ELECTRO OXIDATION OF PALM OIL MILL EFFLUENT (POME): POST TREATMENT

THAM MAU HAN

UNIVERSITI TUNKU ABDUL RAHMAN

ELECTRO OXIDATION OF PALM OIL MILL EFFLUENT (POME): POST TREATMENT

THAM MAU HAN

A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineers (HONS) Environmental Engineering

Faculty of Engineering and Green Technology
Universiti Tunku Abdul Rahman

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DECLARATION

I hereby declare that this project is based on my original work except for citations and quotations which have been duly acknowledged. I also take this opportunity to declare that it has not been previously or concurrently submitted for any other degree award at UTAR or other institutions.

Signature : ________________
Name : Tham Mau Han
ID No. : 10AGB05056
Date : 19th September 2015

APPROVAL FOR SUBMISSION

I certify that this project title “ELECTRO OXIDATION OF PALM OIL MILL EFFLUENT (POME) : POST TREATMENT” was prepared by THAM MAU HAN has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineers (HONS) Environmental Engineering at Universiti Tunku Abdul Rahman.

Approved by,

Signature : ___________________
Supervisor : Dr. Mohammed J.K. Bashir
Date : 19th September 2015

Specially dedicated to my beloved grandmother, mother and father

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ELECTRO OXIDATION OF PALM OIL MILL EFFLUENT (POME): POST TREATEMENT

ABSTRACT

Palm Oil Mill Effluent (POME) wastewater generation has been rocketed in the past few decades due to the ever increasing demand for the usage of fats and oils. Conventional biological treatment has been undoubtedly the best way to reduce the organic matters but insufficient to meet the discharge standard by the local authority. As a result, further treatment is needed to meet more stringent discharge standards. The present study indicates that integrated post-treatment would further treat wastewater so that the wastewater could achieve the required discharge standards. Using response surface methodology (RSM), a few operational parameters would be prioritized such as current density, reaction time and pH that were empirically determined by optimization via RSM. The optimum performance of 69.56% COD, 97.80% colour and 99.64% turbidity removal were obtained under 56 mA/cm^2 of current density and a reaction time of 65 minutes with pH 4.5. Through the regression analysis, R^2, was found to be 0.86, 0.93, 0.97 and 0.86 for colour, COD, turbidity removal efficiency and pH respectively. Upon these findings, electro oxidation process at specified level maybe used as a post treatment technology that is effective and efficient before final discharging so as to meet the requirements.

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LIST OF SYMBOLS / ABBREVIATIONS

AOP	Advanced Oxidation Process
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
ECP	Electro Chemical Peroxidation
EFB	Empty Fruit Branch
FFB	Fresh Fruit Branch
SS	Suspended Solid
POME	Palm Oil Mill Effluent
RSM	Response Surface Methodology
R^2	Regression
^0C	Degree Celcius
mA	Milliampere
mA/cm^2	Milliampere per centimetre square
mg/L	Milligram per Litre
mL	Millilitre
NTU	Nephelometric Turbidity Units
PtCo	Platinum Cobalt
ppb	Parts per Billion
rpm	Round per Minute
NH_3	Ammonia
NH_3-N	Ammoniacal nitrogen
CO_2	Carbon dioxide
H^+	Hydrogen ion
H_2O_2	Hydrogen peroxide
OH^-	Hydroxyl ion
$OH\cdot$	Hydroxyl radicals
O_2	Oxygen

CHAPTER 1

INTRODUCTION

1.1 Background

The palm oil, *elaeis guineensis* originate from the central Africa, at the meantime, Malaysia, a country that are on Mediterranean that consists of tropical lowlands area able to benefits the growth of the palm oil (Pye et al., 2013). As remarkable as it is, the current expansion of oil palm industry in Malaysia has been staggering while it started off as ornamental, and soon, it blossoms its way into the industry and grow to a promising field. In the exertion towards domestication, there are numerous constraints as the crop originally grows in the wild but it is then when arrived in Malaysia that the full potential of the crops' were deeply studied and investigated. This revolution from the wild to being domesticated, where it is grown in neat rows in well-managed plantations, has not been without cost side by side with lots of energy has gone into thoughtful this 'new' crop, and the means of fitting it to its new home (MPOB, 2014).

During the progress of this crop several things has been learnt about its interaction with the environment. After a period of time, the technology used to process the crop had become a new task as success attempt had been made in developing the crop into plantations. Again, being the pioneer, Malaysia has had to take the lead in this new endeavour (MPOB, 2014). In a time frame of 40 years, the hectares of planted palm oil surge from a mere 400 hectares in 1920 to 54,000 hectares in 1960 with an average increase per decade of 13,400 hectares and it is considered to be a phenomenal growth.

Since then, land such as either from virgin jungles, or from the conversion of plantations that originally supported rubber or other crops and several more areas have been unwrapped up for oil palm cultivation (MPOB, 2014).

To accommodate for such a tremendous amount of rise in planted hectares and it leads to the proportional escalation in factory processing the crop. Therefore, treatment of palm oil mill effluent (POME) is essential to avoid environmental pollution. At both end of input and output sides of its activities, POME also significantly contributes to environmental degradation. The extraction of the palm oil of a wet process in a decanter produces a liquid waste. This liquid waste then combined with the wastes from cooling water and sterilizer to form what known as POME (Abdullah and Sulaiman, 2013). As reported by Rupani et al. (2010), 381 palm oil mills in Malaysia generated about 26.7 million tonnes of solid biomass and about 30 million tonnes of POME in 2004.

Discharging the effluents or by products on the lands may lead to pollution and might detriment the surrounding environment. Thus, there is a need for a sound and efficient management system in the treatment of these by-products in a way that can help to conserve the environment and check the deterioration of air and river water quality (Rupani et al., 2010).

For each tonne of crude palm oil (CPO) produced, about an average of 0.9-1.5m^3 POME is generated. The biological oxygen demand (BOD), chemical oxygen demand (COD), oil and grease, total solids and suspended solids of POME ranges from 25000 to 35000 mg/L, 53630 mg/L, 8370 mg/L, 43635 mg/L and 19020 mg/L respectively (Abdullah and Sulaiman, 2013). Therefore, this had created environmental problem because the palm oil mill industry in Malaysia produces the largest pollution load into the rivers throughout the country.

1.2 Problem Statement

Malaysia has a large proportion of global crude palm oil production amounting to 19.9 million tons in 2011 (Saeed et al., 2014) which results in production of excessive industrial wastewater that must be treated to reach the local authority's discharge standards in order to protect the environment. The normal practice in Malaysia in treating the wastewater would be the use of biological treatment whereby aerobic and anaerobic processes is used. However, due to its complex composition, the conventional biological treatment are time consuming and usually ineffective in degrading high molecular weight fraction (Saeed et al., 2014). Thus, scientist had been working in search of other method or technique to be integrated to the current treatment system in order to meet the requirements and regulations of safe wastewater discharge. Physico-chemical treatments are utilized with biological processes for better efficacy (Kokkali, 2011).

Therefore, this study emphasized on using the alternative treatment method to be applied so that the discharge level of the wastewater from the palm oil industries meet the regulations as implemented. An advanced oxidation process of electro oxidation is used to remove the pollutant from the POME. With its potential and efficiency in treating wastewater which had been recognized by many scientists, it is a possible alternative ways to enhance the treatment efficacy and at the same time achieve discharge standard (Bashir et al., 2014).

1.3 Study Objectives

This study is carried out for the following objectives:

i. To investigate the effect of Electro Oxidation of Palm Oil Mill Effluent (POME) as a post treatment.
ii. To study the effect of pH adjustment on the performance of Electro Oxidation.
iii. To build up a suitable prediction model that could describe the treatment performance based on the process variables.

CHAPTER 2

LITERATURE REVIEW

2.1 Palm Oil Industry in Malaysia

Malaysia, the world's second largest exporter for oils and fats with the palm oil as one of the major agricultural activities that are being carried out has a net exports of around 16,000 metric tonnes (MT) on year 2011 and still remain emergent up till today (MPOB, 2014). Not to be forgotten, a single tree of palm oil can produce multiple products ranging from biofuel, feedstock for cosmetics, toiletries, industries cleaning agent to food with its oil approved by World Health Organization (WHO) as meeting the food standards under the Codex Alimentarius Commission Programme that are enriched with Vitamin A and E that can increase the High-Density Lipoprotein (HDL) cholesterol where by it is a type of good cholesterol that are needed by the body and reduce the risk of heart diseases (Oil Palm-Tree of Life, 2006).

Moving on to the economic profit of the palm oil industry, it is the world's most effective oil-bearing crop in the sense of efficiency, productivity and land utilization with 4.19 tonnes per hectares per year average oil yield compare to the rest of the crops which is the soybean, rapeseed and sunflower that has an average of less than 1.00 tonnes per hectares per year oil yield respectively. Other than that, palm oil is also an energy-efficient production whereby the net energy is relatively higher as compare to the soybean and rapeseed (Oil Palm-Tree of Life, 2006).

Of the amount of palm oil produced, 85% of it is used in the food industries and it is one of the 10 products that could be used without or minimal modification. In Malaysia, a total land area of 32.86 million hectares with 62.3% of it are preserved as forest and adding the agricultural cover will be totalled to a sum of 81.3% of greenery while maintaining the title of developing country. In addition to that, the palm oil also serves as a green canopy to help absorbed the ever increasing amount of carbon dioxide (CO_2) with its huge leaf branch that extend widely beside providing numerous job opportunities (Oil Palm-Tree of Life, 2006). Figure 2.1 shows the percentage of forest area comparison between a few Western countries with Malaysia, Indonesia and Colombia.

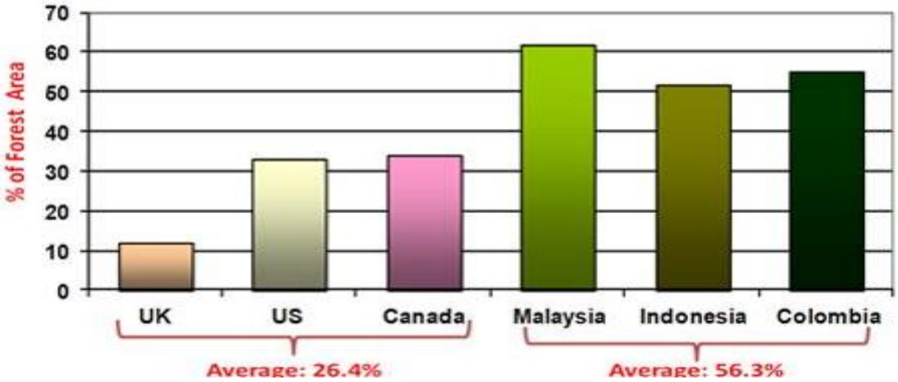


Figure 2.1 Percentage of Forest Area in Various Countries (MPOB, 2012)

This proliferation in hectares is a direct consequence of the government's policy on crop diversification. By 1996, the hectares under oil palm stood at a staggering 2.6 million hectares. By 2005 and 2010 the percentage change in the areas under oil palm was around 20% for each five-year period. In 2011, the hectares reached 5 million hectares, and the change in area in 2011 was only 3% as compared to 2010. This rapid growth in oil palm planting has been seen in five-year period 1975 – 1980, 1980 – 1985, and even in 1985 – 1990 up till 2011 as shown in Figure 2.2, due to the crop diversification programme. It also saw a corresponding growth in the milling and refining sectors. Encouraged further by the government’s incentive to exploit the country's rich agro-based resources, oleo-chemical processing from palm oil and palm kernel oil began to gain prominence in 1980's (MPOB, 2014).

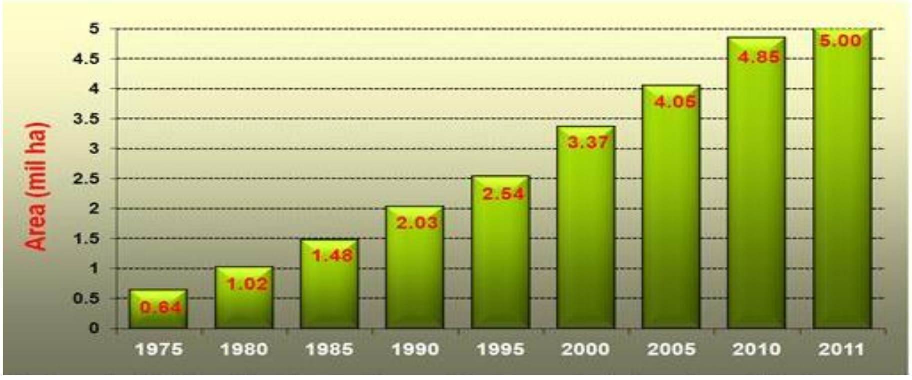
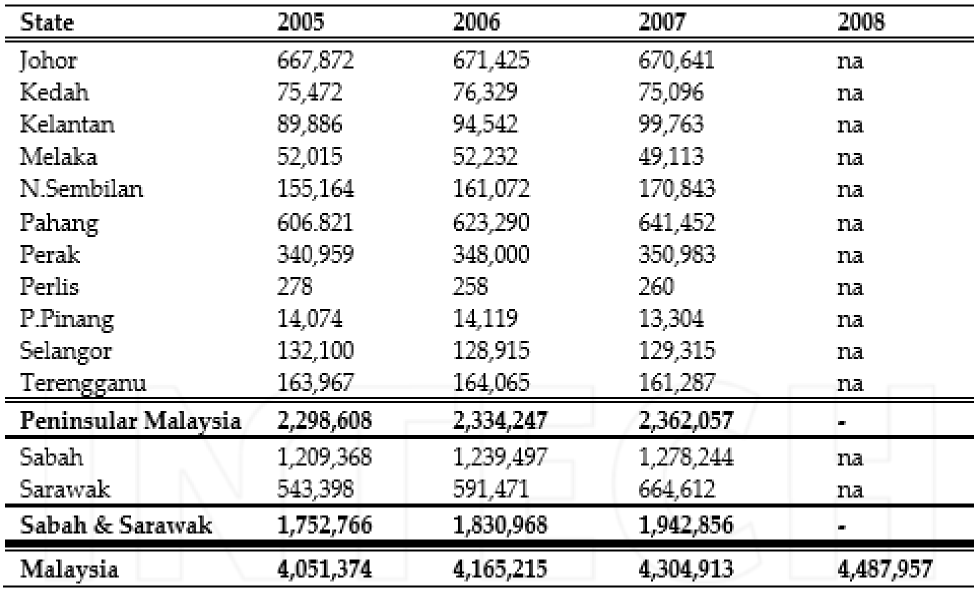


Figure 2.2 Area of Palm Oil Planted in Malaysia throughout the Years (MPOB, 2012)

The yield of Fresh Fruit Brunches (FFB) is about 45-56 % and the fleshy mesocarp of the fruit is used to obtain oil. Yield of oil from the kernel is about 40-50%. Both mesocarp and kernel of fruit produces about 17 tonnes hectares per year of oil. From 5.8 tonnes of FFB, about 1 tonne of crude palm oil (CPO) is produced. The waste products from oil palm processing consist of oil palm trunks (OPT), oil palm fronds (OPF), empty fruit (EFB), palm pressed fibres (PPF) and palm kernel shells, less fibrous material such as palm kernel cake and liquid discharge POME (Rupani et al., 2010). Table 2.1 shows the area of palm oil planted according to state between the year 2005 to 2007 while Figure 2.3 depicts the production of palm oil product throughout the last 30 decades.

Table 2.1 Oil Palm Planted Area 2005 - 2008 (Hectares)

(Abdullah and Sulaiman, 2013)



State	2005	2006	2007	2008
Johor	667,872	671,425	670,641	na
Kedah	75,472	76,329	75,096	na
Kelantan	89,886	94,542	99,763	na
Melaka	52,015	52,232	49,113	na
N.Sembilan	155,164	161,072	170,843	na
Pahang	606.821	623,290	641,452	na
Perak	340,959	348,000	350,983	na
Perlis	278	258	260	na
P.Pinang	14,074	14,119	13,304	na
Selangor	132,100	128,915	129,315	na
Terengganu	163,967	164,065	161,287	na
Peninsular Malaysia	**2,298,608**	**2,334,247**	**2,362,057**	**-**
Sabah	1,209,368	1,239,497	1,278,244	na
Sarawak	543,398	591,471	664,612	na
Sabah & Sarawak	**1,752,766**	**1,830,968**	**1,942,856**	**-**
Malaysia	**4,051,374**	**4,165,215**	**4,304,913**	**4,487,957**

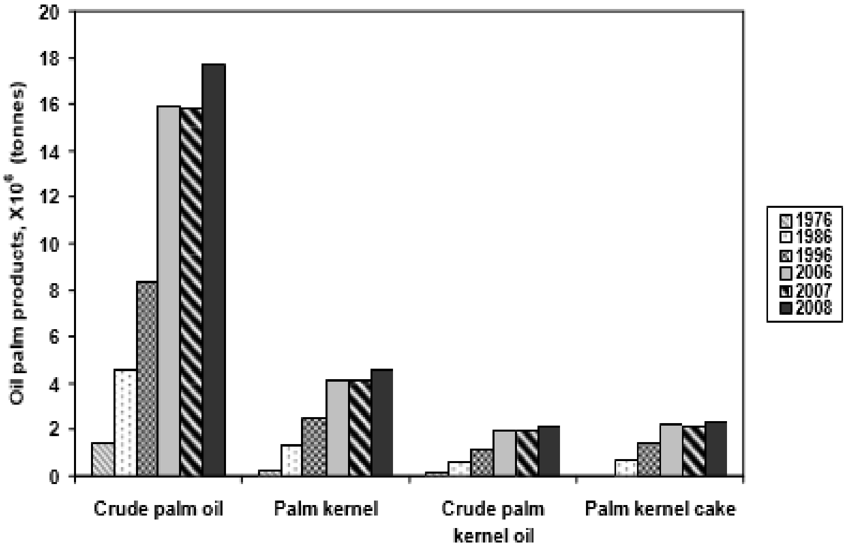


Figure 2.3 Productions of Palm Oil Products Every Ten Years from 1976 – 2006, 2007 and 2008 (Abdullah and Sulaiman, 2013)

2.2 Palm Oil Mill Effluent (POME)

Effluent water is defined as water discharged from industries, which contains soluble materials that are detrimental to the environment such as CH_4, SO_2, NH_3, halogens and insoluble liquid or solid. To be more specific, POME is used as the general phrase referring to the effluent from the final stage of palm oil production. It contains various liquids, residual oil and suspended solids as it has very high strength waste in its untreated form. POME is also actually the sum total of liquid waste which cannot be easily or instantly reprocessed for extraction of useful products and is run down the mill into the internal drainage pipe to be the so called sludge (Igwe and Onyegbado, 2007).

As the number of palm oil mills increase, the generation of waste from the industries poses a threat to the environment as it produces a lot of by-products and wastes besides the liquid waste which is the POME and this could lead to serious contamination if not properly dealt with (Igwe and Onyegbado, 2007). Other than that, the process of oil extraction, washing and cleaning also produces wastewater that contains cellulosic materials, fat, oil and grease which added to the effluent of palm oil mill that sums up to 18,000 to 40,000 mg/L of both the suspended solids and total dissolved solids (Rupani et al., 2010).

2.3 Characteristics of Palm Oil Mill Effluent (POME)

Palm Oil Mill Effluent, or as known as POME is the by-product of processing the palm oil which is used by the society under variety usage such as fertilizer, biofuel, biogas and crude oil which is used to produce toiletries like shampoo and perfumes. POME is made up of about 95–96% water, 0.6–0.7% oil, 4-5% total solid which inclusive of 2-4% suspended solids that are from the debris of palm mesocarp (Wang et al., 2005). Other than that, the physical appearance of the POME appears to be in the form of highly concentrated dark brown colloidal slurry of water, oil and fine cellulosic materials mainly due to the process of the sterilization that induced great amount of heat including some vigorous mechanical process used to separate its constituents such as the kernel, empty fruit brunch (EFB) and also the sludge (Chan et al., 2010).

Due to the immerse heat from the sterilization process, the output from the mill of the wastewater will be thoroughly around 80 to 90°C and it will be then transferred to a tank for cooling and also as a temporary storage tank before further process take place. POME itself is rich with mineral such as phosphorus, potassium, magnesium and calcium thus proper treatment is needed to remove all the mineral rich ions inside it before discharging into the water way to prevent algae bloom from excessive minerals (Wang et al., 2005). This also means that the dried sludge that had been dewatered are recycle back to be used as the fertilizer to the new plant and cost of fertilizer can be reduced due to little usage.

Table 2.2 Typical Characteristic of Palm Oil Mill Effluent (POME) and Discharge Standards Other than Standard A or B of POME According to Environmental Quality Act 1974

Parameter	Mean	Range	Discharge Standards
pH	4.2	3.4 – 5.2	5.0 – 9.0
BOD_5 @ 20^oC (mg/L)	25,000	10,250- 43,750	400
COD (mg/L)	51,000	15,000- 100,000	1000
Suspended Solids (mg/L)	18,000	5,000 – 54,000	400
Ammonical Nitrogen (mg/L)	35	4 – 80	100
Total Solids (mg/L)	40,000	11,500 – 79,000	1,500
Volatile Solids (mg/L)	34,000	9,000 – 72,000	-
Oil and Grease (mg/L)	6,000	130 – 18,000	100
Total Nitrogen (mg/L)	750	180 – 1,400	50

*Colour (PtCo)	-	151	15
*Turbidity (NTU)	-	11,000	< 0.5

***= As of US Environmental Protection Agency (USEPA) standards.**

(MPOB, 2014; EQA, 1974; USEPA, 2015)

2.4 Treatment for Palm Oil Mill Effluent (POME)

The process of processing the POME begins from the intake of the raw effluent produced by the mill and this POME will then be transferred to a pre-treatment process which is the screening either by vibration or mesh screen. After the filtering of the possible coarse particles such as the EFB or shell, it will then be skimmed off the oil and grease by aeration process and also recovery by the oil skimmer. A followed up stabilization process is also take place as to tune the best condition for treatment before applying the biological treatment as shown in Figure 2.4 below.

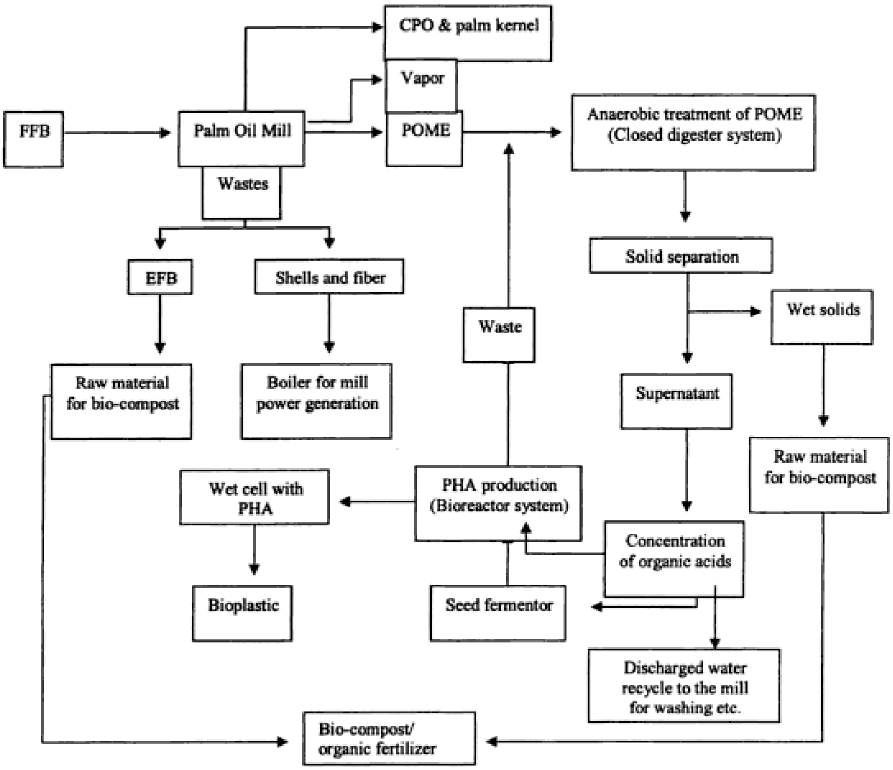


Figure 2.4 Proposed Palm Oil Mill Effluent Wastewater Treatment System (Wang et al., 2005)

2.4.1 Biological Treatment

There are a few types of biological treatment that is available for the POME treatment such as aerobic, anaerobic and facultative. Aerobic pond is generally shallower than the anaerobic pond due to the need of oxygen for the microorganisms to be able to live and also decomposed. As of the anaerobic pond, it doesn't need any oxygen for its activity, thus it needs a deeper pond so that the open air does not penetrate to it and will kill it. Meanwhile facultative ponds are for bacteria that can live with or without the present of oxygen, making it rather easier to be taken care. Thus, it is important to have a control of the condition for the survival and efficiency of the microorganisms.

Usually, if the microorganisms are healthy, the pH is ranging from 7.4 to 7.7 and if it falls below 7.4, it means that the microorganisms are insufficient and draining of wastewater are carried out (Ibrahim et al., 2007). The purpose of having a pH and temperature control is to ensure the microorganisms is working at optimum level. Moving on will be the biogas that are extracted from each tank is directed to the Make-Up-Water tank (M.U.W.), home for the bacteria for mixing of the biogas and the bacteria in that tank before entering the H_2S scrubber for cleansing of the biogas.

The process continues with the biogas entering the chiller, continues the process or by-pass the scrubber and enters the enclosed flare system which burns off the excess biogas. The flare system is advantageous in terms of carbon production as it gives off smokeless combustion and reduced flame visibility with a low noise production. Next, the biogas that goes to the chiller will be cool down with a machine that generates cool air and it continues its path to the buffer tank where the biogas is conditioned to a suitable level before finally enter the gas engine for electricity production and to the thermal boiler. Biogas when it is converted to electrical energy, it will then be supplied to run the thermal boiler, long fibre and decanter which will significantly cuts off the overall costs to run the whole oil palm plant (Wang et al., 2004; Ibrahim et al., 2007).

2.5 The Need of Post Treatment

Due to the increasing number of palm oil mill, a more stringent regulation had been adopted in order to protect the environment from further pollution and also destruction of the natural habitats. Throughout the years, scientist had been working to find a breakthrough in solving this problem and they had finally come across the practice of post treatment (Speitel et al., 1999). To further reduce the toxicity of the POME, an advanced oxidation process (AOP) are required to meet the regulations and standards based on the Environmental Quality Act 1974 and also Industrial Effluents Regulations, 2009 that is established to prohibit pollution and discharge of waste into the water way and other types of treatment method is shown in Table 2.3.

Table 2.3 Other Types of Post Treatment Method

Types of Treatment	Process Details	References
Coagulation-flocculation	Coagulation chemicals are added to increase the rate of floc formation while flocculation is the process of slow mixing to increase the probability of particle collision.	Spellman, 2008
Adsorption	Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate).	Kopecky et al., 2015
Membrane Processes	Use of membrane such as reverse osmosis (RO), Ultrafiltration (UF) and Nanofiltration (NF) to retained larger size particles and allow water molecules to pass through.	Hillis, 2000

Chemical Oxidation-AOP	The potential of AOPs is that it can effectively transform non-biodegradable pollutants into non-toxic biodegradable substances by rapidly oxidizing a wide range of organics pollutants through generation of highly reactive groups of hydroxyl radical, (OH·)	Saeed et al., 2015

2.6 Advanced Oxidation Processes (AOP)

In Malaysia, most of the palm oil mills are implying anaerobic treatment process to treat high organic-loading wastewater such as POME at preliminaries due to its low operation costs as compare to other processes. Nevertheless, there are drawbacks and limitation such as long hydraulics retention time (HRT), large land areas used, digester requirements, utilization difficulty, methane collection in which will lead to a detrimental greenhouse effect released to the environment (Saeed et al., 2015). Furthermore, research proven that an integrated treatment process of anaerobic-aerobic and followed by another aerobic treatment shown to have promising performance in terms of removing the organic compounds from the POME (Chan et al., 2010).

Recently, the advancement in technologies had led to an improved version of treatment processes namely the Advanced Oxidation Process (AOP) that shows promising results after several upgrade in its methodology which can further reduce the organics load of wastewater. This process is still new in the market and not all of it is implemented into the industries and small pilot scale was carried out to extensively understand its effect. In this study, the potential of Electro Oxidation Process (EOP) is that it can effectively transform non-biodegradable pollutants into non-toxic biodegradable substances by rapidly oxidizing a wide range of organics pollutants through generation of highly reactive groups of hydroxyl radical, (OH·) (Saeed et al., 2015). Other than that, researcher in this field has broadened their finding ways to improvise the treatment ability for the wastewater such as replacing the conventional method of treatment of wastewater with electrochemical oxidation and also integration of electrochemical oxidation into the treatment system. As electrical energy is mainly consumed in ECP, photovoltaic (PV) modules can be used as a power supply to eventually reduce the operating costs. In order to reduce the power consumption of the ECP, researcher had suggested that this technique is to be combined with other method either as a pre-treatment or as a polishing step or usage of renewable energy to power up this process (Bashir et al., 2014).

Since oxygen is limited during the in situ biodegradation or organic pollutants, injection of H_2O_2 has been successfully attempted by Calabrese and Kostecki in 1989. As a result, the biodegradation activity had been enhanced by the dissociation of H_2O_2 into water and oxygen which could lead to an increase in removal efficiency (Kokkali, 2011).

2.6.1 Electro Oxidation

As for why AOP is selected is simply because of its efficiency in further reducing of the toxicity level in the POME that they can improve the biodegradability of organic compounds through the use of reactive radical in this case such as the adjustment of pH using acidic buffer. The remarkable ability of the reactive radical to react in a flash with the organic compounds that lead to the production of organic radicals whereby these radical in nature are reactive to the presence of oxygen. While that continues in a series of chain reaction, the end process of mineralization of organics matter to gives of carbon dioxide and water (Mohajeri et al., 2010).

2.6.2 Chemical Reaction of Electro Oxidation

Using this method, the organic pollutants can be eliminated by means of indirect oxidation whereby a mediator is electro generated to carry out the oxidation and direct anodic oxidation where pollutants are being destroyed on the anode surface by the anodic electron-transfer reaction. Hydroxyl (OH) radicals are being produced on the anode surface to enhance the rate of oxidation as it is a strong, non-selective oxidizing agent that reacts instantaneously with organic compounds viz. hydroxylation (oxidative degradation of organic compound in the air which converts lipophilic compounds into hydrophilic products that are more readily excreted) assisted by the addition of hydroxyl group to a non-saturated bond or dehydrogenation with the loss of hydrogen atom following a radical mechanism until their overall mineralization that converts the initial product into carbon dioxide, water and inorganic ions (Mohajeri et al., 2010).

Deng, stated that a set of equipment is need which inclusive of a direct current (DC) power supply, a cathode, an anode, and electrolyte which is used as a mediator that transfer the ion between both electrode in maintaining the electro oxidation process (Bashir et al., 2014).

2.6.3 Factors Affecting Electro Oxidation

There are a few factors that can contribute to the performance and efficiency of the electro oxidation process whereby these factors need to be taken and analyse with care to avoid disturbance to the process.

2.6.3.1 Electrodes

When selecting the type of electrodes, a few of the criteria is needed in order to have an effective performance as an end results such as the electrode have high electrical conductivity, high physical and chemical stability, catalytic activity and selectivity and also of low cost or life ratio (Bashir et al., 2013). Next, the advantages of using the electrochemical peroxidation against the other type of AOP is that it has high efficiency in terms of performance, having simple mechanism in destroying the contaminants leaving no residue when doing so, has suitability to treat wide range of substances, simple and easy equipment needed and also low cost for the materials and equipment.

2.6.3.2 Operational Condition

The possible operational condition for this experiment is current, type of electrodes, reaction time, temperature, and pH. Firstly, the current applied is of constant rate of increase to identify the best possible current density that is needed for an optimum removal. Nevertheless, the contact time, pH buffer and the pH to begin the experiment will also be varied from time to time based on the operational condition. Other than that, the type of electrode and temperature will be a control and is pre-fixed before the start of the experiment (Bashir et al., 2013).

2.6.3.3 Temperature

Based on the state patent above, the temperature that is recommended should be at a range of 20ºC to 70ºC and more ideally at 20ºC to 50ºC. Despite of that, Hawksley in the year 2003 conducted an experiment of temperature between 10ºC to 40ºC on the performance of ECP but it shows no enhancement of the process effectiveness as previously claimed. However, due to the economic viability, it is not wise to raise the temperature unnecessarily as it may increase the operational cost of the process (Kokkali, 2011).

2.6.3.4 pH

As of the recommendation from the US patent for ECP, the ideal range of pH is from 2 to 11 but more ideally at 3 to 5.3. This is due to fact that the average pH level for the POME is 4.2 and thus conducting the test between pH of 3 to 5.3 would results in minimization of operational cost as less chemical are to be used to raise or lower the pH of the POME (MPOB, 2014). By lowering the pH of the treated effluent with strong acid such as the hydrogen peroxide, the conductivity increased due to the presence of more ions. As a results, the current flow increase while the solubility of the iron is enhanced at lower pH values, improving its release from the anode and hence the performance of ECP (Kokkali, 2011).

2.6.3.5 Concentration of H_2O_2

As reported by Scrudato and Chiarenzelli (2000), the optimal concentration of H_2O_2 should not exceed 100ppm in order to achieve the most effective degradation of the organic pollutants. Freeman (2002) demonstrated that adding lower concentrations of H_2O_2 is at the same degree sufficient. Actually, the parameters that must be considered vary each time and dependent mainly on the type of treated effluent. Concerning the way of adding the desired amount of hydrogen peroxide in the ECP system, it must be preferably added in small doses and in different locations, in order to avoid the high accumulations of H_2O_2 at one place and enhance the system‘s efficiency (Kokkali, 2011).

2.6.3.6 Current Density

As claimed by the US Patent for Electrochemical Peroxidation (ECP), the current densities should be in the range of 0.5 to 150 mA/cm^2, preferably between 1 and 100 mA/cm^2, and most preferably between 2 and 50 mA/cm^2 (Scrudato and Chiarenzelli, 2000). Current density will be affecting the effectiveness of the process as it is the electric current per unit area.

2.6.3.7 Contact Time

Based on the research conducted by Awang, et al. (2011), the preferable contact time for the process of ECP would be at 55 minutes for maximum efficiency (Awang et al., 2011). As for time, the reaction would reach an optimum point whereby the process is running at maximum efficiency given that all the variables are in place.

CHAPTER 3

METHODOLOGY

Figure 3.1 shows the methodology flowchart whereby the procedure details are discussed. Starting off with the sample collection, the location was at Tian Siang Oil Mill (Air Kuning) at the retention pond number 10 before discharging to river that had undergone the biological treatment. The sample then tested for initial characteristics such as COD, BOD, colour, turbidity, pH, suspended solids and ammonical nitrogen. Based on that, preliminary experiments were carried out to study the effect of current density, contact time, pH and concentration of H_2O_2. Optimum values that were obtained from the test were used to design the Response Surface Methodology (RSM) experimentation. Following that, the results will be optimized via the RSM and validation process was carried out and ended with the results analysis of the acquired data.

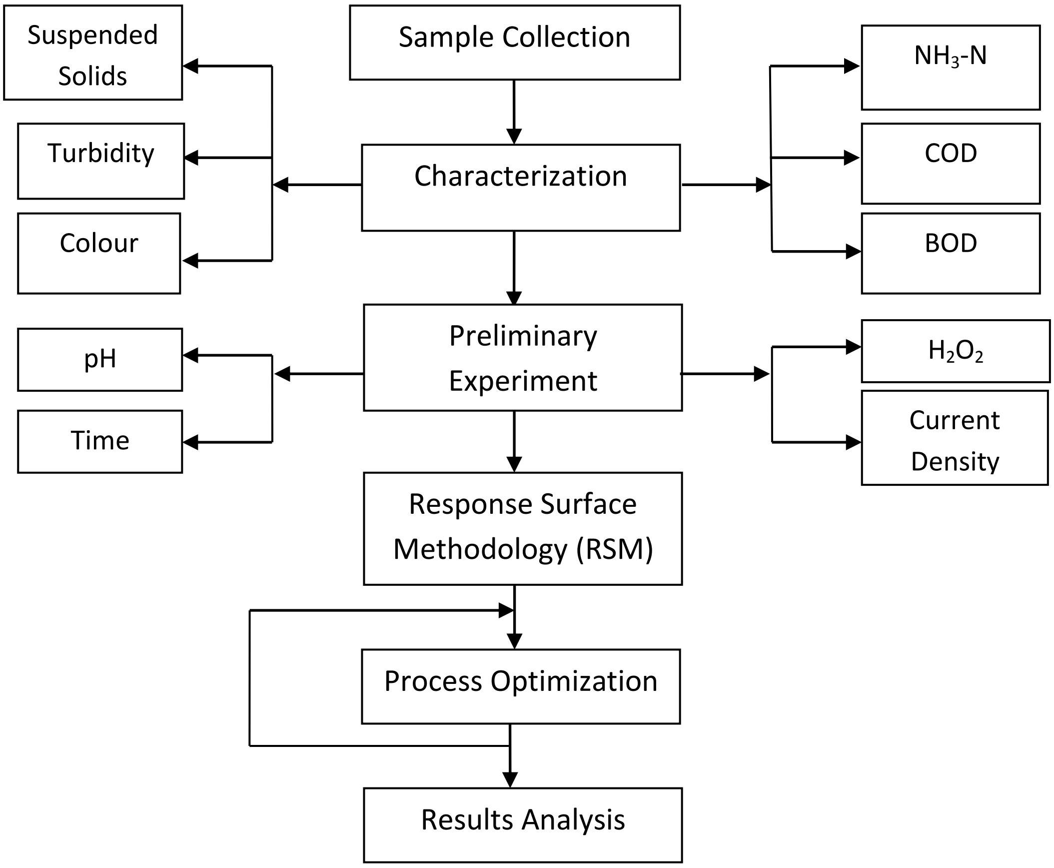


Figure 3.1 Methodology Flowchart

3.1 POME Collection Location

The POME samples were collected from Tian Siang Oil Mill (Air Kuning) Sdn Bhd located in the District of Batang Padang, Perak as shown in Figure 3.2.

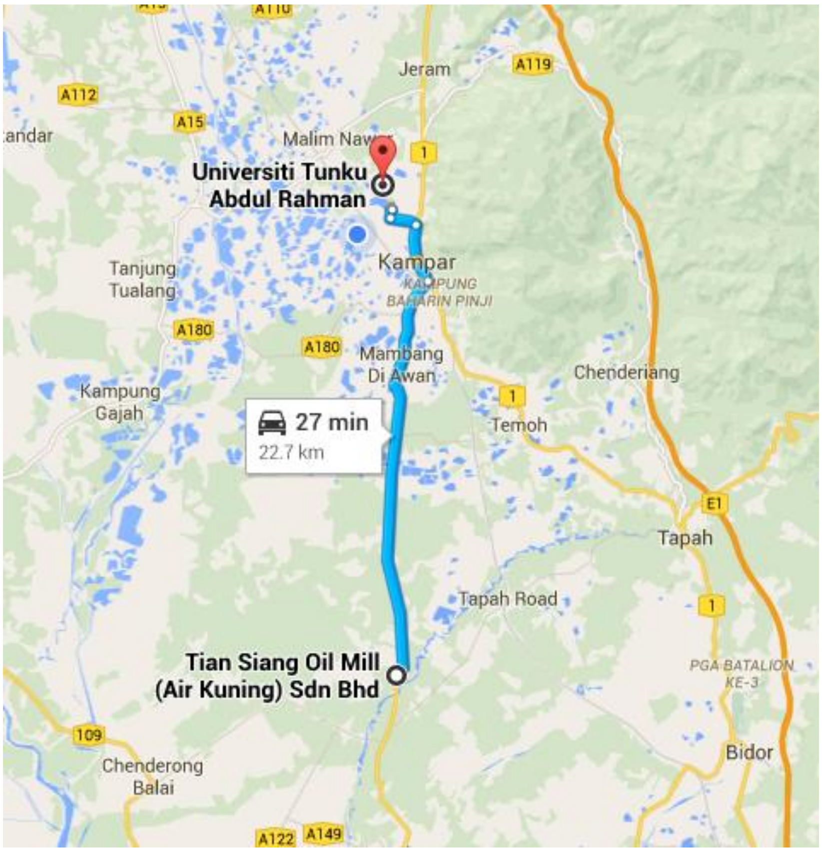


Figure 3.2 Site location of Tian Siang Oil Mill Air Kuning from UTAR Perak Campus (Extracted from Google Maps, Accessed on 27 March 2015)

The mill was commissioned in 2000 with FFB (Fresh Fruit Bunches) processing capacity of 60 tons/hr expandable to 120 tons/hr. Besides the conventional palm oil milling activities, this mill also features the biomass activities like biogas anaerobic digester plant. This company was developed in year 2000 under Tian Siang Group (Tian Siang Oil Mill Air Kuning Sdn. Bhd., 2015).There is numerous collection ponds available for sample collection as there are a total of 11 ponds and the collection is done at pond number 10 as shown in Figure 3.3.

Figure 3.3 Wastewater Sample Collections Pond at Tian Siang Oil Mill Air Kuning

The collected wastewater samples are then transferred to Environmental Laboratory at Faculty of Engineering and Green Technology, UTAR Kampar and was stored at 4ºC in order to minimize the biological and chemical reactions in the wastewater sample and also to avoid inaccurate results when conducting the experiments. The wastewaters are collected using a 1.5L bottle as shown in Figure 3.4.

Figure 3.4 Wastewater Sample Collections with a 1.5L Bottle

3.2 POME Characteristics

Basically, wastewater for POME characteristics are best represented by biological oxygen demand (BOD), chemical oxygen demand (COD), ammonium nitrogen (NH_3-N), pH, colour, turbidity and suspended solids (SS) using the standard method (APHA, 2005). This information is beneficial for the types and design of treatment operations.

3.2.1 Chemical Oxygen Demand (COD)

The most commonly used parameter for the measurement characteristics of wastewater for POME is the chemical oxygen demand due to its high reliability and significant value. The lab scale COD test for leachate was done according to Hach Reactor Digestion Method 8000. The equipment used were COD heat reactor, model DRB 200, USA, and spectrophotometer, model DR 6000, USA, as shown in Figure 3.5 and Figure 3.6, respectively. Firstly, the COD heat reactor was preheated to 150ºC. Then, 2ml of POME sample was pipette into the HR COD Digestion Reagent Vials followed by heating the vials for 2 hours using the COD heat reactor. Then, the vials were cooled to room temperatures and preceded for testing with spectrophotometer using Program 435 COD HR. The COD value was obtained in mg/L.

Figure 3.5 COD Reactor Block (DRB 200, USA)

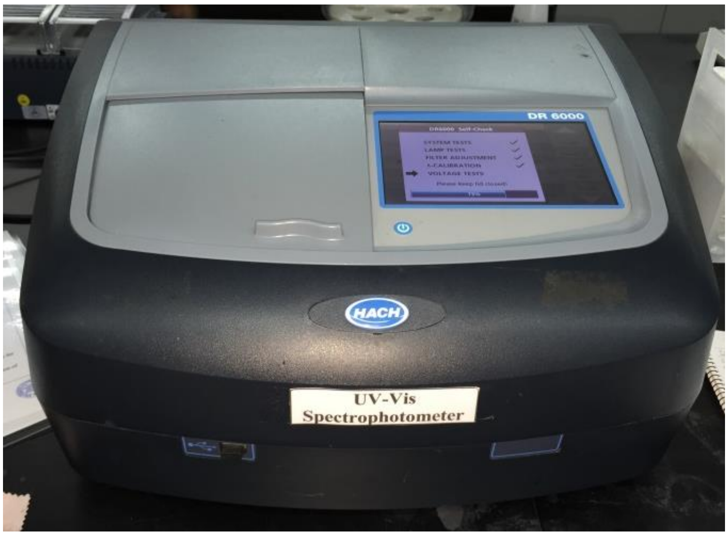


Figure 3.6 UV-Vis Spectrophotometer (DR 6000, USA)

3.2.2 Biological Oxygen Demand (BOD)

Initial BOD_5 measurement of POME sample is important to find the characterization of the POME and its content. The testing method used was dilution method. Initially, dissolved oxygen (DO_0) for the blank and POME sample were tested and the sample was placed in the BOD incubator, model FOC 225E, VELP Scientifica, as shown in Figure 3.7 at 20^oC. The final dissolved oxygen (DO_5) reading was measured again after 5 days using DO meter with BOD probe as in Figure 3.8. BOD_5 value was obtained by the difference of dissolved oxygen values between the 5 days and was calculated using the Equation 3.1 here decimal fraction is the decimal volumetric fraction of sample used.

$$BOD_5 = \frac{DO_5 - DO_0}{Decimal\ Fraction} \tag{3.1}$$

Figure 3.7 BOD Incubator (FOC 225E, Italy)

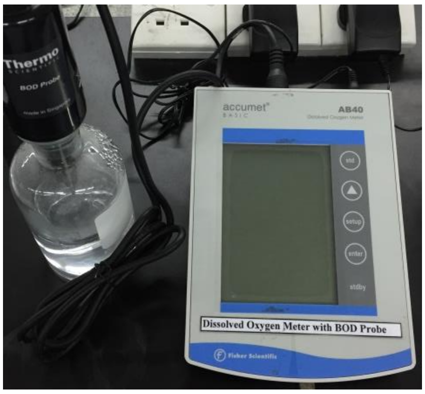


Figure 3.8 DO Meter with BOD Probe (AB40, USA)

3.2.3 Ammonical Nitrogen (NH_3-N)

Ammonical Nitrogen, (NH_3-N), are one of the component that need to be tested out in the wastewater of POME. The Nessler method was used to conduct the test whereby at first, 3 drops of mineral stabilizer were added into a beaker followed by another 3 drops of polyvinyl alcohol and 1mL of Nessler Reagent. The POME sample was diluted into 1: 1000 dilution factors and then 25mL of the diluted sample were added into the earlier solution. The testing was done with spectrophotometer using Program 380 N Ammonia Ness. and the unit measurement would be in mg/L.

3.2.4 pH

pH for the POME sample was tested using pH meter, model HI 2550, Italy, as shown in Figure 3.9.

Figure 3.9 pH meter (HI 2550, Italy)

3.2.5 Colour

The measurement for colour was done using the Hach, Method 8025. According to this standard method, the wastewater sample needs adequate dilution before it is being tested, so that the reading falls in the range of the spectrophotometer test. The reading of spectrophotometer was blanked first using deionised water in a cuvette before the sample measurement was taken. The wastewater sample in sample cell is then measured using 455nm wavelength with spectrophotometer, model DR 6000, USA, using Program 120 Colour. The value of colour test was obtained in Platinum Cobalt scale, Pt/Co.

3.2.6 Turbidity

The measurement for turbidity was done by direct measurement of the wastewater samples using the turbidity meter of model Turbicheck from Lovibond, Germany. Before measurement, the turbidity meter needs to be calibrated. Then, the samples were filled in the 10 ml sample cell and direct measurements were taken from the turbidity meter. The results obtained were in Nephelometric Turbidity Units (NTU). The turbidity meter has a measuring range of 0.01-1100 NTU as shown in Figure 3.10.

Figure 3.10 Turbidity Meter (Turbicheck, Germany)

3.2.7 Suspended Solids

The suspended solids measurement was done using the UV-Vis Spectrophotometer as in Figure 3.6. Wastewater sample was tested directly using the probe to obtain the value of suspended solids. The result was obtained in mg/L.

3.3 Preliminary Experiment

Preliminary experiments were conducted to obtain the suitable range of the independent variables whereby there are a total of 3 parameters to be investigated. Type of electrode used for the electro oxidation was fixed at aluminium electrode plate with a dimension of 12cm x 4.5cm with a total area of 54cm^2. With only 6cm of the length of the electrode plate are immersed in the solution, thus this bring to a total area of 27cm^2 that are contacted with the electric current in 500mL beaker. Meanwhile, the magnetic stirrer speed was set to 300 rpm so that it allows homogeneous mixing of the POME sample while reacting with the anode and cathode terminal of the cell. Other than that, the sample was cooled to room temperature before using it for the experiment. Distance between the 2 electrodes was set to 3cm apart of each other due to the fact that the magnetic bars that are stirring occupy some spaces and also to allow for the reaction to occur in between which is direct anodic oxidation whereby the pollutants are absorbed on the anode surface and destroyed by the anodic electron transfer reaction (Awang et al., 2011). Results from the preliminaries experiment was obtained as shown in Appendix A.

The experiment was conducted in 3 stages. In the first stage, electro oxidation with fixed time and various current density were carried out and meanwhile in second stage, electro oxidation with fixed current density that are optimum obtained earlier with varying time. For the third stage, both the optimum time and current density were used to determine the varying value of pH and to find out the best combination of these 3 variables. The POME sample that were used for the experiments were obtained from the Tian Siang Oil Mill (Air Kuning) Sdn. Bhd. from the pond 10. Before the run for preliminary experiments were conducted, the POME sample was tested for its characteristics and content to ensure that the sample was good to carry on with the experiments and the setup is as shown in Figure 3.11.

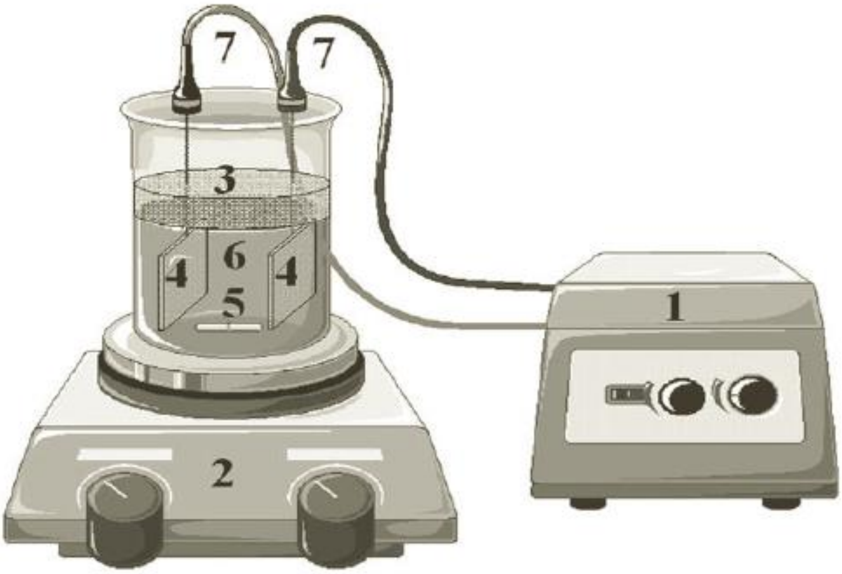


Figure 3.11 Experimental Setup

1) DC power supply 2) Magnetic stirrer 3) Cover 4) Electrodes 5) Magnetic bar-stirrer 6) Wastewater and 7) Electric wire (Bashir et al., 2014)

3.4 Experimental Design and Analysis

In this study, respond surface method (RSM) was used for the experimental design of the process in order to determine the optimum operational condition. Using mathematical and statistical method, RSM was developed for the modelling and analysis of several variables so as to evaluate the relationship between response and process variables. Increasing the efficiency of the processes without increasing the cost is an essential method employed to yield higher performance of operations. This method is described as optimization. Optimization refers to choosing the best elements from sets of available alternatives (independent variables). Thus, using RSM in wastewater treatment process optimization, could contribute significant improvement in the removal efficiency and operational cost reduction (Bashir et al., 2015).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 POME Sample Characteristics

The biological treated POME samples were collected from Tian Siang Oil Mill (Air Kuning) Sdn Bhd just before it is discharged to the river. The collected wastewater samples are then transferred to Environmental Laboratory at Faculty of Engineering and Green Technology, UTAR Kampar and was stored at 4ºC in order to minimize the biological and chemical reactions in the sample and also to avoid inaccurate results when conducting the experiments. The initial measurement of the POME sample resulting in a high COD and colour level. The data is as depict in Table 4.1 below.

Table 4.1 Initial Characterization of POME Sample

Parameters	Units	Values
COD	mg/L	2004
NH_3-N	mg/L	100
Colour	PtCo	4090
Turbidity	NTU	488
BOD	mg/L	6.99
Suspended Solids	mg/L	511
pH	-	8.50
Temperature	ºC	25.00

4.2 Treatment Process Parameters

The experiment started off with the preliminaries work whereby the effect of independent variables such as contact time, current density and adjustment of pH were investigated along with some test on process enhancement using the hydrogen peroxide as it is a strong oxidant. Using the obtained data from the preliminaries experiment, tests were conducted to investigate the effect of current density, contact time, pH adjustment and also addition of hydrogen peroxide on the removal efficiency of the electro oxidation process. Before the treated sample are tested for their removal efficiency, it will first let to settle for approximately 1 hour to allow for the sedimentation of the sludge and to extract the supernatant and filter off for any suspended solids.

4.2.1 Effect of Current Density

First set of experiment was to determine the best current to apply using a pre-fixed contact time of 90 minutes. As summarized in Figure 4.1, the reduction of up to 62% of COD can be obtained using current density of 80mA and the colour removal is relatively high as well reaching 98%. Based on this 2 parameters, the optimum current chosen was at 60mA due to it can achieve the removal of 60% while consuming lesser electricity to produce the almost similar end results. Throughout the observation of the experiment, it is known that the higher the current applied to the treatment, the better the efficiency of parameters for COD, and colour as shown in Figure 4.1. During the experiment, bubble was formed at quite a volume after the sample had been applied with current. These bubbles are due to the degradation of the organic matter inside the sample and thus lead to the production of bubbles as reaction occurs. The increases in current density also affect the degradation of the cellulose which is present in the POME sample.

As the hydrogen bonding reduces, the increase in the temperature will coupled with the increase of efficiency of electrolysis. If pressure over the electrolysis is amplified, then more current permits for the same applied voltage. However, this will results in the decline of the output of gas per coulomb and the heating effect. The improved solubility of the gases and minor bubbles which both are capable of plummeting the cell resistance and increasing recombination reactions are reason behind this effect.

By reducing the distance between electrodes leads to reduction of the resistance of the electrolysis medium, but towards the end, the process may suffer if the closeness allows a build-up of gas between these electrodes. Following that, both the movement of bubbles from the electrode surface and the mass transfer rate in the electrolyte tends to accelerates and the current increases due to the low to higher pulsed potential that occur which in turns lowers the electrochemical polarization in the diffusion layer and further increases hydrogen production efficiency. All this reaction is govern by the reaction of the electrolysis of water as it is the decomposition to give off hydrogen and oxygen gases due to passage of an electric current as shown in Equation 4.1 (Chaplin, 2015).

$$2H_2O + \text{energy} \longrightarrow O_2 + 2H_2 \qquad (4.1)$$

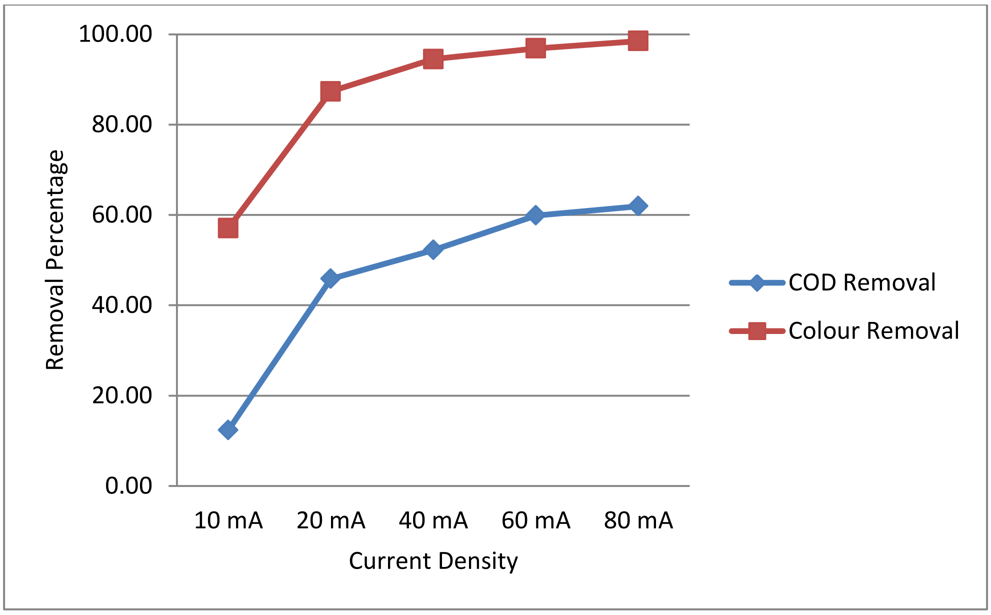


Figure 4.1 Effect of Current Density on COD and Colour Removal Efficiency (Contact Time 90 minutes)

4.2.2 Effect of Contact Time

Pre-determined current density of 60mA was used as it shows to have the optimum effect and also lower cost of operation and a set of experiment using varying time of reaction were conducted. While observing the reaction of the different contact time, it is confirmed that treatment with longer time would provide a better removal efficiency of all the parameters. No doubt that elevating the contact time bring about greater removal efficiency, but the operational cost is one of important factor to be consider along with the treatment efficacy.

COD removal of 66% is obtained from treating the sample for 120 minutes but under just 60 minutes, the removal had already reached 63% which indicates better performance and cost saving measures to be taken into consideration. Meanwhile removal efficiency for colour is at 93% for contact time of 60 minutes as can be seen in Figure 4.2 beneath. Thus, for this stage of the experiment, contact time of 60 minutes is the optimum under 60mA of current applied.

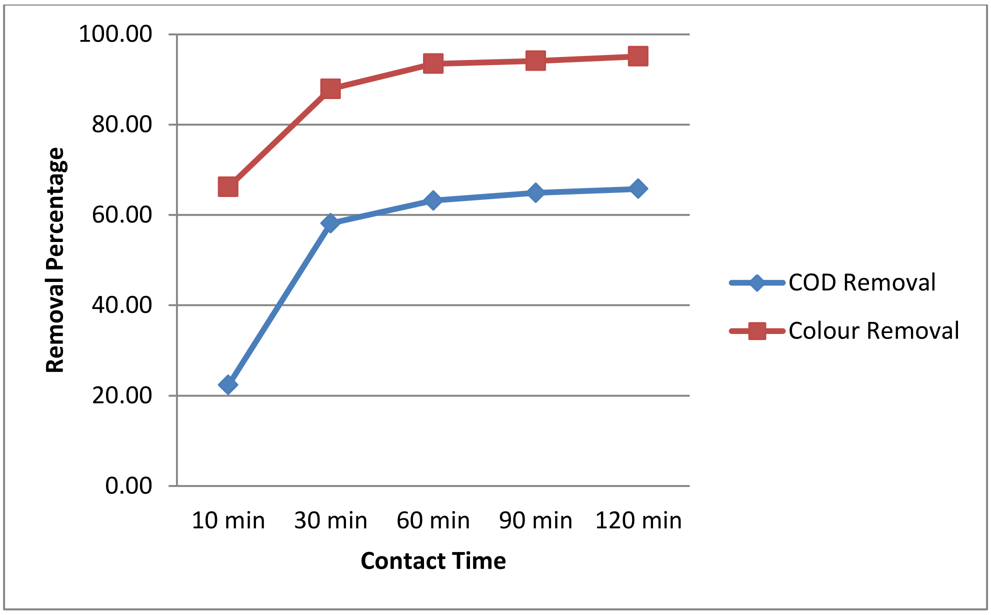


Figure 4.2 Effect of Contact Time on COD and Colour Removal (Current Density 60mA)

4.2.3 Effect of pH Adjustment

In addition, adjustment of the pH was carried out using the optimum time of 60 minutes and current of 60mA to run the varying pH in a set of experiment. When adjusting the pH, it is recommended that adding the acid buffer with care due to the pH would drop significantly upon attaining pH 5 and below. This is to prevent the pH from getting too low as it could affect the overall reaction and when acid buffer is added, there is a response occur upon contact and this would lead to an inconsistent results at the end of the day.

Besides, the formation of bubbles seems to have sky-rocketed after the adjustment of pH and when the current are applied, the bubbles formed rather quickly and in a huge volume. Hydrogen bubbles that are formed as a by-product of the electro oxidation process and addition of acidic buffer as pH adjustment driven the formation as it is a major issue to the process as it lead to the increase of cell voltage. Mass transfer and direct bubble formation on the electrode are dependent factor of the initial bubble sizes (Yannick, 2012).

From here, it is anticipated that lower pH would provide better removal efficiency upon the interaction of the acid and the sample. After the experiment has been conducted, as presented in Figure 4.3 below, it is clear and confirmed that lower pH provide better removal efficiency in terms of COD and colour with each reaching 68% and 98% respectively. Upon great consideration, pH 3 was still chosen as the optimum due to its brilliant removal of COD and colour.

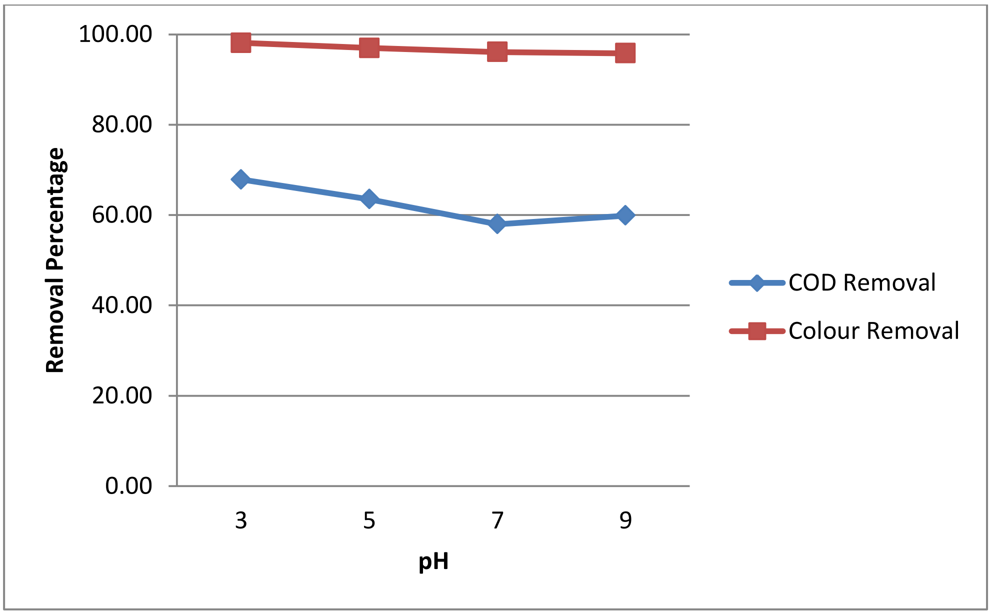


Figure 4.3 Effect of pH Adjustment on COD and Colour Removal Efficiency (Current Density 60mA and Contact Time 60 minutes)

4.2.4 Hydrogen Peroxide (H_2O_2) Addition with pH Adjustment

Meanwhile, the hydrogen peroxide, H_2O_2, itself is a strong oxidant that may boost the oxidation process by means of increasing its efficiency while having a lower reaction time. In this part of the experiment, a set of different concentration of H_2O_2 was tested under the optimum condition of 60mA current density, 60 minutes contact time and pH 3. Figure 4.4 shows the data obtained and it is observed that after the adjustment of pH, when the H_2O_2 was added, it seems to have a small reaction occurred from the sizzling bubble that produced upon contact and stirring would speed up that reaction too. However, the results obtained were not as expectation whereby the performance of the removal efficiency has dropped as compare to the one without the addition of H_2O_2.

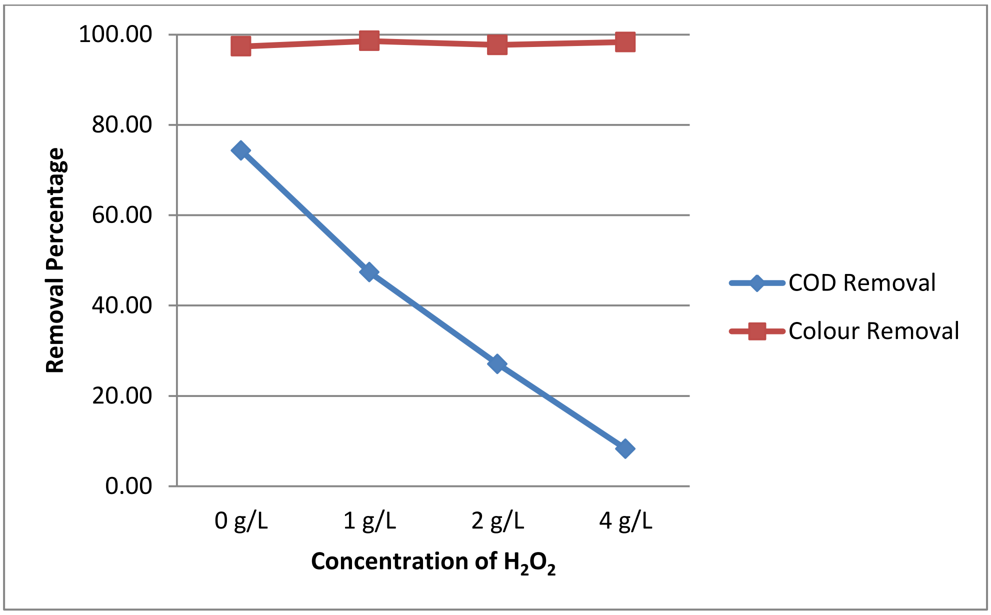


Figure 4.4 Effect of H_2O_2 Addition on COD and Colour Removal Efficiency (Current Density 60mA, Contact Time 60 minutes and pH 3)

4.2.5 Hydrogen Peroxide (H_2O_2) Addition without pH Adjustment

Despite the fluctuating results obtained in the previous experiment, this time around, the sample was not added with the pH buffer instead the H_2O_2 was added directly in 1g/L, 3g/L, 5g/L and 8g/L to test its effect on the removal efficiency of COD and also colour as depict in Figure 4.5 underneath. Results obtained was not of satisfactory due to the fact that the addition of H_2O_2 seems to have retard the removal efficiency and performance which contradict with the findings of a strong oxidant would enhance the overall progress of oxidation. Thus it is decided that the addition of H_2O_2 are to be neglected because of the unsatisfactory results produced and focus on the adjustment of pH along that could bring about a better efficacy via Respond Surface Method (RSM) and its optimization.

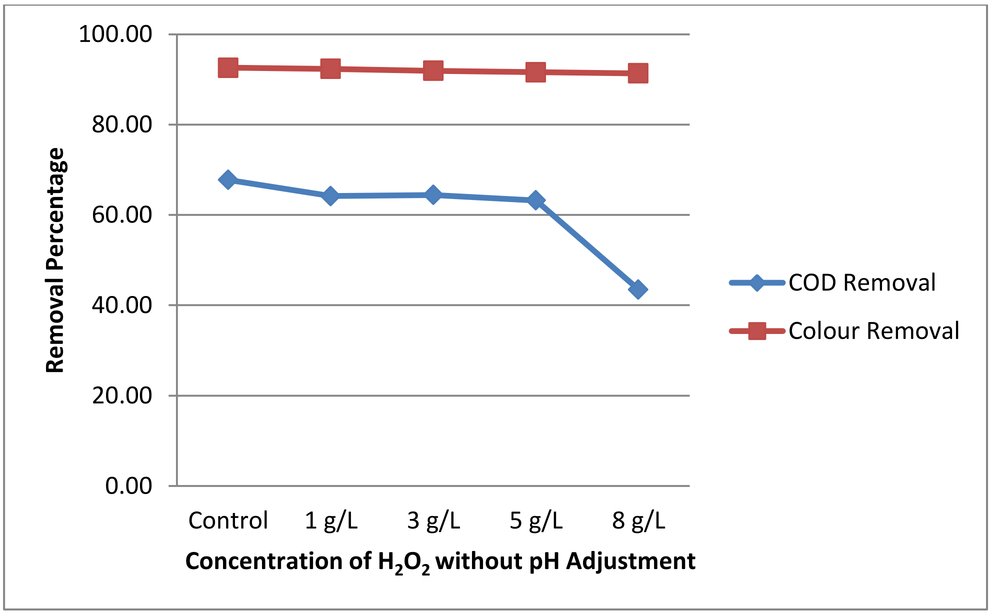


Figure 4.5 Effect of H_2O_2 Addition without pH Adjustment on COD and Colour Removal Efficiency (Current Density 60mA and Contact Time 60 minutes)

4.3 Experimental Analysis and Optimization Using RSM

In this segment of the experiment, data obtained from the preliminaries experiment was used to determine the parameters for the RSM such as test for removal efficiency of colour, turbidity, COD, and pH. The results from the usage of the software namely Design Expert® where data obtained from the preliminaries experiment were inserted and it produces a set of experiment to be conducted as shown in Table 4.2.

Table 4.2 Experimental design matrix for preparation of electro oxidation and removal percentage of the respondents (COD, Colour, Turbidity and pH)

Run	Current	Time(min)	pH	COD (mg/L) Removal	Colour (PtCo) Removal	Turbidity (NTU) Removal	pH After
1	10.00	90	5.00	61.4970	93.7745	97.2689	7.99
11	10.00	90	3.00	67.7975	96.0784	97.4790	7.40
7	60.00	90	5.00	66.5590	95.4167	92.8571	7.92
19	60.00	90	3.00	74.4211	98.0882	98.9496	5.85
2	35.00	70	4.00	70.7054	96.3725	99.8109	6.68
4	47.50	50	4.00	75.1750	97.1814	99.7899	6.97
8	35.00	50	4.00	66.1282	97.1078	99.8992	7.42
9	35.00	50	4.00	66.2359	97.3284	99.9223	7.41
10	35.00	50	4.00	66.5051	97.3039	99.9118	7.42
12	35.00	50	4.00	66.6667	97.2549	99.9160	7.40
15	35.00	50	4.00	66.3436	97.2059	99.9139	7.42
16	35.00	50	4.00	66.2897	97.3529	99.9097	7.43
17	35.00	50	3.50	74.2596	97.5490	99.8908	7.31
18	22.50	50	4.00	70.9208	96.5931	99.0714	6.85
20	35.00	50	4.50	72.2671	96.8137	99.4916	7.20
14	35.00	30	4.00	71.0824	88.6029	68.4874	6.88
3	10.00	10	5.00	32.3640	51.2990	12.1849	6.09
5	10.00	10	3.00	36.7798	54.2157	26.8908	4.17
6	60.00	10	5.00	58.3737	67.5980	15.1261	5.89
13	60.00	10	3.00	67.5821	83.2353	83.1933	5.21

4.3.1 ANOVA Analysis

ANOVA tables present a detailed and comprehensive analysis for the performance of the electro oxidation via the RSM that shows the detailed information on the process such as regression, mean and standard deviation. This can be proven by the significance of the model for removal efficiency of the four response variable of colour, COD, turbidity and pH as of Table 4.3 with value of them are relatively low which indicates that the chances of the model F-values this large could occur due to noise is less than 1% (0.01). Meanwhile, the ‘lack of Fit, p-value’ should be always less than the alpha value of 0.05 which were a significant models for colour, turbidity and pH except for COD whereby the value over 0.05 that lead to an insignificant “lack of fit”. Thus, adjustment has to be made on the COD performance so that not just the removal efficiency can be increase but all the overall treatment process will benefit from this changes which should not be ignore.

Table 4.3 RSM output table for Colour, COD, Turbidity and pH

Sources	Sum of Squares	df	Mean Square	F value	p-value/ Prob > F	Remarks
For colour						
Model	6616.91	6	1102.82	13.91	< 0.0001	Significant
Lack of Fit	1027.56	8	128.45	212.24	< 0.0001	Significant
For COD						
Model	2258.30	5	451.66	36.69	< 0.0001	Significant
Lack of Fit	140.00	9	15.56	2.41	0.1732	Insignificant
For Turbidity						
Model	15975.18	7	2282.17	65.03	< 0.0001	Significant
Lack of Fit	400.13	7	57.16	13.60	0.0055	Significant
For pH						
Model	15.03	5	3.01	17.63	< 0.0001	Significant
Lack of Fit	2.39	9	0.27	1767.45	< 0.0001	Significant

As presented in Table 4.4, the regression, R^2 depicts a good and strong correlation between the three independent variables as the values all exceed 0.80 for a decent correlation and also ensure a satisfactory agreement between the actual and predicted values where the value for colour, COD, turbidity and pH were 0.8652, 0.9291, 0.9743 and 0.8629 respectively. Other than that, the adequate precision was definitely adequate and fit because the data obtained are much more greater than the ratio of 4 with each of them achieving 12.216, 22.085, 26.225 and 16.146 for colour, COD, turbidity and pH respectively.

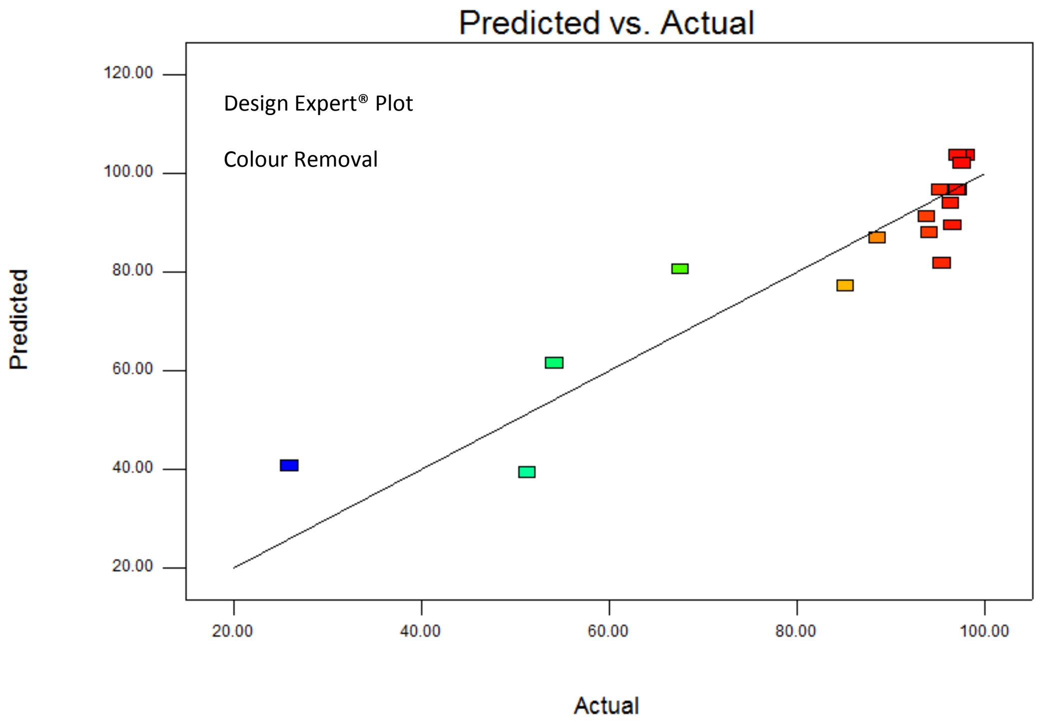
This lead to the findings of extra information whereby the value indicates a sufficient signal as it measures the signal to noise ration and it can be used to navigate the design of the space. Next, the negative value for predicted R^2 means that the overall mean is a better predictor of the response than the current model for the colour removal efficiency. A value of 0.9038 for adjusted R^2 and 0.8929 for predicted R^2 implies that both in a reasonable range and are acceptable model. On the other hand, for turbidity and pH, things are not going good as the difference in value for the predicted and adjusted R^2 are way too far from each other rendering the model not suitable and problem might occur. Thus, actions are to be taken to avoid this by considering model reduction, response transformation and outliers.

Table 4.4 RSM Model Fit Summary

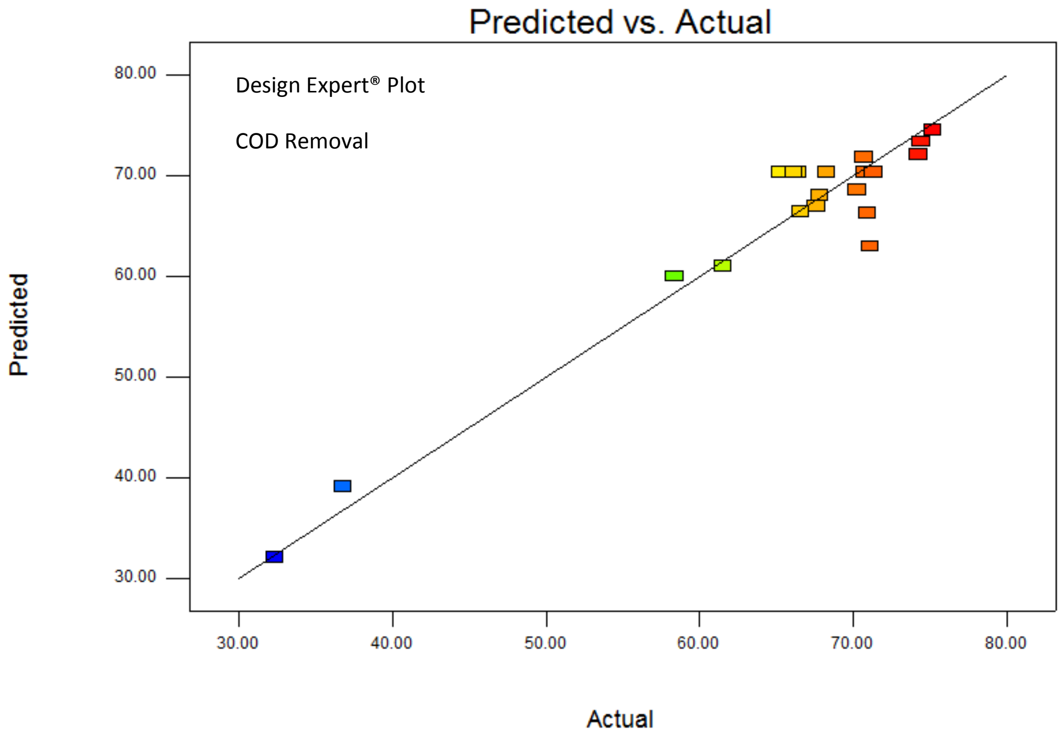
Statistical Figure	Colour	COD	Turbidity	pH
Standard Deviation	8.90	3.51	5.92	0.41
Mean	85.99	65.30	83.78	6.85
Coefficient of Variance	10.35	5.37	7.07	6.03
Predicted residual error sum of square	12131.21	260.26	13072.94	7.95
Coefficient of Determination	0.8652	0.9291	0.9743	0.8629
Adjusted R^2	0.8030	0.9038	0.9593	0.8140
Predicted R^2	-0.5863	0.8929	0.2027	0.5436
Adequate Precision	12.216	22.085	26.225	16.146

Correspondingly, the graph of predicted versus actual value as of Figure 4.6 shows that all the points are located rather close to each other showing that there is a strong correlation between the independent variables of current density, reaction time and also pH. This data lead to the adequacy of agreement between the actual and predicted data whilst using the Design Expert® software.

(a)


Predicted vs. Actual
Design Expert® Plot
Colour Removal
120.00
100.00
80.00
60.00
40.00
20.00
Predicted
20.00
40.00
60.00
80.00
100.00
Actual

(b)


Predicted vs. Actual
Design Expert® Plot
COD Removal
80.00
70.00
60.00
50.00
40.00
30.00
Predicted
30.00
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Actual

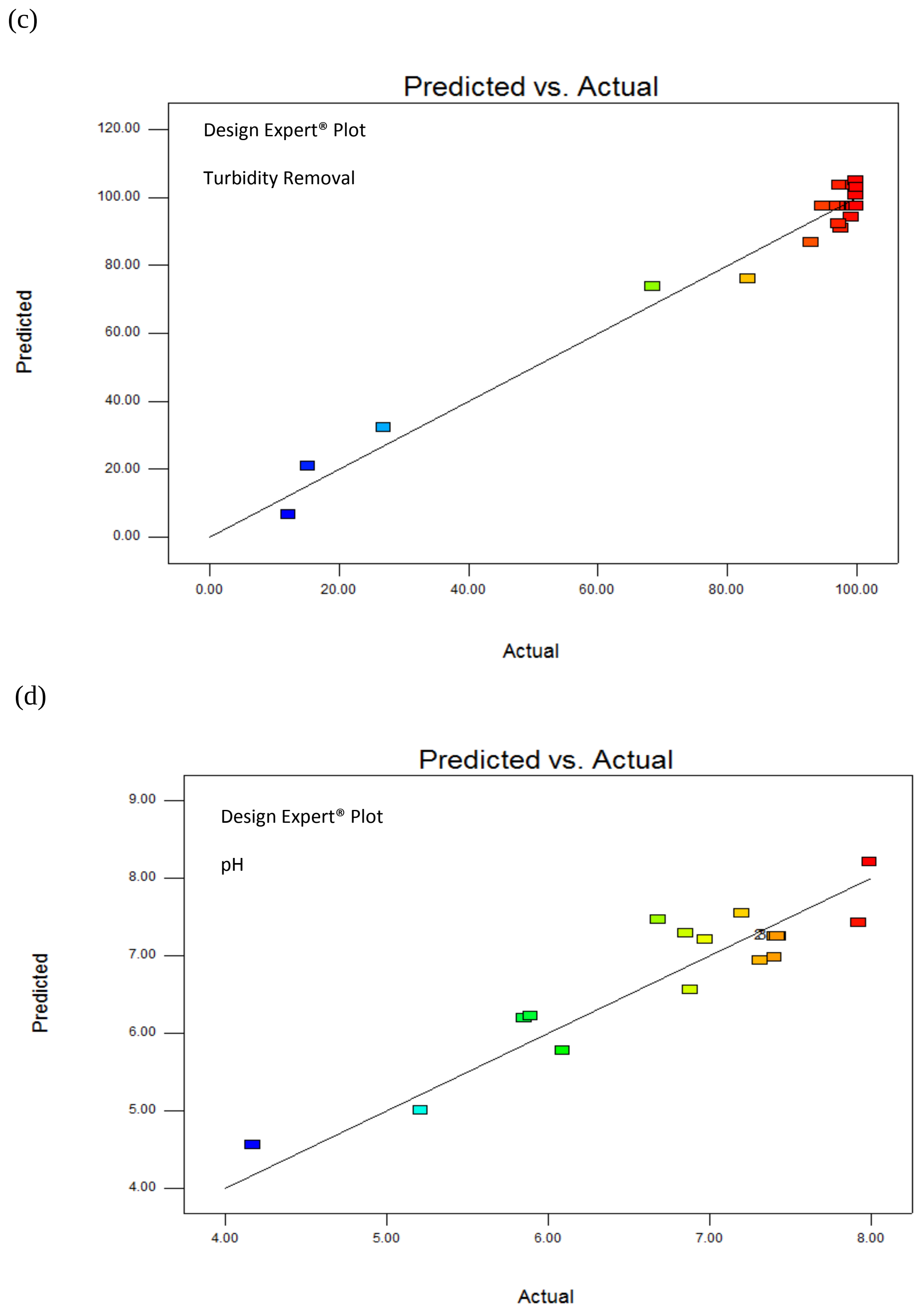

Figure 4.6 Correlation of Actual and Predicted Values of response for removal of (a) colour (b) COD (c) turbidity (d) pH

The interaction among the three independent variables and four dependent variables are illustrated as below as a 3D surface model graphs whereby the maximum point as where the best removal efficiency could be obtained can be seen clearly upon the downward curve of the graphs. As far as the graphs are concern, the abbreviation of CD is given to current density and CT for contact time while the actual factor was the pH itself that can be altered to see the effect on the process efficacy. For colour removal as portrayed in Figure 4.7 below, and efficiency of up to 97.21% are obtained under condition of 35mA/cm^2 of current density, contact time of 50 minutes and at pH 4 that peaks the 3D surface model graphs. It also shows that the reaction can be cost saving with the reduction of the current density to 22.50mA/cm^2 and at the same contact time and pH as the peak condition but it shows a decrement of removal efficiency to 96.59% which sums up to the reduction of 0.64% with 35.71% less usage of current density. As observed on the graph, there is an obvious change in the removal efficiency as the lower the pH drop, the better it is for the removal of colour. This shows that the POME could be treated in a low pH condition to enhance the process efficacy.

Moving on to the COD removal as in in Figure 4.8, the best possible reduction in COD that is obtained from the data sheet is working at a current density of 47.50mA/cm^2, contact time of 50 minutes and pH 4 whereby a removal efficiency of 75.18% is achieved. With cost saving in the design consideration, an alternative condition of efficacy 71.08% can be coupled with 35mA/cm^2 and contact time of 30 minutes under pH 4. The drop of 26% of current density consumption and also 40% of contact time resulted in a decrease of 5.45% of removal effectiveness. Meanwhile, the changes in the pH do in turn affect the COD removal as the graph shows that the drop in pH actually benefits the removal efficiency for COD given that the low pH increases the oxidation process as acidic condition contributes to oxidation.

On the other hand, turbidity removal has display a promising performance as it has the highest percentage of removal in comparison with all the other dependent variables. Referring to the 3D surface model graphs as of Figure 4.9, the prime removal efficiency accomplish is at 97.91% whereby the process runs at a current density of 35mA/cm^2, contact time of 50 minutes with pH 4. But that’s not all to it as enhancement can be made to the efficacy by a boost of 20 minutes of contact up to

70 minutes under the same current density and pH that lead to increment of removal efficiency up to 99.81%. To sum it all up, a rise of removal efficiency by 1.9% requires an upsurge of 28.57% of contact time with the same circumstance of other variables but depending on the cost allocation, both operating state could be used to adjust to the required treatment proficiency. The removal efficiency for turbidity also is affected by the variation in the pH that depicts the lower pH would give a rise in the turbidity removal and also enhance the overall treatment process.

Finally, pH plays an important role in the overall process as it enhanced the treatment by means of lowering down the pH and production of H^+ ions from the addition of acid buffer lend a helping hand in elevating the oxidation process. In terms of the pH value, the final pH are advised to be as close to the neutral value of pH 7 due to the discharge standards according to the Environmental Quality Act 1974 to be of range pH 5.0 to pH 9.0. This is to prevent the disruption to the ecological system and also to avoid any contamination to the aquatic life. Figure 4.10 give a picture of the pH obtained from the experimental work in the form of a 3D surface model graphs and has a peak of pH 6.97 which is as close as it is to the neutral pH of 7 with condition of 47.50mA/cm^2 of current density and contact time of 50 minutes given that the initial pH was adjusted to pH 4. Costing has always been the main consideration when it comes to design and using the same graph, a lower costing operational condition can be attained by pulling down the current density to 35mA/cm^2 and contact time to 30 minutes which contributes to a pH 6.88 by means of the same initial pH value of 4. All in all, a reduction of 26.32% usage of current density and a 40% decrease in contact time would provide a slightly further pH to the neutral value but a significant decline in the budget for the task.

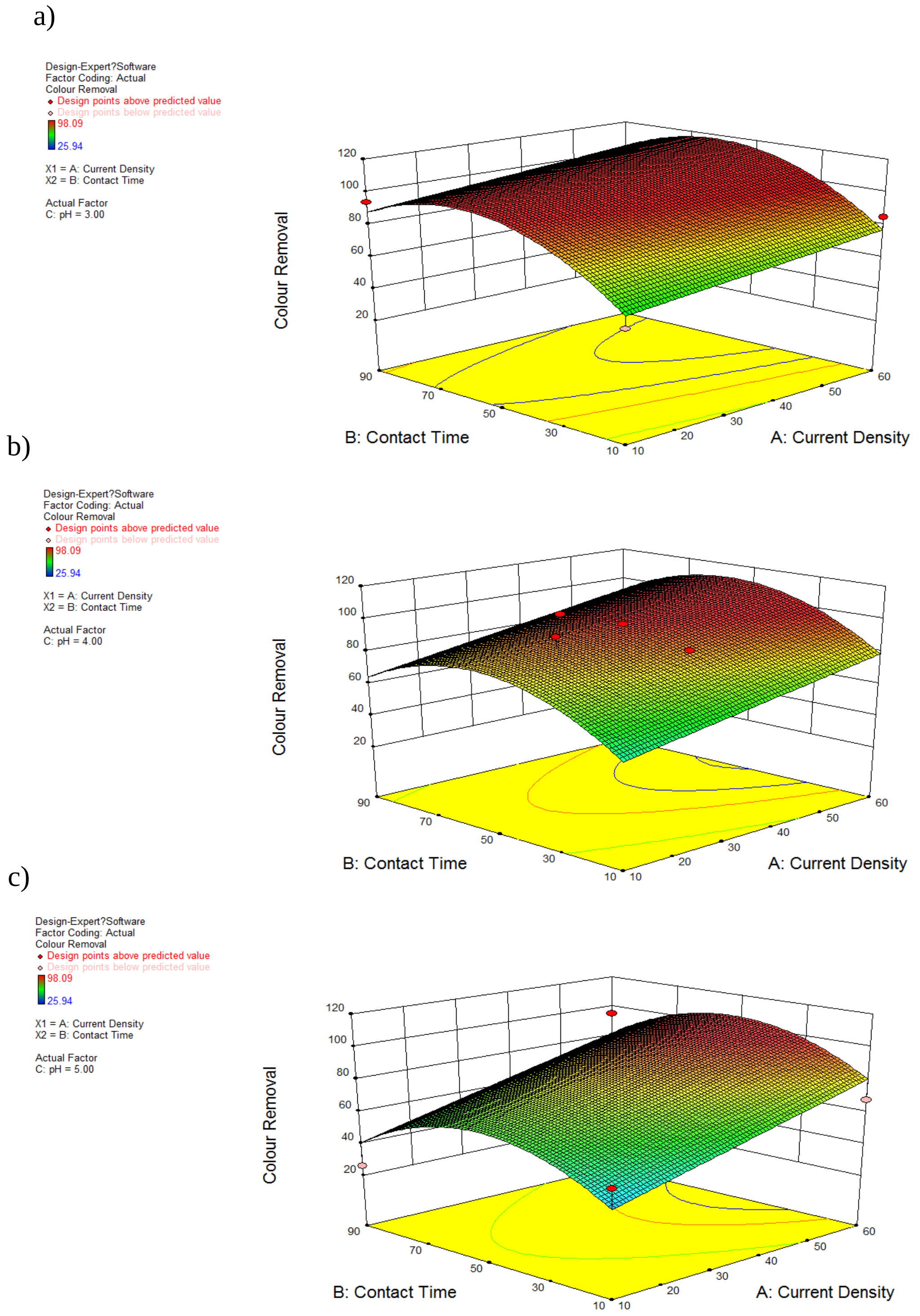

Figure 4.7 3D Surface Plot for Colour Removal Efficiency a) pH 3 b) pH 4 c) pH 5

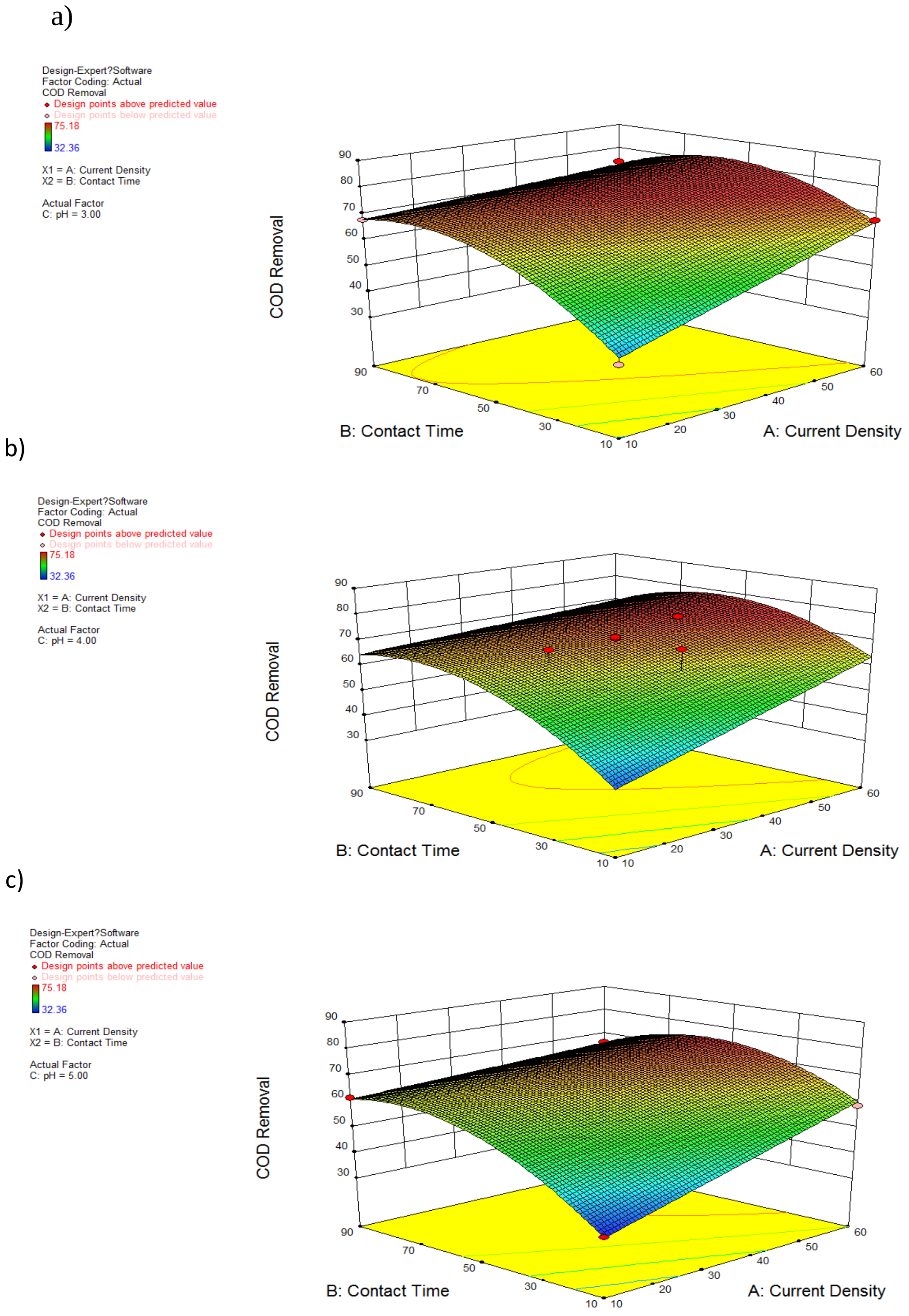

Figure 4.8 3D Surface Plot for COD Removal Efficiency a) pH 3 b) pH 4 c) pH 5

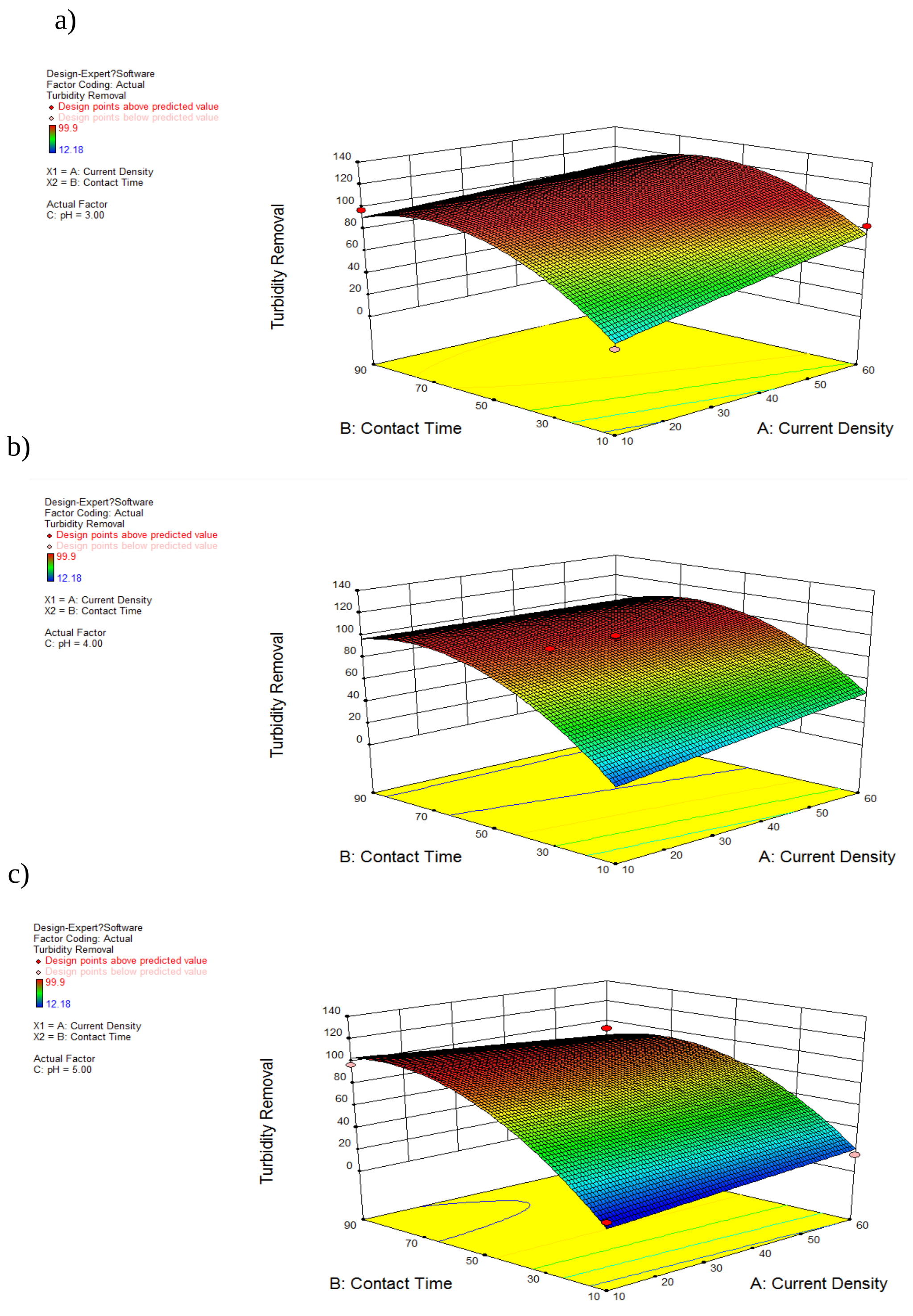

Figure 4.9 3D Surface Plot for Turbidity Removal Efficiency a) pH 3 b) pH 4 c) pH 5

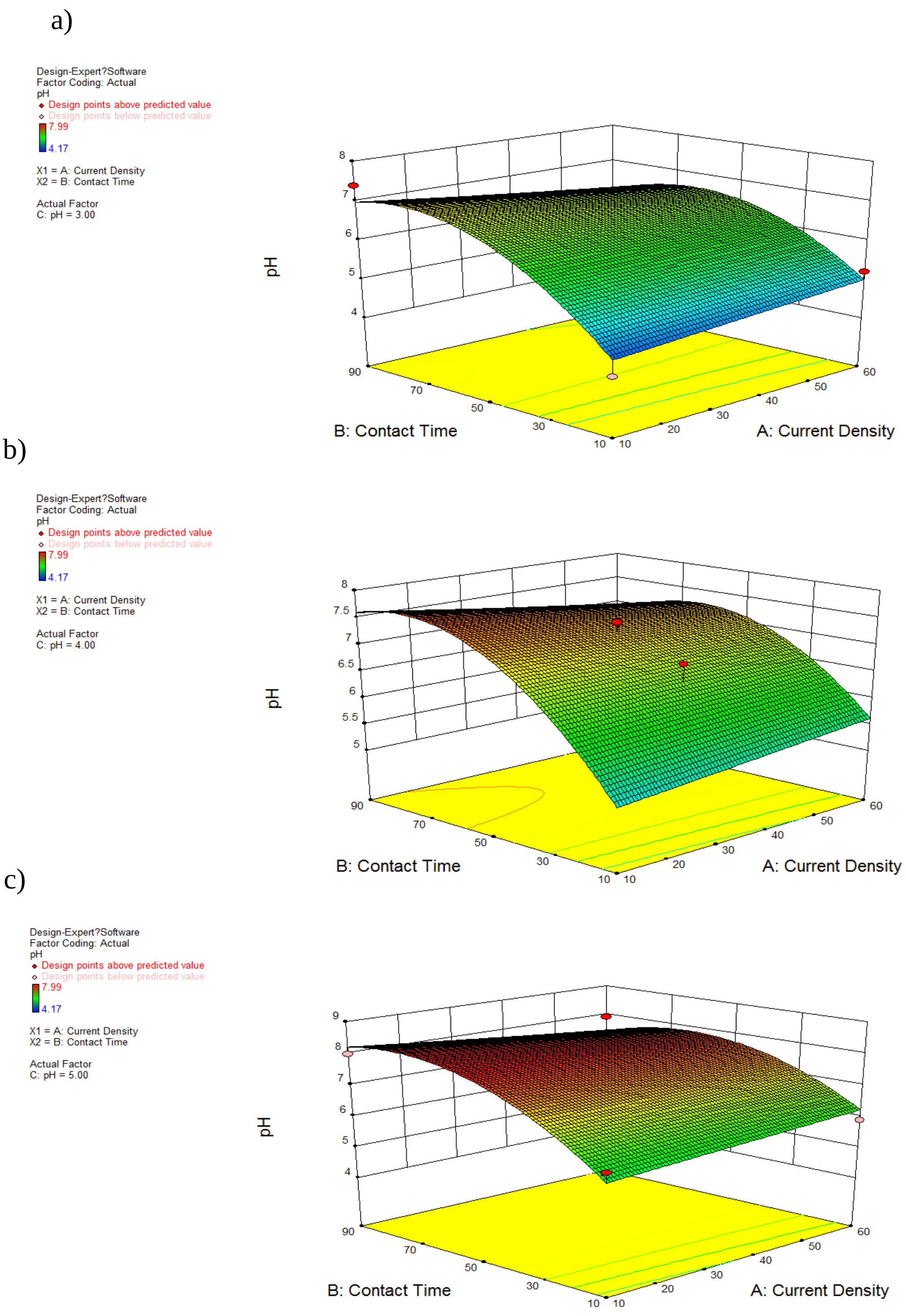

Figure 4.10 3D Surface Plot for Final pH on a) pH 3 b) pH 4 c) pH 5

4.4 Optimization

Based upon the results obtained and generated using Design Expert®, a final step towards the experiment which is the optimization that was carried out by another set of data for confirmation whereby predicted data given by the software would be compared to the actual experimental data.

Table 4.5 Optimization and Laboratory Experiment Validation

Electro Oxidation	**Removal %**	**Removal %**
	Actual*	**Predicted**
COD %	69.56	75.40
Colour %	97.80	100.00
Turbidity %	99.64	100.00
pH	7.48	7.59

* Acquired at laboratory level with 56mA/cm^2, 65 minutes and pH 4.5

As seen in Table 4.5, there are slight different of the actual value as compared to the predicted value due to some human error and environmental factors which indirectly affect the end results. Nevertheless, the actual data were not much of difference apart and it still fall under the range of the treatment efficacy. Complete data for the measurement of the four dependent variables of COD, colour, turbidity and pH that are obtained are then compared with the actual formula obtained in (4.1), (4.2), (4.3) and (4.4) from the ANOVA for the response surface reduced quadratic model, the removal efficiency of the COD, colour, turbidity and pH associated with the three independent variables of current density, reaction time and pH can be safely estimated using the following formulation.

$$\begin{aligned}\text{Colour removal} = {} & 76.89885 - (0.44608*CD) + (2.36519*CT) - \\ & (11.99514*pH) + (0.25395*CD)*pH - \\ & (0.15716*CT)*pH - (0.015628*CT^2)\end{aligned} \qquad \textbf{(4.1)}$$

$$\text{COD removal} = 33.11752 + (0.61439*CD) + (1.16860*CT) - (3.50412*pH) - (5.64125E\text{-}003*CD)*CT - (7.50554E\text{-}003*CT^2) \quad \textbf{(4.2)}$$

$$\text{Turbidity removal} = 33.97814 + (1.83979*CD) + (2.11876*CT) - (12.22826*pH) - (7.77500E\text{-}003*CD)*CT - (0.29610*CD)*pH + (0.23900*CT)*pH - (0.020238*CT^2) \quad \textbf{(4.3)}$$

$$pH = 1.76670 + (0.011987*CD) + (0.092585*CT) + (0.61235*pH) - (3.07500E\text{-}004*CD)*CT - (5.91759E\text{-}004*CT^2) \quad \textbf{(4.4)}$$

First of all, starting from the COD, its removal efficiency had achieved up to 70% and as for the predicted value, it should be treated up to 75% removal efficiency. Secondly, the colour topped the process by a removal efficiency of a staggering 98% and predicted value of the removal based on the software shows up to 100%. Next, through the process of electro oxidation, the removal of turbidity seems promising and it achieved closed to 100% for both the actual and predicted value with a final removal percentage of 99% and 100% respectively. Finally, the pH value after the treatment is estimated to be at 7.59 by the software while the actual value was at 7.50. Test for BOD_5 as shown in Appendix B indicates that the organic matter inside the POME sample was being degraded via the destruction of the organic compound on the process of the electro oxidation. Thus, it prove that this process could had degrade the organic matter as well apart from treating the wastewater to lower COD, colour, turbidity and suspended solids.

Table 4.6 Heavy Metal Content in POME Sample and Other Responses

Heavy Metals	Initial (ppb)	Final (ppb)	Removal %
Aluminium (Al)	32.286	32.859	-1.77
Chromium (Cr)	0.505	0.112	77.82
Iron (Fe)	66.759	34.704	48.02
Nickel (Ni)	0.846	0.141	83.33
Copper (Cu)	0.331	0.180	45.62
Zinc (Zn)	27.076	12.914	52.30
NH_3-N (mg/L)	100	64.5	35.50
Suspended Solids (mg/L)	511	3	99.41

Table 4.6 shows the summary of the removal efficiency of the selected few dependent parameters and also heavy metals. Inductively Coupled Plasma-Mass Spectrophotometer or known as ICP-MS in short was basically used to identify the heavy metal presence in the sample of POME that could lead to the findings of the content with both the raw POME sample and the electro oxidation treated sample. Upon testing, it is discovered that the heavy metal such as Chromium (Cr), Nickel (Ni), and Copper (Cu) was found in a traced amount in the untreated sample while the treated sample shows absence of the 3 heavy metal. On the other hand, Aluminium (Al), Iron (Fe) and Zinc (Zn) was detected on both end of the treatment and it also shows that the treatment did a minor work of removal of this heavy metal contaminant. The removal efficiency of the process towards the heavy metals seems to be promising as most of them are presence in a trace amount except for aluminium that the removal efficiency is negative due to the amount of the elements increase in the sample after treatment. This is due to the fact that the electrode used in this process was aluminium and the process also corrodes the electrode thus inducing more concentration of the aluminium in the treated sample as compare to the untreated ones. Another part of the experiment was to characterize the properties of the sample for before treatment and after treatment so that more information is available to precisely understand and analyse the process. Firstly, other than COD, colour, turbidity and pH, suspended solids was tested for its removal efficiency and

using the electro oxidation process, able to achieve a level of 99% removal efficiency and once proved the effectiveness of this process in treating POME sample. Next, the ammonical nitrate, NH_3-N was also characterized whereby Nessler Reagent Method was used to identify the level of NH_3-N and it could achieve a removal efficiency of up to 35%. The initial concentration of the NH_3-N was not that high in the beginning rendering the reduction are not included as part of the main factor to be studied in the whole process but nevertheless, it is tested to know the properties and for better understanding. As shown in Figure 4.11, the difference of the turbidity and colour of the POME sample before and after treatment using electro oxidation process.

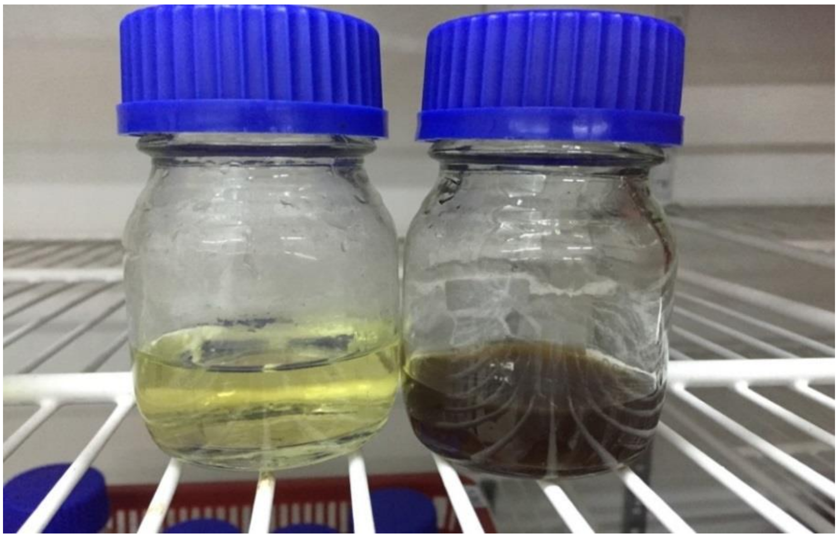

Figure 4.11 Comparisons between Treated (Left) and Non-Treated (Right) POME Sample Using Electro Oxidation Process

Having differences between the actual and predicted value means that there are some deficit in the treatment process which most probably affected by the electrode used as the new plate of the aluminium electrode would provide a better ion exchange capacity and thus increase its performance while a corroded electrode would lower down the ion exchange rate thus resulting in lower removal efficiency as can be observed. As far as the information gathered, the higher the percentage of electrode plating loss, the lower the ability of the electrode to allow current to flow pass and thus affecting the performance of the process with cathode terminal having a faster corrosion formed as compare to the counterpart of anode terminal as of observation. Part of the reason also might be caused by the unstable current that fluctuated during the electro oxidation process given the fact that the aluminium electrode is being corroded while current are flowing through the electrode making the energy loss to surrounding as the current needed would definitely higher.

Moreover, when chemicals such as H_2O_2, acid and alkali buffer are added, the instance where both the chemical and sample are in contact, reaction can be seen and this might prove to be affecting the overall reaction. This eventually led to the affected composition inside the sample and thus produces a varying effect upon the actual experiment. Table 4.7 depicts the comparison of the discharge standard as to the treated sample using the electro oxidation process.

Table 4.7 Malaysia Discharge Standard for Industrial Effluent

Parameters	**Initial**	**Final**	**Removal %**	**Discharge Standard**
COD (mg/L)	2004	610	69.56	1000
BOD_5 @ 20ºC (mg/L)	6.96	6.59	-	400
Turbidity (NTU)	488	1.76	99.64	< 0.5
Colour (PtCo)	4090	90	97.80	15
Suspended Solids (mg/L)	511	3	99.41	100
pH	8.15	7.48	-	5.0 – 9.0
Ammonical Nitrogen (mg/L)	100	64.5	35.50	100

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this study, the optimum operational condition for the post treatment of POME using electro oxidation in terms of current density, contact time and pH were experimentally determined as 56mA/cm^2, 65 minutes and pH 4.5 respectively. Results obtained from the experimental work were compared to the discharge standards in Table 4.7 and all the testing parameter such as COD, colour, turbidity, suspended solids and pH meets the regulation under the Environmental Quality Act 1974. Using the Design Expert® software, a set of 20 experiments was conducted and the regression, R^2, was relatively close to unity of value 0.86, 0.93, 0.97 and 0.86 respectively obtained for colour, COD, turbidity and pH. After that, another set of numerical optimization was carried out and the result was 69.56% removal for COD, 97.80% removal for colour and 99.64% removal for turbidity. Upon these findings, electro oxidation process at specified level maybe used as a post treatment technology that are effective and efficient before discharging so as to meet the requirements.

5.2 RECOMMENDATIONS FOR FUTURE RESEARCH

Present studies unearth the ideal operational condition given by the current density, time of contact and also pH. This give rise to infinite other possibilities and huge research gap that could be yet to explore and discover to further enhanced the treatment efficiency as well as to meet the compelling regulations. Following are some suggestion on research that can be made in future:

- Usage of a different type of electrode that conduct electricity better
- Effective ways of removing the bubble foam produced during experiment
- Providing other sources of energy to run the experiment such as biogas and sunlight

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APPENDICES

APPENDIX A: Tables of Preliminary Experiments

Table of Effect of Current Density on COD and Colour Removal (Contact Time = 90 minutes, Volume Sample = 500mL, Agitation Rate = 300rpm, Temperature = 25ºC and Voltage = 12V)

Current Density \ Parameters	COD (mg/L) Removal %	Colour (PtCo) Removal %
10 mA	12.3731	57.0910
20 mA	45.8756	87.3351
40 mA	52.2208	94.4921
60 mA	59.8985	96.8668
80 mA	61.9289	98.4828

Table of Effect of Contact Time on COD and Colour Removal (Current Density = 60mA/cm^2, Volume Sample = 500mL, Agitation Rate = 300rpm, Temperature = 25ºC and Voltage = 12V)

Time\Parameters	COD (mg/L) Removal %	Colour (PtCo) Removal %
10 min	22.3411	66.1765
30 min	58.1498	87.9085
60 min	63.1844	93.4641
90 min	64.8836	94.1176
120 min	65.7646	95.0980

Table of Effect of pH Adjustment on COD and Colour Removal (Current Density = 60mA/cm^2, Contact Time = 60 minutes, Volume Sample = 500mL, Agitation Rate = 300rpm, Temperature = 25ºC and Voltage = 12V)

pH\Parameters	COD (mg/L) Removal %	Colour (PtCo) Removal %
3	67.8459	98.1238
5	63.4870	96.9717
7	57.9912	96.0829
9	59.8863	95.8196

Table of Effect of Addition of H_2O_2 on COD and Colour Removal (Current Density = 60mA/cm^2, Contact Time = 90 minutes, pH 3, Volume Sample = 500mL, Agitation Rate = 300rpm, Temperature = 25ºC and Voltage = 12V)

H_2O_2\Parameters	COD (mg/L) Removal %	Colour (PtCo) Removal %	pH After
0 g/L	74.3108	97.3667	7.36
1 g/L	47.3684	98.5667	7.10
2 g/L	27.0677	97.6667	6.50
4 g/L	8.2707	98.3333	5.46
1 g/L without pH adjustment	46.3033	18.1333	7.07
2 g/L without pH adjustment	27.0050	20.6667	6.53

Table of Effect of Addition of H_2O_2 without pH Adjustment on COD and Colour Removal (Current Density = 60mA/cm^2, Contact Time = 90 minutes, Volume Sample = 500mL, Agitation Rate = 300rpm, Temperature = 25ºC and Voltage = 12V)

	COD (mg/L)	Colour (PtCo)	pH	
H_2O_2\Parameters	Removal %	Removal %	Before	After
Control	67.7603	92.5680	8.13	8.93
1 g/L	64.1640	92.3358	8.05	8.89
3 g/L	64.4164	91.9044	8.00	8.98
5 g/L	63.2177	91.5727	7.96	9.05
8 g/L	43.4700	91.3404	7.85	9.25

APPENDIX B: Optimization

Table of BOD$_5$ Results

Dilution		100x			500x	
	Before	After	BOD$_5$	Before	After	BOD$_5$
Initial	6.99	6.89	10	6.97	6.37	300
pH 4.5	6.96	6.59	37	6.87	6.33	270
pH 3.6	6.83	6.63	20	6.78	6.43	175