical(s)	Other energy source
Fenton	H_2O_2	Fe(II) ions	None
Fenton-like	H_2O_2	Fe(III) ions	None
Photo assisted Fenton (Photo-Fenton)	H_2O_2	Fe(II) or Fe(III) ions	UV irradiation, visible light or UV/Vis (solar radiation)

2.6. Photochemical Wavelength Range

Sunlight contains about 60% of infrared region, whereas 37% is in visible region and only 3% in the ultraviolet region (Giese, 1976). The electromagnetic radiation is arbitrarily broken down into different region according to wavelength and the various regions are shown in Figure 2.3. Only a small part of the electromagnetic spectrum (above 400 nm to 800 nm) where it can be seen by the naked eye since the light appears as a colour. The ultraviolet rays are divided to the four regions which are UVA, UVB, UVC and Vacuum UV. The UVA range causes tanning, UVB damages the skin which causing sun burn that then may eventually induces skin cancer, while UVC is very effective to kill bacteria, viruses and microorganisms since this range also known as the germicidal range whereas the vacuum UV range which can only be transmitted in a vacuum as it is absorbed by almost all substances, including water and air (Mezughi, 2010).

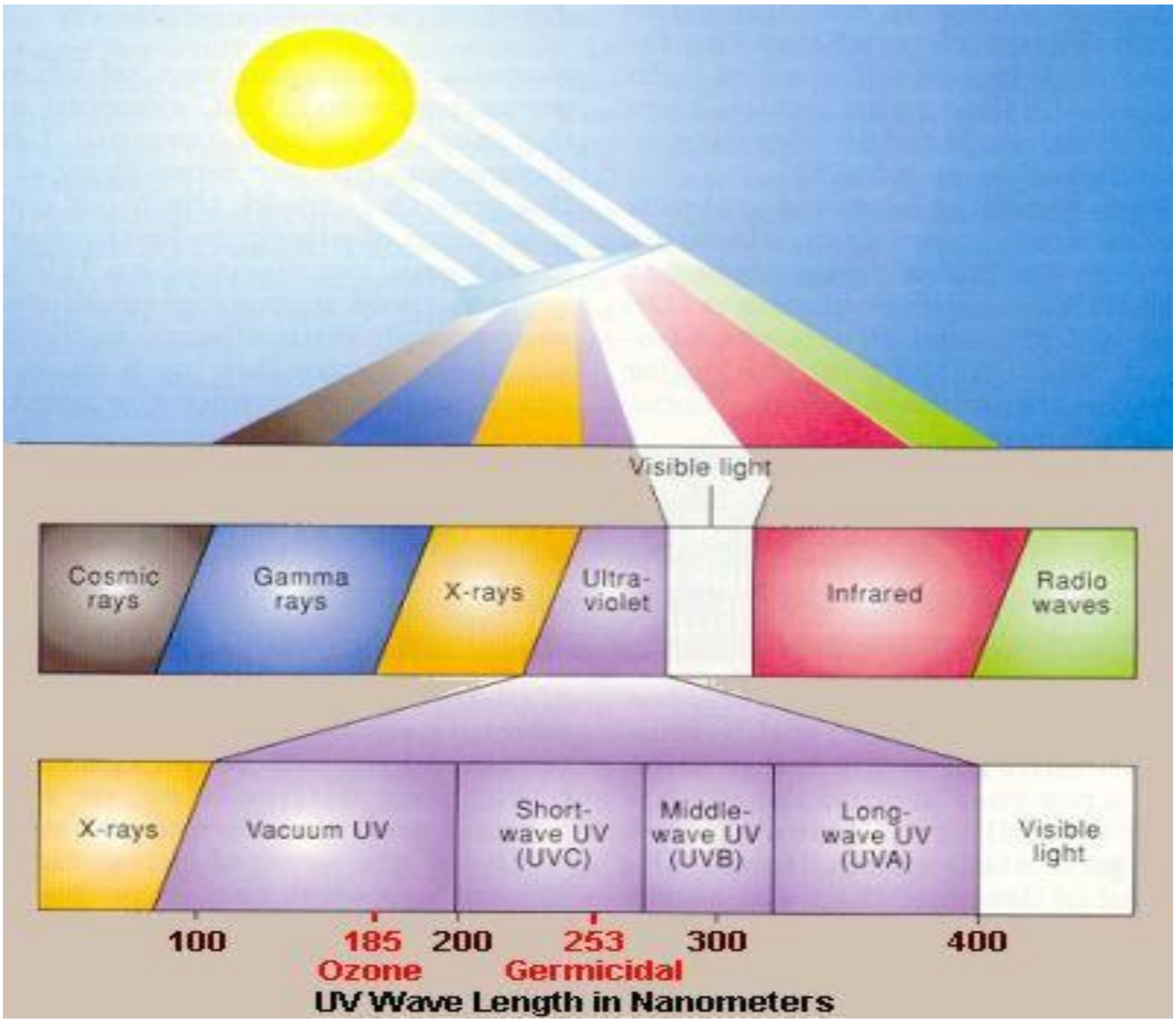


Figure 2.3: The electromagnetic spectrum (Cane, 2013).

2.7. Mercury Lamps

There are many types of lamps that artificially produce UV light where they being used for tanning, for counterfeit money detection, black light stage lamps and germicidal UV lamps and they basically produced by low and medium vapour pressure lamps (AAW, 2013). There are three types of mercury lamps:

2.7.1. Low pressure mercury lamp

The low-pressure mercury lamps contain mercury vapour that is at very low pressure (10^{-3} mmHg) and are operated at room temperature (Mezughi, 2010). The low UV pressure lamps are mostly used in germicidal UV application as they emit most of the energy in the germicidal wavelength of 253.7 nm which also known as part of the UVC spectrum (AAW, 2013).

2.7.2. Medium pressure mercury lamp

Once the mercury pressure in the lamp increases to 1 atm, the lamp is referred to as the medium-pressure lamp which emits the maximum emission at 365 nm. In this study, a medium pressure mercury lamp, purchased from the Photochemical Reactors Ltd, Reading, UK, is used to conduct all the experiment and its spectral distribution provided by the Company is shown in Figure 2.4.

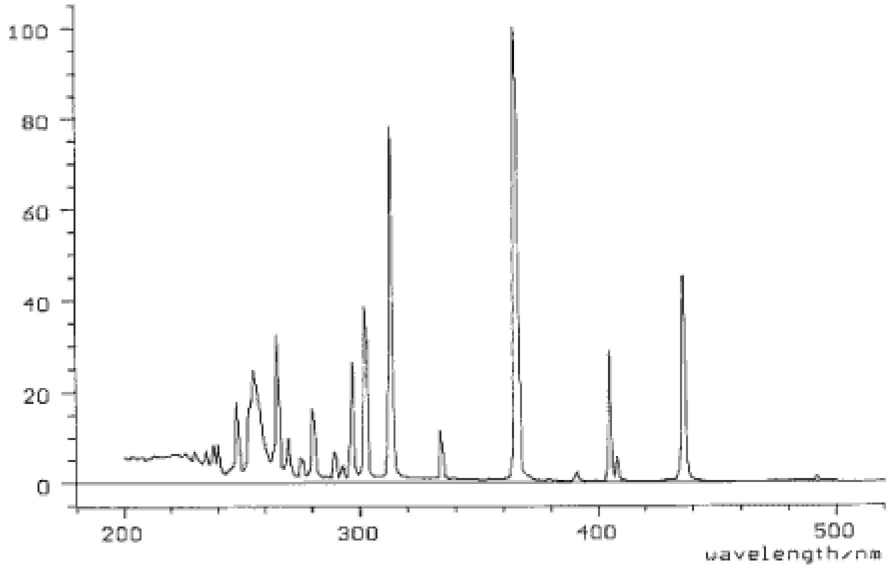


Figure 2.4: The output spectra for a medium pressure mercury lamp.

2.7.3. High pressure mercury lamp

Whereas for the high-pressure mercury lamp, the output is about 10 times of that from medium pressure mercury lamps and about 1000 times of that from low pressure mercury lamp. It is the most intense sources of UV radiation and more versatile lamps since any wavelength may be obtained. Unfortunately, the emission at 253.7 nm in the high pressure mercury lamps, however, is rather low (Mezughi, 2010) and the differences of output spectra is shown in Figure 2.5.

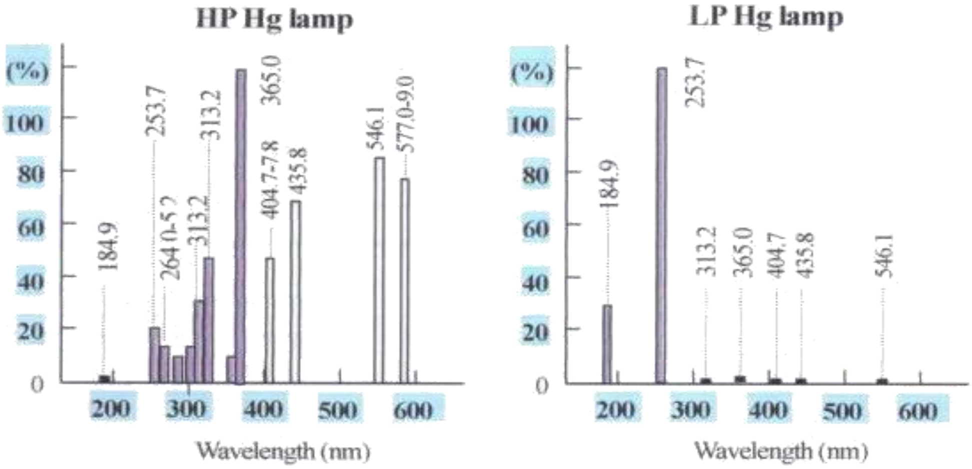


Figure 2.5: The output spectra for high (HP) and low pressure (LP) mercury lamps (SEN light. Corporation, 2013).

2.8. Overview of the Pesticide Usage in Malaysia's Agricultural Sector

Since 2004, the annual pesticide consumption is estimated around 51, 065 metric ton of pesticides; however herbicide dominates the markets in Malaysia as it is being used in plantation crops (Yek, 2013). There are many manufacturers of pesticide in Malaysia and Table 2.2 show several top companies with their products and categories. Most of these companies discharge their wastewater effluent streams into the environment without any treatment. In addition, obsolete pesticides are also disposed off into the environment without any treatment. The Malaysian government has introduced new legislation and most of these chemical industries, including pesticides manufactures, now need to install suitable treatment systems to treat their wastewater streams. The main aim of the work described in this thesis is to optimise a photolytic cell system suitable for the treatment of three most widely produced and used pesticides in Malaysia, namely acephate, glyphosate and malathion.

In Malaysia, large areas of land have been devoted for agriculture where rubber and oil palm are two major plantation crops with 0.1 and 4.8 million ha of cultivation area respectively in 2011 (DOA, 2013). Meanwhile, rice-growing is another important agricultural activity in Malaysia (Mansor, 1996).

Table 2.2: The main manufacturers/distributors of pesticides in Malaysia.

Company name	**Products**	**Category**	**Website**
Fumakilla Malaysia Berhad	Insect repellents Insecticides Rodenticides	Exporter Distributor Manufacturer	*www.texchemgroup.com/business/fumakilla.php*
Halex Industries (M) Sdn. Bhd.	Fungicides Herbicide Insecticides Plant growth Regulators Rodenticides	Importer Exporter Distributor Manufacturer	*www.halex-group.com/section/halex_industri/industri_about_us.html*
Hextar Chemicals Sdn. Bhd.	Other pesticides Algicides Fungicides Herbicides Insecticides Molluscicides Nematicides Plant growth Regulators Rodenticides Virucides	Exporter Distributor Manufacturer Developer Trader	*www.hextar.com/*
Imaspro Resources Sdn. Bhd.	Fungicides Herbicides Insecticides	Exporter Distributor Manufacturer	*www.imaspro.com/*
Kenso Corporation (M) Sdn. Bhd.	Fungicides Herbicides Insecticides Plant growth Regulators Rodenticides	Exporter Distributor Manufacturer	*www.kenso.com.my/*

Malaysia is located in Southeast Asia, close to the equator and shares borders with Thailand, Brunei and Indonesia. The country consists of 14 provincial states; 12 states are in the Peninsular Malaysia (west Malaysia, formerly known as Malaya) and two large states on the island of Borneo (East Malaysia) (Mansor, 1996). There is approximately 329 847 km^2 of land area in Malaysia (CIA, 2013) and the climate is hot (~ 30°C) and humid with considerable rainfall throughout the year. It is drained by more than hundred river systems (Mansor, 1996). Thus, this provides suitable deltas for the rice cultivation activity. The river stream with the distribution of major rice granary area in Malaysia which adapted from Mansor (1996) is shown in Figure 2.6.

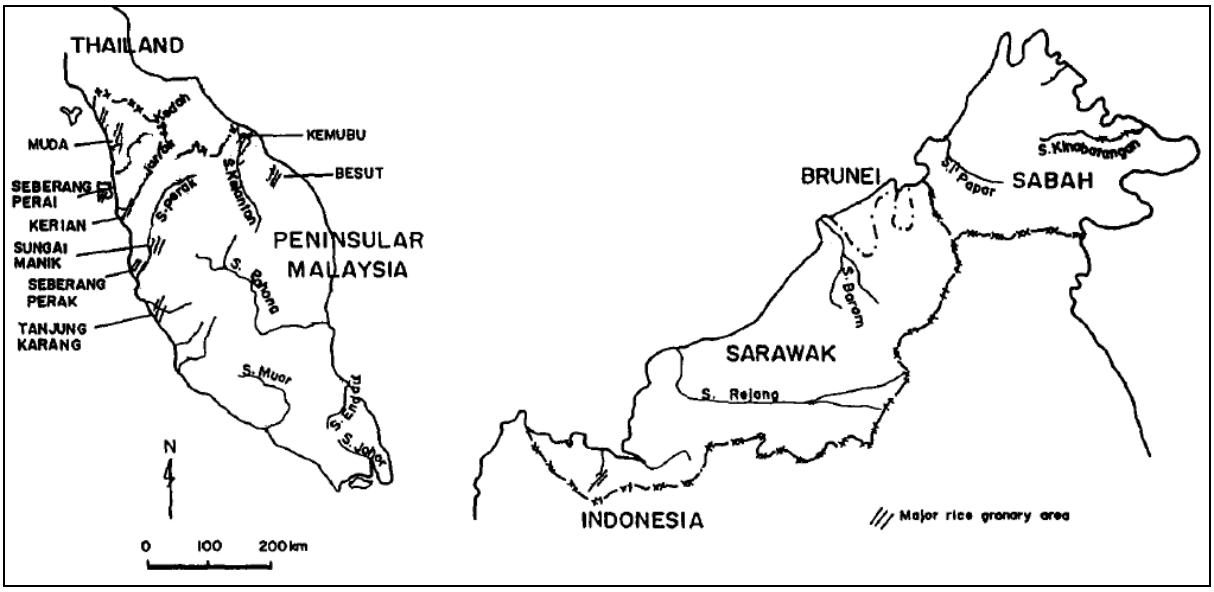


Figure 2.6: The main river systems and major rice granary area in Malaysia.

Rice is grown on a total harvested area of approximately 158 million hectares and about 90% of the rice in the world is grown in Asia (Seck *et al.*, 2012) where around 0.68 million ha is cultivated in Malaysia in 2011 (DOA, 2013). There are four main growth cultivation areas which are irrigated rice field, deep water or floating rice field, rainfed lowland and upland rice field cultivation area; the irrigated system is a dominant system which being used in Malaysia . Three types of rice cultivation areas are shown in Figure 2.7

Figure 2.7: The type cultivation area of (a) irrigated rice field, (b) lowland rice field and (c) upland rice field (Seck *et al.*, 2012).

Due to the nature of the cultivated area (warm and humid environment), it easily attract a proliferation of insects. Of all possible pest control measures, majority of farmers prefer chemical control method due to its immediate results. Acephate is a popular product and widely used to protect rice from pests (Kong *et al.*, 2012). Nevertheless, it is not only insect threat that needs to be treated in the paddy field, as the favourable tropical climate also helps to trigger the massive growth of weeds as well (Mansor, 1996).

Glyphosate herbicide is one of the major weed control products. It is being used in oil palm plantations and other major crop areas (such as paddy field, rubber and coconut plantation) with the total volume of glyphosate marketed in Malaysia is estimated to be about 15 million litres, which is valued around RM 250 (£50) million a year (Raman *et al.*, 2010).

According to the MPOB (2013), the oil palm planted area reached 5.00 million ha in 2011 which is an increase of 3.0% against 4.85 million ha recorded the previous year. Palm oil is one of the 17 major oils traded in the global edible oils and fats market. Palm oil is derived from the mesocarp of the palm fruit (Figure 2.8(a)), while palm kernel oil is derived from the kernel of the fruit (Zainudin, Abu Bakar and Muhamad, 2009). The quality and quantity of the fruits and oil production could be reduced if the oil palm trees are attacked by a variety of insects. Many pesticides are used to control these pests including cypermethrin, acephate and malathion. In oil palm plantations, cypermethrin and acephate are commonly used to control bagworms (*Metisa plana*, *Pteroma pendula*, *Mahasena corbetti*), nettle caterpillars (*Darna trima*, *Setora nitens*, *Darna diducta*, *Setothosea asigna*) and rhinoceros beetles (*Oryctes rhinoceros*) (Zainudin, Abu Bakar and Muhamad, 2009; Yeoh *et al.*, 2006) while malathion is used to control aphids (USEPA, 2004).

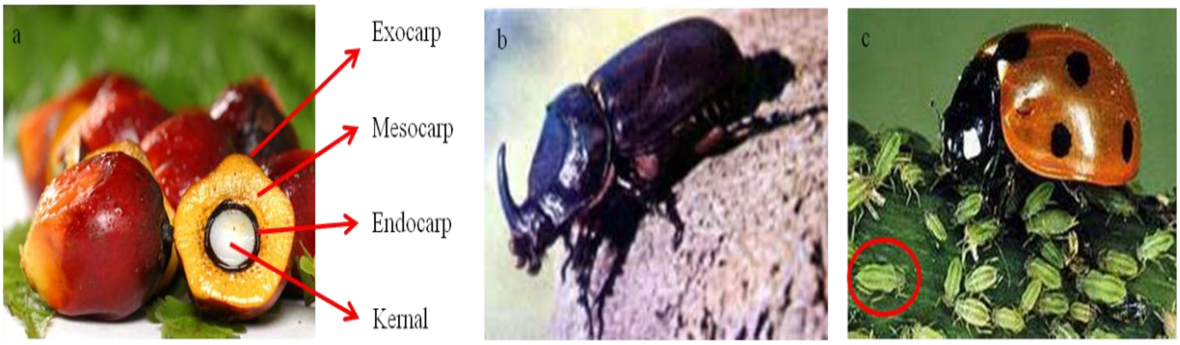


Figure 2.8: (a) Structure of oil palm fruit, (b) rhinoceros beetles and (c) aphids in red circle with a comparison size of ladybird.

It is clear that one type of pesticide will not be able to solve and protect the crops from all pests because different pests required other approaches of treatment. About 250 types of chemicals compound which 100 types of insecticide, 50 types of weed killer, 50 types of fungicide, 20 kinds nematicides and 30 kinds of other chemical substances are being used in the agricultural sector (Fuad *et al.*, 2012).

The recommended typical application rate for the weed control in the oil palm plantation is 1.2 kg/ha (Wibawa *et al.*, 2010). With 5.00 million ha of cultivation area and assuming only a one time application applied to all the area, about 6 million kg of glyphosate active ingredients is being consumed throughout a year.

Another instance is the used of malathion where it is being used on a number of crops, thus it is difficult to characterise its application in every scenario of treatment in which it may be used. Generally, the maximum application rate of malathion to control aphids is 5.8 kg/ha/year (Kawate and Tarutani, 2005). If this rate is being used to control just 1% of the aphids' infestations on the oil palm cultivation area with one time of malathion application, this would lead to about 29×10^4 kg of malathion consumption in a year. This amount is acceptable as malathion is reported to be consumed at a rate of about 25×10^6 kg/year worldwide and of that value, about 2×10^6 kg/year of malathion has been consumed in Mediterranean countries alone (Aaron and Oturan, 2001).

The consumption of pesticide discussed in this section showed that a tremendous amount is being used in the agricultural sector. Therefore, within another year we need to concern their existence and its usage in the environment. There is a study recently reporting the glyphosate resistant weed in Malaysia (Lee and Ngim, 2000). This happened as some farmers desperately rely on intensive use of herbicide with as many as six to eight applications per annum although integrated pest management is introduced by the Malaysian government.

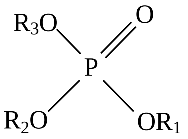
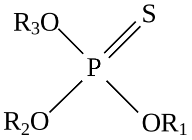
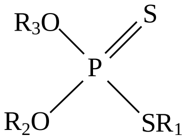
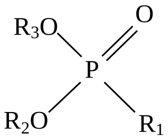
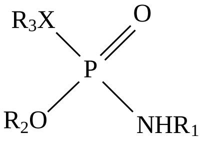
As acephate, glyphosate and malathion are being produced and also widely used in Malaysia, specifically in major crop areas in the agricultural sector, so these three pesticides were selected as the organic pollutants and their details, including physical and chemical properties, are discussed in the next sections.

2.9. Selection of Organic Pollutants

Pesticides are substance that can directly kill an unwanted organism or otherwise control it by inhibiting the reproductive process (Baird, 1999). Their use and dispersion in the environment has mainly occurred since the late 1940s and they have become relatively ubiquitous pollutants in human and animal tissues, in soils and crops, and in groundwater, rivers and lakes (Alloway and Ayres, 1997). It has been known for many years that pesticides sprayed on land reach water courses (Evans, 2009). The large scale applications of these pesticides can lead to situations in which they moved from agricultural fields to the aquatic environment through direct run-off, leaching, careless disposal of empty containers and equipment washing (Konstantinou, Hela and Albanis, 2006).

The four general categories of these pesticides are insecticide, fungicides, herbicides and bactericides (Badawy *et al.,* 2006). In this study, the selected pesticides were acephate, glyphosate and malathion. All of them were classified as organophosphate pesticide. Sud and Kaur (2012) has defined the organophosphate pesticide as synthetic compounds which are usually esters, amides, or thiol derivatives of phosphoric, phosphonic, phosphorothioic, or phosphonothioic acids and the basis of their structure is shown in Table 2.3. It was noticed that glyphosate is not listed in the table given; however, based on United Kingdom Pesticide Action Network, PAN-UK (1996) glyphosate is considered as an organophosphate herbicide as it contains carbon and phosphorous in its molecule structure. Nevertheless, it is not a cholinesterase inhibitor thus, does not affect the nervous system in the same way as other organophosphate insecticides. The detailed description of the three pesticides, acephate, glyphosate and malathion is given in the following subsection.

Table 2.3: Classification of organophosphorous pesticides on the basis of their structure (Sud and Kaur, 2012).

Type	**General structure**	**Pesticides**
Phosphates		Chlorfenvinphos Dichlorvos Monocrotophos
Thiophosphates		Chlorpyrifos Diazinon Fenitrothion Methyl-parathion
Dithiophosphates		Dimethoate Malathion Phorate
Phosphonates		Trichlorfon
Phosphoramides		Acephate Fenamiphos Methamidophos

Where R_1, R_2 and R_3 are any alkyl or aryl groups and X may be S or O.

2.9.1. Acephate

Acephate (*O,S*-dimethyl *N*-acetylphosphoramidothioate), containing P-S, P-N and P-O groups is a broad-spectrum organophosphorus insecticide(Han *et al.*, 2009). It is also known as orthene (Echavia, Matzusawa and Negishi, 2009). Acephate has a high water solubility of 700 mg/mL (Downing, 2000) and it has been reported that acephate is poorly absorbed onto soil therefore it is mobile thus, its leaching to the aquatic environment is highly at risk (Chai *et al.*, 2010). The chemical structure of acephate is shown in Figure 2.9.

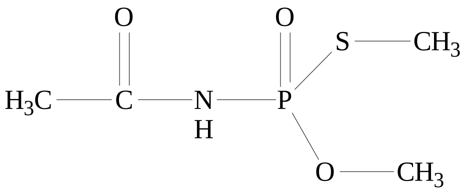


Figure 2.9: Structure of acephate.

Acephate was introduced in Taiwan in 1972 to control insects damaging vegetables, cotton, tobacco, rice and flowers (Yen, Lin and Wang, 2000). Acephate is also being used in food handling establishments, on ornamental plants both in greenhouse and outdoors (such as Christmas trees and cut flowers) and around homes (Han *et al.*, 2009; Rahman *et al.*, 2006). It is also being used in controlling grasshopper, aphids, gypsy moth, bronze and rhinoceros beetles, bagworms and nettle caterpillars (Yeoh *et al.*, 2006).

Acephate is a cholinesterase inhibitor. Generally, when acephate is applied to plants, it is carried to leaf surfaces where it is eaten or comes in contact with pests. According to Pesticide Management Education Program, PMEP (2013), the electrical switching centre which is the synapses are found throughout the nervous systems of humans, other vertebrates, and insects. Muscles, gland and nerve called 'neurons' are stimulated or inhibited by the constant firing of signal across these synapses. Stimulating signals are usually carried by a chemical called 'acetylcholine'. Stimulating signals are discontinued by a specific type of cholinesterase enzyme, acetylcholinesterase, which breaks down acetylcholine. These important chemical reactions are usually going on all the time at a very fast rate, with acetylcholine causing stimulation and acetylcholinesterase ending the signal. If cholinesterase-affecting insecticides are present in the synapse, this situation is thrown out of balance. The presence of cholinesterase inhibiting chemicals prevents the breakdown of acetylcholine which can then build up, causing a "jam" in the nervous system.

According to the application of acephate to control insect in the paddy field, the possibility of it to leach to the ground water is high due to its properties aforementioned. There is 46 million hectares of rice cultivation area and of it, about 30, 783 hectares, ha is an irrigated rice cultivation area in China (Defeng, 2013). The typical application rate of acephate to treat pest like swarming caterpillar is 1.2 kg/ha (Khajuria, 2013) and assuming only 1% of treated area with one application per year, the applied acephate used is 369.4 kg/year. This amount will be considerably higher if it is being used for prolonged time and therefore this will be of a great concern about environmental and health issues (Fu *et al.*, 2012).

Due to this, Rahman *et al.* (2006) who claim that they are the one who did a detailed study of the photocatalytic mineralisation of acephate in aqueous suspensions of TiO_2 has found three intermediates products in their study. They also used various types of oxidising agent such as hydrogen peroxide, H_2O_2 and potassium bromated, $KBrO_3$.

Han *et al.* (2009) have also investigated the influence of substrate and catalyst concentration on acephate decomposition using nano-TiO_2. It was found that the acephate can be degraded and mineralised with 4 g/L concentration of TiO_2. They found three primary products under acidic condition and claimed that their study was the first comprehensive study to provide detail insight on the acephate degradation reaction pathways by photocatalysis. They also reported that both sulphur and the nitrogen in acephate are potential sites for oxidation and the reaction pathway is shown in Figure 2.10. Among the degraded product obtained, there was methamidophos detected in their study which was more toxic to humans and hard to be degraded.

Photocatalytic degradation on acephate using UV light and immobilised TiO_2 has been investigated by Echavia, Matzusawa and Negishi (2009) as well. They reported the photocatalytic degradation of acephate follows the apparent first order kinetic law and confirming the acephate decomposition is due to the photocatalysis process.

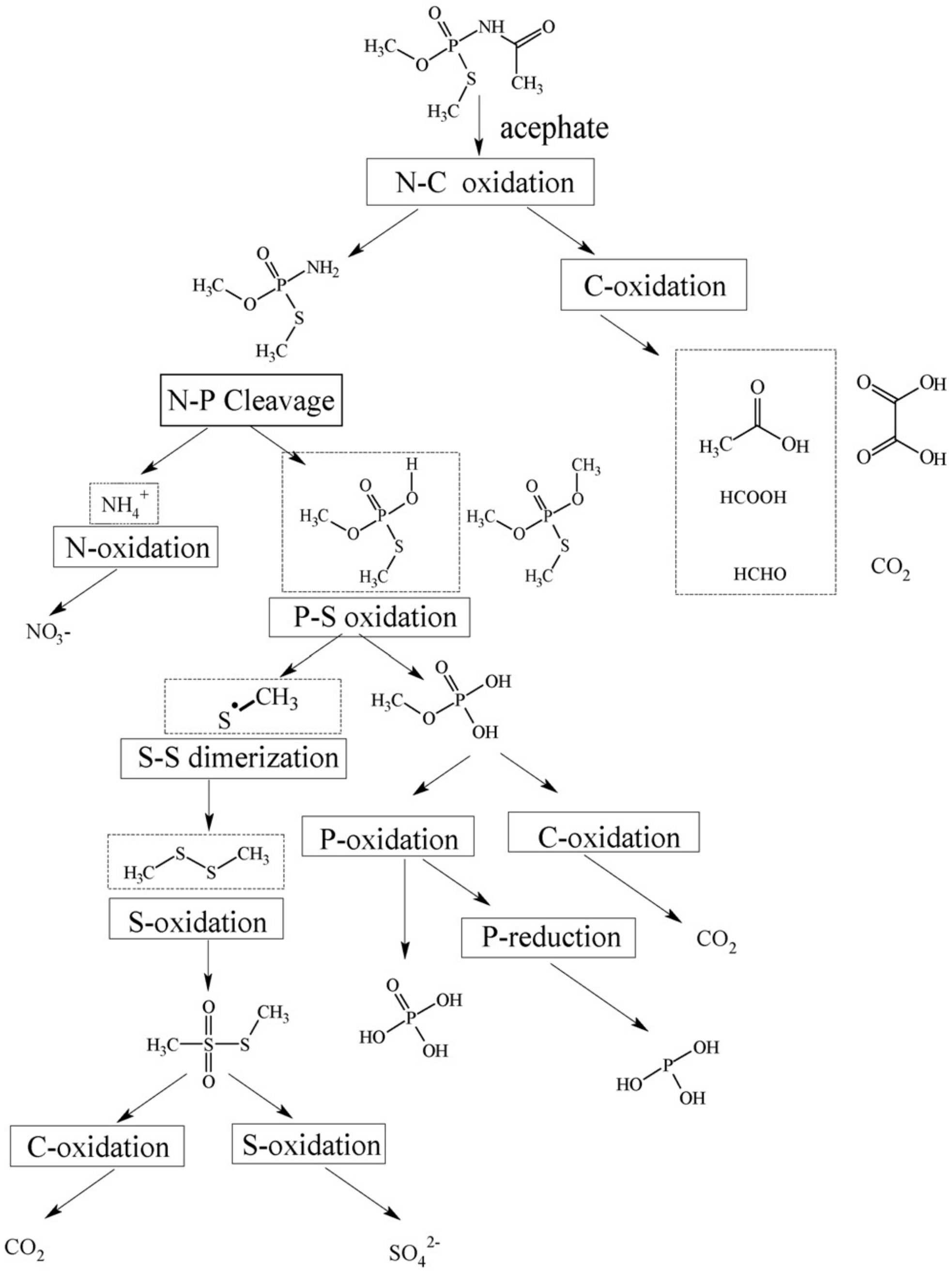


Figure 2.10: Acephate degradation reaction pathways by photocatalysis adapted from Han *et al.* (2009). The dotted squared is the possible product that cannot be measured by the authors.

The limited publications above on photocatalytic degradation on acephate were done under UV light irradiation. However, recent study by Fu *et al.* (2012) has been done on visible light irradiation in the presence of modified $ZnFe_2O_4$-TiO_2 photocatalyst. They reported that the degradation rate of acephate is affected by initial concentration of acephate, pH, catalyst dosage and H_2O_2 dosage.

A List of byproducts detected during photocatalytic studies collected from various publications is shown in Table 2.4.

Table 2.4: List of by-products detected during photocatalytic degradation of acephate according to the literature.

Literature	Name of the compound	Structural formula	Remarks
Rahman *et al.* (2006)	(1-hydroxy-ethyl)-thiophosphoramidicacid *O,S*-dimethylester	$(CH_3)C(OH)(H)NHP(O)(SCH_3)(CH_3O)$	Intermediate
	(1-hydroxy-ethyl)-thiophosphoramidic acid monomethyl ester	$(CH_3)C(OH)(H)NHP(O)(OH)(CH_3O)$	Intermediate
	(1-hydroxy-ethyl)-thiophosphoramidic acid *S*-methyl ester	$(CH_3)C(OH)(H)NHP(O)(SCH_3)(OH)$	Intermediate
Han *et al.* (2009)	Phosphoramidothioic acid, *O,S*-trimethyl ester	$CH_3O(CH_3S)P(O)NH_2$	Intermediate
	Phosphorothioic acid, *O,O',S*-dimethyl ester	$CH_3O(CH_3S)P(O)OCH_3$	Intermediate
	Monomethyl phosphate	$CH_3O(HO)P(O)OH$	Intermediate
	Phosphorous-acid	$P(OH)_3$	Intermediate
	Methyl methanethiosulfonate	$CH_3S(O)_2SCH_3$	Intermediate
	Ethanedioic acid	$(COOH)_2$	Intermediate
	Phosphoric acid	H_3PO_4	Final product
	Carbon dioxide	CO_2	Final product
	Sulphate	SO_4^{2-}	Final product
	Nitrate	NO_3^-	Final product
	Phosphate	PO_4^{3-}	Final product
Echavia, Matzusawa and Negishi (2009)	Acetic acid	$C_2H_4O_2$	Final product
	Formic acid	CH_2O_2	Final product
	Glycolic acid	$C_2H_4O_3$	Final product
	Sulphate	SO_4^{2-}	Final product
	Nitrate	NO_3^-	Final product
Fu *et al.* (2012)	Sulphate	SO_4^{2-}	Final product
	Nitrate	NO_3^-	Final product
	Phosphate	PO_4^{3-}	Final product
	Carbonate	CO_3^{2-}	Final product

2.9.2. Glyphosate

Glyphosate (N-(phosphonomethyl)glycine), is a broad spectrum, post emergence and non-selective foliage herbicide which is commonly used for the control of many annual and perennial weeds, introduced by Monsanto Company, U.S in the early 1970s (Manassero *et al.*, 2010; Chen *et al.*, 2007a; Shifu and Yunzhang, 2007; Baylis, 2000; Woodburn, 2000). Glyphosate is a systemic herbicide (Schuette, 1998) and commonly absorbed into the leaves and translocated through the plant to the roots and rhizomes via the phloem (Merás, Díaz and Franco, 2005). The symptoms of gradual wilting, yellowing plant, complete browning of above-ground growth and deterioration of weeds roots often develop slowly and normally the visible effects on most annual weeds occur within two to four days and may not occur for seven days or more on most perennial weeds (Schuette, 1998). Glyphoste application was at soybean, maize, cotton field, ornamental, turf, right-of-way (Borggaard and Gimsing, 2008; USEPA, 1993) and its structure is shown in Figure 2.11.

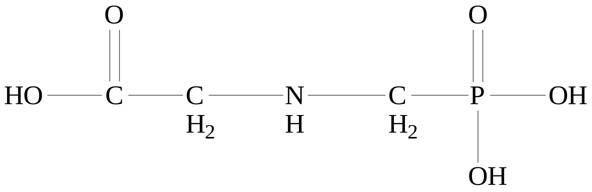


Figure 2.11: Structure of glyphosate.

Glyphosate is among the most widely used pesticide by volume in the U.S. where approximately 5 to 9 million ha were treated with 8.5 million kg of glyphosate annually (USEPA, 1993). This wide use can be ascribed to its low toxicity and very limited risk of leaching due to its strong affinity to bind to soil (Borggaard and Gimsing, 2008). If soil particles containing glyphosate are washed or blown into lakes or streams the majority of the glyphosate will remain adsorbed to the soil although glyphosate is highly soluble in water (12,000 mg/L) (Schuette, 1998). Furthermore, it is readily degraded by soil microbes to aminomethylphosphonic acid (AMPA), which could further degrade to carbon dioxide, phosphate and water (Chen *et al.*, 2007a; USEPA, 1993). Due its low toxicity, the maximum contaminant level for glyphosate in drinking water at U.S was 0.7

mg/L (USEPA, 2013b) which was higher than 0.0001 mg/L for European level set (European Community, 1998). These huge gap permissible levels occurred because the threshold level at European is set for all pesticide while U.S maximum level is based on the toxicity test on the glyphosate itself (Borggaard and Gimsing, 2008).

In spite of glyphosate usage environmentally safe, recent investigations indicate toxicity to amphibians (Puglis and Boone, 2011; Relyea, 2009) and leaching problems (Siimes *et al.*, 2006; Landry *et al.*, 2005) with it usage where the degradation of glyphosate and its soil sorption exhibit great variation depending on soil composition and properties (Gimsing, Szilas and Borggaard, 2007). High soil sorption of glyphosate to solids results in immobilisation, while a weak absorption can leach the glyphosate to the surface and ground water. Furthermore, most of pesticides absorption to the soil particles are of moderately to weakly strength, due to have only one or two functional group unlike gyphosate which have three functional group (carboxylate, amino and phosphonate group), thus strongly absorbed to soil minerals (Borggaard and Gimsing, 2008). However, long term use of glyphosate to control weeds on coarse-textures soil materials for example may leach out glyphosate to water body.

A study by Botta *et al.* (2009) proved that glyphosate and AMPA were most detected in the Orge River, France in 2009 and usually exceeded the European quality standard concentration. They also reported that the contamination was from urban uses rather than agricultural uses due to application on impervious surface like roads, sidewalks and lawn. The occurrence of glyphosate in surface water of two small tributaries of the river Ruhr in North-Rhine-Westphalia, Germany with a maximum concentration of 0.0005 mg/L was also detected (Skark *et al.*, 1998). Therefore, it is worthwhile to reconsidering the fate of glyphosate in the environment since the tremendous quantities of glyphosate used has increased the concerns of its impact on the environment, where the glyphosate might enter through various routes during its manufacture, use and discharge (Chen, Hu and Wang, 2012; Hu, Zhao and Sorohan, 2011; Manassero *et al.*, 2010).

The photodegradation of glyphosate using UV light in water by Lundhoie and Friestad (1986) has shown that glyphosate can be degraded although it has been reported that its photodegradation process in water was negligible (MONSANTO, 2005). The combination of hydrogen peroxide and UV radiation for glyphosate degradation in water was a suitable and very simple process to remove glyphosate from water as well (Manassero *et al.*, 2010). The glyphosate decomposition stable compounds have been identified in their study. Whereas Chen *et al.* (2007a) reported that glyphosate can be efficiently photodegraded in the ferrioxalate system. Whilst the other study by Chen *et al.* (2007b) reported that the presence of Fe(III)-pyruvate and Fe(III)-citrate with UV irradiation have induced photodegradation of glyphosate in aqueous solutions. Photo-Fenton (Fe(III)/H_2O_2/UV) reaction on the degradation of glyphosate also showed a slight total organic carbon (TOC) loss within 120 minutes (min) irradiation (Huston and Pignatello, 1999). The most common study regarding the removal of glyphosate in aqueous solution was by employing a photocatalyst in the degradation process. The study on the photocatalytic degradation of glyphosate by TiO_2 photocatalyst has been studied by Shifu and Yunzhang (2007). This study showed that glyphosate is easily degraded by TiO_2 assisted photocatalysis in aqueous dispersion under irradiation by UV light. It also stated that using various oxidants (H_2O_2, $K_2S_2O_8$ and $KBrO_3$) and heavy metal ions (Fe(III) and Cu(II)) increased the photocatalytic degradation efficiency of glyphosate if complied with the optimum usage. A similar study has been done by Muneer and Boxall (2008) in order to study the degradation products of glyphosate. Another study on the photocatalytic degradation of glyphosate showed that the higher degradation rate is obtained at higher flow rate used in the small scale plug flow simulation reactor (Chen, Hu and Wang, 2012). While Echavia, Matzusawa and Negishi (2009) showed that photocatalytic degradation of glyphosate using TiO_2 immobilised on silica gel appeared to be governed by both adsorption and photocatalytic reaction; they also observed the production of by-products during the photocatalysis process. They suggested that a longer irradiation time of treated water needs to be done since complete mineralisation was not achieved within the 120 min time frame used in their study. A recent study however, used TiO_2 nanotubes doped with 0.15% cerium and the photocatalytic of the glyphosate was enhanced where 76% of degradation was achieved within 1 h UV irradiation compared to 45% when using TiO_2 nanotubes (Xue *et al.*, 2011).

A list of by-products detected during photocatalytic studies collected from various publications is shown in Table 2.5.

Table 2.5: List of by-products detected during photocatalytic degradation of glyphosate according to the literature.

Literature	Name of the compound	Structural formula	Remarks
Manassero *et al.* (2010)	Glycine	$C_2H_5NO_2$	Final product
	Formaldehyde	CH_2O	Final product
	Formic acid	CH_2O_2	Final product
	Ammonium	NH_4^+	Final product
	Nitrate	NO_3^-	Final product
	Phosphate	PO_4^{3-}	Final product
Chen *et al.* (2007a)	Sarcosine	$C_3H_7NO_2$	Final product
	AMPA	$C_7H_{10}N_2O_4$	Final product
Muneer and Boxall (2008)	Sarcosine	$C_3H_7NO_2$	Final product
	Glycine	$C_2H_5NO_2$	Final product
Echavia, Matzusawa and Negishi (2009)	Formic acid	CH_2O_2	Final product
	Glycolic acid	$C_2H_4O_3$	Final product
	Phosphate	PO_4^{3-}	Final product
	Nitrate	NO_3^-	Final product

2.9.3. Malathion

Malathion (diethyl(dimethoxythiophosphorylthio) succinate, one of the most widely applied organophosphorus insecticides (Bavcon *et al.,* 2007; Uygun *et al.,* 2007) , basic uses for insect pest control on cherry, cottonwood, parsnip, walnut, watermelon, wheat, indoor stored commodity and empty storage facilities for barley, corn, oats, rye, ornamental lawns and nonagricultural areas (USEPA, 2009). In 2007, malathion being ranked as the second out of tenth most commonly used organophosphate insecticide in the United States (Grube *et al.*, 2011). The structure of malathion is shown in Figure 2.12.

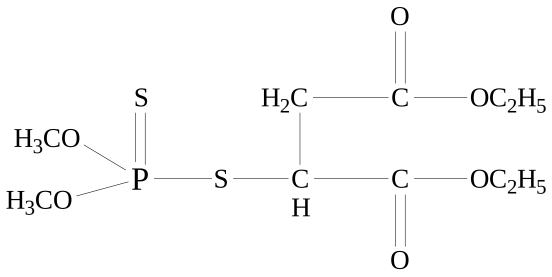


Figure 2.12: Structure of malathion.

Malathion has been used in three major regional eradication programmes in the U.S, specifically Boll Weevil eradication on cotton (5.1 million kg/year), Medfly control (362 874 kg/year) and mosquito control (214 100 kg/year) (Newhart, 2006). It was also being used in the pharmaceutical field as a pediculicide for the treatment of head lice and their ova (USEPA, 2009). Malathion is considered as moderate to high mobility in most soil types including sand, loam, sandy loam and silt loam soil (National Pesticide Information Centre, 2013; Newhart, 2006). Malathion is slightly toxic as its mode of action is through inhibition of cholinesterase enzyme and its metabolite is malaoxon which appeared to be more toxic than its parent compound (Uygun *et al.*, 2007). Due to this matter, the Standing Committee on the Food Chain and Animal Health has voted against the inclusion of malathion in Annex I of Directive 91/414/EEC in September 2006 however, it has been amended to include malathion back in March 2010 (European Community, 2010) as new assessment stated all metabolites of malathion are malathion toxic equivalents (EFSA, 2009).

According to the latest information malathion is still being used in agriculture and had a high request in the market, so there is a need to monitor its usage and dissipation into the environment to avoid pollution in surface or groundwater. Recently, a study showed that the malathion was detected in maximum concentration of 0.02 mg/L in deep wells located at agricultural land in the Qazvin province of Iran (Karyab *et al.*, 2013). However, the contamination does not exceed the health advisory value for the drinking water standard (0.2 mg/L) (USEPA, 2013a). Nevertheless, another study reported that Karaj River (one of the biggest river in Iran) has being polluted with malathion (3.0 mg/L) after a month of its application (Shayeghi, Khoobdel and Vatandoost, 2007). Malathion also among the nine compounds which was frequently detected from 17 compounds studied by Gao *et al.* (2012) in the 16 source water reservoirs of the Haihe

River basin in China. Malathion was also detected in fish tissues samples at levels below the maximum residue limits (Malhat and Nasr, 2011). Beside its contamination of surface water, it also has an adverse effect on semen quality among exposed farmers during usage and handling (Hossain *et al*., 2010). It also increased the mortality of tadpoles (Puglis and Boone, 2011; Gurushankara, Krishnamurthy and Vasudev, 2007). Overall, it can be said that malathion can be a threat if it is not being monitored thoroughly although the current studies just showed the low detection values of malathion.

2.9.4. Suitability of AOPs

In view of this, AOPs is one of the considerable technologies for eliminating organophosphorus pesticide such as malathion. Numerous studies regarding photocatalytic degradation of malathion have been published and among the studies only several deal with the commercial formulation of malathion and most of them using the heterogeneous photocatalysts. They were either in the single or doping mode, for example TiO_2 (Bavcon Kralj *et al.*, 2007; Doong and Chang, 1997; Muszkat and Bir, 1995), TiO_2/ZnO (Ali and Hassan, 2008), Au/Pd/TiO_2 (Yu *et al.*, 2010) and Au/TiO_2 (Fouad and Mohamed, 2011) for the removal of a pollutant. There were also studies using photo-Fenton (Zhang and Pagilla, 2010; Huston and Pignatello, 1999) in order to degrade malathion. The authors compared different factors such as effect of catalyst loading, amount of oxidant used (H_2O_2), pH and effect of light intensity. Meanwhile, photolysis (sunlight and UV light) on malathion has been studied (Shayeghi *et al.*, 2012; Druzina and Stegu, 2007; Chukwudebe *et al*., 1989; Lee Wolfe *et al.*, 1977) as well where the result of kinetics and formation of by-products has been obtained. Moreover, it is important to remark that UV can degrade organic compounds by direct photolysis as a consequences of light adsorption, thus it is a vital to know the photolysis process first in order to control its interference and evaluate the efficacy of the catalyst in the photocatalytic process (Dantas *et al.*, 2010). Studies on the removal of malathion in the presence of oxidants such as hydrogen peroxide (Aires *et al.*, 1992) and ozone (Lin *et al.*, 2012) have been done where the hydrogen peroxide has increased the decomposition rate of malathion at short irradiation times (120 min) at 25°C whereas for the ozone, the highest degradation rate was occurred in the pH 3.5.

However, there is a lack of study on the effect of heavy metal towards photolytic degradation of commercial formulation of malathion. In mixed industrial effluent, it has been reported (Chaudhary, Hassan and Grimes, 2009; Chaudhary and Grimes, 2008; Shifu and Yunzhang, 2007; Chaudhary, Grimes and Hassan, 2001) that the presence of heavy metal ions can significantly influence the removal of the organic pollutant as they are often contained in wastewater.

2.10. Commercial Formulation Pesticide.

Most of the publications mentioned in the previous sections focussed on the use of model concentrated pesticide solutions because the main aims of these studies were to identify the production of intermediate products during the photocatalytic processes. However, a very few studies (Bavcon Kralj *et al.*, 2007; Huston and Pignatello, 1999) have been done on the commercial formulation pesticides. The commercial formulation pesticides basically contain both active and “other” ingredients, which are considered trade secrets and are not public knowledge (Puglis and Boone, 2011). The “other” ingredients in the formulation generally called as adjuvant. Its role in commercial pesticide solutions are (1) to improve the efficiency of the pesticides by increasing the plants or insects’ assimilation in order to develop selectivity towards specific target and (2) to enhance the solubility of the pesticides in water or to stabilize the emulsion mixture. Adjuvant is defined as a substances added separately or within the pesticide solution (Hazen, 2000) in order to modify the biological activity of the compound. Its addition in agrochemical products actually changes the physical and chemical properties of the pesticide mixture products (Green, 2000). Unfortunately, the lack of standardised terminology of adjuvant has created a wide array of terms being used on pesticide and adjuvant label which then get confused among the users; and some of the terminologies adapted from Green (2000) are shown in the Table 2.6. Green (2000) also reported that pesticide active ingredients were not products because the products were complex formulations where manufacturer increasingly use adjuvant to improve product quality and create competitive advantages. Moreover, adjuvants were inexpensive thus; products differentiation today was often based on relatively minor formulation changes that allowed older products to be sold as ‘new and improved’.

Table 2.6: Some of the terminology used for adjuvant on pesticide and adjuvant labels.

Inert	Wetting Agent	Thickener	Buffering Agent
Surfactant	Antifreeze	Additive	Dispersant
Solubiliser	Emulsifier	Neutraliser	Penetrator

Previous research work on the photodegradation of pesticides has been done on concentrated solutions and the main focus was to investigate the effectiveness of the photocatalytic degradation process and to identify the intermediate products. However, formulation pesticides have been used in the present study and the properties of the selected formulation pesticide are reported below.

Acephate formulation was a soluble white powder containing 75% acephate active ingredients and 25% adjuvant. Dilute solutions containing 15 mg/L of acephate in deionised water were clear solutions.

Glyphosate formulation was a viscous light yellow-coloured fluid with only 9.7% of glyphosate active ingredients and 90.3% other ingredients. According to the manufacturer, the other ingredients were tallow alkylamine as a surfactant. Dilution solution showed a clear soluble solution.

Commercial formulation of malathion was an emulsifiable concentrate (viscous yellow-coloured fluid) containing 57% malathion active ingredient and 43% other ingredients. The exact compositions of the other ingredients for the acephate and malathion are not disclosed by the manufacturer as both of the formulations were purchased from the same company located in China. Dilution of commercial malathion produced a clear solution as well which similar to those observed of glyphosate.

2.11. Influence of Adding Materials on the Photodegradation Process

The rapid development of industries such as metal plating facilities, mining operations, fertiliser industries, tanneries, batteries and pesticide industries has discharged wastewater streams containing heavy metals directly or indirectly into the environment (Fu and Wang, 2011). Heavy metals are dangerous because of their persistence, not biodegradable and tend to accumulate in living organisms (Cai *et al.*, 2012; Fu and Wang, 2011). However, the presence of heavy metal ions specifically the transition metal group in the photocatalysis can influence the overall efficiency process as they act as electron scavengers at the semiconductor surface thus preventing electron-hole recombination leading to achieve higher overall rate of removal (Lopez-Munoz, Aguado and Ruperez, 2007). For instance, the presence of Cu(II) ion in the photocatalytic degradation of 4-nitrophenol in aqueous TiO_2 suspension has a detrimental effect (San *et al.*, 2002). Other studies (Chaudhary, Hassan and Grimes, 2009; Chaudhary, Grimes and Hassan, 2001) also reported the detrimental effect by using 100 mg/L of Cu(II) ion and further reduction occurred when the concentration was increased to 500 mg/L due to the copper complexation. In contrast, Lam *et al.* (2007) reported that the complexation of Cu(II) with 1,4-dioxane and its degraded compound, ethylene glycol diformate (EGDF) has a positive role which attributed from ligand-to-metal charge transfer (LMCT) process. The LMCT upon UV irradiation results in the reduction of the metal centre, whereas the ligand will be oxidised to its radical and leave the coordination (Ciesla *et al.*, 2004) for further processes and eventually mineralised.

However, studies by Lopez-Munoz, Aguado and Ruperez (2007); Shifu and Yunzhang (2007); Beydoun *et al.* (2002); Hua *et al.* (1995) have shown that the presence of copper ions increased the degradation rate up to a certain Cu(II) ion concentration and the degradation activity began to decrease if the excessive amount was added to the solution. The reduction was caused due to a decrease in the concentration of hydroxyl radical in the solution (Shifu and Yunzhang, 2007) and this happened due to the formation of Cu(I) from Cu(II) in the Cu(II)-Cu(I) cycle during the UV irradiation (Ciesla *et al.*, 2004; Moffett and Zika, 1987).

Most of the previous work on the effect of Fe ions was conducted on Fe(III) ion rather than Fe(II) as it is more stable. As study by Wahyuni, Mudasir and Hadipranoto (2006) showed that the effectiveness of the photodegradation increased in the presence of Fe(III) due to the formation of hydroxyl radicals through formation of aquahydroxo (can be written as $Fe^{3+}OH^-$ or $[Fe^{III}OH(H_2O)_5]^{2+}$) and further reduced to $Fe^{2+}OH^-$ by electron thus preventing the recombination of an electron with the hydroxyl radicals. However, the production of this aquahydroxo compound was pH dependent when the pH was more than pH 2 (Ciesla *et al.*, 2004). Although Pignatello (1992) agreed that the reaction which used Fe(III) was more pH sensitive instead of Fe(II), however the disappearance of parent compound in the solution was slow. Also that, the excessive amount of Fe(III) ion used also contributes to the detrimental effect (Shifu and Yunzhang, 2007).

Most of the studies (Cernigoj, Stangar and Jirkovsky, 2010; He and Lei, 2004; Huston and Pignatello, 1999) proposed that the use of the photo-Fenton reaction (Fe(III)/H_2O_2/UV) accelerated the decomposition of organic pollutants in aqueous solutions. However, some of the researchers (Zhang and Pagilla, 2010; Badawy, Ghaly and Gad-Allah, 2006) reported that the effectiveness of photo-Fenton reaction basically depend on the ratio of H_2O_2:Fe(II) used in the solution.

Very little research work has been done on the effect of zinc ions in aqueous solutions and the result showed that no obvious effect occurred on the photocatalytic degradation efficiency of glyphosate (Shifu and Yunzhang, 2007) and methamidophos (Wei *et al.*, 2009).

Many studies have been done on aqueous systems containing heavy metal ions, specifically on Cu(II) and Fe(II) whereas only a few on Zn(II) ions. Those studies discussed previously however, focused on the effect of heavy metal ions under TiO_2/UV illumination and some on the removal or recovery of the Cu(II) ions. It is well known that transition metal ions are able to coordinate with most of the organic substances, producing complexes with their higher oxidation state, as Fe(III) and Cu(II) for example, undergo photoreduction to Fe(II) and Cu(I), respectively, which is then accompanied by oxidation of the organic ligand (Ciesla *et al.*, 2004). In view of this, it is worth to emphasize here that the use of heavy metal ions in this study was conducted without TiO_2 as a semiconductor photocatalyst, however, the same principle was adapted in order to understand the effect of the heavy metal ions studied. The three selected heavy metal ions were iron, copper and zinc and some of their sources, uses and properties are given in the following subsections which also include H_2O_2 and other oxidants.

2.11.1. Iron, Fe

Iron is the most abundant metal in the Earth's crust after aluminium which extracted from its oxides such as haematite (Fe_2O_3), magnetite (Fe_3O_4) and carbonate siderite ($FeCO_3$) (Liptrot, 1990; Parish, 1977). Iron being used in the steel industries such as to make bridge, building and most of the skyscrapers.

Iron plays an important role in biology as it helps make red blood cells, which carry oxygen around the body. The source of iron can be present in most dark-green leafy vegetable such as watercress and curly kale, as well as liver, meat and nut. The lack of iron can lead to anemia; however, a sign of constipation, nausea and vomiting are the side effect of iron consuming (NHS, 2013).

Iron shows oxidation state of +3 (the most stable) and +2 (reducing). The presence of four singly occupied 3d orbital in the Fe(II) ion and five singly occupied 3d orbital in the Fe(III) ion (Figure 2.13) is often cited as an explanation of the easy oxidation of Fe(II) to Fe(III) ion (Liptrot, 1990). When iron loses its two electrons in aqueous solution, the remaining electrons are rearranged prior incoming water ligand bonding to make inner orbital octahedral complexes. Thus only one geometry can be formed for Fe(II) ion. Whereas for Fe(III) ion, it has an ability to form two types of coordinated complexes (tetrahedral and octahedral) when three electrons are lost.

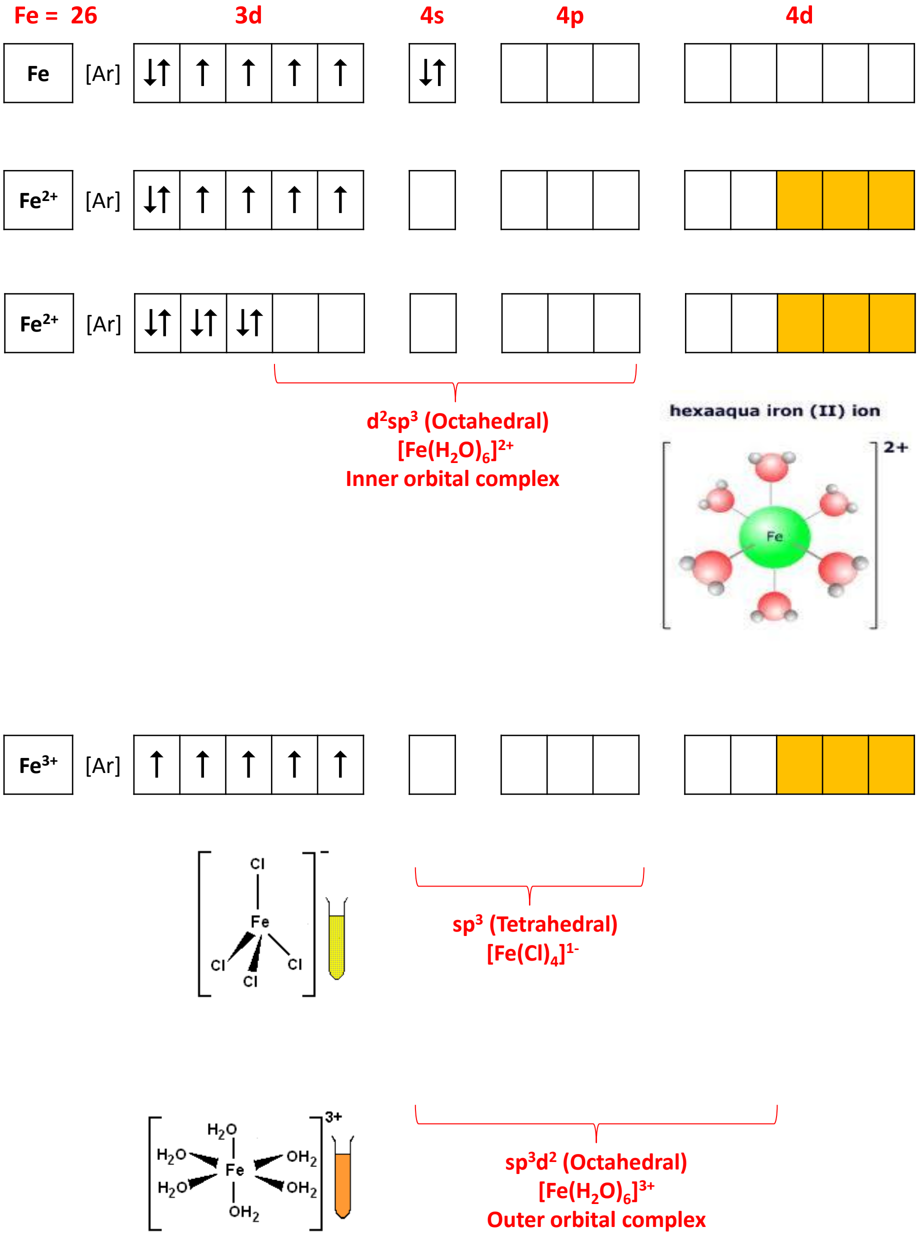


Figure 2.13: The chemistry of Fe(II) and Fe(III) ions in aqueous solution.

2.11.2. Copper, Cu

There are many sources of copper ions pollutions, for example, water in Australia has been found to contain copper ions which have leached from copper water pipes (Beydoun *et al.*, 2002). Copper occurred occasionally in sulphide minerals such as chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), covellite (CuS), chalcocite (Cu_2S), cuprite (Cu_2O) or as basic chlorides or carbonates (Parish, 1977).

It is essential in animal as copper plays a part in the utilisation of iron for haemoglobin formation however the excessive ingestion of copper brings about serious toxicological concerns, such as vomiting, cramps, convulsions, or even death (Fu and Wang, 2011).

Copper is an excellent conductor both of heat and electricity where it is used to make steam piping for water, electrical wires and conductor (Parish, 1977). Copper is commonly alloyed with zinc to make brass, which is used for making cartridge containers and the working parts of watches and clocks whereas bronze, an alloy of copper and tin, is used for fabricating bearings and ships fitting (Liptrot, 1990).

Copper is next to the last member of the first-row transition metals. Copper exhibits oxidation states of +2 (the most common) and +1 (less stable) (Liptrot, 1990). Copper has 29 electrons and when it loses 2 electrons (Cu^{2+}), it can make complexes with other incoming ligands. There are three geometries which can be formed for copper complexes which are tetrahedral, octahedral and square planar. The chemistry of Cu(II) ions in the aqueous solution is shown in Figure 2.14.

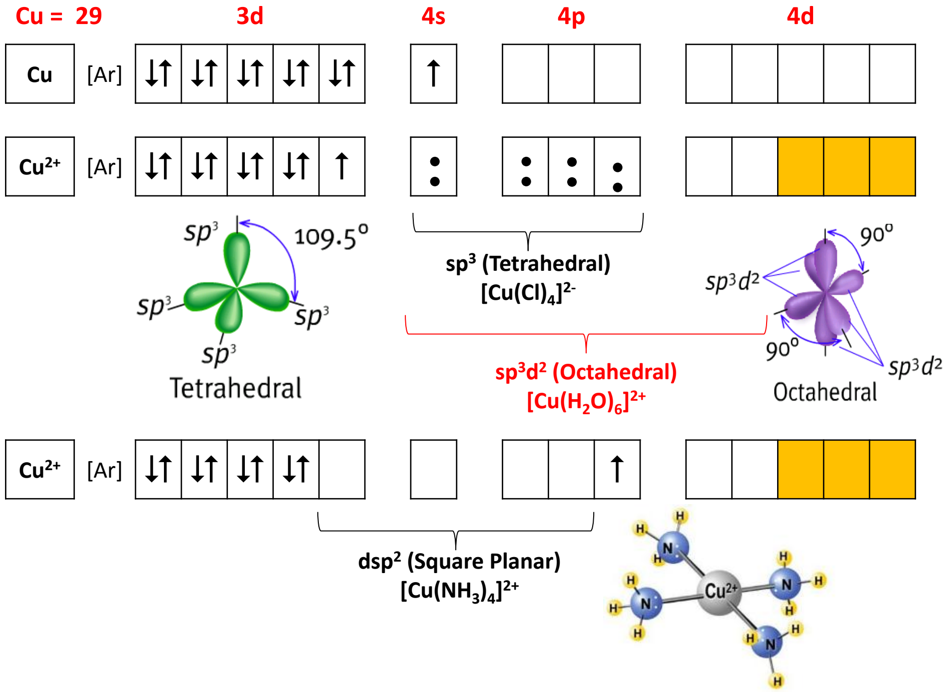


Figure 2.14: The chemistry of Cu(II) ions in aqueous solution.

2.11.3. Zinc, Zn

Although zinc is not very abundance, it is readily available as it occurs in concentrated deposits of sulphide ores, usually with iron, lead and many other metals (Parish, 1977). Zinc enter the environment through natural processes, however, most comes from human activities as zinc is co-product of lead mining (Lajis, 2013). Zinc attaches to soil, sediment and dust particles in the air and it can be moved into groundwater as well as rivers (Lajis, 2013).

Zinc is a nutritionally essential element for human health and it also present in food such as oyster, meat, whole grains, dairy product and legumes. It is important for the physiological functions of living tissue and regulates many biochemical processes. However, too much zinc can cause eminent health problems, such as stomach cramps, nausea, vomiting and skin irritations (Fu and Wang, 2011; Oyaro *et al.*, 2007).

Zinc also has many uses and it is used principally for galvanizing iron, preparation of certain alloys, as a pigment in paints, as a catalyst in rubber industry, die-casting in the automobile industry, roofing and gutters in building construction (Lajis, 2013; Parish, 1977).

Zinc is the last member of the first-row transition metals. Zinc exhibits an oxidation states of +2 and the aqueous solutions of their salt are colourless since a full complement of *d* electrons is present (Liptrot, 1990). Zinc has 30 electrons and when it loses 2 electrons (Zn^{2+}), it can make complexes with other incoming ligands. There are two geometries which can be formed for zinc complexes which are tetrahedral and octahedral. The chemistry of Zn(II) ions in aqueous solution is shown in Figure 2.15.

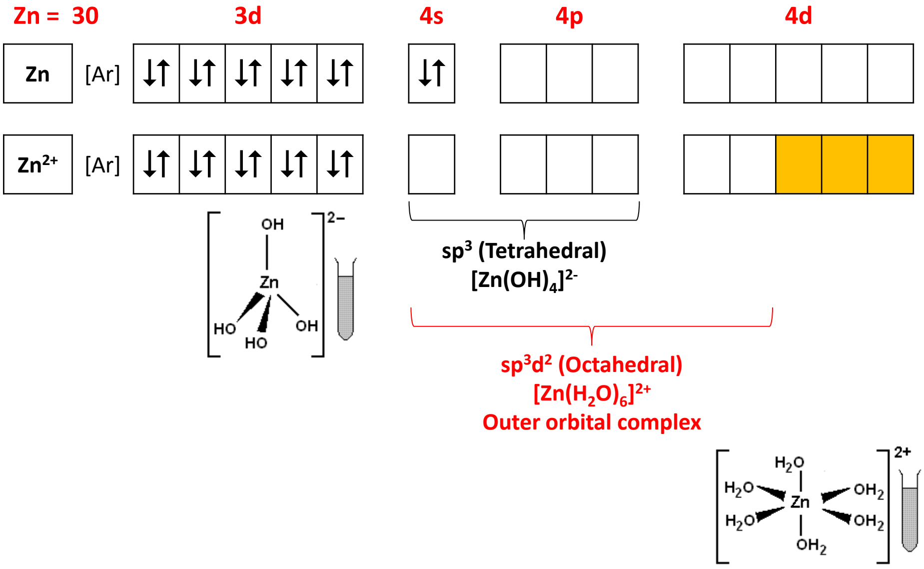


Figure 2.15: The chemistry of Zn(II) ions in aqueous solution.

2.11.4. Hydrogen peroxide, H_2O_2

The effects of H_2O_2 on the AOPs to enhance the degradation of organic pollutants and its usage in the photo-Fenton reaction have already been investigated (Manassero *et al.*, 2010; Zhang and Pagilla, 2010; Shifu and Yunzhang, 2007; Badawy, Ghaly and Gad-Allah, 2006; Pignatello, 1992). In addition to that, the detection of hydroxyl radicals, •OH on irradiated solution by electron spin resonance signals (ESR) studies suggested that hydroxyl radicals are the active radical species (Han *et al.*, 2009) which can propagate the reaction. Hydroxyl radicals are extremely unstable and reactive due to their high reactivity and given that, it must be generated continuously *'in situ'* in the reactor through photochemical reactions (Esplugas *et al.*, 2002). Basically radiation with a wavelength lower than 400 nm is able to photolise H_2O_2 molecules yielding the hydroxyl and hydroperoxyl radicals (Zhang and Pagilla, 2010; Chaudhary and Grimes, 2008; Esplugas *et al.*, 2002).

Another study (Doong and Chang, 1997) reported that in oxygenated solution however, hydrogen peroxide was found as an intermediate compound which accumulate in the system as the concentration of oxygen is decreased. In the contrary, several investigations (Tseng, Juang and Huang, 2012; Zhang and Pagilla, 2010) showed that the addition of H_2O_2 to the solution correspondingly produced the oxygen to the solution and its presence in the irradiated solution eventually lead to the formation of superoxide radicals anions, thus, enhancing the degradation process.

Although it has been agreed, in most studies, that the addition of a small amount of H_2O_2 can greatly increase the generation of •OH, enhancing the degradation efficiency of organic pollutants, several studies indicated that the beneficial effects of hydrogen peroxide deteriorate due to its auto-decomposition and termination process by following reactions (Zhang and Pagilla, 2010; Devipriya and Yesodharan, 2005):

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{2.6}$$

$$\bullet OH + HO_2^{\bullet} \rightarrow H_2O + O_2 \tag{2.7}$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{2.8}$$

$$HO_2^{\bullet} + H^{\bullet} \rightarrow H_2O_2 \tag{2.9}$$

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \tag{2.10}$$

The addition of excess H_2O_2 to the solution also could scavenge the valuable hydroxyl radicals (Zhang and Pagilla, 2010; Shifu and Yunzhang, 2007). Therefore, the amount of

H_2O_2 should be added at the optimal concentration in order to achieve its beneficial effect (Badawy, Ghaly and Gad-Allah, 2006; Zhang *et al.*, 2006).

2.11.5. Other chemical oxidants

Since hydroxyl radicals appear to play an important role in the removal of organic pollutants, several researchers have investigated the effect of other oxidants such as $KBrO_3$, $K_2S_2O_8$ and KIO_4, besides H_2O_2 on the photocatalytic degradation of various pesticide (Zhang and Pagilla, 2010; Liu *et al.*, 2009; Wei *et al.*, 2009; Bahnemann, Muneer and Haque, 2007; Selvam *et al.*, 2007; Shifu and Yunzhang, 2007; Rahman *et al.*, 2006). Zhang *et al.* (2006) studied the UV/oxidant pair such as UV/IO_4^- and $UV/S_2O_8^{2-}$. The author reported that both oxidants were more effective in degrading methamidophos (intermediate product of acephate), however KIO_4 was the most effective. Furthermore, their photolytic decomposition mechanisms involve a number of highly reactive intermediates such as $SO_4^{\bullet -}, \bullet OH, IO_3^{\bullet}$ and $IO_4^{\bullet}$. Selvam *et al.* (2007) also reported the effect of several oxidants on the photocatalytic degradation of 4-fluorophenol and the degradation efficiency was in the order of $IO_4^- > BrO_3^- > S_2O_8^{2-} > H_2O_2 > ClO_3^-$. Meanwhile study by Shifu and Yunzhang (2007) on the photocatalytic degradation of glyphosate by TiO_2 as photocatalyst, revealed that $KBrO_3$ was more efficient electron acceptor than $K_2S_2O_8$ and H_2O_2. The same observation has also been demonstrated in the photocatalytic degradation of phenoxyacetic acid (Bahnemann, Muneer and Haque, 2007). Nevertheless, the results obtained by Wei *et al.* (2009) and Liu *et al.* (2009) revealed that $K_2S_2O_8$ was the most effective oxidant for the photodegradation of methamidophos and trichlorfon, respectively. However, Rahman *et al.* (2006) reported that degradation rate of acephate was higher in the presence of H_2O_2 than of $KBrO_3$, nevertheless both of the oxidants showed a beneficial effect. The addition of oxidant or electron acceptors to the photocatalytic process has been shown to improve the removal of organic pollution by (Ahmed *et al.*, 2011; Bahnemann, Muneer and Haque, 2007):

1) Increasing the number of trapped electrons and consequently avoid the electron-hole recombination
2) Increasing the hydroxyl radical concentration and oxidation rate of intermediate compound
3) Generating more radicals and other oxidising species to accelerate the degradation efficiency of intermediate compounds.

2.12. References

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CHAPTER 3: Materials and Methods

CHAPTER 3: Materials and Methods

3.1. Summary

This chapter describes a series of experimental setups specifically designed to investigate the effects of different parameters on the photodegradation of three pesticides namely acephate, glyphosate and malathion. The description of chromatographic, spectroscopic and other related analytical techniques used to determine the residual concentration of organic pollutants and metal ions in aqueous solution are also reported.

3.2. Chemicals and Reagents

Most pesticides are used as a formulation which is a homogeneous and stable mixture of active and inert ingredients. The use of this stable mixture as pesticide is very effective for target pests.

All three pesticides, acephate, glyphosate and malathion used in this study were of formulation type with the composition acephate (75%), malathion (57%) and glyphosate (9.6%). Two of the formulation pesticides namely acephate (75%), and malathion (57%) were purchased from Shenzen Qinfeng Pesticide Co., Ltd, China. The third formulation glyphosate (9.6%) was purchased from Bayer Garden Company, Cambridge, UK. Analytical standards of acephate, glyphosate and malathion were purchased from Sigma Aldrich, UK. Acetonitrile was of HPLC grade and purchased from Rathburn Chemicals (Walkerburn, UK). Hydrogen peroxide (H_2O_2) (30%), potassium persulphate ($K_2S_2O_8$), potassium periodate (KIO_4) and potassium bromate ($KBrO_3$), used as oxidant, was purchased from Sigma-Aldrich. For studies of heavy metal, $FeCl_2.4H_2O$ (99%), $CuCl_2.2H_2O$ (99%), $ZnCl_2$ (98%) and their standard solutions for calibration were all purchased from Sigma Aldrich, UK. Other chemicals, for example, HCl and NaOH which were used to adjust the pH were obtained from Fluka and FSA supplies Loughborough, UK), respectively. Aqueous solutions of the pesticides were prepared by diluting stock solutions using deionised water obtained from gradient Milli-Q (18.2MΩ)(Millipore, Watford, UK) water purification system.

3.3. The Photolytic System Setups

3.3.1. The mercury lamps

The source of irradiation used in all studies was an ultraviolet (UV) medium pressure mercury lamp. In the case of medium pressure lamps, a few grams of mercury are present. In addition to the mercury, the lamp tube is filled with an inert gas, Argon. When power is applied, Argon is ionised and start the arc, whilst the liquid mercury turn to gases state due to the heated lamp tube. Continuous collision between ionised Argon and mercury gas atoms have excite the mercury atoms. In an excited mercury atom, an electron jumps to a higher energy level. When the electron falls back to its original levels, the atom releases the energy in the form of ultraviolet photon (Figure 3.1 inset). In this study, a mercury lamp of 400/600 W capacity (Figure 3.1) with a maximum emission wavelength at 365 nm was used as a light source in the photolytic system. This lamp was a dual function lamp where it can be used as a 400 or a 600 W by just simply changing the power supply (Figure 3.2). The UV lamp was warmed up for about 15 minutes prior to use in every conducted experiment.

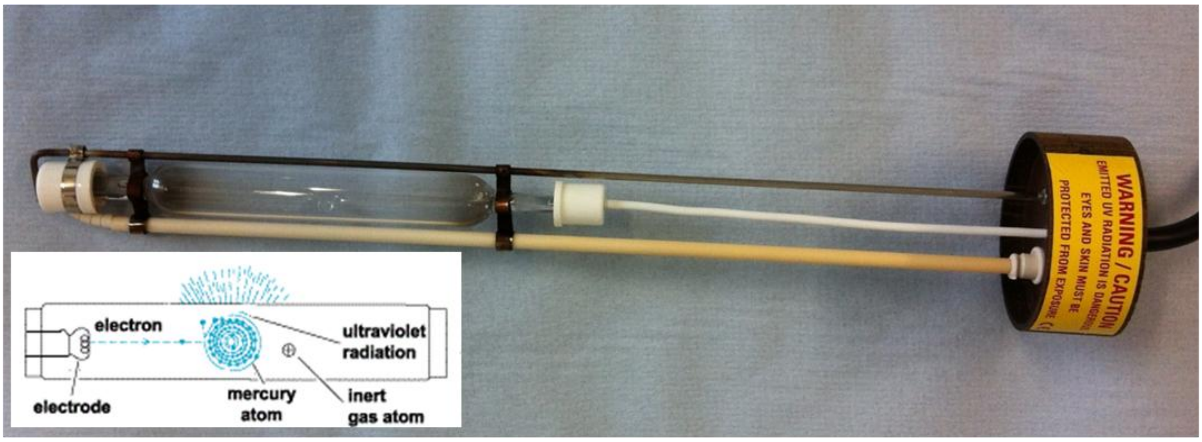

Figure 3.1: A 400/600 W UV medium pressure mercury lamp. Figure 3.1 inset was modified from ELCFED (2013).

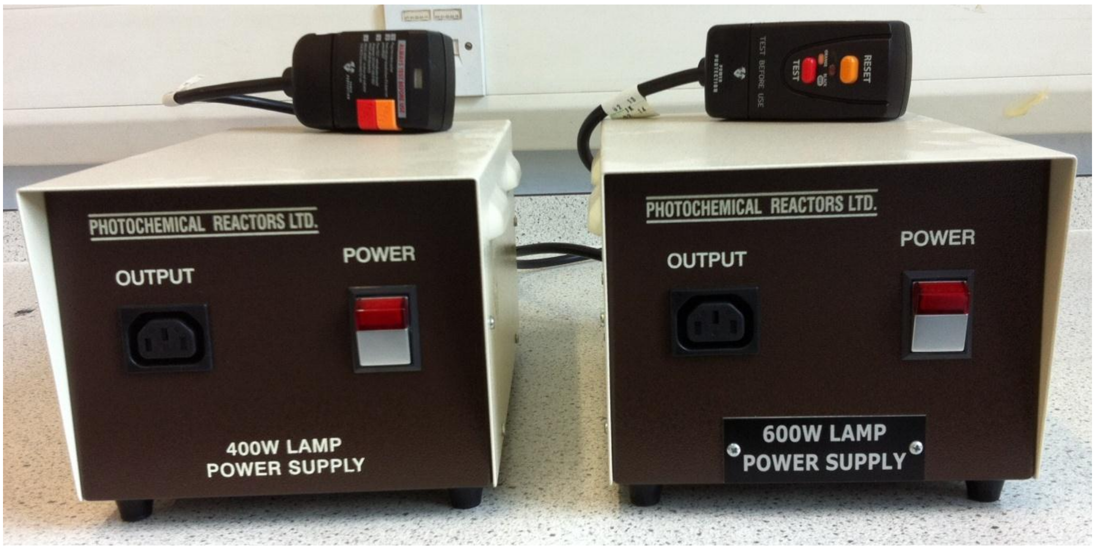

Figure 3.2: Power supplies (400 & 600 W) for a medium pressure mercury lamp.

3.3.2. Immersion well

The immersion well was a double-walled well which acts as a cooling jacket and made from quartz where the UV lamp was hosted in the middle of the cooling jacket (Figure 3.3). The well also fitted with inlet and outlet tubes for water cooling. Inside the cooling jacket a small diameter tube extends to the bottom of the annular space to allow coolant flow from the bottom of the well upwards. This cooling action needed to avoid excessive heating from the lamp and to keep the temperature constant for each experimental setup.

Figure 3.3: Two immersion wells – with and without the UV lamp.

3.3.3. Reaction flask

The reaction flask, made from quartz, has a central large socket to house the immersion well and other smaller sockets which can be used to introduce air, sampling port and temperature probe (Figure 3.4). The flask has a flattened bottom for a magnetic stirring bar and its volume was 400 ml. The assembly of the photoreactor and the schematic are shown in Figures 3.5 and 3.6.

The external surface of the photoreactor was wrapped with aluminium sheet and then placed onto a magnetic stirrer. A magnetic follower was used to agitate the solution and air was introduced into the photoreactor to act as an oxidant. The whole assembly was then placed in the wooden box (Figure 3.7) to prevent dissipation of UV light as the lamp produces dangerous ultraviolet radiations which are harmful to eyes and skin. The reactor, UV lamps and power supply were supplied by Photochemical Reactors LTD, Reading, UK. The temperature in the photoreactor was monitored continuously with a digital temperature controller (MC810B MKII, ThermoFisher Scientific) and maintained at 28.0 ± 2.0°C by passing tap water through the cooling jacket (Figure 3.8). The flow rate of air was 3.0 L/min and controlled by a flow meter connected to the pump (Figure 3.9). The flow meter and the pump were purchased from Fisher Scientific, Loughborough, UK.

Figure 3.4: Reaction flask.

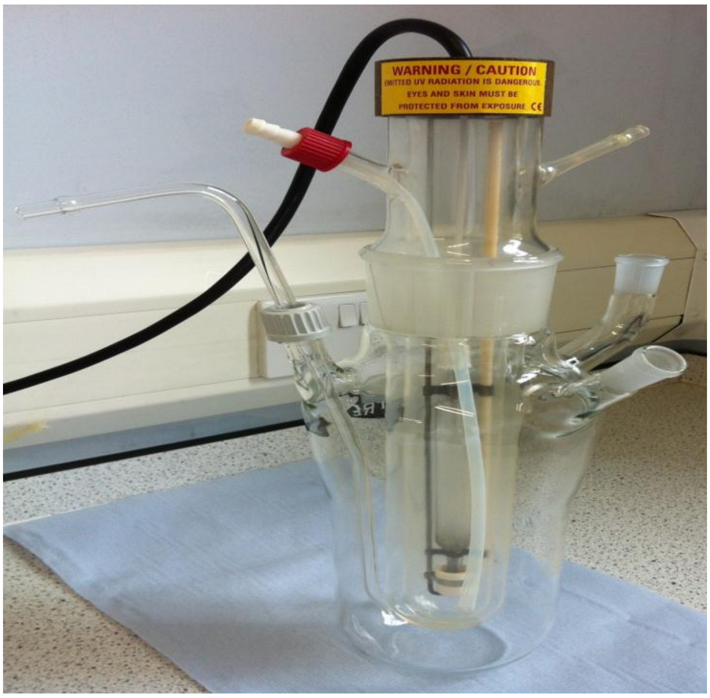

Figure 3.5: Assembled photolytic system.

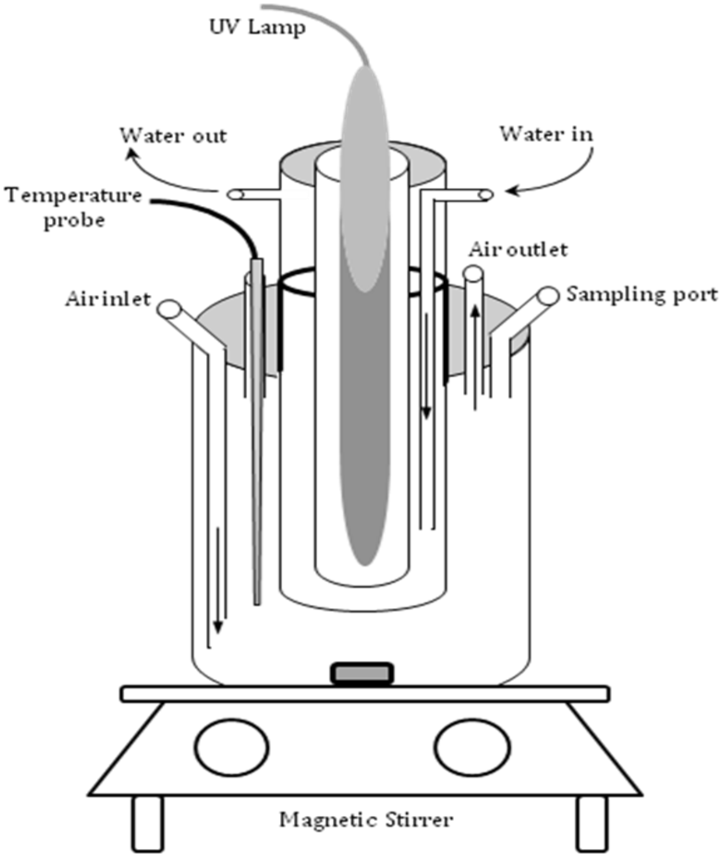

Figure 3.6: Schematic diagram of the photoreactor.

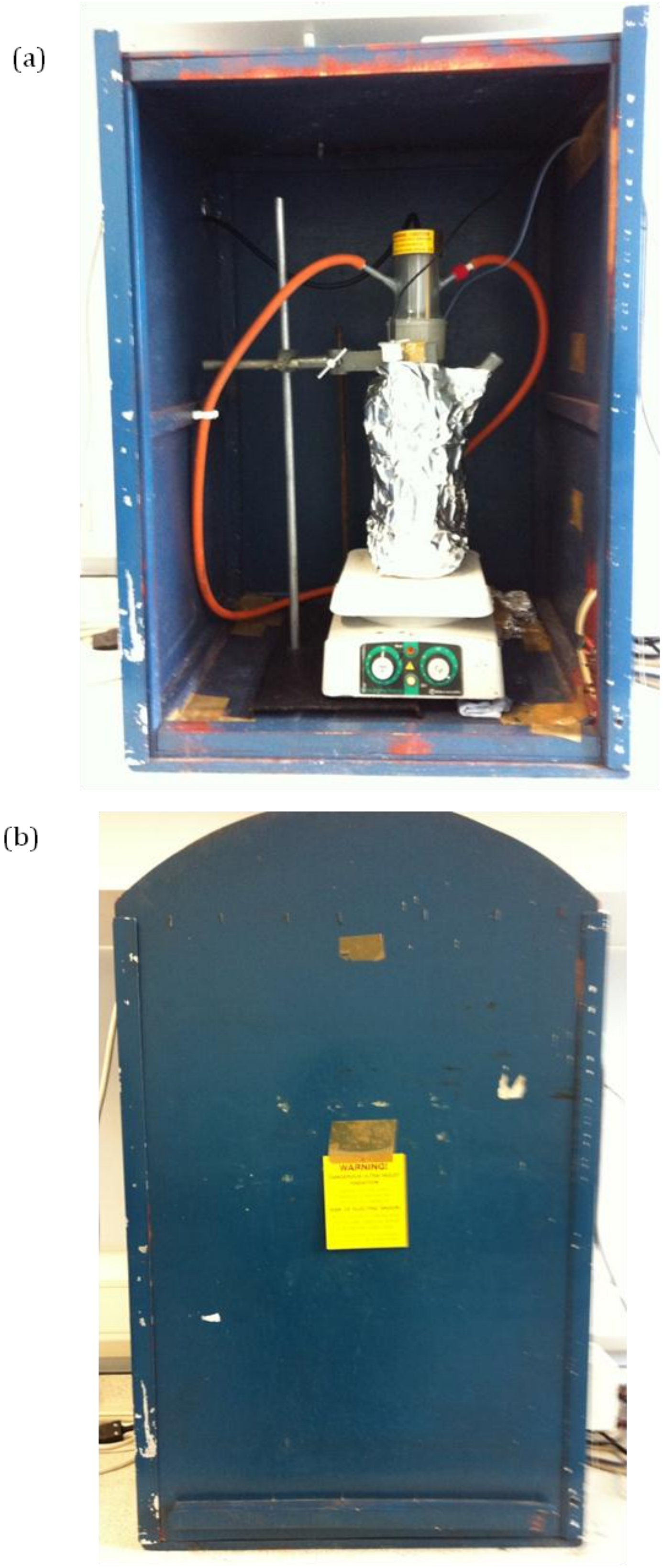

Figure 3.7: Assembled photolytic system wrapped with aluminium sheet (a) in the wooden box and (b) in closed system.

Figure 3.8: Digital thermometer with a probe.

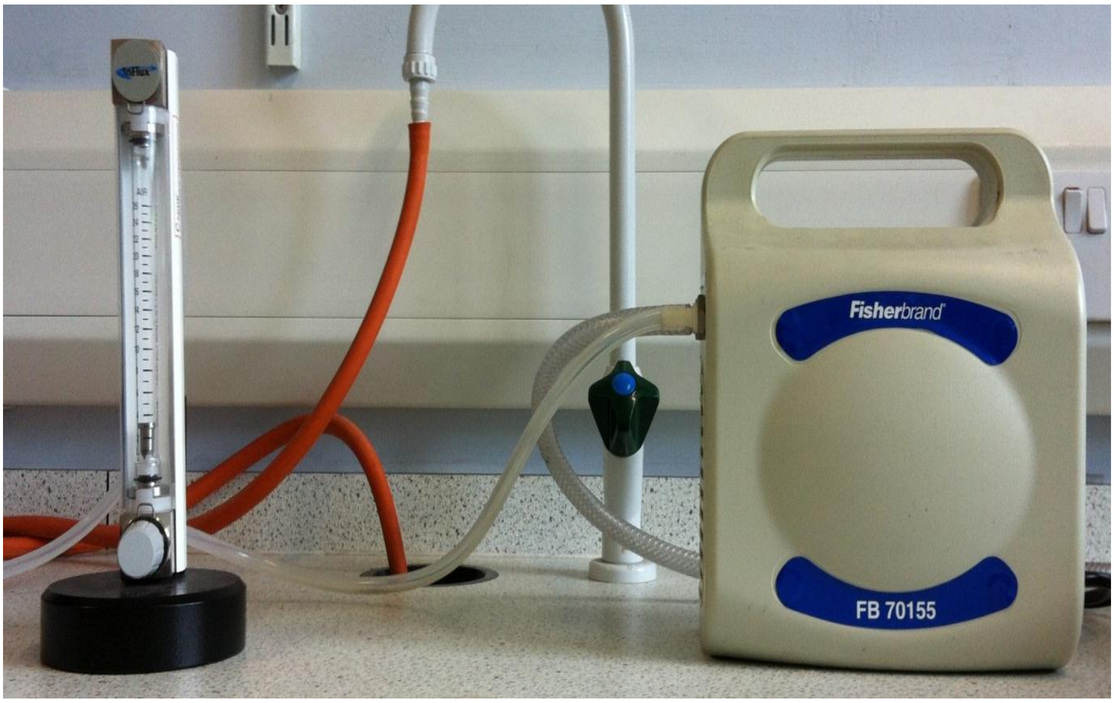

Figure 3.9: Air pump attached to a flow meter.

3.4. Experimental Procedures

3.4.1. Effect of UV source

In each experiment, a total volume of 400 ml solution containing a known concentration of a single pesticide for example, acephate with the initial concentration of 15 mg/L (same initial concentration was used for glyphosate and malathion) was placed in the photoreactor containing the UV lamp (400 W) along with the cooling jacket. The pesticide solution was used as prepared without pH adjustment except for experiments where the pH values were varied by using sodium hydroxide and dilute hydrochloric acid solutions. All experiments were carried out for 5 hours and periodically samples (~20 ml) were collected every hour for analysis and to monitor the degradation. The changes in the pH of the pesticide solutions were monitored with a Mettler Delta 350 pH meter. Replicate experiments were conducted in order to determine the repeatability of the results. All experiments were carried out using a 400 W UV lamp except for those experiments which were specifically designed to investigate the effect of UV source on the photodegradation. For these experiments, a 600 W UV lamp was used under the same experimental conditions. All experiments were carried out under identical conditions and repeated for the three selected pesticides namely, acephate, glyphosate and malathion. The photoreactor was used repeatedly after clean up and series of washing using deionised water.

3.4.2. Effect of pH

The experiments to study the effect of pH followed the same procedures as describe in section 3.4.1. with the exception that the pH of the solution was adjusted at the start of the experiment. The pH was adjusted by adding drops of either diluted hydrochloric acid (0.1 M) and/or sodium hydroxide (0.1 M). The pH was not controlled during the experiment. The self-pH of the model solution containing 15 mg/L of commercial formulation of acephate resulted from the dilution preparation was ≈5.5-5.8 while for glyphosate and malathion were ≈5.1-5.4 and ≈5.0-5.4 respectively. The studied pH values for acephate were 2.5, 4.5, 8.5 and 10.5. Whereas for glyphosate and malathion were at pH 3.0, 7.0 and 8.0.

3.4.3. Effect of pesticide concentration

The effects of initial concentration of the selected pesticides were studied at various initial concentrations. The studied initial concentrations for acephate were at 15, 25 and 50 mg/L while for glyphosate and malathion were at 15, 25, 50 and 100 mg/L.

3.4.4. Effect of various oxidants

The effect of various oxidants such as H_2O_2, $K_2S_2O_8$, KIO_4 and $KBrO_3$ were investigated in the presence and absence of air. The 400 W UV source was used for this study and the concentration of each oxidant was 50 mg/L. These chemical oxidants were used to investigate their effects on the photodegradation of acephate (50 mg/L). This was done in order to determine the vital role of air in the photodegradation system as air also acts an oxidant.

3.4.5. Effect of H_2O_2

Since H_2O_2 gave a beneficial effect among all the other studied oxidants (section 4.3.4.) in the presence of air, set of experiments were carried to investigate the effect of H_2O_2 on the photodegradation of the three pesticides. The studied concentrations of H_2O_2 were 7.5, 15.0 and 30.0 mg/L for acephate and glyphosate whereas for malathion the concentrations were 5.0, 10.0, 15.0 and 30.0 mg/L. The concentration for each of the pesticide was 15 mg/L.

3.4.6. Effect of heavy metal ions

All experiments were carried out under the same experimental conditions as described in section 3.4.1. The experimental conditions to study the effects of single and mixed metal ions are given in Table 3.1. In total 24 experiments were conducted, 8 for each pesticide.

Table 3.1: Conducted experiment for each pesticide in the presence of single metal ions and mixed metal ions at metal ions concentration range between 5.0 and 15.0 mg/L.

Pesticides	Concentration of single metal ions (mg/L)						Concentration of mixed metal ions (mg/L)	
	Fe(II)		Cu(II)		Zn(II)		Fe(II), Cu(II), Zn(II)	
	5.0	15.0	5.0	15.0	5.0	15.0	5.0	15.0
Acephate	√	√	√	√	√	√	√	√
Glyphosate	√	√	√	√	√	√	√	√
Malathion	√	√	√	√	√	√	√	√

These studies were also extended to investigate the effect of H_2O_2 as an oxidant. The added concentration of H_2O_2 was 30.0 mg/L. The effect of H_2O_2 on the photodegradation of pesticides was only studied in the presence of 5 mg/L Cu(II) ions (Table 3.2). This was done because the presence of Cu(II) ions retarded the degradation of the pesticides. The experiments were also conducted to investigate the effect of H_2O_2 in the presence of mixed metal ions. The added concentration for mixed metal ions was 5.0 mg/L for each metal ion.

Table 3.2: Conducted experiment for each pesticide in the presence of single metal ion, Cu(II) and mixed metal ions with the addition of hydrogen peroxide.

Pesticides	Effect of H_2O_2 in the presence of Cu(II) ions concentration (mg/L)		Effect of H_2O_2 in the presence of mixed metal ions concentration (mg/L)	
	Cu(II)	H_2O_2	Fe(II), Cu(II), Zn(II)	H_2O_2
	5.0	30.0	5.0	30.0
Acephate	√	√	√	√
Glyphosate	√	√	√	√
Malathion	√	√	√	√

3.5. Analytical Techniques

The degradation of each pesticide, under various conditions, was followed by analysing the sample solutions, collected at various intervals, using the following five analytical techniques:

1. Total organic carbon (TOC)
2. High performance liquid chromatography (HPLC)
3. Ion chromatography (IC)
4. UV/Visible spectroscopy (UV/Vis spectroscopy)
5. Atomic absorption spectroscopy (AAS)

All collected samples were analysed using a total organic carbon (TOC) analyser in order to quantify the organic carbon concentration of each selected pesticide. The depletion of the parent compound and the formation of intermediate products after five hours irradiation of UV light were observed by using high performance liquid chromatography (HPLC) technique. The mineralisation products such as the formation of sulphate, phosphate and nitrate ions were detected using an ion chromatography (IC) system. The photodegradation of the selected pesticides were also monitored by using a Perkin Elmer Series 200 UV-Visible spectroscopy system. To study the effect of metal ions, an atomic absorption spectrophotometer (AAS) was used to monitor the concentration of metal ions in aqueous solutions.

3.5.1. Total organic carbon (TOC)

Principle of TOC analysis

There are two types of carbon present in wastewater samples which are organic carbon (bonds with hydrogen or oxygen) and inorganic carbon (such as bicarbonate and carbonate ions) and the relationship between them is expressed as (Shimadzu, 2009):

$$TOC = TC - IC \qquad (3.1)$$

Where:

TOC = total organic carbon

TC = total carbon

IC = inorganic carbon

The sample is introduced to the TC combustion chamber, which is filled with an oxidation catalyst and heated to 680°C, and then the sample is converted to carbon dioxide. Carrier gas, which flows at a rate of 15 mL/min, carries the combustion products from the combustion tube to the dehumidifier, where the gas is cooled and dehydrated followed by removing the chlorine and other halogens through the halogen scrubber. Finally, the carrier gas delivers the sample combustion products (carbon dioxide) to the non-dispersive infrared (NDIR) gas analyser, where the carbon dioxide is detected. The peak area is measured by the TOC-Control V software. Once, the TC concentration of the sample is quantified, the IC (consist of carbon contained in carbonates and carbon dioxide dissolved in water) is measured by acidifying the sample with a small amount of hydrochloric acid (HCl) to obtain a pH less than 3. Thus, all carbonates are converted to carbon dioxide and quantified (Shimadzu, 2009).

In this study, the concentration of organic carbon was analysed by using Shimadzu TOC-V_{CPN} analyser (Figure 3.10) equipped with a non-dispersive infrared detector and 8-port sampler. Potassium hydrogen phthalate (KHP) was used as an organic carbon standard whereas a mixture of sodium hydrogen carbonate (Na_2HCO_3) and sodium carbonate (Na_2CO_3) were used as an inorganic carbon standard for the calibration purpose.

Figure 3.10: Total organic carbon analyser.

3.5.2. High performance liquid chromatography (HPLC)

Principle of chromatography

Chromatography involves a sample which is transported by a mobile phase through a column (stationary phase). The distribution of analytes between phases can be described as:

$$X_{mobile} \leftrightarrow X_{stationary} \tag{3.2}$$

And the distribution equilibrium is described by:

$$K = \frac{X_{stationary}}{X_{mobile}} \tag{3.3}$$

Where:

K = equilibrium constant
X_{mobile} = the concentration of component X in the mobile phase
$X_{stationary}$ = the concentration of component X in the stationary phase

Solute with a large K value will be retained more strongly by the stationary phase than those with a small value. As a result of these differences in mobilities, sample components will become separated from each other and the latter (with small K value) will be eluted earlier and more rapidly (Christian, 1994).

The HPLC system (Figure 3.11) equipped with a PerkinElmer series 200 pump, coupled with a UV/VIS series 200 detector, a vacuum degasser and an auto sampler (Gilson model 231) was used to monitor the changes of the pesticides degradation in this study. The injection volume was 100 µl. The optimised conditions for each pesticide are summarised in Table 3.3.

Figure 3.11: High performance liquid chromatography system.

Table 3.3: Optimised HPLC method condition for of each pesticide.

Optimised condition	Pesticides		
	Acephate	Glyphosate	Malathion
Eluent	5% acetonitrile 95% deionised water	10% acetonitrile 90% deionised water/H_3PO_4 pH2.3	60% acetonitrile 40% deionised water
Column	ACE5C18 (150 x 4.0 mm) (Hichrom, Berkshire)	Discovery® Cyano 5µm (250 x 4.6 mm) (Sigma Aldrich)	ACE5C18 (150 x 4.0 mm) (Hichrom, Berkshire)
Flow (mL/min)	1.0	1.0	1.4
Detector (nm)	220	196	220
Retention time (min)	2.85	3.18	2.50

Analysis of acephate

The analytical method used for the determination of acephate was adapted from previous work (Echavia, Matzusawa and Negishi, 2009; Han *et al.*, 2009), however, the size and the type of the column used were different. The chromatograph of a standard solution containing 15 mg/L of acephate is shown in Figure 3.12.

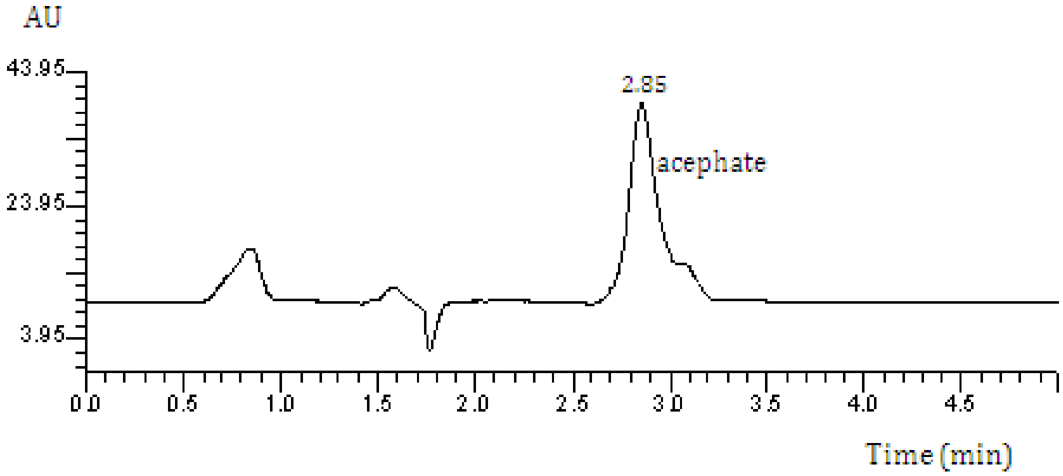

Figure 3.12: Chromatogram of standard solution containing 15 mg/L of acephate.

Analysis of glyphosate

The previous studies (Manassero *et al.*, 2010; Echavia, Matzusawa and Negishi, 2009; Chen *et al.*, 2007a; Chen *et al.*, 2007b; Shifu and Yunzhang, 2007) conducted on the photodegradation of glyphosate only used an ion chromatographic or the molybdenum method to monitor depletion of glyphosate by analysing the concentration of phosphate ions which is one of the products obtained after the complete mineralisation of glyphosate. However, in this study we decided to use both an HPLC and IC systems to monitor the percentage degradation of glyphosate. The HPLC method used was adopted as described by Sigma Aldrich Company, UK. In order to ensure the reproducibility of the measurements, five standard glyphosate solutions containing 15, 50, 100, 500 and 1000 mg/L of glyphosate were analysed. The chromatogram of the highest concentration of glyphosate standard is shown in Figure 3.13. The results obtained show an identical chromatogram as produced by the Sigma Aldrich also at a higher concentration (Figure 3.14).

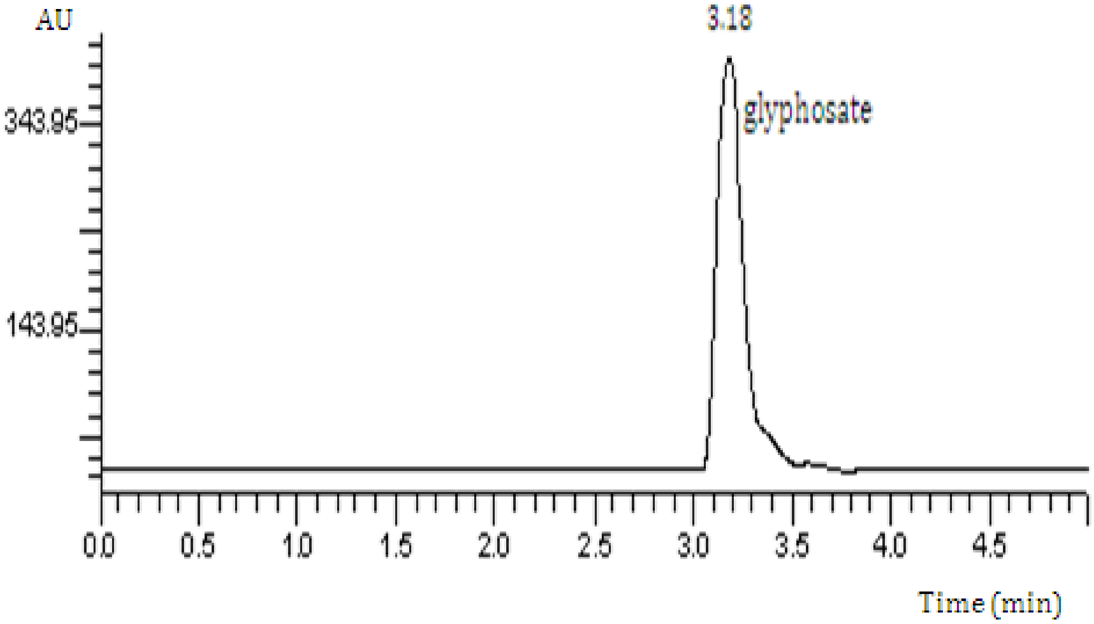

Figure 3.13: Chromatogram of standard glyphosate at the concentration of 1000 mg/L of glyphosate.

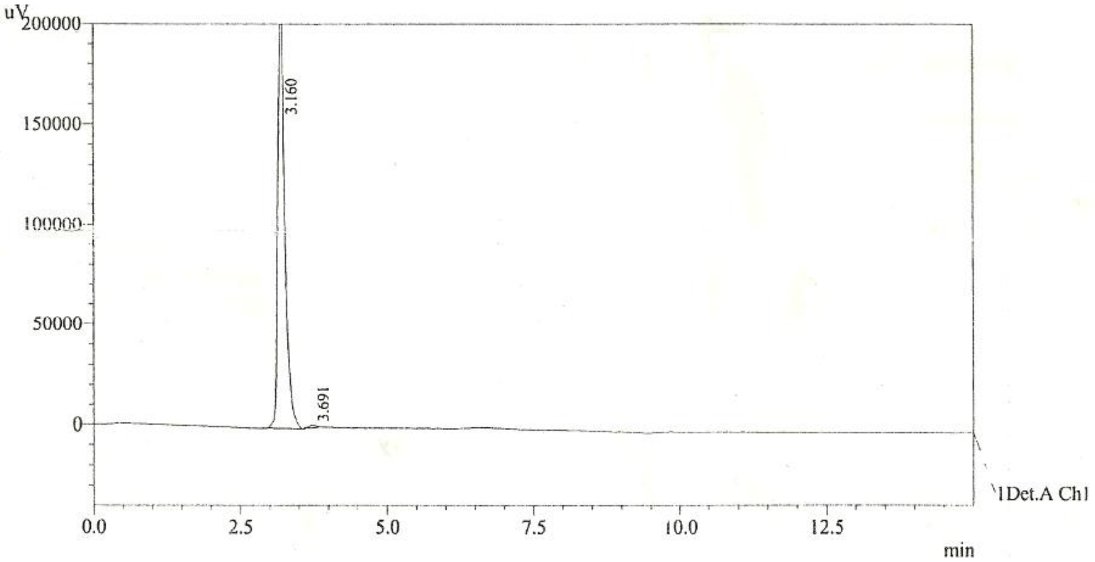

Figure 3.14: Chromatogram of standard glyphosate at high concentration (2 000 mg/L) produced by Sigma Aldrich Company.

However, it was noticed that a peak split occurred when the analysis was done at a lower concentration containing 15 mg/L of glyphosate (Figure 3.15).

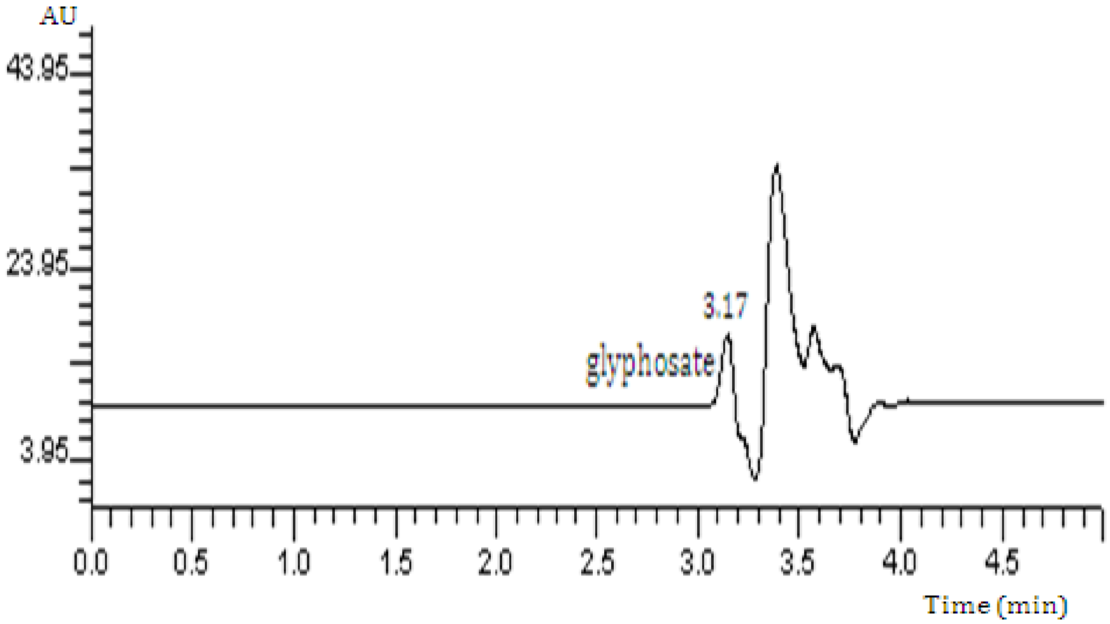

Figure 3.15: Chromatogram of standard glyphosate at the concentration of 15 mg/L.

Thus, the next attempt was to inject blank samples at different eluent percentage ratios of acetonitrile:water. The chromatograms (Figures 3.16 (a), (b) and (c)) show that the peak appeared after glyphosate peak was the eluent (acetonitrile:water) peak. The chromatograms in Figure 3.16 (a), (b) and (c) have low peak area due to the change in the composition of the eluent (different acetonitrile:water ratio).

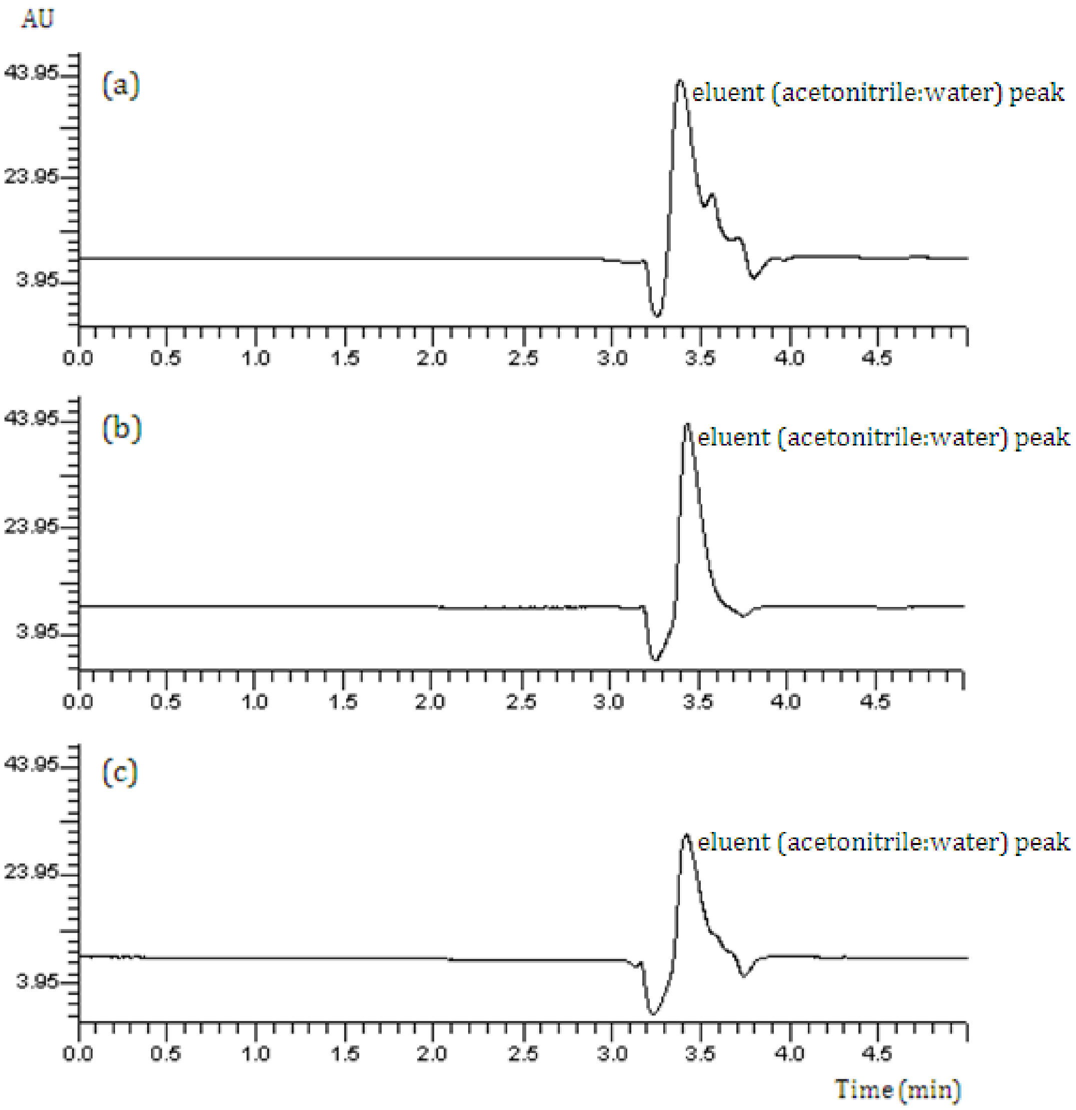

Figure 3.16: Chromatogram of blank samples at eluent concentration of (a) 10% acetonitrile : 90% deionised water/H_3PO_4 pH 2.3, (b) 5% acetonitrile : 95% deionised water/H_3PO_4 pH 2.3 and (c) 1% acetonitrile : 99% deionised water/H_3PO_4 pH 2.3.

Hence, the developed method was used to determine the depletion of glyphosate during the photolytic degradation process.

Analysis of malathion

The analysis of malathion was conducted by injecting standard solutions containing 15 mg/L of malathion at two flow rates *viz:* 1) 1.0 ml/min and 2) 1.4 ml/min. Each of the flow rates was then tested at wavelengths of 210, 220 and 230 nm by using various ratios of acetonitrile-water eluent. The optimised conditions for the analysis of malathion are given in Table 3.3 and the chromatograms for malathion standard and formulation malathion are shown in Figures 3.17 and 3.18 respectively. The optimised method was used to monitor the photodegradation of malathion.

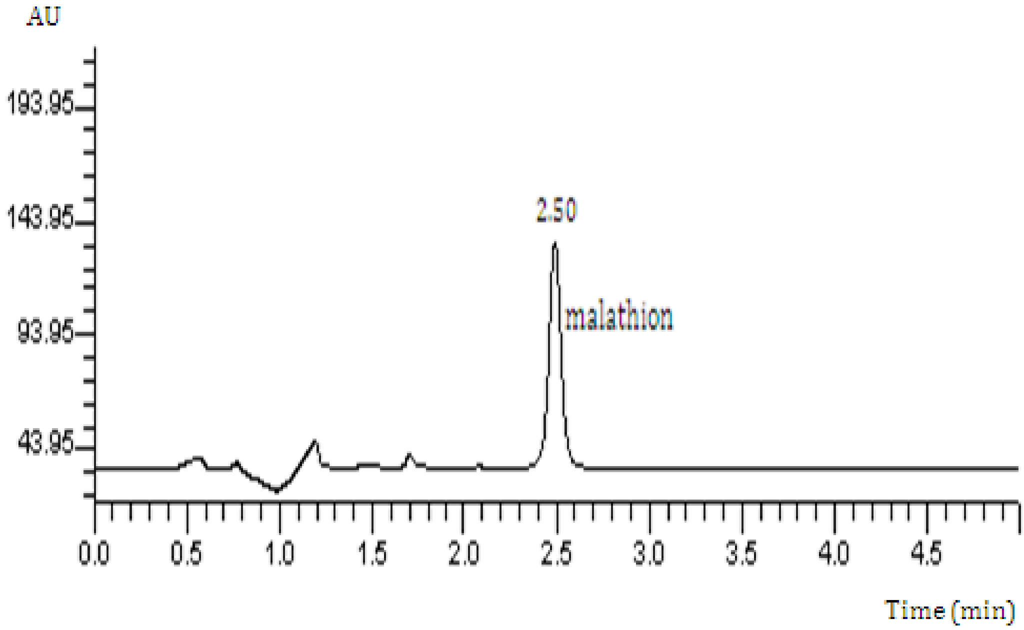

Figure 3.17: Chromatogram of standard malathion at the concentration of 15 mg/L.

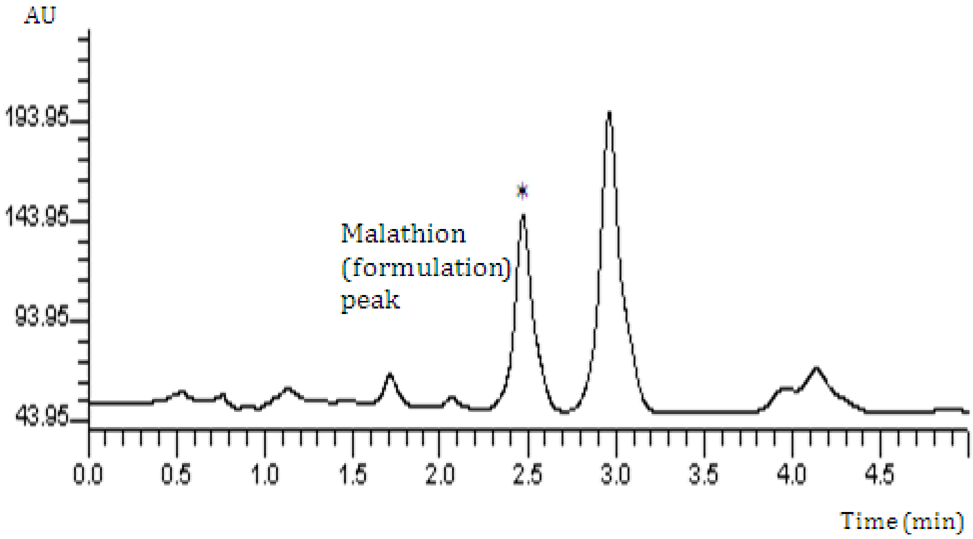

Figure 3.18: Chromatogram of formulation malathion at the concentration of 15 mg/L where peak with * sign is the interest peak.

3.5.3. Ion chromatography (IC)

Principle of IC

Ion exchange chromatography or ion chromatography, is used for the separation of inorganic ions (cations and anions), where separation is based on exchange of ions in the stationary phase (Christian, 1994). In ion chromatography, the stationary phase is a resin exchanger where the surface displays ionic functional groups that interact with analyte ions of opposite charge. As anions (such as sulphate, phosphate, and nitrate) are required to be detected in this study, thus anion exchange resin is used as the stationary phase. Anion exchange chromatography retains negatively charged anions because the stationary phase (column) displays a positively charged functional group as shown in the Figure 3.19 for an example.

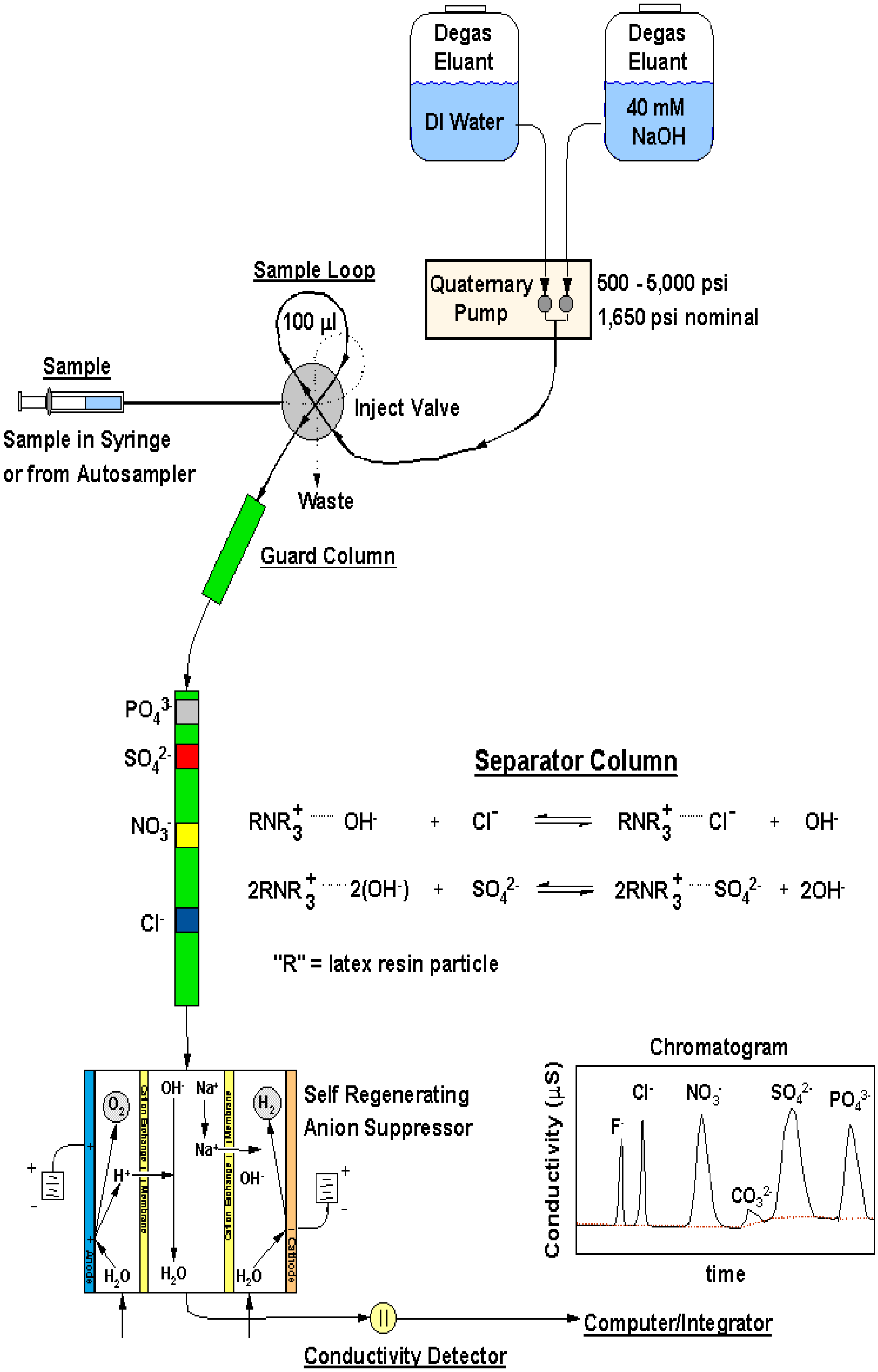

Figure 3.19: Diagram for ion chromatography (Fuller, 2013).

Hence, quantification of the inorganic anions (sulphate, phosphate and nitrate) produced during the photodegradation process were performed on a DIONEX ion chromatography system (Figure 3.20) equipped with GP40 pump, AG0-SC 4 mm guard column, an IonPac AS9-SC 4 mm separator column, a conductivity detector and an anion self regenerating suppressor (ASRS® ULTRA II). An isocratic eluent containing a mixture of 1.7 mM $NaHCO_3$ and 1.8 mM Na_2CO_3 was used with a flow rate of 2.0 ml/min and 50 mA current. The injection volume was 100 µl. Mixed anions were used as a calibrant as to measure the concentration of ions. The concentration of various ions in the mixed anions standard used for the calibration is given in Table 3.4. The chromatograms for both standards solution are shown in Figure 3.21

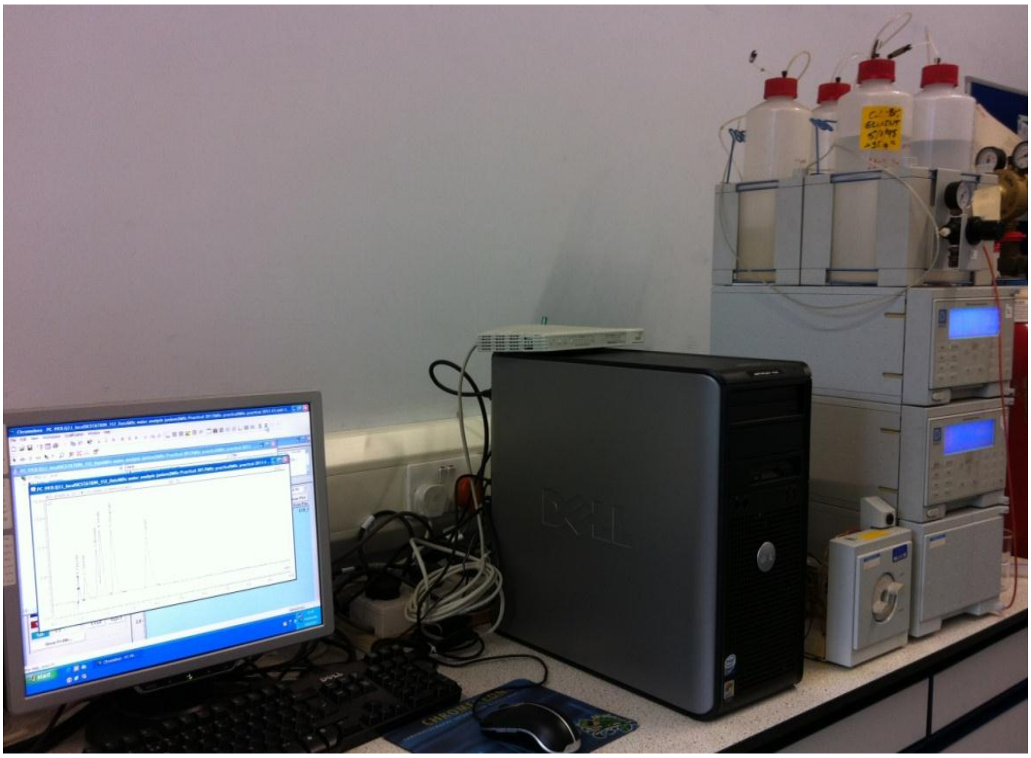

Figure 3.20: Ion chromatography system.

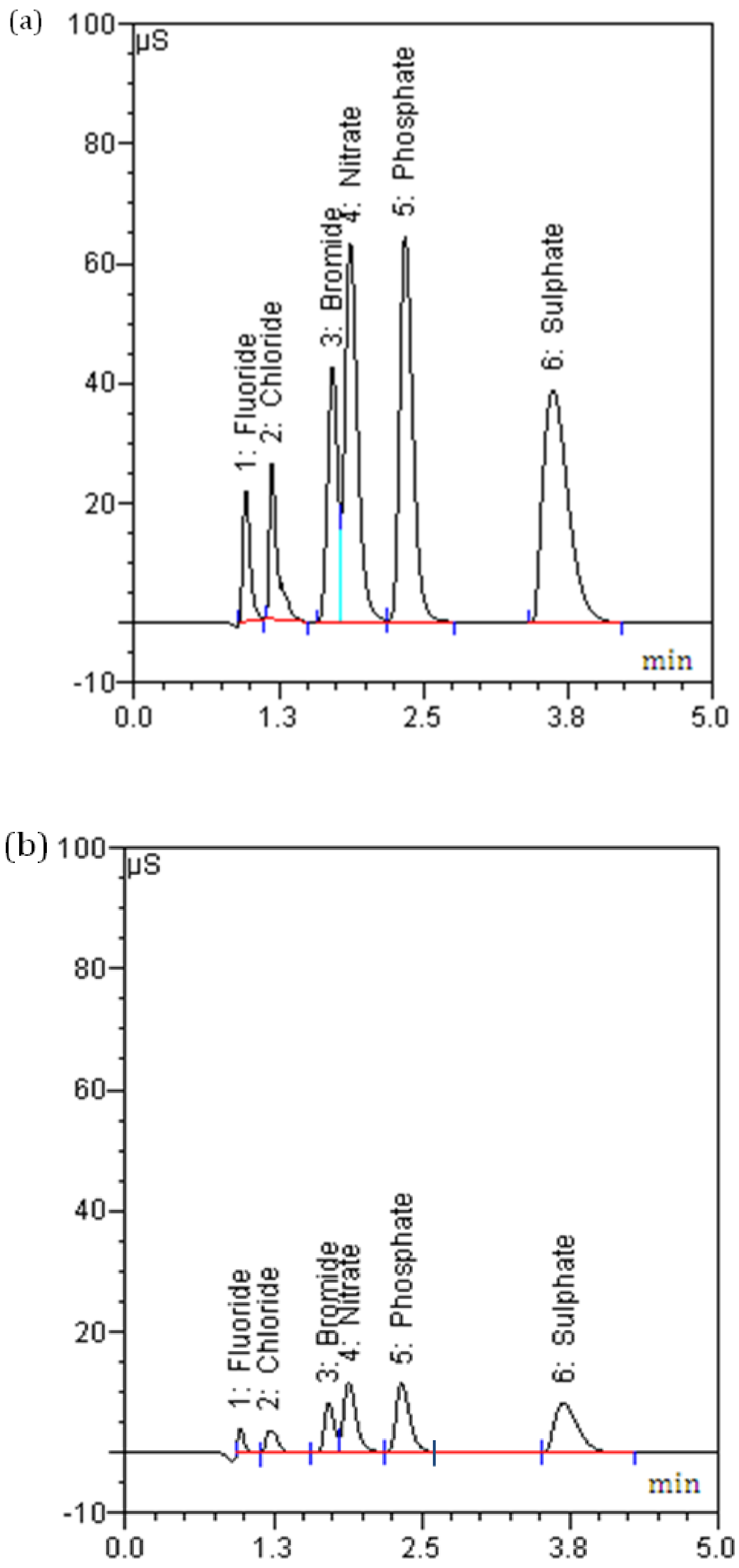

Figure 3.21: The chromatograms of two mixed standard solutions of (a) 10 times dilution and (b) 50 times dilution.

Table 3.4: The concentration of various ions in two mixed standard solutions which were used for the calibration of IC system.

Anions	Standard (mg/L) (1:10 dilution)	Standard (mg/L) (1:50 dilution)
Fluoride	3.0	0.6
Chloride	6.0	1.2
Bromide	25.0	5.0
Nitrate	30.0	6.0
Phosphate	60.0	12.0
Sulphate	30.0	6.0

3.5.4. UV-Visible spectrometer (UV-Vis)

Principle of the UV-Visible spectrometer

A UV-Visible spectrometer is normally used to measure the absorbance of a chemical solution. The Beer-Lambert law states that the fraction of the incident light absorbed by the solution is proportional to its molecular concentration (Figure 3.22) and the law is expressed as (Christian, 1994; Rao, 1975):

$$A = \log_{10} \frac{I_0}{I} = \varepsilon c l \qquad (3.4)$$

Where:

A = Absorbance

I_0 = the intensity of the incident light

I = the intensity of light after passing through the solution

ε = the absorption coefficient

c = concentration of solution

l = the path length of sample cell

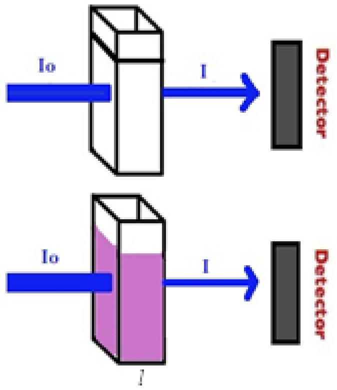

Figure 3.22: Diagram of Beer-Lambert absorption as an incident light travels through a cuvette of width *l*.

A spectrometer is an instrument that will resolve polychromatic radiation in to different wavelength. All spectrometers require (Christian, 1994):

1. a source of continuous radiation over the wavelengths of interest
2. a monochromator for selecting a narrow band of wavelengths from the source spectrum
3. a detector for converting radiant energy into electrical energy
4. a device to readout the response of the detector

A general schematic diagram of a double beam UV-Visible spectrometer is shown in Figure 3.23.

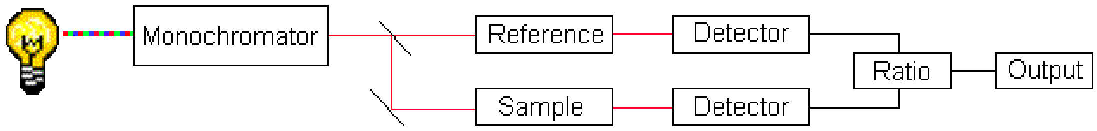

Figure 3.23: General schematic of double beam UV-Visible spectrometer.

All samples of this study, collected periodically during the photodegradation, were analysed using a UV-Vis spectrometer (PerkinElmer, Lambda 25) equipped with the double beam source (Figure 3.24). The standard cell holder used was a quartz cuvette with 1 × 1 cm size. The reference cell contained ultrapure water (18.2 MΩ) obtained from the Millipore system. UV-Vis spectra were recorded from 200 to 400 nm at a scan speed of 480 nm/min using UV WinLab software. The absorption peak at certain wavelength for each pesticide used was obtained before the illumination (Figure 3.25) and the depletion of the absorption peak was monitored qualitatively every one hour for five hours of UV light irradiation.

Figure 3.24: UV-Visible spectrophotometer.

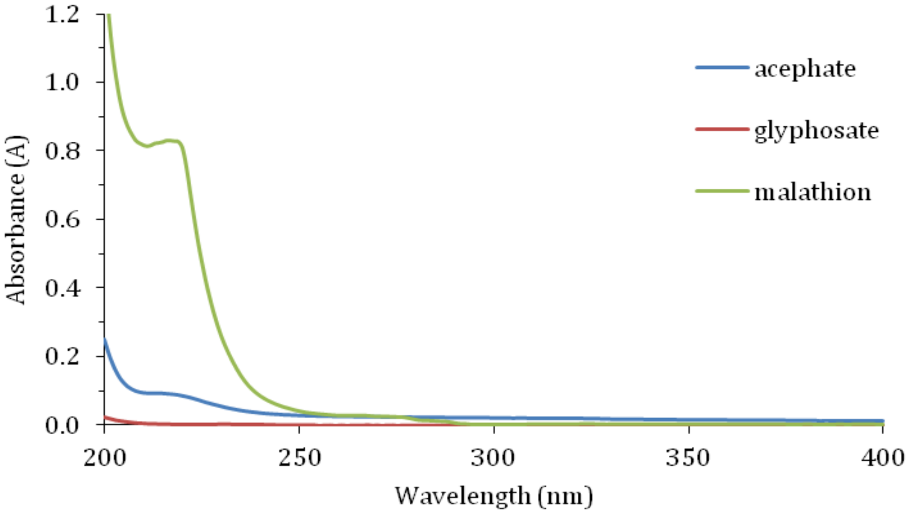

Figure 3.25: UV spectra of each pesticide solution containing 15 mg/L of concentration before illumination.

3.5.5. Flame atomic absorption spectrometer (FAAS)

Principles of FAAS

Every element has a specific number of electrons and the normal and most stable orbital configuration of an atom is known as the ground state. If light energy is applied to an atom, the light energy will be absorbed at a specific wavelength and an outer electron will be promoted to a less stable configuration known as the excited state. In the atomic absorption spectrometer, the sample is subjected to a high energy thermal environment in order to produce gases state free atoms. This environment is provided by a flame. The function of flame is to convert the sample aerosol into atomic vapour which can then absorb light from the primary light source (hollow cathode lamp). The amount of light absorbed is detected by the instrument which is related to the concentration of the element of interest in solution and again Beer-Lambert law is followed in this technique (Perkin Elmer, 1996; Christian, 1994).

Detection of metal ions (Cu(II), Zn(II) and Fe(II)) in solutions were carried out using a flame atomic absorption spectrometer, FAAS (AAnalyst 100-PerkinElmer Instrument) using a hollow cathode lamp (Figure 3.26). The operating parameters for metals detection are summarised in Table 3.5.

Figure 3.26: Atomic absorption spectrometer.

Table 3.5: Operating parameters for the FAAS.

Parameter	**Setting**		
	Copper	**Zinc**	**Iron**
Wavelength (nm)	324.8	213.9	248.3
Calibration standards (mg/L)	2.0, 4.0, 5.0	0.1, 0.5, 1.0	2.0, 4.0, 6.0
Flame	air / acetylene, fuel-lean(blue flame)		

3.6. References

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CHAPTER 4: Results and Discussions

CHAPTER 4: Results and Discussions

4.1. Summary

Photodegradation in water occurs by photolysis or advanced photooxidation. In this chapter, the degradation of acephate, glyphosate and malathion using a photolytic cell system is described. The presence of organic pollutants, including acephate, glyphosate and malathion, arising from both point and non-point sources in aqueous streams is well known. The fate and behaviour of these organic pollutants in water has been documented in literature but very little consideration has been given to the likely effects of heavy metals on their photodegradation. Most previous studies conducted on the degradation of organic pollutants have used titanium dioxide as a catalyst and the main aim was to identify the intermediate products normally produced during the photocatalytic degradation of organic pollutants. The main aim of the work described in this thesis is to optimise the photodegradation process by studying the effect of various parameters and also investigate the effects of Fe(II), Cu(II), and Zn(II) on the photodegradation of acephate, glyphosate and malathion.

4.2. Introduction

This chapter deals with the results obtained for the photodegradation of acephate, glyphosate and malathion using various photolytic systems under different experimental conditions. The percentage degradations of these organic pollutants were studied by monitoring the depletion of total organic carbon (TOC) as a function of irradiation time. The other analytical techniques used to follow the degradation processes are; 1) UV/Visible spectroscopy, 2) high performance liquid chromatography (HPLC), 3) atomic absorption spectroscopy (AAS) and 4) ion chromatography (IC). The results obtained using these analytical techniques are also discussed in this chapter.

Model solutions containing known concentration of the three organic pollutants (acephate, glyphosate and malathion) were prepared and the photodegradation of these pollutants was optimised by studying the effects of 1) UV source, 2) solution pH, 3) initial concentration of the organic pollutants, 4) chemical oxidants including H_2O_2, $K_2S_2O_8$, KIO_4 and $KBrO_3$, 5) Single metal ions of Fe(II), Cu(II) and Zn(II) ions, 6) Cu(II) ions in the presence of hydrogen peroxide and 7) mixed metal ions in the presence and absence of hydrogen peroxide.

The results obtained by studying various factors, for all three pesticides, are discussed in separate sections.

4.3. Photodegradation of Acephate

4.3.1. Effect of UV source

The effect of the UV source on the photodegradation of acephate was studied by carrying out replicates experiments under identical condition using a 400 W and a 600 W UV sources. The results obtained show that only 28.1% and 25.2% degradation were achieved after 5 hours when the solution was irradiated with a 400 W and a 600 W UV light sources respectively (Figure 4.1).

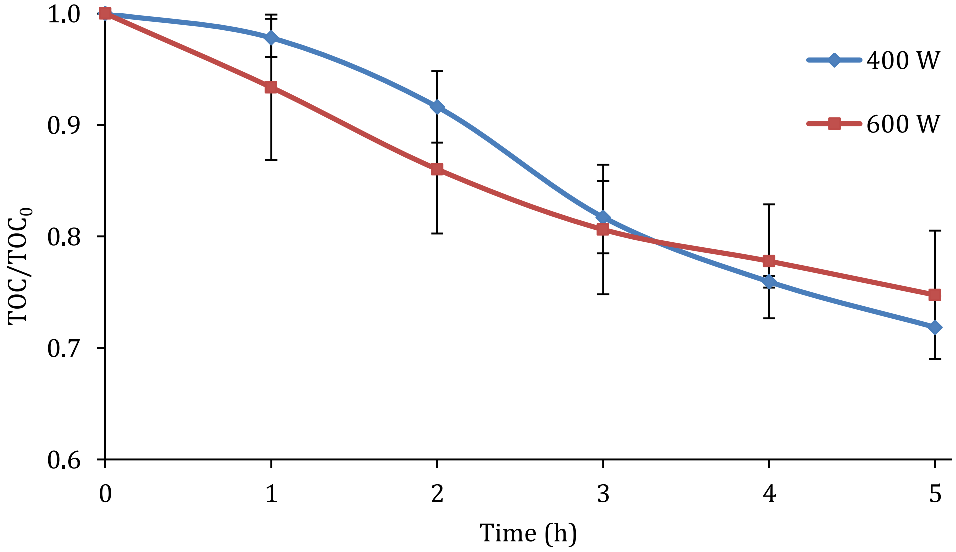

Figure 4.1 Effect of UV irradiation source on photodegradation of acephate. Experimental conditions: [acephate]$_0$ 15 mg/L; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.

Furthermore, the degradation was conducted without any catalyst or additional oxidants. These results show that a similar percentage degradation was achieved using either a 400 or a 600 W UV light. The TOC results are also supported by the UV/visible spectra (Figure 4.2) where similar spectra were achieved for the both lamps after 5 hours of irradiation. Nevertheless, a negative absorbance for the effect of 600 W UV lamp was observed after around 230 nm of wavelength. This could be due to the higher absorption of the blank solution than the sample solution. However, this should not be happened as the blank solution was deionized water. Hence, the negative absorbance could be due to the experimental error. All subsequent studies for the photodegradation of acephate were carried out using a 400 W lamp as a UV irradiation source.

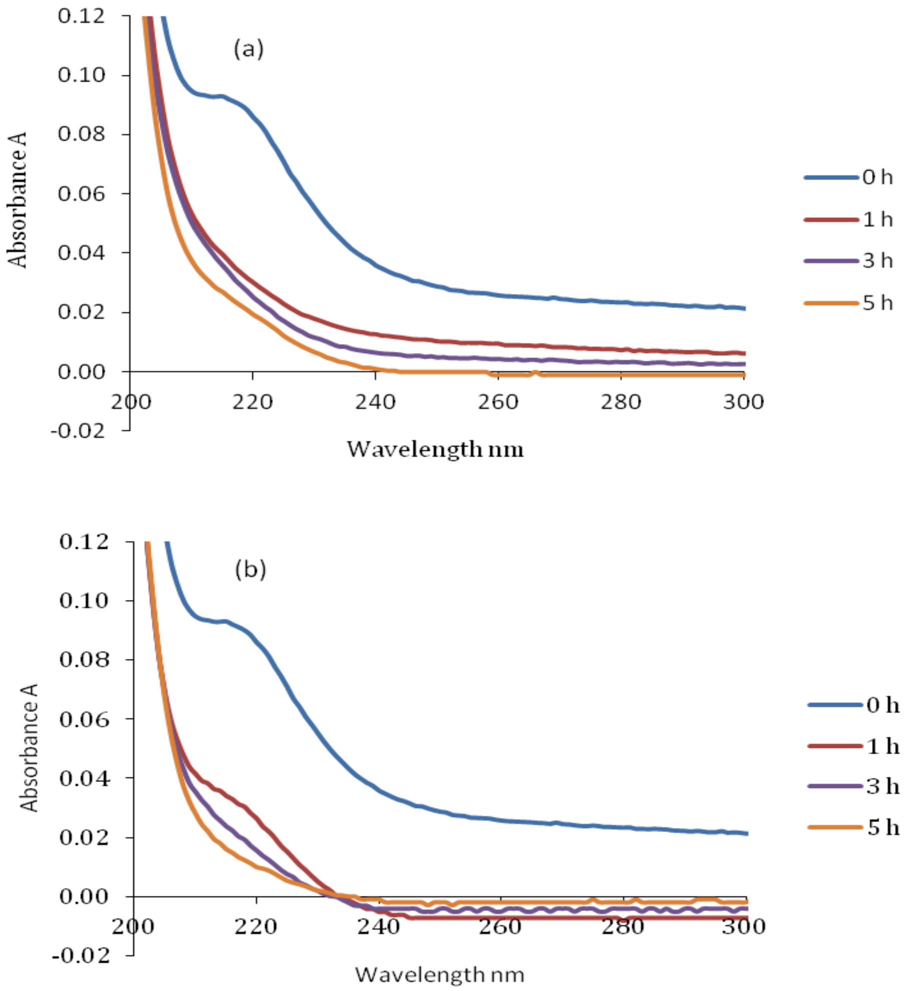

Figure 4.2 **UV spectra for photodegradation of acephate using (a) a 400 W and (b) a 600 W UV source. Experimental conditions: [acephate]$_0$ 15 mg/L; self-pH 5.5; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.**

4.3.2. Effect of pH

The pH is one of the most important parameters that influence the photodegradation of organic pollutant. Therefore, the degradation of acephate was studied at different pH values of 2.5, 4.5, 8.5 and 10.5 using a 400 W UV light. The self-pH of the model solution containing 15 mg/L of acephate was ~5.5-5.8. The results are shown in Figure 4.3.

The results showed that the percentage degradation of acephate decreased if the pH value was lower or higher than the self-pH of acephate. It can be seen that the increment in the photodegradation of acephate only happened at its self-pH 5.5 which was 28.1%. All subsequent studies were therefore conducted at their self-pH (~5.5-5.8) without pH adjustment.

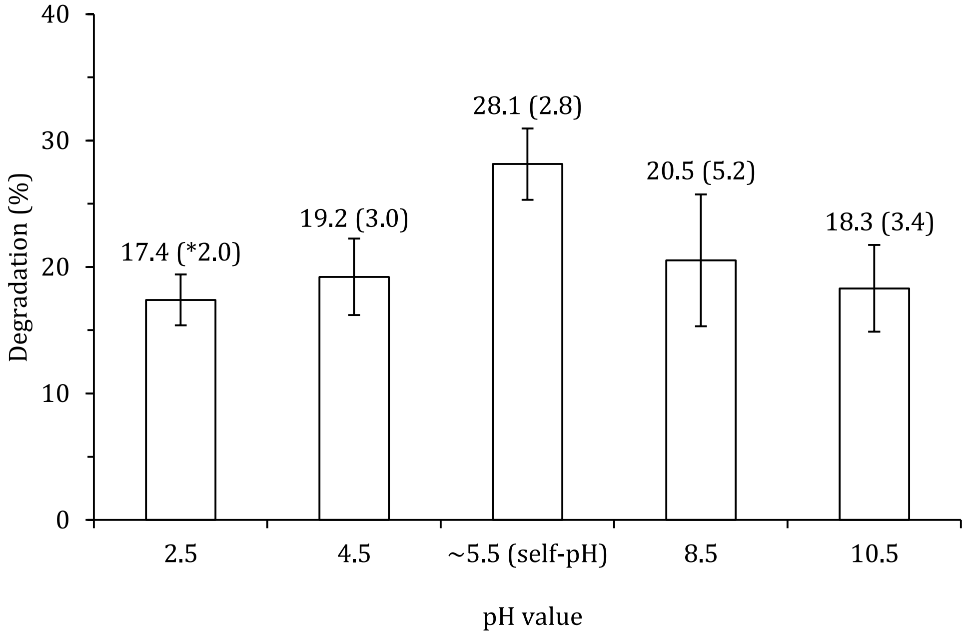

Figure 4.3 Effect of initial pH values on photodegradation of acephate. Experimental conditions: $[\text{acephate}]_0$ 15 mg/L; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h. * Values in parenthesis indicate the standard deviation values.

4.3.3. Effect of initial commercial acephate concentration on photodegradation

The results on the effect of initial concentration on the percentage degradation of acephate are shown in Figure 4.4. It was found that the percentage degradation increased from 28.1% to 54.0% when the initial concentration was increased from 15 mg/L to 50 mg/L after 5 h UV irradiation.

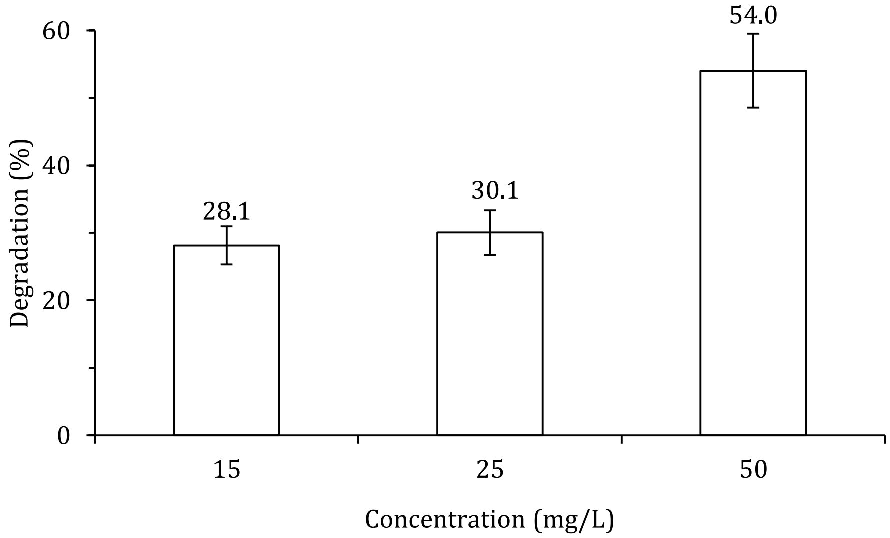

Figure 4.4 Effect of initial concentration of acephate using UV 400 W lamp for 5 hours irradiation at self-pH 5.5 with 3 L/min of air.

Photodegradation of acephate resulted in the mineralisation of the parent molecules and this was observed due to the formation of sulphate, nitrate and phosphate ions (Figure 4.5). Decomposition of acephate in the presence of oxygen normally proceed through the formation of different intermediates, however the complete mineralisation will produce sulphate, phosphate and nitrate ions thus leading to the proposed stoichiometry in equation (4.1):

$$C_4H_{10}NO_3PS + 9O_2 \rightarrow 4CO_2 + NO_3^- + PO_4^{3-} + SO_4^{2-} + 2H_2O + 6H^+ \quad (4.1)$$

The concentration of sulphate increased from 6.7 to 19.0 mg/L whereas concentrations of phosphate and nitrate increased from 3.8 to 16.5 mg/L and 0.4 mg/L to 1.1 mg/L respectively, when the initial acephate concentration was increased from 15 mg/L to 50 mg/L. The values for detected anions were lower than the calculated theoretical values (Table 4.1) since the photodegradation of acephate was not totally completed after 5 h irradiation.

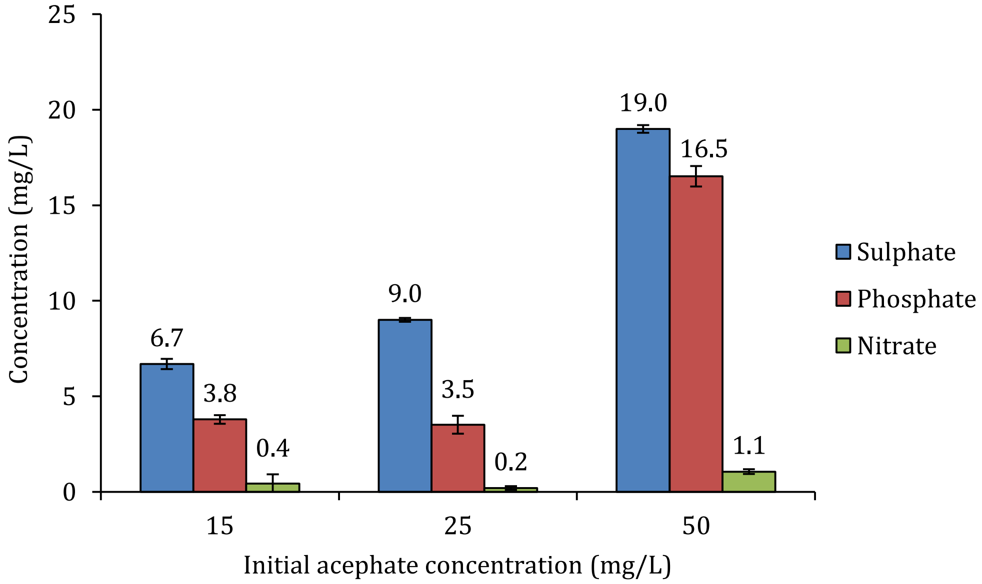

Figure 4.5 Production of inorganic anions after 5 h photodegradation of various initial acephate concentrations at self-pH 5.5 using a 400 W UV light.

Table 4.1 Calculated theoretical values for sulphate, phosphate and nitrate anions concentrations for each initial acephate concentration.

Anions	**Initial acephate concentrations (mg/L) and the corresponding concentrations of sulphate, phosphate and nitrate ions (mg/L)**		
	15.0	**25.0**	**50.0**
Sulphate	7.9	13.1	26.0
Phosphate	7.8	13.0	26.2
Nitrate	5.1	8.5	16.9

To study the kinetics of acephate photodegradation, the Langmuir-Hinselwood kinetic equation was used. The degradation reaction equation can be written as follows (Fu *et al.*, 2012):

$$ln\left(\frac{C_0}{C}\right)=kt \tag{4.2}$$

Where C is the acephate concentration at time t, C_0 is the initial concentration of acephate, k is the rate constant, equivalent to the slope of the linear regression (k in min^{-1}). By plotting $ln\left(\frac{C_o}{C}\right)$ (TOC concentration) as a function of reaction time yielded a straight line in Figure 4.6. These results show that the degradation of acephate at various initial concentrations followed the first order kinetic reaction with rate constants of 0.003, 0.001 and 0.001 min^{-1}, respectively, for 50 mg/L, 25 mg/L and 15 mg/L initial acephate concentrations. Degradation rate of acephate at initial concentrations of 15 and 25 mg/L were very close to each other and the difference can be considered insignificant, meanwhile the removal of acephate at initial concentration of 50 mg/L was significantly higher. However, the initial concentration of 15 mg/L of acephate was selected for all subsequent studies except for the study of section 4.3.4. This value was found to be high enough for the detection of mineralisation products.

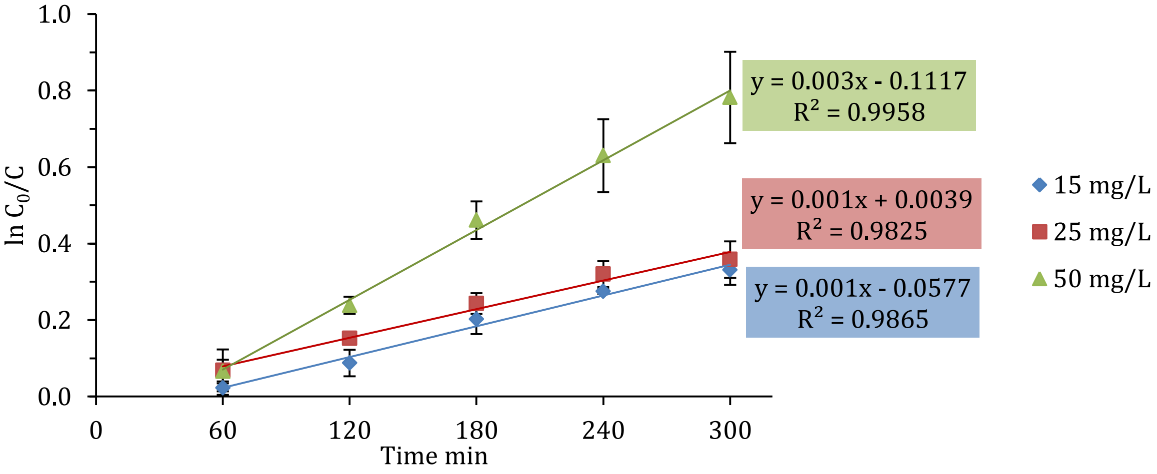

Figure 4.6 Degradation kinetics of various initial commercial formulation acephate concentration showing the rate constants (*k* = slope) and regression coefficients (*R*²) for each based on the TOC reduction under 5 hours irradiation of 400W UV lamp at self-pH 5.5.

4.3.4. Effect of various oxidants

The effects of various oxidants namely H_2O_2, $K_2S_2O_8$, KIO_4 and $KBrO_3$ on the photodegradation of acephate were studied in the presence and absence of air. The results show that percentage degradation value for photodegradation of 50 mg/L of acephate in the absence of air and without any oxidant was only 9.0% (Figure 4.7). Whilst the values for degradation of acephate without air in the presence of H_2O_2, $K_2S_2O_8$, KIO_4 and $KBrO_3$ were 10.0%, 13.6%, 16.6% and 13.9% respectively. The degradation values were very low when photodegradation process occurred without agitating the acephate solution with air. In contrast, when air is introduced to the system, the percentage degradation of acephate was significantly increased from 9.0% to 54.0% for the control experiment. Further increment occurred when 50 mg/L of H_2O_2 was added to the solution (74.0%). It was observed that the percentage degradation of acephate also increased from 13.6% to 27.8% and 16.6% to 38.1% for $K_2S_2O_8$ and KIO_4 respectively. However, a slight decrease occurred for the photodegradation of acephate in the presence of $KBrO_3$ when the non-aerated process is being introduced to the air. Among the oxidants, H_2O_2 in the presence of air show the highest percentage degradation of acephate.

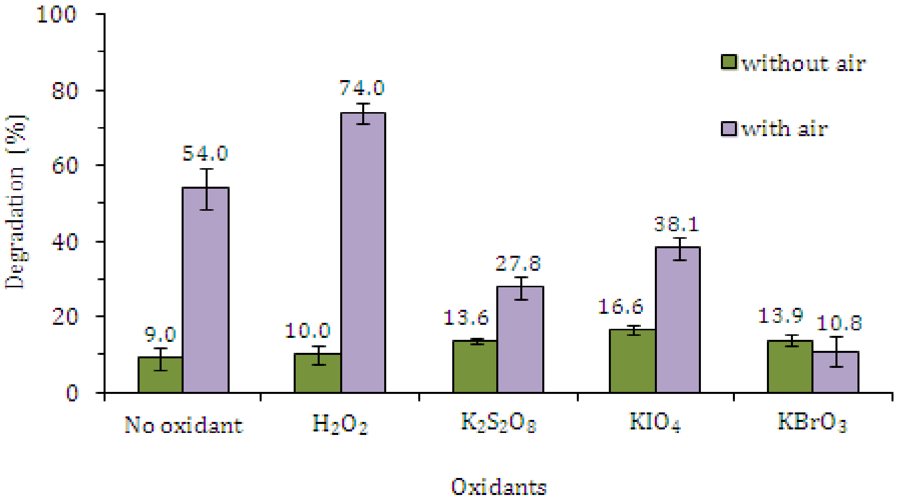

Figure 4.7 Effect of various oxidants in the absence and presence of 3 L/min of air. Experimental conditions: oxidants concentration = [H_2O_2] = [$K_2S_2O_8$] = [KIO_4] = [$KBrO_3$] = 50 mg/L; [acephate]$_0$ 50 mg/L; self-pH 5.5; UV source 400 W; solution volume 400 ml; irradiation time 5 h.

4.3.5. Effect of hydrogen peroxide, H_2O_2 concentration

The effect of adding H_2O_2 on the photolysis of commercial formulation of acephate was investigated by varying the amount of H_2O_2 from 7.5 to 30 mg/L. The results show that percentage degradation (Figure 4.8) increased by increasing the concentration of H_2O_2.

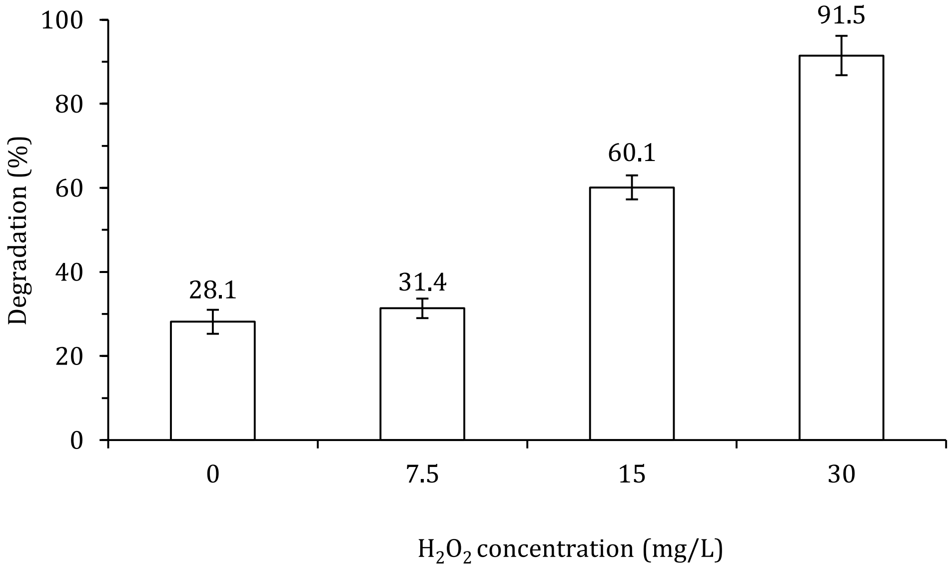

Figure 4.8 Effect of the H_2O_2 concentration on the photodegradation efficiency of acephate. Experimental conditions: $[\text{acephate}]_0$ 15 mg/L; self-pH 5.5; UV source 400 W; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.

4.3.6. Effect of heavy metal ions

Experiments were conducted to investigate the effect in the presence of Fe(II), Cu(II) and Zn(II) ions (5 and 15 mg/L) on the photolytic degradation of acephate (15 mg/L). The results show (Figure 4.9) that there was an increment in the photodegradation of acephate in the presence of single metal ions. In the presence of 5 mg/L of each single metal ion, the degradation increased from 28.1% to 72.0%, 36.9% and 54.7% in the presence of Fe(II), Cu(II) and Zn(II) ions respectively. Further increases were observed when the concentration of Cu(II) and Zn(II) ion increased from 5 mg/L to 15 mg/L. In contrast, the presence of 15 mg/L of Fe(II) ions has slightly decreased the percentage degradation of acephate (from 72.0% to 60.9%) however, the value was still higher compared to the percentage degradation of acephate (28.1%) in the absence of metal ions.

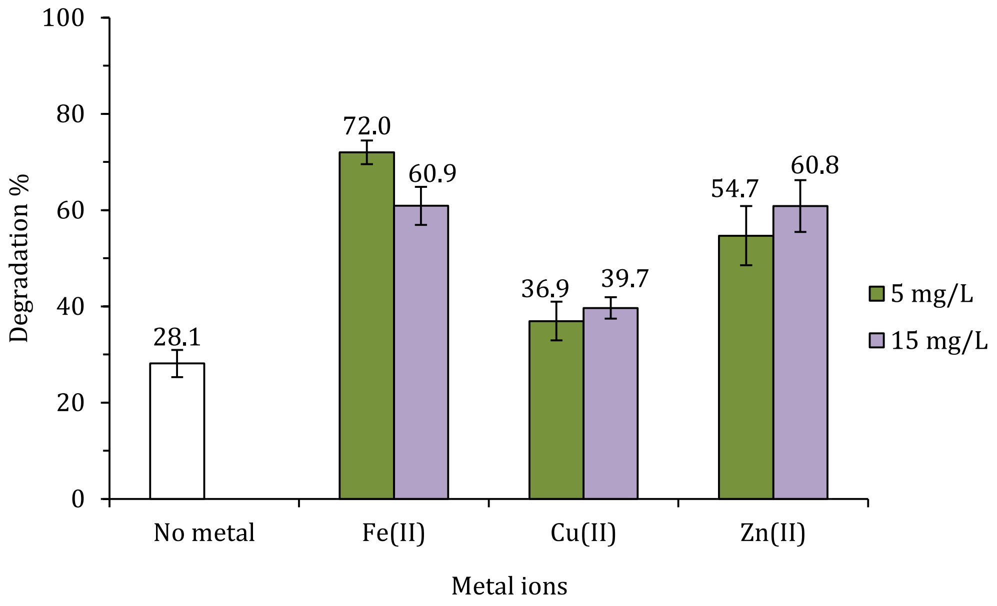

Figure 4.9 **Effect of metal ions on the photodegradation of acephate. Experimental conditions: [acephate]$_0$ 15 mg/L; self-pH 5.5; UV source 400 W; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.**

4.3.7. Effect of copper ions in the presence of hydrogen peroxide

Although all the single metal ions heighten the percentage degradation of acephate, however, copper ions gave the lowest increment among the selected metal ions, hence, the effect of hydrogen peroxide as an oxidant, in the presence of copper ions was investigated. As expected, the TOC removal of acephate increased from 36.9% to 44.6% after 5 h irradiation (Figure 4.10).

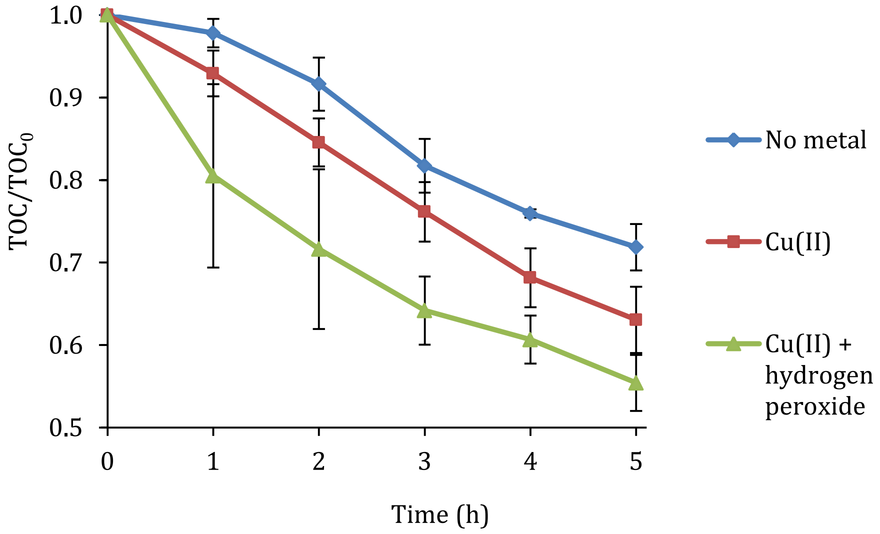

Figure 4.10 Effect of Cu(II) ions on photodegradation of acephate in the presence of H_2O_2. Experimental conditions: [acephate]$_0$ 15 mg/L; [Cu(II)] ions 5 mg/L; [H_2O_2] 30 mg/L; self-pH 5.5; solution volume 400 ml; irradiation time 5 h.

4.3.8. Effect of mixed metal ions in the presence of hydrogen peroxide

A model solution containing mixed metal ions was prepared to simulate a real wastewater which normally contained a mixture of various types of metal ions. The mixed metal ions studied was a mixture of 5 mg/L of each Fe(II), Cu(II) and Zn(II) ions. The presence of mixed metal ions in the photodegradation of acephate gave a slight increment from 28.1% to 36.3% and risen to 51.0% with the addition of 30 mg/L of H_2O_2. The result of the effect of mixed metal ions in the photodegradation of acephate is shown in Figure 4.11. The presence of hydrogen peroxide in the mixed metal ions influence the degradation process, thus, clearly reflected the positive role of hydrogen peroxide in the mixed metal ions solution.

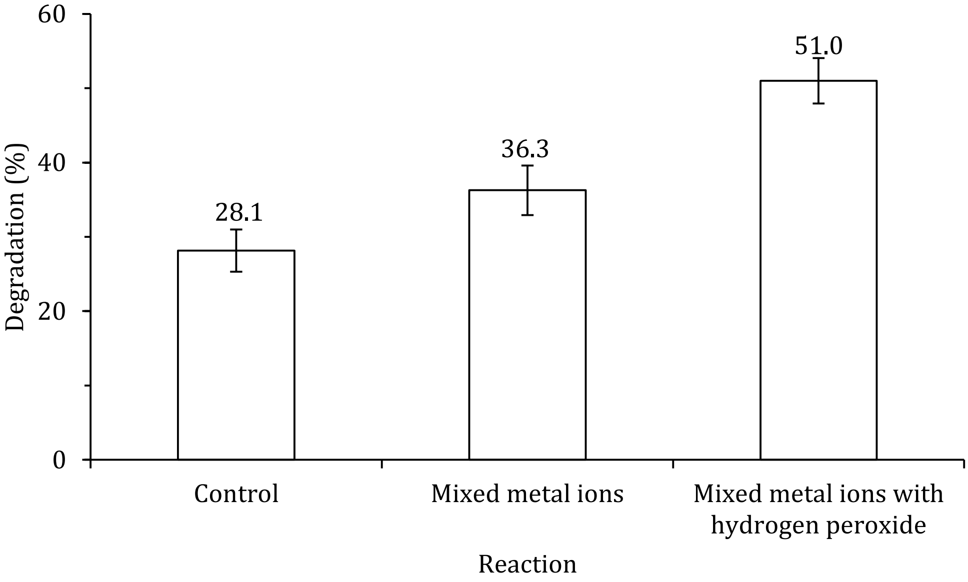

Figure 4.11 Effect of mixed metal ions on photodegradation of acephate in the presence of H_2O_2. Experimental conditions: $[\text{acephate}]_0$ 15 mg/L; mixed metal ions concentration = [Fe(II)] = [Cu(II)] = [Zn(II)] ions = 5 mg/L each; $[H_2O_2]$ 30 mg/L; self-pH 5.5; solution

4.4. Photodegradation of Glyphosate

4.4.1. Effect of UV source

The effect of UV light was studied for the photodegradation of glyphosate and the results are in Figure 4.12. The percentage degradation of glyphosate using a 400 W UV source was 22.3% and this value slightly increased to 30.5% when the UV source was changed from 400 W to 600 W (Figure 4.12).

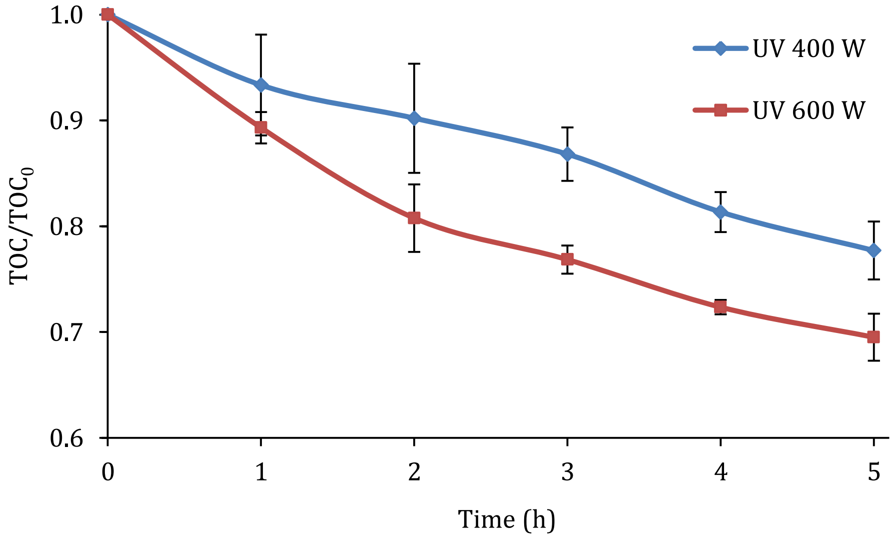

Figure 4.12 Effect of UV irradiation source on photodegradation of glyphosate. Experimental conditions: [glyphosate]$_0$ 15 mg/L; self-pH 5.0; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.

4.4.2. Effect of pH

The self-pH of the model solution containing 15 mg/L of glyphosate was ~5.0-5.4. A set of experiments were conducted to study the effect of initial pH ranging from pH 3 to pH 8. The result (Figure 4.13) was similar to those observed for acephate where the removal of glyphosate from solution was significantly higher at the self-pH value. Thus, all subsequent studies related to the photodegradation of glyphosate were conducted at its self pH without any pH adjustment.

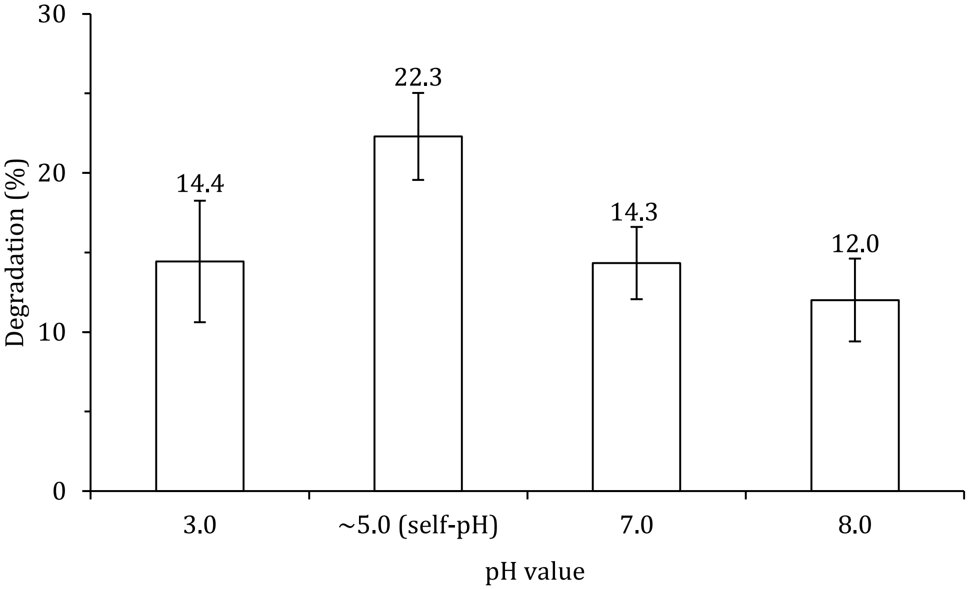

Figure 4.13 Effect of initial pH values on photodegradation of glyphosate. Experimental conditions: [glyphosate]$_0$ 15 mg/L; 400 W UV source; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.

4.4.3. Effect of initial commercial glyphosate concentration on photodegradation

The effect of initial concentration on photodegradation of commercial glyphosate was investigated over the range from 15 to 100 mg/L. The results (Figure 4.14) show a slight drop in the degradation of glyphosate when the concentration was increased from 15 to 100 mg/L.

The mineralisation of glyphosate can also be investigated by measuring the concentrations of phosphate and nitrate ions during the photolytic process. The proposed stoichiometry equation (4.3) is given below:

$$C_3H_8O_5PN + 5O_2 \rightarrow 3CO_2 + PO_4^{3-} + NO_3^- + 2H_2O + 4H^+ \qquad (4.3)$$

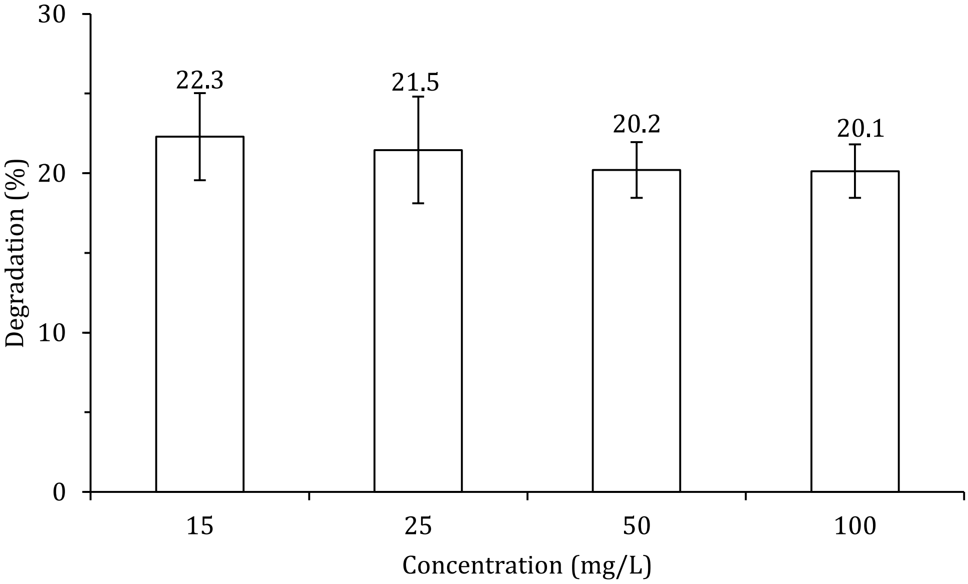

Figure 4.14 Effect of initial concentration of glyphosate using a 400 W UV source for 5 hours irradiation at self-pH 5.0 with the air flow rate of 3 L/min.

The result (Figure 4.15) obtained from an ion chromatography analysis show that the concentrations for phosphate ions were 0.4, 0.6, 0.7 and 0.9 mg/L for the photodegradation of glyphosate at initial concentration of 15, 25, 50 and 100 mg/L correspondingly. Meanwhile, the detected concentrations for nitrate ions were increased from 0.1 to 0.3 mg/L when the initial glyphosate concentration was increased from 15 to 100 mg/L. Although the concentrations of both phosphate and nitrate anions increased with the increase in the initial glyphosate concentration (Figure 4.15), however, detected concentrations were very low compared to the theoretical values (Table 4.2).

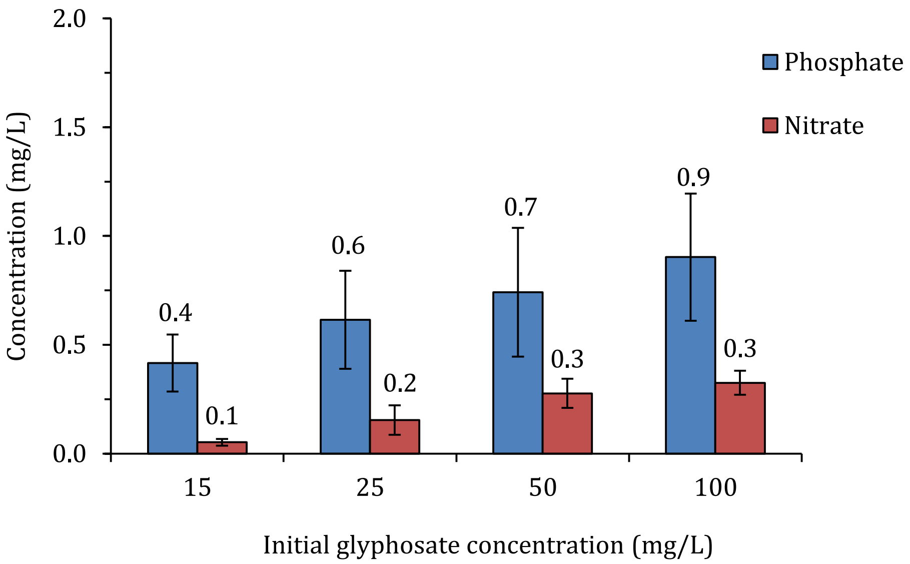

Figure 4.15 Production of inorganic anions after 5 h photodegradation of various initial glyphosate concentrations at self-pH 5.0 using a 400 W UV light.

Table 4.2 Calculated theoretical values for phosphate and nitrate anions concentration for each initial glyphosate concentration.

Anions	**Initial glyphosate concentrations (mg/L) and the corresponding concentrations of phosphate and nitrate ions (mg/L)**			
	15.0	**25.0**	**50.0**	**100.0**
Phosphate	8.9	14.8	29.5	59.0
Nitrate	5.8	9.6	19.3	38.5

The results of kinetic study (Figure 4.16) clearly revealed that the difference in the photodegradation of glyphosate at various initial concentrations was not significant. In view of these results, it was decided to use 15 mg/L of glyphosate for all subsequent studies.

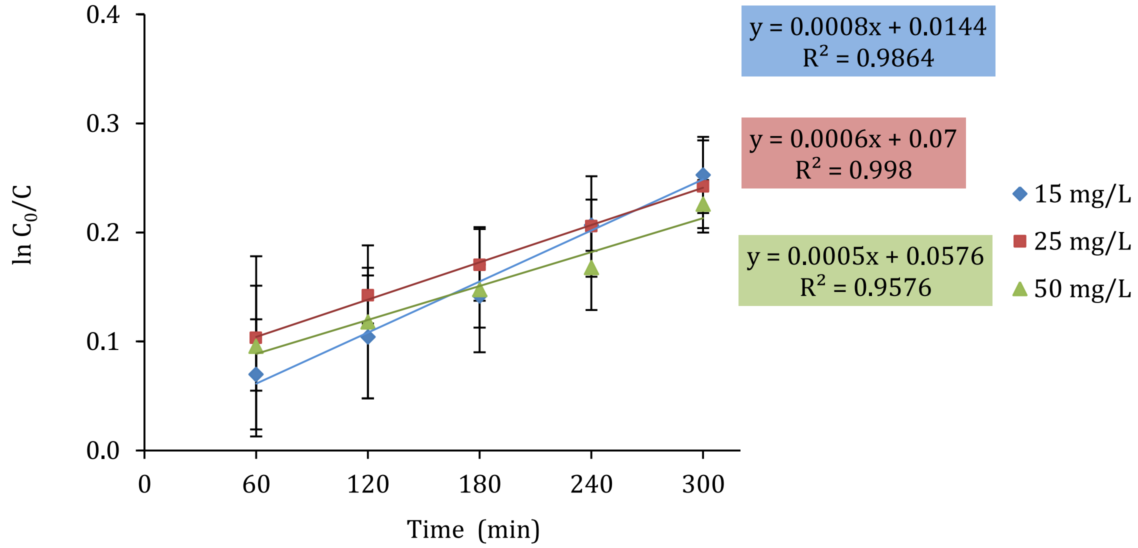

Figure 4.16 **Degradation kinetics of various initial commercial formulation glyphosate concentration showing the rate constant (*k*=slope) and regression coefficients (R^2) for each, based on the TOC reduction under 5 hours irradiation of 400 W UV source at self-pH 5.0.**

4.4.4. Effect of H_2O_2 concentration

The effect of H_2O_2 on the photodegradation efficiency of glyphosate was conducted using 7.5, 15.0 and 30.0 mg/L of H_2O_2. The results (Figure 4.17) show that the degradation efficiency of glyphosate increased by increasing the concentration of H_2O_2 from 0 to 30 mg/L. The percentage degradation values increased from 22.3% to 36.8%, 60.1% and 81.3% when the amount of H_2O_2 increased from 0 mg/L to 7.5, 15.0 and 30.0 mg/L respectively.

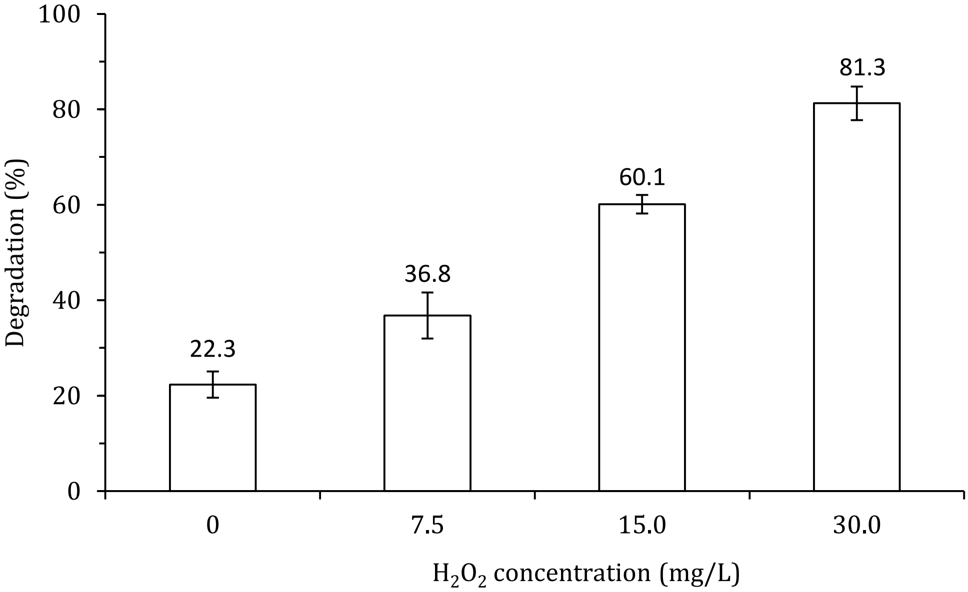

Figure 4.17 **Effect of the H_2O_2 concentration on the photodegradation efficiency of glyphosate. Experimental conditions: [glyphosate]$_0$ 15 mg/L; self-pH 5.0; UV source 400 W; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.**

4.4.5. Effect of heavy metal ions

The effect of adding single metal ions (Fe(II), Cu(II) and Zn(II)) on the photodegradation efficiency of glyphosate was investigated using 5 and 15 mg/L of each metal. The results show that the addition of 5 mg/L of Fe(II) ions significantly increased the degradation efficiency of glyphosate from 22.3% to 82.2% (Figure 4.19). However, when the concentration of Fe(II) ions was increased to 15 mg/L, the percentage degradation reduced to 66.4%, nevertheless, the value was still higher than the value of the photodegradation of glyphosate in the absence of Fe(II) ions. It has also been supported by the HPLC results (Figure 4.18(b2)) where the parent peak (retention time 3.18) corresponding to the original compound disappeared after 5 h irradiation in the presence of 5 mg/L of Fe(II) ion.

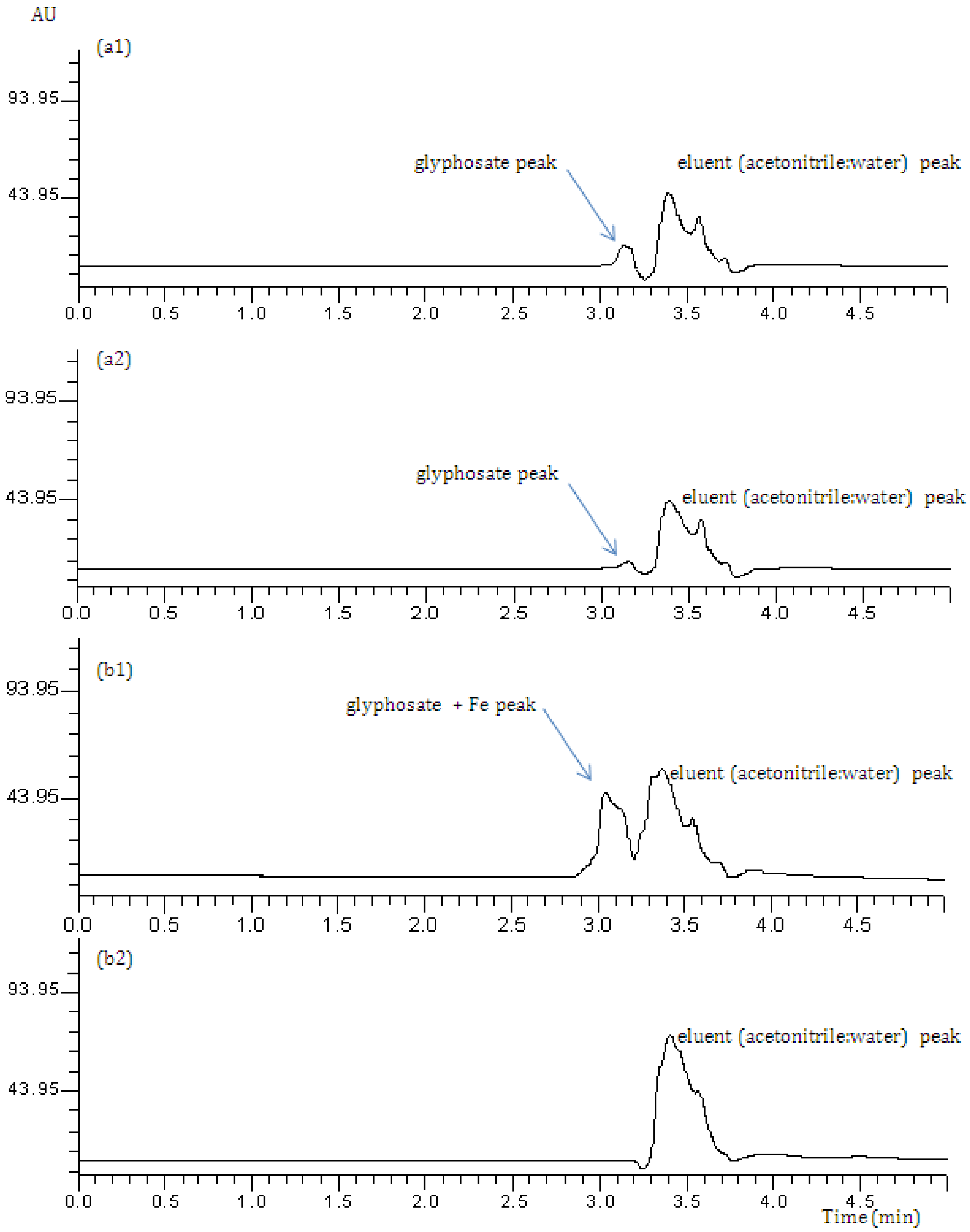

Figure 4.18 **HPLC chromatograms for photodegradation of glyphosate in the absence of Fe(II) ion (a1) before (a2) after 5 h irradiation; and HPLC chromatograms for photodegradation of glyphosate in the presence of Fe(II) ion (b1) before (b2) after 5 h irradiation. Experimental conditions: [glyphosate]$_0$ 15 mg/L; [Fe(II)] 5 mg/L; self-pH 5.0; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.**

The next aim of this task was to investigate the effect of Cu(II) ions (5-15 mg/L) on the photodegradation of glyphosate. The results (Figure 4.19) indicate that the presence of 5 mg/L of Cu(II) ions slightly reduced the efficiency of the degradation of glyphosate. A further reduction was observed when the concentration of Cu(II) ion increased from 5 mg/L to 15 mg/L. The corresponding values after 5 h were 20.0% and 16.4%, respectively. The addition of 5 mg/L of Zn(II) ion also show an increase in the photodegradation of glyphosate, however it was noticed that the percentage degradation value slightly dropped 26.8% to 24.7% when the concentration of Zn(II) ions increased from 5 mg/L to 15 mg/L.

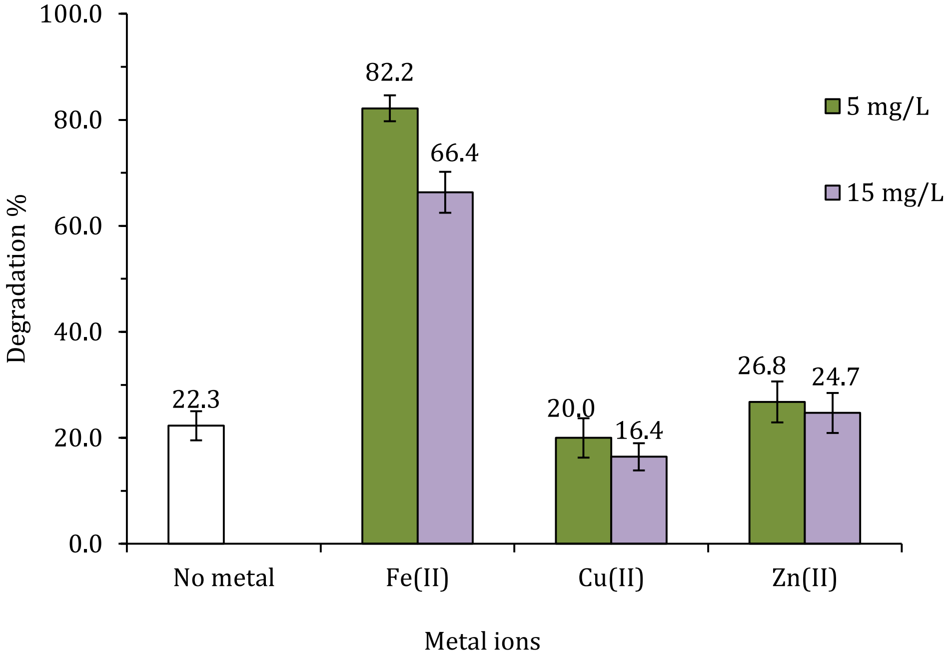

Figure 4.19 Effect of metal ions on photodegradation of glyphosate. Experimental conditions: [glyphosate]$_0$ 15 mg/L; self-pH 5.0; UV source 400 W; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.

4.4.6. Effect of copper ions in the presence of H_2O_2

The reduction in the photodegradation of glyphosate in the presence of copper ions can be overcome by adding hydrogen peroxide to the solution. The addition of 30 mg/L of H_2O_2 to the solution in the presence of 5 mg/L of copper ions increased the degradation of glyphosate from 20.0% to 36.5%. The data in Figure 4.20 show that a considerable increase in the degradation of glyphosate was observed after two hours of irradiation.

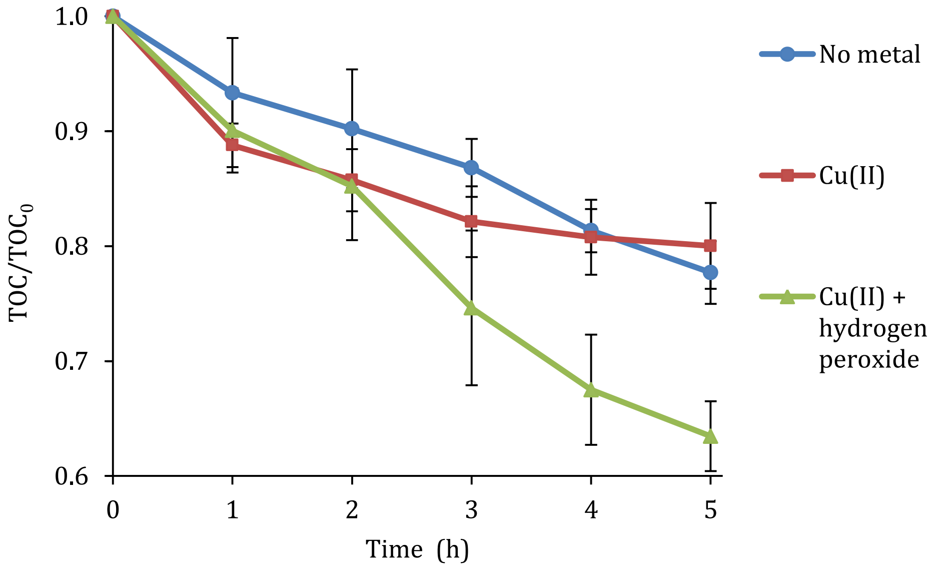

Figure 4.20 Effect of Cu(II) ions on photodegradation of glyphosate in the presence of H_2O_2. Experimental conditions: [glyphosate]$_0$ 15 mg/L; [Cu(II)] ions 5 mg/L; [H_2O_2] 30 mg/L; self-pH 5.0; 400 W UV source; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.

4.4.7. Effect of mixed metal ions in the presence of hydrogen peroxide

The effects of mixed metal ions on the degradation of glyphosate show (Figure 4.21) a slight reduction from 22.3% to 19.7%. However, no significant increase in the percentage degradation of glyphosate was observed (22.5%) in the presence of H_2O_2 an oxidant.

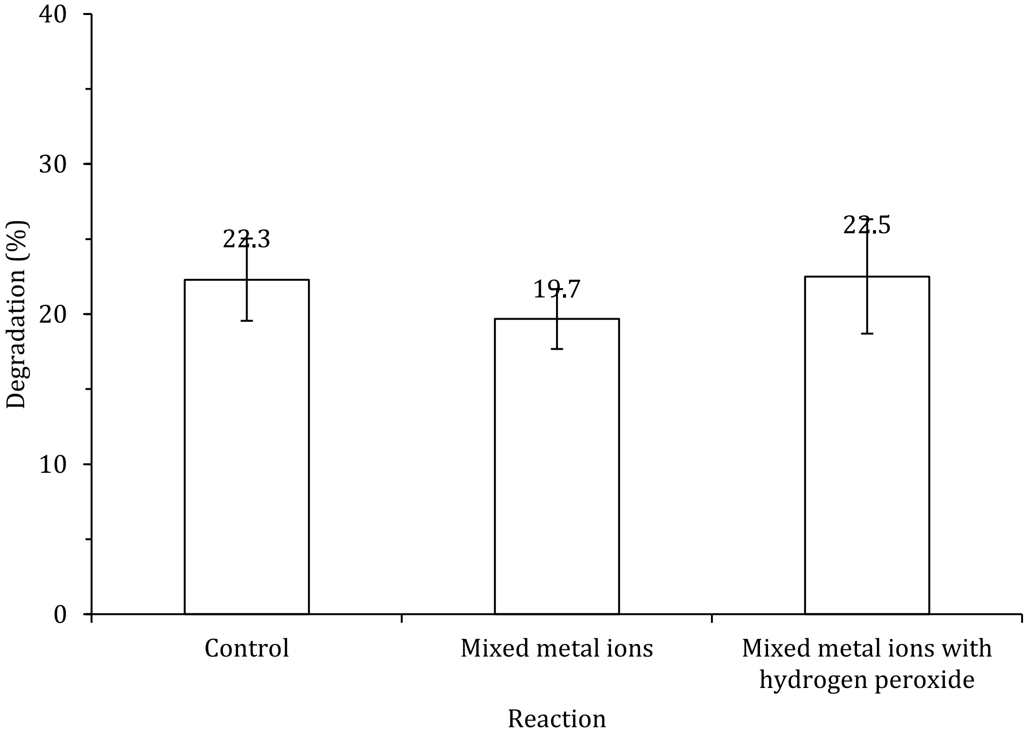

Figure 4.21 Effect of mixed metal ions in photodegradation of glyphosate in the presence of H_2O_2. Experimental conditions: $[\text{glyphosate}]_0$ 15 mg/L; mixed metal ions concentration = [Fe(II)] = [Cu(II)] = [Zn(II)] ions = 5 mg/L each; $[H_2O_2]$ 30 mg/L; self-pH 5.0; 400 W UV source; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.

4.5. Photodegradation of Malathion

4.5.1. Effect of UV source

The results (Figure 4.22) show that the degradation of malathion was slightly higher when a 600 W UV source was used to irradiate the aqueous solution containing 15 mg/L malathion. The percentage degradation of malathion was 89.7% and 87.2% with the use of 600 W and 400 W UV sources respectively. These results were insignificant. However, in order to synchronise this study, the UV 400 W lamp was selected for the rest of the experiments.

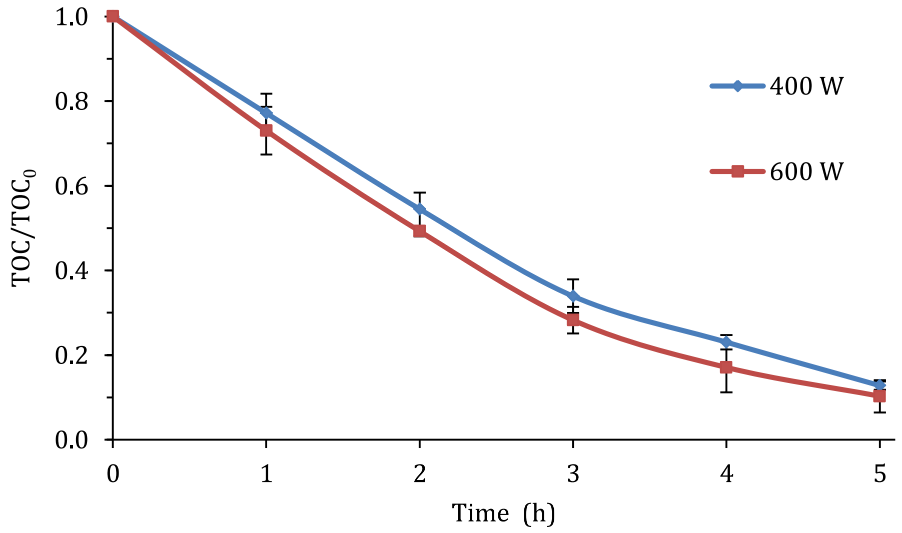

Figure 4.22 Effect of different watt of UV light irradiation on photodegradation of malathion. Experimental conditions: $[\text{malathion}]_0$ 15 mg/L.

4.5.2. Effect of pH

The self-pH of the model solution containing 15 mg/L of commercial formulation of malathion was ~5.0-5.3. Thus, it was decided to investigate the effect of pH 3.0, 7.0 and 8.0 on the photolysis of commercial formulation of malathion using a 400 W UV light as a source of UV irradiation. The pH was adjusted at the beginning of the experiment by adding aqueous solutions of 0.1 M NaOH and 0.1 M HCl and the results are in Figure 4.23.

It can be seen that the photolysis of malathion at its self-pH 5.0 was 87.2%. However, no significant increase in the percentage degradation of malathion was observed when the pH values of the solution were increased or decreased from the natural pH value. The percentage degradation was 42.8%, 57.0% and 43.5% for the pH 3.0, 7.0 and 8.0 respectively. Thus, all the subsequent studies were carried out at the self-pH value of ~5.0.

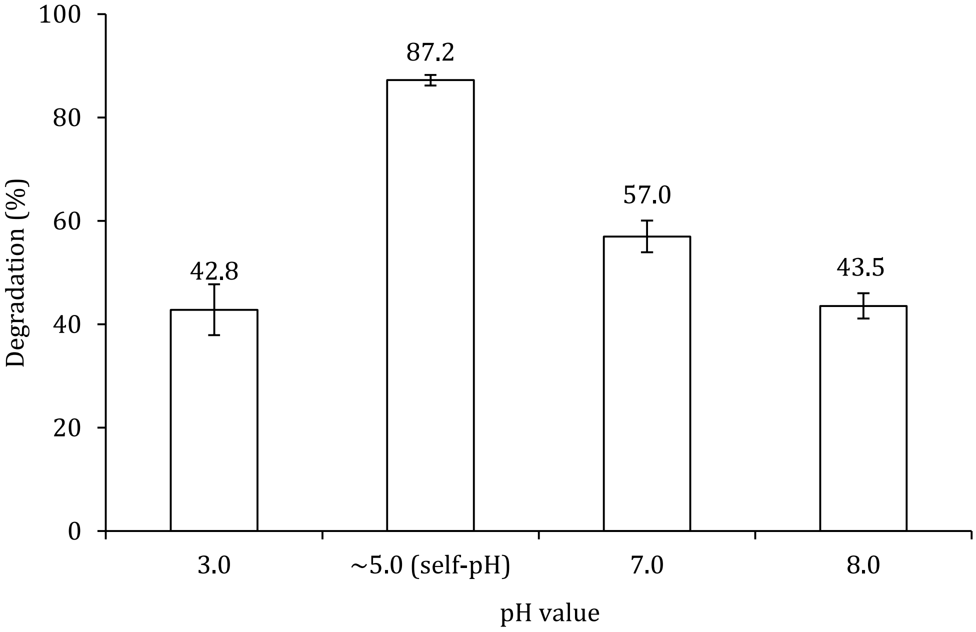

Figure 4.23 Effect of initial pH values on photodegradation of malathion. Experimental conditions: [malathion]$_0$ 15 mg/L; solution volume 400 ml; irradiation time 5 h.

4.5.3. Effect of initial commercial malathion concentration on photodegradation

It is important to study the effect of initial concentration of the substrate in order to know its efficiency towards degradation. The experiments were conducted by varying the initial concentration of commercial malathion at beginning of the experiment from 15 mg/L to 100 mg/L. The results (Figure 4.24) show that the higher the initial commercial malathion concentration (100 mg/L), the lower the percentage degradation (76.9%). When the concentration of malathion reduced to 15 mg/L, the percentage degradation was 87.2%. These results clearly show that the concentration of initial commercial formulation malathion has an effect on the amount of commercial formulation malathion degraded. Hence, in order to determine the reaction rate constants for the effect of initial concentration of commercial formulation malathion, the $ln\left(\frac{C_o}{C}\right)$ (TOC concentration) was plotted as a function of reaction time which then yielded a straight line (Figure 4.25). It demonstrated that the degradation follows the first-order reaction which derived from the Langmuir-Hinshelwood kinetic equation and the rate constant (k in min^{-1}) was equivalent to the slope of the linear regression. The k values for initial concentration of 15, 25, 50 and 100 mg/L were 0.0077, 0.0074, 0.0072, and 0.0063 min^{-1} respectively. Comparing the k values between 100 mg/L and 15 mg/L, it was found that the photolytic degradation rate with 15 mg/L occurred slightly faster than that 100 mg/L. Thus all the subsequent studies were carried out using a 15 mg/L as a concentration of commercial formulation of malathion.

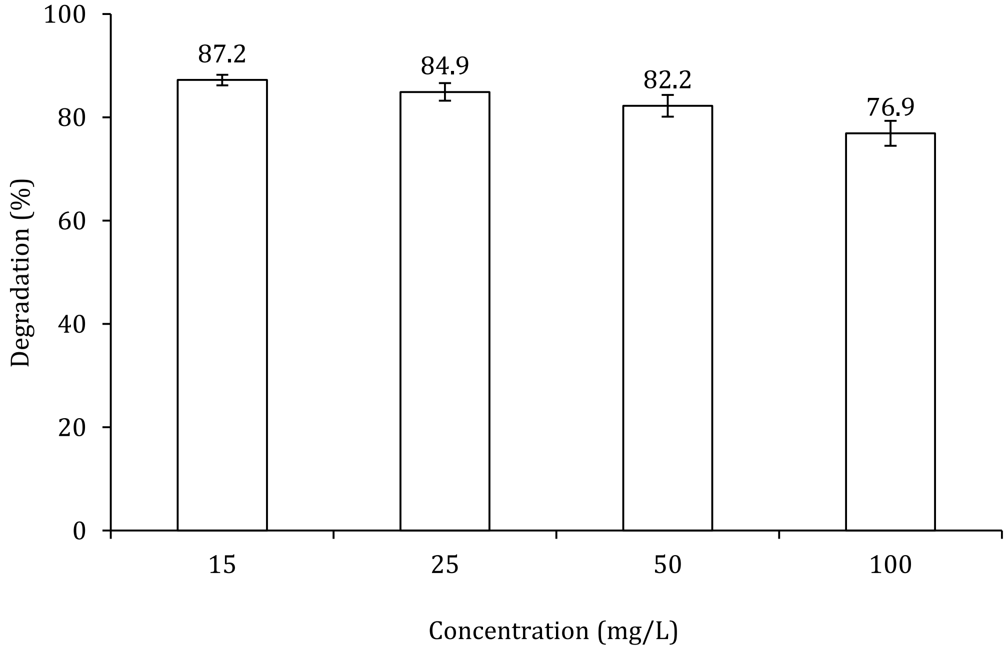

Figure 4.24 Effect of initial concentration of malathion using 400 W UV lamp for 5 hours irradiation at self-pH 5.0 with 3 L/min of air.

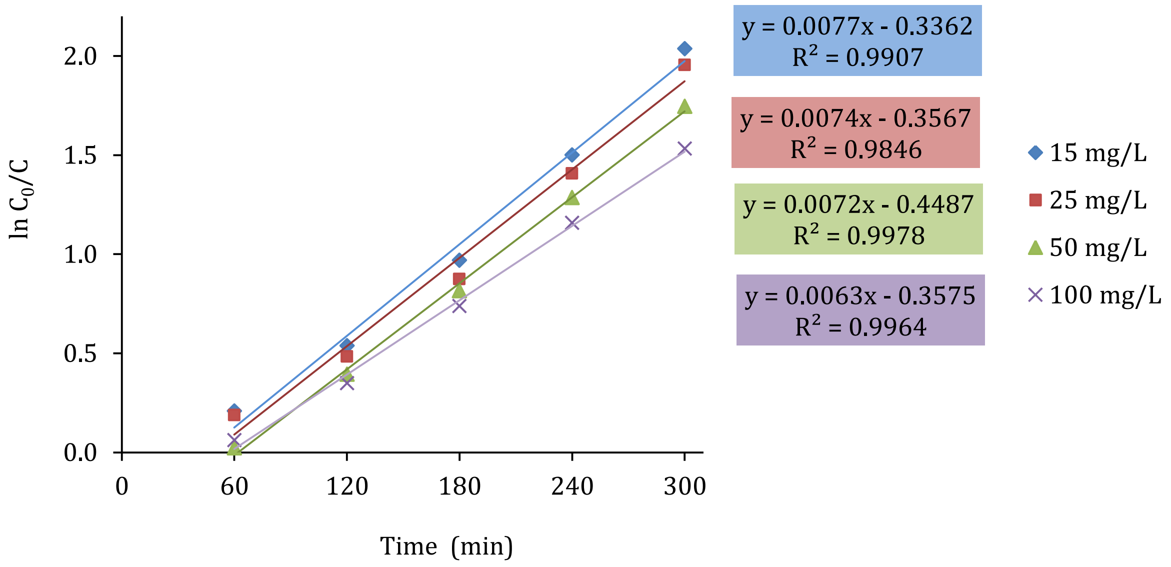

Figure 4.25 Degradation kinetics of various initial commercial formulation malathion concentration showing the rate constants (*k* = slope) and regression coefficients (*R*²) for each based on the TOC reduction under 5 hours irradiation of 400 W UV lamp.

Inorganic anions detected during the photodegradation of malathion were sulphate and phosphate ions. The proposed stoichiometry is shown in equation (4.4):

$$C_{10}H_{19}O_6PS_2 \;+\; 16O_2 \;\rightarrow\; 10CO_2 \;+\; PO_4^{3-} \;+\; 2SO_4^{2-} \;+\; 6H_2O \;+\; 7H^{+} \qquad (4.4)$$

From the equation, the degradation of malathion produced two moles of sulphate and one mole of phosphate ions. The monitored concentrations of these ions achieved after 5 hours of irradiation at various initial malathion concentrations are given in Figure 4.26. The concentration of sulphate and phosphate ions increased with an increase in the initial concentration of malathion. The concentration of sulphate increased from 16.7% to 72.0% whilst phosphate from 4.8% to 28.7%, when the initial malathion concentration increased from 15 mg/L to 100 mg/L. It was noticed that the experimental values, especially for sulphate ion, were significantly higher than the calculated theoretical values (Table 4.3). It is possible that this could be due to the presence of other additives containing sulphur atoms. Study by Bavcon Kralj *et al.* (2007) on comparison of photocatalysis and photolysis of malathion, isomalathion, malaoxon and commercial malathion also measured a higher concentration of sulphate in mineralisation of Radotion, a commercial form of malathion.

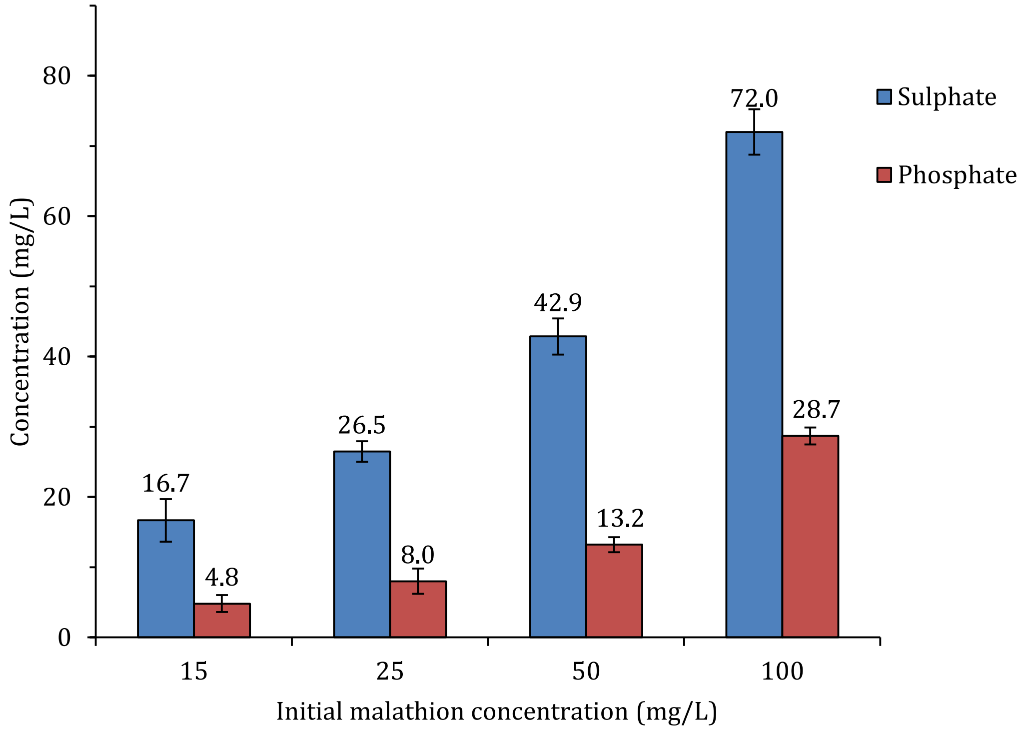

Figure 4.26 Production of inorganic anions after 5 h photodegradation of various initial malathion concentrations at self-pH 5.0 using a 400 W UV light.

Table 4.3 Calculated theoretical values for sulphate and phosphate anions concentrations for each initial malathion concentration.

Anions	**Initial malathion concentrations (mg/L) and the corresponding concentrations of sulphate and phosphate ions (mg/L)**			
	15.0	**25.0**	**50.0**	**100.0**
Sulphate	8.7	14.5	29.1	58.2
Phosphate	4.3	7.2	14.4	28.8

4.5.4. Effect of H_2O_2 concentration

The effect of adding hydrogen peroxide, H_2O_2 on the photolysis of commercial formulation of malathion was investigated as well by varying the amount of H_2O_2 from 5 mg/L to 30 mg/L. The results (Figure 4.27) show that the percentage degradation increased slightly when the concentration of H_2O_2 was increased. The increment was only from 87.2% to 95.7% when 30 mg/L of H_2O_2 was added to the malathion solution.

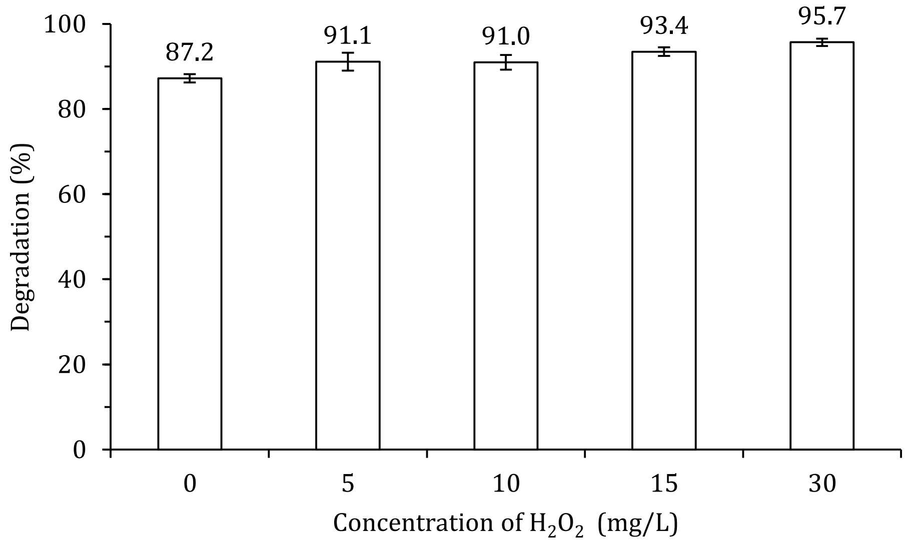

Figure 4.27 Effect of the H_2O_2 concentration on the photodegradation efficiency of malathion. Experimental conditions: $[\text{malathion}]_0$ 15 mg/L; self-pH 5.0; 400 W UV source; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.

4.5.5. Effect of heavy metal ions

It has been reported (Chaudhary, Hassan and Grimes, 2009; Chaudhary, Grimes and Hassan, 2001) that the presence of heavy metal ions can affect the photodegradation of organic pollutants in aqueous solution. The results in Figure 4.28 show that the above 90% degradation of malathion was obtained in the presence of 5 mg/L of Fe(II) ions, however, the percentage degradation of malathion was reduced to 52.5% when the concentration of Fe(II) ions was increased to 15 mg/L. Nevertheless, the photodegradation of malathion in the presence of Zn(II) ions show a slight decrease and the percentage degradation values were 85.7% and 84.1% for 5 and 15 mg/L of Zn(II) ions concentration respectively. The statistical analyses show that the difference in the percentage degradation is due to random variations and is not significant. These results confirm that the presence of Zn(II) ions in malathion solution do not affect the photodegradation process. The presence of Cu(II) ions, however, leads to a significant reduction in the efficiency of the commercial malathion photodegradation. The percentage degradation decreased from 87.2% to 26.1% after 5 hours irradiation. A further reduction was noticed when the concentration of Cu(II) ions increased from 5 mg/L to 15 mg/L (Figure 4.28).

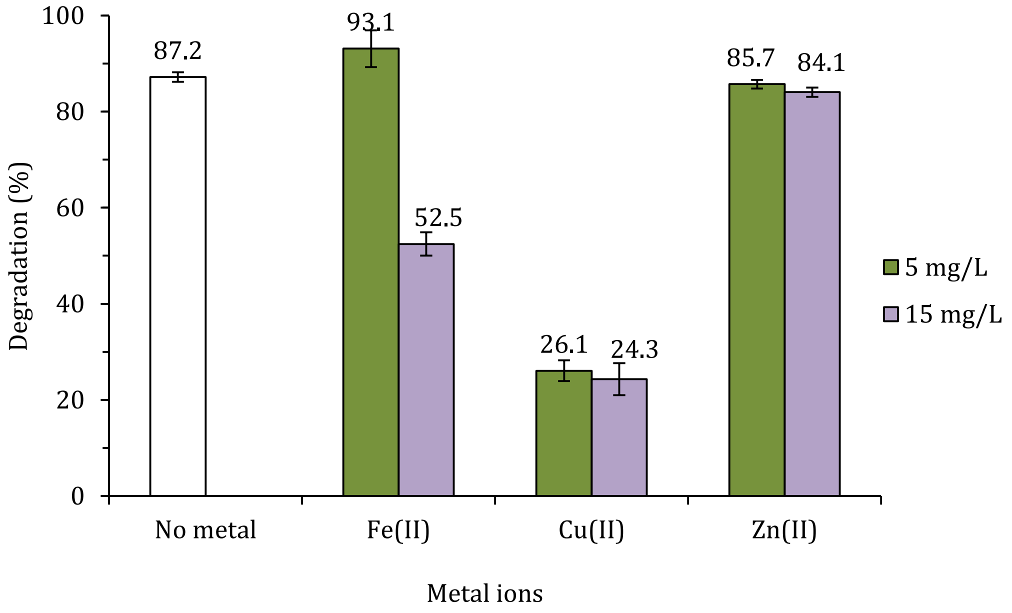

Figure 4.28 Effect of metal ions on photodegradation of malathion. Experimental conditions: [malathion]$_0$ 15 mg/L; self-pH 5.0; 400 W UV source; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.

4.5.6. Effect of Cu(II) ion in the presence of H_2O_2

The results obtained show that the presence of Cu(II) ions retarded the photodegradation of malathion. To overcome this effect, addition of H_2O_2 as an additional oxidant and also an electron acceptor species was investigated and the results are in Figure 4.29. The TOC removal of malathion in the presence of Cu(II) ions has reduced the percentage degradation of malathion from 87.2% to 26.1%. To overcome this, H_2O_2 is added to the solution and a significant increase in the removal of malathion occurred where the value rose from 26.1% to 42.0%. The addition of H_2O_2 as an oxidant does contribute some beneficial effect on the photodegradation of malathion, especially at the initial stages of the reaction.

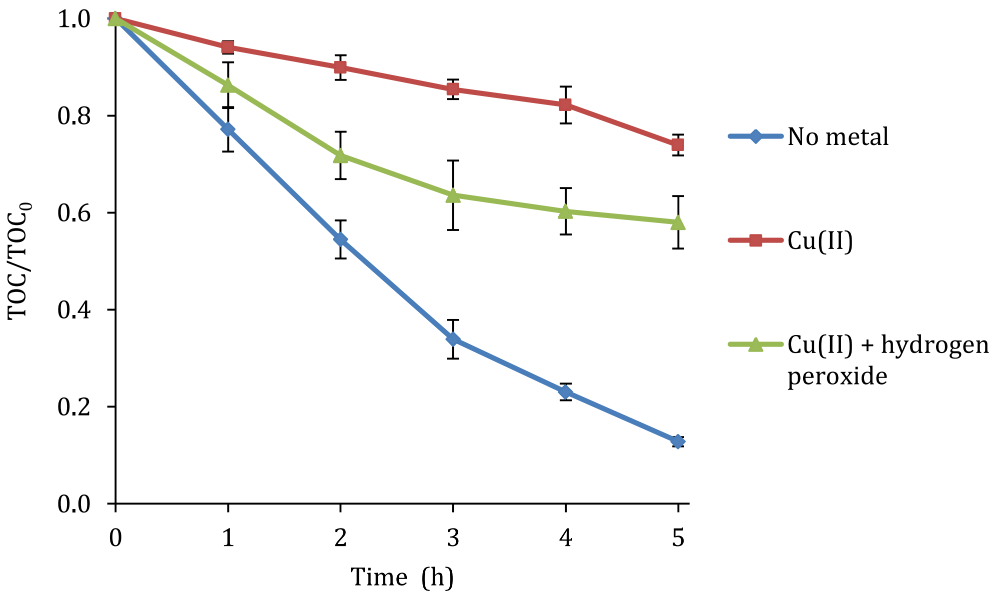

Figure 4.29 Effect of Cu(II) ions on photodegradation of malathion in the presence of H_2O_2. Experimental conditions: $[\text{malathion}]_0$ 15 mg/L; [Cu(II)] ions 5 mg/L; $[H_2O_2]$ 30 mg/L; self-pH 5.0; 400 W UV source; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.

4.5.7. Effect of mixed metal ions in the presence of hydrogen peroxide

The data in Figure 4.30 show the influence of hydrogen peroxide on the photodegradation of malathion in the presence of mixed metal ions. The data show a decrease in the percentage degradation of malathion when mixed metal ions were present in the solution. The percentage degradation decreased from 87.2% to 52.2%. However, when this solution was irradiated in the presence of hydrogen peroxide, the percentage degradation of malathion was 54.1%. Again, these results were similar to the results obtained for glyphosate. The data confirmed that although hydrogen peroxide is known as a powerful oxidant no benefit in the degradation was achieved when malathion was present in a mixed metal solution.

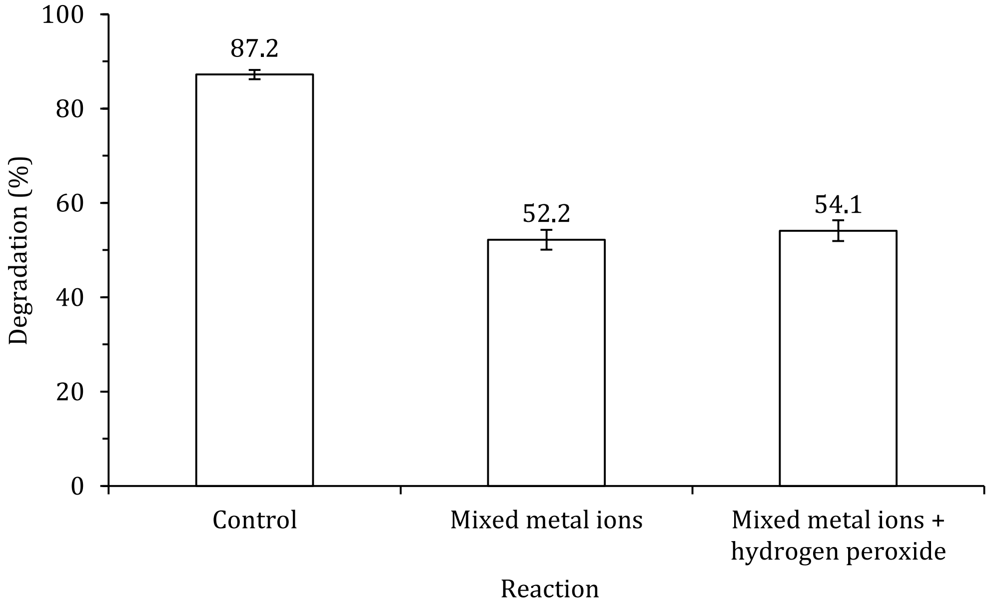

Figure 4.30 Effect of mixed metal ions on photodegradation of malathion in the presence of H_2O_2. Experimental conditions: $[\text{malathion}]_0$ 15 mg/L; mixed metal ions concentration = [Fe(II)] = [Cu(II)] = [Zn(II)] ions = 5 mg/L each; $[H_2O_2]$ 30 mg/L; self-pH 5.0; 400 W UV source; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.

4.6. General Discussion

4.6.1. Effect of UV source

Much research work on the use of different types of medium pressure mercury UV lamps (ranging from 125 W up to 500 W), in the presence of suspended or immobilised titanium dioxide (TiO_2), has been done under different experimental conditions (Chaudhary, Hassan and Grimes, 2009; Han *et al.*, 2009; Senthilnathan and Philip, 2009; Shifu and Yunzhang, 2007; Singh *et al.*, 2007b; Badawy, Ghaly and Gad-Allah, 2006; Rahman *et al.*, 2006; Singh and Muneer, 2004; Doong and Chang, 1998; Aires *et al.*, 1992). In order to compare the effectiveness of TiO_2 used, most researchers have focussed their studies on the photocatalytic degradation of different types of organic pollutants. For instance, Chaudhary, Hassan and Grimes (2009) found no significant degradation of 2,4-dichlorophenoxyacetic acid by using a 125 W medium pressure mercury lamp for 1 h irradiation. However, about 3% degradation of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) was achieved by using a 125 W lamp after 8 h irradiation. Similarly, no degradation of 2,4-dichlorophenoxyacetic acid was observed by Singh *et al.* (2007b) after 2 hours of irradiation when they used a 125 W UV source. Chaudhary, Hassan and Grimes (2009) also reported that the degradation of 2,4,5-T was considerably higher when the UV source was changed from 125 W to 400 W, where 75.8% degradation was achieved after 8 h irradiation. Rahman *et al.* (2006) also found no sign of direct photolysis for acephate after 2 h of irradiation with a 125 W UV source. However, about 10% degradation of acephate was obtained after just 1 h irradiation when 500 W UV lamp was used (Han *et al.*, 2009). These results highlighted the importance of UV sources because the degradation of organic pollutants depends on the nature of these sources. It is very important to use the right UV lamp in order to optimise the degradation of an organic pollutant by studying various parameters.

In this project, attention was focussed to study the effects of a 400 W and a 600 W UV sources. The results for the three pesticides (acephate, glyphosate and malathion) used in this study are summarised in Table 4.4. The results obtained show that both of these sources (400 W and 600 W) were able to degrade the three pesticides. It can be noticed that no significant difference in the degradation of acephate and malathion was observed for both of these sources. However, the degradation of glyphosate increased from 22.3% to 30.5% when the UV source changed from a 400 W to a 600 W.

Table 4.4 Effect of UV source on the photodegradation of acephate, glyphosate and malathion.

Pesticides	**Percentage degradation (%) and standard deviation at different UV sources**			
	400 W		**600 W**	
Acephate	28.1%	2.8	25.2%	5.8
Glyphosate	22.3%	2.7	30.5%	2.2
Malathion	87.2%	1.0	89.7%	3.8

Experimental Conditions: $[\text{acephate}]_0$ = $[\text{glyphosate}]_0$ = $[\text{malathion}]_0$ = 15 mg/L; solution volume 400 ml; self-pH ranging from 5.0-5.5; air flow rate 3 L/min; irradiation time 5 h.

Figure 4.31 show the spectral emission levels for both of these UV sources (provided by the Photochemical Reactors Ltd). Both sources have similar emission spectra and the maximum emission wavelength (λ_{max}) was at 365 nm. The only difference between these two sources is that the intensity for the 600 W lamp was higher compared to the 400 W UV lamp.

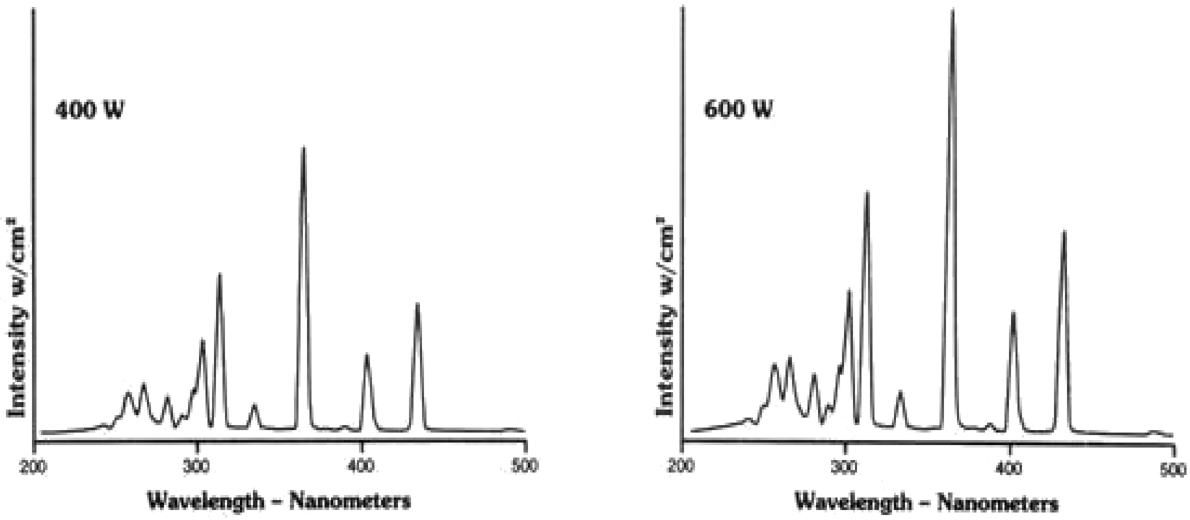

Figure 4.31 Spectral emission levels of the 400 W and 600 W of UV sources.

Among the three pesticides, an increament in the degradation of glyphosate was observed when the degradation was carried out with the 600 W UV source. Although 600 W gave a slightly higher degradation rate compared to the 400 W UV source, nevertheless, it had a tendency to produce intermediate products. Changes in UV/Vis spectra of glyphosate (Figure 4.32(b)) were observed in the range 200-220 nm after 1, 3 and 5 h of irradiation. Furthermore, the HPLC results (Figure 4.33) which show the peak at retention time of 3.18 minutes (before irradiation) has shifted to 5.6 minutes after 5 h irradiations, indicating the production of an intermediate product.

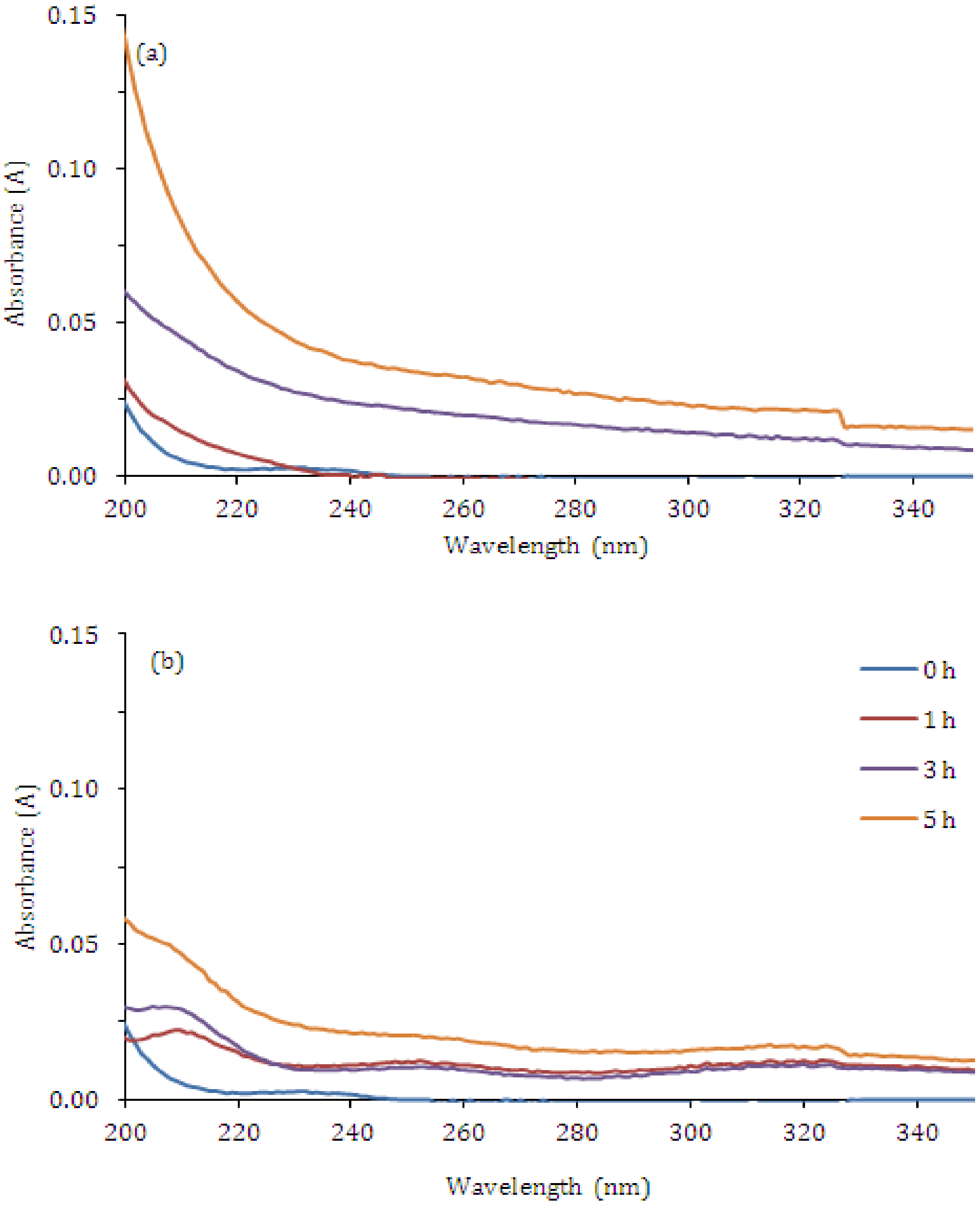

Figure 4.32 UV/Vis spectra for photodegradation of glyphosate using (a) UV 400 W and (b) UV 600 W as a light sources. Experimental conditions: [glyphosate]$_0$ 15 mg/L; self-pH 5.0; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.

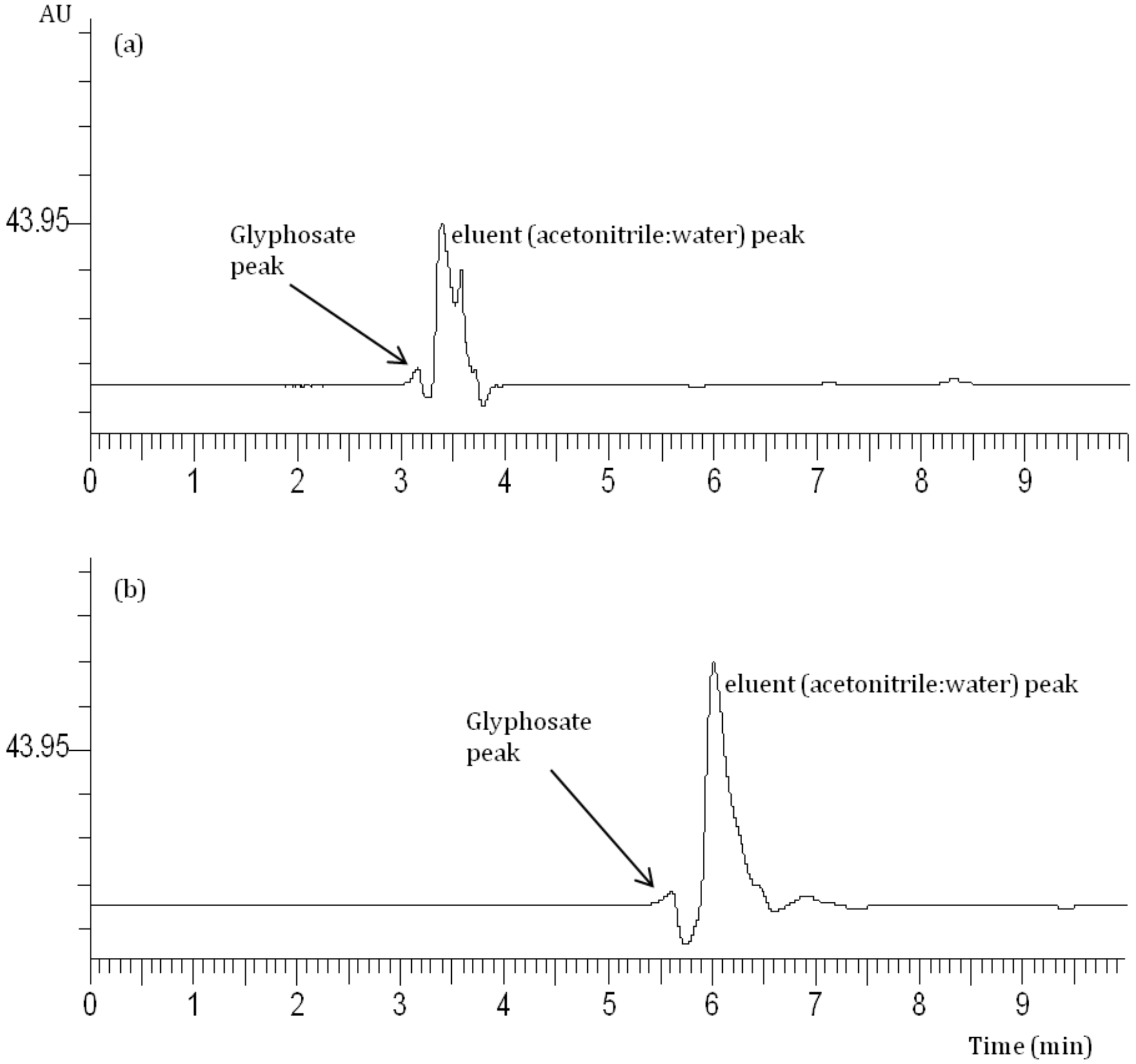

Figure 4.33 HPLC chromatograms for photodegradation of glyphosate using (a) 400 W UV source and (b) 600 W UV source after 5 h irradiation. Experimental condition: [glyphosate]$_0$ 15 mg/L; self-pH 5.0; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.

Muneer and Boxall (2008) reported that the photocatalytic degradation of glyphosate proceeds through the formation of sarcosine and glycine as two intermediate compounds. In another study, the degradation of glyphosate proceeds through the formation of sarcosine, aminomethylphosphoric acid (AMPA) and glycolic acid (Echavia *et al*, 2009). Whereas the production of sarcosine, AMPA, acetic acid and phosphoric acids were detected by Chen *et al.* (2007) who used a UV source with the λ_{max} = 365 nm. A recent publication (Manassero *et al.*, 2010) show the formation of glycine, formaldehyde, formic acid, nitrate anion, ammonium and phosphate anion. From previous findings, it was found that different UV sources produced various types of intermediates or photoproducts. Therefore, it was decided to use the 400 W UV source in all subsequent experiment because it has been reported that this UV source produced fewer stable intermediates with low concentrations (Chaudhary, Hassan and Grimes, 2009).

4.6.2. Effect of pH

In real situations the pH values of wastewater effluent streams vary from acidic to basic depending on the process. Thus, it is important to study its effect since it influences the surface charge of the aqueous solution (Chaudhary, Hassan and Grimes, 2009) and could therefore, change the performance of the reactions responsible for the degradation of organic pollutants from aqueous solutions.

In this study, all pesticide degradation results show that their highest percentage degradations were achieved at their self-pH values (shaded box) and their values are summarised in Table 4.5.

Table 4.5 Effect of pH on the photodegradation of acephate, glyphosate and malathion solution.

Pesticides	**pH values studied and the corresponding degradation values (%) for the three pesticides**								
	2.5	**3.0**	**4.5**	**5.0**	**5.5**	**7.0**	**8.0**	**8.5**	**10.5**
Acephate	17.4	NS	19.2	NS	28.1	NS	NS	20.5	18.3
Glyphosate	NS	14.4	NS	22.3	NS	14.3	12.0	NS	NS
Malathion	NS	42.8	NS	87.2	NS	57.0	43.5	NS	NS

NS = not studied, Shaded box = self-pH value.

Experimental Conditions: $[\text{acephate}]_0 = [\text{glyphosate}]_0 = [\text{malathion}]_0 = 15$ mg/L; solution volume 400 ml; 400 W UV source; air flow rate 3 L/min; irradiation time 5 h.

Similar results have been obtained in previous studies (Kamble, Sawant and Pangarkar, 2007; Pujara, Kamble and Pangarkar, 2007) where the rate of phenol-4-sulfonic acid (self-pH 4.5) and *p*-toluenesulfonic acid (self-pH 3.3) degradations were found to be maximum at their self-pH as well. Several studies (Fu *et al.*, 2012; Han *et al.*, 2009; Rahman *et al.*, 2006) have been done on the effect of pH on the photocatalytic degradation of acephate. However, contradictory results are found among these investigations where Rahman *et al.* (2006) and Han *et al.* (2009) agreed that the highest degradation occurred when pH was around 3.0 but another study by Fu *et al.* (2012), claimed that the degradation rate increased when the pH was increased from pH 3.0 to pH 12.0. These result show that acephate can be degraded in both acidic and basic condition. Moreover, the lone pairs of electrons present on the nitrogen and oxygen atoms in acephate molecule can be protonated and deprotonated under acidic and basic conditions (Rahman *et al.*, 2006). Furthermore, it is well known that some compounds can exist in positive, neutral and negative forms in aqueous solutions (Ahmed *et al.*, 2011). Whereas another study by Shifu and Yunzhang (2007) reported that acidic or alkaline medium were both favourable for the photocatalytic degradation of glyphosate.

Most of the pH studies mentioned previously were conducted in the presence of photocatalyst and normally the surface charge of the photocatalyst and organic pollutant can be profoundly affected by the solution pH. At higher pH values (alkaline medium), the catalyst surface become negatively charged thus the degradation of paraquat and diquat were favourable in basic medium rather than acidic medium as the pollutants were positively charged (Figure 4.34) (Florêncio *et al.*, 2004). Notably, the successful removal of glyphosate in the presence of TiO_2 as the photocatalyst (Echavia, Matzusawa and Negishi, 2009; Shifu and Yunzhang, 2007) was attributed to the strong adsorption of both carboxylate and phosphonate group present in glyphosate molecule, to the positively charged catalyst surface in acidic medium. Hence, the attraction or repulsion between the catalyst's surface and the organic molecule, depending on the organic compound (anionic or cationic) and consequently enhances or inhibits the photodegradation efficiency (Wei *et al.*, 2009).

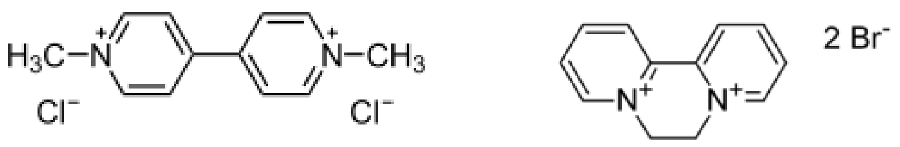

Figure 4.34 Positive charge shown on paraquat dichloride (on the left) and diquat dibromide (on the right) structure.

In this study, the self-pH of acephate (~5.5), glyphosate (~5.0) and malathion (~5.0) were in the acidic medium. This correspond to the study by Han *et al.* (2009) where the amine group in the acephate molecule was protonated in the acidic condition thus, C-N bond in protonated acephate was favourably attacked by •OH radicals which lead to the main products of methamidophos and acetic acid (Figure 4.35). Moreover, the production of sarcosine also resulted from the protonation of NH group in glyphosate molecule under acidic condition (Muneer and Boxall, 2008).

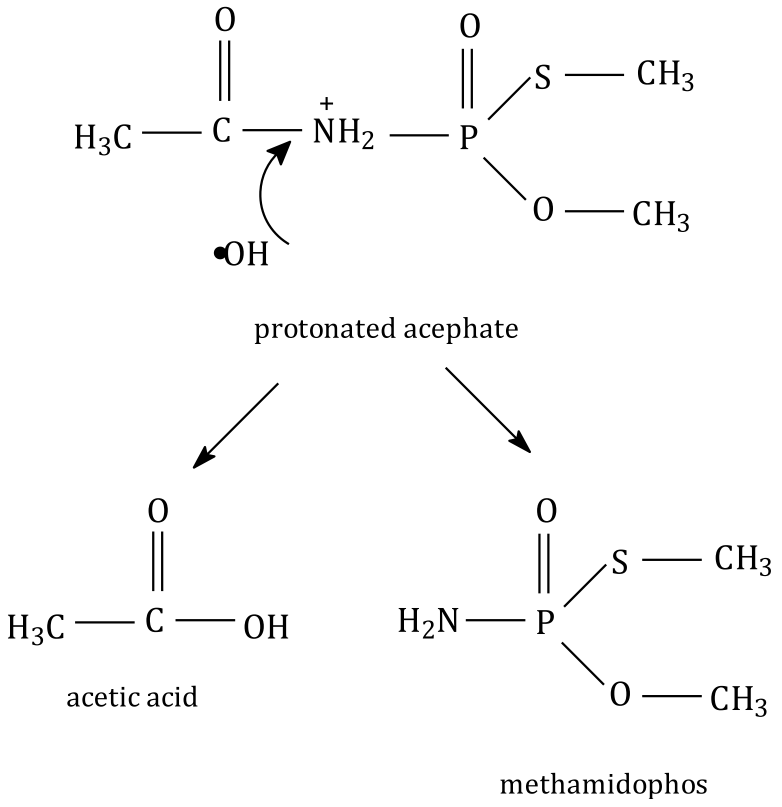

Figure 4.35 Production of acetic acid and methamidophos through C-N bond breaking by •OH radical.

4.6.3. Effect of initial concentration of the substrate

The initial concentration of the pollutant is always an important parameter in any water treatment process; therefore, it is essential to examine the effect of the initial concentration (Pujara, Kamble and Pangarkar, 2007). Most of the photocatalytic study reported that the increment of initial substrates concentrations resulted in the degradation reduction (Abdollahi *et al.*, 2012; Han *et al.*, 2009; Wei *et al.*, 2009; Pujara, Kamble and Pangarkar, 2007; Rahman *et al.*, 2006). The evidence available in the literature points to a reaction between the substrate molecules and radical species generated on the catalyst surface. With increase in initial concentration of substrate, concentration of intermediates also increases with time, thus this intermediate and the parent substrate compete each other for the sites on the catalyst surface in order to be degraded (Pujara, Kamble and Pangarkar, 2007). Since the light intensity, catalyst loading and dissolved oxygen concentration were kept constant, the production of radical species (•OH and $O_2^{\bullet -}$) formed on the surface of catalyst would therefore remain constant (Abdollahi *et al.*, 2012). Thus, as the initial substrate concentration increases, the radical species becomes the limiting reactant which leads to a reduction in percentage degradation (Abdollahi *et al.*, 2012; Wei *et al.*, 2009; Pujara, Kamble and Pangarkar, 2007).

In this study, however, there is no catalyst involved for the production of radical species. Nevertheless, the production of radical species is contributed from the formation of sulphate ion. The increase in the percentage degradation of acephate at higher initial substrate concentrations is mainly due to the rapid formation of sulphate ion (Fu *et al.*, 2012; Echavia, Matzusawa and Negishi, 2009; Han *et al.*, 2009). This sulphate anion, however, can react with hydroxyl radical to produce sulphate radical anions and hydroxyl radical is produced back when the sulphate radical react with water molecule (Ahmed *et al.*, 2011) and all these radicals participate in the degradation process, hence, enhanced the degradation efficiency. All relevant equations are given as follows:

$$H_2O \xrightarrow{hv} 2H^+ + \frac{1}{2}O_2 + 2e^- \qquad (4.5)$$

$$O_2 + e^- \rightarrow O_2^{\bullet -} \qquad (4.6)$$

$$O_2^{\bullet -} + H^+ \rightarrow HO_2^{\bullet} \qquad (4.7)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \qquad (4.8)$$

$$H_2O_2 \xrightarrow{hv} 2\bullet OH \qquad (4.9)$$

$$H_2O_2 + e^- \rightarrow \bullet OH + OH^- \qquad (4.10)$$

$$SO_4^{2-} + \bullet OH \rightarrow SO_4^{-\bullet} + OH^- \qquad (4.11)$$

$$SO_4^{-\bullet} + H_2O \rightarrow \bullet OH + SO_4^{2-} + H^+ \qquad (4.12)$$

$$SO_4^{-\bullet} + e^- \rightarrow SO_4^{2-} \qquad (4.13)$$

The results obtained in the present study (described in section 4.5.3) showed that the photodegradation of malathion decreased with the increase of initial concentration of malathion. These results are in agreement with the study by Aires *et al.* (1992) where they found that the degradation of malathion for 150 min irradiation was reduced from 87.2% to 76.9% when the initial concentration of malathion was increased from 15 to 100 mg/L. Although the result in this study show that the photodegradation of malathion at higher initial concentration (100 mg/L) was slightly decreased, however the percentage value was considerably high (76.9%). This happened as the production of sulphate anions occurred in the solution since malathion molecule contain sulphur atom as well. Again, equations (4.5 - 4.13) are involved in the photodegradation of malathion. At higher initial concentration of malathion, the production of sulphate anions has increased, nevertheless the production of H^+ and e^- are constant (equation (4.5)), thus leads to the constant production of hydroxyl radical (equation (4.9, 4.10)). This synergistic effect has reduced the potential of equation (4.11) although there was abundant of sulphate anions in the solution of malathion at higher initial concentration and ultimately the degradation of malathion at higher initial concentration was decreased.

Among the studied pesticides, glyphosate showed the lowest degradation efficiency (average 20% for initial concentrations of 50 and 100 mg/L) which reflected the low detection of phosphate and nitrate anions in the solution. The mineralisation of 41 mg/L of glyphosate, for 10 h irradiation using UV/H_2O_2, studied by Manassero *et al.* (2010) also detected the concentration of phosphate ions below the stoichiometry value and very low concentration of nitrate ions. A very low detection of nitrate ions also been observed in the degradation of acephate in this study. This observation was mentioned as well by Fu *et al.* (2012) where they suggested the evaporation of nitrogen gas may occur. Regarding the acephate degradation reaction pathway presented in the literature review section 2.9.1, methamidophos is the main product obtained from the acephate degradation where the protonated methamidophos is transformed into NH_4^+ under acidic condition and ultimately should be degraded to NO_3^- and NO_2^- ions, however, it was seldom that NH_4^+ would be transformed to NO_3^- and NO_2^- at low pH values (Han *et al.*, 2009). This condition was also proved in a study carried out by Kim and Choi (2002) on the photocatalytic decomposition of nitrogen compounds, where the authors reported that the formation of NO_3^- and NO_2^- occurred at pH 11-12. These investigations explained the reason of why the measured concentration of NO_3^- ions was very low.

Regarding the kinetic study for the initial concentration for all three pesticides, it was obvious that the degradation of all pesticides in this study followed the first order kinetic reaction. A 15 mg/L of initial concentration was used for the entire conducted experiments for all three pesticides. Based on the kinetic study, the rate constants, *k* value at 15 mg/L for each acephate, glyphosate and malathion were 0.0010, 0.0008 and 0.0077 min^{-1}, respectively. It was found that the photodegradation rates of the three pesticides were comparable. It appeared that the degradation efficiency of all three pesticides followed an order of: malathion > acephate > glyphosate.

4.6.4. Effect of oxidants

It is worth to mention here that, all experiments conducted either to degrade acephate, glyphosate or malathion were agitated with air as mentioned in chapter 3 (Materials and Methods). The presence of air in the irradiated solution acts as an additional oxidant and can lead to the formation of superoxide radical anions when reacted with an electron, hence, increase the degradation process. The reaction is represented in the equation (4.14).

$$O_2 \; + \; e^- \; \rightarrow \; O_2^{\bullet -} \qquad (4.14)$$

This has been proved in the present study (results are given in the section 4.3.4), where the percentage degradation of a solution containing 50 mg/L of acephate was significantly increased from 9% to 54% when air was introduced to the solution. In non-aerated solution, the presence of all oxidants (H_2O_2, $K_2S_2O_8$, KIO_4 and $KBrO_3$) slightly increased the degradation of 50 mg/L of acephate, however, these increments in the percentage degradations were not significant. However, of the oxidants studied, H_2O_2 was demonstrated to be more efficient and $KBrO_3$ was to be less effective for the degradation of acephate in the presence of air (Table 4.6).

Nevertheless, the degradation efficiency of the UV/TiO_2/oxidant have shown that $KBrO_3$ was more efficient than H_2O_2 in order to degrade uracil and 5-bromouracil (Singh *et al.*, 2007a), glyphosate (Shifu and Yunzhang, 2007) and phenoxyacetic acid (Bahnemann, Muneer and Haque, 2007). They postulated that the reduction of bromate ions by electrons does not lead to the formation of hydroxyl radical, however other oxidising agents such as bromite (BrO_2^-) and hypobromous acid (HOBr) were formed. Another reason can be attributed to the maximum number of electron (formed at the surface of catalyst) has been scavenged (equation (4.16)), which then reduced the recombination of electron-hole; hence lead to the enhancement of the degradation efficiency.

$$BrO_3^- \; + \; 2H^+ \; + \; e^- \; \rightarrow \; BrO_2 \; + \; H_2O \qquad (4.15)$$

$$BrO_3^- \; + \; 6H^+ \; + \; 6e^- \; \rightarrow \; \left[BrO_2^-, HOBr\right] \rightarrow Br^- \; + \; 3H_2O \qquad (4.16)$$

Wei *et al.* (2009) examined the effect of H_2O_2, $K_2S_2O_8$ and $KBrO_3$ on the photocatalytic degradation of methamidophos. They found that $K_2S_2O_8$ was the most effective oxidant for the degradation of methamidophos. Another study also reported that $K_2S_2O_8$ has increased the photodegradation efficiency of trichlorfon as well which in the order of: $K_2S_2O_8$ > $KBrO_3$ > H_2O_2 (Liu *et al.*, 2009). This could be due to the capability of persulphate ions which can generate two molecules of sulphate radical anions (equation (4.17)) (Ahmed *et al.*, 2011) and proceed to the production of hydroxyl radical as shown in equation (4.12). All these radicals were responsible for the contribution of high degradation of methamidophos.

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet -} \tag{4.17}$$

Study on the photocatalytic degradation of methamidophos by UV irradiation in the presence of nano-TiO_2 by Zhang *et al.* (2006) has claimed that they were the first to utilise KIO_4 as an oxidant and found that the addition of it was able to degrade almost 83.6% of methamidophos in the first 5 minutes reaction time. They suggested that the presence of IO_4^- in UV/TiO_2/IO_4^- system has led to the formation of highly reactive species such as $IO_3^\bullet$, •OH, IO_3^-, O_3 and $IO_4^\bullet$. In the following year, Selvam *et al.* (2007) also reported the effect of the oxidants on the degradation of 4-flurophenol was in the order of $IO_4^- > BrO_3^- > S_2O_8^{2-} > H_2O_2 > ClO_3^-$.

In all the cases discussed above, air or O_2 was used as an electron acceptor in the photocatalytic degradation and the addition of an additional oxidant increased the pollutant degradation rate. Similar results have been obtained in this study (Table 4.6).

Table 4.6 Effects of various oxidants in the absence and presence of air on the photodegradation of acephate.

Type of oxidants	Degradation of acephate (%)		
	Absence of air and oxidants	Absence of air with oxidants	Presence of air with oxidants
H_2O_2	9.0	10.0	74.0
$K_2S_2O_8$	9.0	13.6	27.8
KIO_4	9.0	16.6	38.1
$KBrO_3$	9.0	13.9	10.8

Experimental conditions: $[\text{acephate}]_0$ 50 mg/L; oxidants concentration = $[H_2O_2]$ = $[K_2S_2O_8]$ = $[KIO_4]$ = $[KBrO_3]$ = 50 mg/L; self-pH 5.5; UV source 400 W; solution volume 400 ml; irradiation time 5 h.

In this study, since H_2O_2 (in the presence of air) demonstrated the highest degradation efficiency, thus the effect of various concentration of H_2O_2 was investigated for 15 mg/L of each acephate, glyphosate and malathion. Hydrogen peroxide demonstrated a significant enhancement in the degradation efficiency of each pesticide. The photodegradation efficiency of acephate and glyphosate tremendously increased in the presence of 30 mg/L of H_2O_2. The effect of H_2O_2 on the degradation of organic pollutant has been a subject of many investigations (Manassero *et al.*, 2010; Chaudhary, Hassan and Grimes, 2009; Liu *et al.*, 2009; Wei *et al.*, 2009; Chaudhary and Grimes, 2008; Chen *et al.*, 2007; Shifu and Yunzhang, 2007; Rahman *et al.*, 2006; Zhang *et al.*, 2006; Chaudhary, Grimes and Hassan, 2001) with the same view of exploiting the hydroxyl radical for enhancing the degradation efficiency.

An important step in the formation of a radical species is the cleavage of H_2O_2 in the presence of UV-light (Chaudhary and Grimes, 2008) and the reaction as follows:

$$H_2O_2 \xrightarrow{hv} 2 \bullet OH \tag{4.18}$$

$$H_2O_2 \xrightarrow{hv} HO_2^{\bullet -} + H^+ \tag{4.19}$$

The •OH could also be produced from the reaction of hydrogen peroxide with an electron (Shifu and Yunzhang, 2007):

$$H_2O_2 + e^- \rightarrow \bullet OH + OH^- \tag{4.20}$$

Correspondingly, the addition of H_2O_2 seemed to act as an oxygen source as well (Tseng, Juang and Huang, 2012; Zhang and Pagilla, 2010).

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{4.21}$$

The simultaneous production of oxygen in the system also contributes to the superoxide radical anions as shown in equation (4.14) and ultimately enhanced the photodecomposition of organophosphorous pesticides. Besides, in an oxygenated solution, hydrogen peroxide was found to function as an intermediate product as well (Doong and Chang, 1997) and resulting in the acceleration of •OH production in the cycle where the equation as follows:

$$O_2^{\bullet -} + H^+ \rightarrow HO_2^{\bullet} \tag{4.22}$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{4.23}$$

$$O_2^{\bullet -} + HO_2^{\bullet} \rightarrow O_2 + HO_2^{\bullet -} \tag{4.24}$$

$$HO_2^{\bullet -} + H^+ \rightarrow H_2O_2 \tag{4.25}$$

Nevertheless, in the case of photodegradation of malathion in the presence of 30 mg/L of H_2O_2, it was noticed that there was only a slight increment occurred from 87.2% to 95.7% when the concentration of H_2O_2 was increased from 5 mg/L to 30 mg/L. The UV/Vis spectra of malathion (Figure 4.36 inset) in the presence of 30 mg/L of H_2O_2 shows the absorption peak after 5 h irradiation still existed. It was expected to be degraded (99.9%), however the TOC result still detected about 4.3% of residual organic carbon (correspond to the formation of intermediate) in the irradiated malathion sample after 5 h, indicating the mineralisation process occurred more slowly than the disappearance of parent compound. This occurrence closely corresponds to other investigations (Shifu and Yunzhang, 2007; Badawy, Ghaly and Gad-Allah, 2006) where they reported the adverse effect of H_2O_2 when it was being used at higher concentrations. At higher concentration, however, the excess H_2O_2 molecules scavenge the valuable •OH (Shifu and Yunzhang, 2007) that was generated earlier. The •OH could also react with hydroperoxyl radical, $HO_2^{\bullet}$ to generate H_2O (Zhang and Pagilla, 2010) and consequently reduce the available hydroxyl radical, thus led to the reduction of the degradation efficiency (equations (4.26, 4.27)).

$$H_2O_2 \quad + \quad \bullet OH \quad \rightarrow \quad HO_2^{\bullet} \quad + \quad H_2O \tag{4.26}$$

$$\bullet OH \quad + \quad HO_2^{\bullet} \quad \rightarrow \quad H_2O \quad + \quad O_2 \tag{4.27}$$

Obviously, the effect of H_2O_2 depends on its concentration in order to have its beneficial effect (Hofstadler *et al.*, 1994).

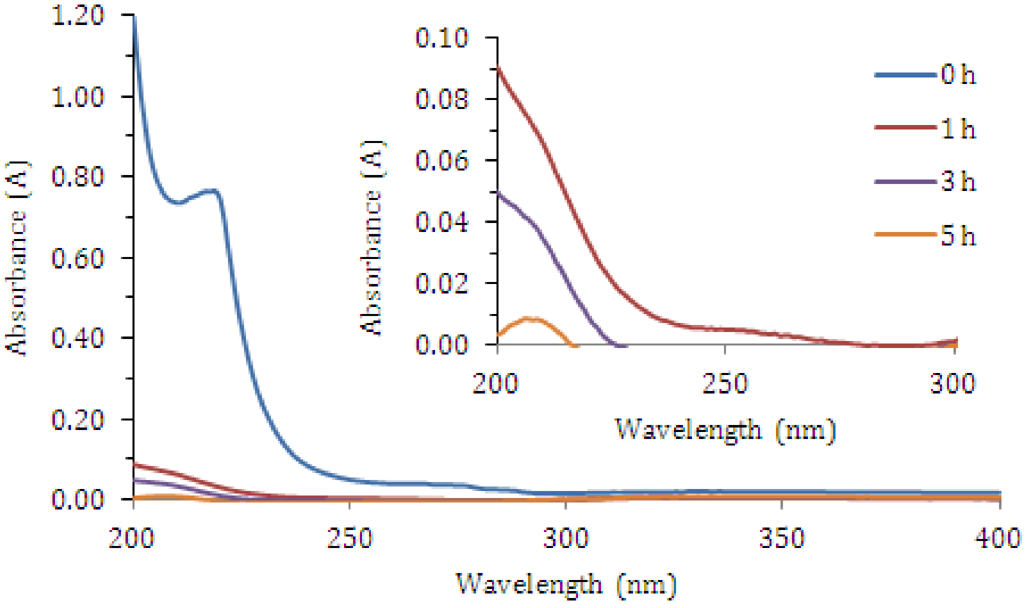

Figure 4.36 UV/Vis spectra of malathion in the presence of H_2O_2. Experimental conditions: $[\text{malathion}]_0$ 15 mg/L; $[H_2O_2]_0$ 30 mg/L; self-pH 5.0; 400 W UV source; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.

4.6.5. Effect of single metal ions

Effect of Fe(II) ion

The results on the effect of various Fe(II) ion concentrations (Table 4.7) show that the presence of 5 mg/L of Fe(II) ions have increased the percentage degradation of all pesticides whereas a further increment of Fe(II) ion concentration (15 mg/L) has increased the degradation of acephate and glyphosate but not malathion. The highest degradation for malathion was achieved in the presence of 5 mg/L of Fe(II) (93.1%) and the HPLC chromatogram (Figure 4.37(b)) show almost a straight line after 5 h irradiation, indicating that the complete disappearance of the parent compound has occurred.

Table 4.7 Effect of various concentration of Fe(II) ion on the photodegradation of acephate, glyphosate and malathion.

Pesticide	**Fe(II) ion concentration (mg/L) and the corresponding percentage degradation (%) of acephate, glyphosate and malathion**		
	0	**5.0**	**15.0**
Acephate	28.1	72.0	60.9
Glyphosate	22.3	82.2	66.4
Malathion	87.2	93.1	52.5

Experimental conditions: $[\text{acephate}]_0$ = $[\text{glyphosate}]_0$ = $[\text{malathion}]_0$ = 15 mg/L; solution volume 400 ml; UV source 400 W; self-pH ranging from 5.0-5.5; air flow rate 3 L/min; irradiation time 5 h.

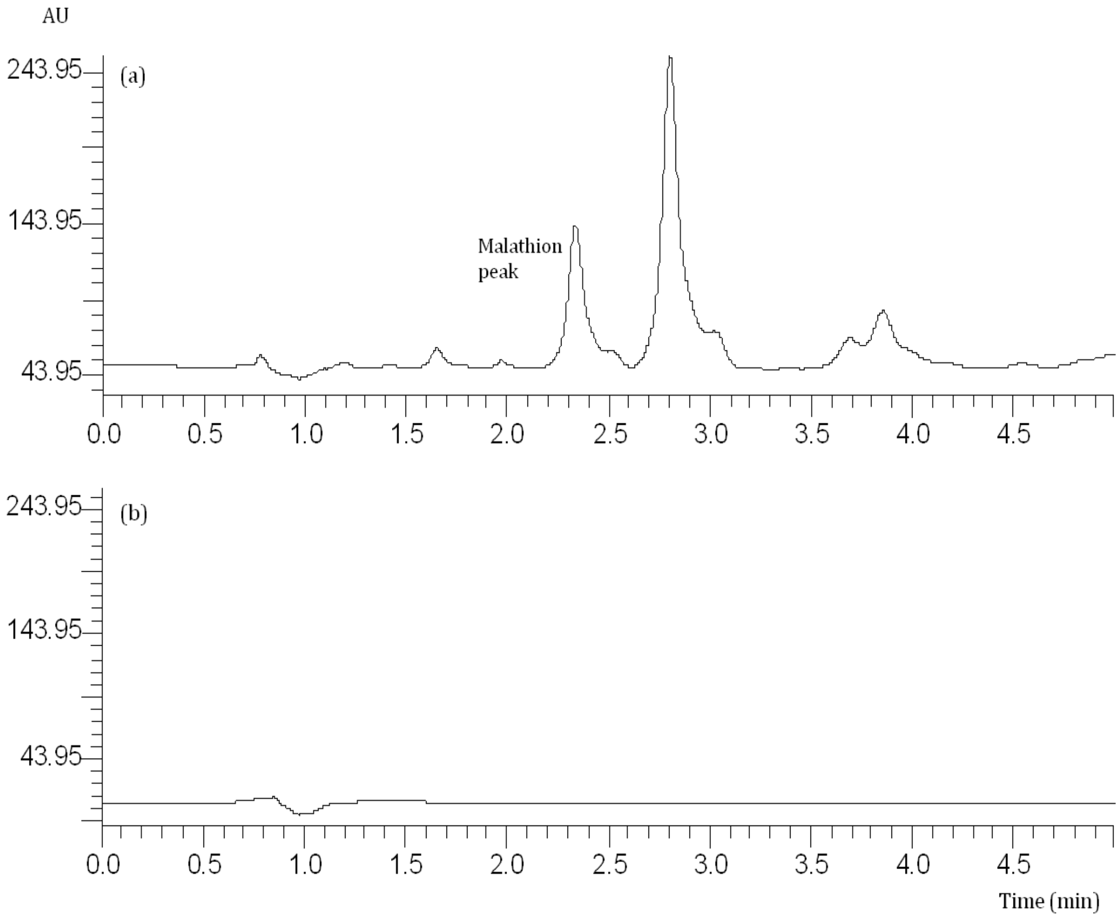

Figure 4.37 Chromatograms of malathion in the presence of Fe(II) ion (a) before and (b) after irradiation. Experimental conditions: [malathion]$_0$ 15 mg/L; [Fe(II)]$_0$ 5 mg/L; self-pH 5.0; 400 W UV source; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.

The increment in the degradation efficiency in the presence of Fe(II) ions is due to the ability of Fe(II) ions to be oxidised to Fe(III) ions (equation (4.28)) and reduce back to Fe(II) ions in the consumption of electron which represented by equation (4.29). The formation of iron(III) hydroxoaqua complex (equation (4.30)) as proposed by Shifu and Yunzhang (2007) can lead to the formation of •OH radical by photolysis process (equation (4.32)) (Kusic, Koprivanac and Bozic, 2011b; Cernigoj, Stangar and Jirkovsky, 2010; Zhang and Pagilla, 2010; Wahyuni, Mudasir and Hadipranoto, 2006; He and Lei, 2004; Brand, Mailhot and Bolte, 2000). All relevant equations are given below:

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-} \tag{4.28}$$

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \tag{4.29}$$

$$Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^{+} \tag{4.30}$$

$$Fe(OH)^{2+} + e^{-} \rightarrow Fe(OH)^{+} \tag{4.31}$$

$$Fe(OH)^{2+} \xrightarrow{hv} Fe^{2+} + \bullet OH \tag{4.32}$$

Hence, the increase in the degradation is attributed to the cyclic reaction in which iron can easily be reduced and oxidised in an aqueous solution containing free electrons. Moreover, the production of $Fe(OH)^{2+}$ complex (equation (4.30)) has the ability to capture the photogenerated electron, thus preventing the recombination process of •OH radicals with free electron, and eventually yielding a reduced form of $Fe(OH)^{+}$ complex (equation (4.31)) (Wahyuni, Mudasir and Hadipranoto, 2006). The synergistic combination of these reactions explained the enhancement of the photodegradation efficiency of malathion in the presence of Fe(II) ions.

The formation of $Fe(OH)^{2+}$ complex in equation (4.30) occurred in the acidic condition between pH range 2.0 and 5.0 (Kusic, Koprivanac and Bozic, 2011a; Shifu and Yunzhang, 2007), thus, this finding has explained the reduction of malathion pH solution which reduced from self-pH 5.0 to pH 3.2 after 5 h irradiation in the presence of Fe(II) ions (Figure 4.38).

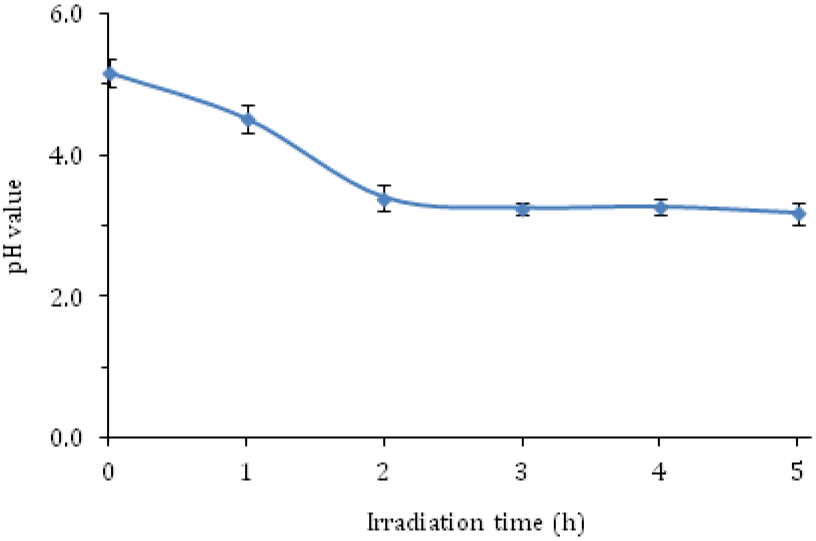

Figure 4.38 The pH changes during the photodegradation of malathion in the presence of Fe(II) ions. Experimental conditions: [malathion]$_0$ 15 mg/L; [Fe(II)] 5 mg/L; self-pH 5.0; 400 W UV source; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.

Nevertheless, most of the researchers have preferred to study the effects of Fe(III) ion rather than Fe(II) ions (Liu *et al.*, 2009; Wei *et al.*, 2009; Shifu and Yunzhang, 2007; Wahyuni, Mudasir and Hadipranoto, 2006) and beneficial effects of Fe(III) ion were observed in their investigations. The preference for Fe(III) ion was probably due to eliminating the step of the equation (4.28). Furthermore, Fe(III) ions are the most stable since it has five singly occupied 3d orbitals (Liptrot, 1990). Some researchers have also studied the effect of Fe(III) and Fe(II) ions where the photocatalytic degradation of 4-fluorophenol in the presence of TiO_2 under pH 4 was compared and it was shown that the degradation efficiency in the addition of Fe(III) was greater than Fe(II) (Selvam *et al.*, 2007).

However, when the concentration of Fe(II) ions was increased to 15 mg/L in the solution, the degradation of malathion was significantly reduced to 52.5%. This happened because the hydroxyl radicals may be scavenged by reaction involving high concentration of Fe(II) ions in the solution (Zhang and Pagilla, 2010; Pignatello, 1992).

$$\bullet OH + Fe^{2+} \rightarrow OH^- + Fe^{3+} \tag{4.33}$$

Effect of Cu(II) ion

The effect of Cu(II) ions have been studied on the photocatalytic degradation of various organic pollutant such as glyphosate (Shifu and Yunzhang, 2007), methamidophos (Wei *et al.*, 2009), 2,4,5-trichlorophenoxyacetic acid (Chaudhary, Hassan and Grimes, 2009), 4-chlorophenol (Chaudhary and Grimes, 2008), 2,4-dichlorophenoxyacetic acid (Chaudhary, Grimes and Hassan, 2001), thiacloprid (Cernigoj, Stangar and Jirkovsky, 2010), trichlorfon (Liu *et al.*, 2009), 4-fluorophenol (Selvam *et al.*, 2007), 4-nitrophenol (San *et al.*, 2002), 1,4-dioxane (Lam *et al.*, 2007), dichlorvos, monocrotophos, parathion and phorate (Shifu and Gengyu, 2005). A number of postulations have been put forward and some studies suggested that the observed enhancement of the photocatalytic degradation rates was due to the electron trapping on the surface catalyst by the copper ions leading to the prevention of electron-hole recombination.

In this study, the beneficial effect of adding Cu(II) ions was demonstrated by acephate. With the increase of the Cu(II) ion concentration, the degradation value of acephate was increased. This observation is in agreement with Lam *et al.* (2007) who reported that the complexation of Cu(II) with 1,4-dioxane and its degraded compound, ethylene glycol diformate (EGDF) have a positive role. They claimed that Cu(II) complexes are readily in the form of hexaaquacopper(II) ions when in water and as soon as 1,4-dioxane interacts with Cu(II) ions, the monodentate water ligands are replaced by the oxygen atom on 1,4-dioxane molecule and $[Cu(H_2O)_5.C_4H_8O_2]^{2+}$ ion is formed (Figure 4.39(a)) acting as a unidentate ligand. On the other hand, complexation of $[Cu(H_2O)_4.C_4H_6O_4]^{2+}$ was formed when two monodentate water ligand is replaced by the oxygen atom on EGDF, thus acting as a bidentate ligand (Figure 4.39(b)).

However, a detrimental effect has been observed on the photodegradation of glyphosate and malathion when 5 mg/L of Cu(II) ions was added to each solution. A further reduction was occurred on both pesticides when the concentration of Cu(II) ions increased from 5 mg/L to 15 mg/L where the lowest degradation value was demonstrated by glyphosate in the presence of 15 mg/L of Cu(II) ions (16.4%). These obtained results are similar with the previous findings (Chaudhary, Hassan and Grimes, 2009; Chaudhary and Grimes, 2008; Chaudhary, Grimes and Hassan, 2001) where they reported a significant drop in the percentage degradation of various organic pollutants in the presence of Cu(II) ions. This drop in the percentage degradation is due to the formation of complexes between Cu(II) ions and the organic species or some of the intermediate products. Some of these complex species are quite stable and need a longer period for complete degradation. The obtained results were also confirmed by the changes in the UV/Vis spectra of glyphosate with time in the presence of Cu(II) ions (Figure 4.40).

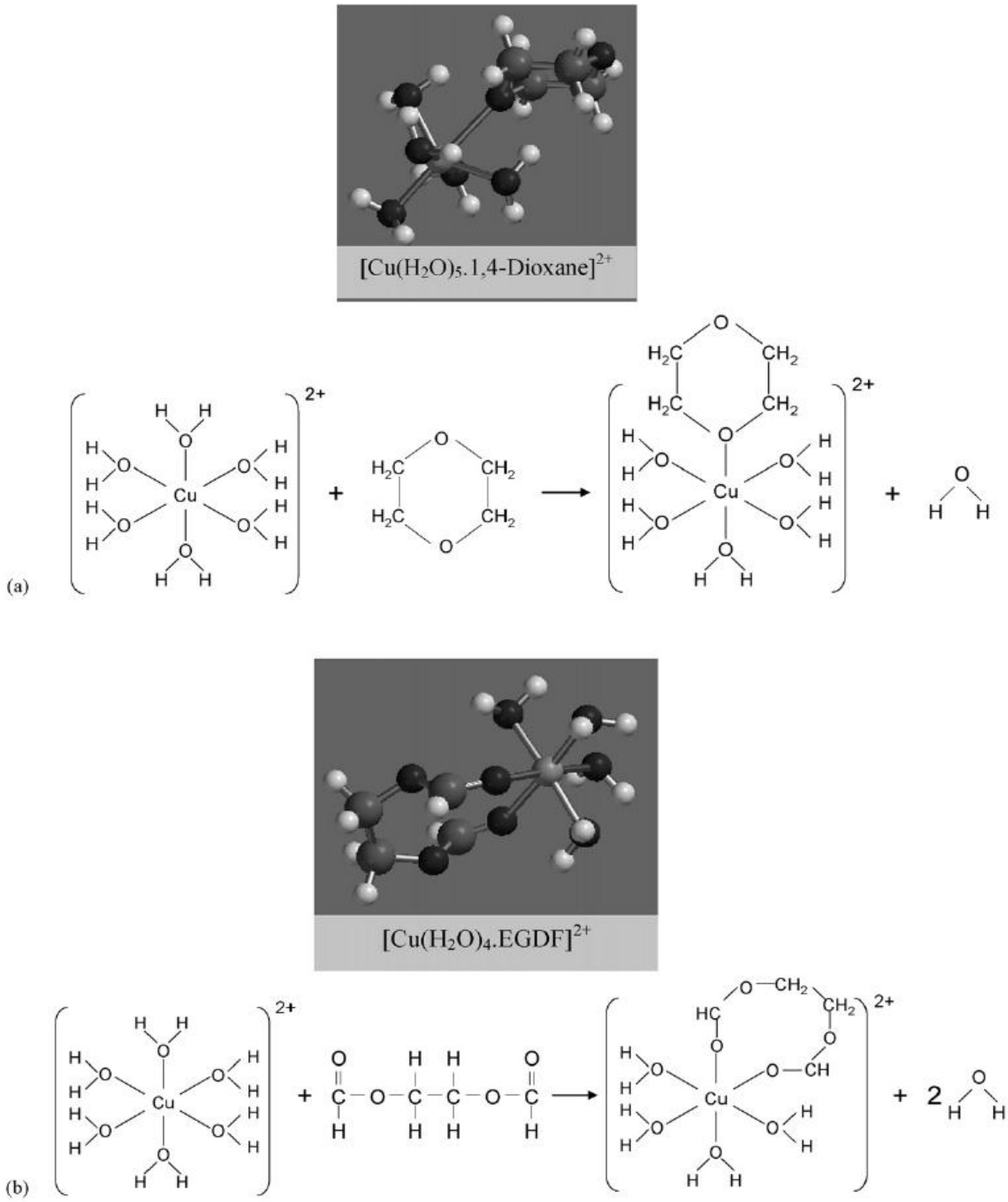

Figure 4.39 Cu complexes structure with (a) 1,4-dioxane and (b) EGDF (Lam *et al.*, 2007).

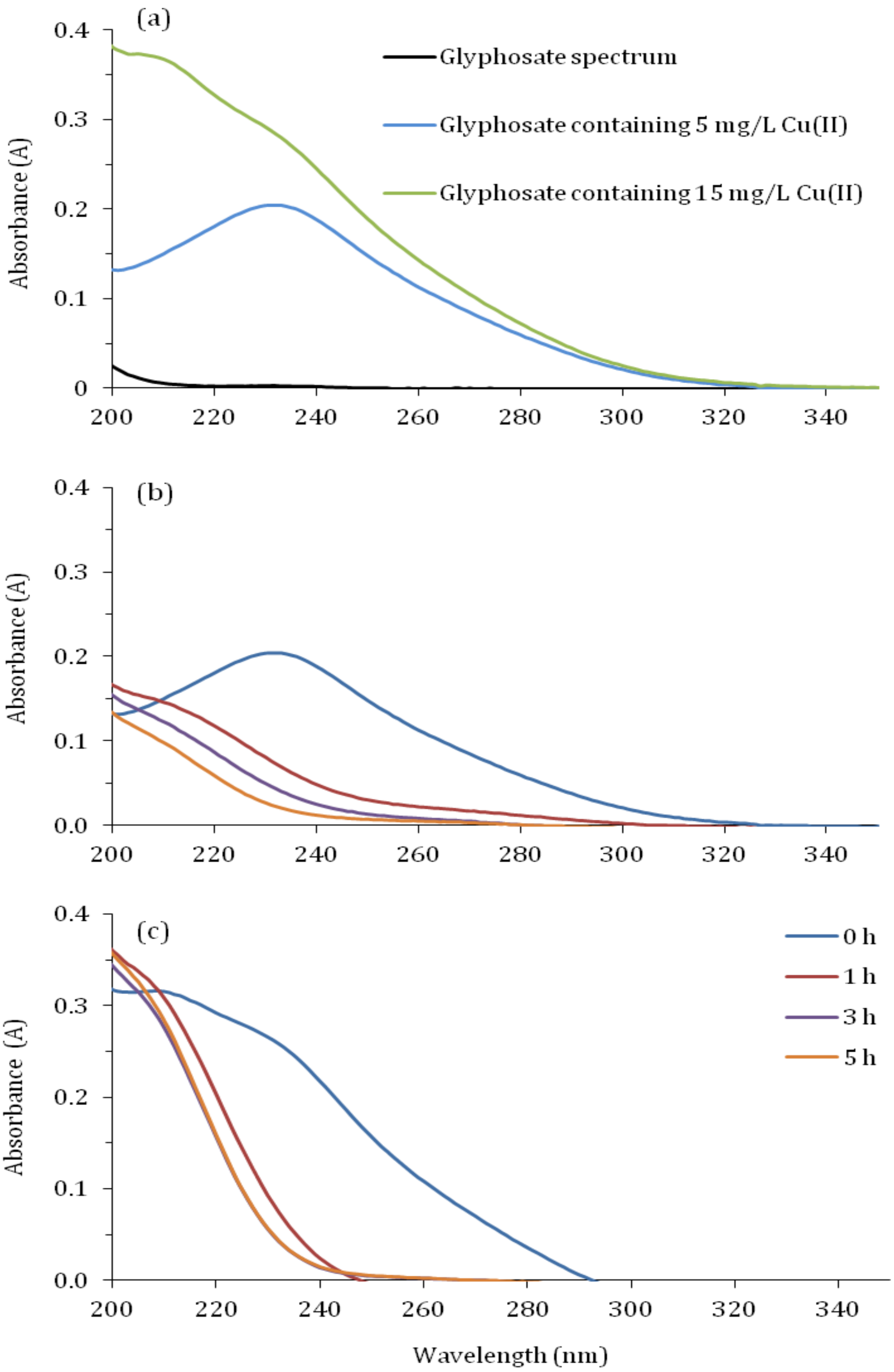

Figure 4.40 **UV/Vis spectra of glyphosate containing Cu(II) ions (a) as a function of concentration between glyphosate and cu(II) ions (variable concentration between 5 and 15 mg/L), (b) as a function of time in concentration of 5 mg/L and (c) 15 mg/L. Experimental conditions: [glyphosate]$_0$ 15 mg/L; [Cu(II)]$_0$ 5 mg/L and 15 mg/L; self-pH 5.0; 400 W UV source; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.**

The formation of Cu(II)-glyphosate complexes is likely to be the factor contributing to the reduction in the degradation efficiency of glyphosate. Furthermore, glyphosate is one of the most capable metallic ion coordinators among the current herbicides (Caetano *et al.*, 2012). Besides, glyphosate has three polar functional groups which are carboxylate, amino and phosphonate group (Caetano *et al.*, 2012; Borggaard and Gimsing, 2008). The structures of glyphosate complexes are proposed by Caetano *et al.* (2012) where the coordination occurred via carboxylate and phosphonate group (Figure 4.41).

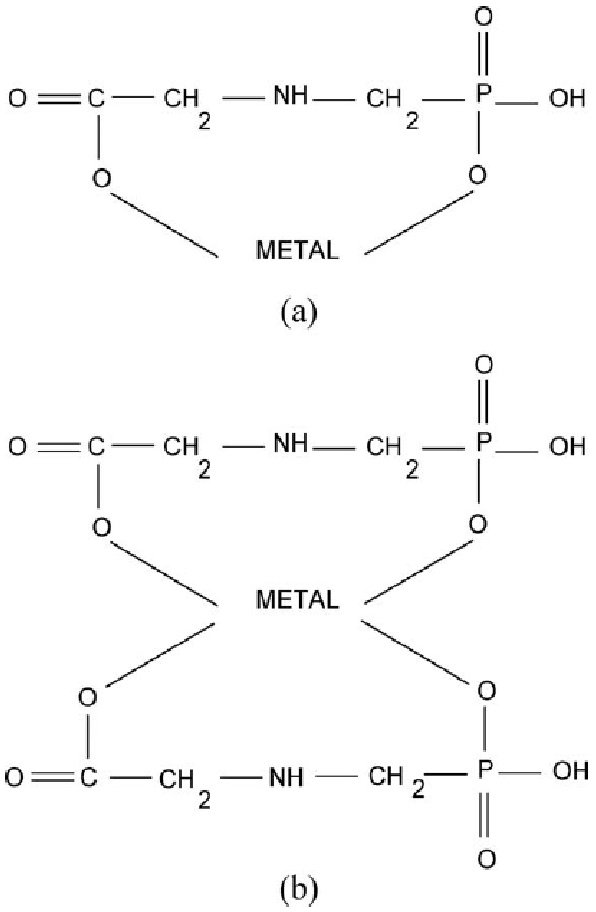

Figure 4.41 Structures of complexes formed by (a) one molecule of glyphosate and metal and (b) two molecules of glyphosate and metal (Caetano *et al.*, 2012).

However, no precipitation occurred in the glyphosate solution after 5 h irradiation indicating the soluble Cu(II)-glyphosate complexes were formed although a slight decrease amount of copper were detected after 5 h irradiation obtained from AAS (Table 4.8).

Table 4.8 Copper concentrations of 5 and 15 mg/L detected by AAS which presence in the glyphosate solution before and after Irradiation.

Time (h)	Cu concentration (mg/L)	
	5.0	**15.0**
0	5.0	15.0
5	4.9	14.8

Experimental Conditions: [glyphosate]$_0$ = 15 mg/L; solution volume 400 ml; UV source 400 W; self-pH 5.0; air flow rate 3 L/min; irradiation time 5 h.

Moreover, Cu(II) ions has an ability to form at least three types of coordinated complexes. However, Fe(II) can form only one complex and Zn(II) can form two coordinated complexes. The formation of these complexes has already been discussed in Chapter 2 (section 2.11.) where the geometry of these complexes could be tetrahedral, square planar or octahedral. In fact, most Cu(II) and Fe(III) complexes with organophosphorous herbicides are octahedral type (Caetano *et al.*, 2012).

In the case of malathion, the significant inhibition in the presence of Cu(II) ions also show a similar pattern with the UV spectra of glyphosate where the absorbance spectra after 5 h irradiation was still high (Figure 4.42) and this could be due to the formation of some stable photoproducts or complexes.

Further explanation is that in the presence of UV light Cu(II) ions behave as electron scavengers thus they reduced to Cu^+ and then the Cu^+ ions oxidised back to Cu^{2+} by consuming •OH radicals through the following reactions (Shifu and Yunzhang, 2007):

$$Cu^{2+} + e^{-} \rightarrow Cu^{+} \tag{4.34}$$

$$Cu^{+} + \bullet OH + H^{+} \rightarrow Cu^{2+} + H_2O \tag{4.35}$$

Due to the Cu^{2+}-Cu^{+} cyclic reactions (equations 4.34 and 4.35), there is a reduction in the overall concentration of •OH radicals in the irradiated solution and ultimately there is a decreases in the concentration of •OH in the photolytic system which then retarded the degradation efficiency. Moreover, Shifu and Gengyu (2005) postulated that the formation of predominant complex, $[Cu(H_2O)_4]^{2+}$ complex only occurred when Cu(II) concentration was higher in the solution where this complex has capability to absorbs UV light. The absorbing competition of UV light lead to the deterioration of H^{+} and e^{-} (equation (4.5)) where both ions are vital in the solution for the production of radical species.

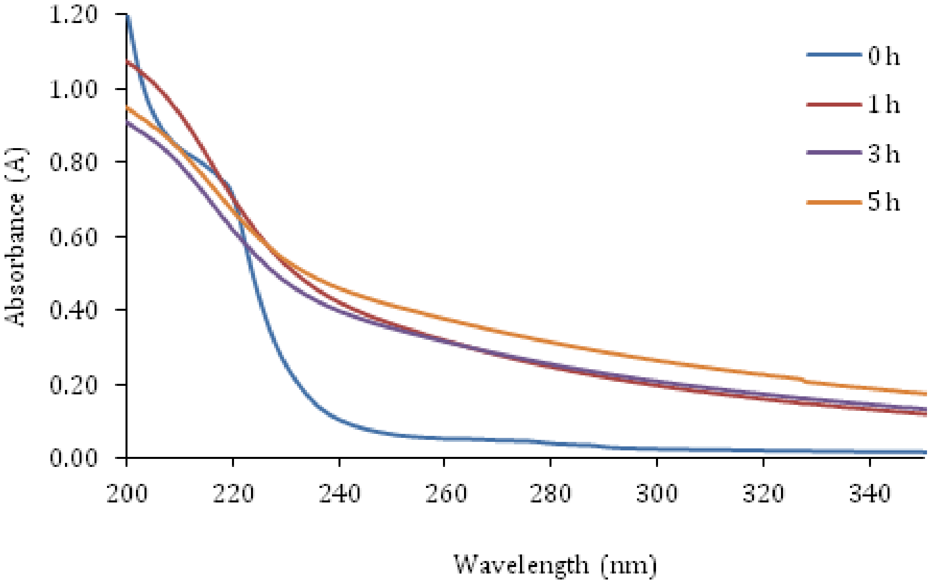

Figure 4.42 UV spectra of commercial formulation of malathion as a function of time in the presence of Cu(II) ions. Experimental conditions: $[\text{malathion}]_0$ 15 mg/L; [Cu(II)] 15 mg/L; self-pH 5.0; 400 W UV source; solution volume 400 ml; air flow rate 3 L/min; irradiation time 5 h.

Another study which reported the detrimental effect in the presence of Cu(II) ions was conducted by San *et al.* (2002). Selvam *et al.* (2007) found that Cu(II) ions has a less beneficial effect where the photocatalytic degradation of 4-fluorophenol was shown to be in the efficiency order of: Mg > Fe(III) > Fe(II) > Cu(II). Other studies (Liu *et al.*, (2009; Wei *et al.*, 2009; Lopez-Munoz, Aguado and Ruperez, 2007; Shifu and Yunzhang, 2007; Shifu and Gengyu, 2005; Beydoun *et al.*, 2002; Hua *et al.*, 1995) have shown dual effect depending on the concentration used where the studies reported the beneficial effect were only obtained at certain concentrations (optimum values) and start to inhibit when higher concentration than optimum values were used.

Effect of Zn(II) ion

An extensive literature review showed that a very limited research work has been done on the effect of Zn(II) ion on the photodegradation of pesticides. It has been found that the presences of Zn(II) ions has no obvious effect on the photodegradation of glyphosate (Shifu and Yunzhang, 2007), methamidophos (Wei *et al.*, 2009), monocrotophos and phorate (Shifu and Gengyu, 2005). Up to this date, there is no publication on the photodegradation of acephate and malathion in the presence of Zn(II) ions.

In this study however, a positive role of Zn(II) ions was only observed for the degradation of acephate. Zn(II) ion needs two electrons to be reduced zinc atom (equation (4.36)). Thus, this could be helped to reduce the recombination of electron and hydroxyl radical yielding the higher degradation efficiency.

$$Zn^{2+} + 2e^{-} \rightarrow Zn \qquad (4.36)$$

Nevertheless, there is no significant effect of 5 and 15 mg/L of Zn(II) ions on the photodegradation of glyphosate and malathion could be due to the complex formation as Zn(II) ions have the ability to form two types of complexes.

4.6.6. Effect of copper ions in the presence of H_2O_2

Overall, the addition of 30 mg/L of H_2O_2 to the solution of each pesticide in the presence of 5 mg/L Cu(II) ions has increased the degradation efficiency. The increase in the degradation efficiency is probably due to the decomposition of H_2O_2 in the presence of Cu(II) ions to produce •OH radicals via a photo-Fenton type like reaction as follows:

$$Cu(II) + e^- \rightarrow Cu(I) \tag{4.37}$$

$$Cu(I) + H_2O_2 \rightarrow Cu(II) + OH^- + \bullet OH \tag{4.38}$$

4.6.7. Effect of mixed metal ions in the presence of H_2O_2

The data on the effect of single metal ions especially in the presence of 5 mg/L of Fe(II) ions act as a catalyst and ultimately increased the degradation efficiency of each pesticides. However, in the presence of mixed metal ions (Fe(II), Cu(II) and Zn(II)), the degradation of glyphosate and malathion were retarded. The addition of 30 mg/L of H_2O_2 to the solution also could not overcome this problem. Thus, I believe that the reduction in the degradation of these pesticides is mainly due to the presence of Cu(II) ions. The presence of Cu(II) ions along with organic compounds are known to form Cu-organic complexes and this clearly show the dominant of copper ions in retarding the degradation efficiency. The Cu-glyphosate complexes have been discussed in section 4.6.5 under the effect of Cu(II) ions.

In contrast, the presence of mixed metal ion in the acephate solution has increased the degradation efficiency and further increment was occurred with the addition of 30 mg/L of H_2O_2. This could be due to the available •OH radicals and positive synergistic effect of Fe(II) and Zn(II) ions in the solution.

4.7. Conclusion

In this chapter, the optimum results of various parameters such as UV source, solution pH, initial concentration of substrates and oxidants (H_2O_2, $K_2S_2O_8$, KIO_4 and $KBrO_3$) on the photodegradation of acephate, glyphosate and malathion have been presented. The effect in the presence of single metal ions namely Fe(II), Cu(II) and Zn(II) ions on the photodegradation of all pesticides have been discussed thoroughly where the studied concentrations were 5.0 and 15.0 mg/L. Effects of mixed metal ions on the degradation of the three pesticides have also been discussed.

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CHAPTER 5: Conclusions and Recommendations

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5.1. Conclusions

Both chemical and product manufacturing industries produce large quantities of waste and effluent streams containing low concentrations of organic pollutants and heavy metal ions (Table 5.1) and these mixed waste effluent streams are difficult to treat with the existing processes (Devipriya and Yesodharan, 2005; Esplugas *et al.*, 2002; Halmann, 1996). The traditional treatment methods for the removal of organic pollutants are very selective and their applications cannot be extended for the treatment of mixed solutions containing both heavy metals and organic pollutants. In addition, most existing treatment methods usually involve the use of additional chemicals and also produce secondary wastes that hinder the extension of existing methodologies to industrial scale due to environmental and economic reasons.

Table 5.1: Examples of hazardous waste generated by different industries (SDWF, 2013)

Waste generator	**Waste type**
Chemical manufacturers	Acids and bases Spent solvents Wastewater containing organic compound
Agrochemical manufacturers	Pesticide residues Concentrated raw animal manures Fertiliser residues
Printing industry	Ink sludge containing heavy metals
Petroleum refining industry	Wastewater containing benzene and other hydrocarbons sludge from refining process
Leather products manufacturing	Toluene and benzene
Paper industry	Chlorine waste from paper bleaching process
Metal manufacturing	Sludge containing heavy metals such Cu, Cd, Zn, Fe, Al, Cr, Sn and etc.

The Malaysian economy is the fastest growing economy in the South East Asian region and has continued to expand over the past many years with the Gross Domestic Product (GDP) recorded a growth of 5.1% in 2011 (DOSM, 2013). The two fastest growing sectors in Malaysia are 1) manufacturing and 2) agriculture sectors (MIDA, 2013). Manufacturing continued to be an important sector in the economy contributing 27.5% of GDP in 2011 (DOSM, 2013). Employment in the manufacturing sector was estimated at 3.5 million persons or 28.7% of total employment in 2011 (DOSM, 2013; MOF, 2013). Similarly, the agriculture sector recorded a growth rate of 5.6% in 2011. This sector contributed 7.3% to the GDP. Employment in the agriculture sector was estimated at 1.4 million persons or 11.5% of total employment in 2011 (MOF, 2013). For decades, the agriculture industry has been one of the economic pillars of the country, playing its role as a catalyst for the development of remote and rural areas. Malaysia was the number one producer of palm oil ten years ago and is today still the number one producer (MPOB, 2013).

The Malaysian government has spent a huge amount of money and effort to encourage foreign investors to invest in both manufacturing and chemicals sectors which include, electrical and electronic products, transport equipment, machinery and equipment, engineering supporting industry, basic metal products, fabricated metal products, textiles and textile products, medical devices industry, agriculture and food processing, oil palm products, chemicals and chemical products, biotechnology industry, petroleum products including petrochemicals, plastic products, rubber products, wood & wood products and furniture, non-metallic mineral products, paper, printing and publishing industry (MIDA, 2013).

The expansion of these industries has created huge environmental pollution problems associated with the management of their waste streams (Daud, 2013). These problems originated due to the lack of proper waste management systems and proper implementation of environmental legislations. The Malaysian government has now introduced and implemented some strict environmental regulations and forced many of these industries to combat the pollution problems associated with the management of both their solid and liquid wastes. To overcome the problems associated with the management of hazardous waste, the Malaysian government has installed a plant which deals exclusively with toxic wastes disposal, including obsolete pesticides, and it is an offence to discharge any toxic waste into the environment (Yek, 2013). In addition, government has also started many initiatives (Abidin, 2004; Hassan, 2004; Ibrahim and Min, 2004) to educate both producers and users of hazardous chemicals, including pesticides, with a specific aim to reduce the release of effluent streams containing hazardous materials into the environment that could give rise to unnecessary containment in the living surrounding. Although all of these initiatives are effective in the management of hazardous materials, there is an urgent need to develop end-of-pipe technologies suitable for the treatment of wastewater effluent streams at this source. The installation of these small treatment units will be able to treat the effluent streams on-site and the treated wastewater can easily be recycled into the main industrial process in a closed loop system and this will ultimately reduce the consumption of raw water or the treated streams can simply be discharged into the environment without causing any environmental damage.

The control of organic pollutants in water is an important issue for the Malaysian government and the implementing of environmental regulations limit the discharge of these compounds into the environment (DOE, 2013). Water contamination with organophosphorous compounds can arises in various ways including effluent from industry such as pesticide and fertiliser manufacturing, runoff from cropland and equipment washing (Konstantinou, Hela and Albanis, 2006). This type of contamination can lead to the formation of effluent containing both heavy metal ions and the toxic organic pollutants. Successful treatment of this type of effluent to achieve legislative compliance will depend upon whether the heavy metals affect the process of degradation of the organic species and whether the presence of organic molecules hinders the removal of the heavy metal. The efficiency of degradation of organic pollutants can be reduced by the presence of heavy metal in the effluent (Chaudhary, Hassan and Grimes, 2009; Chaudhary and Grimes, 2008). This is particularly true if the heavy metal ions can form complexes with the organic pollutant. Methods of organic removal have been mentioned in the introduction chapter however, they are not reliable when the wastewater contains heavy metal ions. Nevertheless, there are many possible approaches such as activated sludge, biological degradation and adsorption but they only transfer the contaminants from one phase to another. Consequently, considerable efforts have been devoted for developing a suitable purification method that can easily destroy these organic pollutants. I believe, that advanced oxidation processes (AOPs) offer the advantages of destroying pollutants by oxidising the organic pollutants into minerals and nontoxic compounds through the utilisation of hydroxyl radicals for environmental remediation. However the removal performance of the AOP is largely dependent on the solution pH, organic substrate type and concentration, oxidants and the type and concentration of heavy metal ions present in mixed effluent streams.

The research work described in this thesis was funded by the Malaysian government. The overall aim of this research work was to develop sustainable and economically viable treatment technology that can be applied on industrial scales to combat the environmental pollution problems associated with the management of wastewater streams containing acephate, glyphosate and malathion. To achieve this aim, a photolytic cell system was designed, developed and optimised by investigating the effect of various parameters. The main findings of my research work are given below:

1. **Effect of UV source**: both 400 W and 600 W UV sources were capable of destroying acephate, glyphosate and malathion in aqueous solutions. No significant enhancement in the percentage degradation was achieved by changing the UV lamp from 400 W to 600 W. In addition, the degradation of these three pesticides, especially glyphosate, showed the presence of intermediate compounds with the use of the 600 W UV source. For economic reasons, all subsequent process optimisation was conducted using the 400 W UV source.

2. **Effect of pH**: Higher degradation of all studied pesticides were achieved at their self-pH values, ranging from 5.0–5.5, No advantages in the percentage degradation were achieved by increasing or decreasing the pH values from this optimum value.

3. **Effect of pesticide concentration**: the degradation efficiency increased by increasing the initial substrate concentration of acephate. In contrast, the degradation efficiency of malathion was decreased when the initial malathion concentration was increased. However, no significant effect occurred for glyphosate when the initial concentration of glyphosate was increased. The kinetic studies demonstrated that photodegradation rates of the three pesticides

based on the total organic carbon reduction followed an order of: malathion > acephate > glyphosate.

4. **Effect of hydrogen peroxide, H_2O_2**: the addition of H_2O_2 (5 - 30 mg/L) as an additional oxidant enhanced the percentage degradation of acephate and glyphosate. However, it was noticed that only an 8.5% increment was obtained for malathion with the addition of 30 mg/L H_2O_2. This clearly revealed that the effect of H_2O_2 depends on its concentration in order to have its beneficial effect.

5. **Effect of single and mixed metal ions**: overall, the presence of 5 mg/L of Fe(II) increased the degradation efficiency for all three pesticides. These results showed that Fe(II) ion acts as a catalyst which led to the formation of $[Fe(OH)(H_2O)_5]^{2+}$ and $[Fe(OH)(H_2O)_5]^{1+}$ complexes which ultimately increased the efficiency of the degradation process. However, the presence of Cu(II) ions significantly inhibited the degradation process in the cases of glyphosate and malathion. Further reduction was observed when the concentration of Cu(II) ions were increased from 5 to 15 mg/L. The presence of Zn(II) ions has no significant effect on the degradation of glyphosate and malathion. The presence of mixed metal ions (Fe(II), Cu(II) and Zn(II)) retarded the degradation of glyphosate and malathion. The presence of mixed metals and single metal ions (Cu(II) and Zn(II)) however, increased the degradation efficiency of acephate.

6. **Effect of Cu(II) and mixed metal ions in the presence of H_2O_2**: Overall, the addition of 30 mg/L of H_2O_2 to the solutions containing just Cu(II) ion increased the degradation of all three pesticides. Whereas, in the presence of mixed metal ions, no significant increase in the degradation efficiencies of both glyphosate and malathion was achieved in the presence of 30 mg/L of H_2O_2. In contrast, the positive role of H_2O_2 in the presence of mixed metal ions was observed in the degradation efficiency of acephate.

The findings above could be due to the degradation of the active ingredient as well. However, this cannot be generalised as there was a study reported that a higher degradation rate was occurred in the pure malathion compared to Radotion (formulation malathion) due to the adjuvants present in the commercial product

(Bavcon *et al.,* 2007). Furthermore, the effect of active ingredient in this study was not monitored.

All the objectives set out in the introduction chapter have been achieved and the outcomes of this work, especially the effect of single and mixed metal ions toward the degradation process of acephate, glyphosate and malathion produced interesting results. Extensive literature research revealed that no previous research work has been done on the effect of Zn(II) ions on the degradation of acephate in aqueous solutions. The effects of Zn(II) ions on the degradation of acephate and malathion has been reported for the first time in this thesis. Furthermore, most previous studies have been done on the effects of single metal ions and, again, no research work has been done on the effect of mixed metal ions on acephate, glyphosate and malation. Thus, the results obtained as part of this project could be useful to understand the impacts of various parameters on the photodegradation efficiency of organic pollutant. The selection of optimum conditions for the treatment of wastewater originating from both point and non-point sources is of paramount importance when a photolytic cell system, based on advanced oxidation process (AOP), is used for industrial applications.

5.2. Application of the Photolytic Cell System

Malaysia's previous environmental record is poor, and the country has not yet been able to back up its commitment to environmental protection with action. However, the present government is determined to combat the environmental pollution problems associated with the management of industrial wastes and effluent streams (Ibrahim and Min, 2004). The Malaysian Government has placed greater emphasis on environmental protection in order to stem the country's environmental degradation and safeguard citizens' health.

The present situation in Malaysia is that apart from a few large and export-oriented industries, which have to meet environmental standards, most of the small to medium size chemical industrial units have no effluent treatment facilities (Daud, 2013). The situation is, however, changing and the governments and regulatory authorities are helping small and medium size industrial units to develop and install appropriate treatment technologies to comply with the stringent environmental quality standards (EQS) as set out by the regulatory authorities. The collection and transportation of effluent streams from these small units to the centralised treatment unit is not an economically viable option due to high cost and the additional emissions of automotive pollutants into the environment. The photolytic system developed as part of this project has the potential to be adopted by these small and medium sized units as an end-of-pipe technology. As most of these industrial units are located in industrial estates and the adoption of this methodology by these units would be the first step to combat environmental pollution problems in Malaysia.

In Malaysia, chemical and agrochemical industries are the two biggest point sources of water contamination containing organic pollutants. Since acephate, glyphosate and malathion are being produced in large quantities and widely used in Malaysia, thus, the possibility of their occurrence in the surface or groundwater will be higher. The photolytic system developed, based on advanced oxidation process, can be used for the treatment of effluent streams originating from these point sources (Figure 5.1) and the treated water can be either recycled or discharged safely into the environment.

Furthermore, it is also possible to apply the developed photolytic cell system for the treatment of surface water at water treatment plants. Typical water treatment plant abstract surface water from rivers or other streams, compressed air is then passed to separate suspended particles. The aerated water is then treated with ozone in the reactor followed by the filtration activity using activated carbon filter and disinfected with chlorine prior the distribution to the users. The photolytic cell system developed as part of this project has the potential to synergistically enhance the efficiency of the ozonation process (Figure 5.2). The synergistic combination of UV/O_3 will be able to completely mineralise the organic pollutant, including pesticides, into H_2O and CO_2.

The optimised result obtained from this study could be useful to other researchers in various fields. Researchers in the field of organic chemistry may extend this study on the formation of complexes since they retarded the degradation process. The production technology field especially pesticide manufacturer may use these results to produce an environmental friendly products in order to meet legislation and management practice. Environmental management field for another instance may use these results in order to build awareness among citizens and users. Responsible body which regulate laws related to the environment issue can be used these result as well in order to enforce or replace the existing legislation. Pollution is hard to be avoided but can be controlled if all parties take their responsibilities.

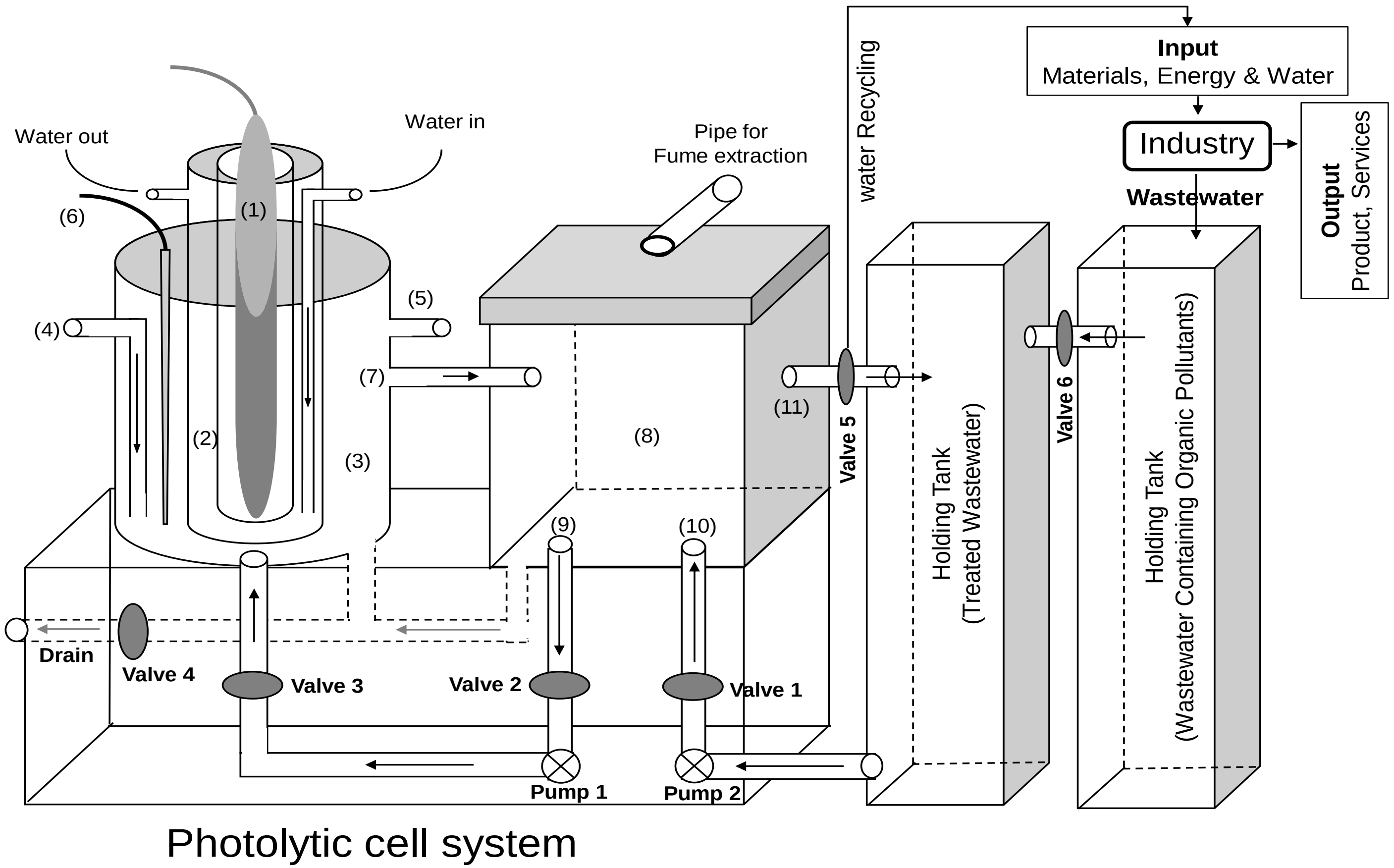

Figure 5.1 Schematic of wastewater treatment using the photolytic cell system.

1. UV lamp; 2. Immersion well; 3. photoreactor; 4. Air inlet; 5. Air outlet; 6. Temperature probe; 7. Overflow into the main reservoir from the photoreactor; 8. Main reservoir; 9. Outlet from the main reservoir to the photoreactor; 10. Inlet into the main reservoir from the holding tank; 11. Inlet into the holding tank containing treated water from the main reservoir.

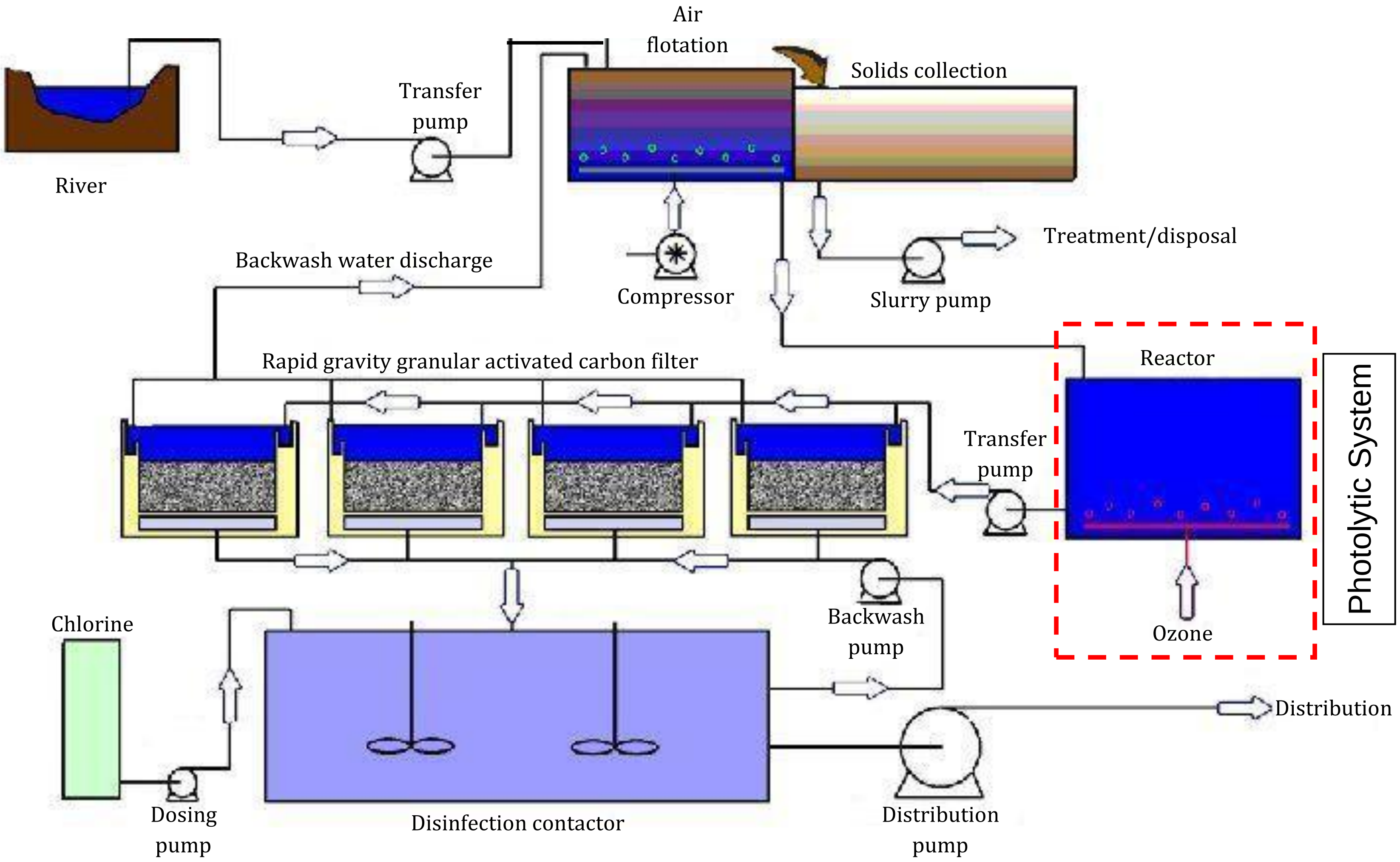

Figure 5.2 **Schematic of water treatment process and the synergistic combination of the photolytic system.**

5.3. Recommendations for Future Work

This thesis describes the photodegradation process used for the removal of three pesticides i) acephate, ii) glyphosate and iii) malathion from model solutions prepared by using the fomulations of these pesticides. Future works may explore the removal of these pesticides from real waste stream using the optimised conditions described in this thesis.

In addition, the photodegradation process could be studied on the removal of mixed pesticides in the presence of mixed metal ions as this would represent real wastewater streams that exist in the environment. As part of this project, preliminary work on the development of an HPLC method which is suitable for the determination of individual pesticide present in a mixed solution has been developed but due to the time constrains and column problem, the work on it has to be suspended. This is an area where future work, related to this project, could also be carried out.

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