EFFECT OF HYDROGEN PEROXIDE ON THE PHOTODEGRADATION OF METAMIFOP IN THE PRESENCE OF Zn(II) IONS.

by

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DECLARATION

I declare that this thesis entitled "Effect of Hydrogen Peroxide on The Photodegradation of Metamifop in The Presence of Zn(II) Ions" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature   : _____

Name   : _____

Date   : _____

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

•OH	Hydroxyl radical
AOP	Advance oxidation process
AOPP	Aryloxyphenoxy propionates
EPA	Environmental Protection Agency
H_2O_2	Hydrogen Peroxide
HPLC	High Performance Liquid Chromatography
ppm	Parts per million
UV	Ultraviolet
UV-Vis	Ultraviolet visible

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ABSTRACT

The photodegradation of metamifop contained in Nominee-M herbicide and the effect of adding Hydrogen Peroxide and Zn(II) ions were studied. Worldwide, the persistence of herbicide and heavy metal contamination in the irrigation water have led to water pollution issues. Thus, the study focused on a photolytic system using UV light to enhance production of hydroxyl radicals (•OH) to degrade the targeted pollutant. The photodegradation process was conducted under UV lamp in the laminar flow chamber for 3 hours and magnetic plate with a magnetic stirrer was used to stir the sample. To monitor the degradation efficiency, the concentration of the organic compound and metal ions were characterized using High Performance Liquid Chromatography (HPLC) and UV-Visible spectrophotometer (UV-Vis). The highest degradation in UV/H_2O_2 was obtained at 97.3% on 5 ppm of metamifop in the presence of 10 ppm of Zn(II) ions and hydrogen peroxide. The result proved that less concentrated solutions of metamifop were easier to degrade and more concentrated solutions of Zn(II) ions and hydrogen peroxide in metamifop promoted the degradation by UV radiation. It was identified that when the concentration of metamifop, Zn(II) ions and hydrogen peroxide is increased, the degradation percentage decreased relatively. Hence, the findings demonstrated that the degradation percentage was conditional on the concentration of samples.

Kesan Penambahan Hidrogen Peroksida untuk Fotodegradasi Metamifop dengan Kehadiran ion Zn(II)

ABSTRAK

Fotodegradasi untuk metamifop yang terkandung dalam racun rumpai Nominee-M dan kesan penambahan hidrogen peroksida dan ion Zn(II) telah dikaji. Di seluruh dunia, ketahanan racun rumpai dan pencemaran logam berat di dalam saliran air mengakibatkan isu-isu pencemaran air. Oleh itu, kajian ini memberi penekanan kepada satu sistem fotolitik yang menggunakan sinar ultra ungu untuk meningkatkan pengeluaran radikal hidroksil (•OH) untuk degradasi pencemar. Proses fotodegradasi berlaku di dalam kabinet laminar flow menggunakan lampu sinar ultra ungu selama 3 jam dan pinggan magnetik digunakan untuk mengacau sampel. Untuk mengawal efisiensi penurunan, kepekatan ion logam dan sebatian organik telah dilaksanakam menggunakan kromatografi cecair prestasi tinggi dan UV spektrofotometer (UV-Vis). Penurunan tertinggi di UV/H2O2 telah diperolehi pada 97.3% untuk 5 ppm metamifop dengan kehadiran 10 ppm ion-ion Zn(II) dan hidrogen peroksida. Ia telah dikenalpasti apabila kepekatan metamifop, ion-ion Zn(II) dan hidrogen peroksida meningkat, peratus degradasi menurun. Oleh itu, dapatan kajian menunjukkan bahawa peratus degradasi bergantung kepada kepekatan sampel.

CHAPTER 1

INTRODUCTION

1.1 Background of study

Rice *(Oryza sativa* L.) has become a staple food and it is one of the most important grain crops for billions of people, especially in Asian, Latin American, and African countries (Kennedy, 2002). In Malaysia, rice or paddy industry had gained special attention by the Government for rice is the staple food commodity (Fatimah *et al.* 2007). With the increasing human population in Malaysia, the demand for continuous food supply has also increased to accommodate the number of population. To increase crop yields, the use of herbicides has been widely used by farmers. This is because the production of crops is restrained by several factors such as insect pests, diseases and weeds, hence, the use of herbicides is crucial for optimum production and quality of crops, especially rice.

Despite their advantages, herbicides pose some risks to the environment if they are not properly handled. Example of herbicide that is commonly used in the production of rice is Nominee-M. Nominee-M contains metamifop whereby metamifop is a type of postemergent aryloxyphenoxypropionic acid herbicide (AOPP) used to kill weeds after they have germinated. In relation with other AOPPs, metamifop provides excellent control on a wide range of annual grass weeds. However, excess of metamifop may lead to bioaccumulation in the crops due to the post emergent use and will also bulk up as pollutants (Sondhia, 2008).

Meanwhile, heavy metals are among the most common inorganic pollutants. Worldwide, heavy metal contamination has become an environmental issue in both developing and developed countries (Zhang *et al.*, 2007; Sun *et al.*, 2010). Based on Smital *et al.*, (2004), the source of heavy metal pollution includes agricultural irrigation made from domestic and industrial wastewater and contamination from fertilizers and herbicides by heavy metals such as lead (Pb), cadmium (Cd), mercury (Hg), copper (Cu), manganese (Mg) and iron (Fe). Due to their toxicity, wide sources, non-biodegradable properties and accumulative behaviours, heavy metals have become a considerable environmental concern (Yu *et al.*, 2008).

In addition to this, Ting discovered that the pollutants containing heavy metal will change the properties of water quality, hence, making the water unsuitable for consumption (Ting *et al.*, 2007). Thus, greater issues may arise when heavy metals, such as zinc (Zn) is present in excessive amounts in the pollutants. Although zinc acts as a micronutrient and is considered as an essential element for life, excessive zinc can be harmful to health. In addition to this, the effect of water contamination can clearly be seen and become hard to overcome especially when it affects the whole hydrological cycle. A typical hydrological cycle is expressed in Figure 1 on how atmospheric water and surface water are interlinked with contamination.
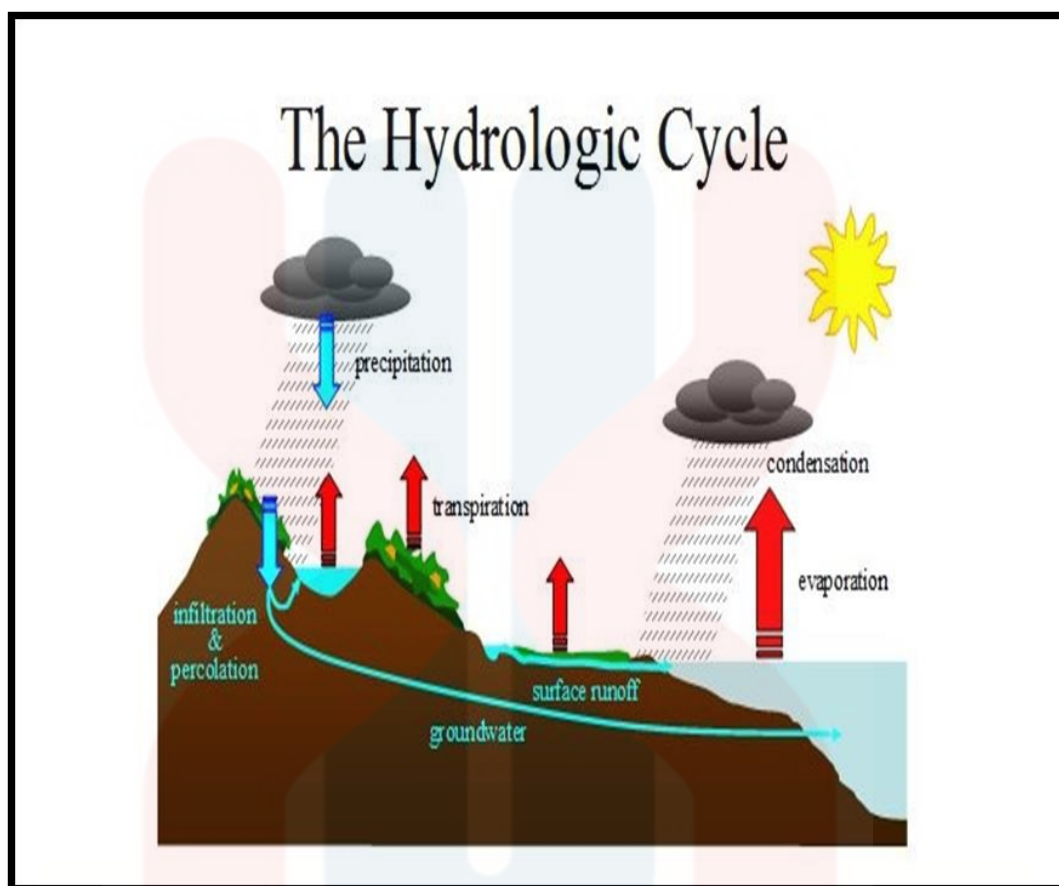
Figure 1.1 : Hydrological Cycle (Sheoran, 2008)

According to Katagi (2004), photodegradation is defined as an abiotic process in the dissolution of pesticides where molecular excitation by absorption of light energy results in various organic reactions or reactive oxygen species such as OH• which will oxidize the functional groups in a pesticide molecule. Hence, in the present study, the effect of Zn(II) ions on the photodegradation of metamifop will be identified along with the presence of hydrogen peroxide.

1.2 Problem Statement

The herbicide Nominee-M contains active ingredient of metamifop that can be contaminated in surface runoff or in groundwater. There are many possible methods which can be applied to remove or destroy these phenolic compounds such as Fenton oxidation, biotreatment, photocatalytic degradation, electrochemical oxidation, biological oxidation and treatment with ultraviolet radiation (Navarro *et al.,* 2009). All of the methods can destroy the harmful compounds in herbicide, however there are several methods such as photocatalysis which is very difficult to be conducted since the catalysts need to be regenerated back from the system. Hence, photodegradation which will not use any catalysts is studied as one of the promising method of water treatment.

1.3 Objectives

1. To investigate on the photodegradation process of metamifop in the presence and absence of Zn(II) ions using High Performance Liquid Chromatography (HPLC) and UV-Visible spectrometer (UV-Vis)

2. To determine the effect of hydrogen peroxide towards the photodegradation of Zn(II) ions.

CHAPTER 2

LITERATURE REVIEW

2.1 Water pollution

Oceans, seas, lakes, rivers and ponds are forms of water resources and they covered three fourths of the Earth's surface. Water is essential for the existence of life on earth. 75% of the earth is covered with water out of which 97% is salty and only 3% is available for drinking, agriculture, domestic and industrial consumption, while the remaining is locked up in oceans as salt water, polar ice caps, glaciers and underground reservoirs. During the last four decades, the major concern on aquatic life has been the alarming rate of discharge of chemicals to the water resources. According to (Vié *et al.*, 2009), native freshwater fish species are at risk of extinction exceeding 50% in some parts of the world, and this is also the case for nearly one-third of the world's amphibians.

In addition, the toxicity and the partially biodegradability characteristics posed by organic chemicals discharged into the environment will cause water resource contamination. Water resource contamination leads to water pollution which is a severe problem facing our world on this 21st century. A study by (Tyagi and Mehra, 1994) stated that the major sources of water contamination were domestic, industrial and agricultural as well as solid waste pollution, thermal pollution, shipping water pollution and radioactive wastes. Water pollution occurs when the water body becomes contaminated by substances and the aquatic organisms cannot keep up with their cleaning responsibilities.

In many developing countries, water pollution is an acute problem which an estimated 95% of untreated urban sewage is directly discharged into surface waters (Pimentel *et al.*, 2004). Water pollution can be categorised as point sources (PS) and non-point sources (NPS). The distinct difference between point sources and non-point sources of water pollution is that point sources are from a direct known source while pollution that comes from various or diffuse sources are called the non-point sources.

Point sources are from factories, wastewater treatment facilities, septic systems, and other sources that are clearly discharging pollutants into water sources. Non-point sources include failing or improperly managed septic systems, leaking sewers, animal wastes, fertilizers and pesticides, leaking underground storage tanks and others (James, 2003). (Meybeck and Helmer, 1996) characterized the source of pollutants as listed in Table 2.1:

Table 2.1: Sources and significance of pollutants resulting from human activities

(Meybeck and Helmer, 1996)

Sources	Bacteria	Nutrients	Trace metals	Pesticides and herbicides	Industrial organic micropollutants	Oils and greases
Atmos. transport	x	xxxG	xxG	xxG		
Point sources						
Urban sewage	xxx	xxx	xxx	x	xxx	
Industrial effluent		x	xxxG	x	xxxG	xx
Diffuse sources						
Agriculture	xx	xxx	x	xxxG		
Urban waste and run-off	xx	xx	xxx	xx	xx	x
Industrial waste disposal		x	xxx	x	xxx	x
Dredging		x	xxx	x	xxx	x
Internal recycling		xxx	xx	x	x	
Navigation and harbours	x	x	xx		x	xxx

Note

x: Low local significance   xxx: High local or regional significance

xx: Moderate local or regional significance   G: Global significance

7

2.2 Herbicides: metamifop

By referring to Table 2.1, the use of pesticides and herbicides have high local or regional and global significance in agricultural sector. This suggests that the consumption of herbicides and pesticides for crops must be always monitored to minimize its impact to living beings and environment. According to Andreu (2004), herbicides are compounds produced to kill certain weeds without giving harm to the host plant. In the production of cereal crops and rice, Nominee-M herbicides act as a control for a wide range of annual and perennial grass weeds. The commonly managed weeds are *Monochoria vaginalis, Sagittarai guyanesis, Limnocharis flava, Jussieae linfolia, Fimbristylus miliacea and Cyperus iria* (Parthipan. *et al*., 2013) In details, active ingredients of 9.5% metamifop and 3.8% bispyribac-sodium are present in Nominee-M.

For this study, a post emergent formulation herbicide newly developed by Dongbu Hannong Chemical Co, Ltd (Korea Republic) called Nominee-M was chosen. A beige Nominee-M will form a suspo-emulsion (SE). SE is a mixture of water insoluble active ingredients dispersed in an aqueous solution whereby the active ingredient is in suspension form and emulsion form. Such emulsion is intended for dilution prior to application. Compared to other form of herbicides, a SE is easy to be handled and measured. It is also a non-flammable substance and offers good miscibility in water.

Metamifop (Oxyphenoxy Acid Esters) is an inhibitor to acetyl coenzyme-A carboxylase introduced from aryloxyphenoxy propionates. Due to high contents of metamifop in Nominee-M, the reaction of metamifop will induce chlorosis selectively in weeds and eventually retard growth of weeds. This active ingredient goes through translocation from point of uptake to the growing meristem in weeds. It inhibits the activity of acetyl coenzyme-A carboxylase (ACCase) leading to retardation of weeds growth.

Meanwhile, (Ravi *et al.*, 2013) in his study has indicated that 100g ai/ hectare for metamifop is the best amount to be applied in paddy field weeds management. In the upcoming study on the photodegradation process, metamifop serves as a base for all the experimental procedures which will further be discussed on the next chapter. Figure 2.1 and Table 2.2 shows the structural formula and chemical properties of metamifop:
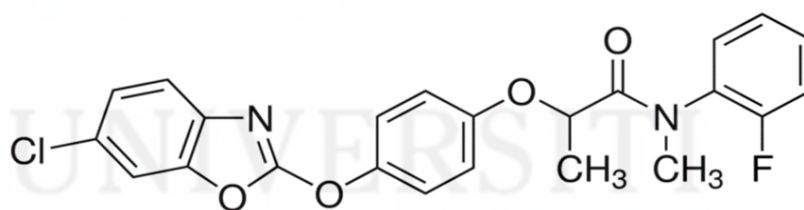
Figure 2.1: Structural formula of metamifop

Table 2.2: The chemical properties of metamifop

Empirical Formula	$C_{23}H_{18}ClFN_2O_4$
Molecular Weight	440.8514 Da
Density	$1.364 g/cm^3$

2.3 Heavy metals: zinc

Any toxic metal may be called heavy metal regardless of their atomic mass or density. According to Raut (Raut *et al*.,2007), the term "heavy metal" is collectively applied to a group of metals and metal-like elements with density greater than 5 g/cm^3 and atomic number above 20. Heavy metals exhibit metallic properties including the transition metals, some metalloids, lanthanides, and actinides. Heavy metals such as iron, cobalt, copper, manganese, molybdenum, and zinc are required by humans (Lane, 2009). However, all metals are toxic at higher concentrations (Lane, 2005) and if ingested at gross amounts it has an emetic effect. Heavy metals will readily accumulate to toxic levels since they are non-biodegradable and non-thermodegradable.

In addition, the concentration of heavy metals is enhanced by rapid industrialization and technological development, posing a significant threat to environment and public health due to their toxicity, accumulation in the food chain and persistence in nature of heavy metals (Ceribasi and Yetis, 2001). Since heavy metals would not break down, the biosphere might be affected for a long period. Heavy metal wastewater exists in various industries, such as metal finishing, electroplating, plastics, pigments and mining, which is a severe threat to the environment and human lives (Kurniawan *et al*.*,* 2006). It is known that heavy metals form an important polluting group and it is urgent to eliminate those toxic heavy metals from waste water.

10

Zinc is a shiny bluish-white metal that originated from natural geological occurrence and wastes (EPA, 2001). In the periodic table, zinc is a Group 12 element. Zinc is represented with the symbol Zn and the atomic number and atomic mass of zinc is 30 and $65.37 g\ mol^{-1}$ respectively. The ground state configuration of zinc is $3d^{10}\ 4s^{2}$ and it is a highly stable filled d-orbitals, hence, its inner d-electrons rarely take part in bonding and oxidation states of Zn beyond +II are hard to achieve.

Zn(II) is proclaimed to be toxic beyond permissible limits. Common symptoms of zinc toxicity are irritability, muscular stiffness, loss of appetite and nausea (NRC, 1977). The recommended level of zinc in drinking water by WHO is 5 mg/L. The metal is then reported to be bioaccumulated into biosphere creating ecological problems. In developing countries, metal mining and metallurgy industrial departments discharge massive quantities of wastewater containing high concentration of Zn(II) (WHO, 1993).

Zinc can also be found in wastewater of pharmaceuticals, galvanizing, paints, pigments, insecticides, cosmetics, etc. that trigger serious problem to the environment (Central, 1986). Therefore, the heavy metal levels in wastewater, drinking water, and water used for agricultural activities should be reduced to the maximum permissible concentration. This study will use $ZnSO_4$ solution in the photodegradation process of metamifop.

2.4 Advanced Oxidation Process (AOP): photodegradation

Advanced Oxidation Process (AOP) is referred to oxidation processes that generate hydroxyl radicals (•OH) in appropriate quantity to influence the water treatment. The hydroxyl radical (•OH) is a powerful, non-selective chemical oxidant, which reacts briskly with most organic compound. The hydroxyl radical (•OH) could play a central role in AOPs for wastewater treatment (Tai *et al*., 2002). Reactions in AOP involves hydrogen atom transfer, electrophilic addition, electron transfer and radical-radical reaction (Quiroz *et al*., 2007). The decomposition of pollutants is the result of atom abstraction or addition reactions and a model on the pathway of hydroxyl radical-induced chain reaction mechanisms in aqueous phase AOP has been developed recently (Li and Crittenden, 2009).

AOP is divided into heterogeneous photo catalysis and homogenous photo degradation (Cardeal *et al.*, 2008). Homogenous photodegradation can be further subdivided into photo-oxidation and direct photodegradation. Photo-oxidation is a light driven oxidation process initiated by hydroxyl radicals. Meanwhile direct photodegradation is a light driven process where degradation proceeds following direct excitation of the pollutant by UV light. For pesticide degradation, it can be divided into three elements which are chemical degradation, photodegradation and microbial degradation (Smital et al., 2004). Photodegradation is defined as the breakdown of pesticides by sunlight which can take place on foliage, surface of soil, water or even air (Kerle *et al*., 1996).

Degradation can occur by direct and indirect photolysis. In direct photolysis, the pesticide absorbs UV light and afterwards reacts with substances in the environment or decomposes by itself. However, indirect photolysis is more common. This is due to oxygen and hydroxy or peroxy radicals, which are produced by photolysis in humic or inorganic compounds (Franko *et al.,* 2005). Among the several factors that influence this process are properties of pesticide, intensity of sunlight, presence of other occurring ions and so forth (Quiroz *et al.*, 2005). Herbicide which has low colour pigment such as Nominee-M which is an off-white viscous suspension has lower affinity towards absorption of photons.

In comparison with other method, AOPs give benefits on high rates of oxidation of pollutant, flexibility concerning water quality variations and feasibility of the equipment used. The main disadvantages are relatively high treatment costs and special safety requirements because of the use of very reactive chemicals such as ozone and hydrogen peroxide and high-energy source like UV lamps and electron beams (Goi, 2005). In general, the AOPs when applied in a right place, give a good opportunity to reduce the contaminants concentration from several hundred ppm to less than 5ppb. Photodegradation or ultraviolet (UV) radiation is a proven method for treating contaminated water that has organic and inorganic pollutants, including pesticides (Ali *et al.,* 2010). Photodegradation process is used to destroy the chemical substance, pesticides and other harmful organisms in polluted water bodies.

2.5 Hydrogen peroxide, H_2O_2

Hydrogen peroxide is a clear, colourless liquid which is a powerful oxidiser that decomposes into an environmental compatible product, which are water and oxygen. Hydrogen peroxide has a melting point of -0.43˚C and a boiling point of 150.2˚C, which the boiling point is slightly higher than water. Hydrogen peroxide contains highly concentrated aqueous solutions (> 65% *m/m)* that are soluble in a range of organic solvents, such as carboxylic esters. Hydroxyl radicals (•OH) of hydrogen peroxide are extremely unstable and has high reactivity.

The active part of hydrogen peroxide is the peroxide group. When dissolved in water, H_2O_2 will spontaneously breaks down into water and oxygen. This decomposition leads to the formation of reactive oxygen species (ROS), which can oxidise certain organics and metal ions and can also kill pathogens (Nederhoff, 2000). Optimisation of conditions using H_2O_2 to destroy these pollutants can involve control of pH, temperature and reaction time and no additional additives are required.

H_2O_2 can be used in combination with catalysts which are UV light and/or other oxidants. The UV light allows the production of an oxidising agent (ROS) called hydroxyl radical (•OH). •OH is one of the strongest oxidants and it is much more efficient than hydrogen peroxide alone (Amin *et al.,* 2008) and is therefore much more efficient in killing microorganisms and degrading organics in water.

14

Previous study (Tseng *et al.*, 2012; Zhang and Pagilla, 2010) has shown that hydrogen peroxide will enhance the degradation process by forming superoxide radicals anions. In addition, most studies have proven that a small amount of H_2O_2 can foster the generation of •OH and intensify the degradation efficiency of organic pollutants, but other studies indicated that beneficial effects of hydrogen peroxide will degenerate due to its auto-decomposition and termination process as shown in the reactions below (Zhang and Pagilla, 2010; Devipriya and Yesodharan, 2005):

$$2\ H_2O_2 \rightarrow 2\ H_2O_2 + O_2 \tag{2.1}$$

$$\text{•OH} + HO_2\text{•} \rightarrow H_2O + O_2 \tag{2.2}$$

$$HO_2\text{•} + HO_2\text{•} \rightarrow H_2O_2 + O_2 \tag{2.3}$$

$$HO_2\text{•} + H\text{•} \rightarrow H_2O_2 \tag{2.4}$$

$$\text{•OH} + \text{•OH} \rightarrow H_2O_2 \tag{2.5}$$

CHAPTER 3

MATERIALS AND METHODS

3.1 Chemicals and reagents

The formulation herbicide used was Nominee-M which contained metamifop (9.5%) was purchased from Agricultural Chemicals (M) Sdn. Bhd. Analytical standard of metamifop was obtained from Sigma Aldrich. The metamifop standard was analysed using High Performance Liquid Chromatography (HPLC). The solvent used for HPLC was acetonitrile, the gradient grade for liquid chromatography obtained from Merck. Next, Zn(II) ions aqueous solutions was prepared using zinc sulphate ($ZnSO_4$). Stock solution was diluted using deionized water in order to get 5 ppm and 10 ppm of solution to prepare aqueous solution of Nominee-M. For UV-Vis, distilled water was used as the blank to neutralize the concentration to zero.

3.2 Characterizations

The instruments used were High Performance Liquid Chromatography (HPLC) and UV-Visible spectrometer (UV-Vis).

3.2.1 High Performance Liquid Chromatography (HPLC)

HPLC model CTO-10ASvp from Shimadzu was used to determine the initial and final concentration standard of metamifop. Upon obtaining the analytical standard of metamifop solution, the standard retention time and percentage degradation on the metamifop were determined. All of the optimized operating condition of HPLC follows the conditions provided by Sigma Aldrich except for the injection volume and type of column used. The injection volume was set to 20μl and the type of column used was C18 with the length of 250 mm. The suitable flow rate for operating condition was 1.4 ml/min.

Figure 3.1: High performance liquid chromatography (HPLC)

Analysis of metamifop

The analytical method used for the determination of metamifop was adapted from Sigma Aldrich. Using HPLC, all degradation values were analysed using the chromatogram obtained from metamifop standard solution with the concentration of 2 ppm, 4 ppm, 6 ppm, 8 ppm and 10 ppm. From the analysis of the metamifop standard solution, the results obtained was really different comparing to the data sheet acquired from Sigma Aldrich.

17

The retention time from Sigma Aldrich was at 4.4 minutes as shown in Figure 3.2 while retention time from analyzed was at 3.1 minutes. The retention time at 3.1 minute was confidently belonged to metamifop because the peak was consistent for all the concentration of the standard solution (2 ppm, 4 ppm, 6 ppm, 8 ppm and 10 ppm) as shown in Figure 3.3. The difference of retention time was due to the different length of column used which was 250 mm in characterization.
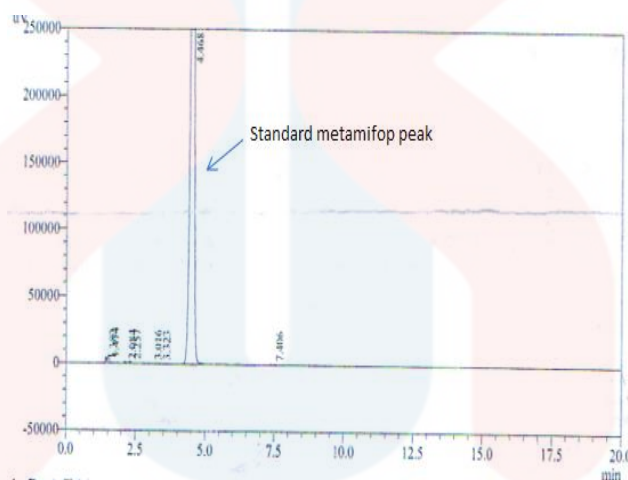
Figure 3.2: Chromatogram of 200 ppm metamifop standard provided by Sigma Aldrich
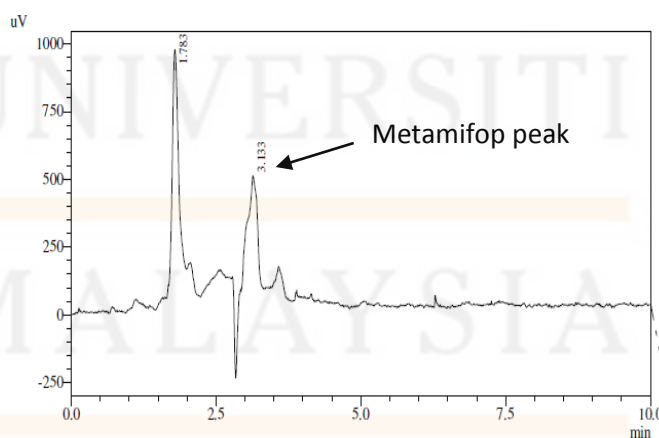
Figure 3.3: Chromatogram of 10 ppm metamifop standard solution

3.2.2 Ultraviolet-Visible spectrophotometer (Spectroquant Pharo 300)

UV-vis model Spectroquant Pharo 300 by Merck was used to determine the concentration level of heavy metal in the waste water solution. Heavy metal that was used was zinc. UV-Vis spectrometer was used to obtain the absorbance. The wavelength ranges were light in the visible and adjacent (near-UV and near-infrared [NIR]) regimes. The standard cell holder used was a cuvette with 1x1 cm size. The wavelength range was between 320 nm to 1100 nm. For the characterization, the use of UV-Vis was to monitor the peak level of metamifop in the samples and detect absorbance spectrum. The spectrum obtained was used to analyse significant deviation in the parent peak of the compound. The blank used to neutralize the concentration to zero was distilled water.
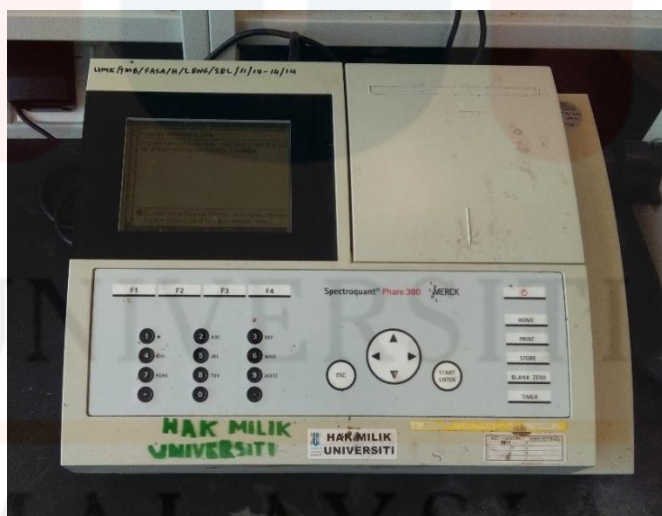
Figure 3.4: Spectroquant Pharo 300 Spectrophotometer

3.2.3 Laminar Flow Chamber

This setup consisted of laminar flow chamber with UV lamp, depicting sunlight. The laminar flow used a UVX radiometer with $40\mu W/cm^2$ and it was covered in aluminium foil in such a way that the UV light was not reflected outside the chamber. The UV wavelength was 300 nm to 400 nm. The operating conditions for UV radiation took 3 hours with the approximate height of 50 cm from UV lamp to the solution. In this research, the samples were kept in the chamber as the photodegradation process has taken place.

Figure 3.5: Laminar flow chamber

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3.3 Method

3.3.1 Preparation of stock solution

3.3.1.1 Stock solution of metamifop formulation

A 1000 ppm of stock solution was prepared by dissolving 10.5 g of Nominee-M formulation in 1L of deionized water. The stock solution was then kept in a 1000 ml volumetric flask covered in aluminium foil to avoid the solution degradation to light surrounding. Finally, the solution was stored in refrigerator at 4°C.

3.3.1.2 Stock solution of 1000 ppm of Zn(II) ions

1000 ppm of Zn(II) ions solution was prepared by dissolving 4.6 g of $ZnSO_4$ salt in 1L of deionized water. The stock solution was then kept in a 1000 ml volumetric flask covered with aluminium foil to avoid the solution degradation to light surrounding. The solution was stored in refrigerator at temperature of 4°C.

3.3.2 Preparation of metamifop solution without Zn(II) ions

3.3.2.1   5 ppm of metamifop solution

1.25 ml of 1000 ppm metamifop stock solution was added into 250 ml volumetric flask. The dilution using deionized water to form 5 ppm metamifop formulation was performed. Cover the volumetric flask with aluminium foil to avoid the solution degradation to sunlight of surrounding.

3.3.2.2 10 ppm of metamifop solution

2.5 ml of 1000 ppm metamifop stock solution was added into 250 ml volumetric flask. It was then diluted using deionized water to form 10 ppm metamifop formulation. The volumetric flask was covered with aluminium foil to avoid the solution degradation to sunlight of surrounding.

3.3.3 Preparation of metamifop solution in the presence of Zn(II) ions

3.3.3.1 5 ppm metamifop with 5 ppm Zn(II) ions

1.25 ml of 1000 ppm metamifop was added from stock solution into 250 ml volumetric flask covered with aluminium foil. Next, 1.25 ml of 1000 ppm Zn(II) ions was added from stock solution. The solution was diluted with deionized water.

3.3.3.2 5 ppm metamifop with 10 ppm Zn(II) ions

1.25 ml of 1000 ppm metamifop was added from stock solution into 250 ml volumetric flask covered with aluminium foil. Next, 2.50 ml of 1000 ppm Zn(II) ions was added from stock solution. The solution was diluted with deionized water.

3.3.3.3 10 ppm metamifop with 5 ppm Zn(II) ions

2.50 ml of 1000 ppm metamifop was added from stock solution into 250 ml volumetric flask covered with aluminium foil. Next, add 1.25 ml of 1000 ppm Zn(II) ions from stock solution. The solution was diluted with deionized water.

22

3.3.3.4 10 ppm metamifop with 10 ppm Zn(II) ions

2.50 ml of 1000 ppm metamifop was added from stock solution into 250 ml volumetric flask covered with aluminium foil. Next, 2.50 ml of 1000 ppm (II) ions from stock solution was added. The solution was diluted with deionized water.

3.3.4 Preparation of stock solution of 1000 pm H_2O_2

A 1000 ppm of stock solution was prepared by diluting 3.33ml of 30%(w/w) H_2O_2 in 1L of deionized water and kept in a 1000 ml volumetric flask. The stock solution of hydrogen peroxide was then stored in refrigerator at 4°C.

3.3.4.1 Stock solution of 5 ppm of H_2O_2

Add 1.25 ml of 1000 ppm H_2O_2 stock solution into 250 ml volumetric flask. It is then diluted using deionized water to mark up 250 ml which forms 5 ppm of H_2O_2 working solution.

3.3.4.2 Stock solution of 10 ppm H_2O_2

Add 2.5 ml of 1000 ppm H_2O_2 stock solution into 250 ml volumetric flask. It is then diluted using deionized water to form 10 ppm H_2O_2 formulation. The volumetric flask was covered with aluminium foil to avoid degradation due to light.

3.3.5 Preparation of metamifop with H_2O_2

3.3.5.1 5 ppm metamifop with 5 ppm H_2O_2

1.25 ml of 1000 ppm metamifop from stock solution was added into 250 ml volumetric flask covered with aluminium foil. Then, 1.25 ml of 1000 ppm of H_2O_2 from stock solution was added. The solution was diluted with deionized water.

3.3.5.2 5 ppm metamifop with 10 ppm H_2O_2

1.25 ml of 1000 ppm metamifop from stock solution was added into 250 ml volumetric flask covered with aluminium foil. Then, 2.50 ml of 1000 ppm of H_2O_2 from stock solution was added.

3.3.5.3 10 ppm metamifop with 5 ppm H_2O_2

2.50 ml of 1000 ppm metamifop from stock solution was added into 250 ml volumetric flask covered with aluminium foil. Then, 1.25 ml of 1000 ppm of H_2O_2 from stock solution was added. The solution was diluted with deionized water.

3.3.5.4 10 ppm metamifop with 10 ppm H_2O_2

2.50 ml of 1000 ppm metamifop from stock solution was added into 250 ml volumetric flask covered with aluminium foil. Then, 2.50 ml of 1000 ppm of H_2O_2 from stock solution was added. The solution was diluted with deionized water.

3.3.6 Experimental Procedures

Photodegradation of metamifop solution was conducted on samples of metamifop exposed to UV light in the laminar flow chamber for 3 hours continuously. Zn(II) ions was added in the experiment to study the effect of Zn(II) ions in degradation process. All collected samples were analyzed using HPLC to determine the concentration peak level of metamifop in the solution. The photodegradation of the metamifop were also monitored using a UV-Visible spectrometer system. To study the effect of Zn(II) ions, UV-Vis spectrophotometry used to obtain the absorbance of Zn(II) ions in aqueous solutions. The experiment was continued by adding hydrogen peroxide to the wastewater solution.

For the photodegradation system, magnetic plate with a magnetic stirrer was used to stir the sample in each beaker of 250 ml. The photodegradation process was conducted under UV lamp in the laminar flow chamber for 3 hours. The samples were placed in the falcon tube for characterization using a UV-Vis spectrometer. Falcon tubes were covered with aluminium foil to avoid the sample degrade to sunlight of surrounding.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Standard calibration curve for standard metamifop

For HPLC system, the results are explained in the percentage of degradation. The areas under graph were detected at 254 nm with retention time at 3.1 minutes. The corresponding concentration of metamifop standard that have been analyzed using (2 ppm, 4 ppm, 6 ppm, 8 ppm and 10 ppm) was determined based on Figure 4.1.
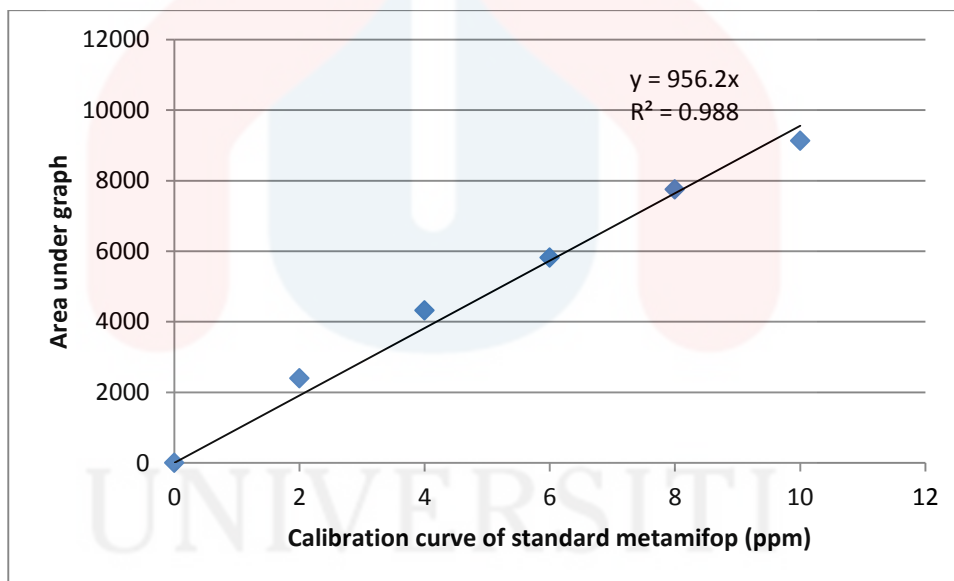

Figure 4.1: The calibration curve for standard metamifop

4.2 Photodegradation of Metamifop

4.2.1 Effect of Initial Concentration of Metamifop

Photodegradation of 5 ppm and 10 ppm of metamifop were studied. The percentage of degradation of 5 ppm and 10 ppm of metamifop were 25.81% and 29.79% over 3 hours irradiation. Based on the experiments conducted, the result has shown that the percentage of degradation slightly increased in 10 ppm of metamifop. This indicated that UV radiation using UV light was able to degrade the sample solutions during photodegradation. The degradation was happened due to the presence of hydroxyl radical. In this experiment, hydroxyl radicals were produced by means of using UV-light which reacts with metamifop. The hydroxyl radical has the strongest effect on the degradation of recalcitrant anthtopogenic pollutants in water and it is the most significant strong oxidant in advanced oxidation processes (Kwon et al., 2009).
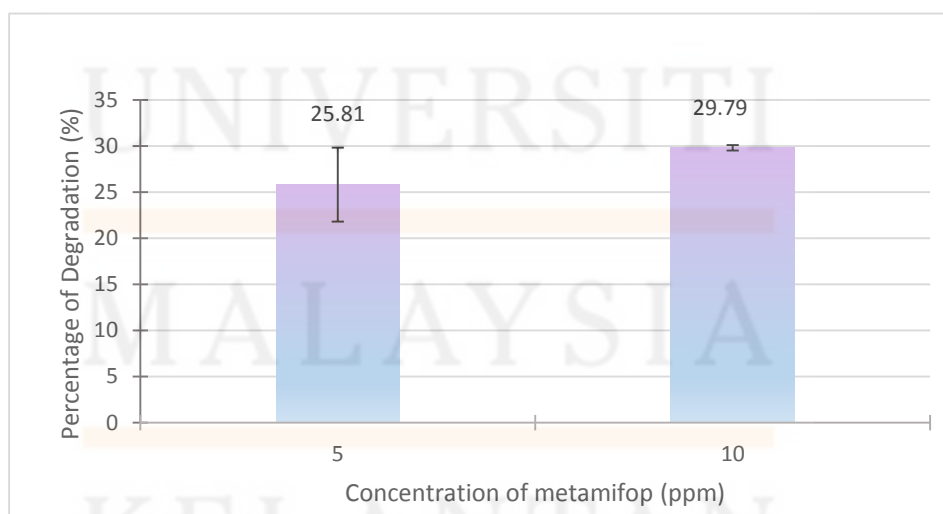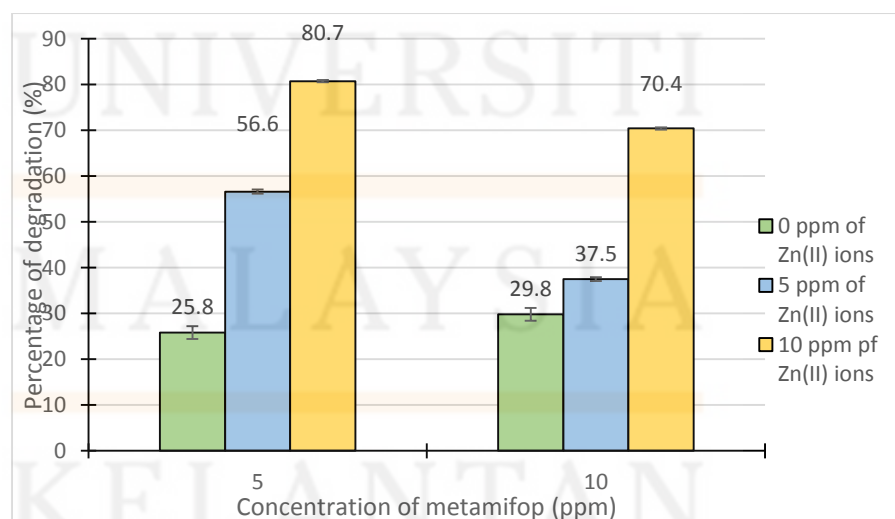

Figure 4.3:   Effect of Zn(II) ions on photodegradation of 5 ppm metamifop. Experimental conditions: [metamifop]$_0$ 5 ppm; [metamifop]$_0$ 10 ppm; solution volume 250 ml; irradiation time 3 hours

4.2.2 Effect of Zn(II) ions on photodegradation of metamifop.

The effects of Zn(II) ions on the photodegradation process of metamifop were studied. The degradation of 5 ppm of metamifop over 3 hours increases from 25.8% to 56.6% in the presence of 5 ppm of Zn(II) ions. Next, the addition of 10 ppm of Zn(II) ions also showed an increment in degradation percentage to 80.7%. By referring to Figure 4.4, similar results were obtained for 10 ppm of metamifop where the percentage of degradation increases in the presence of Zn(II) ions.

The results indicated that the percentage of degradation of metamifop increased as the concentration of Zn(II) ions increased. In addition, it was discovered that the degradation of 5ppm of metamifop was higher compared to 10 ppm of metamifop. The result was significant as more concentrated solutions of Zn(II) ions in metamifop promoted the degradation by UV radiation.

Figure 4.4:   Effect of Zn(II) ions on photodegradation of 5 ppm of metamifop. Experimental conditions: [metamifop]$_0$ 5 ppm; [metamifop]$_0$ 10 ppm; solution volume 250 ml; irradiation time 3 hours

For the reaction, Zn(II) ions needs two electrons to be reduced to zinc atom as shown in equation 4.1. Therefore, the recombination rate of electron and hydroxyl radical were reduced, hence, yielding the higher degradation efficiency (Raihan, 2013). Thus, the findings demonstrated that the presence of Zn(II) ions gave a beneficial effect towards the photodegradation of metamifop.

$$Zn^{2+} + 2e^- \rightarrow Zn \qquad\qquad\qquad (4.1)$$
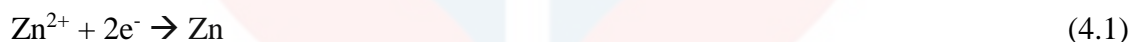
A very few studied were carried on the effect of Zn(II) ions on the photodegradation of herbicide. According to Shifu and Yunzhang (2007), the presences of Zn(II) ions had no apparent effect on the photodegradation of pesticide namely glyphosate. On the contrary, a positive role of Zn(II) ions was observed in this study on the degradation of metamifop.

4.2.3 Effect of hydrogen peroxide on photodegradation of 5 ppm of metamifop in the presence of Zn(II) ions.

In this section, hydrogen peroxide and Zn(II) ions were added in 5 ppm of metamifop. The degradation of 5 ppm of metamifop occur at 31.6% in the presence of 5 ppm of Zn(II) ions and 5 ppm of hydrogen peroxide. It was found that the addition of 10 ppm of hydrogen peroxide significantly increased the degradation of metamifop from 31.6% to 90.4%.

The result has shown that the percentage of degradation of metamifop in the presence of Zn(II) ions decreases when 5 ppm of hydrogen peroxide was present but increased in 10 ppm of hydrogen peroxide. Next, the experiment was repeated using 10 ppm of Zn(II) ions. Likewise, the effect of 10 ppm of Zn(II) ions were correspond to 5 ppm of Zn(II) ions as shown in Figure 4.5:
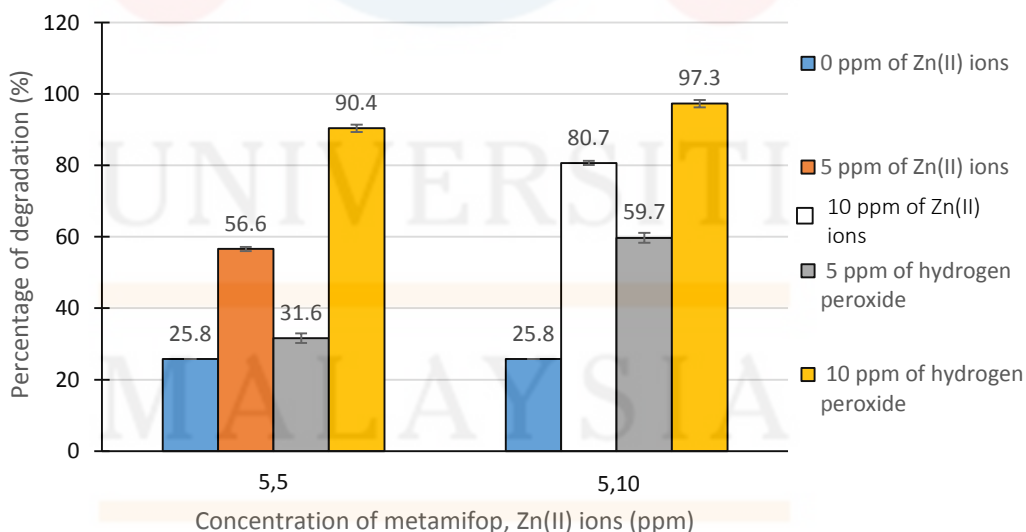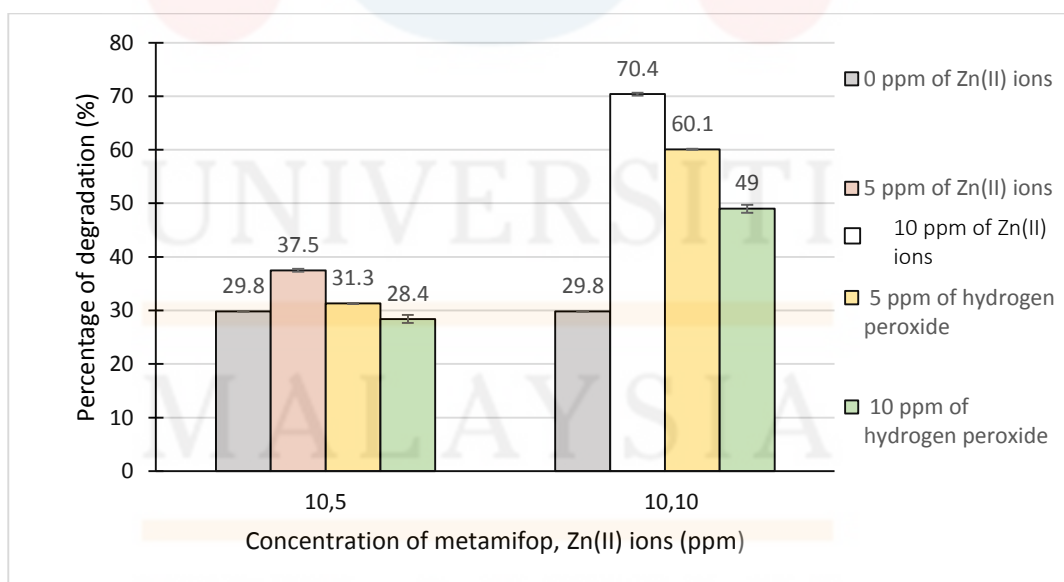

Figure 4.5: Effect of Hydrogen Peroxide and 10 ppm of Zn(II) ions on photodegradation of 5 ppm of metamifop. Experimental conditions: [metamifop]$_0$ 5 ppm; [Zn(II) ions] 5 ppm; [Zn(II) ions] 10 ppm; solution volume 250 ml; irradiation time 3 hours

30

Different concentration of Zn(II) ions and hydrogen peroxide shows different degradation percentage. Referring to the results obtained in part 4.3.3, the result was significant as more concentrated solutions of Zn(II) ions in metamifop promoted the degradation by UV radiation. However, the percentage of degradation of 5 ppm of metamifop in the presence of Zn(II) ions and 5 ppm of hydrogen peroxide were expected to increase too. The highest degradation in UV/H_2O_2 was obtained at 97.3% on 5 ppm of metamifop in the presence of 10 ppm of Zn(II) ions and hydrogen peroxide.

The result proved that less concentrated solutions of metamifop were easier to degrade and more concentrated solutions of Zn(II) ions and hydrogen peroxide in metamifop promoted the degradation by UV radiation. The previous study also showed that the addition of hydrogen peroxide has increased the rates of UV degradation in pesticides namely malathion and diazinon mainly due to the formation of hydroxyl radicals through the photolysis of hydrogen peroxide (Wu *et al*.,2007). In similar, the results obtained from UV-Vis spectrophotometer showed that hydrogen peroxide give an effect towards the photodegradation process of metamifop solution.

4.2.4 Effect of hydrogen peroxide on photodegradation of 10 ppm of metamifop in the presence of Zn(II) ions.

The experiment was repeated by using different concentration of metamifop which was 10 ppm. The effect of hydrogen peroxide in 10 ppm of metamifop in the presence of 5 ppm of Zn(II) ions was observed. The degradation of 10 ppm of metamifop over 3 hours occur at 37.5% in the presence of 5 ppm of Zn(II) ions. However, there was a decrement in percentage degradation of metamifop when 5 ppm of hydrogen peroxide was added, provided percentage from 37.5% to 31.3% after 3 hours irradiation. It was found that the addition of 10 ppm of hydrogen peroxide gradually decreased the degradation of metamifop from 31.3% to 28.4%. Next, the experiment was repeated using 10 ppm of Zn(II) ions. The results also showed a decrement in degradation percentage of 10 ppm of metamifop in the presence of Zn(II) ions and hydrogen peroxide as shown in Figure 4.6:

Figure 4.6: Effect of Hydrogen Peroxide and 10 ppm of Zn(II) ions on photodegradation of 5 ppm of metamifop. Experimental conditions: [metamifop]$_0$ 10 ppm; [Zn(II) ions] 5 ppm; [Zn(II) ions] 10 ppm; solution volume 250 ml; irradiation time 3 hours

For 10 ppm of metamifop, the percentage of degradation of metamifop increased as the concentration of Zn(II) ions increased. The result is significant as more concentrated solutions of Zn(II) ions in metamifop promoted the photodegradation process. Nevertheless, it was discovered that by increasing the concentration of hydrogen peroxide, the percentage of degradation of metamifop decreases. The findings showed that the presence of 5 ppm and 10 ppm of Hydrogen Peroxide retard the photodegradation of 10 ppm of metamifop. This may be explained by the beneficial effects of hydrogen peroxide that degenerates due to its auto-decomposition and termination process (Zhang and Pagilla, 2010; Devipriya and Yesodharan, 2005).

In addition, Linden (Linden at al., 2007) studied the efficacious of UV/H_2O_2 treatment on endocrine-disrupting compunds (EDCs). Direct UV treatment using UV light emitted by a UV lamp is only effective if it is absorbed by the contaminant. Past study had found that the performance of a UV/H_2O_2 process were affected by the reactivity of the target compound towards •OH radical, UV lamp technology itself (high output, low pressure, high output versus medium pressure) and the operational and water quality factors like H_2O_2 dosage, presence of carbonate species, NOM, pH and reduced metal ions (iron and manganese) (Li *et al.*, 2008).

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The effect of hydrogen peroxide and Zn(II) ions towards the photodegradation process of 5 ppm and 10 ppm metamifop have been studied. In this study, HPLC and UV-Vis were used to develop a standard calibration curve and to analyse the absorbance of degraded samples. The highest degradation efficiency was obtained at 97.3% on 5 ppm of metamifop in the presence of 10 ppm of Zn(II) ions and 10 ppm of hydrogen peroxide. The addition of Zn(II) ions and hydrogen peroxide give beneficial effect depending upon the concentration of samples.

5.2 Recommendations

One of the recommendation is to use various combinations of hydrogen peroxide, sonolysis, ultraviolet (UV) radiation, ozone and photocatalytic treatments. This substantial combination is highly capable of oxidizing a wide range of contaminants in water. Next, conventional treatment processes such as chemical precipitation, ion exchange and electrochemical removal can be applied for the removal of heavy metal from inorganic effluent. Advanced further study should be improvised to develop sustainable treatment technologies that can be applied for wastewater treatment.

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APPENDICES

APPENDIX A: CALCULATION FOR STOCK SOLUTION OF METAMIFOP FORMULATION

The calculation for the mass of nominee-M needed and the percentage of metamifop active ingredient in the bottle is:

Mass of Nominee-M needed = 10.5 g

Metamifop active ingredient = 9.5% w/w

The actual value is obtained based on the following calculation formula:

The actual value= 0.095 (active ingredient) x 10.5 g (mass of solution)

$$= 0.9975 \approx 1g$$

1g= 1000 ppm

APPENDIX B: HPLC RESULTS

Table 1: Concentration of standard metamifop

CONCENTRATION (ppm)	Area under graph
2	2401
4	4319
6	5823
8	7751
10	9134

APPENDIX C: UV-VIS RESULTS

1. Results of 5 and 10 ppm of metamifop

Table 1: Absorbance value for 5 ppm and 10 ppm of metamifop

Wavelength (nm)	Concentration of metamifop (ppm)	Absorbance	
		0 hour	3 hour
350	5	0.10	0.069
	10	0.188	0.132

2. Results of 5 and 10 ppm of metamifop in the presence of Zn(ii) ions

Table 2: Absorbance value for 5 ppm and 10 ppm of metamifop in the presence of 5 ppm of Zn(ii) ions

Wavelength (nm)	Concentration of metamifop (ppm)	Concentration of Zn(ii) ions (ppm)	Absorbance	
			0 hour	3 hour
350	5	5	0.083	0.036
	10		0.080	0.050

Table 3: Absorbance value for 5 ppm and 10 ppm of metamifop in the presence of 10 ppm of Zn(ii) ions

Wavelength (nm)	Concentration of metamifop (ppm)	Concentration of Zn(ii) ions (ppm)	Absorbance	
			0 hour	3 hour
350	5	10	0.440	0.085
	10		0.236	0.070

40

3. Results of 5 and 10 ppm of metamifop in the presence of and Hydrogen Peroxide and Zn(ii) ions

Table 4: Absorbance value for 5 ppm and 10 ppm of metamifop in the presence of 5 ppm of Zn(ii) ions and 5 ppm of Hydrogen Peroxide

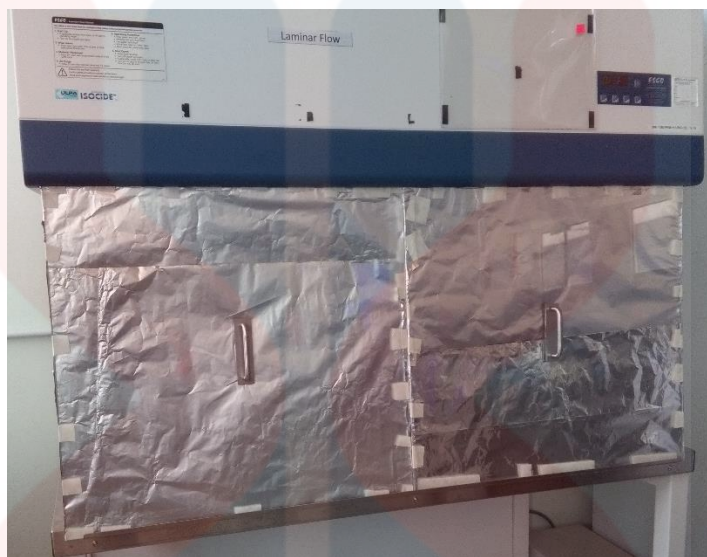| Wavelength (nm)	Concentration of metamifop (ppm)	Concentration of Zn(ii) ions (ppm)	Concentration of Hydrogen Peroxide (ppm)	Absorbance	
				0 hour	3 hour
350	5	5	5	0.098	0.067
	10			0.249	0.171

Table 5: Absorbance value for 5 ppm and 10 ppm of metamifop in the presence of 5 ppm of Zn(ii) ions and 10 ppm of Hydrogen Peroxide

Wavelength (nm)	Concentration of metamifop (ppm)	Concentration of Zn(ii) ions (ppm)	Concentration of Hydrogen Peroxide (ppm)	Absorbance	
				0 hour	3 hour
350	5	5	10	0.114	0.011
	10			0.250	0.179

Table 6: Absorbance value for 5 ppm and 10 ppm of metamifop in the presence of 10 ppm of Zn(ii) ions and 5 ppm of Hydrogen Peroxide

Wavelength (nm)	Concentration of metamifop (ppm)	Concentration of Zn(ii) ions (ppm)	Concentration of Hydrogen Peroxide (ppm)	Absorbance	
				0 hour	3 hour
350	5	10	5	0.119	0.048
	10			0.163	0.065

Table 7: Absorbance value for 5 ppm and 10 ppm of metamifop in the presence of 10 ppm of Zn(ii) ions and 10 ppm of Hydrogen Peroxide

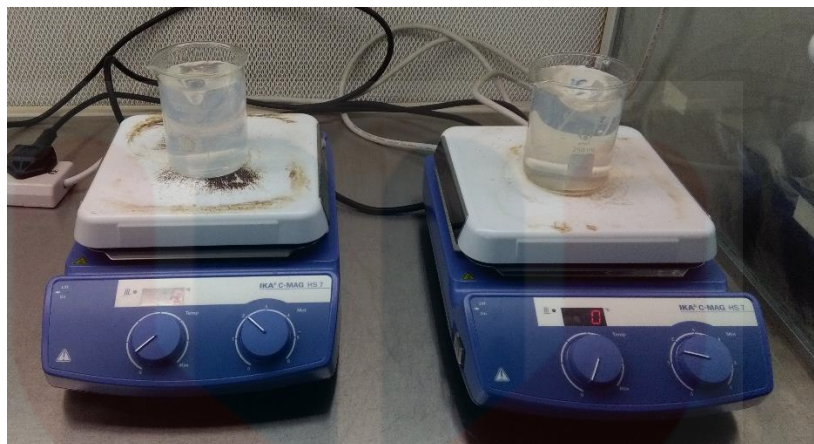| Wavelength (nm)	Concentration of metamifop (ppm)	Concentration of Zn(ii) ions (ppm)	Concentration of Hydrogen Peroxide (ppm)	Absorbance	
				0 hour	3 hour
350	5	10	10	0.150	0.004
	10			0.196	0.100

Figure 1: Laminar flow chamber was covered with aluminium foil

Figure 2: Falcon tubes were covered with aluminium foil to avoid degradation of samples solution to the surroundings.
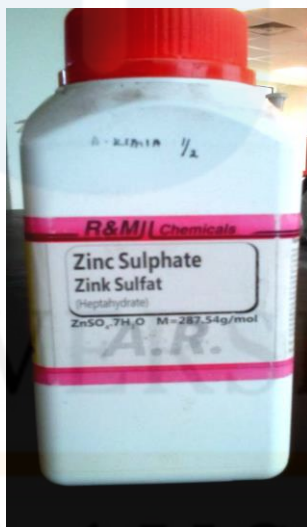
Figure 3: Magnetic plate with magnetic stirrer inside each beaker

Figure 4: Metamifop stock solution were kept in conical flask covered with aluminium foil

Figure 5: Barnstead Smart2Pure water purification system provides deionised water
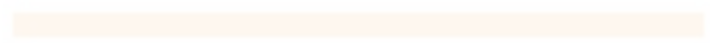

Figure 6: Zinc sulphate salts