DESIGN AND PERFORMANCE ASSESSMENT OF A PHOTO-FENTON REACTOR WITH IMMOBILIZATION OF FE ON NAFION MEMBRANE; FOR REMOVAL OF PAHs FROM THE SUPPLY WATER

By

Ahmad Syafiq bin Zakaria

14319

Dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Engineering (Hons)

(Civil)

JANUARY 2016

Universiti Teknologi Petronas

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CERTIFICATION OF APPROVAL

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Approved by,

____

(AP. Dr. Amirhossein Malakahmad)

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

Ahmad Syafiq bin Zakaria

ABSTRACT

Polycyclic Aromatic Hydrocarbon (PAHs) presence is detected through various medium in Malaysia, however there is no regulation on limitation of PAHs disposition to the water system. Conventional biological treatment are not able to completely remove the pollutants from the water system. Photo-Fenton chemical oxidation treatment which utilizes hydroxyl radical are able to degrade recalcitrant chemicals such as aromatic compounds. A photo-Fenton reactor is designed with immobilization of Fe on Nafion membrane for PAHs removal from supply water and performing assessment based on its effectiveness and efficiency. Assessment was done to obtain the optimum settings including hydrogen peroxide concentrations, UV light, and retention time. Total Organic Carbon and Chemical Oxygen Demand is taken as the observance parameter to determine the degradation of PAHs. PAHs presence were determine using UV-VIS scanning spectrophotometer. TOC degradation is observed at 94.6% pollution reduction with optimum reaction time of 85 sec and H_2O_2 concentration of 0.3 mg/L. COD degradation is observed at 87.7% pollution reduction with optimum treatment time of 70 sec and H_2O_2 dosage of 0.3 mg/L.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1: INTRODUCTION

1.1 Background of Study

Mankind breakthrough during the Industrial Revolution had developed it usage and dependencies on new kind of energy sources, mostly originated from fossil fuels such as crude oil, coal and natural gases[1]. This new sources of energy are used to generate energy for modern technology such as transportation (automobile, vessel, electricity, industrial processes). Wide usage of fossil fuels-based energy and productions resulted in huge deposition of the by-products to the environment. Such petroleum hydrocarbon waste exist in form such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCB), etc[2]. PAHs are among the hazardous substances which are determined to pose the most significant potential threat to human health due to their known toxicity and potential for human exposure; according to Agency for Toxic Substances & Disease Registry (ATSDR) on which PAHs ranked 9th in the Substance Priority List by ATSDR[3]. United States of Environmental Protection Agency (USEPA) enlisted 16 PAHs as priority list on which the compounds can cause harmful health effects[4].

Research on PAHs contamination in water region had been done by many researchers in past years focusing on wide subject and application. Keshavarzi et al. [5] studied the contaminations of PAHs in Karoon river whereby the said river are receiving the effluents from industry such as processing factory, petrochemical and oil plant. Karoon River was in fact the important source of water in Khuzastan Province, Iran. Their research showed the existence of contamination of PAHs with concentrations from 11.54-117,730 µg/kg and mean value of 7034.55 µg/kg across the river. Meanwhile in China, Mopanshan River near the Harbin City in Northeast China was dominated with high percentage of low-molecular weight PAHs and two to three ring PAHs (78.4 to 89.0 %)[6]. In Malaysia, there are also research done for the past decades providing the proof of existence of PAHs in Malaysian water region by these aromatic compound species. Researches done by Zakaria et al. [1, 7, 8], Keshavarzifard et al. [9] conclude that contamination of PAHs in water region is dominated by PAHs originated from both pyrogenic and petrogenic sources. Pyrogenic

PAHs is form through combustion of fossil fuels (coal and petroleum) [8] which are released to the environment in form of exhaust and solid residues. While petrogenic PAHs originated from direct/indirect discharge of oil through accidental spills, from routine tanker , municipal and urban runoff [1].

1.2 Problem Statement

PAHs contamination inaugurate through various ways but which the common cause is anthropogenic activities such as oil spills, discharge from routine tanker operations, municipal and urban runoff [1], urban water storm runoff and sewer containing discharge of petroleum products like petroleum fuels, lubricants and atmospheric disposition [10]. Presence of PAHs in environment mainly in source of water (river, streams, seawater, etc.) introduce them to our food chain, according to Rubio-Clemente et al. [11] which showed that PAHs in water can bind to suspended particles or sediments or bio accumulate in aquatic organisms. Nature of the PAHs which are toxic to living beings including human, animal and plants threaten the health and well-being to the extent of causing mutagenic effects (DNA adducts formation)[12].

Risk exposure of the PAH in our daily life is not an impending threat anymore, as such warns from the institutional that governs the policies and guidelines against environmental hazardous chemical such as ATSDR and USEPA had given their concerns regarding this issues. Warning from regulatory organization should give awareness to the community regarding the possible threat of health to human life against contamination of PAHs. Study against exposure to human being has been done in depth by many researchers, Jedrychowski et al. [13] showed that prenatal exposures may affect immune, metabolic and neurological function of children, and child as one of the most vulnerable groups in society are having high carcinogenic risks [14].

Conventional treatment system for wastewater and water supply system are not able to remove most of the PAHs, mostly high molecular weight (HMW) PAHs due to its resistance to biodegradability [15]. Hence, researches have adopted the advance oxidation process (AOP) as the treatment method to this issue. Oxidation reaction in presence of hydroxyl radicals ($OH\cdot$) are able to degrade most of the organic compounds at ambient conditions [16]. AOP method had been applied at most of the industrial phases in the same consensus which is to reduce the level of contamination of PAHs in its effluent discharge to the river. At current state, there is no standard in water quality guidelines for PAHs in Malaysia. Hence, enforcement in research advances the cause to include the standard which need to be based on individual toxic priority pollutants [17].

1.3 Objective and scope of study

Objective of this research are:

i. To design and fabricate a photo-Fenton reactor for degradation of PAHs from the supply water, and

ii. To assess the photo-Fenton reaction performance for optimum degradation of PAHs in supply water.

Scope of study for this project is collecting samples at study area which is Water Treatment Plant (WTP) Parit, WTP Kampung Senin and WTP Teluk Kepayang. Experimental and analysis work of the collected samples to determine the level of contamination of PAHs in the water region. The samples are treated using the photo-Fenton reactor integrated with Nafion membrane and analyse is done to determine the degradation of the PAHs with comparison of before and after treatment.

1.4 Significance of the project

Since there is no standard quality guidelines for PAHs in Malaysian water, this research is crucial that to provide a benchmark for producing a reliable treatment system that are able to remove PAHs from water system. Research is done accordingly to obtain the most optimum condition (minimum risk, economically viable, maximum efficiency) for the system and for the prototype to work its purpose.

1.5 Relevancy and feasibility of the project

This project is relevant to the author; as a Final Year student in Civil Engineering programme and had taken course related to the respective field of research such as Environmental Engineering and Wastewater Engineering. Research is done accordingly under supervision of Assoc. Prof. Dr. Amirhossein Malakahmad of Civil Engineering & Environmental Department, University Teknologi Petronas. Experimental and analysis are able to be conducted in the laboratory situated within the academic block in the campus. This project are able to be completed within time frame of 28 weeks including Final Year Project 1 semester and Final Year Project 2 semester.

CHAPTER 2: LITERATURE REVIEW

2.1 Polycyclic Aromatic Hydrocarbon (PAHs)

Polycyclic aromatic hydrocarbon (PAHs) are a group of chemical compounds containing two or more fuse benzene rings, which are one of the most important classes of anthropogenic organic contaminants/pollutants[8]. Formation of PAHs can occur naturally under natural condition in oil reservoir/ oil deposition, or through anthropogenic activities. Mainly PAHs is form through incomplete combustion of organic substances, burning coal, oil, gas, wood, garbage and fuel.

Anthropogenic sources are the most concern in which are the primary sources of PAHs in the environment [1]. Petrogenic sources originated from oil spills from discharge from routine tanker operations, oil leakage from the oil reservoir, urban runoff as the leakage from crankcase, oil from automobile and air deposition into the water stream[18]. Pyrogenic sources on the other hand enter the river system through effluents discharge from industrial waste along the river banks. Sewerage system from urban city also contribute to total PAHs contamination as daily products waste are washed out through the sewer into the river. Research conducted by Zakaria et al. [8] shows that in Malaysia the most common sources of PAHs is from the unsupervised handling of used crankcase oil. This major sources enter the system through uncontrolled discharge of used crankcase oil into the river from the automotive workshops, garage and direct discharge from deposition of oil leakage onto urban road to sewer system.

Characteristics of the PAHs can be explained by dividing them to low molecular weight (LMW) and high molecular weight (HMW) PAHs. LMW PAHs are PAHs with two to three benzene ring, with characteristics are to be slightly volatile and susceptible to dilute into the liquid medium. On the other hand, HMW PAHs are low in its solubility due to its hydrophobic nature (log K_{ow}) which gives the reason that HMW PAHs are more adhere to associate with suspended solids and subsequent sedimentation[19]. Table 1 below are adopted from Manoli and Samara [19] which shows the list of the 16 PAH stated by USEPA classification.

Table 1: List of 16 PAHs and its chemical properties.

PAHs	Vapor Pressure (Torr)	Solubility in Water (mg L^{-1})	K_{ow}	Carcinogenic potency IARC/US EPA classification
Acenapthene	10^{-3}-10^{-2} at 20 °C	3.4 at 25°C	21000	
Acenaphthylene	10^{-3}-10^{-2} at 20 °C	3.93	12000	
Fluorene	10^{-3}-10^{-2} at 20 °C	1.9	15000	
Naphthalene	0.0492	32	2300	
Anthracene	2×10^{-4} at 20 °C	0.0.5-0.07 at 25°C	28000	3
Fluoranthene	10^{-6} to 10^{-4} at 20 °C	0.26 at 25°C	340000	3
Phenanthrene	6.8×10^{-4} at 20 °C	1.0-1.3 at 25°C	29000	3
Benzo[a]anthracene	5×10^{-9} at 20 °C	0.01 at 25°C	4×10^{5}	2A/B2
Benzo[b]fluoranthene	10^{-11} to 10^{-6} at 20 °C	-	4×10^{6}	2B/B2
Benzo[k]fluoranthene	9.6×10^{-7} at 20 °C	-	7×10^{5}	2B
Chrysene	10^{-11} to 10^{-6} at 20 °C	0.002 at 25°C	4×10^{5}	3/B2
Pyrene	6.9×10^{-9} at 20 °C	0.14 at 25°C	2×10^{5}	3
Benzo[ghi]perylene	$\sim10^{-10}$	0.00026 at 25°C	10^{7}	3
Benzo[α]pyrene	5×10^{-9}	0.0038 at 25°C	10^{6}	2A/B2
Dibenzo[α,h]anthracebe	$\sim10^{-10}$	0.0005 at 25°C	10^{6}	2A/B2
Indeno[1,2,3-cd]pyrene	$\sim10^{-10}$		5×10^{7}	2B/B2

2A/B2: Probably carcinogenic to humans/ Probable human carcinogen; 2B: Possibly carcinogenic to humans; 3: Not classifiable as human carcinogenicity; Blank: Not tested for human carcinogenicity.

Previous studies which are conducted to measure and investigate PAHs in water are discussed as follows. Studies at Langat Estuary are done accordingly to investigate the sources and concentration of PAHs. Analysis used to determine the concentration is gas-chromatography mass-spectrometry. Whereby methylphenanthrene/phenanthrene (MP/P) ratio where used to identify the sources of PAHs. MP/P value less than 1 indicate pyrogenic sources and MP/P value higher than 1 indicate petrogenic sources. Throughout the samples taken in the area MP/P ratio is observed at range of 0.88 to1.27. Total PAHs sediments samples have concentration in the range of 322 ng/g to 2480 ng/g[1].

Studies done at Straits of Malacca by Zakaria [7] mainly research on utilizing the usage of biomarkers compound of triterpanes to determine the origin of the sources of PAHs. Middle East Crude Oil (MECO) and South East Asian Crude Oil (SEACO) were trace in the tarballs, sediments and mussels. 2 out of 8 tarballs showed signature of MECO petroleum contribution. Source identifier also notified the trace of MECO signature in sediments and mussels samples. It is determine from investigation that MECO is used to formulate Malaysian lubricating oil and leaking of crankcase oil and accumulation in street dust can be trace back to MECO sources.

Research in Malaysia focusing location of rivers and estuaries [8] shows that land-based pollutants are transferred into aquatic environments by means of heavy rainfall and runoffs. Analysis is done using gas-chromatography mass-spectrometry and concentration in the sediments is in the range of 4 to 924 ng/g. MP/P ratio shows that Malaysian water has a unique PAHs sources which contains both petrogenic and pyrogenic sources. PAHs hopanes fingerprint suggested that used crankcase oil is the major contributor in Malaysian water.

Keshavarzifard research specifically in Peninsular Malaysia [9] focusing on distribution and source of PAHs in sediments and hopanes fingerprints. Area of study including Perlis River, Kedah River, Merbok River, Perak River and Klang River. Hereby in this study Perak River is the main concern and it show based on the data that the average concentration of PAHs is 231.2 to 426.7 ng/g. Petrogenic and pyrogenic sources is identified by the diagnostic indicate a significant dominance of pyrogenic sources in the area. Petroleum hydrocarbon major sources is identified to be originated from MECO which in consistent with previous studies.

2.2 Advance Oxidation Process

PAHs characteristics especially those with high molecular weight are resisted to biological treatment due to their chemical stability and low biodegradability [20]. Research done by Trably et al. [15] shows that biological treatment are only able to remove low ring PAHs. This is due to the abiotic loss which significantly contribute to the removal of light PAHs. Low ring PAHs are readily degraded in the treatment whereas high ring PAHs are resisted to the treatment. This is due to the hydrophobicity nature of the high ring PAHs causing low bioavailability and strong absorption onto soil or sediment organic particles. Hence, many researches have applied the advanced treatment process, as a solution to PAHs contamination [15, 21, 22].

AOP are defined as process that involve the generation and usage of hydroxyl radicals (OH·) which is a strong oxidant agent that can degrade almost any organic compound that it came in contact with [23]. Hydroxyl radical is used in this treatment technologies due to the reason that conventional method are not susceptible to remove recalcitrant chemicals such as PAHs, PCB, pesticides, biocides and fertilizers. Hydroxyl radicals attack the dissolved constituents, initiated a series of chemical/oxidation reaction to degrade the compounds until it completely mineralize to form end products of inorganic (Cl^-, NH_4^+, SO_4^{2-}), CO_2 and H_2O [23, 24].

There are various type of AOPs that are available. Their application and its conditions are determined by the types of pollutants and original condition of the contaminated influents.

Fenton process is an old reactive system, and since then many researches underlined to its applications in wastewater treatments. Fenton reagents are able to degrade toxic compounds to less toxic compound in wastewater. Its basic chemistry is that the production of hydroxyl radicals is by means of addition of hydrogen peroxide and ferrous salts (Eq. 1). This simple process does not require any special reactants or equipment. On the other hand hydrogen peroxide are easy to handle and environmentally safe [25]. Despite that, the Fenton reaction requires a specific states to operate which that the pH constraint between pH 2.0 – 4.0[26].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\cdot \qquad \text{(Eq. 1)}$$

Modification on Fenton reaction is done in various ways such as coupling with technology such as UV radiation, solid nano-sized iron catalysed, electrolysis, etc. Details of such modification are presented in Table 2, adopted from Wang et al. [26].

Table 2: Varieties of Fenton chemistry

Reaction	Reagents	pH	Iron loss	Presence of radiation
Classic Fenton	H_2O_2, Fe^{2+}	2-4	Yes	No
Fenton-like	H_2O_2, Fe^{3+}	2-4	Yes	No
Photo-Fenton	H_2O_2,solid complex, free iron ions	Acidic to neutral	Yes	Yes
Heterogeneous Fenton	H_2O_2, solid iron oxide	Wide range	No	No
Electro-Fenton	Electro-generated H_2O_2, free iron ions; H_2O_2, electro-generated Fe^{2+}	2-4	Yes	No
Heterogeneous photo-Fenton	H_2O_2, solid iron oxide	Wide range	No	Yes
Heterogeneous photoelectron-Fenton	Electro-generated H_2O_2, solid iron oxide	Wide range	No	Yes

Photo-Fenton chemistry on the other hand is a modification of typical Fenton reaction. Combination of hydrogen peroxide and ultraviolet radiation with ferrous or ferric ion as catalyst. This AOP system produce more hydroxyl radicals in comparison with other Fenton based chemistry which subsequently showing that Fenton reaction are more efficient and were the most studied AOP subject (31%) [23]. Photo-Fenton reaction have the same basic reaction as Fenton chemistry, only including the UV irradiation in the treatment system. Hydrogen peroxide is added to the system together with iron catalyst to trigger the treatment reaction producing hydrogen radicals. In addition, hydrogen peroxide are degraded into hydrogen radicals in presence of UV light (Eq. 8). The additional features of this reaction is the following reaction:

$$H_2O_2 + (UV) \rightarrow 2\ OH\cdot \quad \text{(Eq. 2)}$$

$$Fe^{3+} + H_2O \rightarrow Fe\ (OH)^{2+} + H^+ \quad \text{(Eq. 3)}$$

$$Fe\ (OH)^{2+} + (UV) \rightarrow Fe^{2+} + OH\cdot + H^+ \quad \text{(Eq. 4)}$$

2.3 Significance of Photo-Fenton

Photo-Fenton reaction is an advance oxidation process which apply the technology of the hydrogen radicals ($OH\cdot$) to mineralize pollutants. Hydrogen radicals are produced through degradation of hydrogen peroxide (H_2O_2) in presence of iron based catalyst which in this case an iron salts (Fe^{2+}) catalyst. This reaction produce ferric ion (Fe^{3+}) as result. The only drawback of a typical Fenton chemistry is that it operating condition that required tight window of pH range from 2.8 – 3.0. On the other hand, continuous addition of catalysts are required since ferrous iron is used up. Natural state of ferric ion at pH higher than 4.0 cause it to precipitate [26]. It show that the system required more catalyst to be used and additional steps to remove sludge, this can cause additional cost. But, photo-Fenton reaction can avoid those problem and additional to that, it able to increase its efficiency and reduce overall cost for the treatment [15, 24].

In addition, photo-Fenton reactions can be operated at ambient temperature and pressure since the operation window for pH value is widen as such that there will be no issues of ferric precipitation; sizeable drop in total iron utilization and sludge generation[27]. Ferrous regeneration in Fenton-like reaction in presence of ultraviolet (UV) radiation and hydrogen peroxide direct photolysis generate extra radicals in the system[28]. On the other hand, hydrogen peroxide is easy to handle and the overall process are easy to implement either as a single or hybrid system [25]. Single Fenton process is able to degrade most of the low ring PAHs due to its biodegradability except a few types of PAHs such as Anthracene and Chrysene which are recalcitrant to both biological and chemical reactions. While the hybrid systems are suitable for removal of low and high ring PAHs [16, 20].

Fenton reaction is considered fast and easy as it chemical reaction between iron catalyst and hydrogen peroxide reagent with a potential of 2.8 V [26]. Activation of hydrogen peroxide in presence of iron catalyst and subsequent generation of hydroxyl radicals are enhanced further in photo-Fenton chemistry due to the presence of UV radiation which contribute in ferrous regeneration and direct photolysis of hydrogen peroxide which produce extra radicals. Another importance factor of Fenton process is that it is cheap, chemicals ($Fe^{2+,}$, Fe^{3+}, H_2O_2) which are easy to obtain and handle, leaving no residue and enhance stability to treat a range of substance given one of the most promising oxidation methods [29].

Research done by Beltran et al. [30] shows prove of successfulness of PAHs removal using Fenton reagent. Aqueous oxidation of three PAHs; fluorine, phenanthrene and acenaphthene with hydrogen peroxide and ferrous salts were investigated. Variables that is tested including concentration of both reagents, pH, presence of bicarbonate and humic substances. Concentration of PAHs in water was followed by high performance liquid chromatography and detection using Hewlett-Packard programmable fluorescene detector. Hydrogen peroxide is analysed iodometrically and remaining ferrous ion concentration is analysed using addition of 2,4,6 tripyridyl-s-triazine when PAH reaches a minimum and constant value. Fenton reagents play both role as initiator of hydroxyl radicals production and also as inhibitor at high concentration. Presence of bicarbonate ions and humic substances inhibit the oxidation rate of PAHs which suggest that further research is required in this particular matter. Oxidation rates of Fenton oxidation is of a similar capability to other advanced oxidation system involving high energy consumption (ozonation and UV). Fenton oxidation of PAHs is less expensive and can be recommended to eliminate this type of priority pollutants.

2.4 Nafion Membrane

Nafion perfluorosulfonic acid (PFSA) membrane have been recently developed because of its vast application in various industrial use such as in electrochemical devices and biomedical application[31]. Nafion membrane have been studied in previous years in chemical treatment for wastewater. For example; study on propane partial oxidation[32], degradation of 2,4-dichlorophenol[33], etc. Integration of Nafion membrane and photo-Fenton reaction is necessary to overcome the problem of excess Fe ions in the solution. According to research done by Sabhi and Kiwi[33], Fe^{3+}/H_2O_2 homogeneous catalysed reactions required 50-80 ppm of Fe ions in solution which is well above the European Economic Community directives which only allow 2 ppm Fe ions in treated water to be discharged directly into the environment[34].

Membrane-support catalysts have been developed for the purpose of to provide more stable chemically-kinetic reaction. These silica structured surfaces are able to withstand corrosion due to the high oxidative potential in the treatment solution. In the case of its application in photo-Fenton process, its function is to fixed the Fe-ions on a stable support as a way to not allow them to leach during the reaction process[33]. Fenton-mediated catalysis also are able to proceed at acceptable kinetic rates[35]. On the other hand, Nafion membrane are able to withstand repeated usage and long term stability [36, 37].

Using this technology, it has widen the range of operating condition of the treatment system which allow the treatment to run in range of pH 2.0 – 11.0. Addition of Nation membrane in photo-Fenton water treatment improve the condition of the system. Initial pH reduction to acidic media is not included and excess of Fe ions on the water media is not an issue[38]. Immobilizing of Fe ions on Nafion membrane allow the reaction to be more flexible and having a consistent kinetic reaction at a wide pH range from pH 2-11[33, 38]. The chemical reaction taking place at the surface of the Nafion membrane, the mechanism of the reaction is mass transfer through diffusion of the Fe ions from the inner layer of the membrane[37]. The reaction mechanism can be define as per described in Figure 2.1, adopted from Parra et al. [37] which in his research subject of study is 4-chorophenol.

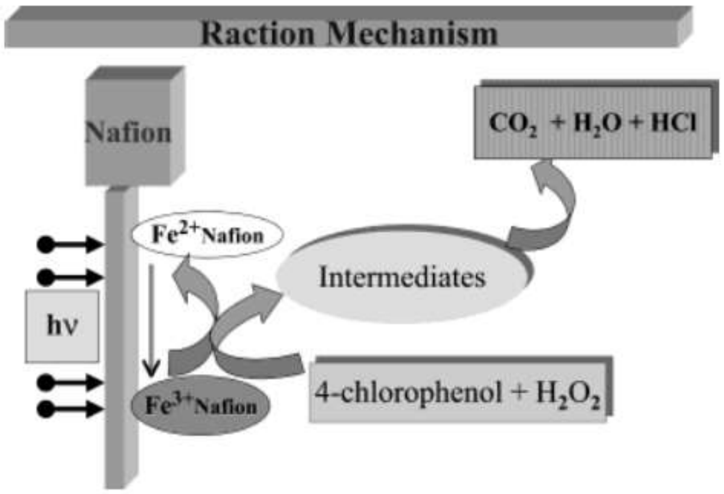

Figure 2.1: Reaction Mechanism

According to research done by Parra et al. [37], performance of Nafion in improving the photo-Fenton process can be seen in his finding where the 4-chorophenol as the subject TOC is reduced by 94% in reaction approximately 40 min. Compared to only 6% degradation in 40 min for dark degradation setup. Comparison of the performance shows that the accessibility of iron species is significantly improved with respect to the Dupont 117 Nafion/Fe.

Findings by Parra et al. [37] and Sabhi and Kiwi [33] agrees with conclusion that treatment condition in wide pH range from pH 2.0-11.0 have the mineralization takes place with practically the same kinetics. Solution with initial pH values between 3 and 10 shows same trend at final pH values after photodegradation which converged to value pH of approximately 3.5. This shows the reason behind the similarity in the kinetics of the degradation. Shifting of the pH to a more acidic medium can be attributed to the formation of HCl and short-chain carboxylic acids generated in the solution preceeding the final mineralization [37], see Figure 2.2. According to Sabhi and Kiwi [33] residual intermediates after photodegradation is determine to suggested species like: $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH)_2^+$ and $[Fe_2(H_2O)_4(OH)_2^+]$ in solution at pH > 3.

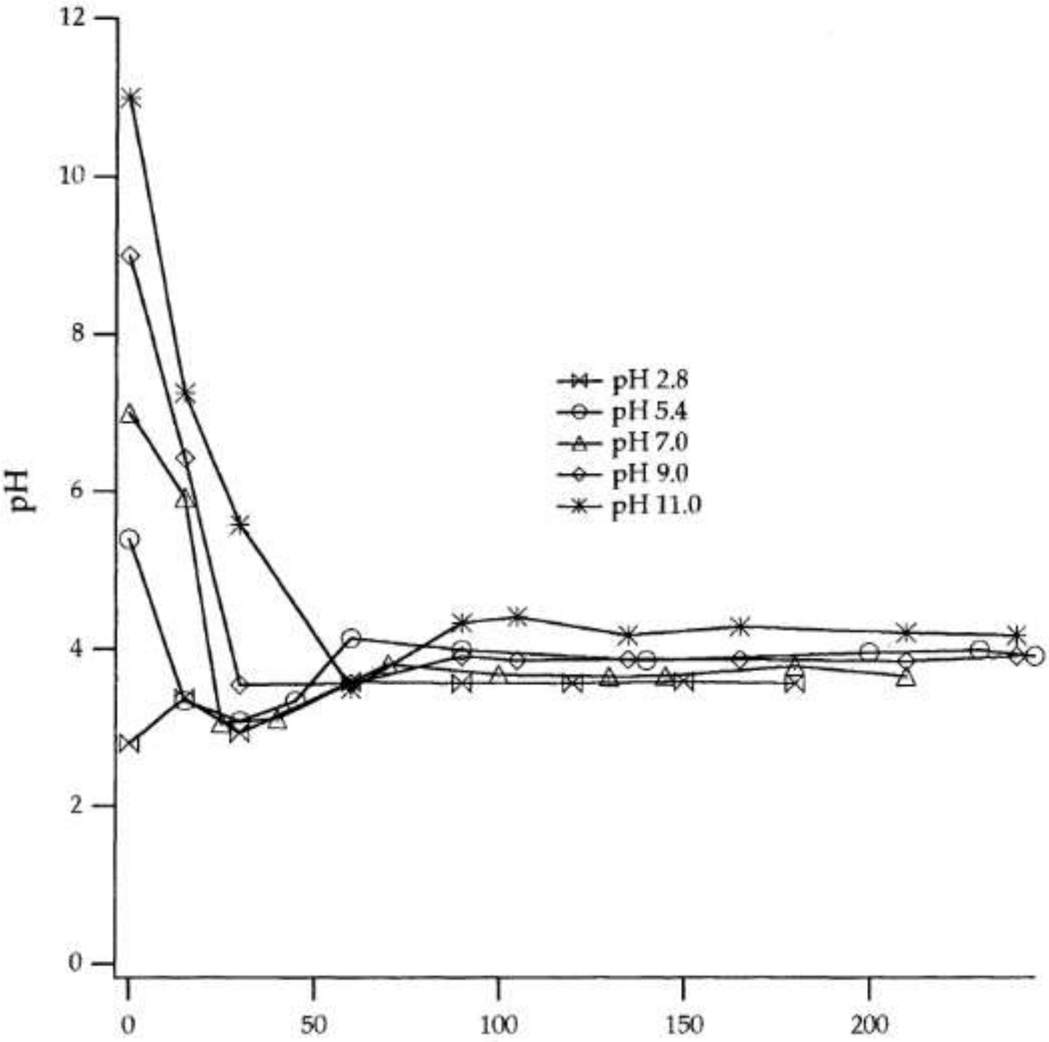

Figure 2.2: Shift of solution pH during Nafion-Fe mediated photo-degradation of 2,4 DCP in a solution H_2O_2 under Suntest light irradiation.

2.5 Hybrid systems

Research study on AOP for PAHs treatment is a common topic nowadays as many researches had study various kind of complexes hybrid with other treatment system and introducing modifications to current techniques to improve its effectiveness and efficiencies. Table 3 shows some of the researches done to combine conventional treatment with AOP.

Table 3: Examples of research on hybrid system

Researchers	Research description	Hybrid system used
Nam et al.[16]	Enhanced degradation of a mixture of PAHs by combining biodegradation with hydrogen peroxide oxidation in a former manufactured gas plant soil. By the combined treatment, more than 98% of 2 or 3 ring hydrocarbons and between 70% and 85% of 4 or 5 ring compounds were degraded while maintaining pH about 6-6.5	A modified Fenton-type reaction at near neutral pH by using ferric ions and chelating agents. Biodegradation followed by modified Fenton treatment was superior to the reverse-order sequence in the degradation of PAHs.
Liu et al. [39]	Effective degradation of aniline wastewater using single biological oxidation, single photo-Fenton and combined biological and photo-Fenton is test for its efficiencies. More than 94% removed of aniline and Chemical Oxygen Demand (COD) were obtained by combined photo-Fenton and biological oxidation processes.	A photo-Fenton reactor with pH pre-adjusted (3-4) in plexiglass storage tank to adjusting tank to adjust pH to neutral for biological treatment in the following sequencing batch reactor.
Sakulthaew et al. [21]	Treatments of water inputs from urban runoffs using combined chemical approach of ozonation and biological process. Objective is to mineralize PAHs. Degradation rates were observed transforming a mixture of PAHs within 10 mins. But it shows different biodegradability of each PAHs species. Overall results showed that the combined process increase the biodegradability of the PAHs.	Using a system flow-through ozone system that simultaneously ozonated and trap emitted gases from reactors. End process of the system is followed by catalytic ozone destroyer.

Previous studies indicated that addition of hydrogen peroxide before bioremediation was not effective in removal of aged PAHs [16]. This was reflected with their outcome of the research whereby biodegradation followed by modified-Fenton's treatment was superior to the reverse order sequence in degradation of PAHs. These facts need to be look into details chemistry of the reaction between Fenton reagent and the said PAHs in treatment environment which show that natural organic matter in the environment scavenged the radicals which prevent effectiveness of the PAHs treatment. This is the reason of the later arrangement are better compared to the other sequence.

Hybrid system with chemical pre-treatment followed by biological treatment are not feasible due to several reasons. Excess oxidant or catalyst by oxidation reaction are toxic to microorganisms which can hinder the biological treatment [20]. Uncontrolled and unregulated effluents from pre-treatment reactor might cause the overall wastewater treatment to fail. Thorough study need to be done specifically to the contaminated study to obtain the original information of the organic composition to determine the correct treatment system [40]. This is due to reason that poor selection of treatment conditions might cause generation of an effluent with too little metabolic value which inhibit the biological process. Direct application of the Fenton reaction are not suitable due to reason that radicals are in fact able to attack most organic matter hence, it lacks of selectivity for preferential attack on the more bio resistant fraction. Reaction with natural organic compounds might produce intermediate products which are potentially hazardous or a stable intermediate which are resist to biodegradation.

2.6 Reactor design

Before come up with design of photo-Fenton reactor, the design of other researches in producing photo-Fenton chemistry related bioreactor was gathered (Table 4).

Table 4: Example of Reactor Design

Researchers	Research Title	Descriptive of the design
Andreozzi et al. [25]	Advance oxidation processes (AOP) for water purification and recovery	- Stirred photochemical tank reactor - Proper sizing of the path length between quartz sleeve (housing of UV lamp) and reactor walls - Quartz cleaning device - Residence time determine by means of simplified first-order kinetics for the substrate consumption - Powers in range 5/100 W l^{-1} used with UV lamp of 40-1.5 × 10^3 W
Sabhi and Kiwi [33]	Degradation of 2,4-Dichlorophenol by Immobilized Iron Catalysts	- Nafion-Fe loading (1.78%) - Dupont Nafion 117, 0.007 inch thickness, area 48 cm^2 - 60ml cylindrical pyrex flask containing 40 ml reagent solution - Suntest solar simulator with intensity of 80mWcm^{-2}, wavelength 290-800nm
Krutzler et al. [41]	Optimization of a Photo-Fenton Prototype Reactor	Figure and table available at Appendix A-A and A-B. - Two coaxial glass cylinder (top and bottom) - Inner centre UV-lamp

		- Two different inner cylinder studied; Quartz and Duran glass Wastewater pumped at flow rate of 300L/h.
Gogate et al. [42, 43]	A review of imperative technologies for wastewater treatment II: hybrid methods	- 400ml capacity double wall cylindrical reactor irradiated with 16 fluorescent black lamps of capacity 14W each. - Operating temperature 25^{o}C - pH 2.75 - Concentration of Fe^{3+} is 1 mM. - Effective pre-treatment for the biological oxidation - 3 h treatment time

A few criteria is considered based on the research done to determine the design of the reactor. Which is describe as follows.

Material for the photo-chemical reactor must have the acid-resistant capability.

- To be specific the material for the photochemical reactor must have considerable resistance to chemical, physical and oxidation[37].

pH adjustment are required at end of the process.

- Final pH after treatment procedure is around pH 4. Hence, pH adjustment are required to change the pH to neutral medium at the end of the treatment; addition of NaOH[33].

Reagents used are need to be regulated to avoid excess in the reactor.

- This could save operation cost, avoid scavenging affect, dilution factor and subsequent reduction in treatment effectiveness[24].
- Reagents used in the treatment is calculated beforehand and is determine according to the literature.

- Final optimum amount of reagents for the treatment is to be obtained after experimentation.

Ensuring radical contact with the contaminants molecules.

- Magnetic stirring mechanisms is provided to ensure homogeneous solution in the treatment environment.

UV-lamp housing.

- Material chosen are needed to be resistance to chemical, physical, oxidation and irradiation[44].
- High transparency from the violet to the infrared spectral range (quartz glass).

Economically feasible.

- Material chosen and capacity of the reactor is compared and selected based on the most suitable design with economic feasibility and project limitation.

CHAPTER 3: METHODOLOGY

3.1 Collecting samples and analysis

This research project have adopted study area at River Perak which includes WTP Parit, WTP Kg Senin and WTP Teluk Kepayang. On each of the WTP we take samples from raw water originated from river and treated water as water supply to the community.

Figure 3.1: Sampling Points

Sampling were done according to Standard Method 6010 B that emphasized on preparation of sampling preservation method[45]. TOC and UV-absorbance were tested as an indicator of aromaticity and chemical reactivity for aquatic organic matter samples from a wide range of water sources[46]. TOC measurements were done using catalytic combustion-based TOC analyser (TOC-5000, Shimadzu, Japan) and ultraviolet absorbance (UVA254) were determine using UV-VIS scanning spectrophotometer (T80, Oasis Scientific Incorporation, US) with 1-cm cells at 254 nm wavelength.

Sample container of 1 litre glassware bottle is pre clean first before use. Sample container(s) is wash with phosphate-free detergent and then rinse with tap water. Next, wash with 1 mol HNO_3 then rinse with tap water. Wash again with 1 mol HCl then wash with tap water. Sample container is rinsed with sample water before it is filled up with sample water. Sample is kept in an icebox at sampling location then transfer to cooler room with temperature at 4^oC. Sample is kept in for analysis for duration of 2 weeks after sampling[45].

3.2 Reactor Design

Photo-Fenton design:

Table 5: Design Specification

Design Specification	
Photochemical reactor volume: 2.0 L	Water sample treated (1 cycle): 1L
Diameter: 14.5cm	Height: 18cm
Wavelength : 360nm	2 X HITACHI F4T5BLB 4W
Nafion membrane: Dupont Nafion 115 (5 mil thickness)	1 piece, Area: 10cm x 10cm
Reagent: H_2O_2 (30%) , 0.1mg/L ~ 1.0mg NaOH (1 mol)	Retention time: 1-10min.
pH operating system: 2.0 – 11.0	Magnetic stirrer: CORNING Laboratory Stirrer, 150rpm

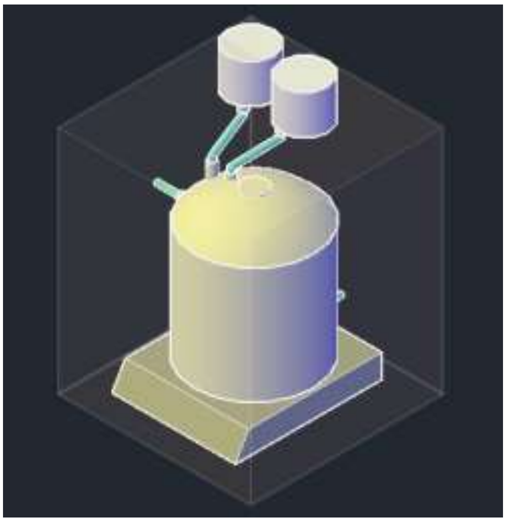

Figure 3.2: Photochemical reactor (Exterior)

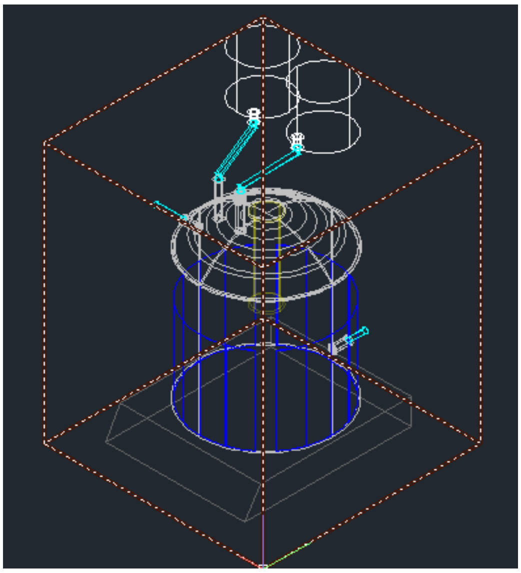

Figure 3.3: Photochemical reactor (Interior)

3.3 Total Organic Carbon (TOC)

TOC analysis is measured for raw water, supply water and treated water. Sample water is taken from cooler at 4°C and let the temperature settles at room temperature before proceed to analysis. Water samples is transferred to a 10 ml vial precisely for TOC measurement using TOC analyser (TOC-5000, Shimadzu, Japan). Using auto-sampler for the TOC analysis which give estimation of the time for analysis roughly 25 mins per sample. Units for TOC reading is ppm.

3.4 Chemical Oxygen Demand (COD)

COD analysis is measured for supply water and treated water. Supply water COD is necessary for determination of initial concentration of hydrogen peroxide by theoretical calculation. Distilled water is used as blank. 5 ml of water sample was taken and precipitate for 30 min. 2 ml of sample is poured into low range COD vials. Vials were digested at 150 °C for 2 hours. Vials is let to cool down to room temperature. Analysis is perform using HACH DR 2800 with settings to LR COD.

3.5 Ultraviolet-Visible Spectrophotometry (UV-VIS)

UV-VIS analysis is run for raw water, supply water and treated water after photo degradation treatment. Water sample is filtered through filter paper (Whatman, No. 1) and transfer to to 1ml vial and measured the ultraviolence absorbance (A cm^{-1}) using UV-VIS scanning spectrophotometer (T80, Oasis Scientific Incorporation, US) at 254nm wavelength. The Specific Ultraviolet Absorbance (SUVA) is calculated using the following formula (Eq. 11).

$$\text{SUVA (L/mg.M)} = \text{UVA } (\text{cm}^{-1})/\text{TOC (mg/L)} * 100\text{cm/M} \qquad \text{(Eq. 5)}$$

3.6 Photo-Fenton treatment

Dupont Nafion 115 membrane is preloaded with Fe ion beforehand. Nafion 115 is purchased from Fuel Cells Etc, Texas and preconditioned with working environment for 24 hour before package is opened. Three steps membrane preparation: (a) membrane was washed with H_2O_2 (10%) and subsequently with H_2SO_4 (5N), (b) next membrane is immersed in $FeCl_3$ (0.1M) for 30 min and washed repeatedly until all Fe^{3+} and Cl^- ion are removed, (c) membrane is immersed in NaOH (0.01M) for 30 min to convert the exchanged Fe^{3+} to its hydrated form[33].

1 L beaker is used as reactor container and HITACHI F4T5BLB 4W is used as source of UV light. 1 L water sample is filled in the beaker, and subsequent hydrogen peroxide amount is added. Amount of hydrogen peroxide to be used in the experiment is determine hypothetically using theoretical oxygen demand (ThOD) method [47] of the following equation: COD = α ThOD. Therefore, theoretically dissociation of one mole of H_2O_2 will produce one mole of oxygen radical. Hence, one mole oxygen required will be equals to the number of moles of H_2O_2 used for degradation. Based on the theoretical amount of hydrogen peroxide we determine the optimum amount of hydrogen peroxide from variation of amount of hydrogen peroxide used.

Experiment is conducted in three phase which described as follows. Phase 1 is to determine the experimental condition and pattern of the degradation. Treatment of the photo-Fenton process for 1 h duration and sample taken for analysis at an interval of 5 min. Phase 2 is based on the pattern and data analysis of the first phase. Third phase is the same condition as Phase 2 except the concentration of hydrogen peroxide is increased by two-fold.

3.7 Project Timeline

Detail is presented in Appendix B-A and B-B.

CHAPTER 4: RESULTS & DISCUSSION

4.1 Water Characterization

Water characterization analysis is done to obtain the parameter of the water sample before any treatment is done. Based on the parameter obtain initially, we can compare it with water parameter after treatment is done to analyse the performance of the photo-Fenton treatment. Table 6 shows that WTP Parit has the highest TOC of supply water, 1.817 ppm and WTP Kampung Senin has the lowest TOC of supply water, 1.200 ppm. On the other hand, Kampung Senin has the highest UVA of supply water, 0.015 and Parit has the lowest UVA of supply water. We can observed here that there is no direct correlation between TOC and UVA. TOC is the analysis to determine the organic carbon but, UV-VIS analysis at 254 nm is specifically to estimate the presence of PAHs in water.

Table 6: Water Characterization

Parameters	WTP Parit	WTP Kampung Senin	WTP Teluk Kepayang
Raw water, TOC (ppm)	1.898	1.663	1.804
Supply water, TOC (ppm)	1.817	1.200	1.559
Raw water, UVA (A cm^{-1})	0.053	0.042	0.044
Supply water, UVA (A cm^{-1})	0.010	0.015	0.011
Supply water, COD (mg/L)	20	17	14

4.2 Effect of pH on photo-Fenton reaction

Photo-Fenton reaction is tested initially with 1 h treatment duration. From this experiment, we can observed that pH is increasing with time. This is not the same with the literature. In the research done by Sabhi and Kiwi [33] pH is observed to converge to acidic media around pH 4.0. This is due to the formation of the peroxyl radical (HO_2^-) and carboxylic acid. Both compound have the character of acidic and it will reduce the pH. That is not the case in this experiment. As shows in Figure 4.1, pH is increasing linearly. Research done by Sabhi have the pattern of the pH converging to pH 4 due to the formation of hydrochloric acid by the degradation of 4-chlorophenol. Sample in this research on the other hand is taken from supply water which have less organic compound. pH is observed to be increase over time is due to the formation of hydroxyl in the Fenton reaction which can be observed in Equation 1.

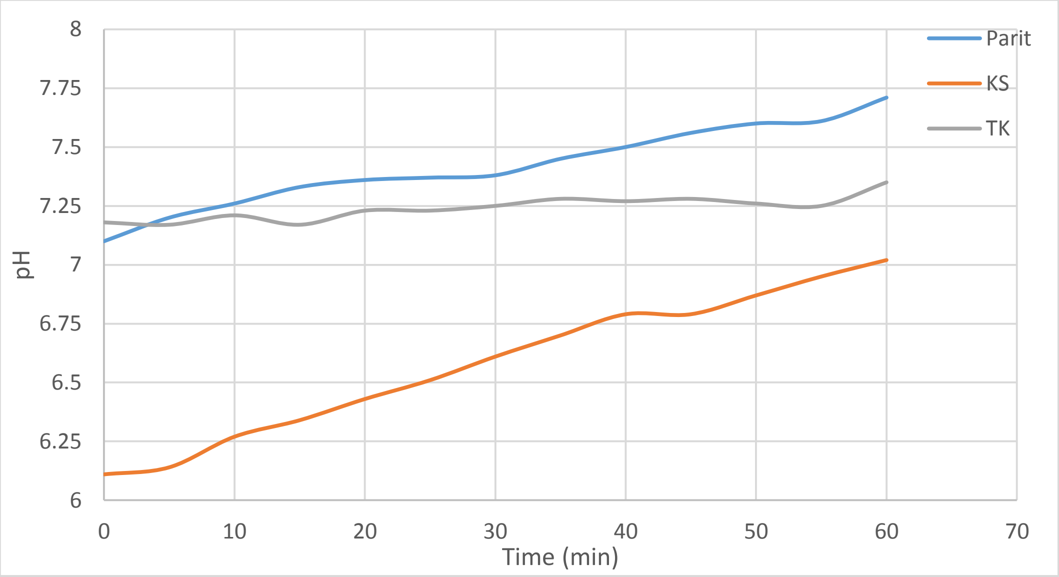

Figure 4.1: pH reading during 1 h treatment

pH for photo-Fenton reaction with supply water is considered not a significant parameter in this context of experiment because of the integration of the nafion membrane which allow the reaction to occur at wide range at pH 2.0 – 11.0 [38], pH is not included on the next phase of experimentation.

4.3 Photo-Fenton's Performance on TOC removal

TOC analysis is done for both experiment which we tested the treatment for 1 h and 5 min. For the treatment in which we run for 1 h, based on Figure 4.2, we observed that the TOC degradation is decreasing inversely proportional. But from the pattern of the graph, we can see that the TOC is staggering. This is due to the phase reaction of the photo-Fenton reaction which the catalyst; ferrous salts is being used up in the initial reaction and being regenerate back in presence of UV light. Since the TOC is quite small, we can determine that even small change of the composition of the reaction would give significance changes to the result of the analysis obtain. TOC is observed to be reduce at most for the first 5 min of the treatment and the rest of the time is practically constant over the time. We take 5 min as the next retention time for the next phases of the experiment to determine the optimum reaction time since 1 h duration is exceedingly overboard.

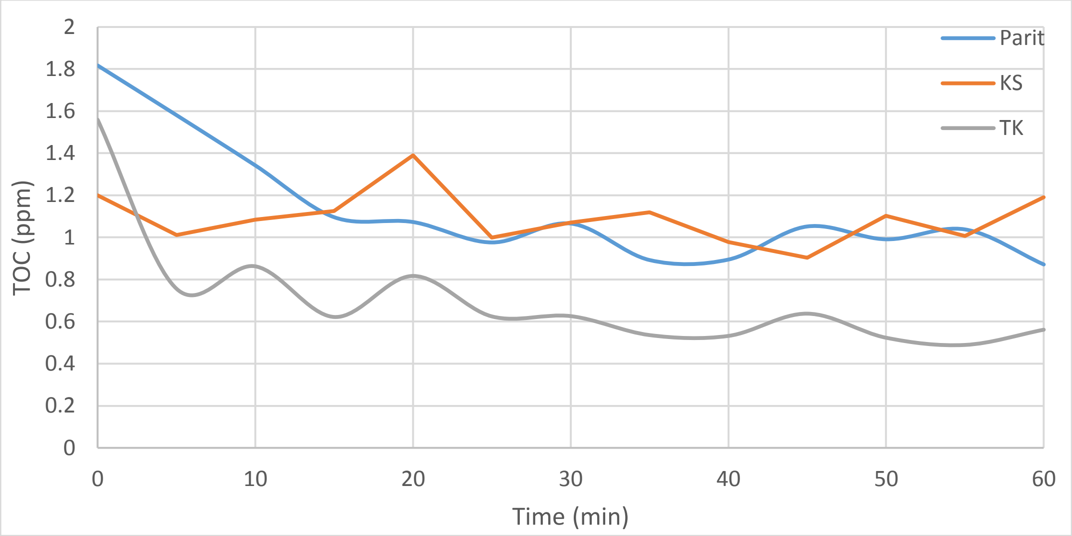

Figure 4.2: TOC reading of 1 h treatment

Hence, we run the second experiment with 5 min duration to assess the performance of the photo-Fenton reaction. Based on Figure 4.3, it shows that the degradation of the TOC is quite large compared to the graph shown in Figure 4.2. TOC is decreasing inversely proportional and the degradation of the TOC is observed as 95.63%, 93.18% and 95.11% respectively to WTP Parit, WTP Kampung Senin and WTP Teluk Kepayang. In overall performance, we can observe that the optimum duration for the treatment is at 85 sec in reference to the degradation of the TOC.

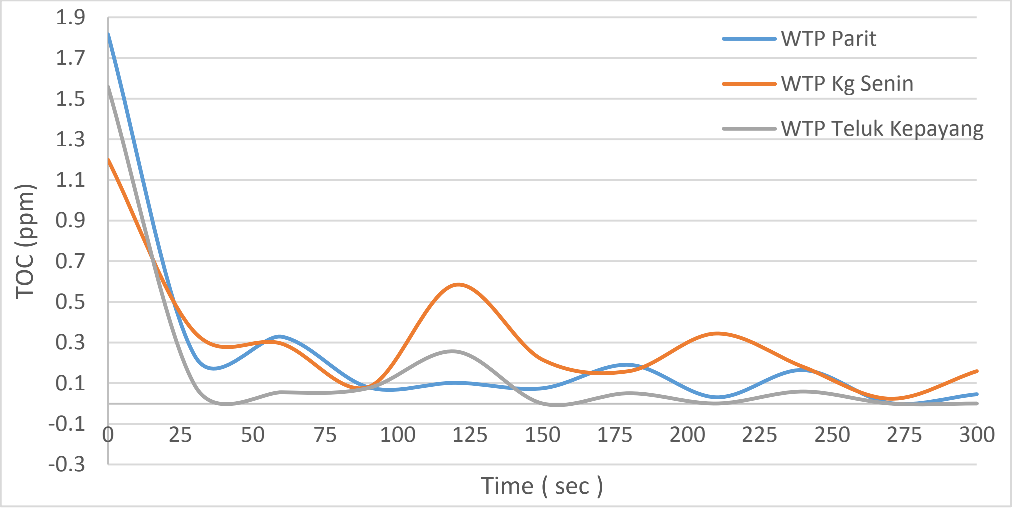

Figure 4.3: TOC reading of 5 min treatment (0.3 mg/L H_2O_2)

4.4 Photo-Fenton's Performance on COD removal

COD analysis is done for phase 1 and phase 2 of the experiment whereby the treatment duration is 1 hour and 5 min respectively. Based on phase 1 of the experiment, in Figure 4.4 we can observe that the COD degradation is occurring most at the first 5 min of the treatment. Degradation of COD is staggering at the following time recorded after the major degradation at the first 5 min. The cause of it is also due to the phase reaction of the photo-Fenton reaction. Hydroxyl is produced and consumed at the changes of the step of the reaction. Since the COD of the water sample is low, even small changes in the chemical reaction can be observed in reading of the COD taken.

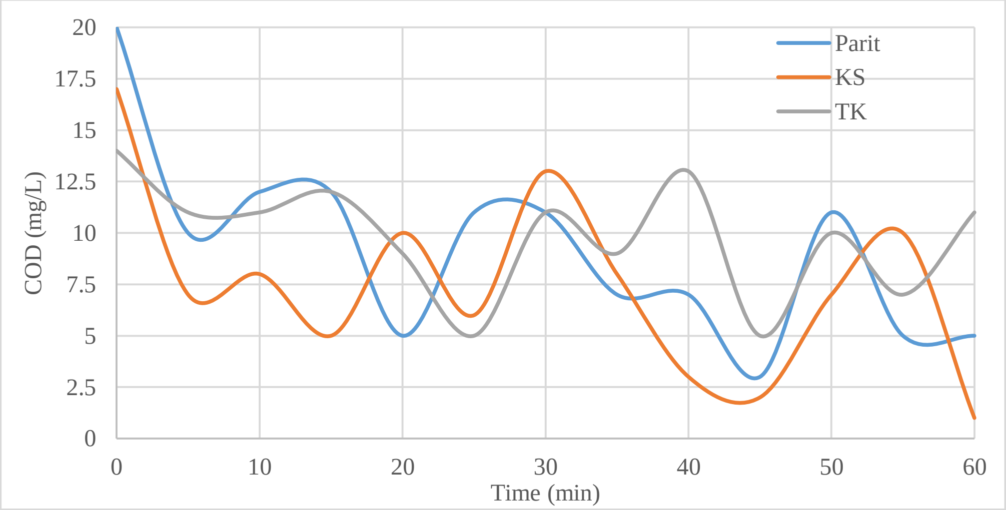

Figure 4.4: COD reading of 1 h treatment

On the other hand, phase 2 of the experiment shows a better degradation declination since we already established that for 1 hour treatment, degradation occur mostly at first 5 min. In phase 2, we are going to determine the optimum time for COD removal based on the data represented in Figure 4.5. COD removal is observed to be in high percentage at 90% removal for WTP Parit, 94% removal for WTP Kg Senin and 79% removal WTP Teluk Kepayang. Based on the pattern in the graph, for overall performance optimum time of treatment for COD removal is observed at 70 sec.

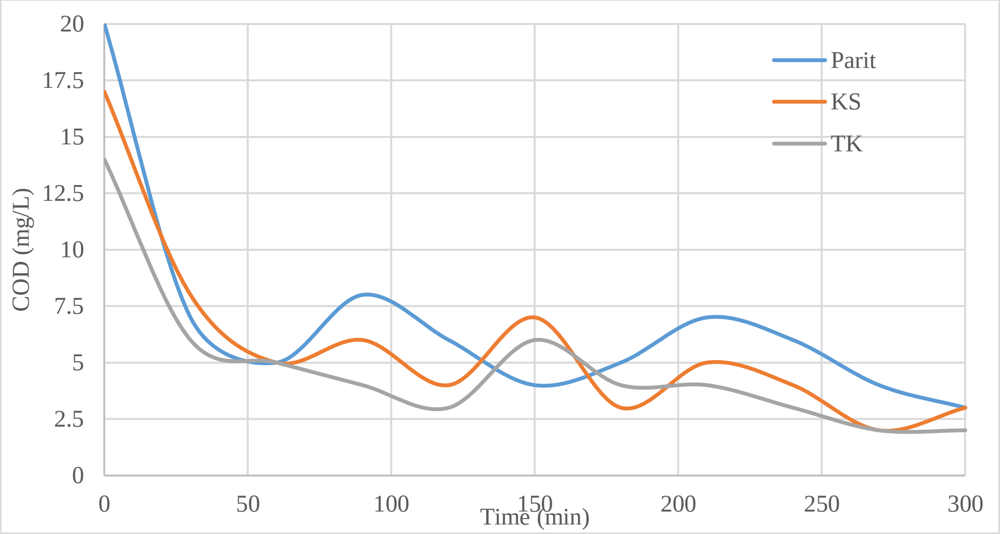

Figure 4.5: COD reading of 5 min treatment (0.3mg/L H_2O_2)

4.5 Effects of Hydrogen Peroxide concentrations in photo-Fenton reaction

Hydrogen peroxide concentrations that is used earlier is 0.3 mg/L. Theoretical amount of hydrogen peroxide is calculated based on the Eq. 6 and Eq. 7 [47] in Appendix C. Based on the calculation theoretical amount of hydrogen peroxide is 0.127 mg/L. But stereochemistry calculation is considered as the minimum amount. Hence we take the upper part of the value; 0.3 mg/L. We used the same concentration for all the water samples from 3 WTP. Calculation of the concentration of hydrogen peroxide used is available in Appendix C.

To get the optimum concentrations of hydrogen peroxide for the reaction, we tested the treatment with two-fold concentration; 0.6 mg/L of hydrogen peroxide and 5 min treatment duration. Based on the graph in Figure 4.4, we observed that the degradation of the TOC is decreasing inversely proportional. Degradation of TOC is observed at 91.44%, 81.83% and 97.99% respectively to WTP Parit, WTP Kampung Senin and WTP Teluk Kepayang. Overall performance we can observe that the optimum duration is 125 sec. To compare experiment using hydrogen concentration 0.3 mg/L and 0.6 mg/L, we can conclude that hydrogen peroxide concentration of 0.3 mg/L has the optimum performance precede the other. Excess amount of hydrogen peroxide cause the scavenging effect when hydrogen peroxide used in the experiment is 0.6 mg/L which is the reason for the reduce performance of the treatment.

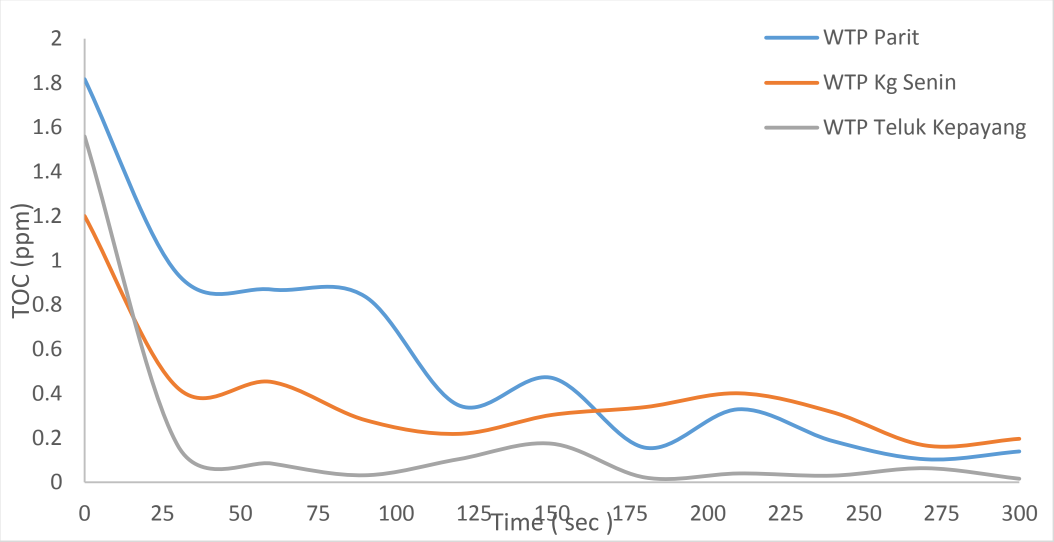

Figure 4.6: TOC reading of 5 min treatment (0.6 mg/L H_2O_2)

4.6 Ultraviolet-Visible Absorbance (UVA) Analysis

UV Absorbance value provide estimation on the presence of PAHs. Based on research by Zakaria [7], observance at 254 nm wavelength would be able to collect absorbance value by the PAHs compound. Based on the UVA chart in Figure 4.5, we can observe that the UVA value is decreasing further after the photo-Fenton treatment.

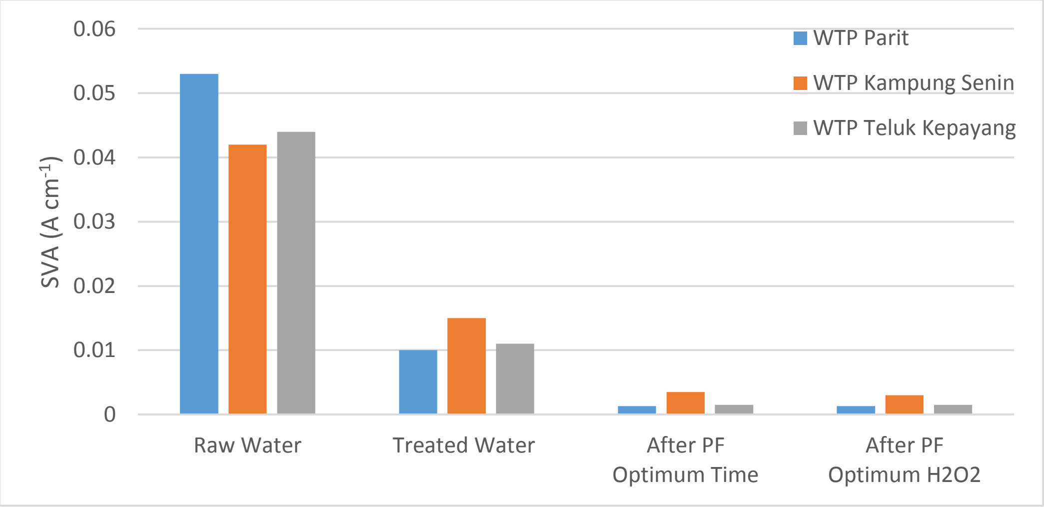

Figure 4.7: UVA

4.7 Specific Ultraviolet-Visible Absorbance (SUVA) Analysis

Results from SUVA analysis is obtain through calculation using TOC and UVA data as describe in the formula Equation 5. Based on the chart shows by Figure 4.6, we can observe that the SUVA is decreasing after the photo-Fenton treatment. The same pattern is shown on the UVA reading. This shows that the treatment are able to reduce the amount of PAHs from water sample tested. Nevertheless, SUVA analysis will get the estimation of the presence of the PAHs and according to Edzwald and Tobiason value of SUVA less than 3 indicate that the solution mainly contain hydrophilic material which is the low molecular PAHs [48].

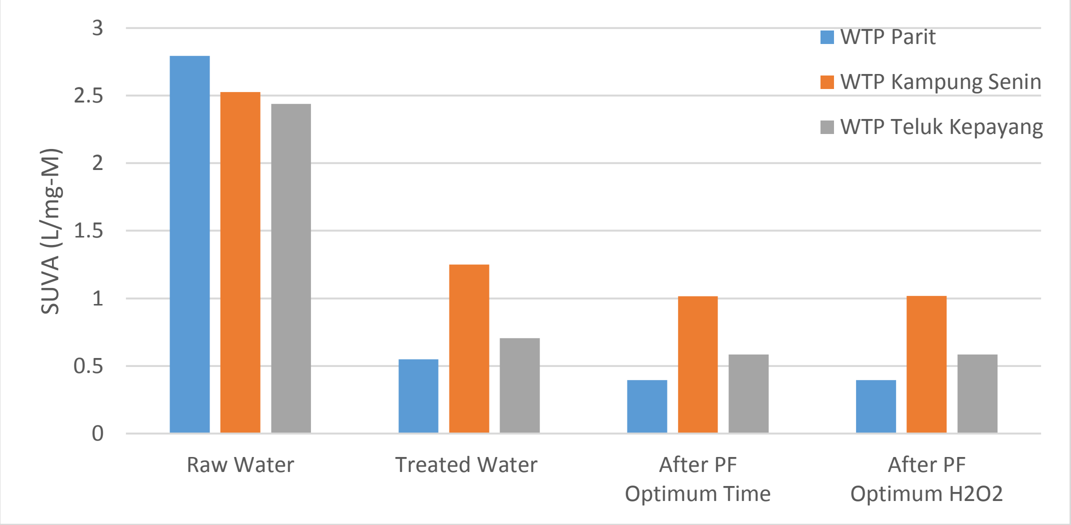

Figure 4.8: SUVA

4.8 Nafion Performance

There is no analysis done to the membrane, only physical observation and the performance of the photo-Fenton reaction is used to determine the functionality of the membrane. Throughout the experiment, there is no leakage of ferrous observed. No formation of sludge and no brown colour formation is observed which represent the presence of iron ion in the solution. Nafion is proved able to be used multiple times without reduction in its performance in the photo-Fenton reaction.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

Photo-Fenton reactor integrated with Nafion membrane is designed and fabricate to investigate the performance of the reactor in treating supply water contaminated with PAHs taken from 3 WTP. Nafion performance shows that it is functioning well in this research as there is no leakage occurring in the treatment. It is proved that drawback of photo-Fenton in formation of sludge is avoidable. Factors affecting the performance of the reactor is the time and hydrogen peroxide and based on performance for TOC removal it is determined that optimum time for treatment of PAHs is 85 sec and optimum dose of hydrogen peroxide is 0.3 mg/L. Whereby for COD removal performance the treatment time is 70 sec and dosage of hydrogen peroxide is 0.3 mg/L. This research shows that TOC and COD analysis are able to provide early and convenient data to determine the degradation of the organic contamination. It is observed that degradation of TOC for all water samples at an average of 94.64% reduction and 87.67% reduction for degradation of COD. SUVA analysis on the other hand helps in providing estimation of the presence of PAHs. Based on the findings, we had determine that the water sample in our research are contaminated by low molecular PAHs.

Photo-Fenton reaction integrated with Nafion are proven to be a good method to reduce PAHs contamination in supply water. However, we observe the limitation of degradation of PAHs that can be done in low level of contamination. Recommendation that can be made is that research on PAHs removal from Malaysian water region is necessary since many research has shown presence of PAHs contamination in various places in Malaysia. Plus whereby that there is no regulation on limitations of PAHs in water. Photo-Fenton reactor are able to be improve further requiring of it to improve its performance in treating low concentration of PAHs. Possibly, more detail comparison with performance of other Advance Oxidation Process in treating low concentration of PAHs. Detail analysis and experimentation are required to obtain more pleasing results to determine the performance of the photo-Fenton reaction.

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