

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY

School of Engineering

Chemical and Process Engineering

Master's Thesis

**STUDY ON THE DEGRADATION OF ACESULFAME  
POTASSIUM BY UV-LED/CATALYST**

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**ABSTRACT**

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**Study on the degradation of Acesulfame Potassium by UV-LED/Catalysts**

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This master's thesis mainly focuses on the experiments of the degradation of acesulfame potassium under UV-LED and catalysts/oxidizing agents. Acesulfame potassium is defined as an artificial sweetener which can be found in diet foods, beverages and some drugs. The most important benefit of acesulfame potassium is the sweetness which can sweeten than normal sugar 200 times. Although having a very high benefit, the persistence after discharged to environment of artificial sweeteners in general and acesulfame potassium in particular is very long. Acesulfame potassium can be considered as contaminants of emerging concern which substance hardly recognize in environment. Due to the development of technology, there are some method which can recognize the presence of it in environment with a very small concentration (from ngr/l to mgr/l). The most concern about substances is the unknown long-term effect. In this thesis, acesulfame potassium is prepared at concentration from 1 ppm to 6 ppm with pH from 2 to 6. The treatment time from 5 minutes to 120 minutes represents the degradation rate of acesulfame concentration. HPLC method is used to check the concentration before and after treatment. Also catalysts and oxidants (0.5 mg, 1 mg, 1.5 mg) are added for treatment optimization. Finally, the TOC and GC-MS are tested at optimal conditions. The conclusions and suggestions are presented.

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Lappeenranta University of Technology

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**NOMENCLATURE**

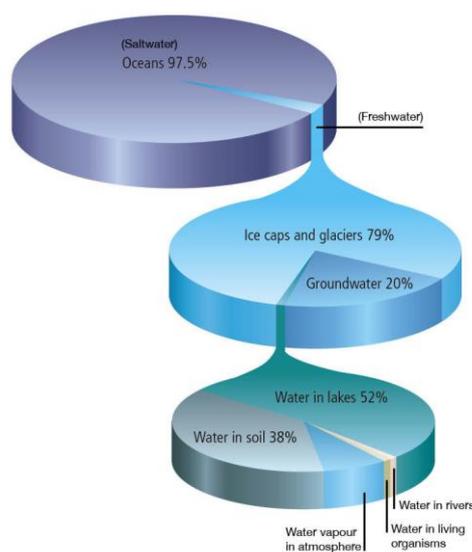
EEA	European Environment Agency
CECs	Contaminants of Emerging Concern
Ace-K	Acesulfame Potassium
UV-LED	Ultraviolet Light Emitting Diodes
HPLC	High-performance Liquid Chromatography
GC-MS	Gas Chromatography – Mass Spectrometry
TOC	Total Organic Carbon
VB	Valence Band
CB	Conduction Band
TiO <sub>2</sub>	Titan Dioxide
ZnO	Zinc Oxide
PDS	Potassium Peroxodisulfate
PMS	Potassium Peroxomosulfate
CO <sub>2</sub>	Carbon Dioxide
H <sub>2</sub> O	Water
$\cdot OH$	Hydroxyl Radical
$\cdot SO_4^-$	Sulfate Radical

## 1 INTRODUCTION

In the current era, the world witnesses a lot of change in all field, for example technology, pharmaceutical, environment and so on. Followed by that, the effect of global megatrends on the environment are increasing that lead to global warming and climate change. In details, as mentioned in preparation for SOER 2015, European Environment Agency (EEA) shows that there are some megatrends which have direct effects on the environment. For instance: (EEA, 2017)

- Technology: accelerating technological change
- Society: increasing and distributing global population
- Economy: increasing of multipolar world
- Environment: pressure on ecosystems by growing uncontrollable environmental pollution (water, air, noise, etc..)
- Politic: diversifying approaches to governance

Following those above information, the jump of technology and some developments will result in the increase the environment and ecosystem pressure. The EEA gave the relationship between those megatrends and their effect on environment. In details, the growth of global population will lead to the increase of energy consumption and amount of daily released pollutants.



*Figure 1. Distribution of Earth's water (Sharma, 2012)*

Based on the data which is published, one of the most concern in this era is the water pollution. As shown in figure 1, the amount of freshwater all over around the world occupy 2.5%. In that 2.5%, there is 1% surface water and 20% is groundwater, the rest belongs to ice caps and glaciers with 79% (Sharma, 2012). Based on the information above, the amount of available freshwater is less. In the future, if there is no recycled and reused method to increase the amount of freshwater, the world will face lack of freshwater, lead to various serious problems such as, lack of food, hygiene and many diseases. National Geographic gives some fast facts about the recent reality of water pollution: (Geographic, 2017)

- 70% of industrial waste in developing countries is released directly to the environment without any treatment which is harmful for human the ecosystems.
- On average, 22 million tons of fertilizers and chemicals are being used every year.

Also mentioned in the same reference, National Geography shows the goal for removing pollutants. Followed by that, scientists concentrate to detect and remove more pollutants at smaller concentration (Geographic, 2017). Based on that purpose, contaminants of emerging concern (CECs) is now the most concern due to the unknown long-term effects and the very small concentration stored for a very long time. CECs which can be found in foods, beverages, pharmaceuticals and personal care products, are defined as the substances that have potential to affect adversely to human and environment.

CECs are compounds which can easily being found in daily used products such as shampoo, soap, skin care and even in pharmaceuticals products which are released to the environment after uses or after absorb in human body. CECs are known as new compounds which are exposed to aquatic organisms at the very beginning and may not be detected until adulthood. There are some new drawback of CECs: (Manttari & Kallioinen, 2017)

- Release to environment for a long time without being recognized and concerned due to its small concentration (commonly found in the  $\mu\text{g/l}$  range or even  $\text{ng/l}$  range).
- Unknow long-term effects.
- The present of CECs will cause hamfer for used water.
- Influece to the aquatic organism without any detection until adulthood
- Can be released to the environment easily by medical products, healthcare and skin care products and hard to detect and remove by physical method

Artificial sweeteners are known as an CEC which can be observed for human daily products such as beverages, diet food, medicines and are released to the environment without any concern about its environmental impacts. In addition, there are some health effects that can cause the balanced disruption of gut microbiota which lead to the series of human diseases such as obesity, diabetes and inflammatory bowel disease. However, the specific influences of artificial sweeteners on the gut microbiota and its metabolism still need more researches. (Bian, et al., 2017)

Acesulfame Potassium is introduced as a compound which usually can be found in normal diet products due to its low-calorie. However, Bandyopadhyay and Pfeffer (Bandyopadhyay, et al., 2008) (Pfeffer, et al., 1985) mentioned in their research about the genotoxicity and the inhibiting anaerobic fermentation of acesulfame potassium. Thus, there are many specific benefits of artificial sweeteners in general and acesulfame potassium in particular such as, additives for food and beverages containing less calorie and keeping the same sweetness comparing with sucrose. In spite of its advantages for food field and pharmaceutical fields, there are still remaining unclear disadvantages which need more studies. Also being mentioned by the United States Food and Drug Administration (FDA), the long-term exists of acesulfame potassium in environment has not been studied (Wikipedia, 2017).

Because of unknown long-term effects of CECs in general and acesulfame potassium in particular, there are some studies which focused on this issue by using some water treatment method such as: (EPA, 2010)

- Activated Sludge Process
- Granular Activated Carbon Adsorption
- Chlorine Disinfection
- Ultraviolet Disinfection
- Ozone Disinfection
- Reverse Osmosis (RO)

In this thesis, the degradation of acesulfame potassium (Ace-K) concentration in wastewater was mainly focused and the effects of catalysts and oxidants to accelerate the experiments were also mentioned.

HPLC, TOC and GC-MS are special device which are used in this thesis in order to recognize the smallest concentration and the byproduct pathway of Ace-K before and after treatment. Followed by that, the best result experiment is added catalysts and oxidants to optimize the final result.

## 2 THEORITICAL EXPERIMENTS

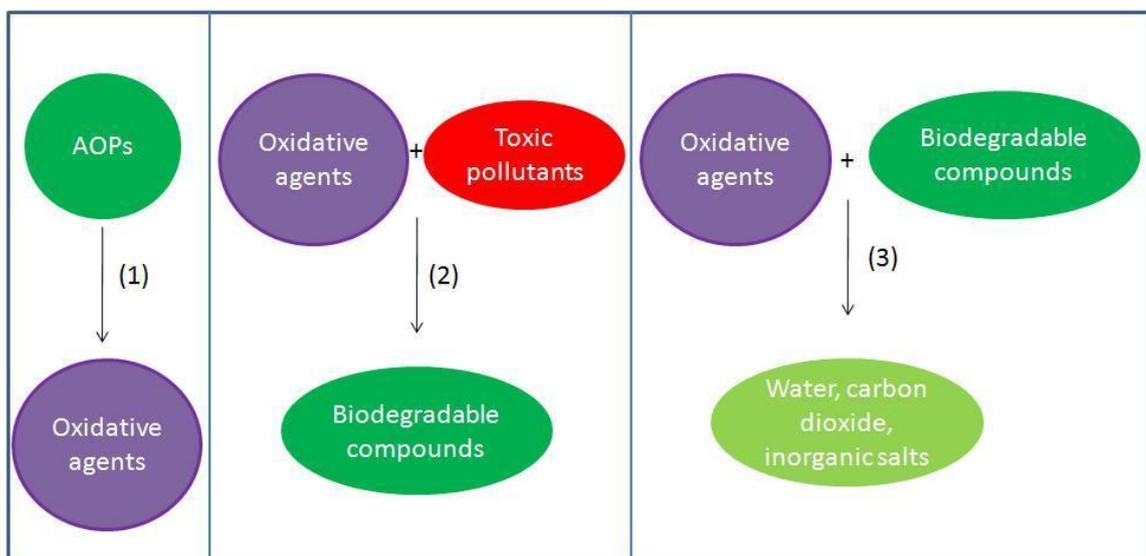
### 2.1 Advanced oxidation process

With an increase in the fresh water demand and releasing wastewater to the environment, reduced, recycled wastewater are the most concerns in this century. The main source of wastewater comes from daily life activities and manufacturing. Among a lot of processes to degrade the pollutants in wastewater, advanced oxidation processes (AOPs) proved to be the most effective way for degrading wastewater. AOPs aim to remove organic pollutants which cannot be decreased by using biological processes. Following that, AOPs use external sources such as electricity, ultraviolet radiation (UV) or solar light to treat organic contaminants in wastewater. (Dorfman & Adams, 1973)

AOPs include 3 stages as shown below: (Mazille & Spuhler, 2011)

- Creation of powerful oxidizing agents ( e.g. hydroxyl radicals, sulfate radicals)
- Reaction between agents and organic comtaninants in wastewater to form biodegradable compounds
- Reaction between agents and biodegradable compounds to form water production, carbonsioxide and inorganic salts

The steps also can be expressed as figure 2 below:



*Figure 2. Main stages of AOPs to decrease organic pollutants in wastewater. (Mazille & Spuhler, 2011)*

Based on that concept, oxidation is defined as the transfer from a reductant (electron donor) to an oxidant (electron acceptor) which lead to the change of chemical for oxidant and reductant. Studies show that the most powerful oxidizing agents for photocatalytic process are fluorine, hydroxyl radicals ( $\bullet OH$ ), ozone and chloride with redox potentials are 2.8 eV, 2.73 eV, 2.07 eV and 1.49 eV, respectively. (Dorfman & Adams, 1973)

The overall concept of AOPs is using hydroxyl radical ( $\bullet OH$ ) to oxidize the organic pollutants in wastewater. This method is based on using UV radiation with common catalysts, e.g. Titan (IV) dioxide ( $TiO_2$ ), Zinc dioxide ( $ZnO$ ), Hydrogen peroxide ( $H_2O_2$ ), Ozone ( $O_3$ ) or the combination of  $H_2O_2$  and  $O_3$  to produce  $\bullet OH$ . Followed by that, AOPs can be divided into established and emerging technologies depending on the wastewater treatment industry and existing conditions. Table 1 presents two categories of technology of AOPs. (Kommineni, et al., 2008)

Table 1. Technology of AOPs (Kommineni, et al., 2008)

<b>Established Technologies</b>	<b>Emerging Technologies</b>
<ul style="list-style-type: none"> <li>- Hydrogen Peroxide/Ozone (<math>H_2O_2/O_3</math>)</li> <li>- Ozone/Ultraviolet Irradiation (<math>O_3/UV</math>)</li> <li>- Hydrogen proxide/Ultraviolet Irradiation (<math>H_2O_2/UV</math>)</li> </ul>	<ul style="list-style-type: none"> <li>- High Energy Electron Beam Irradiation (E-beam)</li> <li>- Caviatation (Sonication and Hydrodynamic)</li> <li>- <math>TiO_2</math> – catalysed UV Oxidation</li> <li>- Fenton’s Reaction</li> </ul>

## 2.2 Photocatalysis

Photocatalysis was discovered for the first time in 1972 by Fujishima and Honda bringing up a new era for heterogeneous photocatalysis. When the photocatalyst absorbs the lights with the balance energy is higher than the band gaps energy, the electron ( $e_{CB}^-$ ) is excited from the valence band (VB) to the conduction band, creates the positive-charge hole ( $h_{VB}^+$ ) in VB. Being known as strong oxidant,  $h_{VB}^+$  can react with organic compounds in contaminant resulting in the reduction of organic compound and ending up with carbon dioxide ( $CO_2$ ) and water ( $H_2O$ ). Followed by that, the  $h_{VB}^+$  decrease the concentration of organic compound in the contaminant by reacting with water in wastewater to produce hydroxyl radical ( $\cdot OH$ ) or sulfate radical ( $\cdot SO_4^-$ ) with redox potentials are 2.73 V and 2.6 V, respectively. The product after oxidizing is ended up with  $CO_2$  and  $H_2O$ . (Zhang, 2015). Figure 3 presents the mechanism of photocatalysts. In addition, the nature, concentration, chemical structure and existence of other compounds affect the ability of photocatalytic degradation. The photocatalytic process is capable for degrading a wide range of organic contaminants such as herbicides, pesticides and micropollutants. (Umar & Aziz, 2013)

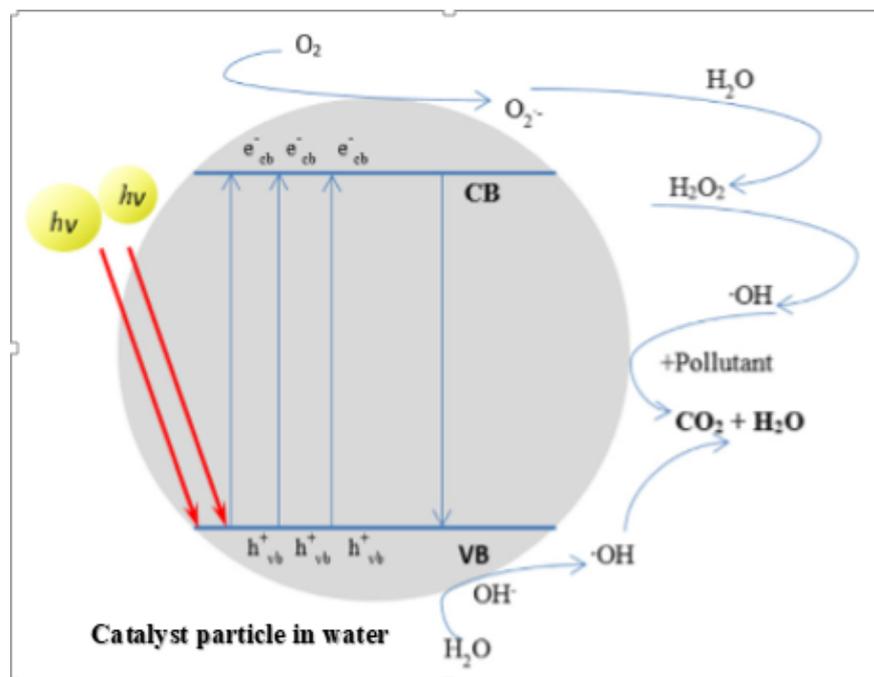


Figure 3. Photocatalysts working mechanism (Zhang, 2015)

Photocatalysis is a combined words with two parts, “photo” and “catalysis”, defined as the photoreaction accelerated by using catalyst as a substance accelerating a reaction without being consumed as a reactant. Besides, catalyst is also known as the substance which increases the reaction rate by deducting the activation energy. In details, the catalysts used in this topic are  $\text{TiO}_2$ ,  $\text{ZnO}$  and two other oxidizing agents called Potassium Peroxodisulfate (K-PDS) and Potassium Peroxomonosulfate (K-PMS). (Bengtsson, 2011). Oxidizing agents are used in reactions in order to produce sulfate radical ( $\bullet\text{SO}_4^-$ ) and  $\bullet\text{OH}$  which have been known as strong electron oxidizing agents because of their high standard redox potential (Luo, et al., 2015).

Photocatalysis is currently known as a process which can be improved by using variable catalysts in order to optimize the photocatalytic reaction. However, the limitation of photocatalysis is that it cannot occur in night time due to the lack of sunlight, because the electron can only excite with the high energy from sunlight. (Loeb, 2013). To enhance the solar energy and optimize the treatment, a catalyst is needed. This research mainly focuses on using titan dioxide ( $\text{TiO}_2$ ) and zinc oxide ( $\text{ZnO}$ ) for photocatalysis reaction.

Besides the photocatalysis method using  $\text{TiO}_2$  and  $\text{ZnO}$  as catalysts, in this thesis, the discussion about the affect of sulfate radical is also mentioned by using PDS and PMS. The main purpose of using oxidizing agents is the oxidization process which has the ability to remove one or more electrons from another atom and leave positive charge holes for the further reaction. Basically, catalysts and oxidizing agents will bring the same result, that is the generation of positive charge holes in another atom. However, the main difference between a catalyst mechanism and an oxidizing agent mechanism is the different band gap under the attack of UV light will excite the electron in VB to CB and the attack of UV light on oxidizing agent to remove electrons from another atom. (Umar & Aziz, 2013).

## 2.3 UV-LED

Being known as radiation source, UV lights and sunlight can be used in order to produce radiation source for photocatalytic process. Ultraviolet is an alternative process for traditional chemical process in wastewater treatment with the temperature and pH requirement (Bilenko, et al., 2010). UV radiation can be found in some common daily stuffs, such as radio, cell phones, microwaves, lights and so on. The most common form of UV radiation is sunlight which produces three types of UV radiation: (FDA, 2013)

- UVA: The longest wavelengths from 315 – 400 nm, less affected by the atmosphere and able to reach the Earth's surface
- UVB: The wavelengths is between 280 – 315 nm, with 90% is absorbed by ozone, water vapour, O<sub>2</sub> and CO<sub>2</sub>
- UVC: The shortest wavelengths from 100 – 280 nm, with all UVC radiation is absorbed by ozone and other factors (Anon., n.d.)

Studies show that UV radiation gives some benefits for human body. For instance, UVB radiation help body synthesis vitamin D3 which plays the main role to support transporting calcium to bone and muscle (FDA, 2013). However, the benefit of UV radiation depends on the spectra and fluence rates. If the spectra and fluence rate are higher than the limit such as UVA and UVB, there will be negative effect for human skin, such as, cancer (FDA, 2013). Artificial UV lights used as a source of UV irradiation contains mercury. Those can be divided into low, medium and high pressure lamp. As mentioned above, sunlight also can provide UV irradiation in photocatalytic process. About 4 - 5% of sunlight can reach to the earth with wavelength approximately 300 - 400 nm as close as UV light range. (Umar & Aziz, 2013). However, due to the daytime length, the limitation of sunlight is the continuation of photocatalytic process. For instance, for those countries surrounding equator, the length of daytime and nighttime are nearly the same and constant while those countries near to North Pole and Antarctic, such as Finland, Norway, Canada and so on, the length of daytime and nighttime depends on the seasons. Thus sunlight is not a good option although sunlight may be a natural source providing UV radiation. (Acra, et al., 1984)

In this research, ultraviolet light emitting diode (UV-LED) is used as an agent which create UV radiation with the wavelength is 265 nm to degrade the concentration of an artificial

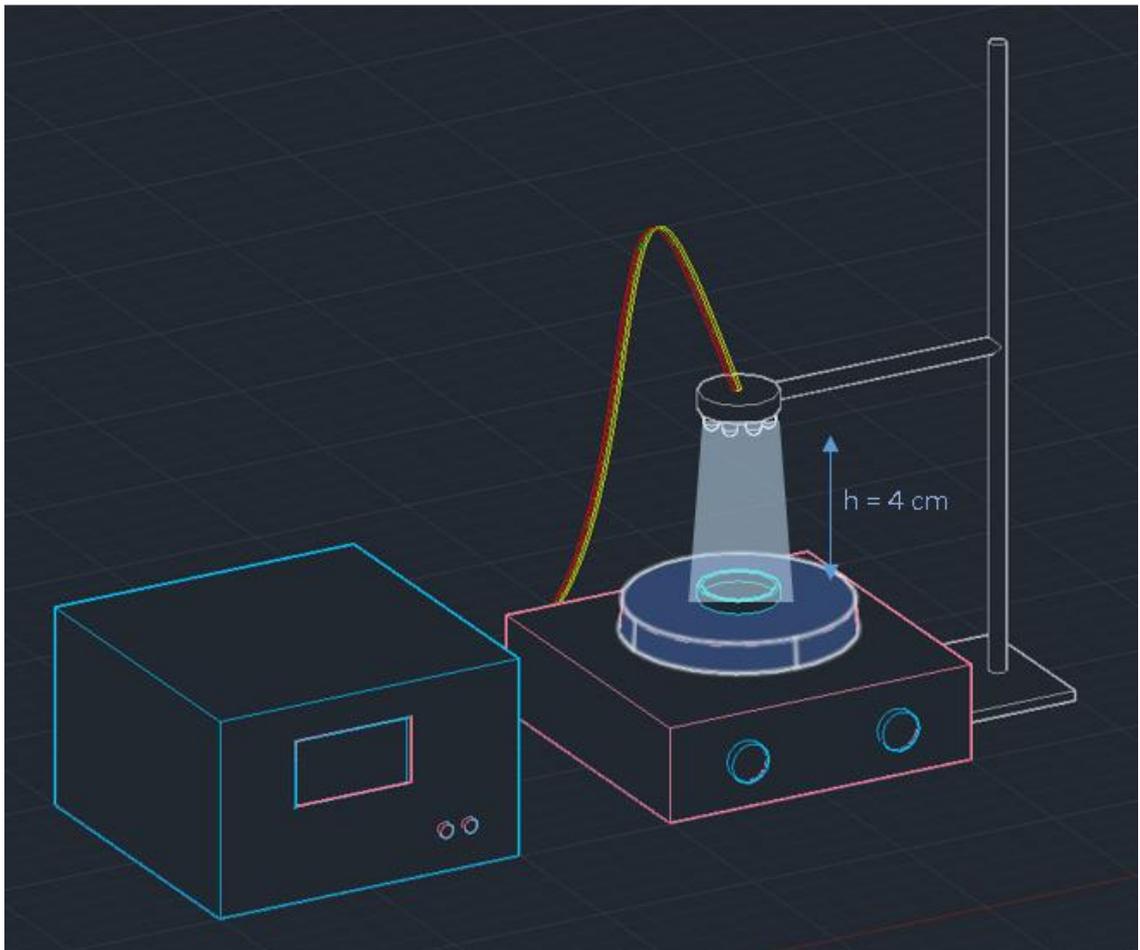
sweetener called Acesulfame Potassium (Ace-K). Effect of  $\text{TiO}_2$ ,  $\text{ZnO}$ , PMS and PDS on degradation Ace-K were investigated. The concept of this research is using UV-LED to reduce the artificial sweetener concentration at the normal condition, without catalysts. Then, adjusting the pH value and concentration in order to choose the optimal condition to add the catalysts. After that, the catalysts were used in order to finalize the optimal condition with the qualified catalyst which gives the highest degradation rate of the contaminants.

Table 2 below is the summary of the advantages and disadvantages of UV-LED system (Mark, 2018)

Table 2. Advantages and disadvantages of UV-LED system (Mark, 2018)

Advantage	Disadvantage
<ul style="list-style-type: none"> <li>- Long life</li> <li>- Environmental-friendly</li> <li>- Higher efficiency with low operation and investment cost</li> <li>- Lower heat output</li> <li>- Easy for changing and replacing</li> </ul>	<ul style="list-style-type: none"> <li>- Not all LED bulbs are dimmable</li> <li>- Light output and colour quality can degrade over the life of the bulb</li> </ul>

Figure 4 describes the structure of an UV-LED system. Following that, the energy source supplies the energy and transform the electricity energy into the optical energy. The UV-LED is put 4 cm high with the petri dish containing the wastewater. The stirring bar in the petri dish stirs the wastewater while treating under UV-LED. The experiments will run from 5 minutes to 120 minutes. Because of the harmfulness of UV-LED, the system must be covered in a close space.



*Figure 4. UV-LED system mechanism*

## 2.4 CATALYSTS AND OXIDIZING AGENTS

### 2.4.1 Catalysts

#### 2.4.1.1 Titan(IV) dioxide (TiO<sub>2</sub>)

Titan(IV) dioxide (TiO<sub>2</sub>) is known as a powerful catalyst for heterogeneous photocatalysis based on their photon adsorption energy about 3.2 eV and wavelengths is lower than ~ 390 nm because of their cost effectiveness, thermal stability, non-toxic compound and capability for oxidation of almost all organic compounds. The ability of TiO<sub>2</sub> depends on its chemical structure, properties, surface area, particle size distribution and band gap energy. When the photon energy is equal or higher than the TiO<sub>2</sub> band gap energy (3.2 eV), the electron will be excited to conductive band and leave a photon hole in valance band. (Umar & Aziz, 2013). Table 3 shows the physical properties of TiO<sub>2</sub> used as catalyst in this research.

Table 3. Physical properties of TiO<sub>2</sub> (Anon., ei pvm)

<b>Chemical formula</b>	TiO <sub>2</sub>	<b>Producing company</b>	Sigma–Aldrick, USA
<b>Molecular weight</b>	79.866 g/mol	<b>Particle size</b>	~ 21 nm
<b>Band gap energy</b> (Umar & Aziz, 2013)	3.2 eV	<b>Wavelength</b> (Umar & Aziz, 2013)	388 nm
<b>Chemical structure</b>	$\text{O}=\text{Ti}=\text{O}$		
<b>Application</b>	<ul style="list-style-type: none"> <li>- crystalline form</li> <li>- developed coated surface</li> <li>- photocatalytic studies on organic compounds</li> <li>- titanium dioxide-cell interations</li> </ul>		

Equation 1 – 3 illustrate the reaction concept of TiO<sub>2</sub> in wastewater. Followed by that, after being reacted by UV radiation, electron in valance band is excited to conductive band and create a positive hole which reacts with water in contaminant to produce hydroxyl radical ( $\bullet OH$ ). Hydroxyl radical attracts and reacts with organic compound and ends up with CO<sub>2</sub> and H<sub>2</sub>O. Moreover, in conductive band, electron can react with oxygen (O<sub>2</sub>) to form anion radical superoxide. (Umar & Aziz, 2013)



Hydroxyl radical and



where R represents for Acesulfame Potassium

The appearance of oxygen in the last equation is necessary for the effectiveness of photocatalytic degradation on organic contaminants which is shown from equation 6-11. The presence of oxygen aims to create an anion radical superoxide which brings to the formation of  $\bullet OH$ . (Abdollahi, et al., 2012)

Table 4 is the advantages and disadvantages of UV/TiO<sub>2</sub> system

Table 4. Advantages and disadvantages of UV/TiO<sub>2</sub> system (Kommineni, et al., 2008)

<b>Advantages</b>	<b>Disadvantages</b>
<ul style="list-style-type: none"> <li>- Can be done at the higher wavelength than other UV process</li> <li>- Can be used in variety of organic pollutants under variety of water qualities</li> <li>- Photostable, cheap and reusable</li> <li>- High activity</li> <li>- Ideal to treat trace micro pollutants</li> </ul>	<ul style="list-style-type: none"> <li>- No full-scale current applications</li> <li>- Required pre-treatment to avoid fouling and destructive restriction of TiO<sub>2</sub>.</li> <li>- The process performance is mostly based on pH.</li> </ul>

In this research, TiO<sub>2</sub> nanopowder is purchased from Aldrich Chemistry (Germany) with the 99.5% purity and particle size is 21 nm

#### **2.4.1.2 Zinc Oxide (ZnO)**

Zinc oxide (ZnO) is irradiately easily under UV light to create the electron and photon-hole pairs as same concept as TiO<sub>2</sub> since a wide-band gap energy is from 3.2 to 3.7 eV. ZnO is an environmental friendly materials, no risks for human and animals. Those equations can be found in the same equation in TiO<sub>2</sub> segment. (Lee, et al., 2016). Table 5 and 6 shows the physical properties of ZnO used as catalyst in this research and its benefits and drawbacks

Table 5. Physical properties of ZnO (Anon., ei pvm)

<b>Chemical formula</b>	ZnO	<b>Producing company</b>	Sigma–Aldrick, USA
<b>Molecular weight</b>	81.408 g/mol	<b>Particle size</b>	< 50 nm
<b>Band gap energy</b> (Umar & Aziz, 2013)	3.6 eV	<b>Wavelength</b> (Umar & Aziz, 2013)	335 nm
<b>Chemical structure</b>	<b>Zn=O</b>		
<b>Application</b> (Wang, 2004)	<ul style="list-style-type: none"> <li>- inorganic compound</li> <li>- soluble in water</li> <li>- additive for producing rubbers, plastics, ceramics, glass,...</li> <li>- used in optics, optoelectronics, catalysis and piezoelectricity.</li> </ul>		

Table 6. Benefits and drawbacks of UV/ZnO system (Lee, et al., 2016)

<b>Advantages</b>	<b>Disadvantages</b>
<ul style="list-style-type: none"> <li>- Cheap catalyst</li> <li>- Wide range to absorb light spectrum than some other metal oxides</li> </ul>	<ul style="list-style-type: none"> <li>- Limit in the visible light region due to its wide band gap energy</li> </ul>

ZnO nanopowder used in this research is supplied by Aldrich Chemistry (Germany) with 97 % and particle size < 50 nm.

## 2.4.2 Oxidizing agent

### 2.4.2.1 Peroxodisulfate (PDS – $S_2O_8^{2-}$ )

Peroxodisulfate (PDS) is a strong oxidizing agent being used in petroleum fields for treating hydraulic fluids (Salari, et al., 2009). PDS usually is found as a salt associated with sodium (Na) or Potassium (K). In this thesis, Potassium Peroxodisulfate (K-PDS) is used. Under the impact of UV-LED radiation,  $S_2O_8^{2-}$  is transformed to  $\bullet SO_4^-$ , similar to  $\bullet OH$ ,  $\bullet SO_4^-$  is able to interact with organic compounds. (Raharinirina, et al., 2009). The detail descriptions is shown from Eq 4 to 7. Table 7 shows the characteristics of K-PDS.

Table 7. Characteristics of PDS

<b>Chemical formula</b>	$K_2S_2O_8$	<b>Producing company</b>	Sigma-Aldrich
<b>Molecular weight</b>	270.32 g/mol	<b>Particle size</b>	No data
<b>Oxidation potential</b> (Gao, et al., 2012)	2.01 V	<b>Wavelength</b> (Gao, et al., 2012)	350 nm
<b>Chemical structure</b> (Sigma-Aldrich, 2017)	$  \begin{array}{c}  \text{O} \qquad \qquad \text{O} \\  \parallel \qquad \qquad \parallel \\  \text{KO}-\text{S}-\text{O}-\text{O}-\text{S}-\text{OK} \\  \parallel \qquad \qquad \parallel \\  \text{O} \qquad \qquad \text{O}  \end{array}  $		
<b>Application</b> (Wikipedia, 2016)	<ul style="list-style-type: none"> <li>- PDS can be used as initiator for many alkenes, curing agents in polymerization, surface preparation for coating processes, adhesive preparation.</li> <li>- PDS is known as strong oxidants producing sulfate radicals to interact with organic pollutants in wastewater.</li> </ul>		

Equation 4 to 7 present the PDS reaction with UV-LED radiation (Gao, et al., 2012)



Table 8 shows the benefits and drawbacks of PDS. PDS is purchased from Sigma (Germany) with 99% purity.

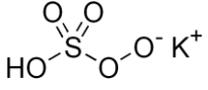
Table 8. Advantages and disadvantages of PDS

<b>Advantages</b> (Khan & Adewuyi, 2011)	<b>Disadvantages</b> (Sessa, et al., 2006)
<ul style="list-style-type: none"> <li>- Oxidizing agent produces <math>\cdot SO_4^-</math> for treating wastewater.</li> <li>- Stable compounds as chemical oxidation for decreasing pollutants</li> </ul>	<ul style="list-style-type: none"> <li>- High cost to apply in field applications</li> </ul>

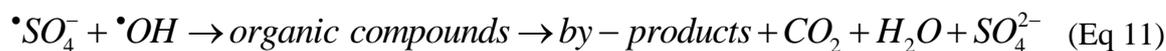
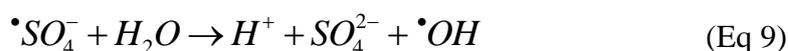
#### **2.4.2.2 Peroxomonosulfate (PMS – HSO<sub>5</sub><sup>-</sup>)**

Peroxomonosulfate (PMS) can be the combination of peroxomonosulfuric acid and salt, e.g. Sodium (Na) or Potassium (K). PMS is known as a powerful oxidant which is capable to oxidize variety of organic compounds. During treating contaminant under UV light, PMS create sulfate radical ( $\cdot SO_4^-$ ) and hydroxyl radical ( $\cdot OH$ ) with the high standard redox potentials are 2.6V and 2.73V, respectively. (Luo, et al., 2015). Table 9 presents the physical properties of potassium peroxomonosulfate (KHSO<sub>5</sub>).

Table 9. Physical properties of potassium peroxomonosulfate

<b>Chemical formula</b>	$H_3K_5O_{18}S_4$	<b>Producing company</b>	ACROS Organics
<b>Molecular weight</b>	614.78 g/mol	<b>Particle size</b>	No data
<b>Oxidation potential</b> (Verma, et al., 2016)	1.82 eV	<b>Wavelength</b> (Verma, et al., 2016)	260 nm
<b>Chemical structure</b>			
<b>Application</b> (Ghanbari & Moradi, 2017)	<ul style="list-style-type: none"> <li>- PMS can be used for real wastewater treatment</li> <li>- PMS can be applied for polluted air, soil and sludge</li> <li>- PMS is a strong oxidant being used in photolysis method to remove organic contaminants by producing <math>\bullet OH</math> and <math>\bullet SO_4^-</math>.</li> </ul>		

Equation 8 – 11 represent the formation of hydroxyl radicals ( $\bullet OH$ ) and sulfate radicals ( $\bullet SO_4^-$ ) which react with wastewater. Based on the equations below, the PMS reactions will end up with  $CO_2$ ,  $H_2O$ , sulfate ( $SO_4^{2-}$ ) salts and by-products (if any) (Ghanbari & Moradi, 2017)



Benefits and drawbacks of PMS is shown in table 10 below

Table 10. Advantages and disadvantages of PMS (Kennedy &amp; Stock, 1960)

<b>Advantages</b>	<b>Disadvantages</b>
<ul style="list-style-type: none"><li>- Stable compound</li><li>- Wide range of applications (cleaning, disinfection, wastewater treatment and so forth)</li></ul>	<ul style="list-style-type: none"><li>- Cause unexpected compound while using in pools</li></ul>

PMS is obtained from ACROS Organics (extra pure, minimum 4.5% active oxygen)

## 2.5 Artificial sweeteners

Artificial sweeteners are the compound of synthesis chemical containing no-calories can be used as a substituted sugar in food industry, drink industry, pharmaceutical and sanitary products (Gan, et al., 2013). Artificial sweeteners have been known as emerging contaminants as they can be used in various sectors and persist in water (Li, et al., 2016). Known as sugar substituted compound, artificial sweeteners are usually sweeter than sugar in order to decrease the material cost and the sweet taste is still remaining. In this research, acesulfame potassium (Ace-K) is used as a contaminant reduced by using photocatalysis and catalysts.

## 2.6 Acesulfame potassium (Ace-K)

Acesulfame potassium (Ace-K) is known as an artificial sweetener which is approximately sweeter than sucrose 200 times, has no calories, cannot be metabolized in human body and unchanged when excreted (Whitehouse, et al., 2008). Ace-K was found in 1967 by chemist Karl Clauss accidentally. It can be found in beverages, frozen products and baked ingredients (Whitehouse, et al., 2008). Formula of Ace-K is  $C_4H_4KNO_4S$  with the molecular weight of 201.24 g/mol, with the chemical structure presented in figure 5. Ace-K is an odourless, white and crystalline powder which is very soluble in water and slight soluble in ethanol (Anon., 2017). Ace-K is commonly determined in ground, surface and wastewater (Liu, et al., 2014). Studies have proved that absorbing Ace-K with high dose results to clastogenic and genotoxic (Whitehouse, et al., 2008).

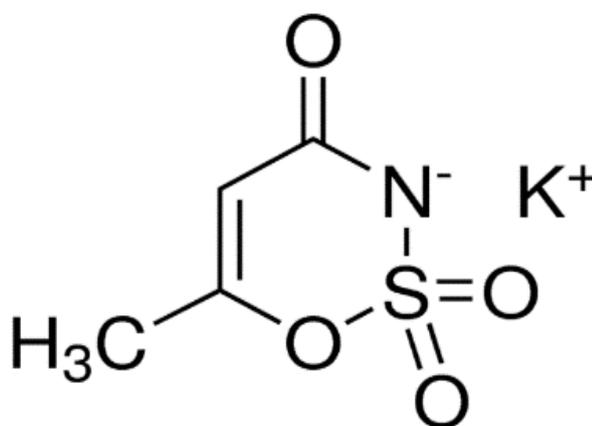


Figure 5. Chemical structure of acesulfame potassium (Anon., 2017)

Ace-K is proved to be very persistent in wastewater during treatment of drinking water. Thus, the presence of UV radiation and catalysts in order to reduce the amount of Ace-K in wastewater are very important. As mentioned in (Scheurer, et al., 2014), Ace-K transformation after treating can be ended up with amidosulfonic acid, sulfate, hydroxyl acesulfame or iso-acesulfame by UV light. (Scheurer, et al., 2014). Ace-K was reported that can be degraded by using photolysis under UV light; however, the compound is considered to be very persistent in wastewater with activated sludge process as well as soil passage (Castronovo, et al., 2017). Table 11 shows the applications, benefits and drawbacks of Ace-K.

Table 11. Advantages and disadvantages of Ace-K

<b>Application</b>	<ul style="list-style-type: none"> <li>- Artificial sweetener in beverage and food</li> <li>- Personal care products</li> <li>- Medicine industry</li> </ul>
<b>Benefit</b>	<ul style="list-style-type: none"> <li>- Artificial sweetener which is sweeter than sucrose 200 times.</li> <li>- Used as a flavor-enhancer.</li> <li>- Prevent the sweetness in food and beverage.</li> </ul>
<b>Drawback</b>	<ul style="list-style-type: none"> <li>- Long-term exposure can cause headache, depression, nausea, mental confusion, liver and kidney effects, visual disturbances and cancer.</li> </ul>

## 2.7 Method

### 2.7.1 TOC

Total Organic Carbon (TOC) measures the organic molecule's presence as carbon in wastewater indirectly. TOC is understood as the amount of carbon found in an organic compound. The TOC analyser includes three functions: (Tekmar, n.d.)

- Oxidize organic carbon in wastewater to CO<sub>2</sub>
- Measure the amount of CO<sub>2</sub> produced.
- Analyze and convert the result in mass of carbon out of a volume of sample.

Because of the strong relationship of Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD), TOC measurement was built in 1970s. Nowadays, TOC is known as a wide-used method for testing the amount of organic molecule's presence (as carbon) in wastewater. (Tekmar, n.d.).

In this topic, the samples are prepared as followed description:

- Adding 2ml wastewater into the digestion cuvette cell, shake the cuvette cells in 5 minutes.
- Closing the double cap tightly with the CO<sub>2</sub>-permeable membrane side covering the digestion cuvette.
- Changing the cap of the indicator cuvette to another side of the double cap above.
- Leaving the those sample with the indicator cuvette above the digestion cuvette (do not scratch and remove the barcode in the double cap).
- Putting all samples in the oven at 100°C for 120 minutes.
- After heating, leaving those samples outside in order to cool down
- Using the spectrophotometer to test the amount of CO<sub>2</sub>
- Depending on the CO<sub>2</sub> inflow rate, the color of the indicator solution in the indicator cuvette changes

The spectrophotometer used in this topic is Hach DR2800 portable spectrophotometer.

### 2.7.2 GC – MS

Gas chromatography – Mass Spectrometry (GC-MS) is a composite word between Gas Chromatography (GC) and Mass Spectrometry (MS). Function of GC is to classify volatile and non-volatile organic compounds; however, GC cannot detect them. Thus, MS is included in the system in order to optimize the function of the system, because of its detection ability which detect variety of compounds. (Sneddon, et al., 2007). GC – MS can be divided into two main phases: (Piantanida & Barron, 2014)

- The stationary phase: depending on the form of the stationary phase, there are two types of GC, 1) GSC is the gas-solid chromatography with the solid stationary phase and 2) GLC using liquid stationary phase is standed for gas-liquid chromatography.
- The mobile phase: transports the vapourized sample to column. The separation of different compounds depends on their relative vapour pressure and the attraction of stationary phase.

There are 4 units in GC – MS system: (Piantanida & Barron, 2014)

- Carrier gas (mobile phase): transport the sample molecules through column while the stationary phase can not dissolved or adsorbed them. Carrier gas plays role as an inert that does not contact with sample →the separation and selectivity of GC is occurred in stationary phase only.
- Injector: where the samples is volatilized. Injecting the sample can be done manually or automatically by using syringe.
- Column: where the sample components after separation sits. There are two main type of used columns: packed column and capillary column. Since the higher benefits, nowadays, capillary comlumn is commonly used.
- Detector: after separation, the result is sent to detector as an electronic signal in order to produce a chromatogram.

Table 12 below presents the pros and cons of GC-MS (Piantanida & Barron, 2014)

Table 12. Advantages and disadvantages of GC-MS method

<b>Pros</b>	<b>Cons</b>
<ul style="list-style-type: none"> <li>- Suitable for separating complex mixture.</li> <li>- Accurate quantitation</li> <li>- Mature technique → a lot of application for various demand</li> </ul>	<ul style="list-style-type: none"> <li>- Thermally stable and volatile compounds limitations.</li> </ul>

In this thesis, GC – MS (Agilent – GC 6890N, MS 5975) with agilent DB-5MS column dimensions 30 mm, 0.25 mm, 0.25  $\mu\text{m}$  is used.

- The inlet temperature is 250°C
- The injection volume is 1  $\mu\text{l}$
- The oven temperature is 65°C in 2 minutes and raises to 180°C (hold in 1 minute) with the rate of 30°C/min. After that, the temperature is raised up to 280°C (hold in 1 minute) with the rate of 7°C/min. Finally, the temperature is increased to 300°C (hold in 3 minutes) with the rate of 40°C/min.

The samples were prepared by using 3 ml of methanol, pure water, wastewater (after treating under UV-LED) and methanol filtrate to sample tubes, respectively. Then, all sample were added 20  $\mu\text{l}$  of N-methyl-N-(trimethylsilyl). After that, all samples were placed in the oven at 50°C in 40 minutes before measuring.

### 2.7.3 HPLC

High Performance Liquid Chromatography (HPLC) is a separation technique which is built in 1950s and 1960s due to the purpose not only to synthesize and purify compound but also for crystallization, extraction and distillation techniques. At that time, the first chromatography system involves a column and an eluent container which is installed above the column. Followed by that, the sample was put manually in the head of the column and also the column was installed with the containers. However, that chromatography version was lack of high level with automation and did not have pump. Thus, in 1970s, in order to

increase the separation power, HPLC system was improved with high-pressure pump and the column with smaller particle size. (Huber & Majors, 2007)

Nowadays, HPLC is developed and becomes a standard method which is used in a lot of fields for analysis and experiment, e.g. pharmaceutical, biotechnology, chemical, environmental and food technology (Bhanot, 2012). Because of the wide application fields, HPLC becomes a priority choice of method for analysing various compounds. (Blitz, 2000). HPLC is known as a separation technique including 3 units: (Blitz, 2000)

- The input board: small amount of liquid sample is injected.
- Stationary phase: a tube packed with polar tiny particles (3 – 5  $\mu\text{m}$ )
- Column is packed tube which the samples are moved along with liquid (mobile phase) affecting on column by high-pressure pump

There are four main process using in HPLC system: (Giri, 2015)

- *Normal Phase*: is defined by the transportation from non-polar mobile phase to polar stationary phase. Thus, the stationary is usually silica and mobile phase is usually organic compounds, such as, hexane, methylene chloride, chloroform, diethyl ether or even the mixture of them.
- *Reverse phase*: in contrast with normal phase, the transportation is from the mobile phase as a polar liquid to stationary as non-polar (hydrophobic) in nature. In this case, the mobile phase can be the mixtures of water and methanol or acetonitrile.
- *Size-exclude*: The pore sizes fills the column and the particles are differentiated based on their molecular size. Large moleculars are washed in column and smaller ones are adsorbed to the packing particles and elute.
- *Ion-exchange*: The stationary phase is a surface with ironical charges which contrast with the charge to the ions in samples. The technique can be understood as the stronger charges the samples have, the more attractive it will be to the stationary phase → as long as they spent, as much as it takes to be cleaned. The mobile phase is an aqueous buffer where can control the elution time by pH and the strength of ion.

Reverse phase HPLC is the most common used because of their ease to use, the application in wide range of molecules. There are 6 main components in an HPLC equipment:

- *Solvent container*: where mobile phase is taken place.
- *Pump*: which forces the mobile phase to the column and detector
- *Injection*: where syringe inject the liquid sample automatically to bring to the column with the mobile phase solvent by pump.
- *Column*: usually polished stainless steel from 50 to 300 milimeter long with internal diameter from 2 – 5 mm.
- *Detector*: is taken place at the end of the column in order to detect the signal from column. Used detectors are usually UV-spectroscopy, fluorescence, mass-spectrometric and electrochemical detectors.
- *Data acquisition*: the signal is detected by detectors is transferred to peek and return the result as peek in graph for the data acquisition.

In this research, HPLC system supplied by SHIMADZU® with Phenomenex C18 column (5  $\mu\text{m}$ , 150 mm x 4.6 mm) with UV detector at wavelength 230 nm was used to measure the concentration of Ace-K and initial Ace-K solution. The mobile phase solvent was prepared by mixing ammonium acetate and methanol with ratio of 95/5. Injection flow rate was maintained at 1 ml/min.

The given table below presents the pros and cons of using HPLC method.

Table 13. Advantages and disadvantages of HPLC method (Burdick, 2018)

<b>Pros</b>	<b>Cons</b>
<ul style="list-style-type: none"> <li>- Beter sensibility</li> <li>- Beter selectivity</li> <li>- Quantification of analytes</li> <li>- Faster speed than reverse phase</li> <li>- Possibility to use elution gradient</li> </ul>	<ul style="list-style-type: none"> <li>- Coelution due to the different polarities of two compounds with same structure can exit at the same time.</li> <li>- Adsorbed compounds</li> <li>- Cost</li> <li>- Complexity</li> </ul>

## 2.8 Experiment stages

Those stages below describe the experimental steps to treat Ace-K under UV LED

- (1) Prepare the Ace-K solution with the normal pH (around 5.5 – 5.7), pH2, pH3, pH4 and pH5 (with the concentrations of 1 ppm, 2 ppm, 3 ppm, 4 ppm, 5 ppm, 6 ppm).
- (2) For each sample, 10 ml Ace-K solution is taken in order to do treatment under UV-LED in 5 minutes, 10 minutes, 15 minutes, 30 minutes, 45 minutes, 60 minutes, 75 minutes, 90 minutes, 105 minutes and 120 minutes.
- (3) After treatment under UV-LED, each sample is taken to cuvette to test HPLC. The result is shown as a concentration of solution before and after the treatment. The result in this research is the degradation rate with the equation can be found in Eq 12. Followed by the result after testing HPLC, the optimal condition (with the optimal pH and concentration) is figured out in order to prepare samples for doing treatment with catalysts and oxidizing agents. HPLC preparing samples and measurement are mentioned in HPLC segment.
- (4) The optimal condition is used to add catalysts/oxidizing agents. In details, in order to research the optimal amount of added catalysts, 0.5 mgr, 1 mgr and 1.5 mgr catalysts/oxidants are added for each sample.
- (5) Repeat the step 2 by taking 10 ml Ace-K solution with catalysts/oxidants and doing treatment under UV-LED with the same time in step 2.
- (6) Samples are taken to the cuvettes and tested HPLC as same as step 3. Also, the degradation in the result is used to compare and choose the optimal condition (with the optimal pH, concentration and amount of used catalysts/oxidants)
- (7) After all treatment and testing, TOC test and GC test are used in order to test the amount of CO<sub>2</sub> and by-product pathway containing in the solution before and after treatment. The TOC and GC measurements are mentioned in TOC segment and GC segment above.

$$Deg. rate = \frac{(C_i - C)}{C_i} \times 100 \quad (Eq 12)$$

As mentioned in (Coiffard, et al., 1999), there are two optimal pH value for degrading the concentration of Ace-K solution, pH3 and pH12. At those pH value, the  $\frac{C}{C_i}$  is about 0.455 and 0.355, respectively (Coiffard, et al., 1999). Thus, this thesis focuses on degrading the Ace-K concentration in the solution with pH ranges from 2 to 5. And because of the time limitation, pH12 is not researched and mentioned as a result in this thesis.

As mentioned in (Scheurer, et al., 2014), the concentration of Ace-K is proved to be very persisted up to 2.5 ppm. Thus, in this thesis, the concentration of Ace-K will be tested around 2.5 ppm in order to study the stability of Ace-K in wastewater and the optimal treatment conditions to treat the low concentration of Ace-K in wastewater.

### 3 RESULT AND DISCUSSION

#### 3.1 HPLC Result for treatment without catalyst/oxidant

##### 3.1.1 Ace-K at normal pH (5.5-5.7) concentration 1 ppm – 6 ppm

From previous researches, the pH range of Ace-K was about 2.5 to 9. Also Coiffard mentioned in his research, the optimal pH value in order to degrade the concentration of Ace-K in their wide pH range was 3, 9 and 12 ppm (Coiffard, et al., 1999). In this research, due to the limitation of time, the pH range was decided around 3ppm. Followed by that, the pH range tested was from 1 – 6 ppm. Moreover, as mentioned in (Scheurer, et al., 2014), Ace-K was not perceptible to absorb UV light if the concentration of Ace-K was from 10 ppm to 50 ppm.

At the first time, the experiment was started with the normal and standard conditions of the solutions (pH form 5.5 – 5.7) and the concentration was tested from 1 – 6 ppm. Figure 11 presents the degradation rate of standard Ace-K with concentration from 1 – 6ppm and treatment is from 5 minutes to 120 minutes.

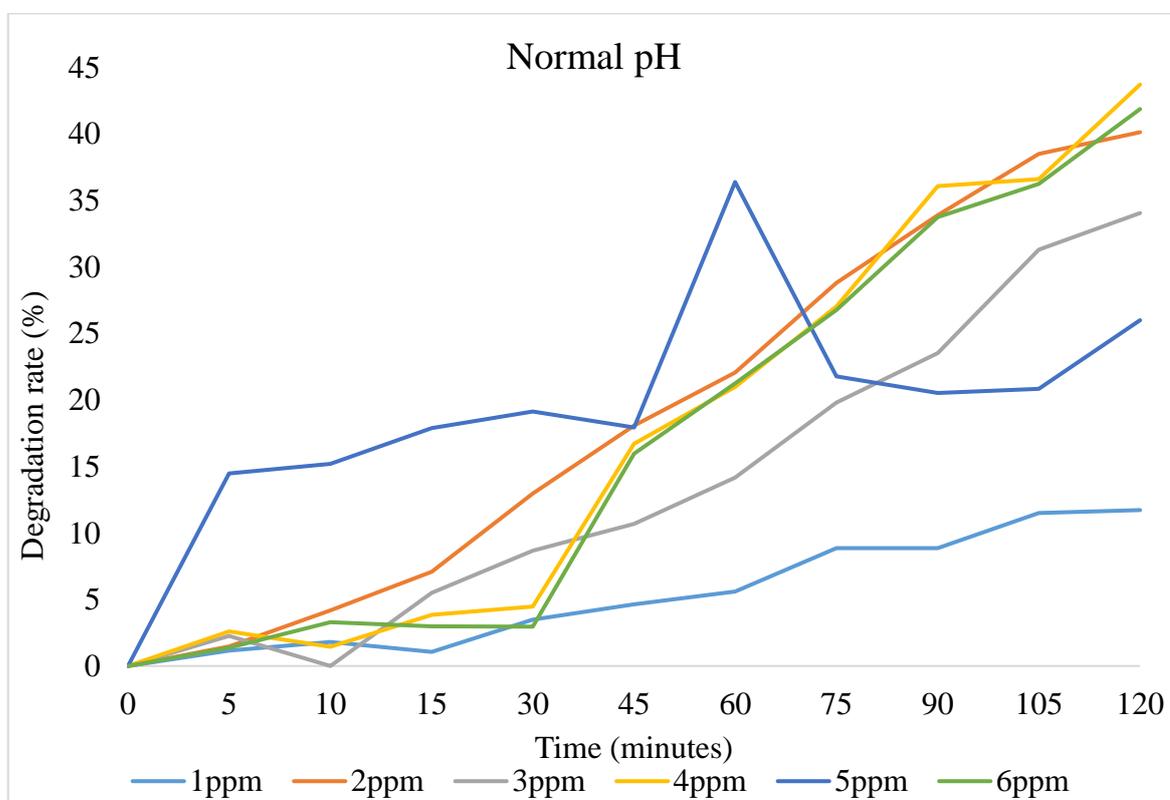


Figure 6. Degradation rate of Ace-K in normal pH (5.5 – 5.7) at concentration 1 – 6 ppm

As observed from figure 6, with normal pH (5.5 – 5.7), 2 ppm, 3 ppm, 4ppm and 6 ppm could be considered to be the optimal condition for further experiments due to the increasing ability. In details, the increase of degradation rate at 2, 3, 4 and 6 ppm was dramatic through time while at 1 ppm, the degradation rate increases steadily and at 5 ppm, the increasing rate was unstable.

In conclusion, after the first treatment result, concentration 2, 3, 4 and 6 ppm were chosen for adjusting pH value in order to figure out the highest and most stable condition for adding catalysts and oxidants.

After observing the result of Ace-K at normal pH (5.5 – 5.7), experiments of Ace-K are repeated with pH 2, 3, 4 and 5 at the same concentrations.

### 3.1.2 Ace-K at pH 2 concentration 2 ppm, 3 ppm, 4ppm and 6 ppm

pH was studied as an influence agent which affect the transformation of Ace-K as anion in solution. The anions in aqueous phase were formed into acceptable end products, such as CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, etc. Following the formation stage, the concentration of Ace-K contaminants in solution decreased.

Firstly, pH2 was used to treat in order to test the influence of pH for the degradation ability. The result of the degradation of Ace-K with pH2 is shown below.

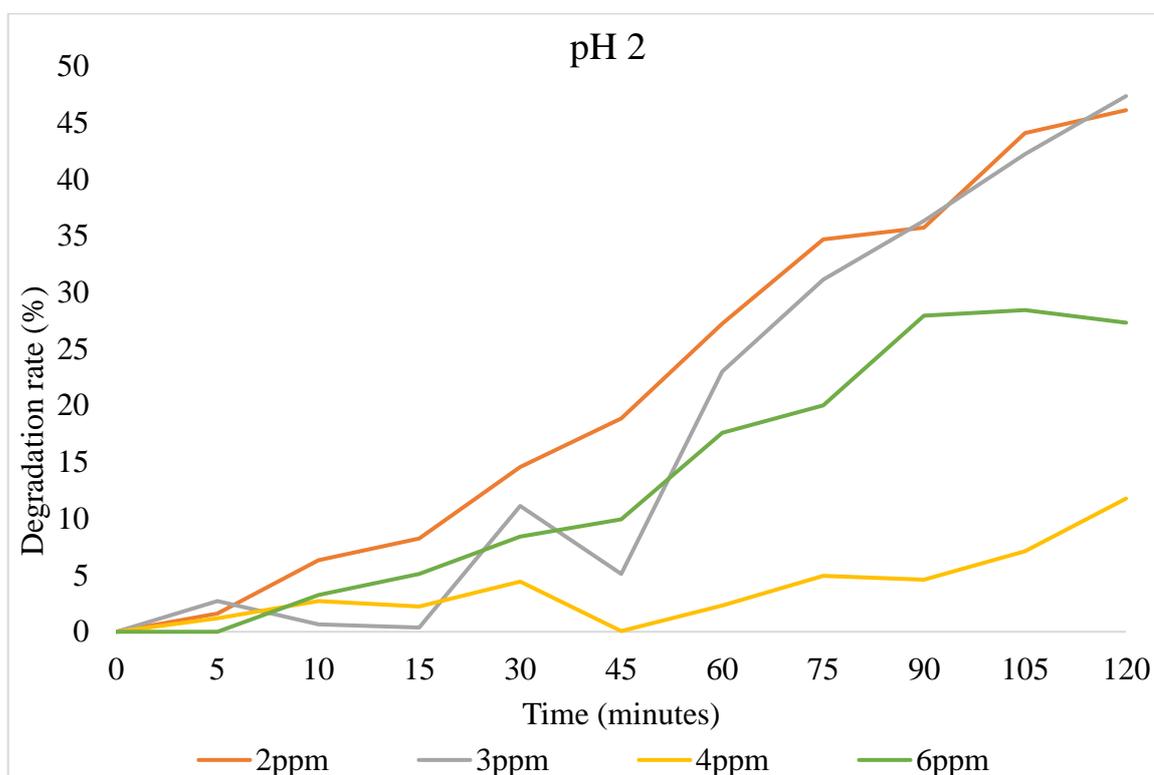


Figure 7. Degradation rate of Ace-K in pH 2 at the concentration 2, 3, 4 and 6 ppm

pH 2 at 2 ppm, 3ppm, 4 ppm and 6 ppm is shown in figure 7. Based on that, the increase in the degradation rate of Ace-K was higher than normal pH for 2 ppm and 3ppm. However, the increase was not significant due to the optimal pH for treating Ace-K in solution at 3 ppm (Coiffard, et al., 1999). In addition, the degradation rate at 4 and 6 ppm was smaller than the degradation rate at normal pH condition. This might occur due to the high concentration of Ace-K which was brought to the limitation of UV light absorption and the incomplete effect of low pH value (Scheurer, et al., 2014).

### 3.1.3 Ace-K at pH 3 concentration 2 ppm, 3 ppm, 4 ppm and 6 ppm

Second, pH3 was used for the next treatment and the result is shown below

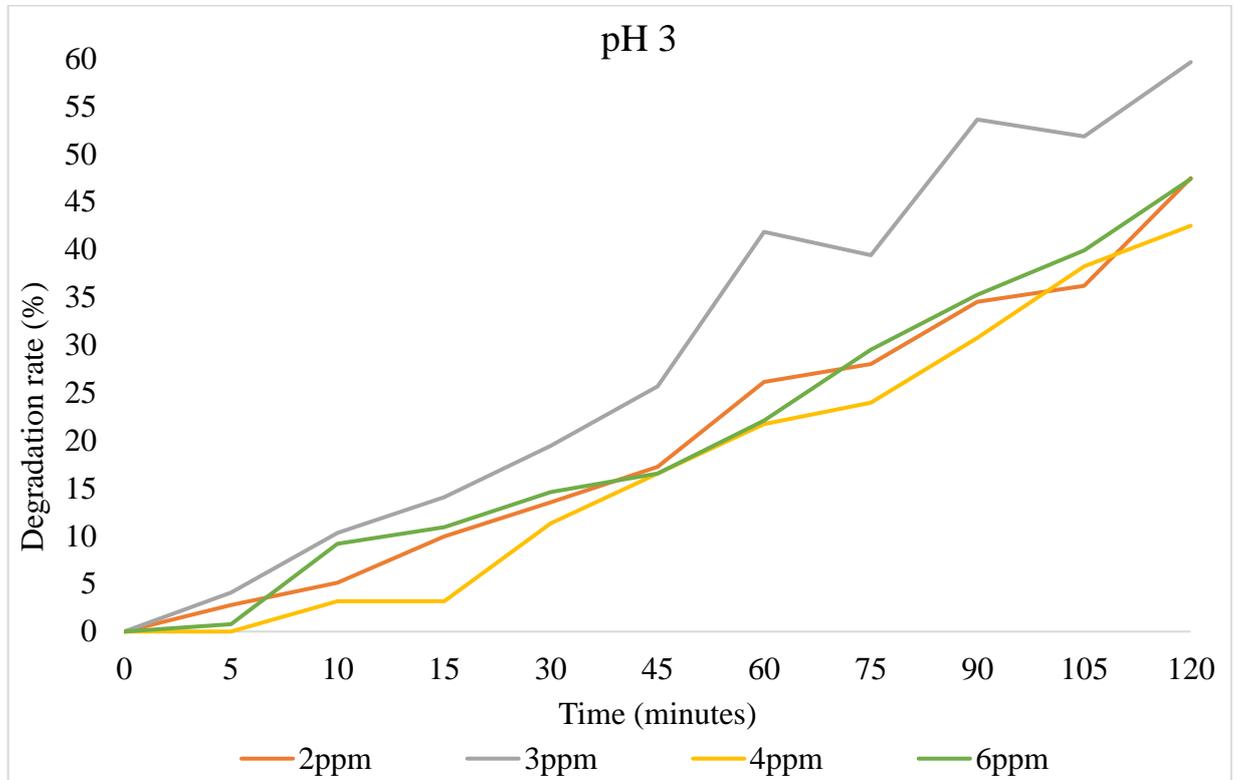


Figure 8. Degradation rate of Ace-K in pH 3 at the concentration 2, 3, 4 and 6 ppm

As observed from figure 8, the degradation rate of Ace-K in solution increased dramatically. This shows the same result which is studied in (Coiffard, et al., 1999). Followed by that, at pH 3 and pH 12, the decrease of Ace-K concentration was highest. pH 3 was shown the optimal condition for experience in this research. Moreover, the degradation at 3 ppm was significantly higher than the concentration at 2, 4 and 6 ppm as in figure 8 above.

In conclusion, between pH 2 and pH 3 with concentration 2, 3, 4 and 6 ppm, 3 ppm at pH 3 is the best result with 120 minutes treatment (more than 55% comparing with 30% degradation rate for normal pH and 45% degradation rate for pH 2).

### 3.1.4 Ace-K at pH 4 concentration 2 ppm, 3 ppm, 4 ppm and 6 ppm

The increasing in the pH value also brought to the influence in the concentration degradation. Figure 9 presents the degradation rate of Ace-K with pH4.

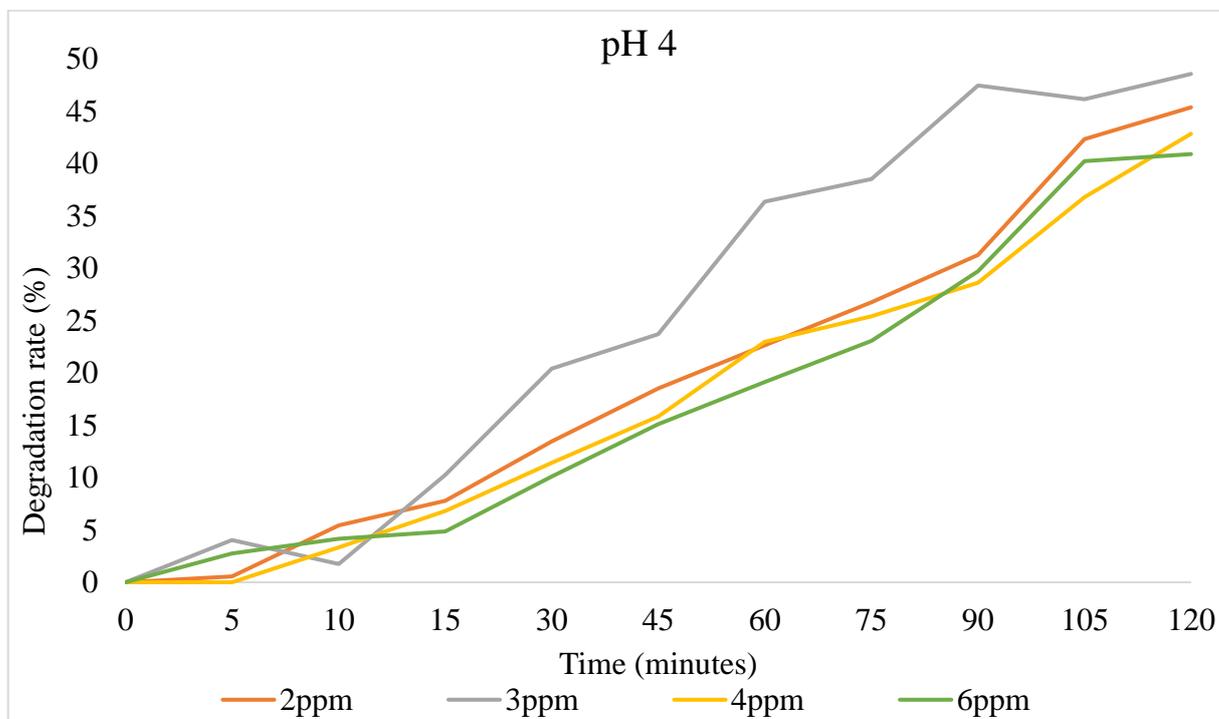


Figure 9. Degradation rate of Ace-K in pH at the concentration 2, 3, 4 and 6 ppm

Based on the figure above, the increase of degradation was significant. In details, the anions Ace-K forming in solution, which reformed to acceptable end products, were higher than the amount of the end products at normal pH, pH2 and same with pH3.

Besides, the degradation ability at 3ppm for pH4 reached the highest value compared with 2, 4 and 6 ppm. However, compared with 3ppm, pH3, the degradation rate of Ace-K in 3 ppm, pH4 was lower. As mentioned in (Scheurer, et al., 2014), with the high concentration of Ace-K, the limitation of UV light absorption was proved due to the treatment time, pH value.

### 3.1.5 Ace-K at pH 5 centration 2 ppm, 3 ppm, 4 ppm and 6 ppm

Figure 10 illustrates the degradation rate of Ace-K at pH 5 and concentration 2 ppm, 3 ppm, 4 ppm and 6 ppm.

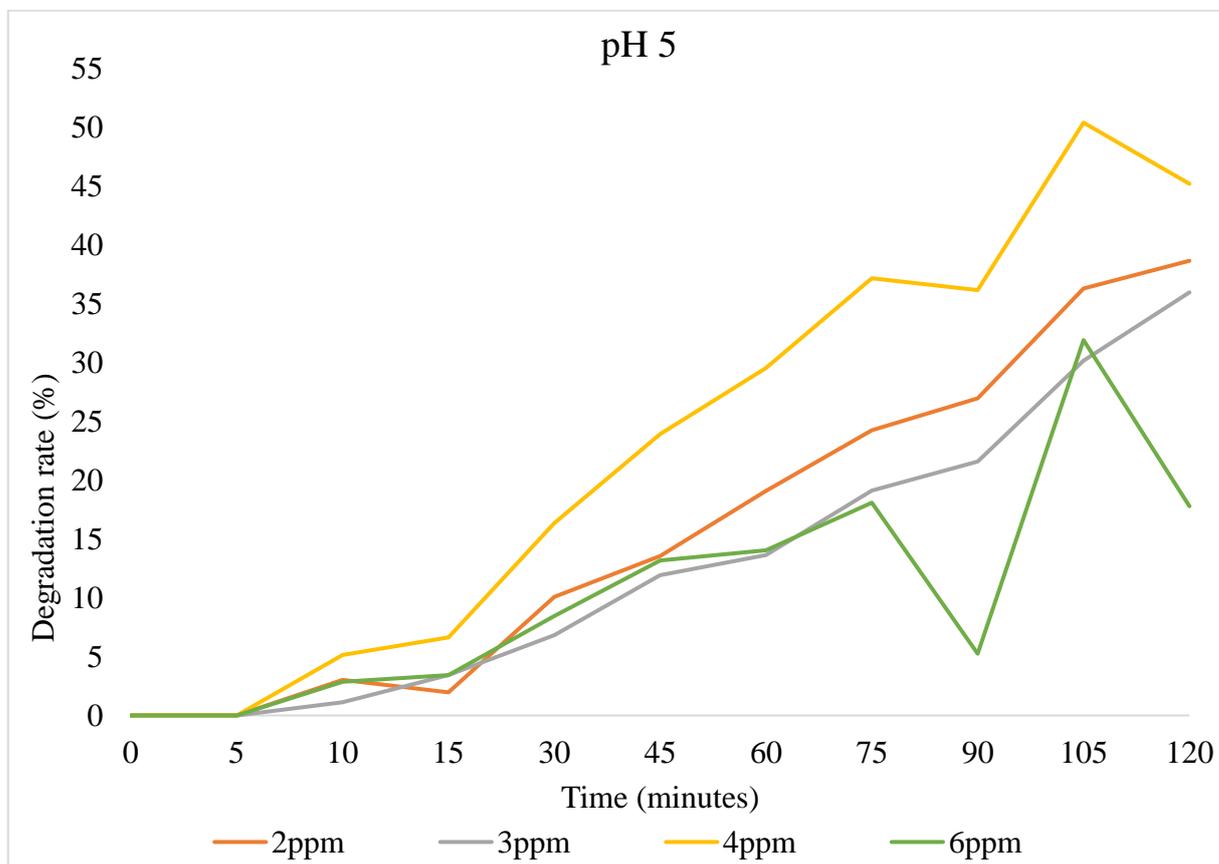


Figure 10. Degradation rate of Ace-K in pH 5 at the concentration 2, 3, 4 and 6 ppm

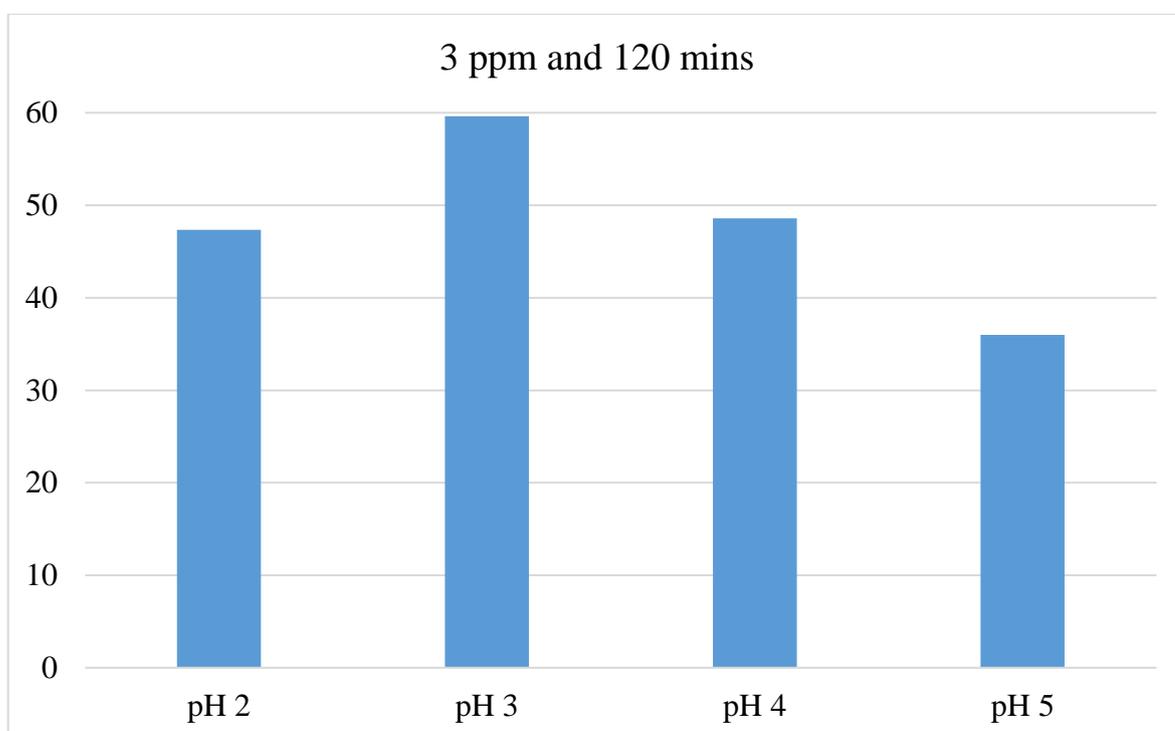
Based on figure 10, as similar with the degradation rate of Ace-K at pH 2, pH 3 and pH 4, in pH5, the increase of the degradation rate of Ace-K was compared with the degradation rate of Ace-K at normal pH condition. However, there was a sharp fluctuation at the end of 4 ppm and 6 ppm. The result could be shown in figure 10 due to the high reformation of anion Ace-K in solution. In addition, Coiffard also mentioned in his research, the optimal pH values for the best degradation rate of Ace-K were pH 3 and pH 12 (Coiffard, et al., 1999). Thus, degradation rate of Ace-K at pH 5 could not reach the optimal result.

In conclusion for the first stage of treatment, treating Ace-K pollutants in solution by adjusting pH and the suitable concentration were concerned. Due to the effect of UV light to treat Ace-K contaminant in solution, normal pH showed the basic phototransformation of

Ace-K with the highest degradation rate is 45%. By adjusting pH value, the degradation rate of Ace-K increased due to the effect of pH to anion of Ace-K in solution.

Based on the result above, after normal pH treatment, 2 ppm, 3 ppm, 4 ppm and 6 ppm were chosen in order to use for adjusting pH treatment. Because the HPLC results of 1 ppm and 5 ppm were not positive for the next experiment stage and also for the time limitation, the adjusting pH experiments for 1 ppm and 5 ppm were not done. Following all the result after adjusting pH experiments, 3 ppm at 120 minutes of Ace-K showed the optimal concentration with.

The figure 11 below is the comparison between pH 2, pH 3, pH 4 and pH 5 at concentration 3 ppm and pH3



*Figure 11. The comparison between pH 2, pH 3, pH 4 and pH 5 at 3 ppm and 120 minutes*

As studied from figure 11, at pH 3, the highest degradation was shown which is nearly 60%. The next stage of experiment would use the optimal conditions at 3 ppm, pH 3 in 120 minutes.

### **3.2 HPLC Result of treatment with catalyst/oxidant**

After the previous treatment, the optimal condition with the pH value, concentration were figured out with pH3 of the solution and 3 ppm concentration of Ace-K. These next experiments below were aimed to find out the highest and the most beneficial catalyst/oxidizing agent and its dosage using optimal condition as mentioned earlier. The experiments were done with three amounts of catalysts/oxidizing agents (0.5 mgr, 1.0 mgr and 1.5 mgr).

Because of the high efficient photoactivity, stability, low-cost, humans and environmental safety,  $\text{TiO}_2$  was used as suitable catalyst for almost all the degradation of contaminants in the environment (Hashimoto, et al., 2005). For ZnO, C, N and S non-metals were doped with ZnO by the effect of UV-LED process (Hossaini, et al., 2017). The combination of  $\text{TiO}_2$  or ZnO as catalysts and UV-LED generates hydroxyl radicals which could react with the organic contaminants in solution to produce acceptable end products. Besides, the effect of PDS and PMS was also researched in this thesis with the generation of sulfate radicals (in both PDS and PMS) and hydroxyl radicals (in PMS) reacting also with organic contaminants in solution and ending up with acceptable end products (Luo, et al., 2015).

#### **3.2.1 Ace-K at pH 3 centration 3 ppm with $\text{TiO}_2$**

As mentioned above,  $\text{TiO}_2$  was observed as the most commonly used catalyst with its high photoactivity which could be used to degrade the concentration of compound in solution. Figure 12 below describes the degradation rate of Ace-K in solution with three amount of  $\text{TiO}_2$ : 0.5 mgr, 1.0 mgr and 1.5 mgr.

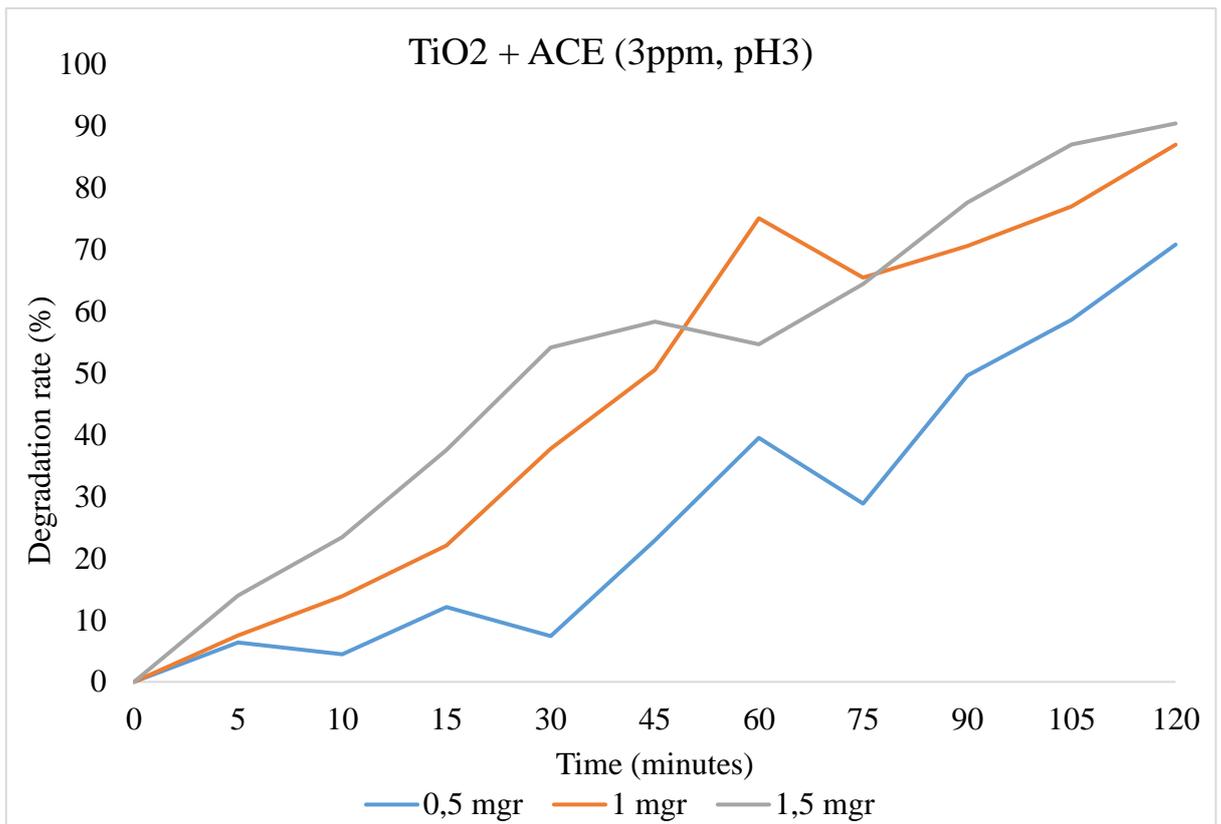


Figure 12. Degradation rate of Ace-K in pH 3, 3ppm and TiO<sub>2</sub>

As observed in figure 12, the degradation rate trend increased significantly. As easily compared between the treatment without TiO<sub>2</sub> and with TiO<sub>2</sub>, the degradation rate was increased from 59% (without TiO<sub>2</sub>) to nearly 70%, over 80% and 90% for 0.5 mgr, 1.0 mgr and 1.5 mgr of TiO<sub>2</sub>, respectively. The changes might happen due to the hydroxyl radicals reactions which are expressed from equation 1 to equation 3. Followed by that, the TiO<sub>2</sub> would be decomposed to create hydroxyl radicals under ultraviolet radiation, reacted with wastewater and ended up with acceptable end products. (Umar & Aziz, 2013)

In this result, at 1.5 mgr of TiO<sub>2</sub>, the degradation was reached the highest rate with 90.4% of Ace-K solution degraded in 120 minutes.

### 3.2.2 Ace-K at pH 3 centration 3 ppm with ZnO

After TiO<sub>2</sub>, ZnO was known as a second strong and highly efficient compound in reducing the organic contaminants under ultraviolet conditions with its photoactivity ability. Figure 13 demonstrates the effect of ZnO on the degradation rate of Ace-K in solution at the optimal conditions as found in the beginning.

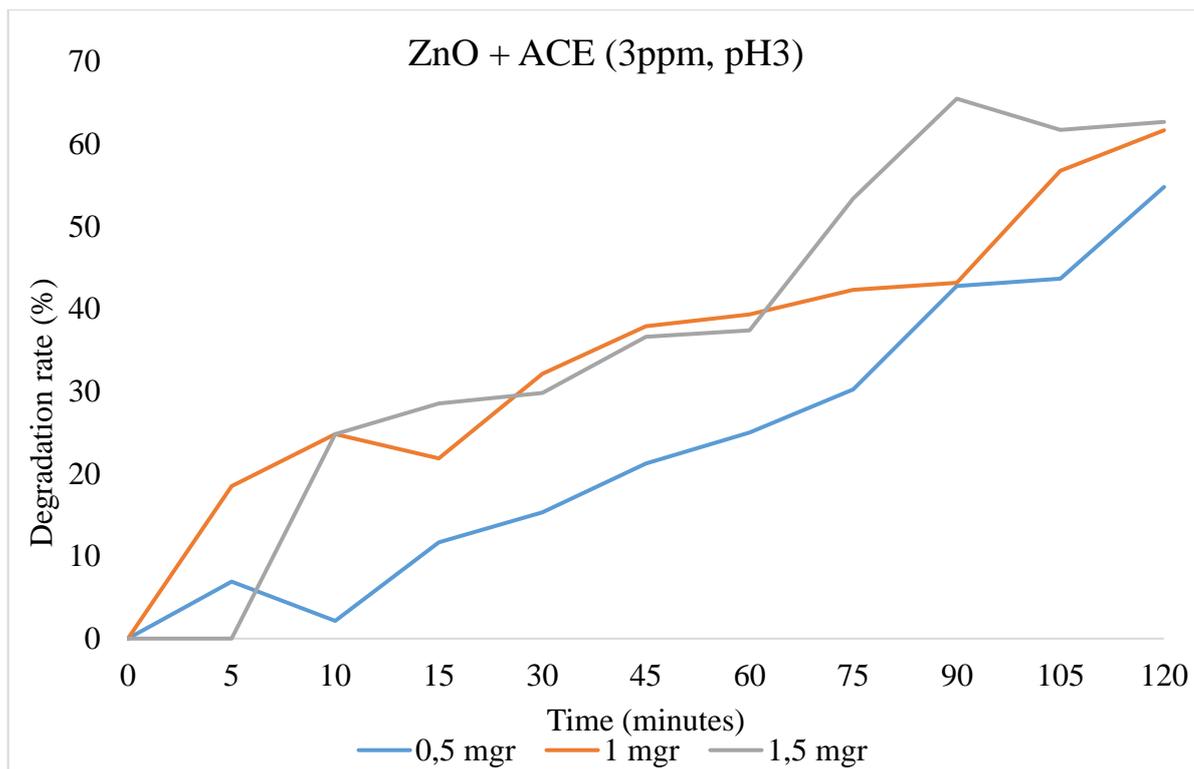


Figure 13. Degradation rate of Ace-K in pH 3, 3ppm and ZnO

As illustrated in the figure above, the increase of the degradation rate of Ace-K was observed easily. Followed by that, the degradation rates reached about 55% for 0.5 mgr of ZnO, over 60% for 1.0 mgr of ZnO and nearly 65% for 1.5 mgr of ZnO. As compared with the result without ZnO, ZnO affected on the decomposition reactions and interaction of Ace-K under UV light by producing hydroxyl radicals. As same as TiO<sub>2</sub>, the decomposition reactions were described from equation 1 to equation 3 and ended up with CO<sub>2</sub>, H<sub>2</sub>O and some other harmless compounds. (Umar & Aziz, 2013)

There were some differences between using TiO<sub>2</sub> and ZnO as catalysts. The differences of the photoactivity, wavelength, kinetics and rate constants between them might cause the

different effect on the treating result. Followed by that, with the same amount of catalyst (0.5 mgr, 1.0 mgr and 1.5 mgr), the effect of  $\text{TiO}_2$  on experiments was more significant than the effect of  $\text{ZnO}$  which could be easily figured out in 120 minutes treatment. The comparison summary table can be found below.

Table 14. Comparison of degradation rate of  $\text{TiO}_2$  and  $\text{ZnO}$  in 120 minutes treatment

<b>120 minutes treatment</b>	<b>Without catalyst</b>	<b><math>\text{TiO}_2</math> (%)</b>	<b><math>\text{ZnO}</math> (%)</b>
<b>0.5 mgr</b>	59.632	70.818	54.806
<b>1.0 mgr</b>		86.984	61.681
<b>1.5 mgr</b>		90.421	62.707

As observed from the comparison table,  $\text{TiO}_2$  played a high role to degrade the concentration of Ace-K solution with its high photoactivity and more efficient than  $\text{ZnO}$  with the same amount.

### 3.2.3 Ace-K at pH 3 centration 3 ppm with PDS

The next stage of experiment was added oxidizing agents with the oxidation ability to react with contaminant in order to oxidize Ace-K concentration. PDS and PMS were used in this research due to their high electron removal ability. For PDS, oxidation potential is 2.01 V (Gao, et al., 2012). Figure 14 illustrates the degrading potential of Ace-K concentration by using PDS.

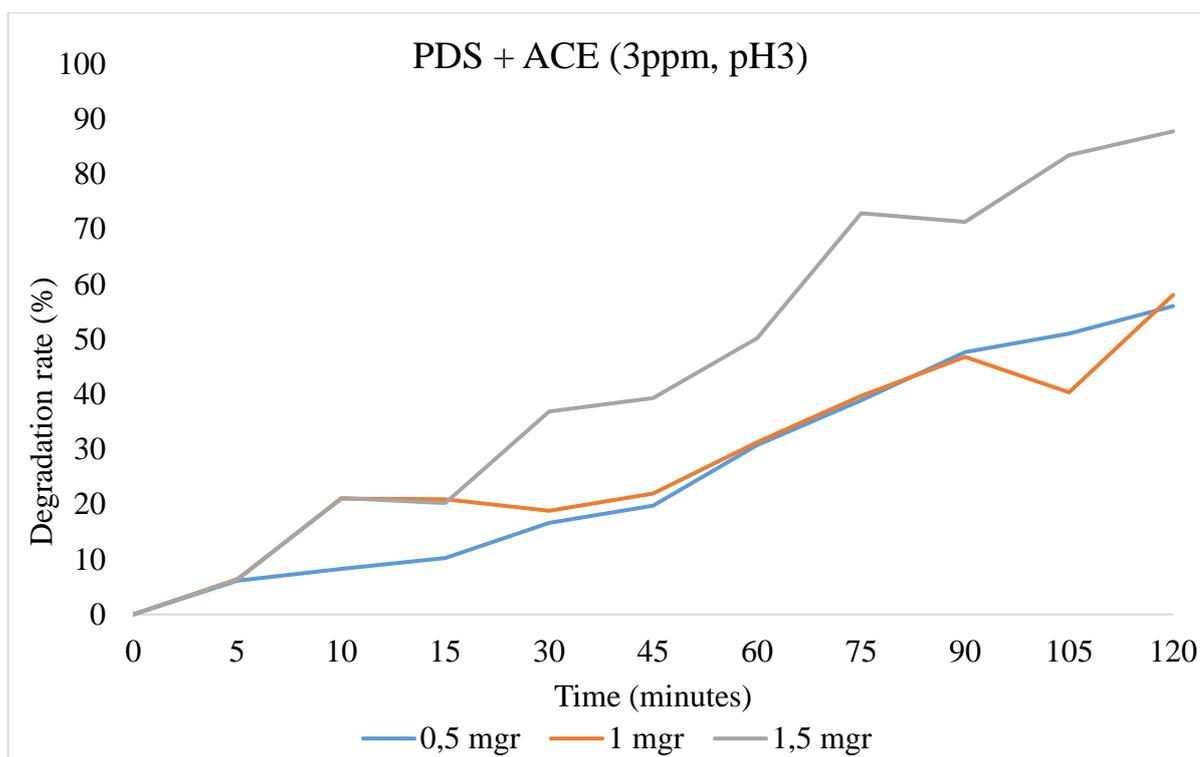


Figure 14. Degradation rate of Ace-K in pH 3, 3ppm and PDS

Followed by that, the increase of degradation rate of Ace-K was dramatic. The trend might happen due to the effect of sulfate radicals reacted with wastewater containing Ace-K as mentioned in equation 4 to equation 7. Following those equations, the sulfate radicals created due to the interaction of the decomposition of  $S_2O_8^{2-}$  under ultraviolet radiation and Ace-K in solution by some intermediate reactions and ended up with acceptable by products. (Gao, et al., 2012)

In this result, at 1.5 mgr of PDS, the degradation was reached the highest rate with 87.7% of Ace-K solution degrade in 120 minutes.

### 3.2.4 Ace-K at pH 3 centration 3 ppm with PMS

For the last oxidizing agents, PMS was known as an oxidizer with oxidation potential is 1.82V and PMS could oxidize organic compounds by taking and reducing the electron containing in those compounds (Wikipedia, 2017). As same as PDS, PMS could be decomposed to create sulfate radicals, besides, hydroxyls radicals was also produced the decomposition of PMS by the attack of ultraviolet radiation. Figure 15 below gives the degradation rate of Ace-K concentration after treating under UV-LED with the support of PMS

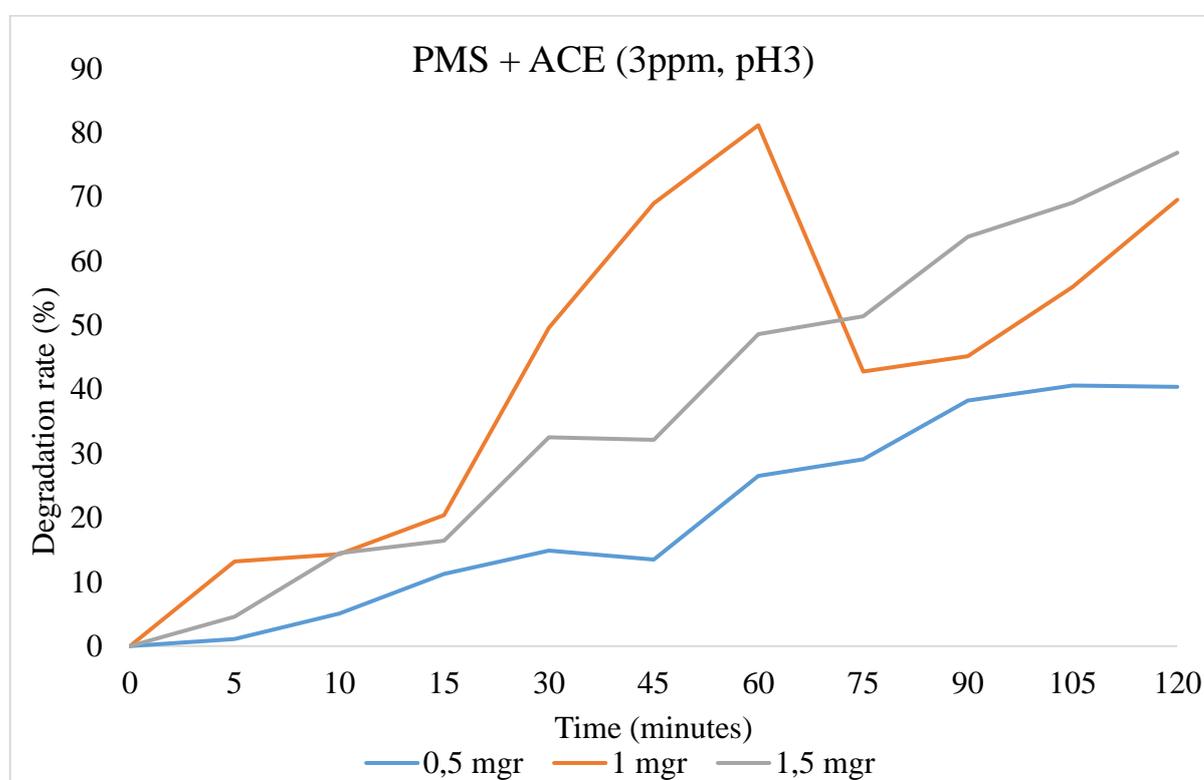


Figure 15. Degradation rate of Ace-K in pH 3, 3ppm and PMS

As shown in the above figure, the degradation rate of Ace-K increases and reaches up to 40%, nearly 70% and over 70% in 0.5 mgr, 1.0 mgr and 1.5 mgr of PMS, respectively. The generation of sulfate radicals and hydroxyl radicals with some intermediate reactions were mentioned from equation 8 to equation 11. Followed by those equations, the both radicals were generated by the decomposition of PMS under UV light and they reacted with each other and the organic contaminant then, in order to end up with some acceptable compounds. (Ghanbari & Moradi, 2017)

The table 15 below is the comparison of the degradation rate between PDS and PMS were used as oxidizing agents.

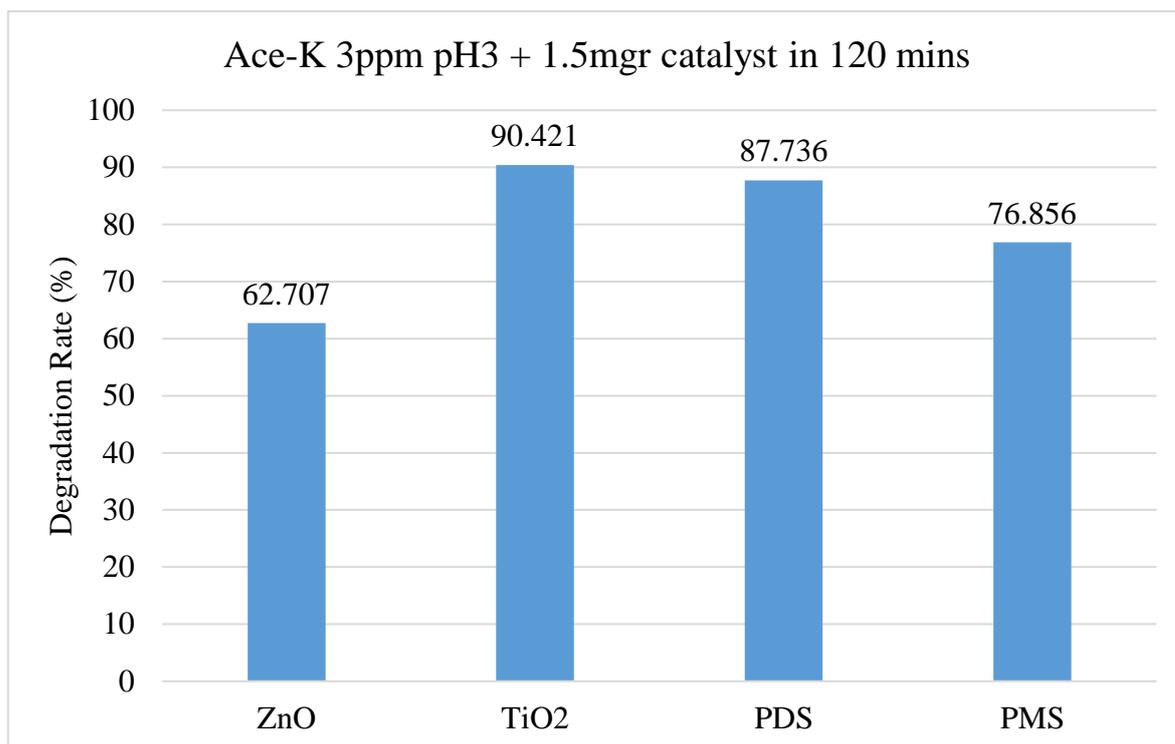
Table 15. Comparison of degradation rate of PDS and PMS in 120 minutes treatment

<b>120 minutes treatment</b>	<b>Without catalyst</b>	<b>PDS (%)</b>	<b>PMS (%)</b>
<b>0.5 mgr</b>	59.632	55.998	40.410
<b>1.0 mgr</b>		58.028	69.537
<b>1.5 mgr</b>		87.736	76.856

As observed from the comparison table, PDS showed better condition while using 1.5 mgr comparing with PMS at the same amount. The difference might occur due to the effect of sulfate radicals which generate after decomposed from PDS. PMS also showed the increase after using 1.5 mgr of PMS. However, the generation of both radicals might cause to the amount of each radical containing in the decomposed compound which could not adapt to degrade more Ace-K than PDS.

In conclusion, the effect of hydroxyl radicals (in TiO<sub>2</sub>, ZnO and PMS) and sulfate radicals (in PDS and PMS) supported for the treatment of degrading Ace-K concentration in solution under UV light. The absorption of light energy brought from ultraviolet radiation excited electrons from VB to CB in the catalysts (TiO<sub>2</sub> and ZnO) and produced photon charge holes which could attracted and reacted with organic contaminants in solution, besides, the UV light could also react with oxidizing agents (PDS and PMS). This UV oxidation method aimed to break the organic contaminant and react with sulfate radicals and hydroxyl radicals which were also produced by the decomposition of PDS and PMS by UV-LED.

Figure 16 below is the comparison summary about the degradation rate of Ace-K at the optimal condition (3 ppm, pH3) and 1.5 mgr of catalysts/oxidizing agents in 120 minutes treatment.



*Figure 16. Comparison degradation of Ace-K at the optimal conditions of each catalyst/oxidant*

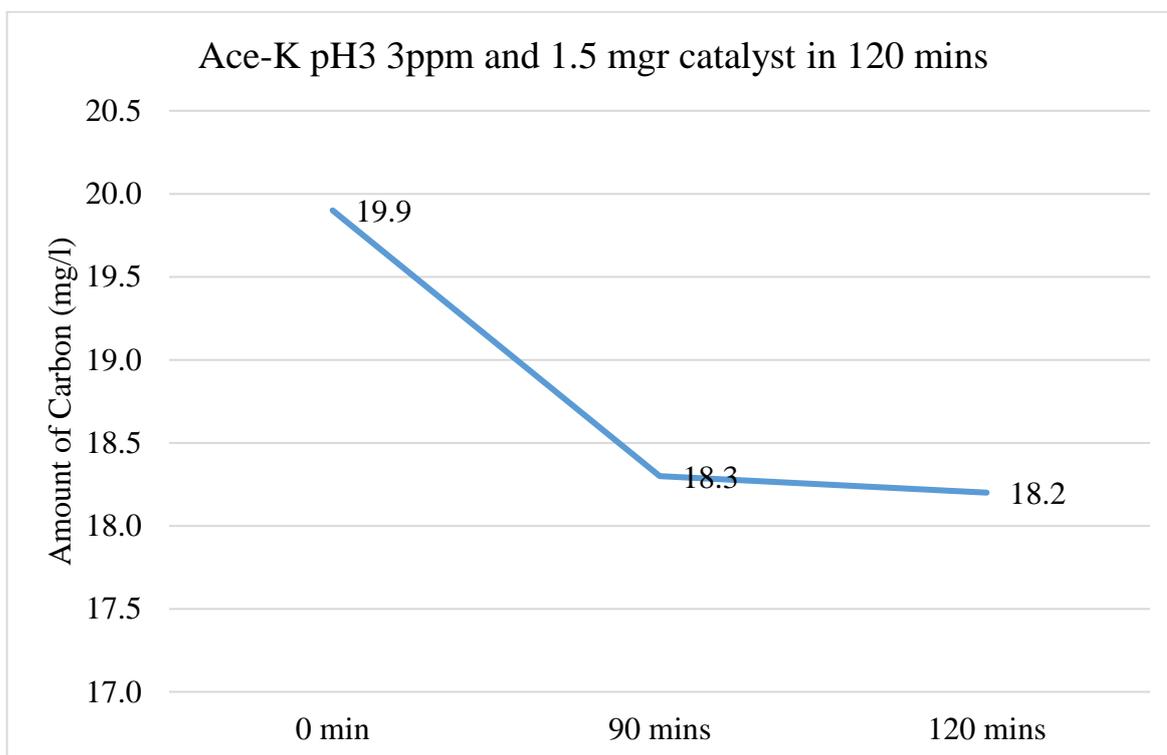
Based on the figure above, at concentration was 3 ppm, pH 3, in 120 minutes treatment, with 1.5 mgr of TiO<sub>2</sub>, the treatment got the best conditions with 90.4% degradation of Ace-K concentration.

For the next testing result, the TOC was done in order to test the amount of organic carbon contains in the optimal condition treatment. After that, we could give conclusion for the rest organic containing in the compounds after treatment.

The last part was GC-MS result which provided the general idea about that pathway of Ace-K from the first formula, degrading and forming to another formula during treatment time from 5 minutes to 120 minutes.

### 3.3 TOC Result

TOC is known as the method to test the amount of organic carbon is the contaminants due to the color changing in the indicator solution. The prepared samples and testing stages were mentioned in the theoretical part of TOC. Figure 17 below shows the amount of carbon during three specific times (0 minute, 90 minutes and 120 minutes). Due to the time limitation, the TOC result presents some specific time in order to prepare the total amount carbon remained in solution before and after treatment.



*Figure 17. TOC result comparison of optimal conditions of  $TiO_2$  at specific time*

Based on the figure above, after adding 1.5 mgr  $TiO_2$  as catalysts, the total amount of carbon at the beginning before treated was 20 mg/l. After treated, the amount of carbon was reduced to 18.2 mg/l. It was due to the amount of treated carbon in the pollutants was reduced after every treatment and the remaining carbon in the solution after preparing sample would change color in the indicator cuvette.

In conclusion, combining HPLC result and TOC result, the optimal condition to treat Ace-K in solution by using catalyst/oxidizing agent under UV-LED condition is:

- Concentration: 3ppm
- Amount of TiO<sub>2</sub>: 1.5 mgr
- pH value: 3
- Treatment time: 120 minutes
- Catalyst/Oxidizing agent: TiO<sub>2</sub>

Followed by that condition, the degradation rate of Ace-K after treated was 90.4% with the total organic carbon is 18.2 mg/l. The last test in this research was GC-MS which was used to detect the by-products after a period of treatment time. GC-MS results can be found in the next chapter, following the result is the explanation about the pathways which is obtained from the pathway figure.

### 3.4 GC Pathway

As mentioned above, GC-MS is defined the by-products pathways after treatment. In this case, as generally obtained from the below pathway in figure 18, there were fourth stages of the pathway due to the attack of hydroxyl radicals which were decomposed  $\text{TiO}_2$  by using UV-LED. Also as obtained from the GC-MS result, the by-products were generated after 5 minutes treatment until 45 minutes treatment. Followed by that, from 60 minutes treatment, no more by-products were generated leading to the higher efficiency for the treatment from 60 minutes to 120 minutes. Below the figure of Ace-K transformation, there are the explanation of the transformation and the abbreviation table of compound names which will explain clearly about the Ace-K pathway.

Compared to the results of HPLC and TOC, GC-MS result is acceptable with the higher efficient treatment from 60 minutes to 120 minutes.

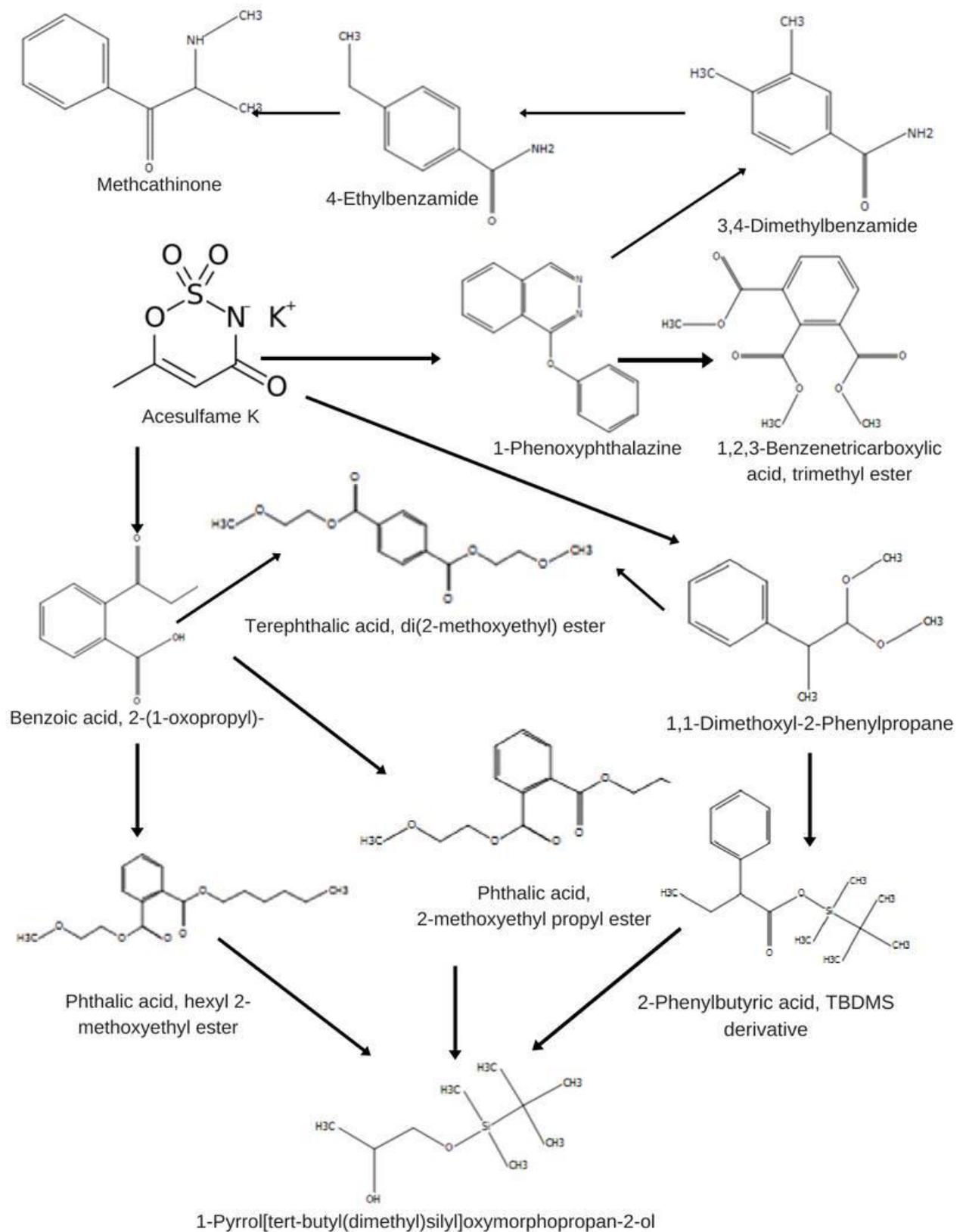


Figure 18. GC pathway of Ace-K transformation

Table 16. Summary table of GC pathway compound names and their abbreviation

<b>Compound number</b>	<b>Abbreviation</b>	<b>Compound name</b>
Compound 1	C1	Benzoic acid, 2-(1-oxopropyl)-
Compound 2	C2	1,1-Dimethoxyl-2-Phenylpropane
Compound 3	C3	1-Phenoxyphthalazine
Compound 4	C4	Phtalic acid, hexyl 2-methoxyethyl ester
Compound 5	C5	Phtalic acid, 2-methoxyethyl propyl ester
Compound 6	C6	Terephthalic acid, di(2-methoxyethyl) ester
Compound 7	C7	2-Phenylbutyric acid, TBDMS derivative
Compound 8	C8	3,4-Dimethylbenzamide
Compound 9	C9	1-Pyrrol[tert-butyl(dimethyl)silyl]oxymorphopropan-2-ol
Compound 10	C10	4-Ethylbenzamide
Compound 11	C11	Methcathinone
Compound 12	C12	1,2,3-Benzenetricarboxylic acid, trimethyl ester

❖ *GC pathway explanation*

- The first stage of degrading Ace-K
  - Ace-K was degraded by UV-LED process and the support of TiO<sub>2</sub>. Those first intermediate compounds created after the hydroxyl radicals are C1 to C3.
- The second stage of degrading Ace-K
  - C1 was continuously attacked by hydroxyl radicals and derived into C4, C5 and C6.
  - C6 and C7 were generated due to the interaction with hydroxyl radicals of C2
  - C3 after the derivation of Ace-K by the opening of two benzene rings generated C12.
  - There were two possible ways which could generate C8.
    - + By the combination of one amine in C3 and C2.
    - + The breaking of the amine from Ace-K by the hydration attached with C2 to generate C8.
- The third stage of degrading Ace-K
  - C10 was made by the breaking down of one methyl in C8.
  - Based on the pathway, there were three ways to generate C9
    - + The breaking of benzene ring and the attack of hydroxylation which could generate not only C4 but C9 as well.
    - + Also at the same time, the hydroxylation affected to break down the benzene ring of C5, C7 in the second stage and C9 in the third stage
- The last stage of degrading Ace-K
  - C11 was generated by the breaking down of the last methyl in C10 and the attach of amine which generated from C3 after the attack of hydroxyl radicals mentioned in the first and second stage of degrading Ace-K.

## 4 CONCLUSION AND SUGGESTION

### 4.1 Conclusion

Speaking generally, global warming and climate change currently are the most concerns which attract a lot of consideration from not only developed countries, but developing countries as well (Kirby, 2013). Followed by a lot of researches, along with developing technology, the environment need to be protected and the pollution need to be reduced. The pollutants is discharged uncontrolled which pollute the human and surrounding ecosystems and results to the ecological imbalance (Agudo, 2017). In addition, the amount of discharges waste will accumulate in environment a lot of substance which may not effect directly. The longer-term effects may be more serious. Thus, due to the future of the world, scientists currently consider more about the CECs compound which can cause serious problems in the future if it is not be concerned in the present. The questions are what is the effect of CECs on the public health and what is the ecological exposure. (Spangenberg, et al., 2007). To find the answer for those questions and due to the development in technology of the last three decades, scientists decide to discover to concentrations of CECs in streams, groundwater, drinkingwater, air, food and daily products. As mentioned in their research, Arroyo demonstrated about the detection of artificial sweeteners in wastewater in United States in 1998 which can easily be found in daily products, such as, food, beverage or even drugs. Many CECs are found very persistent in normal degradation processes of environment. (Reghav, et al., 2013).

Nowadays, there are a lot of advanced method which can degrade the concentration of CECs. In this research, Acesulfame potassium is used as CECs in wastewater after released and persisted in the normal degradation conditions of environment. The research defines the concentration of contaminants in solution and treated the solution under UV-LED with:

- Wavelength: 265 nm
- Number of lights: 11 units
- Distance from the light source to petri dish: 4 cm
- Due to the harmfulness of the UV radiation, the experiments were proceed in the lack of light conditions.

The experiment is taken from 5 minutes for 120 minutes at different concentrations 1 ppm, 2 ppm, 3 ppm, 4 ppm, 5 ppm and 6 ppm and adjusting pH from 2 – 5. For the first group of experiments, the purpose is testing and choosing the optimal condition (highest degradation rate at suitable treatment time, concentration and pH value). In conclusion for the first group of experiment, at 3 ppm, pH3, the degradation rate shown the better result (59.6% in 120 minutes) compared to the rest conditions. As observed from Coiffard's article (Coiffard, et al., 1999), the effect of pH on the degradation rate of Ace-K is very important. In details, at pH3 and pH12, the  $C/C_0$  ratio reduces faster than pH6 and pH9. Because of the time limitation, only pH3 is tested.

After observed the first optimal condition, catalysts and oxidizing agents are tested to increase the degradation rate. The catalysts and oxidizing agents are used at 0.5 mgr, 1.0 mgr and 1.5 mgr. In this case, catalysts and oxidizing agents which were used are  $TiO_2$ , ZnO, PDS and PMS. There are two different concepts of decomposition of catalysts and oxidizing agents. In details, based on the effect of ultraviolet radiation, electrons in catalysts ( $TiO_2$  and ZnO) particles are excited from VB to CB and leave positive charge holes in VB. For oxidizing agents (PDS and PMS), the agents will remove one or more electrons from another atoms by absorbing UV light, leading to the positive charge holes is remained (Wikipedia, 2017). Followed by that the creation of hydroxyl radicals and sulfate radicals will attract and react with organic contaminants to break the Ace-K compounds, the degradation rate increases better. The attack of hydroxyl radicals and/or sulfate radicals to break Ace-K compounds are mentioned under the support of UV-LED (Umar & Aziz, 2013) (Gao, et al., 2012) (Ghanbari & Moradi, 2017). Followed by that,  $TiO_2$  showed the best result with 90.4% of degradation in 120 minutes treatment with 1.5 mgr of  $TiO_2$  used.

After HPLC test, TOC and GC-MS are used to test the optimal condition. For TOC, due to the time limitation, the total organic carbon is test for treatment in 0 minutes, 90 minutes and 120 minutes. At 120 minutes, the total organic carbon the least with 18.2 mgr/gr. For GC-MS pathway, the by-products are shown based on the treatment time. In details, Ace-K pathway is shown is forth stages with the treatment time from 5 minutes to 45 minutes. Based on that information, the treatment time from 60 minutes to 120 minutes will show the higher efficiency without any by-product. Those results support to conclude the final optimal condition.

In conclusion, after HPLC, TOC and GC-MS, at 120 minutes with 1.5 mgr of TiO<sub>2</sub>, in 3 ppm, pH 3, the degradation rate increase from 59.6% to 90.4%. Based on the conclusion, the decomposition of TiO<sub>2</sub> under ultraviolet radiation will attract the organic contaminants and generate hydroxyl radicals which degraded Ace-K by breaking down the organic compound structure. However with the short treatment time, Ace-K compound could not be break completely. Therefore, from 5 minutes to 45 minutes, some by-products were generated. Hydroxyl radicals continuously reacted and broke down the remaining Ace-K concentration and some new generated by-products. From 60 minutes treatment, there is no more by-products. Thus, 60 minutes to 120 minutes gives the better result. Also TOC result decrease significantly at the first time, after that, there is decrease in TOC value; however, the decrease is slower and stop at 18.2 mgr/gr in 120 minutes treatment time.

## 4.2 Suggestion

Based on the result and explanation above, the degradation rate is affected by the changing of pH value, amount of used catalysts/oxidizing agents, the UV-LED conditions and other AOPs method. The final result shows 90.4% concentration of Ace-K degraded can be increased. Following recommendations below can be considered for further researches.

### 4.2.1 Adjusting pH value

As mentioned in Coiffard's article, pH 3 and pH 12 are concluded to be the optimal pH value for treating Ace-K under UV light. In details, the  $C/C_0$  ratio are 0.455 in 12 minutes treatment and 0.355 in 6 minutes treatment for pH 3 and pH 12, respectively. Due to the time limitation, only pH 3 is studied in this thesis. Based on Coiffard's result, at pH 12 the degradation rate of Ace-K is faster which can be expected to bring a good result. (Coiffard, et al., 1999)

### 4.2.2 Catalysts/Oxidizing agents

Besides  $TiO_2$  and  $ZnO$  commonly known as catalysts which generate hydroxyl radicals, there are some more metal oxide which can form hydroxyl radicals such as  $MgO$ ,  $La_2O_3$ ,  $Nd_2O_3$ ,  $Sm_2O_3$ ,  $Yb_2O_3$  and  $CeO_2$  (Hewett, et al., 1996). Those compounds are studied to generate hydroxyl radicals as a radical chain carrier.

For oxidizing agents, there are several type of oxidizing agents which can replace PDS and PMS. For instance: (Wikipedia, 2017)

- Ozone ( $O_3$ )
- Oxygen ( $O_2$ )
- Sulfuric acid ( $H_2SO_4$ )
- Nitric acid ( $HNO_3$ ) and nitrate compounds
- Fluorine ( $F_2$ ), chlorine ( $Cl_2$ ) and other halogens
- Hydrogen peroxide ( $H_2O_2$ ) and other inorganic peroxides, Fenton's reagents

Followed by that, all that agents above can remove one or more electrons in the main reaction and react with organic compounds to degrade its concentration. Besides, the consideration of amount of catalyst/oxidant is needed in order to optimize the effect of hydroxyl and sulfate in treating solution.

### 4.2.3 UV-LED condition

In this research, the fixed UV-LED condition is used:

- Wavelength: 265 nm
- Number of lights: 11 units
- Distance from the light source to petri dish: 4 cm

Recommendation in this case is changing the number of light bulbs. 11 bulbs due to the design of supplier. The change in the number of bulbs may affect to the degradation efficiency. And also the distance between the light source to the petri dish can also be adjusted to figure it out the best height.

### 4.2.4 Another AOPs methods

Besides photocatalysis which is used in this thesis, there are some more AOPs which can apply to reduce the organic pollutant concentration in wastewater by producing hydroxyl radicals, such as: (Sillanpaa & Repo, 2017)

- UV/Ozone AOP: Photon of UV transform ozone in the presence of water to oxygen and peroxide → peroxide reacts with ozone to form hydroxyl radicals → molecular ozone and direct photolysis causes organics destruction.
- H<sub>2</sub>O<sub>2</sub>/UV: H<sub>2</sub>O<sub>2</sub> is injects and mixed with the treatment of UV light → O-O bond in H<sub>2</sub>O<sub>2</sub> is separated by UV radiation and generate hydroxyl radicals. However, the overdosing of H<sub>2</sub>O<sub>2</sub> brings to the reverse reaction (hydroxyl radical with its formation)
- Fenton's reactions: the concept of this reaction is the combination of catalyst (ferrous iron) with oxidizing agent (H<sub>2</sub>O<sub>2</sub>). In details, the process includes the hydroxyl radical formation from H<sub>2</sub>O<sub>2</sub> by photolysis process and the Fenton reaction. The presence of UV irradiation convert Fe<sup>3+</sup> (ferric ion) → Fe<sup>2+</sup> (ferrous ion) and form hydroxyl radical.

In addition, the combinations of some other methods can also apply in this case. For instance, the combination of ultrasound with other oxidation processes. However, in some case, the combination may not bring the expected result. Thus, it may need some consideration before combining the above methods.

#### **4.2.5 Concentration adjusting**

Besides those above suggestions, the higher concentration can be consider as another recommendation. The concentration can be adjust at 5 ppm, 10 ppm, 15 ppm, 20ppm and so on instead of using low concentration. The purpose of concentration adjusting is figuring it out the optimal range of the concentration. In this research, the concentration is adjusted from 1 ppm to 6 ppm in order to show the best concentration. However, the concentration from 1 ppm to 6 ppm cannot cover the degradation ability of Ace-K under UV-LED with catalysts/oxidizers. The concentration can be studied from 10 ppm to 100 ppm in order to figure out the suitable pH value and other conditions to illustrate the best treatment conditions and compare the difference with the low concentration. After that, the comparison table can be considered to create in order to give the standard table of treatment Ace-K in variable treatment conditions.

On the other hands, the smaller concentration adjusting can be considered. However, the shortage may come from the solution preparation due to its small amount for scaling.

#### **4.2.6 Combination**

Due to the demand on degrading the concentration of Ace-K, the combination of two to more above suggestions can be considered in order to have the best result. However, the optimal of each suggestion may not be the best for the combination. Thus, the combination method need to be done in the real condition of the laboratory.

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