



# **EFFECTS OF MIXED METAL IONS ON THE PHOTODEGRADATION OF METAMIFOP**

by

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## DECLARATION

I declare that this thesis entitled “Effects of Mixed Metal Ions on the Photodegradation of Metamifop” 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.

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## LIST OF ABBREVIATIONS

Fe	Iron
Zn	Zinc
Pb	Lead
Ag	Silver
Cu	Copper
As	Arsenic
Cd	Cadmium
Hg	Mercury
Cr	Chromium
ZnSO <sub>4</sub>	Zinc Sulphate
Fe <sub>2</sub> SO <sub>4</sub>	Iron (III) sulfate
•OH	Hydroxyl radical
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	Copper (II) Nitrate Trihydrate
AOP	Advance oxidation process
AOPP	Aryloxyphenoxy propionates
ACCase	Acetyl coenzyme-A carboxylase
AAS	Atomic Absorption Spectrometer
HPLC	High performance liquid chromatography

## Effects of mixed metal ions on the photodegradation of metamifop

### ABSTRACT

Photodegradation is one of develop system that believed to be capable of destroying compound suitable for reducing the concentration of pesticides in the wastewater. The system can be utilized for organic compounds treatment which can lead to complete mineralization under the optimum conditions. However, the heavy metal can influence the photodegradation of organic pollutants in aqueous solution. The purpose of this study is to identify the impact of mixed metal (Fe(II), Cu(II), Zn(II)) ions on the photodegradation of metamifop. Hence, to monitor the degradation efficiency of the system, the residual concentrations of these organic compounds and metal ions were analyzed using high performance liquid chromatography (HPLC) and UV-Visible spectrometer (UV-Vis). The data show that the presence of mixed metal ions on the photodegradation of metamifop is greatly increased the degradation values. It was identified that, photodegradation of 5 ppm of metamifop in the presence of 5 ppm mixed metal ions achieved 71.51% degradation and 10 ppm of mixed metal ions achieved 96.32% degradation respectively. The hydrogen peroxide was also added into metamifop solution in order to identify the effect on the photodegradation of metamifop in the presence of mixed metal ions. The result indicated that the presence 5 ppm of H<sub>2</sub>O<sub>2</sub> was achieved 68.81% degradation and further addition of 10 ppm of H<sub>2</sub>O<sub>2</sub> was drastically dropped to 29.82%. Basically, the presence of mixed metal (Fe(II), Cu(II), Zn(II)) ions on metamifop solution was given a positive feedback in which it help to increase the degradation process of metamifop as expected. However, there is no significant beneficial is observed when hydrogen peroxide is added to metamifop solution.

## Kesan ion logam campuran ke atas fotodegradasi metamifop

### ABSTRAK

Fotodegradasi adalah salah satu sistem yang dipercayai mampu untuk memusnahkan dan mengurangkan kepekatan racun perosak di dalam air kumbahan. Sistem ini boleh digunakan untuk rawatan bahan organik yang boleh membawa kepada mineralisasi lengkap di bawah keadaan optimum. Walaubagaimanapun, kehadiran logam berat mempengaruhi sistem fotodegradasi bahan pencemar organik dalam larutan akueus. Tujuan kajian ini adalah untuk mengenal pasti kesan ion logam campuran (Fe (II), Cu (II), Zn (II)) terhadap proses fotodegradasi metamifop. Kromatografi cecair berprestasi tinggi (HPLC) dan UV-nyata spektrometer (UV-Vis) telah digunakan untuk memantau sistem degradasi dan mengenal pasti kecekapan sistem ini. Data menunjukkan bahawa kehadiran ion logam campuran (Fe(II), Cu(II), and Zn(II)) keatas fotodegradasi ini membantu dalam meningkatkan nilai degradasi metamifop. Ia telah dikenalpasti bahawa 5 ppm metamifop dengan kehadiran 5 ppm ion logam campuran telah mencapai 71.51% degradasi dan 10 ppm ion logam campuran mencapai sehingga 96.32% degradasi. Seterusnya, hidrogen peroksida telah ditambah bertujuan untuk mengenal pasti kesannya ke atas fotodegradasi larutan metamifop. Data menunjukkan apabila 5 ppm  $H_2O_2$  ditambah ke dalam larutan metamifop ia mencapai 68.81% degradasi sahaja. Peratus degradasi menurun secara drastik kepada 29.82% apabila 10 ppm  $H_2O_2$  telah ditambah dalam larutan metamifop. Pada asasnya, kehadiran ion logam campuran (Fe (II), Cu (II), Zn (II)) secara keseluruhannya memberi kesan yang positif dimana ia membantu dalam meningkatkan proses degradasi metamifop. Namun begitu, tiada kesan yang signifikan diperoleh apabila hidrogen peroksida di tambah kepada larutan metamifop.

## CHAPTER 1

### INTRODUCTION

#### 1.0 Background of Study

Nowadays, the application of pesticides in agricultural sector is too common. A pesticide is a modern technology that assists to enhance the quality of yield, to control pest on crop production as well as design to kill specific pests, such as weeds and insects. However, ordinarily a pesticide is not particularly focusing on the pest but also affect non-target plants and animals. The use of pesticides can lead to the loss of biodiversity. Generally, the greater part of the pesticides are not effectively degradable, they are continuously persistence in soil and can leach to surface water and groundwater and also contaminate the wide environment.

Metamifop is one of the pesticides that can be utilized against insects and pests. However, the frequent applications of pesticides such metamifop can cause contaminate the groundwater, water surface and soil. In addition, the pesticides rely upon their chemical properties in which they enter to the organisms and bioaccumulate on the food chains. Basically, heavy metals properties such as iron, copper, and zinc regularly shape a part of the dynamic mixes of pesticides. As indicated by Lenntech (2016) heavy metals refer to any metallic element that has a relatively high density and it is poisonous or toxic even in low concentration. Heavy metals including arsenic (As), lead (Pb), mercury (Hg), zinc (Zn), chromium (Cr), silver (Ag), cadmium (Cd), copper (Cu) iron (Fe), and the platinum bunch components (Duruibeet *al.*, 2007). An overflow of heavy metals in soils often caused

the utilization of chemical substances such as fertilizers. Besides, Industrial activities, sewage sludges, and also metallo-pesticides are the causes of the presence of heavy metal in soils. The concentration of heavy metals in soils can be enhanced by the repeating use of fertilizer and also by excessive fertilizer and pesticide applications (Eugenia *et al.*, 1995). Heavy metal known to be most toxic that could adverse effect to human health and environment itself.

Advanced Oxidation Processes (AOP) or Photocatalytic degradation utilizing UV alongside a suspended  $\text{TiO}_2$  catalyst have the advantage of producing the hydroxyl radicals (Jong,2008). It also believed as one of the promising method for water contamination treatment. AOP is depend on the generation and consequent responses of a powerful oxidizing agent the hydroxyl radical ( $\text{HO}\bullet$ ) and responds quickly with most organic compounds, by hydrogen abstraction or addition to double bonds, initiating a sequence of oxidative degradation reactions which may prompt the complete mineralization of natural contaminations (Neamtu *et al.*,2002).

However the existence of metal particles can impede the annihilation of organic contaminants and the productivity of recuperation of the metal is diminished by the presence of organic pollutant. The diminishment in the proficiency of these method is because formation of complexes between the organic species and the metal ions in solution (Chaudhary, 2009).

## 1.2 Problem statement

Pesticides have played a key role in agricultural sectors in which it help to improve the quality of product in agricultural. Pesticides are developed to provide reasonable function and minimal risk to human health and environment. The usages of pesticides increased the production of heavy metal compound in water and soil.

Generally, polluted wastewater by pesticides can be treated with various treatments such as biodegradation, photo Fenton, filtration and photocatalytic degradation. The presence of heavy metal ions can influences the overall process of photodegradation. However, among these methods especially photocatalytic degradation has the major drawback. The catalyst used in the process need to recover back. Thus, in this study photodegradation process is proposed one of the suitable methods to treat the polluted wastewater.

Basically, heavy metal ions may influence the photodegradation of organic pollutants in aqueous solution. However, the heavy metal may become a catalyst for photodegradation process. Copper compounds may act as catalysts for the photodegradation of various pollutants in irradiated systems (Sykora, 1997). Other previous studies demonstrates that detrimental effect by utilizing of 100 mg/L of Cu(II) and further reduction occurred when the concentration was increased to 500 mg/L due to the copper complexation (Chaudhary *et al.*, 2009). The presence of heavy metal ions can influences the photodegradation of organic pollutants in aqueous solution. For instance, a portion of the metals like iron are known increase the degradation of pesticides and diminish their half-lives (Rafique and Tariq, 2015).

Heavy metals play two roles in the process of degradation of pesticides in soil which it can improve levels of some pesticides in the soil. For example,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  may decrease the dissemination while metals like iron may upgrade their rate of scattering (Rafique *et al.*, 2015).

Advanced Oxidation Process (AOP) method such as photodegradation is believed as an effective method to treat water contamination by pesticide since it can generation of hydroxyl radicals attack to virtually all organic compounds and leading to mineralization of the organic compound. Hence, the objectives of this study is to identify the effect of mixed metal ions on the photodegradation of pesticides namely metamifop.



### 1.3 Objectives

- i) To identify the effect of mixed metal ions ((Fe(II), Cu(II) and Zn(II)) on the photodegradation of metamifop.
  
- ii) To determine the effect of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) on the photodegradation of metamifop.

### 1.4 Significance of study

From this study, the effect of mixed metal ions on the photodegradation of metamifop will be investigated by using two varied concentration consisting of 5 ppm and 10 ppm of mixed metal ions. It was expected that in the presence of mixed metal ions ((Fe(II), Cu(II) and Zn(II)) will increased the photodegradation of metamifop after 3 hours irradiation. Besides, the addition 5 ppm and 10 ppm of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as a catalyst was also expected to increase the photodegradation of metamifop.



## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Pesticide Pollution

Scientists, politicians, legislators, enforcers and the public freely define pollution as too high convergence of any chemical in environment which it has an antagonistic impact, straightforwardly or in a roundabout way, on life or on quality of life (Javaid, 2006). Pollution additionally refers to be anything that influences the hydrosphere, lithosphere and atmosphere while the pollutants are allude to the materials that influence the worldwide environment with an adverse impact on the biosphere. They might be synthetic in nature however results could likewise be destructive of environment that leading to global warming (Javaid, 2006).

Basically, industrial activities and agricultural activities is fundamentally the major of anthropogenic sources that identified to be causes of excessive amounts of chemical element that can possibly harmful in water, soil or the atmosphere. For instance, refining process, electroplating, purifying, metal mining, power generation, manufacturing, combustion process and the utilization of fertilizers and pesticides lead to the increasing of the presence of chemical compound on the environment. Globally, an alarming level of pesticides has been accounted for in air water and soil. Some of these pesticides have been accounted for to be toxic, persistent, carcinogenic and mutagenic (Yusoff, 2013).

Nowadays, an agricultural activity is growing by day to day as well as the production and the consumption of food in which leads to the increasing usage of fertilizer and pesticides. A pesticide is well known to provide benefit such as controlling and destroying unwanted insect and improving the quality of the yields. However, the extravagant usage of pesticides in agriculture sector can cause impact such contamination of groundwater and surface water resources.

A pesticide is basically a source that contains phenols and phenolic compounds. Phenol and its subsidiaries are another group of natural toxins in pesticides which is one of the dangerous pollutants because it can be destructive to life forms at low concentrations and potentially to harmful human health. Pesticides from this compound can be further grouped into phenoxyacetic, phenoxybutyric, phenoxypropionic and the latest aryloxyphenoxypropionic (Barlow, 2007). Human utilization contaminated water that contains phenol compounds can result serious pain that prompting to the capillaries which at last causing demise (Javaid, 2006).

Pesticides for the most part cause unintended ecological impacts since they are not completely particular target on organisms. Organisms can be exposed to pesticides through many paths such as ingestion of water and food, respiratory, and skin contact. The chemical that crosses the different boundaries of the body reaches the metabolizing tissue or storage (Hayo, 1996). In recent years, the presence of these pesticides in water and food show a great concern about the possible adverse effect towards human health and also the environment (Burrows *et al.*, 2002).

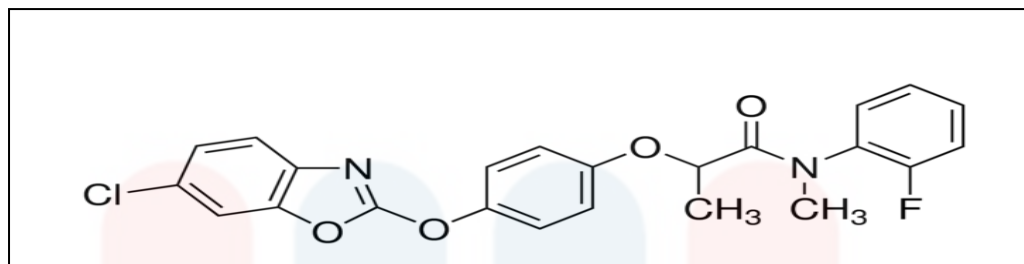
## 2.2 Introduction of pesticides: metamifop

According to Janaki (2014), metamifop is a new generation synthetic herbicide belonging to aryloxyphenoxy propionic acid group. Metamifop widely used to manage annual and perennial grass in cereal crops and rice. It is a post emergent aryloxyphenoxypropionic acid herbicide (AOPP) that is normally used to kill weeds after they have sprouted. Metamifop is a moderately new herbicide created in Korea and is generally used to control weeds in numerous spots, for example, timberland parks and gardens golf courses (Moon *et al.*, 2010).

Metamifop (Oxyphenoxy Acid Esters) was recently introduced from aryloxyphenoxy propionate which is a phenol. Metamifop is the active ingredient that 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 and killing plants. The chemical properties of metamifop is described in the Table 2.1

**Table 2.1:** The chemical properties of metamifop

Empirical Formula	$C_{23}H_{18}ClFN_2O_4$
Molecular Weight	440.8514
Density	1.364 g/cm <sup>3</sup>
Flash Point	310.373 °C
Enthalpy of Vaporization	87.986 kJ/mol
Boiling Point	589.59 °C at 760mmHg



**Figure 2.1:** Structural formula of metamifop

### 2.3 Advanced Oxidative Processed (AOP) – Photodegradation

In recent years, photocatalytic oxidative degradation processes (AOP) have been studied for the purposed of treatment contaminated wastewaters with biocidal or non-biodegradable organic compounds (Braun& Oliveros, 1996). Glaze.,*et al* (1987) defined AOPs as “near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radicals in sufficient quantity to effect water purification. AOPs can frequently accomplish oxidative decimation of compounds refractory to conventional ozonation or H<sub>2</sub>O<sub>2</sub> oxidation. AOPs are suited for wrecking broke down organic contaminants, for example, halogenated hydrocarbons (trichloroethane, trichloroethylene), aromatic compound (benzene, toluene, ethylbenzene, xylene – BTEX), pentachlorophenol (PCP), detergents, nitrophenols, pesticides and can likewise be utilized to oxidize inorganic contaminants, for example, cyanide, sulfide, and nitrite AOPs are to be imperative devices for environmental innovation and they should be put on more solid investigative and designing premise.

The hydroxyl radical (OH) that produced in AOPs is an effective, non-particular which acts quickly with most organic compound. These technique depend on the creation and consequent responses of an intense oxidizing specialist the hydroxyl

radical ( $\bullet\text{OH}$ ). This species responds quickly with most natural mixes, by hydrogen deliberation or expansion to double bonds, starting a grouping of oxidative debasement responses which may prompt the complete mineralization of organic pollutants (Braun & Oliveros, 1996). Albeit numerous techniques have been utilized to expel organic contaminants from the waste water material, advance oxidation processes such as photodegradation are believed as the best technique that that can be used (Fernandez *et al.*, 2013).

Photodegradation is one of AOPs method that useful process in wastewater treatment because it can be used to kill or eliminate the chemical substances in wastewater. Generally, photodegradation included the breakdown of molecules then convert the molecules into smaller pieces by photon. Active species such as superoxide radicals ( $\text{O}_2\bullet$ ), hydroxyl radicals ( $\bullet\text{OH}$ ), and electrons involved in the photodegradation process. According to Katagi (2004) photodegradation is an abiotic process in the scattering of pesticides where atomic excitation by assimilation of light vitality results in different organic responses or receptive oxygen species such  $\text{OH}^-$  which particularly or non-particularly oxidizes the functional groups in a pesticide particle. The  $\bullet\text{OH}$  is a strong oxidant to assault the state with high electron density. It can be created in various ways. Among these, surface hydroxyl groups are the imperative sources for generation.

It is surely understood that the hydroxyl group of some metal oxides are at the origin of the acidic or fundamental properties of these solid (Li *et al.*, 2012).The diminishing amount of the surface hydroxyl groups lessened the generation of  $\bullet\text{OH}$  and after that affected the photocatalytic activities (Li *et al.*, 2012).

## 2.4 Mixed Metal Ions (Iron, Copper and Zinc)

In this study, effect of the presence of mixed metal ions in photodegradation of metamifop is investigated. The mixed metal ions that will be utilized as a part of this study comprise of iron, copper and zinc. Fundamentally, the heavy metal can be transmitted into the earth through both natural and anthropogenic causes. Industrial activities and agricultural sectors likewise contribute the expanding of heavy metal on nature. Heavy metals are essential in numerous regards to man, particularly in manufacturing of certain important products of human use, however it known to be toxic to most organisms when present in excessive concentrations.

In term of photodegradation, heavy metal occur on environment like a cocktail in which it consist a variety types of metal ion such cadmium, copper, zinc, iron, and lead and all the metal ions is mixed together on the environment. Generally, the presence of heavy metal may be able to enhance the photodegradation process or it may cause negative effect on the process of photodegradation such as retarding the process of photodegradation. Rafique and Tariq (2015) reported that  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  decreasing the dissipation of deltamethrin and cypermethrin while some other metals like iron may improve the rate of dissipation.

Besides, Liu *et al* (2007) also reported that the existence of  $\text{Cu}^{2+}$  in the soil may restrain the degradation of a-cypermethrin that might be as the reduction inactivity of bacterial biomass due to  $\text{Cu}^{2+}$ . Nevertheless,  $\text{Cu}^{2+}$  particles strongly inhibited the degradation process of ethylenethiourea (ETU) which is a vital degradation product of ethylenebisdithiocarbamate fungicides while 2,4-D-corrupction by *Variovorax* was very quickened by  $\text{Cu}^{2+}$  particles (Rafique and Tariq, 2015).



However, a portion of the metals like iron are known increase the degradation of pesticides and decrease their half-lives. Iron is one of the major components present in the soil for formation of hydroxides, oxides, chlorides that known to accelerate the photolysis of pesticides through the photosensitizing effect. Iron can play a dual role in which it can accelerate the photodegradation process by producing the HO radical or retard the photodegradation process.

A previous study shows that the presence of iron on the photodegradation of a-cypermethrin in soil was more efficient when soil iron levels were improved. The degradation is up to around 94% to 96% of initial concentration after 4 days of nonstop UV radiation within the sight of  $\text{Fe}^{2+}$  (Rafique *et al.*, 2016). Besides, the expansion of  $\text{Zn}^{2+}$  decreased the photodegradation of a-cypermethrin however the inhibitory effect was less extreme than  $\text{Cu}^{2+}$  (Rafique and Tariq, 2015). Hence, the mixed metal ions that will be used in this study is Zn (II) ions from  $\text{ZnSO}_4$ , Cu (II) ions from  $(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and Fe (II) ions from  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . Basically, it is important to investigate the effect of mixed metal ions on the photodegradation of metamifop to identify whether the process of photodegradation will be enhanced or the process will be retard.

### 2.4.1 Iron, Fe

Iron is accepted to be the tenth most bottomless component in the universe and it exists generally in the fresh water, soil, sea and air. Iron is malleable, ductile, lustrous, silver-gray metal. Iron is known to exist in four particular crystalline structures. Iron is chemically active and forms two major series of chemical compounds, the ferrous, bivalent iron (II), mixes and the trivalent iron (III), or ferric mixes. It assumes a vital part in environmental and biochemical frameworks (Changbo, 2009). It happens in oxidation numbers from  $-II$  to  $+VI$  with coordination quantities of 3 to 8 (Hawker and Twigg, 1994).

In fluid arrangement the most plenteous iron species have an oxidation number of  $+II$  (ferrous iron) and  $+III$  (ferric iron) (Changbo, 2009). Fe (II) has the capacity for photosensitizing so it can help the photodissipation of various halogenated herbicides and pesticides (Rafique *et al.*, 2015). Iron may bring choroiditis, retinitis and conjunctivitis if it contacts and stays in the tissues. Constant inward breath of over the top convergences of iron oxide fumes or dusts may cause a benign pneumoconiosis, called siderosis which is detectable as x-ray change.

Besides, the existence of iron, for example, Iron (III)- O-arsenite, pentahydrate in the environment is dangerous to the environment. A major attention ought to be given to plants, air and water. It is emphatically prompted not to give the chemicals substances a chance to enter the environment since it is persistence in the environment.



## 2.4.2 Copper, Cu

Copper is a ruddy metal that occurs naturally in rock, soil, water, residue, and at low levels air. Copper additionally occurs naturally in all plants and creatures. Copper is a transition metal, one of a few components found in rows 4 through 7 between Groups 2 and 13 in the periodic table and reddish-brown tint as being copper colored. Copper metal is genuinely delicate and flexible. Both electricity and heat pass through copper easily. The high electrical conductivity makes it perfect for some electrical purposes. Copper boiling point of 2,595°C (4,703°F) and the melting point is 1,083°C (1,982°F). The density of copper is 8.96 grams for each cubic centimeter.

The electroplating industry and metallurgy industry expanded the presence of copper. It is likewise found in numerous blends of metals, called composites, for example, metal and bronze. Copper comprise 29 electrons and when it loses 2 electrons ( $\text{Cu}^{2+}$ ), it can make edifices with other approaching ligands. Copper can likewise enter the nature through local waste water, waste dumps, combustion of fossil fuels and wood creation production, phosphate manure production copper is crucial for good health.

However, exposure of higher measurements of copper can give an adverse consequence. A long-term exposure to copper dust can irritate the mouth, eyes, and nose and cause nausea, diarrhea, headaches and dizziness.

### 2.4.3 Zinc, Zn

Zinc is parts of heavy metal ions that can occur naturally. Zinc is a lustrous, blue-white metal that burns in air with a bluish-green flame. Zinc can be found in group IIb of the periodic table and it has a solid inclination to respond with acidic, soluble, and inorganic mixes. It is crystalline and brittle at ordinary temperatures, however it gets to be bendable and pliant when warmed somewhere around 110°C and 150°C.

Zinc is naturally occurring component found in the earth surface rocks because of its reactivity, zinc metal is not found as the free component in nature. There are around 55 mineralized types of zinc. The most imperative zinc minerals on the planet are sphalerite, smithsonite and hemimorphite. Zinc has two basic oxidation states, Zn (0) and Zn(+2). Zinc is forms a variety of different compounds for example zinc chloride, zinc oxide, and zinc sulfate.

Basically, zinc regularly utilized as a part of material and canals in building development and vehicles industry. In animals and human, zinc is a key supplement that assumes a part in layer soundness, in more than 300 compounds, and in the digestion system of proteins and nucleic acids (WHO, 2001).

## 2.5 Hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>

Hydrogen peroxide photolyzes cleanly to deliver hydroxyl radicals who then respond with numerous organic compounds to create low-atomic weight oxygenated substances that are effortlessly biodegradable in the oceanic environment. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) fundamentally promising an advantage to the photodegradation process.

Previous studies have asserted that hydrogen peroxide can significantly enhance the underlying response rates of photocatalysis of an assortment of organic compounds. The expansion H<sub>2</sub>O<sub>2</sub> to a reaction solution has the impact of expanding the degradation rate. An important step in the formation of a radical species is the cleavage of H<sub>2</sub>O<sub>2</sub> within the sight of UV-light. The expansion of H<sub>2</sub>O<sub>2</sub> expands the rate of radical formation (both hydroxyl (•OH) and hydroperoxyl (HO<sub>2</sub>•) radicals) which can degrade the pesticides (Chaundry *et al.*, 2005).

A past study demonstrate that the attacks by the OH radical, within the sight of oxygen, initiates a complex cascade of oxidative reactions lead to mineralization of the organic compound and the rate of destruction of a contaminant is around corresponding to the rate consistent for the contaminant with OH radical (Munter, 2001). Hydrogen peroxide is a generally economical and readily available chemical oxidant. It is created by electrolysis of ammonium bisulphate or by oxidation of alkyl hydroanthraquinones.

## CHAPTER 3

### MATERIALS AND METHOD

#### 3.1 Chemical and reagent

Metamifop is an active ingredient of formulation pesticides of nominee-M. High Performance Liquid Chromatography (HPLC) were used in order to analyze the standard of metamifop that obtained from Sigma Aldrich while Ultraviolet-Visible spectrometer were used to identify the percentage degradation. The mixed metal ions were used in this studies is Zn(II) ions from ZnSO<sub>4</sub>, Cu(II) ions from (NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and Fe(II) ions from FeCl<sub>3</sub>·6H<sub>2</sub>O.

#### 3.2 Characterization

##### 3.2.1 High Performance Liquid Chromatography (HPLC)

In this study, High Performance Liquid Chromatography (HPLC) were used to identify the parent peak of standard metamifop. The standard retention time was determined by injecting the analytical standard of metamifop. The HPLC system was Shimadzu SIL-20AC HT Auto sampler equipped with a sample cooler with a built-in dehumidifier to minimize condensation problems was used to monitor the changes of the metamifop degradation in this study. The eluent used is an acetonitrile and deionized water as the eluent ratio was 70% acetonitrile and 30% deionized water. Type of column used was Eclipse Plus C18 while the detector used were D2 (deuterium) and W (tungsten). Table 3.1 shows the operating condition of HPLC.

**Table 3.1:** Operating conditions of HPLC

Parameters	Conditions
Column	L = 75mm, Eclipse Plus C18 3.5 $\mu$ l
Flow	1.4 ml/min
Eluent	75% Acetonitrile, 25% water
Detector	UV-235 nm
Injection Volume	10 $\mu$ l
Pump	Seal wash pump

### 3.3.2 Analysis of metamifop

The analytical method used for the determination of metamifop was adopted 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.

### 3.2.3 Ultraviolet-Visible spectrometer, UV-Vis (HACH DR 5000)

A UV-Visible spectrometer is normally used to measure the absorbance of a chemical solution. UV-Vis spectrometer model HACH DR 5000 as shown in Figure 3.1 can characterize almost all chemical parameters such as zinc. UV-Vis spectrometer means that the absorption spectrometer or reflectance spectrometer in the ultraviolet-visible spectral region. It used light in the visible and adjacent (near-UV and near-infrared [NIR]) ranges. The standard cell holder used was a quartz cuvette with 1x1 cm size. To get the accurate reading, make sure wearing gloves to hold cuvette to avoid the cuvette dirty or fingerprint. For the characterization, UV-

Vis was used to monitoring the peak level of metamifop in the sample. The blank used to neutralize the concentration to zero was distilled water.



**Figure 3.1:** Ultraviolet-Visible spectrometer, UV-Vis (HACH DR 5000)

### 3.3 Laminar Flow Chamber

This experiment set-up consists of laminar flow chamber shown in with ultraviolet lamp. The UV lamp was warmed up for about 15 minutes prior to use in conducted experiment it will wrap with aluminium foil to avoid dissipation of UV light as the lamp produces dangerous ultraviolet radiations which are harmful to eyes and skin. Table 3.2 shows operating condition of UV lamp.

**Table 3.2:** Operating condition of UV lamp

Parameter	Condition
Source lamp	Gas-filled Tungsten (visible) and Deuterium (UV)
Wavelength range	190-1100 nm
Duration	3 hours





**Figure 3.2:** Laminar Flow chamber fully covered by aluminium foil

### 3.4 Experimental Procedures

A photodegradation system was set-up by preparing the stock solution of all samples. Photodegradation of metamifop solution were conducted by exposed different concentration of metamifop to UV light in the laminar flow chamber for 3 hours continuously. Then, different concentrations of mixed metal ions were added into the metamifop solution and exposed to UV light in the laminar flow chamber for 3 hours. The entire laminar flow chamber was covered in aluminium foil to concentrate the UV irradiation for treatment purpose. The UV lamp was turned on for 15 minutes for warm up before starting the experiment. Hydrogen peroxide were added into metamifop and mixed metal ions solution to identify the effect of hydrogen peroxide ( $H_2O_2$ ) on the photodegradation of the metamifop in the presence of mixed metal ions. The solution was allowed for treatment for 3 hours continuously under UV irradiation. The samples were analyzed using UV-Vis.



**Figure 3.3:** Magnetic plate with magnetic stirrer inside each beaker

#### **3.4.1 Effect of mixed metal ions**

All experiments were carried out under the same experimental conditions as described in section 3.4. The experimental conditions to identify the imprint of mixed metal ions on the photodegradation of metamifop. The mixed metal ions is made up by a mixture of Fe(II), Cu(II) and Zn(II) .The concentration of mixed metal used is 5 ppm and 10 ppm of each metal ions . Table 3.3 show the conducted experiment for metamifop in the presence of mixed metal ions at metal ions concentration of 5 ppm and 10 ppm. In total there are 18 experiments were conducted.



**Table 3.3:** Experiment for metamifop in the presence of mixed metal ions at different concentration 5 ppm and 10 ppm.

Pesticides		Concentration of mixed metal ions	
Metamifop		Fe(II),Cu(II),Zn(II)	
5ppm	10ppm	5 ppm	10 ppm
√			
	√		
√		√	
√			√
	√		√
	√	√	

### 3.4.2 Effect of H<sub>2</sub>O<sub>2</sub> on the photodegradation of metamifop

Since H<sub>2</sub>O<sub>2</sub> is believed to give a beneficial effect to the photodegradation process then experiments was conducted to identify the effect of hydrogen peroxide on the photodegradation of metamifop. 5 ppm and 10 ppm of H<sub>2</sub>O<sub>2</sub> were added into 5ppm and 10 ppm of metamifop solution to identify the effect of H<sub>2</sub>O<sub>2</sub> on the photodegradation process.

### 3.4.3 Effect of H<sub>2</sub>O<sub>2</sub> on the photodegradation of metamifop in the presence of mixed metal

This study also extended by adding mixed metal ions into the metamifop solution together with H<sub>2</sub>O<sub>2</sub>. The concentration of mixed metal ions was added is 5 ppm and 10 ppm while the concentration of H<sub>2</sub>O<sub>2</sub> is 5 ppm and 10 ppm. The purpose of adding mixed metal ions is to investigate the effect of H<sub>2</sub>O<sub>2</sub> on the existence of mixed metal ions on the photodegradation of metamifop. Table 3.4 shows the conducted experiment for metamifop in the presence of mixed metal ions with the addition of hydrogen peroxide.

**Table 3.4:** Experiment for metamifop in the presence of mixed metal ions and hydrogen peroxide at concentration 5 ppm and 10 ppm.

Pesticides		Concentration of mixed metal ions		Concentration of Hydrogen peroxide	
Metamifop		Fe(II),Cu(II),Zn(II)		H <sub>2</sub> O <sub>2</sub>	
5ppm	10ppm	5 ppm	10 ppm	5 ppm	10 ppm
√				√	
√					√
	√			√	
	√				√
√		√		√	
√		√			√
√			√		√
√			√	√	
	√	√			√
	√	√			√
	√		√	√	
	√		√		√

### 3.4.4 Preparation of stock solution

#### 3.4.4.1 Stock solution of metamifop formulation

In order to make calculation the mass of nominee-M was determined and the percentage of metamifop active ingredient in was obtained.

Mass of nominee-M needed = 10.5 g

Metamifop active ingredient = 9.5% w/w

The actual value was obtained based on the following calculation formula.

The actual value = 0.095 (active ingredient) x 10.5 g (mass of solution)  
= 0.9975 = 1g

1 g = 1000 ppm

10.5g of Nominee-M formulation will be dissolving in 1L of deionized water to prepare 1000 ppm of stock solution. Aluminium foil is used to prevent the interference of light of the stock solution and keep in a 1000 ml volumetric flask. The stock solution of metamifop was then stored in refrigerator at 4 °C.

### 3.4.5 Preparation of mixed metal ions solution

#### 3.4.5.1 Stock solution of 1000 ppm of Cu (II) ions

3.805g of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  salt was dissolved in 1 L deionized water in order to have 1 L of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  stock solution containing 1000 ppm of Cu(II) ions. In order to preserve the content of Cu (II) ions, 10 ml of 25% nitric acid was added. The stock solution was kept in a 1000 ml volumetric flask covered in aluminium foil to avoid the interference of light from the surrounding. It was then placed in the refrigerator at 4 °C.

#### **3.4.5.2 Stock solution of 1000 ppm of Fe(II) ions**

The 1000 ppm of Fe (II) ions solution was prepared by dissolving 4.8400 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 200ml of deionized water and then dilute to 1 liter in volumetric flask with deionized water. The stock solution was kept in volumetric flask and covered in aluminium foil to prevent interference of light. It was then placed in the refrigerator at 4°C.

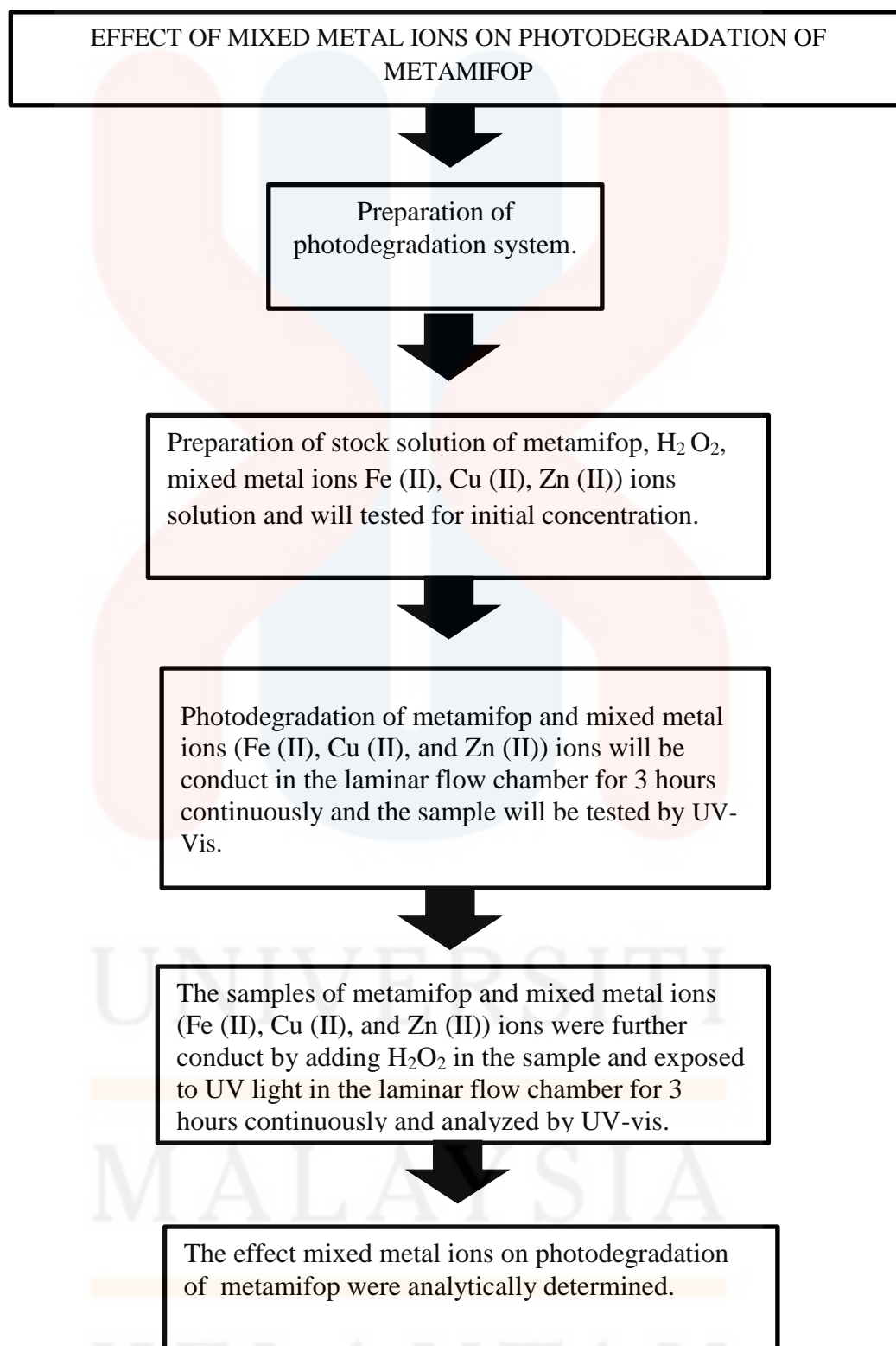
#### **3.4.5.3 Stock solution of 1000 ppm of Zn(II) ions**

The 1000 ppm of Zn(II) ions solution was prepared by dissolving 4.67 g of  $\text{ZnSO}_4$  salt in 1L of deionized water. The stock solution was kept in a 1000 ml volumetric flask covered with aluminium foil to avoid the solution degradation to light surrounding. The solution was then placed in the refrigerator at 4°C.

#### **3.4.6 Preparation of stock solution of 1000 pm of $\text{H}_2\text{O}_2$**

A 1000 ppm of stock solution was prepared by dissolving 3.33 ml in 1L of deionized water. Aluminium foil will be used to prevent the interference of light of the stock solution and keep in a 1000 ml volumetric flask. The stock solution of hydrogen peroxide was then placed in refrigerator at 4°C

### 3.5 Experiment flow chart



**Figure 3.4:** Flowchart of the experiment

## CHAPTER 4

### RESULTS AND DISCUSSION

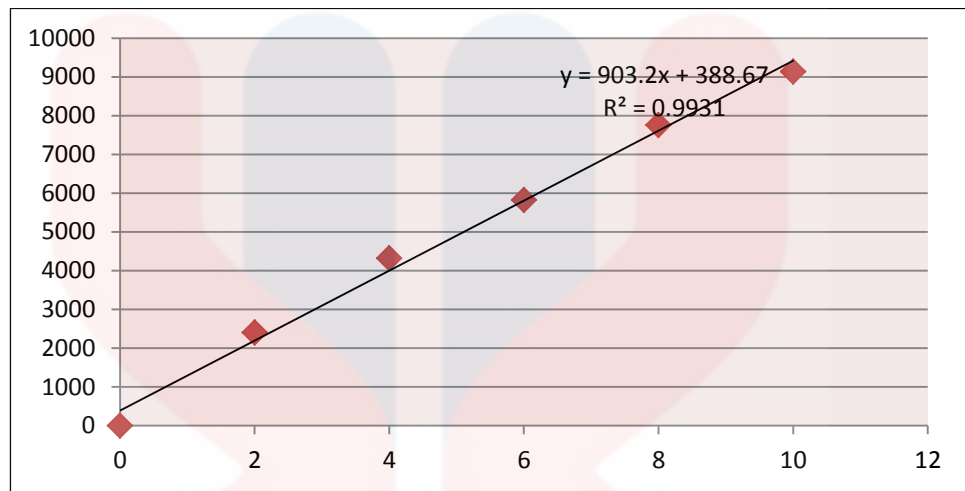
#### 4.1 Introduction

In this section, photodegradation of metamifop is discussed in terms of percentage of degradation (%). The analytical interpretations were carried out by using High Performance Liquid Chromatography (HPLC) and UV-Vis Spectroscopy (UV-Vis). High Performance Liquid Chromatography (HPLC) is used to determine the parent peak of the standard metamifop while the UV-Vis Spectroscopy (UV-Vis) is used to determine the percentage of degradation of metamifop. The wavelength of UV-Vis Spectroscopy (UV-Vis) used is about 350 nm.

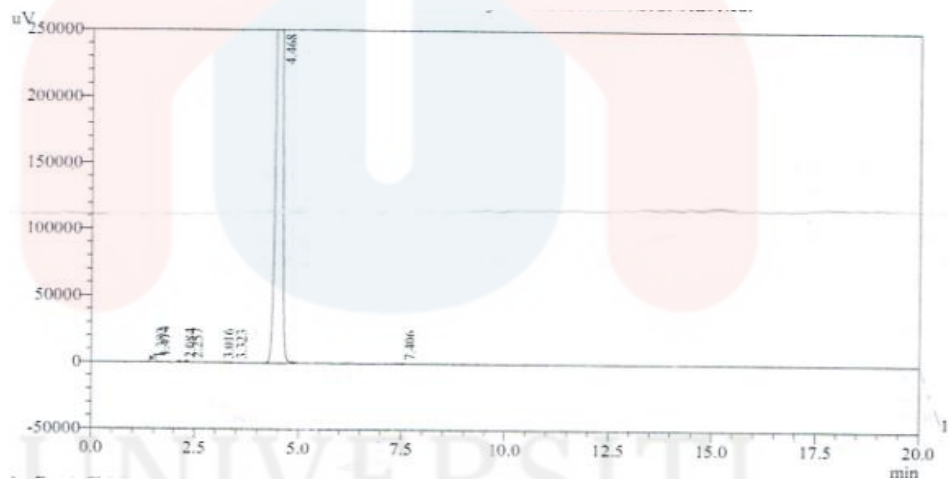
#### 4.2 Standard calibration curve for standard metamifop

For HPLC system, the results are explained in the percentage of degradation. The areas under graph were detected at 350 nm with retention time at 3.1 minutes. The corresponding concentrations of metamifop standard that have been analyzed using (2 ppm, 4 ppm, 6 ppm, 8 ppm and 10 ppm) were determined based on Figure 4.1. From the analysis of the metamifop standard solution, the results obtained from this experiment is quite different compared to the data sheet chromatogram provided by Sigma Aldrich in figure 4.2. Basically, the retention time obtained from Sigma Aldrich (Figure 4.2) was 4.4 minutes however; the retention time that acquired from this experiment was 3.1 minute. This difference of the retention time is could be due

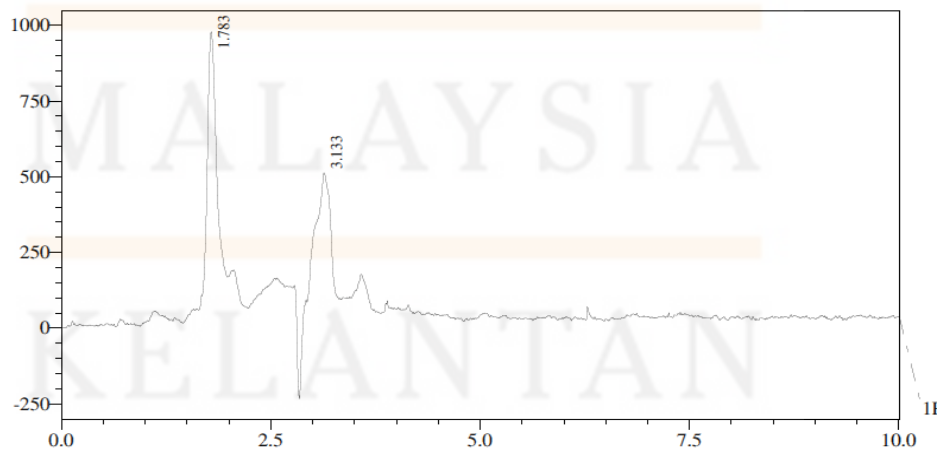
to the different type of column used. The Figure 4.3 showed the chromatogram of 10 ppm metamifop standard solution.



**Figure 4.1:** Calibration curve of standard metamifop



**Figure 4.2:** Chromatogram of metamifop standard obtained from Sigma Aldrich

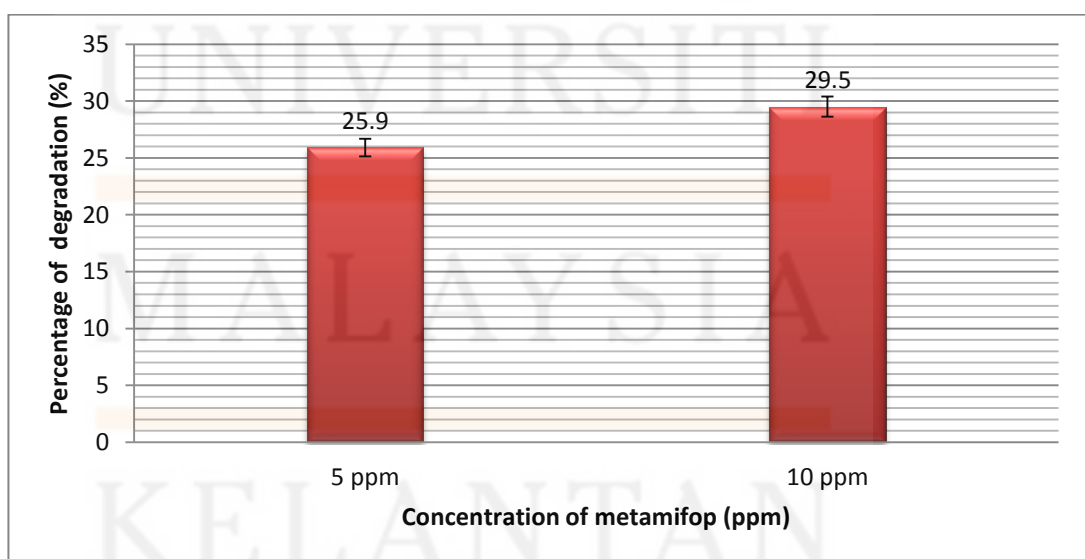


**Figure 4.3:** Chromatogram of 10 ppm metamifop standard solution.

### 4.3 Photodegradation of metamifop

#### 4.3.1 Effect of initial concentration on photodegradation of metamifop.

In this study, different concentrations of metamifop were used in order to identify the effect of the mixed metal ions on the photodegradation of metamifop. The concentration of metamifop used in this experiment is 5 ppm and 10 ppm. Basically, the effects of initial concentration on photodegradation metamifop were obtained from 3 hours irradiation under the photodegradation system. The result in Figure 4.4 showed the effect of initial concentration of the photodegradation of metamifop. It indicated that the percentage of photodegradation of 5 ppm metamifop is slightly lower than 10 ppm of metamifop in which the value of percentage degradation of 5 ppm is 25.9 % and 29.5% for 10 ppm of metamifop. The results obtained indicate that the higher the concentration of metamifop the higher the degradation percentages were obtained. The photodegradation of 5 ppm and 10 ppm metamifop were increased is believed due to the exposure of ultraviolet (UV) light.



**Figure 4.4:** Effect of photodegradation of metamifop. Experimental conditions: [metamifop]<sub>0</sub> 5ppm and 10ppm; volume 250 ml; irradiation time 3 h.



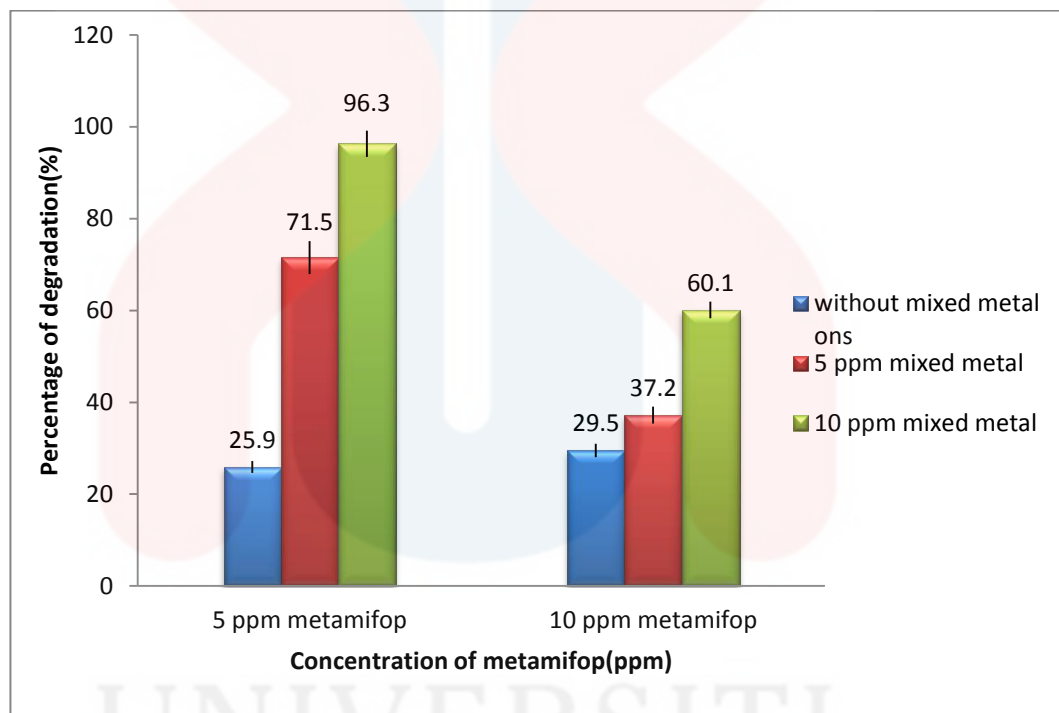
According to the previous study conducted by Yousif & Haddad (2013), they reported that the exposure to UV light causes a degradation of many materials and UV radiation will causes a photo oxidative degradation in which results the breaking of the polymer chains, production of OH radicals and reduces the molecular weight, causing deterioration of mechanical properties and leading to useless materials after an unpredictable time. Hence, the exposure of UV radiation on metamifop solution in this experiment is believed enhanced the degradation.

#### **4.3.2 Effect of mixed metal ion on the photodegradation of metamifop**

The effect of mixed metal ions on photodegradation of metamifop conducted by added 5 ppm of each metal ions (Fe(II), Cu(II) and Zn(II)) to the 5 ppm and 10 ppm of metamifop, separately followed by further addition of 10 ppm of mixed metal ions. The result in Figure 4.5 showed that the addition of 5 ppm of mixed metal ions (Fe(II), Cu(II) and Zn(II)) on the 5 ppm metamifop were drastically increased the percentage of degradation from 25.9% to 71.5%. In order to identify the effectiveness of mixed metal ions on the photodegradation of metamifop, further addition of 10 ppm of mixed metal were tested. The result demonstrated that the presence of 10 ppm of mixed metal ions on the 5 ppm of metamifop drastically rise to 96.32%.

Nevertheless, the addition of 5 ppm of mixed metal ions to the 10 ppm of metamifop was also investigated. The result indicates that the addition of 5 ppm mixed metal ions in the 10 ppm metamifop solution were help to increase the percentage degradation from 29.5% to 37.2%. Besides, the result showed the

increment of the degradation value increased from 29.5% to 60.5% when 10 ppm of mixed metal ions were added into the metamifop solution. Basically, both of 5 ppm mixed metal ions and 10 ppm of mixed metal ions were increased the photodegradation of metamifop, however, increment in degradation value for 10 ppm metamifop is lower compared to 5 ppm metamifop this is probably due to the higher concentration of metamifop in the solution.



**Figure 4.5:** Effect of mixed metal ions in photodegradation of metamifop. Experimental conditions: [metamifop]<sub>0</sub> 5 ppm 10 ppm; mixed metal ions concentration = [Fe(II)] = [Cu(II)] = [Zn(II)] ions = 5 ppm and 10 ppm each; volume 250 ml; irradiation time 3 h.

The result of the effect of mixed metal ions in the photodegradation of metamifop is shown in Figure 4.5. The presence of mixed metal ions influence the degradation process, thus, clearly reflected the positive role of mixed metal ions solution. According to the previous study by Yusoff (2013) it reported that the presence of mixed metal ions in the photodegradation of acephate gave a slight

increment from 28.1% to 36.3%. This increment is due to the positive role of mixed metal ions. Thus, I believe that the increment of the photodegradation of metamifop is mainly due to the presence of Fe(II), Zn(II), Cu(II) ions in the solution.

Basically, the photodegradation of metamifop were increased is might due to the presence of Cu(II) ions in the solution. Yusoff (2013) reported that Cu(II) ions increase of the the degradation value of acephate . A previous studies by Lam *et al.* (2007) reported that the complexation of Cu(II) with 1,4-dioxane and its degraded compound, ethylene glycoldiformate (EGDF) have a positive role. The effect of adding  $\text{Cu}^{2+}$  on the photodegradation efficiency of glyphosate was investigated by Shifu and Yunzhang (2007) they claimed that the addition of a small amount of  $\text{Cu}^{2+}$  (up to 0.01 mM) the photodegradation efficiency of glyphosate increases rapidly from 36.2% to 88.5%, but if the  $\text{Cu}^{2+}$  concentration is larger than 0.01 mM, the photodegradation efficiency decreases markedly.  $\text{Cu}^{2+}$  behaves as electron scavenger which preventing the recombination of electron-hole pairs, thus increasing the chances of the formation of OH on the  $\text{TiO}_2$  surface. This is favorable for the photocatalytic reactions. But when the  $\text{Cu}^{2+}$  concentration is higher, the photodegradation efficiency decreases (Shifu and Yunzhang, 2007). Other studies show the effect of Cu on photodegradation of a-cypermethrin was decreased from 95.69 to 79.5% after 8 days of continuous UV irradiation. In fact, Cu compounds are known to catalyze the photodegradation of various pesticides under UV irradiation (Tariq *et al.*,2014). When the soil-incorporated chlorpyrifos was spiked with  $\text{Cu}^{2+}$  at a concentration of 20 mg kg the rate of its photodegradation was increased from  $3.5 \times 10$  to  $1.6 \times 10$  day. Copper is known to enhance the photodegradation of pyrethroids in the presence of UV light (Tariq *et al.*,2014).

Besides, according to Sykora (1997) copper compounds may act as catalysts for photodegradation of various pollutants in irradiated systems. Copper ions have been reported to strongly inhibit the degradation process of ethylthiourea (ETU). Besides, the photodegradation of metamifop was increased due to the exposure of UV radiation since it can produce the hydroxyl radical that help to degrade the metamifop. Basically, the effect of mixed metal ion is rarely investigated.

#### **4.3.3 Effect of Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>) towards the photodegradation of metamifop**

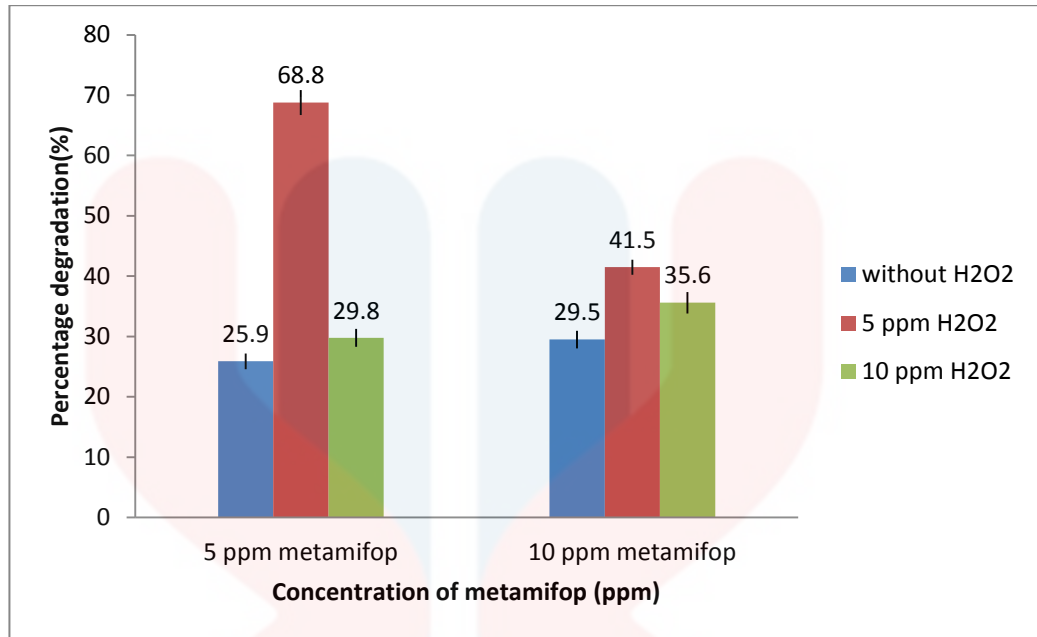
The experiment was further continued by the addition of hydrogen peroxide in the metamifop solution at concentration of 5 ppm and 10 ppm. Basically, the concentration of 5 ppm metamifop without H<sub>2</sub>O<sub>2</sub> is 25.9%. However, based on the result obtained (Figure 4.6) the presence of 5 ppm of H<sub>2</sub>O<sub>2</sub> on 5 ppm of metamifop result were greatly increased to 68.81%. Further addition of 10 ppm of H<sub>2</sub>O<sub>2</sub> on 5 ppm of metamifop was decreased to 29.8%. It was expected that the further addition of 10 ppm of H<sub>2</sub>O<sub>2</sub> will increased the photodegradation since the addition of H<sub>2</sub>O<sub>2</sub> into the photocatalytic system was expected to promote the degradation. However, the result indicated that the addition of 10 ppm of H<sub>2</sub>O<sub>2</sub> dropped the value of percentage degradation.

The photodegradation of 10 ppm of metamifop with the addition of 10 ppm H<sub>2</sub>O<sub>2</sub> were also investigated. The result indicated an exhibits a slight increase which the value of degradation is 35.6%. However, it was noticed that the percentage

degradation value slightly escalated to 41.5% when the concentration of 5 ppm of  $H_2O_2$  were added into the 10 ppm of metamifop solution.

Based on the observation in this study, we can observe that the concentration of 10 ppm of  $H_2O_2$  achieved small degradation percentage values compared to the 5 ppm. This is might due to the optimum dosage of  $H_2O_2$ . 5 ppm is seemed suitable dosage for degradation of metamifop because the lower dosage acted as electron acceptor to enhance the degradation efficiency (Tseng *et al.*, 2012) while 10 ppm is exceeding to the optimum dosage. Generally, the excess of  $H_2O_2$  concentration would trap the  $\bullet OH$  radicals to form weaker oxidant  $HO_2\bullet$  radicals. When the dosage was high the degradation was suppressed due to the capture of  $\bullet OH$  radicals and the competitive adsorption of  $H_2O_2$  (Tseng *et al.*, 2012).

$H_2O_2$  is formed as an intermediate in many photocatalysed reactions was found to undergo simultaneous decomposition resulting in the generation of OH radicals, which enhance the photodecomposition of many pollutants in water (Rauf & Asyraf, 2009). Ravelli *et al.*, (2009) previous studies showed that  $H_2O_2$  assists the degradation while its overdose retards the rate, possibly due to the competition for OH radicals. Hence,  $H_2O_2$  were proven to have slight contribution on the degradation of metamifop.



**Figure 4.6:** Effect of hydrogen peroxide towards photodegradation of metamifop. Experimental conditions: [metamifop]<sub>0</sub> 10ppm; 5ppm; hydrogen peroxide = 5 ppm; 10 ppm; solution volume 250 ml; irradiation time 3 h.

Besides, the effect of H<sub>2</sub>O<sub>2</sub> on the photocatalytic degradation of organic pollutants has been a subject of many investigations, the results is same in which it help for enhanced the degradation rates (Devipriya & Yesodharan, 2005). The effect of adding H<sub>2</sub>O<sub>2</sub> on the photodegradation efficiency of glyphosate were also investigated by Chen and Liu (20107) they reported that the addition of a small amount of H<sub>2</sub>O<sub>2</sub> (up to 0.1 mM) increase the photodegradation of glyphosate which the result rapidly increased from 36.2% to 60.3%, but if the H<sub>2</sub>O<sub>2</sub> concentration is larger than 0.1 mM, the photodegradation efficiency decreases gradually (Chen & Liu, 2007). It is the same case in this experiment, the addition of 5 ppm of H<sub>2</sub>O<sub>2</sub> were enhanced the photodegradation of metamifop, however the efficiency of photodegradation were reduced when 10 ppm of H<sub>2</sub>O<sub>2</sub> were added. According to Chu and Wong (2004) the rate improvement at lower H<sub>2</sub>O<sub>2</sub> dosages is probably due the following reasons. First, direct photolysis of H<sub>2</sub>O<sub>2</sub> by UV light can generate OH



radicals, which are likely to be the dominant rate-improving mechanism in this process. Another minor mechanism may partially contribute to the rate enhancement, in which  $\text{H}_2\text{O}_2$  is suggested to be a better electron acceptor than oxygen addition, the high dose of  $\text{H}_2\text{O}_2$  might absorb and attenuate the incident UV light available for the photocatalysis process. Therefore, the total oxidation capabilities of the system are largely reduced and the rates retarded. Hence, the  $\text{H}_2\text{O}_2$  should be added at optimum dosage in order to avoid reduction of the photodegradation rate.

#### **4.3.4 Effect of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) on the photodegradation of 5 ppm of metamifop in the presence of mixed metal ions**

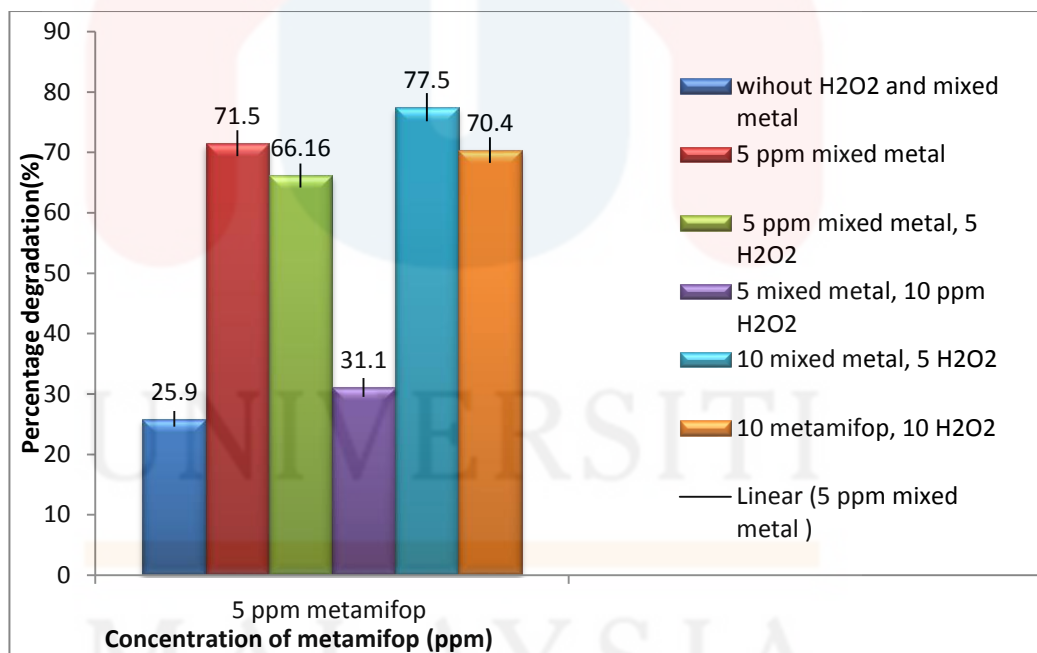
The effect of hydrogen peroxide on the photodegradation of metamifop in the presence of mixed metal ions is further investigated. In this experiment, different concentration of metamifop, mixed metal ions and hydrogen peroxide were tested. In order to determine the effect of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) on the photodegradation of metamifop in the presence of mixed metal ions different concentration were used in this experiment. The concentration were used is 5 ppm and 10 ppm.

The investigation was firstly conducted by adding different concentration of mixed metal ions and  $\text{H}_2\text{O}_2$  on 5 ppm of metamifop solution. Basically, the initial concentration of 5 ppm metamifop after 3 hour irradiation is 25.9 % and the concentration of metamifop in the presence of 5 ppm of mixed metal ions is 71.5%. The result (Figure: 4.7) indicates that the percentage of degradation of 5 ppm metamifop with the presence of 5 ppm of mixed and 5 ppm  $\text{H}_2\text{O}_2$  were increased to 66.16% after 3 hour irradiation. However, the percentage value degradation of 5 ppm



metamifop showed reduction when 5 ppm mixed metal and 10 ppm of  $\text{H}_2\text{O}_2$  were added into the 5 ppm metamifop solution where the value of percentage obtained were 31.1%.

Nevertheless, 10 ppm of mixed metal ion and 5 ppm of  $\text{H}_2\text{O}_2$  were also added into 5 ppm metamifop solution in order to investigate the effectiveness of the photodegradation of metamifop. The results showed that the percentages of degradation value were increased significantly to 77.5 %. However, the percentages of degradation value were slightly decreased to 70.4% when 10 ppm of mixed metal and 10 ppm of  $\text{H}_2\text{O}_2$  were added on the 5 ppm metamifop solution.



**Figure 4.7:** Effect of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) on the photodegradation of 5 ppm metamifop in the presence of mixed metal ions. Experimental conditions:  $[\text{metamifop}]_0$  5ppm; mixed metal ions concentration =  $[\text{Fe(II)}] = [\text{Cu(II)}] = [\text{Zn(II)}]$  ions =5 ppm and 10ppm each ; hydrogen peroxide concentration = 5 ppm; 10 ppm, solution volume 250 ml; irradiation time 3 h.

Based on the observation of this experiment, we can conclude that the highest percentage of degradation was achieved when 10 ppm of mixed metal ions and 5 ppm of  $H_2O_2$  were added into the 5 ppm of metamifop solution. The result proved that the concentration of 10 ppm mixed metal and 5 ppm of  $H_2O_2$  ions were very effective in the photodegradation of 5 ppm of metamifop. An experiment conducted by Yusoff (2013) reported that the presence of mixed metal ion in the acephate solution has increased the degradation efficiency and further increment was occurred with the addition of  $H_2O_2$  30 mg/L of. This could be due to the available  $\bullet OH$  radicals and positive synergistic effect of Fe(II) and Zn(II) ions in the solution.

In contrast, the lowest value of degradation percentage is when 5 ppm of mixed metal ions and 10 ppm of  $H_2O_2$  were added into the 5 ppm of metamifop solution. This believed due to concentration of mixed metal ions and  $H_2O_2$  in the solution. The the combination of 5 ppm of mixed metal ions and 10 ppm of  $H_2O_2$  were not effective in the photodegradation of metamifop since the amount of 5 ppm of mixed metal were compact compared to 10 ppm and it also because the concentration of 10 ppm of  $H_2O_2$  that exceed to the optimum dosage that previously discussed in section 4.3.3. Yusoff (2013) reported that the presence of mixed metal ions (Fe(II), Cu(II) and Zn(II)) retarded the photodegradation of glyphosate and malathion. The addition of 30 mg/L of  $H_2O_2$  in the solution also not provide a significant effect on the photodegradation of glyphosate and malathion. Hence, the concentrations of  $H_2O_2$  affect the photodegradation system and the concentrations of mixed metal ion play a crucial role on the photodegradation of metamifop.

#### **4.3.5 Effect of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) on the photodegradation of 10 ppm of metamifop in the presence of mixed metal ions**

Further investigations were conducted by added different concentration of mixed metal ions and H<sub>2</sub>O<sub>2</sub> on the photodegradation of 10 ppm metamifop. The initial percentage degradation value of 10 ppm metamifop is 29.5% and the percentage degradation of 10 ppm metamifop with 10 ppm of mixed metal is 60.12%. Based on the result we can identify that the percentage of degradation of 10 ppm of metamifop were slightly increased from 29.5% to 68.63% when 10 ppm of H<sub>2</sub>O<sub>2</sub> and 10 ppm of mixed metal ions were added.

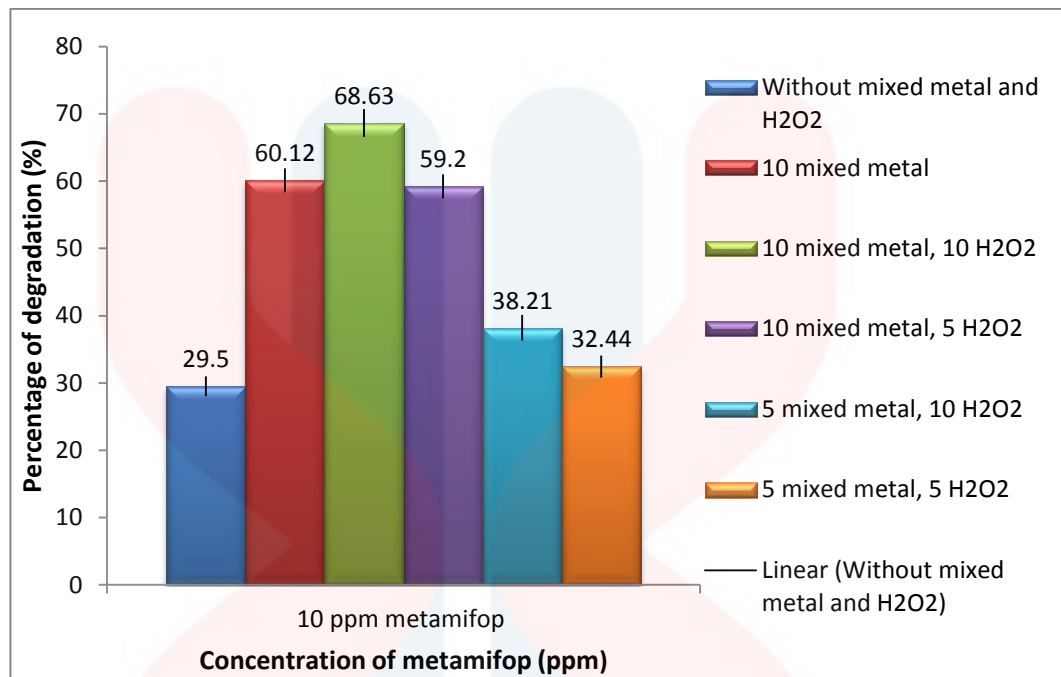
The result in Figure 4.8 also showed that percentage of degradation of 10 ppm of metamifop with the presence of 10 ppm of mixed metal and 5 ppm of H<sub>2</sub>O<sub>2</sub> were slightly decreased to 59.2%. Nevertheless, the investigation was continued by adding 5 ppm of mixed metal ions and 10 ppm of H<sub>2</sub>O<sub>2</sub> in the solution of 10 ppm of metamifop. The result obtained showed that the percentages of degradation value were drastically dropped to 38.21%. The reduction of percentage degradation also occurred when 5 ppm of mixed metal ions and 5 ppm of H<sub>2</sub>O<sub>2</sub> were added into the 10 ppm of metamifop solution. However, the result indicated that the highest percentage of degradation is when 10 ppm of mixed metal ions and 10 ppm of H<sub>2</sub>O<sub>2</sub> was added into 10 ppm of metamifop solution. The combination of 10 ppm of mixed metal ion and 10 ppm of H<sub>2</sub>O<sub>2</sub> were effective on the photodegradation of 10 ppm metamifop. This increment of the photodegradation was believed due to the positive role of mixed metal ions in the solution. Basically, the effect of mixed metal ions on the photodegradation of acepate, glyphosate and malathion has been explored by Yusoff (2013). It reported that the presence of mixed metal ions (Fe(II), Cu(II) and

Zn(II)) was retard the photodegradation of glyphosate and malathion. However, the presence of mixed metal ions on the photodegradation of the acephate solution were reported increased the degradation efficiency and further increment was occurred with the addition of  $H_2O_2$ . This believed due to the available  $\bullet OH$  radicals and positive synergistic effect of Fe(II) and Zn(II) ions in the solution.

Basically, the presence of Fe(II) in the solution is accepted improved the photodegradation rate.  $Fe^{2+}$  known to help the photo dissipation of various halogenated herbicides and pesticides because of its photosensitizing capacity (Rafique and Tariq 2014). Previous studies by Rafique *et al.*, (2016) reported that the increment in the degradation efficiency in the presence of Fe(II) ions is due to the capability of Fe(II) ions to be oxidised to Fe(III) ions and reduce back to Fe(II) ions in the consumption of electron. The formation of iron(III) hydroxo aqua complex can prompt to the formation of  $\bullet OH$  radical by photolysis process (Shifu and Yunzhang, 2007). Besides, Esplugas *et al.*, (1994) studied the influence of Fe(II) in the photodegradation using UV radiation nitrobenzene in aqueous solution. Fundamentally, the concentration of Fe(II) showed great impact on the rate photodegradation. It is apparent that the photo Fenton type reaction relies heavily on the UV irradiation to initiate the generation of  $\bullet OH$ . If desired, organic pollutants can be mineralized completely with UV/visible irradiation. For example, Ruppert *et al.* ,(1993) demonstrated that various herbicides and pesticides can be completely mineralized by the Fe(II) and  $H_2O_2$  process. Hence, I believed that the presences of Fe(II) in mixed metal ions upgraded the productivity of the photodegradation of metamifop.

Nevertheless, the result indicates that the addition of mixed metal ion enhanced the photodegradation of metamifop. For example, 60.12% were achieved when 10 ppm of mixed metal ions added on 10 ppm of metamifop solution however the percentage of degradation showed reduction when 5 ppm of mixed metal ions were added on the metamifop solution. The reduction of the value of degradation is believed due to the compact amount of mixed metal ions on the solution. The increment of the photodegradation on metamifop is probably due to the presence of Zn(II) in the solution. 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. In any case, it has been found that positive part of Zn(II) particles was effective in degradation of acephate (Yusoff, 2013). A previous studies by Latiff (2015) also reported that there was an increment in the photodegradation of metamifop in the presence of Zn(II) ions. The addition of Zn(II) ions with 5 ppm shows that the degradation of metamifop was increased from 48.43% to 64.40% and the addition of Zn(II) ions with 10 ppm shows that the degradation percentage were increased from 64.4% to 72.14% (Latiff, 2015) . Hence, I believed that the presence of Zn(II) on the mixed metal ions increased the photodegradation of metamifop.

In contrast, the result in Figure 4.8 indicated that the lowest percentage of degradation occurred when only 5 ppm of mixed metal ions and 5 ppm of H<sub>2</sub>O<sub>2</sub> was added into 10 ppm of metamifop solution. The concentration of 5 ppm of mixed metal and 5 ppm of H<sub>2</sub>O<sub>2</sub> were not effective on the the photodegradation of metamifop since the concentration of mixed metal added was compact. Hence, it was believed that the concentration of mixed metal ions were important on the the photodegradation of metamifop.



**Figure 4.8:** Effect of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) towards the photodegradation of 10 ppm metamifop in the presence of mixed metal ions. Experimental conditions: [metamifop]<sub>0</sub> 10ppm; mixed metal ions concentration = [Fe(II)] = [Cu(II)] = [Zn(II)] ions =5 ppm and 10ppm each ; hydrogen peroxide concentration = 5 ppm; 10 ppm, solution volume 250 ml; irradiation time 3 h.



## Chapter 5

### CONCLUSION AND RECOMMENDATION

#### 5.1 Conclusion

In this study, the photodegradation technology was implemented in order to identify the effect of mixed metal ions (Fe(II), Cu(II), Zn(II)) ions towards the photodegradation of herbicide containing the active ingredient metamifop. The UV-light from laminar flow chamber were applied as a precursor for ( $\bullet$ OH) in order to degrade metamifop. An analytical method was developed by using UV-Vis spectrum to verify that the increment of the significance of the percentage degradation value. In order to study the effect of mixed metal ions (Fe(II), Cu(II), Zn(II)), two different concentration were used which were 5 ppm and 10 ppm. The result indicates that the mixed metal ions increased the photodegradation of metamifop where it achieved 71.5% of degradation when 5 ppm was added. Besides, the further addition of 10 ppm of mixed metal ions were increased the percentage of degradation to 96.3%. Hence, the result showed that the mixed metal ions (Fe(II), Cu(II), and Zn(II)) were help to increase the photodegradation of metamifop solution and it have has a positive impact on the photodegradation of metamifop. The result also indicated that the higher the concentration of mixed metal ions, the higher the percentage of degradation was obtained.

Nevertheless, hydrogen peroxide was also added on the metamifop solution as oxidant catalyst in order to identify the effect on the photodegradation of metamifop. The concentration of  $H_2O_2$  used was 5 ppm and 10 ppm. The results demonstrate that



the addition of 5 ppm increased the photodegradation of 5 ppm metamifop where it achieved 68.8% of degradation. However, the result showed that the percentage of degradation was drastically reduced to 29.8% when 10 ppm of H<sub>2</sub>O<sub>2</sub> was added. In this study, it showed that the concentration of 5 ppm of H<sub>2</sub>O<sub>2</sub> was given positive effects on the photodegradation of metamifop while the concentrations of 10 ppm of H<sub>2</sub>O<sub>2</sub> were not given significant effect on the photodegradation of metamifop. Hence, the result indicated that concentration of H<sub>2</sub>O<sub>2</sub> added should be added at suitable dosage in order to achieve it beneficial effect.

The expected outcome of this study was achieved in which the mixed metal ions help to increase the photodegradation of both 5 ppm and 10 ppm of metamifop. Besides, the effect of hydrogen peroxide was also increased the photodegradation of metamifop however it should be added at suitable dosage.

## 5.2 Recommendation

Although 5 ppm and 10 ppm of mixed metal ions (Fe(II), Cu(II), Zn(II)) ions enhanced the photodegradation process, the metamifop was not fully degraded. The addition of hydrogen peroxide in the solution was also not fully degraded the metamifop. So, to increase the effectiveness of photodegradation of metamifop, the presence of ultraviolet radiation and the combination of ozone and hydrogen peroxide as catalysts element is probably can be an effective system to upgrade the degradation metamifop.

A previous research reported that ozonation and its combinations with hydrogen peroxide and UV radiation are excellent treatment methods for different hazardous wastes. They also reported that Ozone, ozone with UV, and ozone with  $H_2O_2$  are able to reduce the acute toxicity of the effluents from the pulp and paper industry. For example, UV or oxidation technology ( $O_3/H_2O_2/UV$  system) has been applied successfully for the removal of volatile organic contaminants (VOC) (benzene, acetone, dichloroethane, tetrachloroethane, etc.) from groundwater in San Jose, CA (USA).

Hence, UV radiation with  $O_3$  and  $H_2O_2$  combination gives a good yield of OH radicals, so it probably can be a good and effective catalyst to degrade metamifop.

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## APPENDIX : UV-VIS RESULTS

### 5ppm Metamifop

Wavelength (nm)	Absorbance (nm)			
	Replicate 1	Replicate 2	Replicate 3	Average
350	31	23.33	23.33	25.85

### 10ppm Metamifop

Wavelength (nm)	Absorbance (nm)			
	Replicate 1	Replicate 2	Replicate 3	Average
350	29.79	29.41	29.41	29.54

### 5 ppm Metamifop with 5ppm of mixed metal ions

Wavelength (nm)	Absorbance (nm)			
	Replicate 1	Replicate 2	Replicate 3	Average
350	71.43	71.73	71.30	71.51

### 10 ppm Metamifop with 10 ppm of mixed metal ions

Wavelength (nm)	Absorbance (nm)			
	Replicate 1	Replicate 2	Replicate 3	Average
350	59.94	59.94	60.47	60.12

### 5 ppm metamifop with 10 ppm of mixed metal ions

Wavelength (nm)	Absorbance (nm)			
	Replicate 1	Replicate 2	Replicate 3	Average
350	96.26	96.34	96.37	96.32

### 10 ppm Metamifop with 5 ppm of mixed metal ions

Wavelength (nm)	Absorbance (nm)			
	Replicate 1	Replicate 2	Replicate 3	Average
350	37.54	36.11	37.97	37.20

### 5 ppm metamifop with 5 ppm of H<sub>2</sub>O<sub>2</sub>

Wavelength (nm)	Absorbance (nm)			
	Replicate 1	Replicate 2	Replicate 3	Average
350	68.38	68.75	69.29	68.81



**10 ppm Metamifop with 10 ppm of H<sub>2</sub>O<sub>2</sub>**

Wavelength (nm)	Absorbance (nm)			
	Replicate 1	Replicate 2	Replicate 3	Average
350	36.27	35.58	34.88	35.58

**5 ppm of metamifop with 10 ppm of H<sub>2</sub>O<sub>2</sub>**

Wavelength (nm)	Absorbance (nm)			
	Replicate 1	Replicate 2	Replicate 3	Average
350	28.86	30.59	29.82	29.76

**10 ppm Metamifop with 5 ppm of H<sub>2</sub>O<sub>2</sub>**

Wavelength (nm)	Absorbance (nm)			
	Replicate 1	Replicate 2	Replicate 3	Average
350	41.16	40.36	42.91	41.48

**5 ppm Metamifop and 5 ppm of mixed metal with the addition of 5 ppm of H<sub>2</sub>O<sub>2</sub>**

Wavelength (nm)	Absorbance (nm)			
	Replicate 1	Replicate 2	Replicate 3	Average
350	65.77	66.51	66.20	66.16

**10 ppm Metamifop and 10 ppm of mixed metal with the addition of 10 ppm of H<sub>2</sub>O<sub>2</sub>**

Wavelength (nm)	Absorbance (nm)			
	Replicate 1	Replicate 2	Replicate 3	Average
350	67.48	69.34	69.07	68.63

**5 ppm Metamifop and 5 ppm of mixed metal with the addition of 10 ppm of H<sub>2</sub>O<sub>2</sub>**

Wavelength (nm)	Absorbance (nm)			
	Replicate 1	Replicate 2	Replicate 3	Average
350	31.54	30.87	30.87	31.10

**10 ppm Metamifop and 10 ppm of mixed metal with the addition of 5 ppm of H<sub>2</sub>O<sub>2</sub>**

Wavelength (nm)	Absorbance (nm)			
	Replicate 1	Replicate 2	Replicate 3	Average
350	59.39	59.26	58.95	59.20

**5 ppm Metamifop and 10 ppm of mixed metal with the addition of 5 ppm of H<sub>2</sub>O<sub>2</sub>**

Wavelength (nm)	Absorbance (nm)			
	Replicate 1	Replicate 2	Replicate 3	Average
350	77.45	77.52	77.52	77.50

**10 ppm Metamifop and 5 ppm of mixed metal with the addition of 10 ppm of H<sub>2</sub>O<sub>2</sub>**

Wavelength (nm)	Absorbance (nm)			
	Replicate 1	Replicate 2	Replicate 3	Average
350	38.38	38.19	38.07	38.21

**5 ppm Metamifop and 10 ppm of mixed metal with the addition of 10 ppm of H<sub>2</sub>O<sub>2</sub>**

Wavelength (nm)	Absorbance (nm)			
	Replicate 1	Replicate 2	Replicate 3	Average
350	70.60	70.52	70.26	70.46

**10 ppm Metamifop and 5 ppm of mixed metal with the addition of 5 ppm of H<sub>2</sub>O<sub>2</sub>**

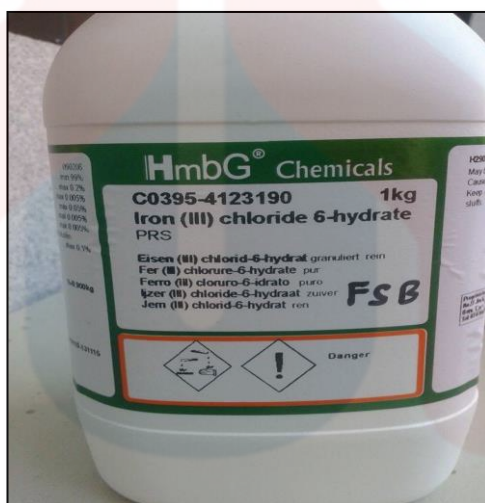
Wavelength (nm)	Absorbance (nm)			
	Replicate 1	Replicate 2	Replicate 3	Average
350	32.09	32.32	32.44	32.28

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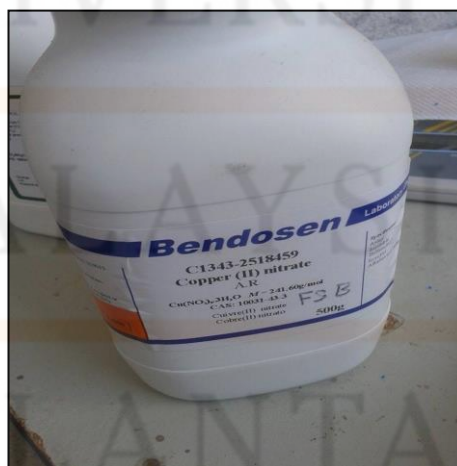
## APPENDIX B



**Figure 1:** Stock solutions of metamifop, Zinc, Copper, Iron, and Hydrogen Peroxide.



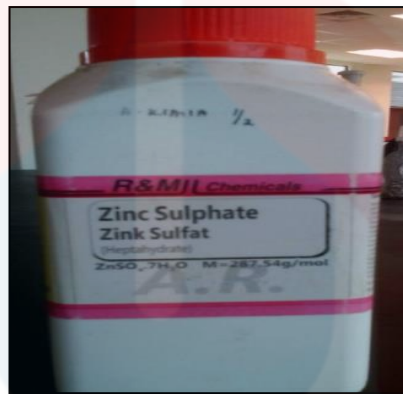
**Figure2:** Iron (III) chloride 6-hydrate



**Figure 3:** Copper (II) nitrate



**Figure 4:** Hydrogen Peroxide



**Figure 5:** Zinc sulphate



**Figure 6:** Laminar flow chamber