PHOTOCATALYTIC DEGRADATION PROCESS OF WASTE WATER USING TITANIUM DIOXIDE AS CATALYST

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A thesis submitted in fulfillment of the requirement for the awards of the degree of Bachelor

Faculty of Chemical and Natural Resources Engineering
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"I hereby declare that this thesis entitled "*Photocatalytic Degradation Process of Waste Water using Titanium Dioxide as Catalyst*" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidate of any other degree".

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ABSTRACT

Photocatalytic degradation is a process where the organic contaminant in water is degraded by UV light. UV photo oxidation acts to degrade and remove organic compound through the ultraviolet radiation to activate the catalyst. The catalyst used in this study is titanium dioxide (TiO_2) which is chosen based on its properties that are low toxicity, low resistance to corrosion and semiconductor. The semiconductor will absorb the UV light and attract electrons across the energy gap into the conduction band. This electron will change into hydroxyl radicals which can decompose organic compounds while still in the waste water stream. So this is the basic concept that applied in industrial to treat the waste water or any pollutant in water in order to protect the environmental. Simulated oils waste water was used to replicate the Palm Oil Mill Effluent (POME). The studied parameters are the effect of catalyst concentration and irradiation time. The effect of both parameters has studied using Design Expert 7 to determine the optimum condition of degradation activities. The degradation activities were measured through the change of initial and final COD and dissolved oxygen in sample. Through Analysis of Variance (ANOVA) and optimization application of Design Expert 7, it was found that the optimum condition to achieve maximum degradation activities.

ABSTRAK

Penggunaan teknologi proses penguraian sisa air merupakan kaedah yang terbaik untuk merawat sisa buangan air. Teknologi proses penguraian ini adalah dimana bahan organik di dalam air akan di uraikan menggunakan sinaran ungu, (UV). Sinar UV ini bertindak sebagai penyingkir untuk menyingkirkan bahan organik melalui sinaran ungu untuk mengaktifkan pemangkin. Pemangkin yang digunakan ialah titanium dioksida (TiO_2) dimana ia mempunyai sifat-sifat seperti kurang toksik, tidak mudah terhakis dan semikonduktor. Semikonduktor akan bertindak menyerap sinar UV dan di situ berlakunya mekanisme dimana elektron akan berubah kepada ion hidroksida yang radikal yang mampu menguraikan bahan organik. Inilah konsep yang diguna pakai dalam industri untuk merawat sisa air buangan atau apa sahaja sisa untuk memelihara alam sekitar. Sampel disediakan dengan kepekatan yang sama dengan kepekatan sisa buangan dari kilang sawit (POME). Parameter yang dikaji ialah kesan kepekatan pemangkin dan masa sinaran UV terhadap aktiviti penguraian dan kedua-dua parameter ini dianalisis menggunakan perisian Design Expert 7 dalam menentukan aktiviti yang optimum untuk aktiviti penguraian. Aktiviti penguraian ini diukur melalui perbezaan COD awal dan COD akhir sample dan perubahan oksigen terlarut didalamnya. Melalui analisis varian (ANOVA) dan optimism dari perisian Design Expert 7 telah menemukan keadaan yang optimum untuk mencapai aktiviti penguraian yang maksimum.

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COD   -   Chemical Oxygen Demand

DO   -   Dissolved Oxygen

TiO_2 -   Titanium Dioxide

UV   -   Ultra Violet

PCA   -   Photocatalytic Activity

WQI   -   Water Quality Index

DOE   -   Department of Environment

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CHAPTER 1

INTRODUCTION

1.1   Background

Water pollution is the contamination of water bodies such as lakes, rivers, oceans, and groundwater caused by either human activities or industrial activities, which can be harmful to organisms and plants which live in these water bodies. It has always been a major problem to the environment. With industrialization in major areas and an urban city growing the water around them just keeps getting polluted. A lot of water pollution is caused by factories near rivers and lakes doing illegal dumping.

One type of water pollution is Palm oil mill effluent (POME) that contains high concentration of organic matter. COD concentration is in the range of 45,000 to 65,000 mg/l, 5-day BOD 18,000 to 48,000 mg/l and oil and grease greater than 2,000 mg/l. The COD: N: P ratio is around 750:7.3:1 (K.K. Chin, S.W. Lee, H.H. Mohammad, 1996).

On average, about 0.1 tonne of raw Palm Oil Mill Effluent (POME) is generated for every tonne of fresh fruit bunch processed. POME consists of water soluble components of palm fruits as well as suspended materials like palm fiber and oil. Despite its biodegradability, POME cannot be discharged without first being treated because POME is acidic and has a very high biochemical oxygen demand (BOD).

One of the methods found in photocatalytic degradation is a process where the organic contaminant in water will be degraded by using the UV light. Photocatalytic oxidation is one of the most effectively clean technologies for the degradation of waste water and any pollutants or contaminant in water. However, the application of heterogeneous photocatalytic for waste water treatment on an industrial scale has been impeded by a lack of mathematical models that can be readily applied to a reactor design and scale up (Gianluca Li Puma and Po Lock Yue, 2002).

UV photo-oxidation acts as eliminator to removing organic compound through the ultraviolet radiation to activate the catalyst. The catalyst that will use in this method is titanium dioxide (TiO_2) which is consider to it's properties that have low toxicity, low resistance to corrosion and semiconductor. The semiconductor will absorb the UV light and attract electrons across the energy gap into the conduction band. This electron will change into hydroxyl radicals which can decompose organic compounds while still in the waste water stream. So this is the basic concept that applied in industrial to treat the waste water or any pollutant in water in order to protect the environmental.

The purpose of this research is to study about the effects of temperature and irradiation time of the waste water towards the photodegradation process by measuring the chemical oxygen demand (COD) value and dissolve oxygen (DO) value. COD is a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals such as ammonia and nitrite. COD measurements are commonly made on samples of waste water or of natural water contaminated by domestic or industrial wastes in order to protect the quality of water. Chemical oxygen demand is measured as a standardized laboratory assay in which a closed water sample is incubated with a strong chemical oxidant under specific conditions of temperature and for a particular period of time.

1.2   Problem Statement

The growth of the industrial field and development of country especially in economic and investment give the huge effect to our environment including organisms and plant. However, in contexts of environmental awareness, there are still several authorities and people who are irresponsible in protect the environment from any pollution. Besides that the primary and secondary treatment of POME seems not much efficient because its still have the higher value of COD, BOD and the others composition that can harm marine life. The purpose of this research is to venture the tertiary treatment in addition to secondary and primary treatment to further to reduce the COD and BOD value in order to protect the environment. This technology process must be developed in order to enhance treatment in an industrial scale instead of laboratory scale.

1.3   Objective

The objectives of this research are

1. To study the effect of time irradiation of UV light towards degradation activities.

2. To study the effect of catalyst concentration towards the photocatalytic degradation.

1.4   Scope of Research

This study will concentrate on determining the effect of temperature and time irradiation towards the photocatalytic degradation process. The equipment that use in this experiment is COD digester and UV lamp. The function of COD digester is to determine the initial COD value of waste water prior to catalyst addition and the final value after irradiation with catalyst, TiO_2.

- For the time irradiation, we use the UV lamp to emit to the sample in certain time at range 0 to 150 minutes.
- The catalyst concentration that used for this experiment is between 0 to 2.5mg/L
- The value of COD will be measured using COD digester and the oxygen consumed is measured by using the DO (dissolve oxygen) meter.

1.5   Rational and Significant

The rational of this research is to study potential of a new technology that can be developed and applied for waste water treatment. Relating to the current situation that our industrial activities are growing every year, the production of waste water also must be consider in order to protect the environment, resident and especially marine life from the hazardous waste. For the further research and development, the study potential of this process can be applied to treat the contaminant and pollutant waste water at industry which is more hazardous than POME. Photocatalysis on TiO_2 represents a promising alternative technology for degradation of organic pollutant and inactivation of microorganisms in water through the photogeneration of separated electrons and positive holes in semiconductor particles (Josef Krysa *et al.*, 2005). In this research, the photocatalytic degradation process is expected to produce the simplest and non-toxic product which is carbon dioxide (CO_2) and water (H_2O) respectively. Using the

interaction between ultraviolet radiation and titanium dioxide (TiO_2) has a strong potential for destruction of toxic in water (Sixto Malato Rodriguez *et al.*, 1996).

CHAPTER 2

LITERATURE REVIEW

2.1 Photocatalytic Degradation

Photocatalytic degradation process is an eliminating process of organic compound in water by using the interaction between ultraviolet radiation and titanium dioxide (TiO_2) as catalyst. It has the potential for treating of toxic organics in waste water. While UV photo-oxidation is a destructive method of removing organic compounds, like oil, that uses ultraviolet radiation to activate a catalyst. (Alexia Patsoura *et al.*, 2007).

In the last few years, research on new methods for advanced waste water treatment has gone from processes involving phase transfer of a contaminant (e.g. activated carbon, air stripping, pyrolysis) to complete destruction of the contaminant. The possible application of photocatalytic for destruction of the organic mater in water has been extensively investigated. (Ollis et *al.*, 1991; Matthews, 1991). It has been found that the production of CO_2 and H_2 from this process. The problem with toxic organic compounds in waste water is becoming an increasing threat to people's health.

UV photo-oxidation does not require a separation step to remove the contaminant because the organic contaminant is destroyed while still in the waste water stream. (Jauregui *et al*., 1998). This eliminates the costs and time associated with this

additional step. There are three different oxidizers are currently used in industry, UV light, hydrogen peroxide and ozone. .

2.2   Titanium Dioxide as a Photocatalyst

Titanium dioxide is attractive because of this ability and because of its low toxicity and resistance to corrosion (Alfano *et al*., 1970). Titanium dioxide is considered a semiconductor because it takes UV light to promote electrons across the energy gap into the conduction band. These electrons may then form hydroxyl radicals, which can decompose organic compounds. Many studies have been published on the use of TiO_2 as a photocatalyst for the decomposition of organic compounds. TiO_2 is active under UV light. Photocatalytic activity (PCA) is the ability of a material to create an electron hole pair as a result of exposure to ultraviolet radiation. The resulting free-radicals are very efficient oxidizers of organic matter. Photocatalytic activity in TiO_2 has been extensively studied because of its potential use in sterilization, sanitation, and remediation applications.

Titanium dioxide, particularly in the anatase form, is a photocatalyst under ultraviolet light. Recently it has been found that titanium dioxide, when spiked with nitrogen ions, or doped with metal oxide like tungsten trioxide, also act as photocatalyst under visible and UV light. The strong oxidative potential of the positive holes oxidizes water to create hydroxyl radicals. It can also oxidize oxygen or organic materials directly. It is also used in the Graetzel cell, a type of chemical solar cell (Xu Zhao *et al*., 2007; Efthalia C. *et al*., 2007; C. Fotiadis *et al*., 2007; A.R. Mohamed *et al*., 2004; Heqing Tang et al., 2008).

The photocatylic properties of titanium dioxide were discovered by Akira Fujishima in 1967. The process on the surface of the titanium dioxide was called the Honda-Fujishima effect.   Titanium dioxide has potential for use in energy production:

as a photocatalyst, it can carry out hydrolysis for example break water into hydrogen and oxygen. Were the hydrogen collected, it could be used as a fuel. The efficiency of this process can be greatly improved by doping the oxide with carbon, as described in "Carbon-doped titanium dioxide is an effective photocatalyst" produce electricity when in nano particle form. Research suggests that by using these nano particles to form the pixels of a screen, they generate electricity when transparent and under the influence of light. If subjected to electricity on the other hand, the nano particles blacken, forming the basic characteristics of a LCD screen. According to creator Zoran Radivojevic, Nokia has already built a functional 200-by-200-pixel monochromatic screen which is energetically self-sufficient (Masaaki Kitano *et al.*, 2007)

As TiO_2 is exposed to UV light, it becomes increasingly hydrophilic; thus, it can be used for anti-fogging coatings or self-cleaning windows. TiO_2 incorporated into outdoor building materials, such as paving stones in noxer blocks or paints can substantially reduce concentrations of airborne pollutants such as volatile organic compounds and nitrogen oxides

2.3   Mechanism of TiO_2

The photocatalytic reaction proceeds via a series of chemical events following the initiation step of pair electron hole formation. This leads to the utilization of both the electron hole, h^+ for oxidation processes and eventually to the capture of the e^- electron for reduction processes, as well as the potential formation of super oxides anions and hydrogen peroxide from oxygen (Hugo de Lasa *et. al.,* 2005).

Unfortunately, there is a competing electron and electron hole recombination step the reverse of equation (1-1), and this result in process inefficiencies and the waste of energy supplied by the photon. The electron hole recombination can be considered as

one of the major factors limiting the efficiency of the photocatalytic processes. (Hugo de Lasa *et. al.,* 2005).

$$photocatalyst \ \rightarrow \ e^- \ + \ h^+ \tag{2.1}$$

Every effort to prevent electron and electron hole recombination will improve the efficiency of photocatalytic processes and will considerably help to achieve the application of this technique for water purification (Hugo de Lasa *et. al.,* 2005).

The photocatalytic reaction can be represented as a number of mechanistic steps (M. Saquib *et. al.,* 2007). A photo excited TiO_2 generates an electron and an electron hole.

$$TiO_2 \ \xrightarrow{h\nu} e^- \ + h^+ \tag{2.2}$$

Electron transfer from the adsorbed substrate (RX_{ad}), absorbed water or the OH_{ad} ion to the electron hole.

$$h^+ + \ RX_{ad} \ \rightarrow \ RX_{ad}^+ \tag{2.3}$$

$$h^+ + \ H_2O_{ads} \ \rightarrow \ O_{ads}^{\bullet} \ + \ H^+ \tag{2.4}$$

$$h^+ + OH_{ad}^- \ \rightarrow \ OH_{ad}^{\bullet} \tag{2.5}$$
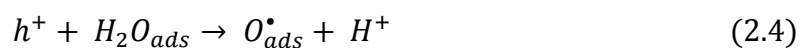
2.4   Wastewater Remediation

Photocatalytic degradation and TiO_2 as photocatalyst offers great potential as an industrial technology for detoxification or remediation of wastewater due to several factors such as the process occurs under ambient conditions very slowly, direct UV light exposure increases the rate of reaction, the formation of photocyclized intermediate products, unlike direct photolysis techniques, is avoided, oxidation of the substrates to CO_2 is complete, the photocatalyst is inexpensive and has a high turnover and lastly TiO_2 can be supported on suitable reactor substrates.

2.5   Palm Oil Mill Effluent (POME)

Palm oil mill effluent (POME), from a factory site in India contained about 250,000 mg/L chemical oxygen demand (COD), 11,000 mg/L biochemical oxygen demand, 65 mg/L total dissolved solids and 9000 mg/L of chloroform-soluble material. Treatment of this effluent using Yarrowia lipolytica NCIM 3589, marine hydrocarbon-degrading yeast isolated from Mumbai, India, gave a COD reduction of about 95% with a retention time of two days. Treatment with a chemical coagulant further reduced the COD and a consortium developed from garden soil clarified the effluent and adjusted the pH to between 6 and 7. The complete treatment reduced the COD content to 1500 mg/L which is a 99% reduction from the original. Palm oil mill effluent (POME) is an important source of inland water pollution when released into local rivers or lakes without treatment.   POME contains lignocellulolic wastes with a mixture of carbohydrates and oil (N.Oswal *et al*, 2001).

Chemical oxygen demand (COD) and biochemical oxygen demand (BOD) of POME are very high and COD values greater than 80,000 mg/L are frequently reported. Incomplete extraction of palm oil from the palm nut can increase COD values substantially. POME has generally been treated by anaerobic digestion resulting in methane as a value added product (Sinnappa, 1978; Borja *et al.,* 1995). The raw POME may also be used in crop irrigation (Wood *et al.* 1979) and treated it using a pond system (Chin *et al.*, 1996). The aerobic digestion of POME decreases carbon content and inorganic nitrogen and changes pH from the acidic range to an alkaline one (Agamuthu *et al.*, 1986). Such treatment also increases the ratio of organic nitrogen leading to the production of a better fertilizer.

The sample palm oil mill effluent (POME) can be treated using other process which is membrane technology but it require a lot of process and it maintenance and fouling which will increase overall cost of plant. Waste water treatment is one of the most important components in POME because the facility to treat it is being generated in large volume during the production of crude palm oil (CPO) (Chin *et al.*, 1996).

2.6   Measurement of Water Quality

The complexity of water quality as a subject is reflected in the many types of measurements of water and Wastewater quality indicators. These measurements include (from the simplest and basic to more complex):

- Dissolved Oxygen(DO)
- Chemical oxygen demand (COD)

2.6.1   Dissolved Oxygen (DO)

Dissolved oxygen analysis measures the amount of gaseous oxygen (O_2) dissolved in an aqueous solution. Oxygen gets into water by diffusion from the surrounding air, by aeration (rapid movement), and as a waste product of photosynthesis. When performing the dissolved oxygen test, only grab samples should be used, and the analysis should be performed immediately. Therefore, this is a field test that should be performed on site.

Adequate dissolved oxygen is necessary for good water quality. Oxygen is a necessary element to all forms of life. Natural stream purification processes require adequate oxygen levels in order to provide for aerobic life forms. As dissolved oxygen levels in water drop below 5.0 mg/l, aquatic life is put under stress. The lower the concentration, the greater stress. Oxygen levels that remain below 1-2 mg/l for a few hours can result in large fish kills. Measure DO in water sample by using Winkler test, oxygen probe or by iodometric titration. DO is inversely proportional to temperature, and the maximum amount of oxygen that can be dissolved in water at 0°C is 14.6 mg/L.

Table 2.1 Solubility of Oxygen in Water
(Ruth F.W. and Robin M, 4th edition)

Water Temperature (°C)	Saturation concentration of oxygen in water (mg/L)
0	14.6
2	13.8
4	13.1
6	12.5
8	11.9
10	11.3
12	10.8
14	10.4
16	10.0
18	9.5
20	9.2
22	8.8
24	8.5
26	8.2
28	8.0
30	7.6

Based on the table 2.1 shows that when the temperature increases the concentration of oxygen in water will decrease. This is because the temperature will affect the amount of oxygen in water. Related to this research when the temperature of waste water is high the degradation process will decrease because the oxygen present in the sample is less. This DO value also related to the COD value in order to determine the photodegradation process.

2.6.2   Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals such as ammonia and nitrite. COD measurements are commonly

made on sample of waste water or of natural waters contaminated by domestic or industrial wastes (Guiying Li *et al*., 2006).

Chemical oxygen demand is measured as a standardized laboratory assay in which a closed water sample is incubated with a strong chemical oxidant under specific condition of temperature and for a particular period of time. As the COD value increase the quality of water is decrease. This is because the amount of oxygen are consume for decomposition during the photodegradation process. When the concentration of oxygen is less the water are not suitable for aquatics. (Guiying Li *et al*., 2006)

2.7   Department of Environment (DOE) Water Quality Index Classes

Table 2.2 and 2.3 describe that the water quality index (WQI) and general rating scale for WQI. There are five difference classes which is the class I is very clean compared to the class V that is much polluted. Several criteria are considered to determine which class is suitable for the difference type of water. If the WQI is less than 90 the water is considered as polluted and when COD of that water is high, it show that the water is highly polluted and there are no aquatics life in it. So, based on this table the degradation process is needed in order to decompose the organic compound in water to ensure that the quality of water is high.

Table 2.2 Water Quality Index

Parameter	Unit	Class				
		I	II	III	IV	V
Ammoniacal Nitrogen	mg/l	< 0.1	0.1 - 0.3	0.3 – 0.9	0.9 – 2.7	> 2.7
Biochemical Oxygen Demand	mg/l	< 1	1 - 3	3 – 6	6 – 12	> 12
Chemical Oxygen Demand	mg/l	< 10	10 – 25	25 – 50	50 – 100	> 100
Dissolved Oxygen	mg/l	> 7	5 – 7	3 – 5	1 – 3	< 1
pH	mg/l	> 7.0	6.0 - 7.0	5.0 – 6.0	< 5.0	> 5.0
Total Suspended Solid	mg/l	< 25	25 – 50	50 – 150	150 - 300	> 300
Water Quality Index		> 92.7	76.5 – 92.7	51.9 – 76.5	31.0 – 51.9	< 31.0

Table 2.3 General Rating Scale for the Water Quality Index (WQI)

Usage	10	20	30	40	50	60	70	80	90	100	WQI
General	Very polluted				Slightly polluted				Clean		
Water class			v		iv		iii		ii	i	
Public water supply	Not acceptable				Doubtful	Necessary treatment becoming more expensive			Minor purific required	Purification not necessary	
Recreation	Not acceptable		Obvious pollution occurring	Only for boating	Doubtful for water contact	Becoming polluted still acceptable need bacteria count		Acceptable for all sport			
Fish, Shellfish & wild life	Not acceptable			Coarse fish only	Handy fish only	Doubtful for sensitive fish	Marginal for trout		Acceptable for all fish		
Navigation	Not acceptable			Obvious pollution occurring	Acceptable						

CHAPTER 3

METHODOLOGY

3.1   Material

The material that involved in this experiment is the sample of waste water that classified palm oil as raw material and titanium dioxide (TiO_2) as a catalyst.

3.2   Equipment

In this experiment of photocatalytic process, the major equipment that will use is UV lamp, HACH spectrophotometer and the COD digester. The function of UV lamp is to irradiate and generate the catalyst (TiO_2) in the sample of waste water and the reaction between them will produce the hydroxyl radicals that can decompose organic compounds. The COD digester is used to perform the standard condition for the sample at temperature 30 -150°C and duration 0-120 minutes. The final and initial value of COD will be determined as the percentage of degradation.

3.3   List of Equipment

The equipments used for this experiment are high range COD reagent, DO meter, COD digester, HACH spectrophotometer and UV lamp

Figure 3.1 Dissolved Oxygen Meter

The DO meter was used in this experiment to measure the quantity of oxygen that dissolved in the sample solution. If the value is low means that the water is not suitable for the aquatic life or to discharge from industrial. The temperature also gives the effect to the reading of dissolved oxygen meter. If the water has high temperature, it can be decrease the quantity of oxygen in that water.

Figure 3.2 High Range COD Reagent

High range COD reagent contains strong chemical oxidant under specific conditions of temperature and for a particular period of time. A commonly used oxidant in COD assays is potassium dichromate ($K_2Cr_2O_7$). Because this chemical oxidant is not specific to oxygen consuming chemicals that are organic or inorganic, both of these sources of oxygen demand are measured in a COD assay.

Figure 3.3 HACH Spectrophotometer

Figure 3.4 shows the HACH spectrophotometer that used to determine the COD value after the sample is running in COD digester. The HACH DR 2800 Portable Spectrophotometer can be used for more than 240 analytical methods.

Figure 3.4 COD Digester

COD digester was used to digest the sample in the standard condition. 2ml of sample will added to COD reagent and placed in COD digester within 120 minutes at temperature 150 °C.
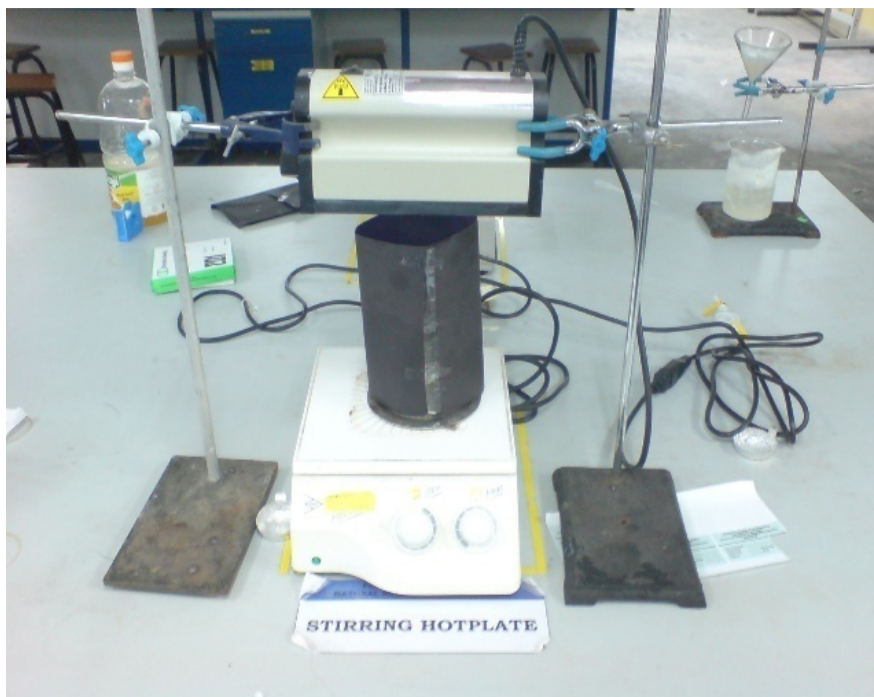
Figure 3.5 Set up of the experiment photodegradation

Figure 3.6 shows that the design of experiment for photocatalytic degradation process. The sample was coating with paper to avoid the source of light from surrounding. Only the UV light is going to irradiate the sample.

3.4 Reagent and Chemical

The reagent and chemical used for experiment are titanium dioxide, TiO_2 and palm olein. The simulated waste water was used to replicate the Palm Oil Mill Effluents (POME).

3.5   **Design of Experiment Set-Up**

3.5.1   Effect of Irradiation Time and Concentration of Catalyst

Preparation of sample

⬇

The initial COD and initial compositions of the sample were measured

⬇

The sample were added with catalyst (TiO$_2$) and placed under UV lamp for 75 minutes.

⬇

Then, the TiO$_2$ was filter and the sample was analyzed to check the final COD value and dissolved oxygen.

⬇

The procedure 1 until 4 was repeated with the different irradiation time, and catalyst concentration.

Figure 3.6 Simplified flow diagram of the experiment

The concentration of sample is fixed to 4% v/v of oily waste water. 4 ml of oil is mixed with 96 ml of water. The concentration of sample based on actual content of oil in POME (Palm Oil Mill Effluent). Next, the initial COD and initial DO without catalyst were measured using COD digester followed by HACH spectrophotometer and dissolved oxygen was determined using DO meter.
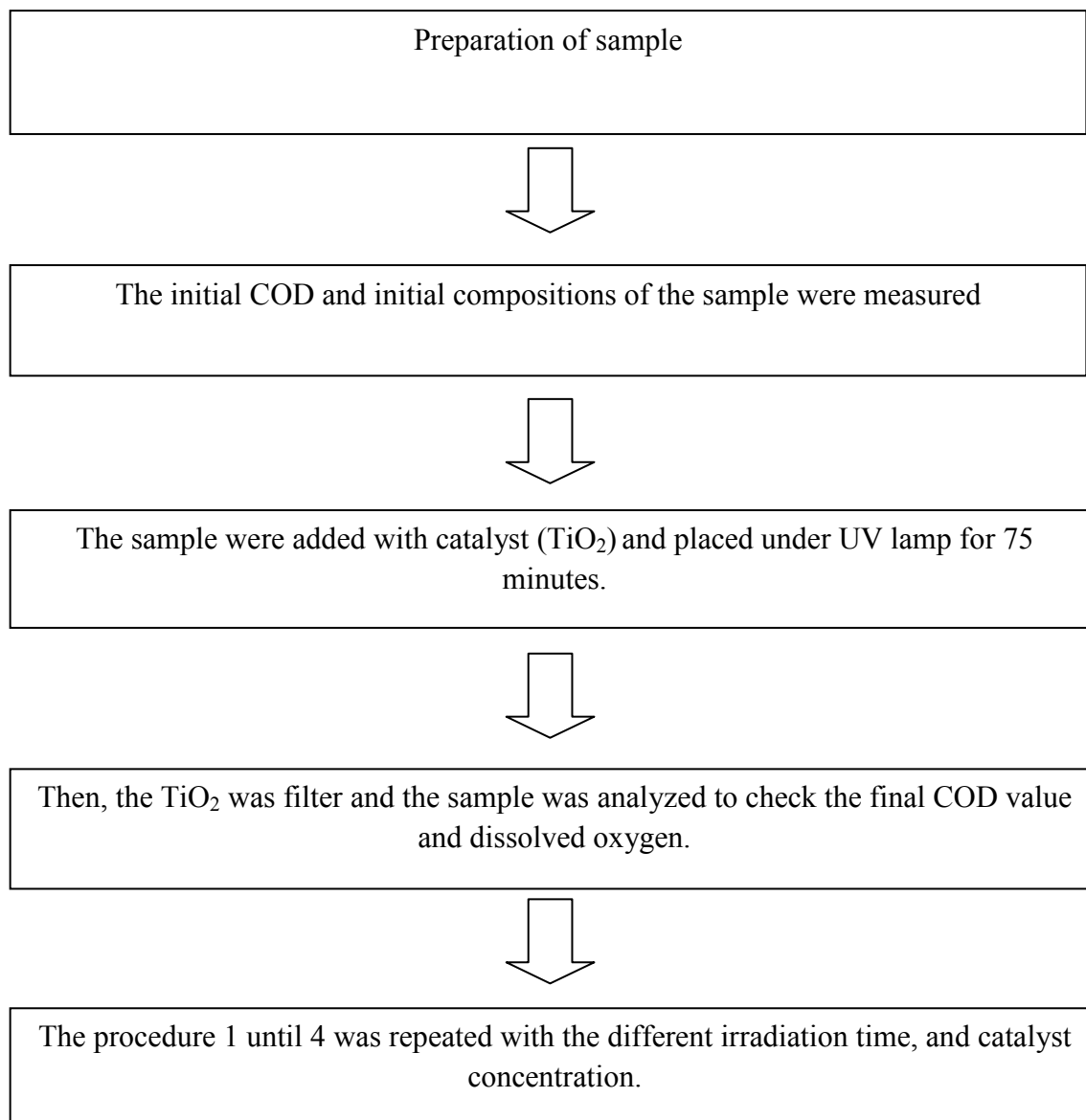
After that the sample is added with catalyst, TiO_2 and placed under the UV light for 75 minutes. The UV light will emit and react with sample and catalyst in order to degrade the organic compound in the sample. Finally the TiO_2 is filter out and the sample is analyzed to check the final COD and final DO. The value of initial and final COD and DO are compared in order to determine the activity of degradation.

The procedure 1 until 4 is repeated with various irradiation time, and catalyst concentration. Than the graph final COD versus irradiation time and the graph DO versus time are plotted to show their relationship.

3.6   Analysis

The photodegradation activity was determined by the percentage of change in COD or by comparing the initial and final COD of waste water sample. The sample was digesting using the COD digester at the standard condition with temperature 150°C and duration 120 minutes. Then the sample will analyze using the HACH spectrophotometer to check the value of COD. While for determine the dissolved oxygen, DO meter was used to determine the DO change in the sample.

$$\% \, Degradation = \frac{COD_i - COD_f}{COD_i} \times 100\%$$ (3.1)

CHAPTER 4

RESULT AND DISCUSSION

4.1   Introduction

The result was divided into two part which is the first part was the effect of studied parameter toward COD of sample and the second was the effect of studied parameter toward dissolved oxygen (DO) of sample. The result of the experiment were summarize in the table below.

Table 4.1: Result of Experiment

Run	Catalyst Concentration (mg/L)	Irradiation Time(minutes)	Temperature(°C)	Degradation (%)	Dissolved Oxygen Change (%)
1	0.5	0.0	30	0.054	0.36
2	1.5	75.00	30	81.53	1.97
3	1.5	75.00	30	79.33	3.15
4	1.5	75.00	30	77.31	0.79
5	0.5	150.00	30	90.26	9.9

6	2.5	0.0	30	0.054	0.12
7	2.5	150.00	30	98.91	10.02
8	0.5	150.00	30	85.11	13.05
9	2.5	0.0	30	0.061	0.26
10	0.5	0.0	30	0.018	0.36
11	2.5	150.00	30	95.18	17.05
12	1.5	75.00	30	61.18	9.13
13	1.5	75.00	30	63.69	6.51
14	1.5	75.00	30	82.38	5.66

4.2 Effect of Irradiation Time and Catalyst Concentration toward Degradation Process.

Based on the data from the Table 4.1 above by using the software Design Expert 7, all the data were analyzed and the graph of interaction of both irradiation time and catalyst concentration were plotted in order to study the relationship between them. After we interpret the data the model were derived based on the result that obtain in the Table 4.1

Degradation (%)   =0.56876 × Irradiation

= 0.010500 × Catalyst Concentration

=0.031130 ×Irradiation × Catalyst Concentration   (4.1)

Based on the equation 4.1, the desired percentage of degradation activities can be determined by using this model by multiplying the constant variable with the manipulated variable. So it is the simplest analysis of model that summarize from the

data of result from experiment. The catalyst concentration and irradiation time are proportional to the percentage of degradation
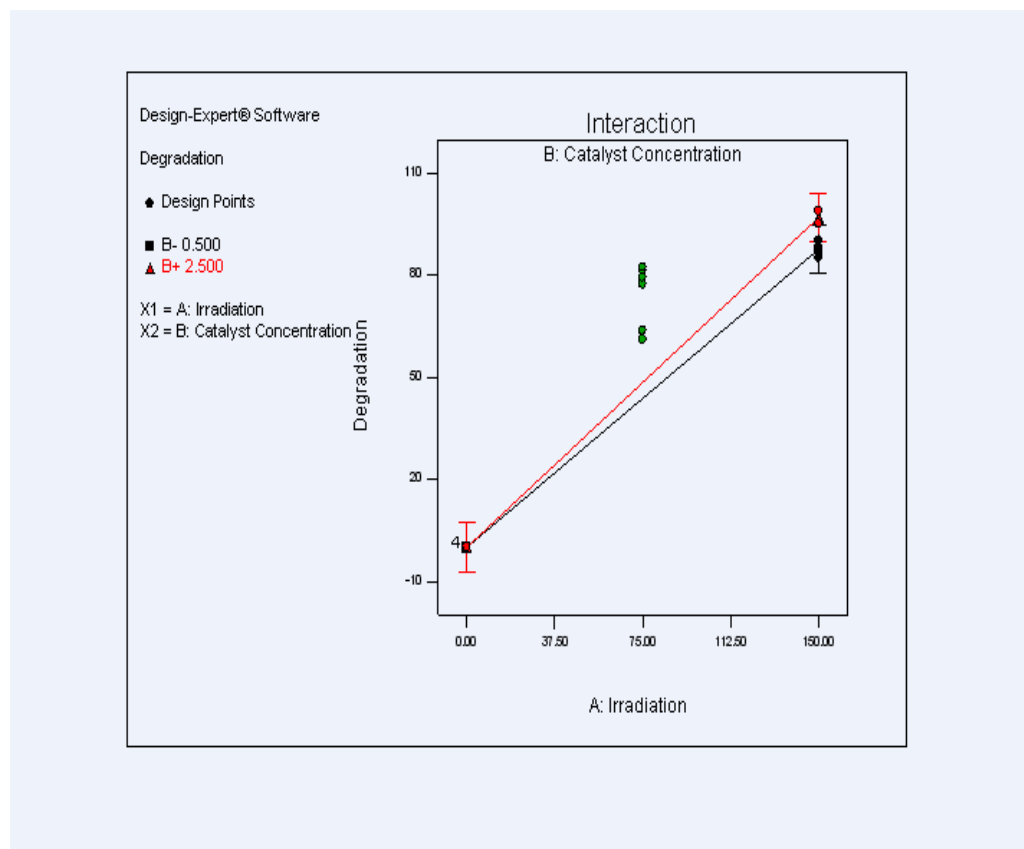
Figure 4.1 Graph of Interaction between Catalyst Concentration and Irradiation Time toward Degradation Activities

Based on the graph above by increasing the catalyst concentration and irradiation time of UV light, the optimum state of degradation process can be achieve. The reaction between catalyst and UV light is the main part of degradation process at optimum temperature 30 °C.

$$TiO_2 \rightarrow e^- + h^+ \qquad (4.2)$$

$$h^+ + H_2O_{ads} \rightarrow OH^._{ad} + H^+ \qquad (4.3)$$

$$h^+ + OH^-_{ad} \rightarrow OH^._{ad} \qquad (4.4)$$
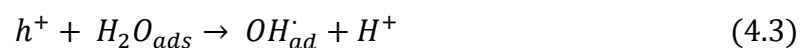
Titanium dioxide will absorb the UV light and attract electrons across the energy gap into the conduction band. This electron will change into hydroxyl radicals which can decompose organic compounds including carbon dioxide. (Al-Ekabi *et al,.*1993)

4.3. Effect of Irradiation Time and Catalyst Concentration toward Dissolved Oxygen Change.

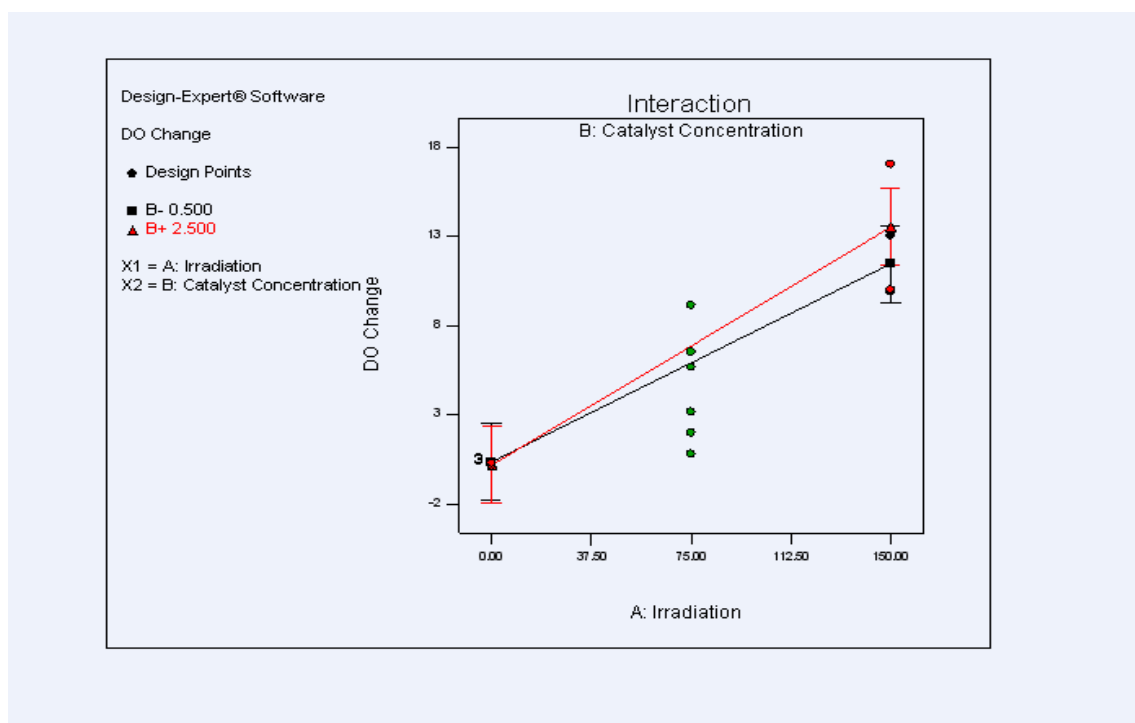**Figure 4.2** Graph of Interaction between Catalyst Concentration and Irradiation Time toward Dissolved Oxygen in Sample

As we can see from the graph above, when the degradation is optimum the change of DO also increase since the photocatalytic can treat the waste water and increase the quality of waste water. The reaction involved is

$$H_2O \rightarrow OH_{ad}^- + H^+$$
(4.5)

In this photocatalytic process the reaction will produce the high concentrations of OH^- and water also dissociation into ions. Molecular oxygen act as acceptor species in the electron transfer reaction

$$e^- + O_2 \rightarrow O_2^- \tag{4.6}$$

Super oxide anions can subsequently be involved in the following reaction

$$O_2^- + H^+ \rightarrow HO_2^{\cdot} \tag{4.7}$$

$$H^+ + O_2^- + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \tag{4.8}$$
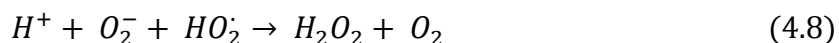
Photoconversion of hydrogen peroxide gives more $OH^{\cdot}$ free radical groups

$$H_2O_2 + h^+ \rightarrow 2OH^{\cdot} \tag{4.9}$$

Finally $OH^{\cdot}$ radicals oxidize organic adsorbed pollutants (RX_{ad}) onto the surface of the titanium dioxide particle. The $OH^{\cdot}$ radicals as described by equation above are very reactive and attack the pollutant molecule to degrade it into mineral acids including carbon dioxide and water (Al-Ekabi $et\ al$,.1993).

For the dissolved oxygen change the math model that we derive based on the result obtain were shown below;

DO Change (%)   =0.070383 × Irradiation

=0.085000 ×Catalyst Concentration

=7.43333 × 10^{-3} ×Irradiation ×Catalyst Concentration   (4.10)

Based on the equation 4.10, the desired DO change can be determined by using this model by multiplying the constant variable with the manipulated variable. So it is how the model analyzes the data from result of the experiment using the Design Expert 7. The catalyst concentration and irradiation time are proportional to the DO change.

4.4   Photodegradation Activity Optimization
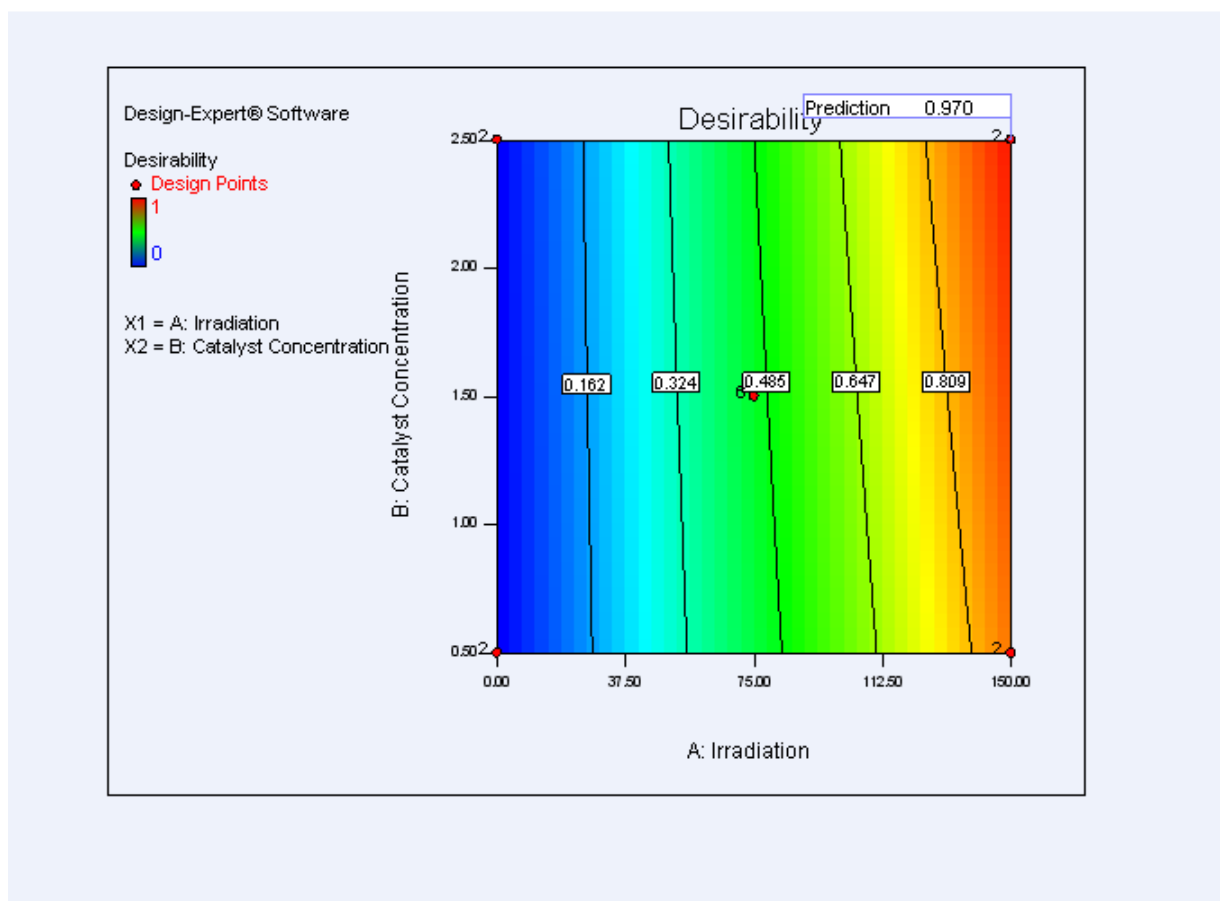
Figure 4.3 Desirability Graph

Based on the graph above shows that the optimization condition when the both parameter which are irradiation time and catalyst concentration were applied. At the highest desirability is when the both parameter at the high concentration of catalyst and long duration of irradiation time. As the line is approach the red region shows that the condition of two parameters is at the optimum condition. So, it can conclude that when the optimum condition of desirability, the 97 % degradation activity is achieved. While at the cool blue region the desirability is lower at condition that the catalyst concentration and irradiation time are less. The minimum degradation activity is about 16.2%.
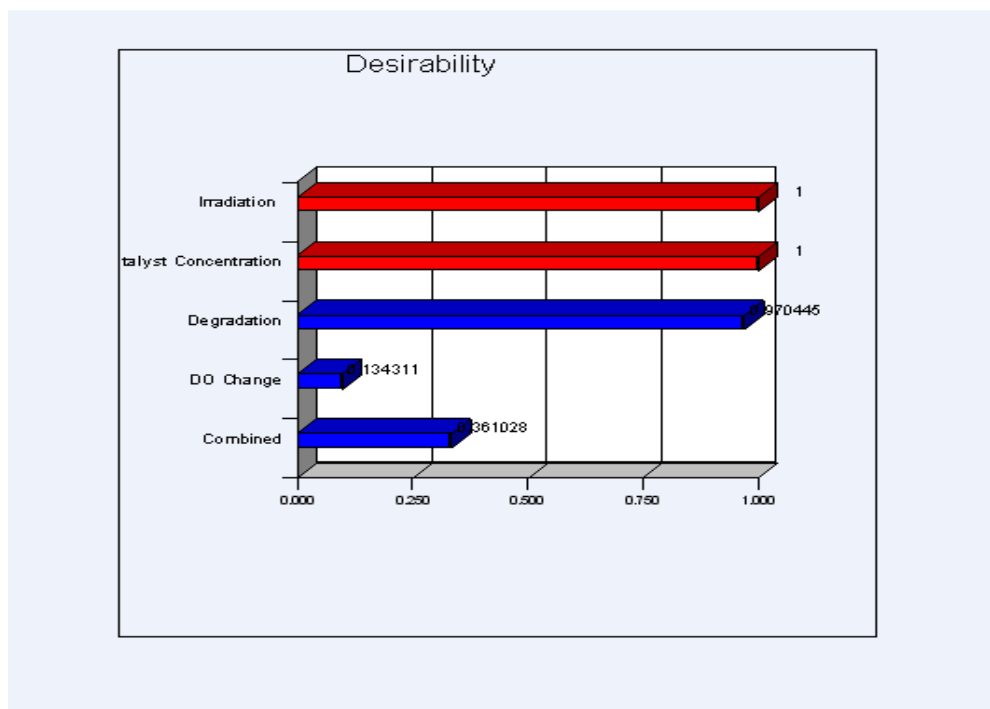
Figure 4.4 Desirability Chart

The bar graph shows the multiple responses optimization variable that satisfied the criteria and the overall combined desirability, when the values is approach one that will be considered good. So according to this chart the irradiation time, catalyst concentration and degradation satisfied this combined desirability. However the dissolved oxygen change is slightly lower even though at the optimum condition with high degradation activities. So the combination of two parameters basically gives a large effect to degradation process compared to dissolved oxygen change. By increasing the degradation activities seems that can increases the quality of water and can be utilized for waste water treatment.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Based on the result that obtain from the experiment, the effects of irradiation time towards the degradation process is directly proportional and for increasing of catalyst concentration can increase the percentage of degradation process. The optimum degradation activity is on temperature at 30°C. TiO_2-mediated UV photocatalysis is capable of completely degrading waste water and it is considerably effective in term of COD removal

With the combination of two parameters for this experiment can give the highest desirability and the optimum condition for us to determine the optimum degradation process that would be achieved. By applying this method in a large scale seems that can replace in addition to the primary and the secondary treatments which is less efficient compared to this technology.

5.2 Recommendations

Make sure that when running the experiment there is no source of light from surrounding except UV light that can give effect to our result. So the experiment must

be conducted in the dark and run in the fume hood while handling experiment with high temperature.

It is hope that this technology will used widely and further develop in industrial scale instead of laboratory scale. During the filtration process make sure all the catalyst are well filter in order to avoid it to mix with COD reagent that can give effect to the result.

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Appendix A

Analysis of Variance for Degradation Process

Use your mouse to right click on individual cells for definitions.
Response   1   Degradation

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Square	DF	Mean Square	F- Value	Prob > F
Model	17133.02	3	5711.01	132.37	0.0001
A-Irradiation	17045.41	1	17045.41	395.08	0.0001
B-Catalyst Concentration	44	1	44	1.02	0.3421
A-B	43.61	1	43.61	1.01	0.3442
Curvature	2691.38	1	2691.38	62.38	0.0001
Residual	345.15	8	43.14		
Lack of Fit	66.62	4	16.66	0.24	0.9026
Pure Error	278.53	4	69.63		
Cor Total	20283.31	13			

The Model F-value of 132.37 implies the model is significant. There is only

a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.

In this case A, Center Point are significant model terms.

Values greater than 0.1000 indicate the model terms are not significant.

If there are many insignificant model terms (not counting those required to support hierarchy),

model reduction may improve your model.

The "Curvature F-value" of 62.38 implies there is significant curvature (as measured by

difference between the average of the center points and the average of the factorial points) in

the design space. There is only a 0.01% chance that a "Curvature F-value" this large

could occur due to noise.

The "Lack of Fit F-value" of 0.24 implies the Lack of Fit is not significant relative to the pure

error. There is a 90.26% chance that a "Lack of Fit F-value" this large could occur due

to noise. Non-significant lack of fit is good -- we want the model to fit.

Std. Dev.	6.57	R-Squared	0.9803
Mean	58.21	Adj R-Squared	0.9728
C.V. %	11.28	Pred R-Squared	0.9586
PRESS	722.76	Adeq Precision	23.886

The "Pred R-Squared" of 0.9586 is in reasonable agreement with the "Adj R-Squared" of 0.9728.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your

ratio of 23.886 indicates an adequate signal. This model can be used to navigate the design space.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	46.21	1	2.32	40.85	51.56	
Block 1	2.85	1				
Block 2	-2.85					
A-Irradiation	46.16	1	2.32	40.80	51.51	1.00
B-Catalyst Concentration	2.35	1	2.32	-3.01	7.70	1.00
AB	2.33	1	2.32	-3.02	7.69	1.00
Center Point	28.02	1	3.55	19.84	36.20	1.00

 Final Equation in Terms of Coded Factors:

Degradation   =

+46.21

+46.16 * A

+2.35   * B

+2.33   * A * B

Final Equation in Terms of Actual Factors:

Degradation   =

+0.030750

+0.56876   * Irradiation

+0.010500   * Catalyst Concentration

+0.031130   * Irradiation * Catalyst Concentration

The Diagnostics Case Statistics Report has been moved to the Diagnostics Node.

In the Diagnostics Node, Select Case Statistics from the View Menu.

Proceed to Diagnostic Plots (the next icon in progression). Be sure to look at the:

   1) Normal probability plot of the studentized residuals to check for normality of residuals.

   2) Studentized residuals versus predicted values to check for constant error.

   3) Externally Studentized Residuals to look for outliers, i.e., influential values.

   4) Box-Cox plot for power transformations.

If all the model statistics and diagnostic plots are OK, finish up with the Model Graphs icon.

Constraints

Lower Upper Lower Upper

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Irradiation	is in range	0	150	1	1	3
Catalyst Concentration	is in range	0.5	2.5	1	1	3

| Degradation | | maximize | 0.018 | 100 | 1 | 1 | 3 |

Solutions

Number	Irradiation	Catalyst Concentration	Degradation	Desirability
1	150.00	2.50	97.045	0.970
2	150.00	2.45	96.8285	0.968
3	150.00	2.40	96.5575	0.966
4	150.00	2.36	96.4016	0.964
5	150.00	1.51	92.4198	0.924

5 Solutions found

Number of Starting Points: 35

Irradiation	Catalyst Concentration
150.000	0.500
75.000	1.500
0.000	2.500
0.000	0.500
150.000	2.500
91.455	1.223
136.155	2.331
45.120 1	.240
94.680	1.532
20.190	0.746
19.980	0.798

81.915	2.043
14.160	2.246
83.955	0.786
124.590	2.198
130.425	0.754
38.955	0.626
119.310	1.359
114.435	1.242
40.950	0.960
51.285	1.796
80.100	2.034
147.675	1.142
94.410	1.278
95.715	0.637
68.685	0.695
105.615	2.435
67.575	0.736
67.995	2.234
85.575	1.549
40.995	1.050
117.480	1.408
22.710	1.566
98.040	2.381
44.970	1.631

Appendix B

Analysis of Variance for Dissolved Oxygen Change

Use your mouse to right click on individual cells for definitions.
Response   2   DO Change

     ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Square	DF	Mean Square	F- Value	Prob > F
Model	303.42	3	101.14	25.88	0.0002
A-Irradiation	299.15	1	299.15	76.53	< 0.0001
B-Catalyst Concentration	1.79	1	1.79	0.46	0.5181
A-B	2.49	1	2.49	0.64	0.4481
Curvature	11.80	1	11.80	3.02	0.1205
Residual	31.27	8	3.91		
Lack of Fit	21.94	4	5.49	2.35	0.2138
Pure Error	9.33	4	2.33		
Cor Total	393.70	13			

The Model F-value of 25.88 implies the model is significant. There is only

a 0.02% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.

In this case A are significant model terms.

Values greater than 0.1000 indicate the model terms are not significant.

If there are many insignificant model terms (not counting those required to support hierarchy),

model reduction may improve your model.

The "Curvature F-value" of 3.02 implies the curvature (as measured by difference between the

average of the center points and the average of the factorial points) in the design space is not

significant relative to the noise. There is a 12.05% chance that a "Curvature F-value"

this large could occur due to noise.

The "Lack of Fit F-value" of 2.35 implies the Lack of Fit is not significant relative to the pure

error. There is a 21.38% chance that a "Lack of Fit F-value" this large could occur due

to noise. Non-significant lack of fit is good -- we want the model to fit.

Std. Dev.	1.98	R-Squared	0.9066
Mean	5.59	Adj R-Squared	0.8715
C.V. %	35.34	Pred R-Squared	0.6305
PRESS	123.68	Adeq Precision	13.149

The "Pred R-Squared" of 0.6305 is not as close to the "Adj R-Squared" of 0.8715 as one might

normally expect. This may indicate a large block effect or a possible problem with your model

and/or data. Things to consider are model reduction, response tranformation, outliers, etc.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your

ratio of 13.149 indicates an adequate signal. This model can be used to navigate the design space.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	6.39	1	0.70	4.78	8.00	
Block 1	-1.84	1				
Block 2	1.84					
A-Irradiation	6.11	1	0.70	4.50	7.73	1.00
B-Catalyst Concentration	0.47	1	0.70	-1.14	2.08	1.00
AB	0.56	1	0.70	-1.05	2.17	1.00
Center Point	-1.86	1	1.07	-4.32	0.61	1.00

 Final Equation in Terms of Coded Factors:

DO Change   =

+6.39

+6.11   * A

+0.47　* B

+0.56　* A * B

Final Equation in Terms of Actual Factors:

DO Change　　=

+0.40250

+0.070383　　* Irradiation

-0.085000　　* Catalyst Concentration

+7.43333 × 10^{-3}　　　* Irradiation * Catalyst Concentration

The Diagnostics Case Statistics Report has been moved to the Diagnostics Node.
In the Diagnostics Node, Select Case Statistics from the View Menu.

Proceed to Diagnostic Plots (the next icon in progression). Be sure to look at the:
  1) Normal probability plot of the studentized residuals to check for normality of residuals.

  2) Studentized residuals versus predicted values to check for constant error.

  3) Externally Studentized Residuals to look for outliers, i.e., influential values.

  4) Box-Cox plot for power transformations.

If all the model statistics and diagnostic plots are OK, finish up with the Model Graphs icon.

Constraints

Lower Upper Lower Upper

Name	Goal	Limit	Limit	Weight	Weight	Importance
Irradiation	is in range	0	150	1	1	3
Catalyst Concentration	is in range	0.5	2.5	1	1	3
Degradation	maximize	0.018	100	1	1	3
DO Change	maximize	0.12	100	1	1	3

Solutions

Number	Irradiation	Catalyst Concentration	Degradation	DO Change	Desirability
1	150.00	2.50	97.045	13.535	0.361
2	150.00	2.47	96.8976	13.5026	0.360
3	150.00	2.44	96.7579	13.4718	0.360
4	150.00	2.40	96.5562	13.4274	0.359

4 Solutions found

Number of Starting Points: 35

Irradiation	Catalyst Concentration
75.000	1.500
0.000	0.500
0.000	2.500
150.000	0.500
150.000	2.500
148.350	1.510
92.040	1.382
94.215	0.860
47.985	1.696
137.400	1.050
67.695	0.664
67.095	2.241
100.425	1.899
139.590	2.431
15.870	0.835
56.460	1.566
48.270	2.219
149.160	1.419
92.250	1.520
29.670	0.803
49.095	2.331
94.455	0.673
46.785	0.819

91.275	0.689
32.055	1.293
136.185	1.803
108.150	1.941
40.455	2.417
66.555	0.808
84.330	0.696
86.400	1.082
147.630	0.585
149.490	1.727
34.005	2.090
144.900	0.560

Appendix C

Attachment of Figures

| **Figure C1**: Before | **Figure C2:** After |

Sample of waste water figure C1 before photocatalytic degradation process and figure C2 after the degradation process.

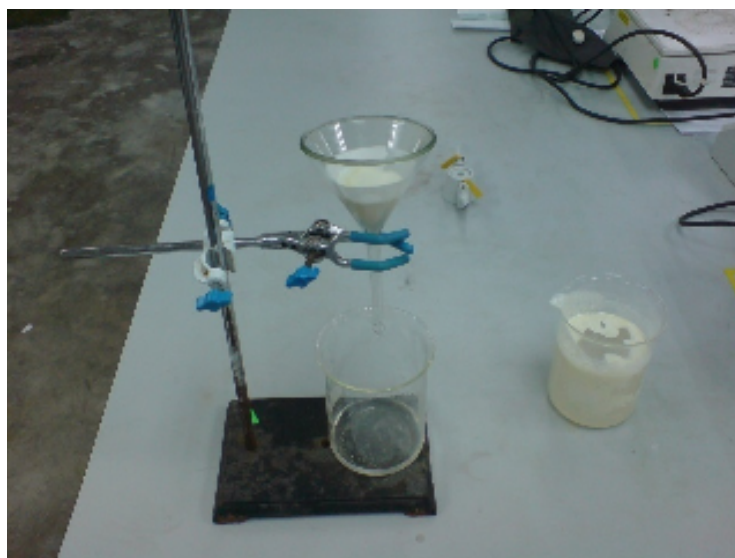**Figure C3**; Design of experiment of Photocatalytic Degradation process.

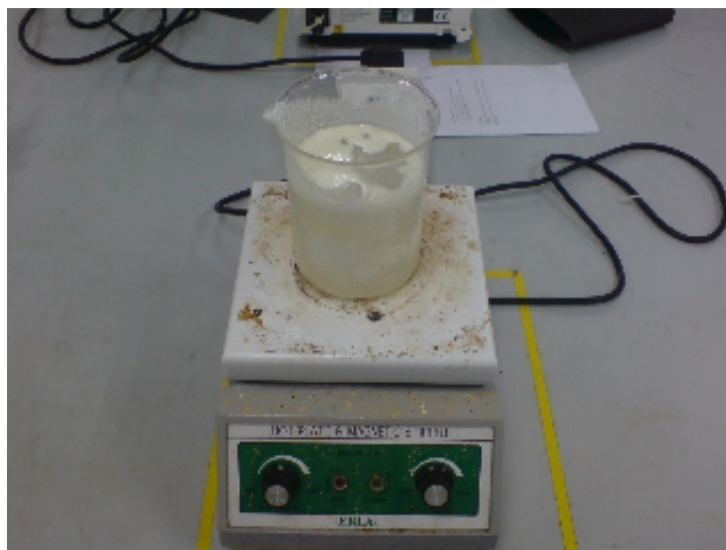**Figure C4**: Filtration process to remove the catalyst from sample

Figure C5: Sample was stirred using magnetic stirrer
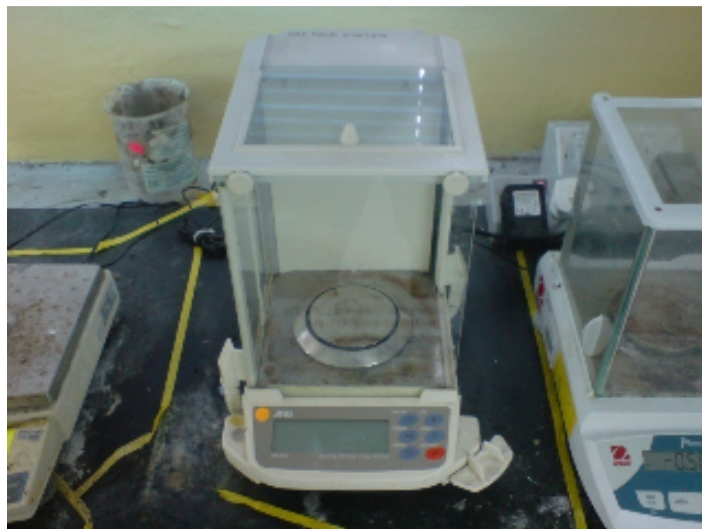

Figure C6: Bottle of samples

Figure C7: Weighing Scale