

**Faculty of Science and Engineering  
Department of Chemical Engineering**

**Development of an Efficient Integrated System for Industrial Oily  
Wastewater Treatment**

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**This thesis is presented for the Degree of  
Doctor of Philosophy  
of  
Curtin University**

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## DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgement has been made.

This thesis contains no material where has been accepted for the award of any other degree or diploma in any university.

Signature: .....

Date: .....

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This work is dedicated to my mother for her loving support.

This work is also dedicated to my husband, my lovely kids and all my family in Indonesia in appreciation of their lovely encouragement during my PhD study.

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## PUBLICATIONS

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## ACRONYMS

AOPs	Advanced oxidation processes
API	American petroleum institute
BOD	Biochemical oxygen demand
BP	British petroleum
BTU	Biological treatment unit
CaO	Calcium oxide
$C_0$	Initial concentration
$C_e$	Concentration at equilibrium
$C$	Concentration of component
cm	Centimetre
COD	Chemical oxygen demand
$C_t$	Concentration at any time
DAF	Dissolved air floatation
DOC	Dissolved organic carbons
$E_b$	Energy band-gap
EDS	Energy Dispersive X-ray Spectroscopy
EPA	Environmental protection agency
EU	European Union
$Fe^{2+}$	Ferrous iron
$Fe^{3+}$	Ferric iron
FTIR	Fourier transform infrared
g	Gram
h	Hour

H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
K	Degree kelvin
kg	Kilogram
$k_1$	Pseudo-first order constant
$k_2$	Pseudo-second order constant
$K_d$	Distribution coefficient
$K_f$	Freudlich constant related to adsorption capacity
$K_{fd}$	Film diffusion rate constant
$K_{id}$	Intra particle diffusion rate constant
$K_L$	Langmuir constant
L	Litre
$\lambda$	Wavelength
m	Metre
mg	Milligram
min	Minute
mW	Milliwatt
Q <sub>overall</sub>	Overall quantum yield
PVDF	polyvinylidene difluoride
$q_e$	Adsorption capacity at equilibrium
$q_m$	Maximum adsorption capacity
$q_t$	Oil adsorbed at specific time
R <sup>2</sup>	Linear regression coefficient
$R_L$	Separation factor
rpm	Revolutions per minute
SEM	Scanning electron micrograph

$t$	Time
TDS	Total dissolved salts
TiO <sub>2</sub>	Titanium dioxide
TOC	Total organic carbon
TPH	Total petroleum hydrocarbon
TSS	Total suspended solid
USEPA	United states environmental protection agency
UV	Ultra violet
UF	Ultrafiltration
V	Volume
ZnO	Zinc oxide
°C	Degree Celsius
M	Micro
$\beta$	Constant related to adsorption energy
$\Delta G^{\circ}$	Gibb's free energy
$\Delta H^{\circ}$	Enthalpy change
$\Delta S^{\circ}$	Entropy change

## ABSTRACT

Oily wastewater generated from various industries such as petroleum refinery, canola oil, food and restaurants which contains hazardous pollutants is a matter of great concern in the field of wastewater treatment. The untreated or partly treated oily wastewater discharged to water bodies could significantly affect the aquatic life and human health. Different methods and technologies have been applied, individually or combined, for oily wastewater treatment, such as membrane filtration, advanced oxidation processes (AOPs), and adsorption. The quality of the oily wastewater also has a significant effect on the performance of the selected treatment technology. Therefore in this work, different oily wastewater qualities (petroleum refinery wastewater, resultant wastewater, canola oil wastewater and synthetic oily wastewater) were used to understand and suggest the most efficient oily wastewater treatment technology.

In this work the polymeric ultrafiltration (UF) membrane was first applied as single effective treatment method for oily wastewater. Different transmembrane pressure (TMP) and initial oil concentration associated with permeate flux and fouling mechanism of UF membrane also were analyzed in order to study the efficiency of the UF membrane filtration process in oily wastewater treatment. Based on the results, the TOC, COD and oil content decreased more than 90 % and UF membrane works very well at higher TMP value (3 bars). However, the fouling problem was the major problem that affects the UF membrane performance. Furthermore, the effectiveness of the advanced oxidation processes (AOPs), represented by photo-Fenton process, was also investigated for oily wastewater treatment. The experiments were performed at different hydrogen peroxide concentration (650 mg/L, 1500 mg/L and 2000 mg/L), irradiance time and UV light sources (solar simulator and natural solar light). The

experimental results showed that this method is reliable to treat oily wastewater. The achieved TOC and COD removal efficiencies were more than 82 % and 70 %, respectively, after 80 min natural solar light irradiance and the optimum conditions of pH 3, 650 mg/L H<sub>2</sub>O<sub>2</sub>, 8 mg/L FeSO<sub>4</sub>.7H<sub>2</sub>O. However, the high cost of chemicals used for this treatment method may limit the process when applied in a large scale.

Different agro-waste materials were suggested for oil removal, such as eucalyptus bark, watermelon shell and chicken bone. The eucalyptus bark was found to be the best oil sorbent, then it was characterised and applied under different operating conditions and analysed the adsorption isotherm and kinetics models. Based on the experimental results, oil adsorption onto eucalyptus bark increases with the increase of adsorbent dosage, contact time and temperature while, it reaches best performance at acid condition (pH 3). The adsorption isotherms were analysed by using Langmuir, Freundlich and Dubinin-Radushkevich isotherm models where Dubinin-Radushkevich model is found to be the best applicability with  $R^2$  value of 0.8695. Then, the analysis proved that this adsorption kinetic follows the second order reaction model.

An integrated treatment system was proposed to evaluate the improvement of the polymeric UF membrane performance by integrating the membrane with Fenton-flocculation as pre-treatment process for efficient petroleum refinery wastewater (PRW) treatment. The results show that the integrated- UF membrane system not only reduces the permeate flux decline but also improve the permeate quality. The COD and the oil content removal efficiencies of the PRW sample increased 55% and 4.23% respectively, when the Fenton and flocculation pre-treatment process was integrated with the UF membrane. The integrated system was further investigated under different conditions of transmembrane pressure (TMP) (1, 1.5, 2 bar) and cross flow velocity (CFV) (250, 300, 600 ml/min). Hermia's models have been used to study the fouling

mechanism of the membrane. The results show that cake formation model is the dominant fouling mechanism regardless the applied TMP and CFV conditions. FTIR, SEM and EDS were applied to analyse and characterize the foulant and the fouling mechanism. The SEM demonstrated different morphologies between fresh and fouled membranes (in both the sole and integrated membrane systems) has shown irregularly distributed micro particles/oil droplets on membrane surface and pores that were dominant in the fouled membrane.

Furthermore the EDS analysis identified that cake layer components are C, O, Na, Mg, Si, S, Cl, Ca and Fe. The pre-treatment stage is essential to enhance the polymeric UF membrane performance treating oily wastewater and particularly the raw PRW.



# **CHAPTER 1**

## **Introduction**

## **1.1 Introduction**

The ever increasing human population and industrial manufacturing for many sectors have caused several impacts on the environment due to hazardous contamination to ecological elements such as water sources, air and soil. Industries such as petroleum refineries, vegetable oils, pharmaceuticals, paper, food and beverages, pesticides, herbicides and insecticides are among the major industries that produce various wastewater qualities (Nieto et al., 2011, Chen et al., 2000, Chong et al., 2010). The typical wastewater of manufacturer contains different pollutants such as alcohols, aromatic compounds and inorganics including heavy metals (Gogate and Pandit, 2004). Thus, it is important to implement the efficient treatment technologies to address such pressing issues.

One of the major sources of hazardous pollutants in industrial wastewater is oily compound which can be generated from major industries including petroleum refineries, edible oil and restaurant industries. Discharging oily wastewater to the water bodies without proper treatment could lead to serious environmental problems for both aquatic life and human health due to its low biodegradability and hazardous nature. To overcome these environmental problems caused by oily wastewater disposal, there are some treatment methods available for oily wastewater that can be divided into some categories such as physical, biological and chemical processes (Mahamuni and Adewuyi, 2010). Usually, the oily wastewater was treated by coagulation or filtration to eliminate suspended solid and volatile materials followed by biological treatment. However, there are several restrictions for such treatments with regards to phase transference of pollutant that needs further post-treatment, low efficiency, longer reaction time and large space requirement (Chen et al., 2000). Physical method such as adsorption has also been applied for different oily wastewater treatments.

Commercial activated carbon (CAC) is the most renowned adsorbent which has been comprehensively implemented for adsorption process due to its effectiveness for wastewater purification (Moazed and Viraraghavan, 2005). However, there remains some limitations such as the high regeneration cost of the saturated AC and contaminants phase change without destroying them (Kusvuran et al., 2005). This limitation has led to development of other low cost adsorbents from new biomaterials originating from agricultural waste as a replacement of commercial activated carbon (Crini, 2006).

Another method known as advanced oxidation processes (AOPs) is also the preferred alternative technique for oily wastewater treatment. AOPs are characterized by hydroxyl radicals production that are responsible for organic pollutants reduction to be mineralized into water, carbon dioxide and other harmless products. Different AOPs have been applied for industrial wastewater treatment such as Fenton ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ), Fenton-like ( $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ ), electrochemical oxidation, photo assisted Fenton ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{Fe}^{3+}/\text{UV}$ ) or photocatalysis process ( $\text{TiO}_2/\text{O}_2$ ,  $\text{O}_3/\text{H}_2\text{O}_2$ ,  $\text{O}_3/\text{UV}$ ,  $\text{H}_2\text{O}_2/\text{UV}$ )(Andreozzi et al., 1999). AOPs methods can be classified into two main processes, homogeneous and heterogeneous processes that can be performed with or without light irradiation. Photo-Fenton reactions between iron ions, hydrogen peroxide and light irradiation is a typical homogeneous process (Czaplicka, 2006). Meanwhile, the use of photocatalysts such as titanium dioxide ( $\text{TiO}_2$ ) and zinc oxide ( $\text{ZnO}$ ) with UV irradiation has also been stated as an efficient heterogeneous process (Saien and Nejati, 2007). However, some challenges need to be further considered such as high chemical cost, intermediates generation and application difficulties in term of proper mixing and chemical amount (Babuponnusami and Muthukumar, 2014, Nieto et al., 2011).

Furthermore, oily wastewater treatment using membrane technology is also increasing due to its outstanding permeate quality, separation based on manageable size dismissal (Ahmad and Chan, 2009), high removal of bacterial and toxic residue, simpler apparatus needed, no special chemicals addition and can be operated by moderately skilled operators (Xia et al., 2004). The work of the membrane is dependent on pressure difference. However, membrane technology has a common problem represented by membrane fouling where the pollutant particles deposit onto membrane surface or membrane pores lowering the performance of the membrane. This problem results in higher operational cost and significant permeate flux reduction.

Membrane fouling can be caused by pore blocking, gel layer generation and particles adsorption. These limitations could be solved by applying effective and efficient pretreatment process for the wastewater before entering the membrane system. Even though several treatment methods have been proposed to purify oily wastewater (Jamaly et al., 2015), limited information exists on photo-Fenton, UF membrane and integrated UF membrane application to refinery and restaurant wastewater treatment. Some factors such as transmembrane pressure, velocity and solution pH have been investigated widely, however the analysis of fouling mechanism and the impact of oil concentration and cleaning process on permeate flux tend to be disregarded. In this work, different treatment methods such as ultrafiltration (UF) membrane, photo Fenton and low cost adsorption as a single or combined treatment will be thoroughly investigated and optimized for oily wastewater treatment. To the best of our knowledge, only a few studies have been dealt with comparison of various treatment methods for different oily wastewater quality.

## **1.2 Research objectives**

The overall purpose of this study is to propose and suggest an effective technique for oily wastewater treatment based on photo Fenton, low cost adsorbents, UF membrane and an integration Fenton - UF membrane. The specific objectives include:

- Investigate the efficiency of polymeric UF membrane for synthetic and raw oily wastewater treatment.
- Optimize the influence of transmembrane pressure (TMP), cross flow velocity (CFV) and pH of oily feed on the UF membrane filtration performance.
- Study membrane fouling mechanism and foulant characterization
- Evaluate the efficiency of photo-Fenton process for industrial oily wastewater treatment.
- Propose a low cost agricultural based waste material as an effective adsorbent for dissolved oil removal.
- Evaluate the performance of integrated system of Fenton-flocculation followed by polymeric UF membrane for oily wastewater treatment.

## **1.3 Significance of the work**

The adsorbents selected for removal of oil from wastewater are novel and the plan of integrating Fenton process with membrane module is also an original one. Reports on the treatment of real restaurant wastewater containing used edible oil are very rare. The significance of the thesis as a contribution to knowledge or understanding of knowledge in the field of study: Removal of oil from wastewater is a problem to the environmentalists, though most of the studies are on the spill of petroleum oil on the sea and its removal by mechanical or biotechnical methods. This thesis included

restaurant wastewater containing used edible oil that is less common and selection of chicken bones as adsorbent may lead to an integrated wastewater system for the restaurants using its own solid waste. Use of photochemical techniques for oily wastewater is also a significant contribution to the domain.

## **1.4 Thesis organization**

The thesis consists of eight chapters which are systematically organized as:

*Chapter 1.* A general overview of the thesis background, objectives and thesis organization. The schematic diagram of thesis organization can be found in Figure 1.1.

*Chapter 2.* Literature review of the relevant published research, fundamental and current state of UF membrane filtration, photocatalysis processes, adsorption and integrated membrane system.

*Chapter 3.* Describes the research methodology, materials, experimental set up and analytical equipment used in this study.

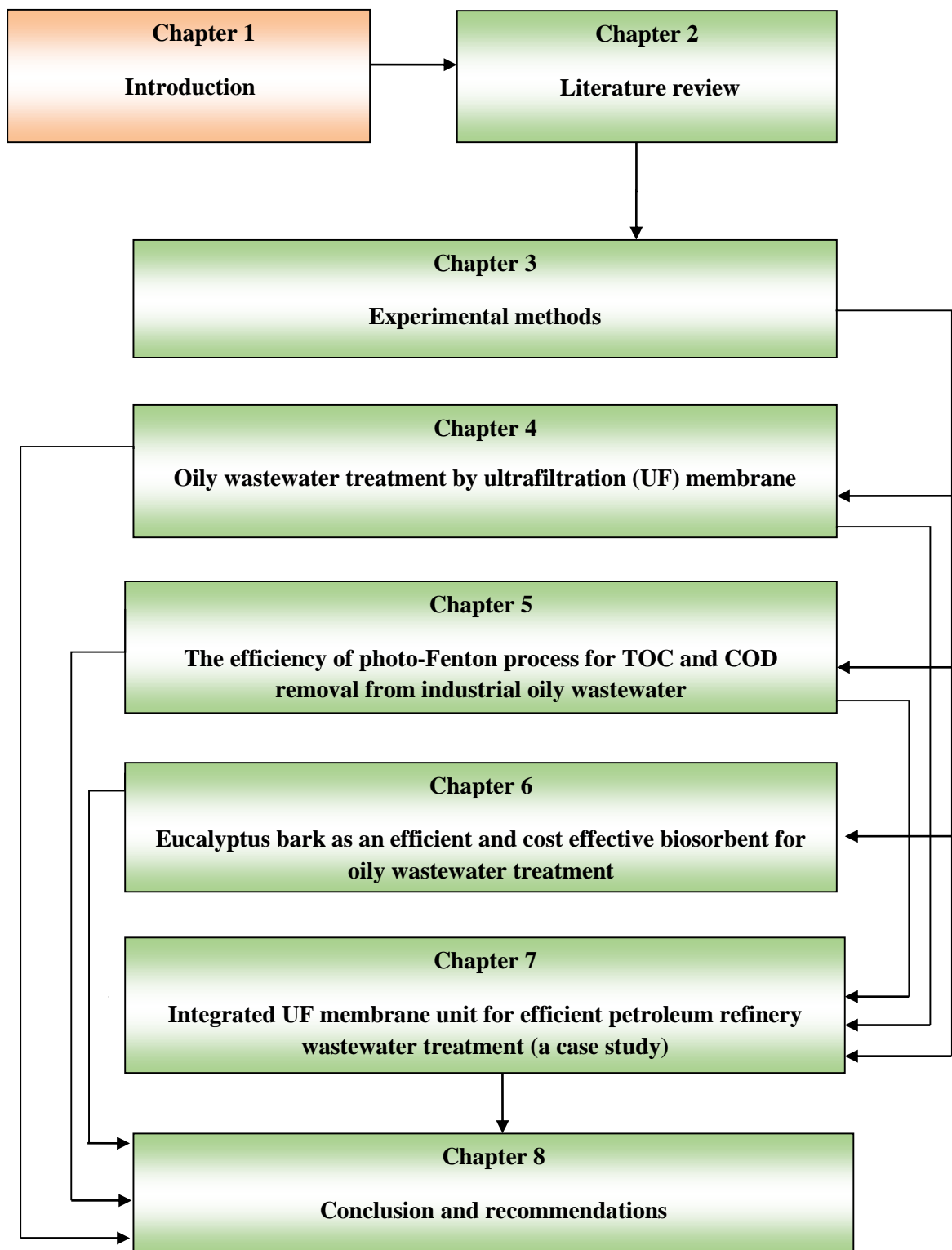
*Chapter 4.* Reports and discusses the experimental results of membrane performance, organic degradation and fouling mechanism.

*Chapter 5.* Covers the experimental results of photo-Fenton method in order to be integrated with UF membrane as a pretreatment process.

*Chapter 6.* Reports the investigation of several low cost adsorbents for oil adsorption and discusses the experimental results including adsorption isotherms, kinetic models and thermodynamic study.

*Chapter 7.* Reports the application of integrated UF membrane. The discussion of operating conditions, foulant characterization and permeate quality is also documented in this part.

*Chapter 8.* Summarizes the major conclusions of this study and recommendations for future work.



**Figure 1.1** Schematic diagram of the thesis organization



## **CHAPTER 2**

### **Literature Review**

## **2.1 Introduction**

This chapter will be divided into two parts. The first part will focus on the oily wastewater sources and their impact on the environment. The second part will present the state of the art for different treatment technologies applied for oily wastewater treatment.

## **2.2 Sources of oily wastewater**

Generally, oily wastewater refers to oil and water mixture in any composition which is no longer useful for productive process. Fats, waxes and mineral oils solution could be included as oil. Specifically, oil can be classified into; mineral oil that is a viscous liquid and soluble in alcohol/ether but insoluble in water, petroleum oil, animal oil that is known as fats and vegetable oil which is derived from parts of plant materials such as canola oil and palm oil (Alther, 2008).

Oily wastewater presence in the environment has created serious environmental problems. Oily wastewater can be generated from two main sources, industrial and municipal liquid wastes. For oily wastewater discharged from industrial sources, significant amounts are produced by petroleum refinery, food and beverage, textiles, metal, pharmacy, cooling and heating industries which can result from some processes such as production, refining, storage, transportation and sewage collection (Patterson, 1989, Liu and Liptak, 2000). In food industry, oily wastewater can be derived from various processing steps that involve activities with fruit, oils, dairy, meat and fish. The following sections will demonstrate the most common oily wastewaters and their formation (edible oil wastewater, petroleum refinery wastewater and oily restaurant wastewater)

### 2.2.1 Edible oil wastewater (EOW)

Edible oil is made from part of plant materials which are nonhazardous for human consumption. Palm oil, canola oil, and olive oil are the common edible oils produced in significant amount throughout the world. These huge productions result in large amount of oily wastewater. EOW can be generated in several production stages such as sterilization, stripping and oil extraction. The problem of EOW is the poor discharge quality that exceeds the acceptable discharge standard limit stated by the governments. Table 2.1 shows the general physical-chemical characteristics of edible oil wastewater.

**Table 2.1** Characteristics of raw edible oil wastewater (El-Abbassi et al., 2009, Martini et al., 2014, Malaysia, 1999, Rupani et al., 2010)

<b>Parameters</b>	<b>Average discharge values</b>	<b>Acceptable discharge standard</b>
COD (mg/L)	330 – 183,000	100
BOD (mg/L)	300 – 44,000	100
Oil (mg/L)	200 – 7,800	50
pH	3.5 – 11	5 - 9
Temperature (°C)	80 - 90	45
Suspended Solid (SS), (mg/L)	5,000 – 18,000	400

**Palm oil:** Palm oil is produced in significant quantities in Indonesia, Malaysia and Nigeria. As an impact, these countries are facing environmental issues regarding palm oil mill effluent (POME) (Gobi et al., 2011). Physically, POME is the thick viscous liquid waste disposed from palm oil mills during palm oil production from oil palm fruits and has foul odor. The POME is characterized by high COD, BOD and oil

content (Gobi et al., 2011, Ahmad et al., 2003). Governments have to regulate POME discharges so as to maintain a safe healthy environment. Malaysia, one of the highest palm oil producing countries, started regulating POME discharge standards into the environment since 1977. The regulated discharge standard of POME is shown in Table 2.2.

**Table 2.2** Characteristics of raw POME and acceptable discharge standard (Rupani et al., 2010, Malaysia, 1999)

Parameters	Raw POME	Regulatory limits
Temperature (°C)	80 -90	45
BOD (mg/L)	25,000	100
COD (mg/L)	50,000	-
Oil (mg/L)	4,000	50
Total Solids (mg/L)	40,500	-
pH	4.7	5 - 9
Total Kjehdal Nitrogen (mg/L)	750	200

**Canola oil:** Canola oil made from rapeseed plant is another edible oil which is widely used for cooking oil and also as an additive for candles, inks and medicinal application (Jenab et al., 2014). European Union, Canada, China and Australia are the countries which produce a total of more than 50 million tons per year of canola oil. In the process of canola oil production, the rapeseed is slightly heated, crushed and extracted using hexane, refined using water precipitation and organic acid to remove gums and deodorized using steam distillation. Generally, canola oil wastewater (COW) generated from extraction and refining stage has lower COD, TOC, suspended solid

and oil content than other edible oils (palm oil and olive oil wastewater) but it still exceeds the minimum wastewater discharge limit. The characterization of the selected COW is summarized in Table 2.3.

**Table 2.3** Characteristics of raw canola oil wastewater (Martini et al., 2014)

<b>Parameter</b>	<b>Range</b>
COD (mg/L)	330
TOC (mg/L)	90
Oil (mg/L)	250
pH	9

**Olive oil:** As one of the edible oils produced in huge amounts, the treatment of olive oil mill wastewater (OMW) is important, especially in the Mediterranean countries that produce more than 2.4 million tons per year of olive oil or more than 95% of the total world production. The specific characteristics of raw OMW are listed in Table 2.4.

**Table 2.4** Characteristics of raw olive oil mill wastewater (El-Abbassi et al., 2012, El-Abbassi et al., 2009).

<b>Parameter</b>	<b>Range</b>
pH	4 - 5
TOC (mg/L)	1800 - 3200
COD (mg/L)	129000 - 183000
Conductivity (mS/cm)	16 - 32
Oil (mg/L)	5200 - 7800
Total phosphorus (mg/L)	350 - 830

Its organic fraction also consists of sugars, tannins, polyphenols, polyalcohols, pectins, lipids and proteins which contribute to the high COD, TOC and oil content in OMW.

### ***2.2.2 Petroleum refinery wastewater (PRW)***

The main purposes of the petroleum refineries is to convert the crude oil through refining into higher value products for various applications. Despite the great effort dedicated to replace fossil fuels by renewable energy sources such as solar energy, crude oil is still the main source of energy. Therefore, the world oil demand may reach 107 mbpd in the next two decades. As a consequence, PRW will continually increase leading to more contamination of the world's water bodies (Yan et al., 2010). Petroleum refineries usually need large amounts of water to operate numerous processes from crude distillation to numerous downstream processes (Coelho et al., 2006).

The quantity of the oily wastewater generated in the refineries from different collection systems is almost 50 % of the used fresh water (Coelho et al., 2006). PRW can be characterized by high content of toxic compounds such as oil, hydrocarbons, sulfides, ammonia and large quantities of inorganic salts depending on the type of processed crude oil and process system (Santos et al., 2006). Table 2.5 shows the general physical-chemical characteristics of petroleum refinery wastewater.

**Table 2.5** Characteristics of raw petroleum refinery wastewater (Mota et al., 2008)

<b>Parameters</b>	<b>Average discharge values</b>	<b>Acceptable discharge standard</b>
COD (mg/L)	3340	140
BOD (mg/L)	280	17
Oil (mg/L)	200	23
pH	10.6	6.2
Temperature (°C)	41	22
Sulfide (mg/L)	38	0
Phosphorus (mg/L)	97	0

### ***2.2.3 Restaurant oily wastewater (ROW)***

Restaurant industry also produces huge quantities of oily wastewater. ROW could be generated from restaurant operational activities such as washing kitchen utensils, cleaning and cooking food materials (Kang et al., 2011). Most of the restaurants discharge their wastewater into foul sewers leading to public sewage treatment plants or into storm drains without proper treatment process (Zulaikha et al., 2014). The wastewater composition that is usually heavily loaded with organic matters will vary with time and also on the type of food they serve or prepare. Thus, it is very difficult to characterize their properties. High oil content in restaurant wastewater tends to clump together, generate unpleasant odor, block drain pipes and grease traps which severely impact wastewater management. Chemical coagulation was also found to be low efficiency in dispersed oil particles reduction (Chen et al., 2000). Thereby, appropriately efficient and effective treatment of restaurant wastewater is still

necessary to be improved for reducing its impact on the environment. Table 2.6 shows the general physical-chemical characteristics of restaurant wastewater.

**Table 2.6** Characteristics of raw restaurant oily wastewater (Kang et al., 2011)

<b>Parameters</b>	<b>Range</b>
COD (mg/L)	750 - 6800
BOD (mg/L)	600 - 2500
Oil (mg/L)	500 - 4700
pH	6.1 – 8
Suspended solid (mg/L)	250 - 650
NH <sub>2</sub> -N (mg/L)	4.8 – 10.4

### **2.3 Environmental impact of oily wastewater**

The effect of oily wastewater to the environment is influenced by its characteristics and compositions. The untreated or less treated industrial and municipal wastewater can endanger public health and ecological systems due to hazardous components contained with their acute toxic effects (Tansel and Pascual, 2011). Even though the composition of different oily wastewaters vary in the amount and type, the presence of oil in the emulsified form is often difficult to treat. The characterization of the discharged oily wastewater to the water bodies should meet the minimum level stated by the government before disposal to protect the environment from harmful compounds. Several characteristics of oily wastewaters that have environmental impact can be described as shown in Table 2.7:



**Table 2.7** General characteristics of oily wastewater (Greenberg et al., 1998)

<b>Parameters</b>	<b>Description</b>
Temperature	The important parameter that affects the chemical reaction time needed in treatment processes
Solid compounds	Solid contained in wastewater in various forms such as suspended and dissolved solids can be classified by their size, chemical characteristic and size distribution. Membrane filtration is the common technology applied to remove suspended and dissolved solid in wastewater
Turbidity	The water clarity level in relation to optical property affecting absorbed or transmitted light caused by the availability of suspended and colloidal matter such as minute organic and inorganic matter, clay, silt and microscopic organisms
Biochemical oxygen demand (BOD)	The amount of oxygen needed by aerobic biological organisms to decay organic material in the polluted wastewater
Chemical oxygen demand (COD)	The indirect analysis of the chemical decaying of organic and inorganic pollutants, dissolved or suspended, in water which can be oxidized chemically. This parameter implies the water-dissolved oxygen amount (mg/L) to be consumed by the contaminants
Total organic carbon (TOC)	Any compound containing carbon atoms except CO <sub>2</sub> including related substances such as carbonate, bicarbonate and the like. It involves dissolved organic pollutants such as hydrocarbons
Oil content	The content of fats, grease and oils in wastewater in certain concentration can interfere aerobic and anaerobic biological process and decrease the wastewater treatment effectiveness
Solution pH	By knowing solution pH, the treatment of wastewater can be optimized to obtain maximum contaminant removal
Metal compounds	Heavy metal compounds such as cadmium, ferrous, ferric and others could be contained in industrial wastewater. Their presence in significant amount will be hazardous to the environment

## **2.4 Oily wastewater treatment technologies**

Wastewater treatment is essential for human and environmental protection. The advancement of analytical techniques has made the detection of possible toxic organic or inorganic compounds at ppb levels. This is supported by the increasing demand of regulation regarding industrial wastewater discharge quality. Some progress has been made by government and academic area worldwide such as developing new technologies to minimize waste production, water networking, performance improvement of existing methods and creating highly efficient wastewater treatment process converting the discharge into a usable resource. The effective solutions for industrial wastewater treatment are needed to meet the regulatory standards for discharge and to ensure wastewater reuse such as for irrigation and other industrial application. Several technologies are available and can be implemented to obtain better wastewater quality.

### ***2.4.1 Physical treatment methods***

Physical treatment process such as air flotation, membrane filtration and adsorption is one of primary wastewater treatment methods that can be defined as a process in which a material is removed from a solution or mixture by physical ways (Georgy, 2006).

#### ***2.4.1.1 Air flotation***

Air flotation treatment is a purification method to treat wastewater by bubbling air through wastewater tank or pond in order to increase the specific gravity difference between pollutant particles and water. For oily wastewater treatment, this method can be applied for reducing the amounts of fat, oil and grease. The effectiveness of air

flotation has been widely reported (Rubio et al., 2002). In this process, suspended particles and oil globules can be floated to the wastewater surface and then removed by skimming. There are some techniques of air flotation like dissolved air flotation (DAF), dispersed air flotation (DispAF) and electro-flotation. For DAF, wastewater should be saturated under pressure with air generated by granular media filtration. Then, the pressure is released through needle valves into flotation cells resulting in air bubbles with approximately 30 – 120  $\mu\text{m}$  in diameter (Benito et al., 1998). It is also common that prior to DAF process, pretreatment such as rapid mixing between water/wastewater solution and coagulant/flocculant agent is applied (Edzwald, 2010). Meanwhile, in DispAF technique, air bubbles are produced through the pores of sintered glass disks with diameter ranging from 75 to 655  $\mu\text{m}$  (Dafnopatidou and Lazaridis, 2008). For electro-flotation process, electrolysis of water is used with bubbles produced at the electrodes having diameters ranging from 22 to 50  $\mu\text{m}$  (Burns et al., 1997). An author applied the air flotation principle for emulsified oil removal from an oil field reported that the separation process in flotation column can improve the contact of oil droplets and air bubbles. Then, oil demulsification using combined chemical treatment and flotation column successfully resulted in 90 % of oil removal efficiency (Li et al., 2007).

#### *2.4.1.2 Membrane separation process*

Membrane filtration can be defined as a separation process which is based on the presence of semi permeable membranes. The principle of the membrane is for the pollutant to be trapped on membrane surface or in membrane pores within a specific size range (Georgy, 2006). The membrane performance is mainly driven by the pressure difference as an average value of inlet and outlet pressure, named trans

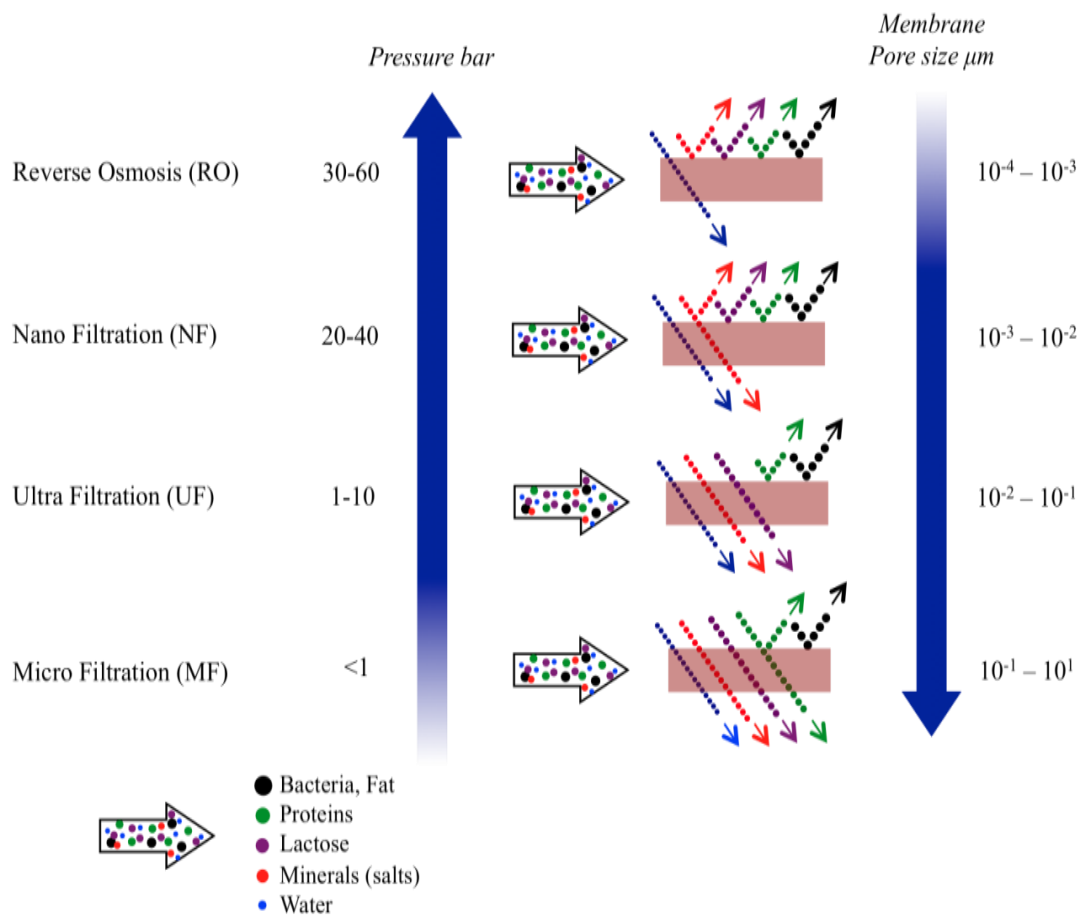
membrane pressure (TMP). TMP generated from applied pressure or vacuum is promoted by other operating condition such as cross flow velocity (CFV) which can be interpreted as the average speed value of membrane feed solution (Mohammadi and Esmaelifar, 2004, Mohammadi et al., 2003). Other parameters that affect the effectiveness of membrane filtration processes are temperature, pH, oil and salt concentration (Abbasi et al., 2010, Hua et al., 2007). According to their pore size, membrane can be categorized into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (Table 2.8).

**Table 2.8** Typical characteristics of the membranes (Arthur et al., 2005)

<b>Filtration membrane</b>	<b>Molecular weight cut-off range (Dalton)</b>	<b>Applications/Removal</b>
Microfiltration (MF)	>500,000	Bacteria, viruses and suspended solids
Ultrafiltration (UF)	1,000 – 1,000,000	Proteins, starch, viruses, organics, dyes, fats and paint solids
Nanofiltration (NF)	100 – 20,000	Starch, sugar, pesticides, divalent ion, organics and detergents
Reverse osmosis (RO)	<200	Metal ions, acid, sugars, dyes, resin and salts.

MF and UF should be favorable for larger suspended or colloidal particles via a sieving mechanism whilst NF and RO are more suitable for dissolved salt removal by diffusion mechanism (Tchobanoglous et al., 2003). UF is more effective for the removal of oil, proteins, organics, suspended and dissolved solid than MF. UF and MF can work at low trans membrane pressure (0.06 – 2.06 bars) but they are not effective for salt removal (Bilstad and Espedal, 1996). For some UF membranes, the ability to trap

larger organic macromolecules is characterized by a molecular weight cut off (MWCO) rather than by a particular pore size. The MWCO can be defined as a measure of the membrane removal characteristic regarding atomic weight or mass rather than pore size. Thus, membrane MWCO is presumed to act as a barrier to filter any molecule with a molecular weight exceeding the membrane MWCO (Allgeier, 2005, Wu and Imai, 2012). Membrane filtration types have specific characteristics related to the filtration ability, pressure and pore size range (Figure 2.1).

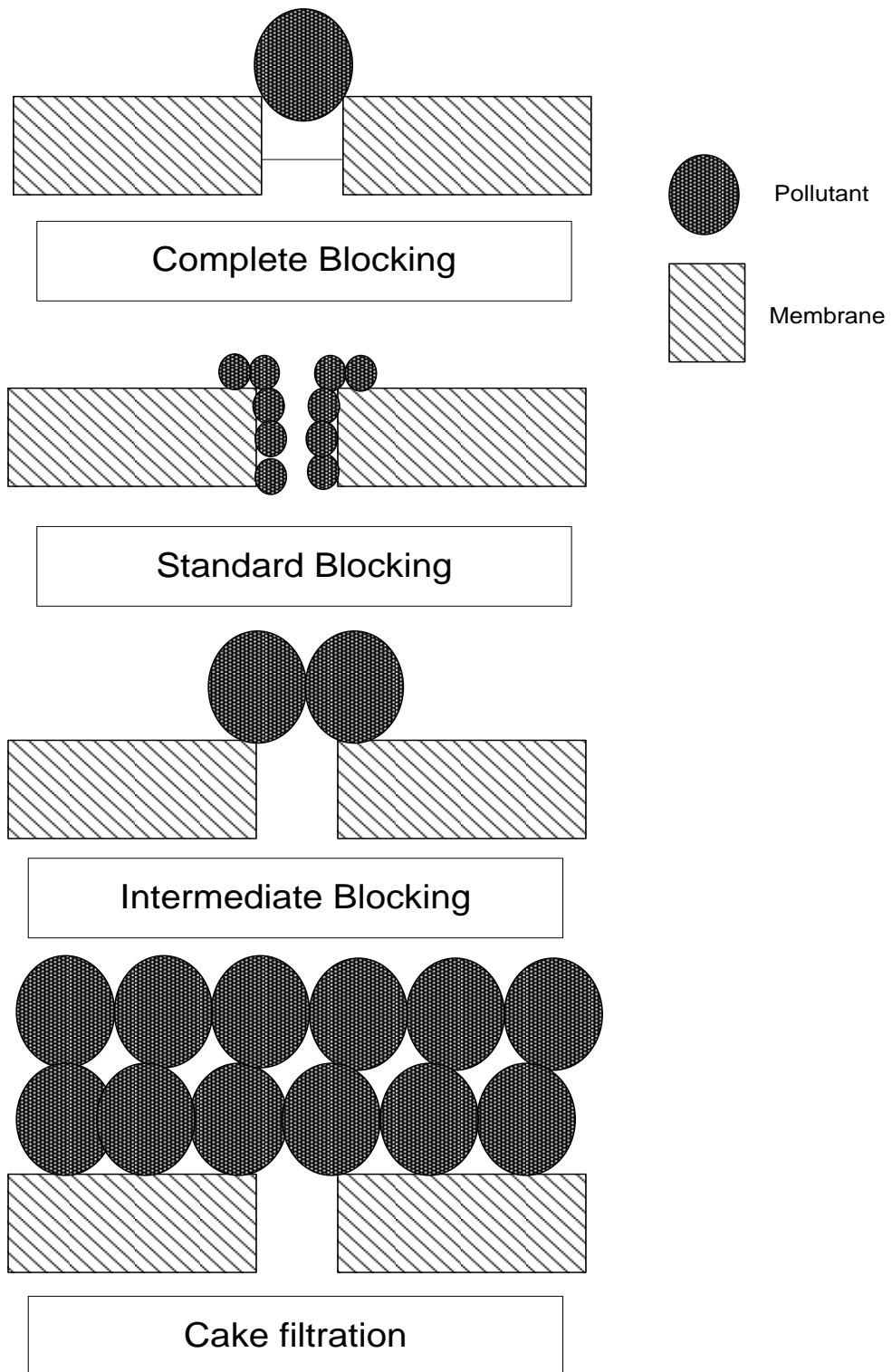


**Figure 2.1.** The mechanism of membrane filtration (Wu and Imai, 2012)

For oily wastewater purification, membrane usage has several advantages including excellent contaminant removal percentage, automatic operation system, molecule

separation based on manageable size dismissal, no specific chemical needed for the oil emulsion stabilization and can be operated by moderately skilled operators (Chang et al., 2001, Madaeni et al., 2012, Ahmad and Chan, 2009). However, membrane fouling is the most common issue in the membrane separation technology. Membrane fouling is caused by pollutant particles depositing onto membrane surface or membrane pores lowering the performance of the membrane. This problem results in higher operational cost and significant permeate flux reduction. Membrane fouling formation could be due to pore blocking, gel layer generation, particles adsorption and concentration polarization.

Fouling resistance can be categorized into reversible and irreversible fouling based on the bond between trapped pollutant particle and membrane pore. The effect of reversible fouling is less detrimental as the membrane can be reused after chemical or physical cleaning even though with decreasing initial flux, while irreversible fouling is permanent fouling condition. Membrane fouling mechanism can be analyzed using Hermia's models consisted of cake formation model, intermediate pore blocking model, standard pore blocking and complete pore blocking models (Figure 2.2).



**Figure 2.2** The mechanism of membrane fouling

Several strategies have been applied to mitigate membrane fouling problem and to lengthen membrane usage such as employing pretreatment stage, periodically back or forward washing and applying double membranes system (Zhong et al., 2003, Vincent Vela et al., 2009). Some work related to membrane application for oily wastewater purification had been conducted, particularly for UF and MF membranes. Several authors (Madaeni et al., 2012, Mohammadi et al., 2003, Abadi et al., 2011, Yuliwati et al., 2011) have investigated the effect of different operating conditions on membrane efficiency related to flux, fouling resistance and certain organic removal. In some studies, researchers reported that membranes can remove more than 90 % oil content in the oily wastewater (Abbasi et al., 2010, Ebrahimi et al., 2010).

Literature also reported the application of integrated membrane separation with other methods as pre-treatment to degrade membrane fouling and enhance permeate flux such as flocculation (Zhong et al., 2003). Employing nanoporous membrane (NPM) combined with powdered activated carbon (PAC) was conducted for oily wastewater. The study demonstrated that NPM-PAC system can enhance the removal efficiency of TSS, COD and TOC with steady permeation flux (Sarfraz et al., 2012).

The study of membrane performance in treating oil in water emulsion or high strength industrial wastewater was also investigated (Fakhru'l-Razi et al., 2009, Mutamim et al., 2012) and proved that membrane has an outstanding permeate quality that fulfills government regulatory standard for wastewater discharge.

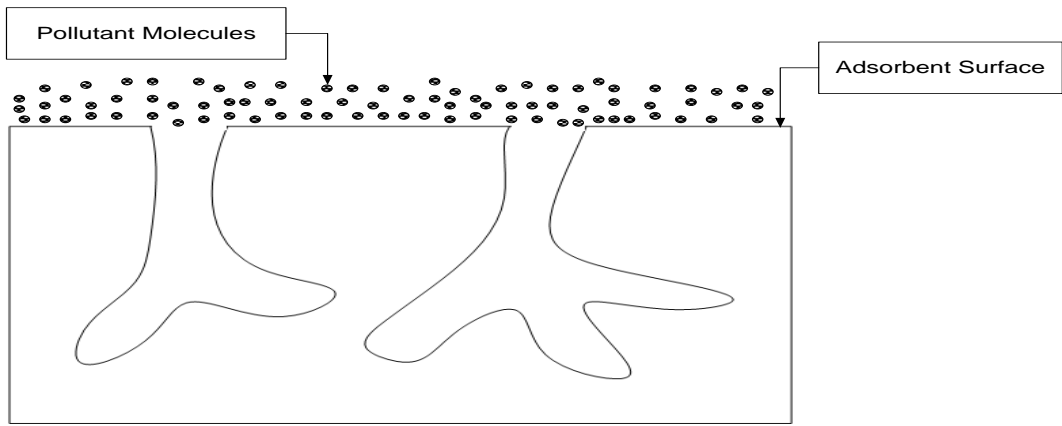


#### *2.4.1.3 Adsorption process*

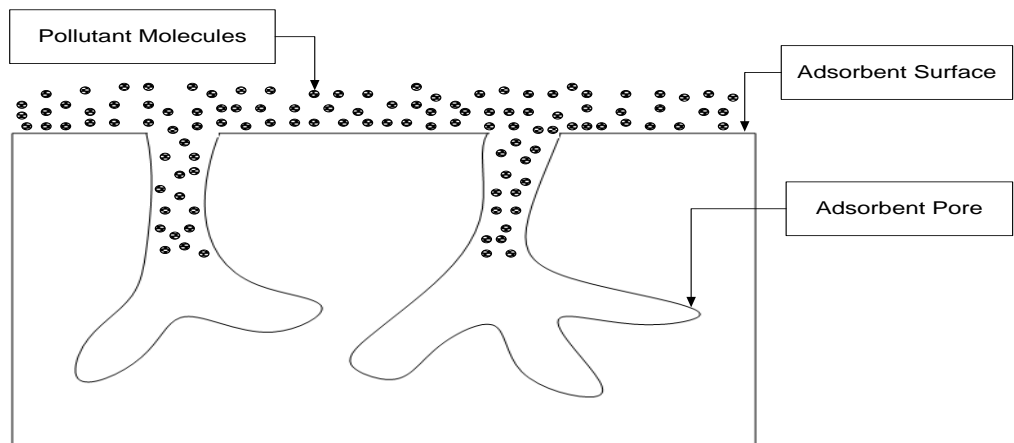
No single method is extremely outstanding to eradicate all contaminants in wastewater to meet the environmental regulation. Each technique should be efficient to remove certain pollutant constituents. Adsorption as one of wastewater treatment methods is a simple way to reduce the contaminants contained in oily wastewater. Adsorption can be defined as the adhesion process of atoms, ions or molecules from a gas, liquid, or dissolved solid to adsorbent surface when they are in contact for a specific time (Weber and Beck, 1973).

Adsorption can be categorized into two types, physical and chemical adsorption. Physical adsorption is the existence of interparticle bonds between adsorbate and adsorbent that tend to be reversible, while chemical adsorption can be characterized by strong ion or molecule aggregation due to, generally, electron exchange causing irreversible condition.

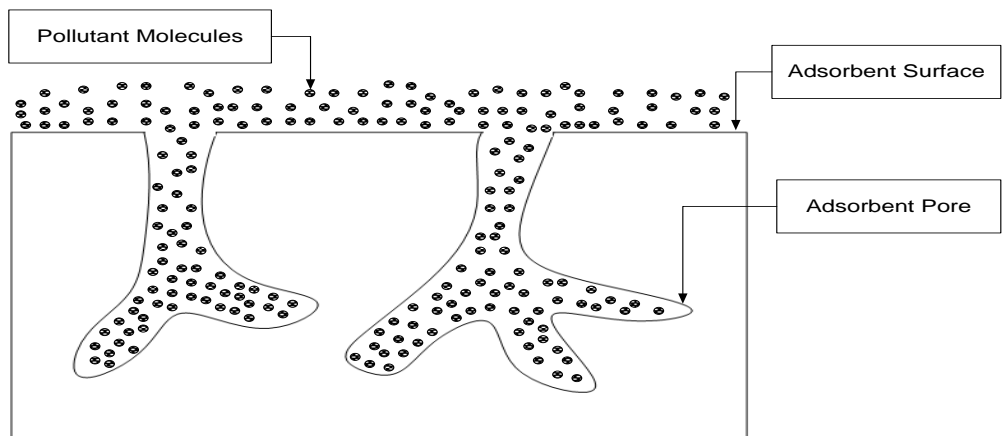
The removal efficiency in adsorption depends also on several factors such as pollutant chemical structure, solubility, pH, contact time, adsorbent dosage, adsorbent surface area, temperature and other physical-chemical parameters (Crini, 2006, Sanghi and Bhattacharya, 2002). The mechanism of adsorption process can be divided into three steps (Figure 2.3): (i) Diffusion process of pollutant molecules (adsorbate) to adsorbent surface. (ii) Migration of the adsorbate into adsorbent pores. (iii) Monolayer build up of adsorbent and adsorbate.



(i)



(ii)



(iii)

**Figure 2.3** The mechanism of adsorption

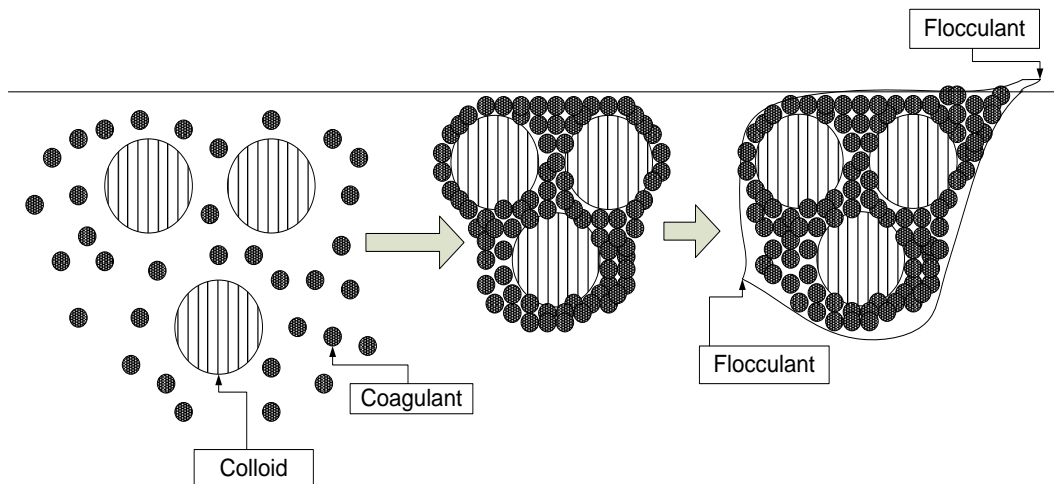
To date, the most popular adsorbent for pollutants removal from wastewater is activated carbon (AC) (Babel and Kurniawan, 2003). This adsorbent can be prepared from various natural organic materials such as coal, coconut shells, lignite, wood and has been widely applied in many studies (Bansal and Goyal, 2005, Carrott et al., 2003, Nguyen-Phan and Shin, 2011). However, the regeneration cost of the saturated AC is relatively expensive and it has been a challenge to many researchers to look for more cost effective adsorbents. Several adsorbent materials were studied for certain impurities uptake from wastewater (Denizli et al., 2005, Cengeloglu et al., 2007). Researchers are also still exploring for low cost adsorbents especially from the environment perspective such as agricultural wastes that provide several advantages such as economic value, simple usage, availability and high biodegradation level in the environment (Bhatnagar and Sillanpää, 2010, Khalid et al., 2000, Hameed et al., 2008). Main agricultural based material, named lignocellulosic, contains cellulose, hemicellulose and lignin which have binding site action (Afroze et al., 2015). Then, to increase the possibility of pollutant removal, some modification or integration process had been investigated. Chemical modification using cationic surfactant was applied to agricultural waste such as barley straw to treat oily wastewater and the study proved that the adsorption efficiency of modified barley straw increases compared to its raw material (Ibrahim et al., 2010). Esterification process also has been applied to increase natural adsorbent efficiency such as sago bark and reported that the oil removal capability of esterified bark is more efficient than raw bark (Wahi et al., 2014). The natural adsorbents made of agricultural waste and animal waste materials tend to be used in wastewater treatments due to its availability, effectiveness, cheap and simple process.

### 2.4.2 Chemical treatment methods

This technique includes chemical coagulation/flocculation and advanced oxidation processes (AOPs).

#### 2.4.2.1 Chemical coagulation/flocculation

Chemical coagulation/flocculation is a process utilizing chemicals in an aqueous system in order to create a rapid-settling aggregate out of finely divided suspension. Generally, the aim of this method is to eliminate trace organic contaminants from the wastewater. The principle mechanism of chemical coagulation consists of destabilization, entrapment and aggregation or colloids binding processes (Drinan and Spellman, 2012). Then, the larger or heavier flock particles can be removed by subsequent settling and filtration (Figure 2.4).



**Figure 2.4** The mechanism of coagulation/flocculation

Some studies have employed this method for various purposes such as reducing natural organic matter, turbidity, color and pathogens. Different coagulants or flocculants such as lime, magnesium, aluminum salts, calcium oxide and aluminium sulphate have been widely investigated by its addition to the water system (Gheraout, 2014, J., 1988).

For oily wastewater, this technique can be applied when dealing with chemically stable emulsified oil to promote the break up of the oil emulsion (Cañizares et al., 2008). These techniques are simple and cost-competitive but relatively low efficiency if applied as a single treatment method. To solve this problem, some researchers applied a combination such as integrated chemical coagulation and physical methods that can increase the mechanical treatment performance by emulsifying agent precipitation, interfacial tension effect or electrical charge neutralization (Hanafy and Nabih, 2007).

#### *2.4.2.2 Advanced Oxidation Processes (AOPs)*

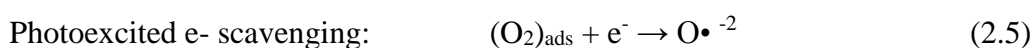
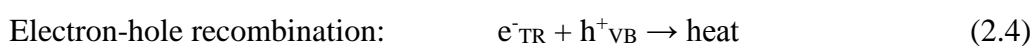
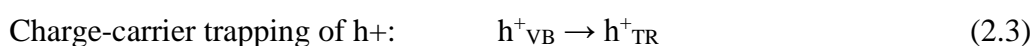
Advanced oxidation processes (AOPs) can be defined as the oxidation process of aqueous phase based on the reaction between dissolved natural organic contaminant and active radical agents including hydroxyl radical substances in order to mineralize the organic pollutant into water, CO<sub>2</sub> and other harmless products (Andreozzi et al., 1999). In comparison to other wastewater treatment techniques, AOPs are still an efficient and potential technology due to the availability of various catalysts and oxidant types to be utilized as well as significant result of organic contaminant degradation. AOPs including photocatalytic process; (TiO<sub>2</sub>/O<sub>2</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/UV, H<sub>2</sub>O<sub>2</sub>/UV), Fenton (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>), Fenton-like (H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup>) and photo assisted Fenton (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>/Fe<sup>3+</sup>/UV) and ozonation (Andreozzi et al., 1999, Elmorsi et al., 2010).

##### *(i) Photocatalytic process*

Photocatalytic process is based on photocatalysts addition into the wastewater under UV irradiation. This method has been known as one of the outstanding techniques to degrade highly refractory compounds including TOC and COD removal of various industrial wastewaters. Photocatalytic technology offers several advantages in being

cost effective, abundant energy sources such as solar light, ultraviolet (UV) or near-UV, relatively less usage of chemicals, operation at near room temperature and simple application (Nguyen-Phan and Shin, 2011).

AOPs methods can be classified into two main processes, homogeneous and heterogeneous that can be performed with or without light irradiation. In term of heterogeneous photocatalytic degradation process, the interaction of photon which has suitable wavelength with a semiconductor particle plays an important role in the wastewater treatment (Gaya and Abdullah 2008). Several metal oxides and chalcogenides such as TiO<sub>2</sub>, ZnO, MgO<sub>3</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, SnO<sub>2</sub>, WO<sub>3</sub>, α-FeO<sub>3</sub>, ZnS, CdS, CdSe, WS<sub>2</sub>, and MgS<sub>2</sub> are commonly used as photocatalysts (Serpone et al., 1995). The mechanism of photocatalysis has a relation to band gap energy. When the energy of photons ( $h\nu$ ) is equal to or greater than the band gap energy ( $E_b$ ) of the photocatalyst, electrons are excited and transferred from the valance band (VB) to the conduction band (CB). This step creates holes in the valance band ( $h^+$ ) and free electrons ( $e^-$ ) in the conduction band. This mechanism can be represented by the following equations (Konstantinou and Albanis 2003):



The energy required for the electron excitation varies according to the specific characteristics of the semiconductor and the minimum wavelength needed for the photo-excitation depends on the band-gap of the photocatalyst. Among these semiconductors, TiO<sub>2</sub> has been reported as a suitable photocatalyst used to degrade organic pollutants in aqueous solutions due to its safety, resistance to photo corrosion, catalytic efficiency, low cost and the ability to absorb radiation at wavelengths below 400 nm (Czaplicka, 2006).

**Table 2.9** Band-gap energy and wavelength ( $\lambda$ ) of different photocatalysts (Bhatkhande et al. 2002).

<b>Photocatalyst</b>	<b>Band-gap (eV)</b>	<b>Wavelength (<math>\lambda</math> nm)</b>
Si	1.1	1127
WSe <sub>2</sub>	1.2	1033
Fe <sub>2</sub> O <sub>3</sub>	2.2	564
CdS	2.4	517
WO <sub>3</sub>	2.7	459
SnO <sub>2</sub>	3.5	354
$\alpha$ -FeO <sub>3</sub>	3.1	400
ZnS	3.7	335
ZnO	3.2	388
SrTiO <sub>3</sub>	3.4	365
TiO <sub>2</sub> (rutile)	3.0	413
TiO <sub>2</sub> (Anatase)	3.2	388

Some studies had reported the efficacy of photocatalysts in various oily wastewater remediation. For instance, oily wastewater from restaurants was treated using TiO<sub>2</sub> combined with vacuum ultraviolet (VUV). The result clearly proved that under the optimum conditions of irradiation for 10 min, VUV treatment achieved removal efficiencies of COD, BOD<sub>5</sub> and oil as 50 %, 37 % and 86 % respectively, meanwhile

combined TiO<sub>2</sub>/VUV reached 63 %, 43 % and 70 %, respectively (Kang et al., 2011). Other wastewater such as paper mill wastewater, textile and olive mill wastewater also showed promising result when treated by TiO<sub>2</sub> mediated solar photocatalysis (Zhang et al., 2014).

Furthermore, as an alternative, ZnO which has similar band gap to TiO<sub>2</sub> also showed good performance, especially for chlorinated, phenolic compounds and dyes contaminant in textile wastewater (Shukla et al., 2010, Villaseñor et al., 1998) because the combination between the oxidant and photocatalyst has the ability to oxidize several highly refractory compounds. In some studies, several pesticide solutions were purified using combined H<sub>2</sub>O<sub>2</sub>/TiO<sub>2</sub>/UV and reported that H<sub>2</sub>O<sub>2</sub> has the potential capability to enhance the rate of reaction (Doong and Chang, 1997). However, one of the main disadvantages of TiO<sub>2</sub> is the wide band-gap which needs short wavelength of UV light (<388) leading to the limitation of employing the solar light. Band-gap narrowing by the introduction of non-metal anions (N, C, S, P and F) into TiO<sub>2</sub> was recently found to be efficient to yield catalyst with high catalytic activity under visible light irradiation (Znad and Kawase, 2009).

Fenton, Fenton-like, UV oxidant and photo Fenton methods have also been acknowledged as homogenous processes which are effective and efficient to treat wastewater. There are still limited data available for Fenton-like system in oily wastewater treatment, especially under near neutral pH condition, where the Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub> or UV/ Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub> system alone is not effective for more oxidant generation and pollutant oxidation due to the low solubility of ferric ions in the aqueous solution via a non-radical mechanism (Aljubourya et al., 2016).

Meanwhile, for Fenton technique which is based on the use of Fenton's reagents (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>), the presence of oxidizing agents such as H<sub>2</sub>O<sub>2</sub> in wastewater has more positive



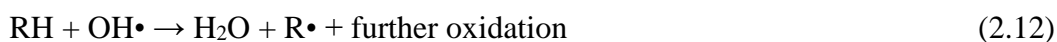
effect on the degradation rate of the organic pollutants due to the more generations of hydroxyl radicals. The activity of  $\text{H}_2\text{O}_2$  can be increased in the presence of other metal ions such as ferrous and ferric ions (Adán et al., 2009). The oxidation process can destroy organic pollutants to become harmless compounds such as  $\text{CO}_2$ , water and inorganic salts. It produces hydroxyl radicals that can be represented as follow (Bianco et al., 2011):



According to Equations 2.8 and 2.9, the ferrous iron ( $\text{Fe}^{2+}$ ) starts the reaction and catalyzes decomposition of  $\text{H}_2\text{O}_2$  into hydroxyl radicals. Furthermore, the newly formed ferric ions ( $\text{Fe}^{3+}$ ) decompose  $\text{H}_2\text{O}_2$  into water and oxygen:



The organics (RH) are oxidized by hydroxyl radicals proton abstraction ending with the production of organics radicals ( $\text{R}\cdot$ ). These last reactive products can be further oxidized:

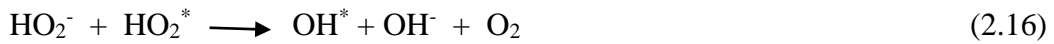
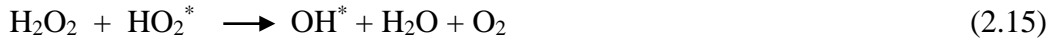


Similar to Fenton process, UV/oxidant also disintegrates  $\text{H}_2\text{O}_2$  to obtain active hydroxyl radicals by irradiating the solution with UV radiation. The reaction mechanism can be described via three stages: initiation, propagation and termination as given below (Benitez et al., 2000) :

Initiation reaction



Propagation reaction

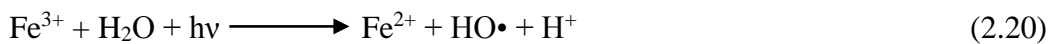
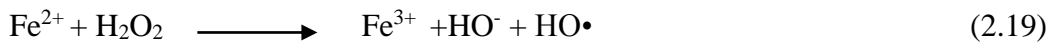


Termination reaction



The  $\text{H}_2\text{O}_2$  concentration needs to be properly selected to reach higher pollutant removal efficiency and to reduce the scavenging effect of hydroxyl radical.

Furthermore, in order to produce larger quantity of hydroxyl radical, Fenton and UV/ $\text{H}_2\text{O}_2$  system can be combined and named photo-Fenton process. It can be described by the following equations (Guedes et al., 2003, Feng et al., 2003, Lucas and Peres, 2007, Lucas and Peres, 2009).



Equation 2.19 is a reaction which generates powerful hydroxyl radicals and oxidizes  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ , meanwhile Equation 2.20 is a reaction of  $\text{Fe}^{3+}$  with water when light is irradiated to the system. These hydroxyl radicals can oxidize the organic substrates (RH) in the wastewater as following:



Then, the new radical (R·) will be oxidized by  $\text{Fe}^{3+}$  to produce environmentally friendly products (Canizares et al., 2007).

There are some factors affecting Fenton, UV/oxidant and photo-Fenton reactions in wastewater treatment application such as:

***The need for lower pH condition:*** A low pH of near 2.5 and 3 has been notably reported as the best operating condition for reducing different contaminants in complex industrial wastewater (Bianco et al., 2011, Guedes et al., 2003). During the process, the possibility of the pH value for slight increase is reported. Thus, using this technique will require additional cost for pH control (Wadley et al., 2004).

***Iron salts and H<sub>2</sub>O<sub>2</sub> ratio:*** Iron in its ferrous and ferric forms serves as photocatalyst agents and works with H<sub>2</sub>O<sub>2</sub> which will decompose into oxygen and water. The active radical tends to react with the oxidant themselves then introducing an upper limit for oxidant amount to be added to the system. The increase of molar ratio  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  at constant H<sub>2</sub>O<sub>2</sub> concentration will lead to higher hydroxyl radicals production in the reaction (Răileanu et al., 2013).

***Ferric ion precipitations:*** Ferric ion precipitation can prevent  $\text{Fe}^{2+}$  regeneration thus decreasing the effectiveness of Fenton/photo-Fenton process during the treatment. Controlling the pH reaction and applying the rotating magnetic field could minimize the possibility of ferric ion precipitation as the insoluble oxide – hydroxide complex.

***Wavelength and Light intensity:*** Light is an energy source for the photocatalysis and photo-Fenton processes to commence the pollutant degradation. The relationship

between wavelength ( $\lambda$ ) and the energy band-gap ( $E_b$ ) or the energy difference can be represented by Equation 2.23 (Gaya and Abdullah, 2008).

$$\lambda = \frac{1.24 \times 10^3}{E_b} \quad (2.23)$$

Where  $E_b$  is the energy band gap (eV) and  $\lambda$  is the wavelength of light (nm). Based on Equation 2.23, the photons of light must be equal to or greater than the energy band-gap of the semiconductor photocatalyst. Then, light intensity ( $\Phi$ ) relies on the photon energy flux, which is the energy of photons per second per unit area radiated on the suspension, and quantum yield of the photo process. The overall quantum yield ( $Q_{overall}$ ) of light absorbed by any photocatalyst can be described by Equation 2.24 (Herrmann, 2005):

$$Q_{overall} = \frac{\text{rate of reaction}}{\text{rate of absorption of radiation}} \quad (2.24)$$

In general, the influence of light intensity on the photocatalytic degradation rate could be complicated due to the other factors related to the process such as the photoreactor configuration and the photocatalyst loading.

#### (ii) Ozonation process

Ozonation is one of the effective wastewater treatment methods which utilizes ozone molecule consisting of three negatively charged oxygen atoms. Ozone can be artificially produced using an oxygen generator with bubbling through the wastewater in order to reduce the concentration of some contaminants including chlorinated hydrocarbons, pesticides, alcohol, ethers, microorganism and aromatic hydrocarbon (Mehrjouei et al., 2015, Lazarova and Bahri, 2004). For oily wastewater treatment, the

oxidation by ozone can be interestingly attractive and effective due to its work mechanism by direct attack of molecular ozone and indirect attack by free radicals. Generally, the direct process occurs under acidic condition of pH less than 4 and the indirect oxidation works above pH 9 (Rein, 2001). However, some previous studies used integrated ozonation system with other oxidation agents or technique for better wastewater discharge quality. For instance, the investigation of the olive oil mill wastewater treatment by integrated ozone – UV method proved that more than 80 % of phenol compounds can be reduced and around 10 - 60 % of COD removal achieved depending on oxidant dosage (Karageorgos et al., 2006).

#### ***2.4.3 Biological treatment methods***

Biological treatment for oily wastewater is applicable for degrading fat, oil and grease into miscible molecules, dissolved oil and stabilized oil in water emulsion that cannot be destabilized by chemical coagulation/flocculation. This biological treatment offers some advantages such as being inexpensive and non-toxic end products but this technique is restricted by the requirement of large plant area, longer reaction time, oxygen transfer blocking by lipid formation and limited flexibility in operation and design (Lemmer and Baumann, 1988, Forgacs et al., 2004, Crini, 2006). Therefore, pretreatment process prior to biological treatment to hydrolyze oil and grease has been considered and reported as an effective way for accelerating the process and enhancing time efficiency (Camarota and Freire, 2006). Compared to aerobic, anaerobic treatment tends to attract more attention since it generates more biogas and less biomass (Manahan, 2010). However, anaerobic treatment still has some issues such as disintegration of sludge and limitation on bacteria efficiency by the oils and fats overload (Zhou et al., 2008). To overcome these problems, researchers have tried to

apply the combination of up flow anaerobic and aerobic system for high strength oily wastewater because it offers relatively lower hydraulic retention time and higher bacteria performance.

#### ***2.4.4 Integrated treatment methods***

Treating oily wastewater using single treatment techniques such as membrane, adsorption and chemical oxidation have several shortcomings which are severe membrane fouling, high chemical cost, intermediates generation, upper limit of feed concentration and application difficulties in term of proper mixing (Babuponnusami and Muthukumar, 2014, Nieto et al., 2011, Coca-Prados et al., 2013, Gryta et al., 2001, Karhu et al., 2013). In order to address these problems, the integrated technology has been proposed as a promising efficient system.

Adsorption has been extensively applied as a pretreatment method due to its large surface area and abundant micro pores quantities (Coca-Prados et al., 2013, Jamaly et al., 2015). For instance, the use of combined powdered activated carbon (PAC) – membrane filtration has been investigated (Sarfaraz et al., 2012, Mohammadi and Esmaelifar, 2005). They reported that the use of PAC in feed circulation even in low concentration can create shear stress on the membrane surface. This effect could reduce cake layer thickness which leads to the high permeation flux and pollutant removal efficiency as well as low fouling. Integrated PAC - ceramic MF membrane had also shown a significant improvement of membrane flux. However, this study mentioned that the use of PAC has no influence on TOC and p-Xylene removal efficiency (Yang et al., 2011). Furthermore, chemical technique including coagulation/flocculation or Fenton reaction can also be used as a pretreatment method for membrane based hybrid process. This technique is the important step for the

performance of the following membrane stage to keep a high flux and to reduce membrane fouling. The addition of coagulant/ flocculant agents such as calcium chloride ( $\text{CaCl}_2$ ) and sodium hydroxide ( $\text{NaOH}$ ) for the pretreatment of emulsified oils contained in aqueous wastewaters has been investigated (Benito et al., 1999). This study proved that some organic pollutants can be eliminated using the integration of coagulation/ flocculation and membrane yielding more than 90% of the oils and 75% of the COD reduction. For the application of integrated photo Fenton – membrane separation, it has been reported that this combined system successfully degraded COD by 91 % (Zhang et al., 2013). Furthermore, the involvement of dissolved air flotation (DAF) as pretreatment stage could remove a large proportion of oil droplets and suspended solid particles. In flotation mechanism, different organic constituents may form colloids in the flotation tank surface by the rising air bubbles where it can be removed. Some studies have reported that integrated DAF - membrane system can increase the performance of membrane filtration by reducing organic pollutant loading in the solution before entering membrane system (Peleka et al., 2006, Blöcher et al., 2003).

Another way which can be employed as hybrid system is dual membrane process. For instance, UF/RO membrane which was applied for the oily wastewater treatment containing 107 mg/L and 1765 mg/L of initial oil and COD concentration, respectively. The study reported that this dual membrane application yields about only 7 % of permeate flux decline with oil content below 10 mg/L, free suspended solid, high TOC and cations removal efficiency (Tomaszewska et al., 2005). Other study investigated the efficiency of the integration polyacrylonitrile (PAN) UF and polyamide RO membrane (Sarfaraz et al., 2012). This study achieved only 5 % of flux decline during 7.5 hours, excellent removal efficiency of oil, COD, TOC and turbidity

of 100 %, 98 %, 98 % and 95 %, respectively. They also found that TMP, CFV, temperature and pH optimum values are 3 bars, 1 m/s, 40 °C and 9, respectively. A hybrid PVDF MF/ polyethersulfone UF membrane was applied to treat oily wastewater containing 3.591 mg/L and 2.698 mg/L of oil content and COD, respectively. Then, the study reported excellent permeate quality with 99 % of both COD and oil content removal efficiency with lower fouling than single membrane application (Masoudnia et al., 2015). In addition, a comparison study amongst four commercial UF and NF membranes with different pore size to treat high loading of oily restaurant wastewater having 10.300 mg/L COD concentration also reported promising result of more than 90 % of COD removal achieved. They concluded that NF is less susceptible to fouling than UF (Zulaikha et al., 2014). However, the main weakness of dual membrane system is restricted to the high cost for constructing and maintaining the system.

In the current study, we investigated the treatment of oily wastewater by UF membrane, photo Fenton or adsorption technique. Furthermore, as a case study, raw petroleum refinery wastewater purification using integrated Fenton/flocculation - UF membrane was conducted.

## **2.5 Summary**

This chapter demonstrates the problems related to oily wastewater from various sources and its impact on the environment. To date, several treatment methods are available including physical, chemical and biological with reports of good results for oily wastewater purification, but each of them has drawbacks. Despite the fact that membrane application has been found to be an excellent and modern technology for oily wastewater treatment, fouling generation as an effect of trapped pollutant in the



membrane surface has been a serious issue significantly decreasing membrane efficiency and increasing the operational cost. Furthermore, enormous studies proved that adsorption technique utilizing commercial activated carbon is also highly efficient for pollutant removal in oily wastewater but some shortcomings such as high activation cost, regeneration and long contact time need to be solved by exploring other low cost materials as the replacement of activated carbon. Thus, certain low cost adsorbents from agricultural material and animal waste seem potentially good candidates. In addition, advanced oxidation processes (Fenton and photo Fenton) have also been reported as good treatments for oily wastewater treatment. However, there are some challenges such as high cost for chemicals, upper limit of feed concentration and intermediates generation that need to be addressed. To overcome these problems, the enhancement of single or combined technology can be a solution for efficient oily wastewater treatment. Therefore, the aim of this study is to thoroughly investigate the treatment of oily wastewater using single treatment technology (adsorption, photo-Fenton, membrane) and an efficient integrated technique (Fenton-flocculation – membrane). As far as the author is concerned, to date, only very few studies focused on finding efficient and effective ways as pretreatment step for an UF membrane integrated system.

## **CHAPTER 3**

### **Experimental Methods**

### 3.1 Introduction

This chapter describes the experimental procedures, analytical techniques, chemicals and equipment that were used in this research project. The performance of UF membrane, photo-Fenton, adsorption and integrated UF membrane was investigated to propose efficient and cost effective treatment strategy for oily wastewater. Different analytical techniques were applied to measure the physicochemical properties of raw and treated oily wastewater samples.

### 3.2 Materials

The following chemicals were used as received without any further treatment: HACH COD reagent vials HR 0-1500 mg/L for COD measurement, Potassium hydrophthalate (KHP) for COD standard solution, Sodium sulphite ( $\text{Na}_2\text{SO}_3$ ) for Fenton quenching solution, HACH Phenanthroline reagent pillow ferrower (total iron) for total iron analysis, Phenanthroline reagent pillow ferrous for ferrous salt measurement, reagent grade hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%) as oxidizing agent, Ammonium ferrous sulphate ( $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ) for iron standard solution, Sodium oxalate ( $\text{Na}_2\text{C}_2\text{O}_4$ ) for potassium standard solution, Sodium hydroxide (NaOH) pellets and sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98 %) for pH adjustment, Potassium permanganate ( $\text{KMnO}_4$ ) for peroxide analysis. All these chemicals were purchased from Sigma Aldrich and Rowe Scientific, Australia. Analytical grade iron (II) sulphate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) was purchased from Ajax Finechem, Australia. Dry ice for oil content analysis was purchased from BOC, Australia. De-ionized water was used in all experiments. All glassware used was cleaned and rinsed using de-ionized water, then stored in a laboratory oven at 60 °C before using.

### 3.3 Characterization of oily wastewater

The characterization of oily wastewater before and after treatment was conducted in order to evaluate the treatment effectiveness. For adsorption, oil analysis was used as a key factor to check the treatment efficiency, while TOC, COD and oil content were used for UF membrane, photo-Fenton and integrated membrane experiments. For each experiment, two repeated analyses were conducted for better result.

#### 3.3.1 Oil content analysis

The oil content in the oily wastewater was measured by a gravimetric method. Oily sample (20 mL) was transferred to a separating funnel. Then few drops of sulphuric acid solution were added to obtain pH 2 before adding 3 mL of n-hexane. The separating funnel was mechanically shaken for 2 min and left to form two separate layers. The mixture of organic solvent and oil layer was collected onto weighed round bottomed flask that contained 10 g of anhydrous sodium sulphate. Furthermore, the hexane in oil was separated using rotary evaporator (Butchi Rotavapor R-210 series) (Figure 3.1). Oil sample in the round flask was dried at 103 °C for 15 min then cooled to room temperature in the desiccator.



**Figure 3.1** Rotary evaporator (Butchi Rotavapor) for oil content analysis

The oil removal efficiency was determined based on the following equations:

$$\text{Oil removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \% \quad (3.1)$$

Where  $C_0$  and  $C_e$  are the initial and final oil content concentration (mg/L) in the oily wastewater sample (mg/L), respectively.

$$\text{Adsorption capacity (mg/g), } q = \frac{(C_0 - C_e)V}{m} \quad (3.2)$$

Where  $V$  and  $m$  are the volume of oily wastewater sample (L) and mass of the adsorbent (g), respectively.

### 3.3.2. Total organic carbon (TOC) analysis

TOC concentration (mg/L) was analyzed using Shimadzu TOC-V CPH analyzer (Figure 3.2) set to operate at a pressure of 200 kPa, a temperature of 700°C, a flow rate of 150 mL/min with a solution of potassium phthalate as a standard of calibration. Previously, the samples (20 mL) were filtered by PTFE 0.45  $\mu\text{m}$  membrane filter to separate any catalyst particle. Then, the sample bottles were put in the TOC analyzer for injection system. The Standard deviation showed in TOC analyzer system was less than 0.5.



**Figure 3.2** TOC analyzer for TOC measurement

### 3.3.3 Chemical oxygen demand (COD) and Fe analysis

COD concentration (mg/L) was measured by HACH DRB200 reactor and DR890 colorimeter (Figure 3.3) according to the manufacturer's standard procedure of sample digestion (standard method 5220 D). The mg/L results are defined as the mg of oxygen consumed per liter of sample. Filtered sample (2 mL) was added to the COD digestion solution (HACH COD reagent vials HR 0-1500 mg/L) which is commercially available. The vial is heated for two hours by HACH DRB200 reactor. After cooling process at room temperature, the COD value of the sample contained in the vial was measured using DR890 colorimeter. This equipment can also be used to determine the concentration of ferric and ferrous ions by phenanthroline method in the solution. The 1,10-phenanthroline indicator in ferrous iron reagent will react to ferrous iron ( $\text{Fe}^{2+}$ ) forming an orange color. To determine ferric ion ( $\text{Fe}^{3+}$ ) concentration, total iron concentration is deducted by ferrous ion concentration detected.



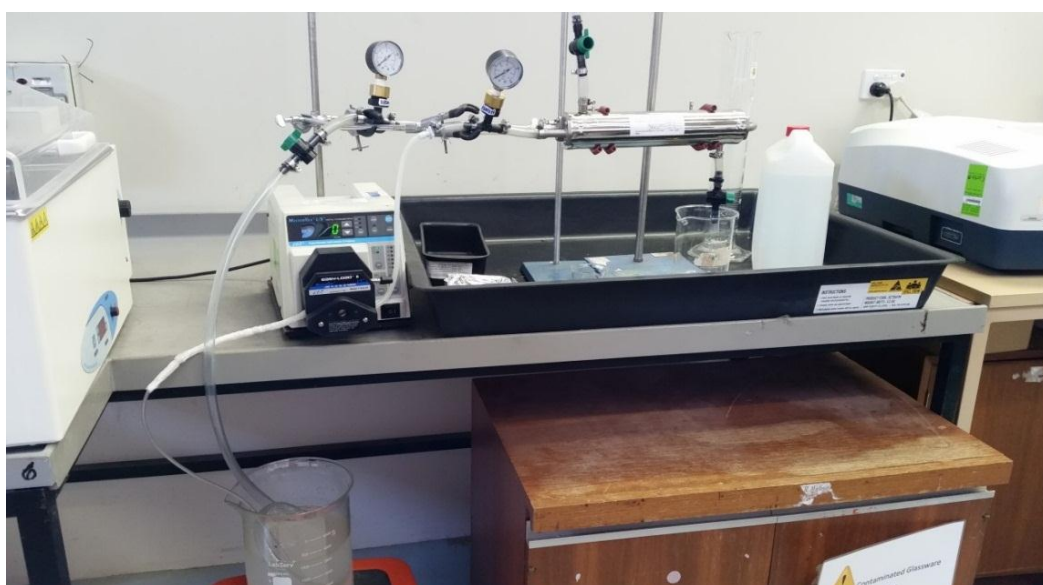
**Figure 3.3** HACH DRB200 reactor and DR890 colorimeter for COD and Fe analysis

### 3.3.4 pH

The pH was measured using a pH meter glass electrode (SP-701LI 120). The measurements for pH were performed immediately to avoid any changes that might occur due to contact with air. The pH meter was calibrated periodically using buffer solutions.

## 3.4 Polymeric UF Membrane

In order to investigate the efficiency of UF membrane made of polymeric polyvinylidene fluoride (PVDF) material at different operating conditions, synthetic oil in water emulsion and raw restaurant wastewater were used as feed solution. For each experiment, two pieces of a 30 cm length of UF membrane that has active area of 0.024 m<sup>2</sup> and molecular weight cut-off (MWCO) of 100 kDa were used and placed inside the membrane holder (Micro 240, made of 316 stainless steel) which has two membrane holes sealed by nitrile tube seals. Each piece of membrane was tested with de-ionised (DI) water prior to use. New membranes were used in each experiment to ensure homogenous starting condition for membrane performance.

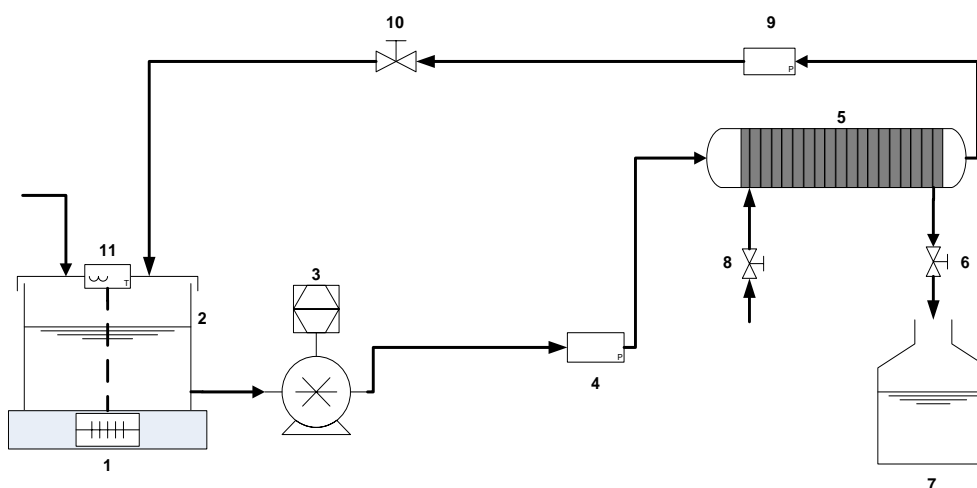


**Figure 3.4** Experimental set up for UF membrane.



**Figure 3.5** Polymeric UF membrane

The experimental sets up of the UF membrane-only and integrated UF membrane methods are shown in Figures 3.6 and 3.7, respectively. In the first method, the UF membrane-only method, oily sample was fed directly to the membrane without any pretreatment.



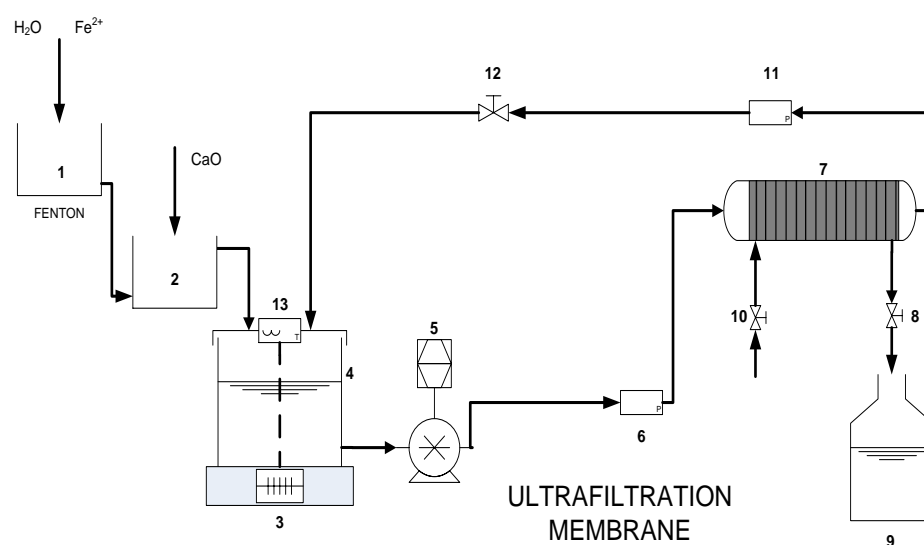
(1) Digital thermally controlled stirrer (2) Feed tank (3) Programmable digital peristaltic pump (4) Pressure gauge inlet (5) UF Membrane (6) Permeate valve (7) Permeate vessel (8) Closed valve (9) Pressure gauge outlet/Retentate (10) Retentate Valve (11) Thermometer

**Figure 3.6** Schematic diagram for UF membrane-only method



In the second method, the integrated membrane mode, the oily sample was first pre-treated using Fenton (1 mL/L  $\text{H}_2\text{O}_2$  and 0.5 g/L  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and flocculation (0.5 g/L CaO) processes before being passed through the UF membrane.

The initial volume of the oily sample was 6 L, and the experiments were run in a recycle system. The volume of the collected permeate was measured every 10 min in order to investigate the permeate flux. The retentate sample was returned to the feed tank. During the experiment, temperature, pressure and flow rate were fully controlled. The flow rate was adjusted using a programmable peristaltic pump and the pressure was controlled using valves. Blank experiment using DI water was also conducted before and after experiment in order to analyze the condition of fresh and fouled membrane.



(1) Fenton batch process (2) Coagulation batch process (3) Digital magnetic stirrer with heat adjustment, (4) Feed tank, (5) Programmable digital peristaltic pump, (6) pressure gauge inlet, (7) UF Membrane, (8) Permeate valve, (9) Permeate vessel, (10) Closed valve, (11) Pressure gauge /Retantate, (12) Retantate Valve, (13) Thermometer

**Figure 3.7** Schematic diagram for integrated UF membrane method

Membrane cleaning was conducted in some parts of the experiments. This process was done according to the procedure recommended by manufacturer's recommendation:

(1) sanitizing the membrane using 75 mg/L of hypochlorite solution for 10 min, (2) initial rinse of the fouled membrane with deionised water, (3) rinse with acid solution by flowing 0.3 % nitric acid solution at 45 °C for 30 min, (4) rinse membrane with distilled water as a final step.

The UF membrane system was operated under different operating conditions. The removal of a certain pollutant is expressed as follows:

$$\text{Removal efficiency, (\%)} = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (3.3)$$

Where  $C_p$  (mg/L) is the concentration of a certain pollutant in permeate and  $C_f$  (mg/L) is its feed concentration.

To determine the permeate flux of the membrane during the filtration process (L/m<sup>2</sup> h), the following equation was applied (Hua et al., 2007):

$$\text{Permeate flux, } J = \frac{V}{At} \quad (3.4)$$

where  $J$  is the permeation flux (L/m<sup>2</sup> h),  $V$  is the collected permeate volume (L),  $A$  is the membrane area (m<sup>2</sup>), and  $t$  is the time taken to collect the permeate (h). According to Darcy's Law, the water and feed solution flux can also be determined by the following equation (Sarfaraz et al., 2012) :

$$J = \frac{TMP}{\mu R_t} \quad (3.5)$$

where TMP is the trans membrane pressure (TMP) or pressure difference between the inlet and outlet of the membrane (bar),  $\mu$  is the viscosity of water at room temperature (m Pas), and  $R_t$  the summation of membrane resistance (1/m), respectively.

Trans membrane pressure (TMP) applied in the system can be measured as follows:

$$TMP = \frac{P_i + P_o}{2} \quad (3.6)$$

Where  $P_i$  and  $P_o$  (bar) are the inlet and outlet pressure of membrane modules, respectively.

Hermia's model, the most applicable model for predicting flux decline, can then be used to investigate the influence of the membrane fouling on the permeate flux. The general equation for Hermia's model can be written as follows (Charfi et al., 2012):

$$\frac{d^2t}{dV^2} = K \left( \frac{dt}{dV} \right)^n \quad (3.7)$$

Using Equation 3.7 for the derivation of permeation flux ( $J$ ) with time ( $t$ ), Hermia's model can be rewritten as follows:

$$\frac{dJ}{dt} = -K (J - J_{ss}) J^{2-n} \quad (3.8)$$

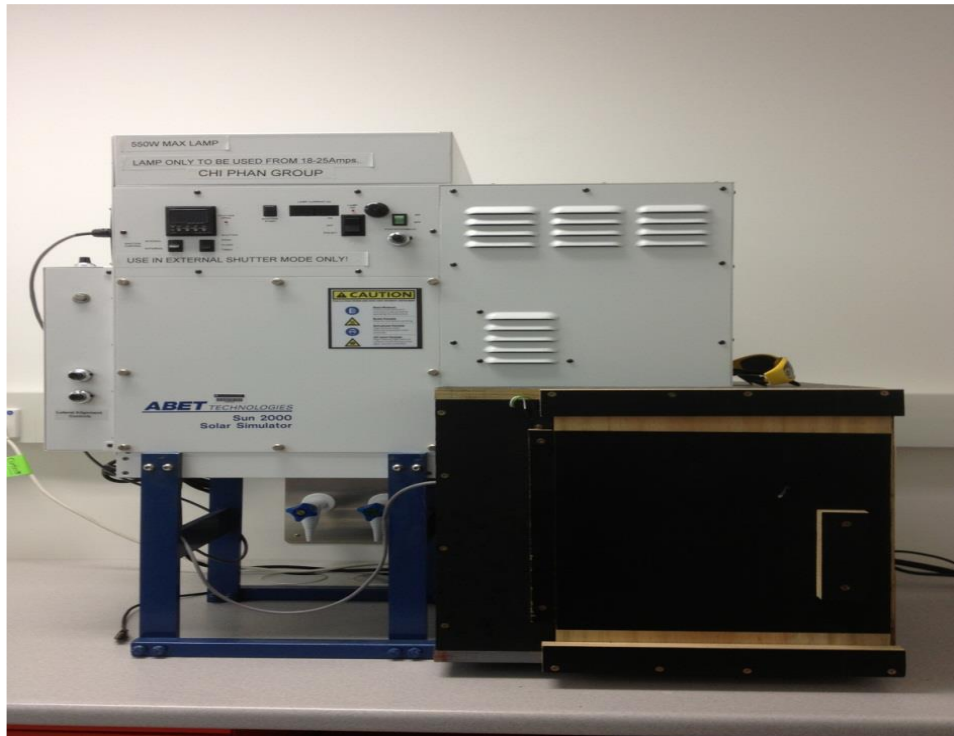
where  $K$  is a constant,  $J_{ss}$  is the steady state permeation flux,  $n = 0$  for cake filtration,  $n = 1$  for incomplete blocking of the membrane's pores (intermediate fouling),  $n = 1.5$  for standard blocking, and  $n = 2$  for complete blocking.

The cake formation model ( $n = 0$ ) assumes that fouling is caused by cake building up on the membrane surface, the way the cake forms will determine the flux decline. In the intermediate blocking model ( $n = 1$ ), particles block some membrane pores creating intermediate fouling. In the standard model ( $n = 1.5$ ), there is a decrease in the pore diameter caused by particle adsorption on the pore wall, leading to a flux decline. The complete blocking model ( $n = 2$ ) assumes that the settled particles on the membrane surface will block pores, leading to a flux decline (Mah et al., 2012).

### 3.5 Experimental studies of photo-Fenton system

To study the effect of oxidant concentration and irradiation sources on the efficiency of oily wastewater purification, photo-Fenton experiments were conducted by using raw wastewater from a local canola oil producing plant. The samples were collected from Alba Edible Oil Company, Western Australia and were taken from the outlet of dissolved air flotation (DAF) unit. Upon arrival, all samples were stored at 4 °C then characterized before further experiments were conducted. Each experiment was carried out in a Pyrex glass beaker as a reactor, equipped with a magnetic stirrer. The initial solution pH was adjusted to 3 as the optimal value for Fenton and photo-Fenton reaction (Tokumura et al., 2008) and no further pH adjustment was carried out during the degradation process since the change of pH was insignificant. The pH values of the solutions were monitored using a pH meter (SP-701LI 120). All samples were withdrawn from batch reactor at specific time using a gas tight syringe and filtered through a 0.45 µm polyvinylidene difluoride (PVDF) membrane before analysis. TOC and COD were measured and used as indicators for measuring the degradation efficiency.

For UV light source, the experiments were carried out in the dark box equipped with 4 UV lamps having 18 watt of power each (light intensity 45 µmoles/m<sup>2</sup>/s). For solar simulator light source, the experiments were conducted in the dark box (light intensity 80 µmoles/m<sup>2</sup>/s) (Sun 2000 x 210 mm, Abet Technologies Model 11044) (Figure 3.8). For natural solar light source (light intensity 1450 µmoles/m<sup>2</sup>/s), the experiments were performed on clear days and at ambient temperature (Figure 3.9). Light intensity was measured by using Licor Light Meter, model Li-250A (Figure 3.10). Blank experiments using oily sample that treated by various light sources (natural solar light, UV lamp and solar simulator) without Fenton's reagent were also conducted.



**Figure 3.8** Solar simulator (Sun 2000 210 × 210 mm, Abet Technologies Model 11044)



**Figure 3.9** Photo Fenton experiment for oily wastewater treatment samples using natural solar light



**Figure 3.10** Light meter (Licor LightMeter Model Li-250A)

### **3.6 Adsorption experiments**

Three different bio waste materials (eucalyptus bark (EB), watermelon shell (WS) and chicken bone (CB)) were selected as potential biosorbents for oil removal from oily aqueous solution. The best one will be implemented in different operating conditions for oily wastewater treatment. The oily wastewater samples were collected from an Asian restaurant located in Perth, Western Australia.

#### **3.6.1 Biosorbent preparation**

Eucalyptus bark (EB) was collected from yard environment of Curtin University – Bentley Campus, Western Australia. Watermelon shell (WS) and chicken bone (CB) were collected from household environment. The EB and WS were washed several times with distilled water to remove any impurities, then dried at 105 °C for 24 h in a laboratory oven. CB materials were cooked at 200 °C for 24 h and then washed to clean away the attached meat and fat. EB, WS and CB were crushed by a mechanical grinder (RETSCH, GmbH & Co. KG, West Germany) to obtain powder form then passed through British standard sieves (BSS) of 250 µm. Figure 3.11 shows the waste materials used before and after preparation.



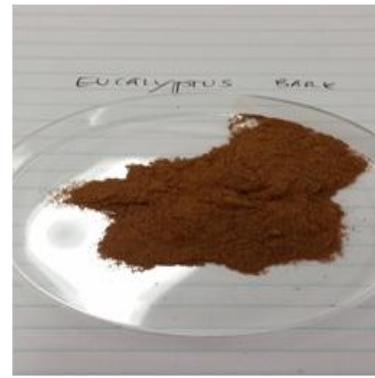
(a-before)



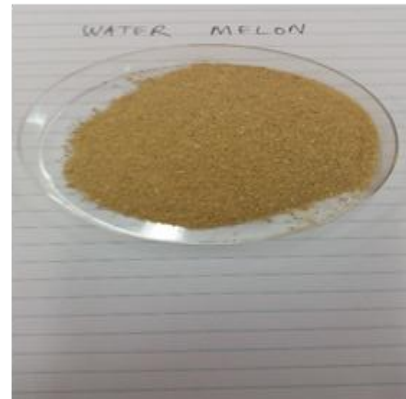
(a-after)



(b-before)



(b-after)



**Figure 3.11** Biosorbent materials, (a) Chicken bone, (b) Euclyptus bark and (c) Watermelon shell

The biosorbent material was kept in an airtight plastic container and ready to be used in adsorption experiments.

### ***3.6.2 Biosorbent characterization***

Biosorbent materials were characterized using different types of analytical techniques such as surface area (BET), Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR) and elemental analyzer.

#### *3.6.2.1 Surface area (BET) and total pore volume*

The specific surface area and total pore volume were determined using the multi-point Brunauer-Emmet-Teller (BET) method. Before analysis, the sample was degassed to eradicate any trace of volatile elements at temperature 25 °C for 60 min then increasing the temperature to 120 °C for 360 min. The sample was transferred to the BET analysis system.

#### *3.6.2.2 Scanning electron microscopy (SEM)*

A Scanning Electron Microscope (SEM) Gemini Zeiss NEON 40 ESB was applied in order to investigate the adsorbent morphology before and after adsorption. Some amount of adsorbent was put on a 10 mm diameter of aluminum stub. Every sample was laid on a double side carbon adhesive placed on the stub. Sample was coated with platinum (Pt) then screened using SEM machine.

#### *3.6.2.3 Fourier transform infrared (FTIR)*

In order to analyze the functional groups of the biosorbent, the Perkin-Elmer spectrum one FTIR spectrometer was used. A small portion of the biosorbent was put on the hydraulic press which was cleaned using ethanol solution. The film should be homogeneous in appearance.



### ***3.6.3 Adsorption experimental procedure***

100 mL of restaurant oily wastewater was measured using a measuring cylinder, then poured into a 250 mL glass screw cap bottle through a glass filter funnel. Some biosorbent was weighed and added to the bottle. The oily sample bottles including a bottle of blank experiment containing oily sample without biosorbent were put in the incubator shaker (Thermo line scientific) arranged at 200 rpm for 100 min. After contact time, the liquid was filtered and analyzed for oil content. The biosorbent that did not result in significant oil degradation was phased out. The effect of several operating parameters that were designed including contact time (0, 10, 30, 50, 70, 100, 150 and 180 min), initial solution pH (3, 5, 7, 9 and 10), temperature (25 °C, 30 °C, 35 °C, 40 °C and 45 °C) and adsorbent dosage (0.25 g, 0.5 g, 1 g, 1.5 g and 2 g) was all investigated.

## **CHAPTER 4**

### **Oily Wastewater Treatment by Ultrafiltration (UF) Membrane**

## 4.1 Introduction

This chapter presents the application of polymeric ultrafiltration (UF) membrane for the treatment of raw restaurant oily wastewater and synthetic oil in water emulsion, the assessment of the influence of different operating conditions, and the evaluation of membrane cleaning influence on the permeate flux recovery.

Restaurant oily wastewater (ROW) and oil in water emulsion from various industries have been a major concern due to its impact on environment quality and general public health. In order to meet the environmental discharge standards, different treatment technologies have been applied including gravity settling, adsorption, flotation, pH adjustment, electrostatic coalescence and membrane filtration (Feng et al., 2003, Mohammadi and Esmaelifar, 2005, Salahi et al., 2010b). However, most of these methods have limitations for the emulsion separation efficiency with oil droplets and wettability of the media by dispersed phase (Mohammadi and Esmaelifar, 2004, Salahi et al., 2011).

Membrane separation technology has been considered as one of the most effective treatment methods for oily wastewaters due to its simple apparatus needed, separation based on manageable size dismissal, high removal of bacterial and toxic residue, no special chemicals used, small area requirements and can be operated by moderate skilled operators (Xia et al., 2004, Ahmad et al., 2005a). The use of polymeric membrane which is feasible for the treatment of aqueous solution is significantly less expensive than ceramic membrane (Allgeier, 2005). Some studies have also reported the outstanding results of membrane separation process for oily wastewater treatment (Table 4.1).

**Table 4.1** Performance of various membranes for oil removal from oily wastewater

<b>Membrane type</b>	<b>Oily wastewater type</b>	<b>Results</b>	<b>Reference</b>
Polymeric MF (polyvinylidene fluoride)	Oil in water emulsion	TOC removal: 94 %, COD removal 94 %, oil removal: 98.4 %, TMP: 3 bars, time for steady state flux: 90 min	(Masoudnia et al., 2015)
Polymeric UF (polyethersulfone)	Oil in water emulsion	TOC removal: 97.9 %, COD removal 98 %, oil removal: 99.5 %, TMP: 3 bars, time for steady state flux: 90 min	(Masoudnia et al., 2015)
Polymeric UF (polyvinylidene fluoride)	Oily restaurant wastewater	BOD removal: 79.2 %, COD removal 98.4 %, TMP: 2-4 bars, T: 25 °C time for steady state flux: 180 min	(Zulaikha et al., 2014)
Nanofiltration membrane	Oily restaurant wastewater	BOD removal: 82.2 %, COD removal 98.4 %, TMP: 2-4 bars, T: 25 °C time for steady state flux: 150 min	(Zulaikha et al., 2014)
Ceramic MF	Petrochemical wastewater	BOD removal: 72.4 %, COD removal 60.6 %, TMP: 15 bars, T: 25 °C, CVF: 2 m/s time for steady state flux: 100 min	(Madaeni et al., 2012)
Polymeric UF (Polyvinylidene fluoride)	Oil in water emulsion	TOC removal: 87 %, COD removal 01 %, TMP: 3 bars, time for steady state flux: 50 min, CFV: 0.33 m/s	(Mohammadi and Esmaeilifar, 2004)
Ceramic MF	Oil in water emulsion	TOC removal: 92.4 %, TMP: 0.2 Mpa, time for steady state flux: 70 min, CFV: 0.95 m/s	(Hua et al., 2007)
Ceramic UF	Oil in water emulsion	COD removal: 92 %, TMP: 0.35 Mpa, T: 25 °C, time for steady state flux: 70 min, CFV: 3.4 m/s	(Lobo et al., 2006)
Polymeric UF (polyvinylidene fluoride)	Oil refinery wastewater	TOC removal: 98 %, COD removal 90 %, TMP: 0.1 Mpa, CVF: 7 m/s, time for steady state flux: 200 min	(Li et al., 2006)
Ceramic MF	Palm oil mill wastewater	Suspended solid removal: 97 %, TMP: 2 bars, T: 25 °C, time for steady state flux: 40 min	(Ahmad et al., 2005a)
Polymeric UF (Polyvinylidene)	Palm oil mill wastewater	Suspended solid removal: 97 %, TMP: 2 bars, T: 25 °C, time for steady state flux: 40 min	(Ahmad et al., 2005a)
Polymeric flat sheet UF	Oil in water emulsion	TOC removal: 87 %, COD removal 91 %, TMP: 3 bars, CVF: 0.33 m/s, time for steady state flux: 50 min	(Mohammadi and Esmaeilifar, 2004)

To evaluate and assess the polymeric UF membrane for both ROW and synthetic oil in water emulsion, the effect of several operating conditions such as initial oil concentration, temperature and applied pressure on flux profile and pollutant removal was thoroughly investigated. Furthermore, the fouling characterization and mechanism were also studied through morphological and Hermia's models analysis.

## **4.2 Materials**

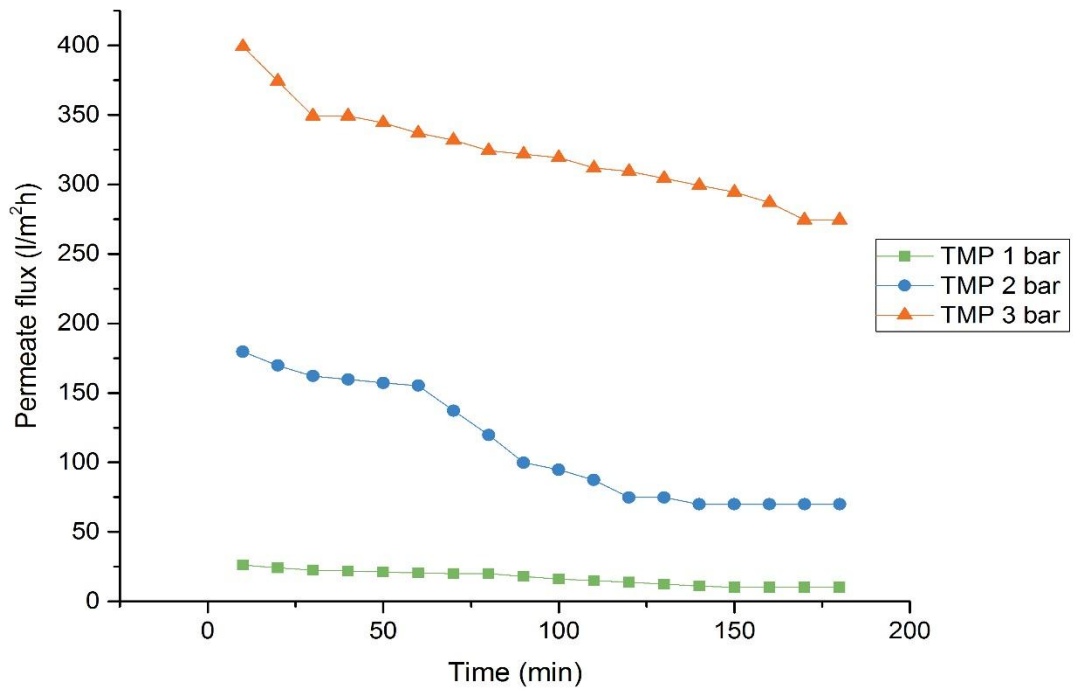
Synthetic oil in water emulsion was prepared by mixing commercial canola oil (Coles vegetable oil, Australia) with distilled water and non-ionic emulsifier (Palmolive-Ajax dishwashing, Australia) for 20 min at a high speed mode using a blender (Breville, Italy) to homogenize it. ROW used was collected from an Asian restaurant located in Perth, Western Australia.

More detail of experimental set up and analytic procedure can be seen in Chapter 3.

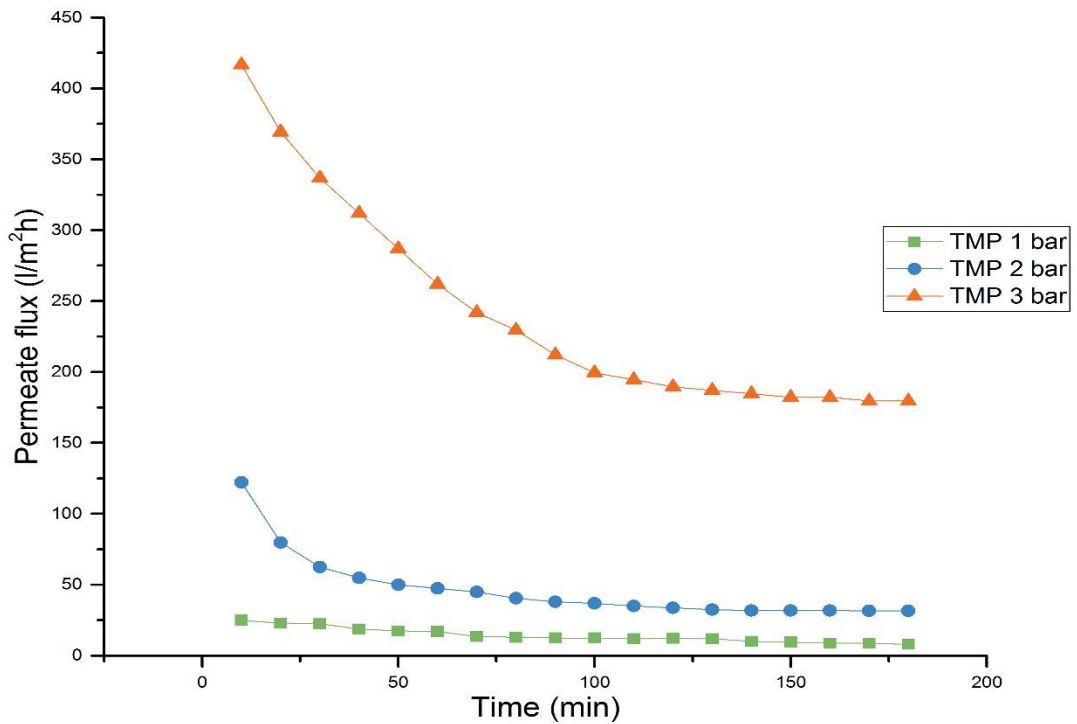
## **4.3 Results and Discussion**

### ***4.3.1 Effect of trans membrane pressure (TMP) on permeate flux***

The influence of TMP on permeate flux for both synthetic oily wastewater and raw ROW are shown in Figures 4.1 and 4.2, respectively.



**Figure 4.1** Effect of TMP on permeate flux during 180 min of filtration time using synthetic oil in water emulsion (Oil concentration: 2 g/L, T: 25 °C, pH: 3, CFV: 400 mL/min)



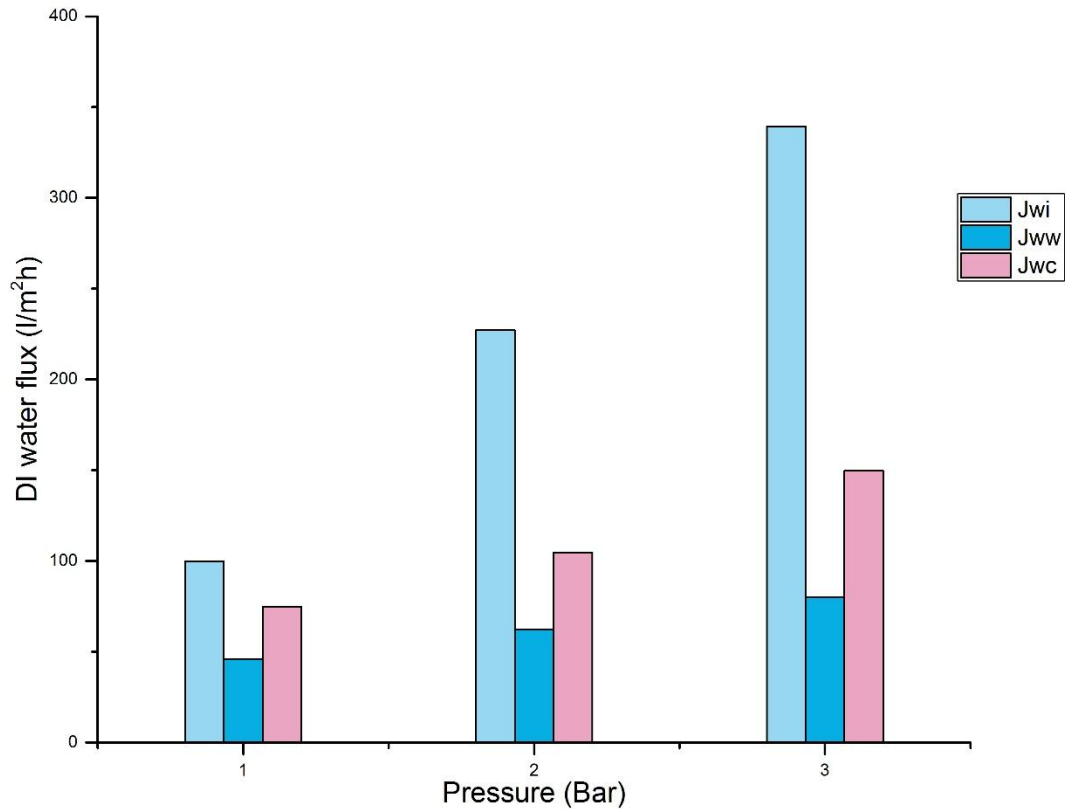
**Figure 4.2** Effect of TMP on permeate flux during 180 min of filtration time using raw restaurant oily wastewater (Oil concentration: 2 g/L, T: 25 °C, pH: 3, CFV: 400 mL/min)

TMP significantly affects permeate flux values since increasing TMP increases permeate flux by producing more power for solute particles or oil droplets passing through the membrane pores. This is supported by Darcy's law even though membrane fouling probably could restrain this effect (Zhen et al., 2006). In most cases, the flux increases linearly with increasing TMP until it achieves the limiting flux (Elmaleh and Ghaffor, 1996). The quality of the oily wastewater to be treated shows no permeate flux reduction for both synthetic and raw oily wastewaters at low TMP (1 bar). However, at high TMP (3 bars), the permeate flux reduction for raw oily wastewater was 51.3% while it reduced only 31.25% when treating synthetic wastewater under the same operating conditions.

The significant permeate flux reduction of raw ROW can be caused by its characterization which has more complex compounds such as dissolved solid, fat, grease and other heavy hydrocarbons than the synthetic oily wastewater. Therefore, the filtered raw oily permeate passing through the membrane is less than that of the synthetic oily wastewater.

#### ***4.3.2 Effect of TMP on membrane permeability***

Membrane permeability is the ability of membrane pores or membrane surface to pass in and out of some substances related to the strength of membrane usage under certain conditions. Membrane permeability is also influenced by membrane type, membrane material and operating conditions such as TMP, feed concentration and velocity. De-ionized (DI) water can be applied to measure membrane permeability.



**Figure 4.3** Effect of TMP on membrane permeability using de-ionised (DI) water (T: 25 °C, pH: 3, CFV: 400 mL/min,  $J_{wi}$ : initial DI water flux,  $J_{ww}$ : DI water flux after treating oily wastewater before cleaning,  $J_{wc}$ : DI water flux after treating oily wastewater after cleaning)

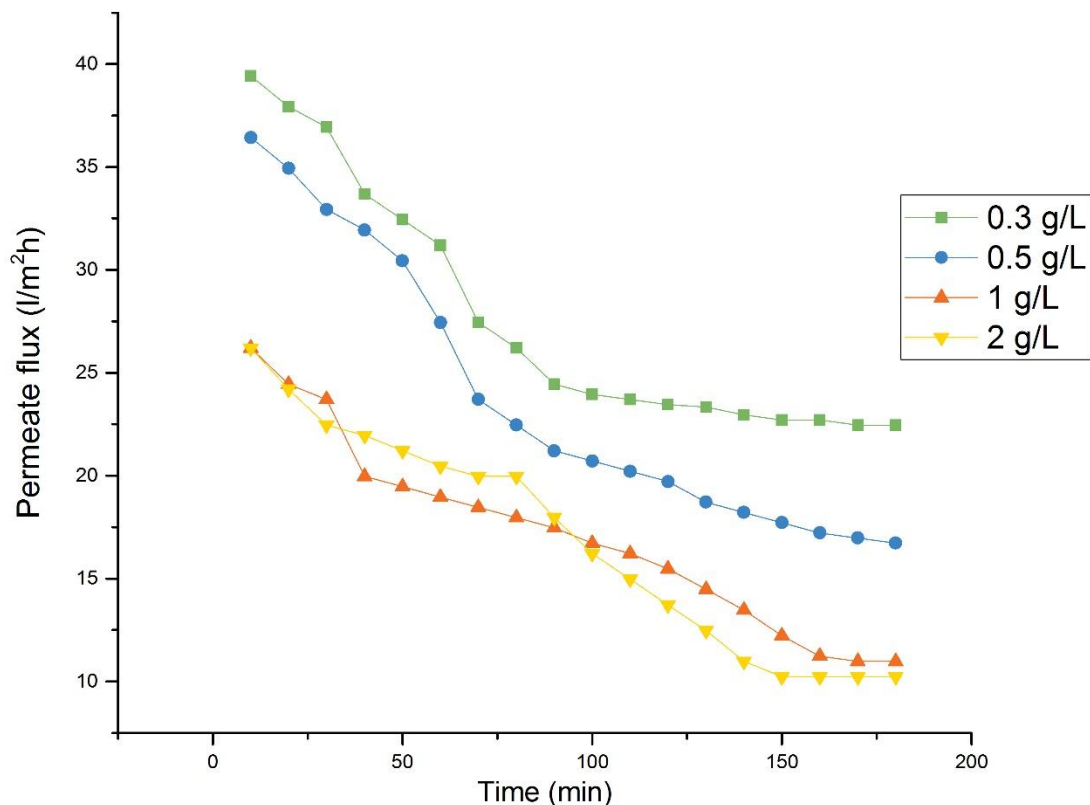
Figure 4.3 shows the influence of TMP on the DI water flux for three different cases. For fresh membrane ( $J_{wi}$ ), for used membrane after treating 0.3 g/L oily wastewater before chemical cleaning ( $J_{ww}$ ) and for used membrane after treating 0.3 g/L oily wastewater after chemical cleaning ( $J_{wc}$ ). Figure 4.4 indicates that increasing TMP increases membrane permeability and consequently the permeate flux. At all TMP levels, DI water flux after treating oily wastewater ( $J_{ww}$ ) declined severely due to plugged pores in membrane surface layer. After the application of chemical cleaning, the DI water flux ( $J_{wc}$ ) noticeably increased due to the removal of trapped pollutants on membrane pores. However, DI water flux after chemical cleaning ( $J_{wc}$ ) was still lower than its initial flux ( $J_{wi}$ ). This can be attributed to the strong bonding between



residual pollutants and membrane pores after chemical cleaning (Yin et al., 2013, Ahmad et al., 2005).

### 4.3.3 Effect of initial oil concentration on permeate flux

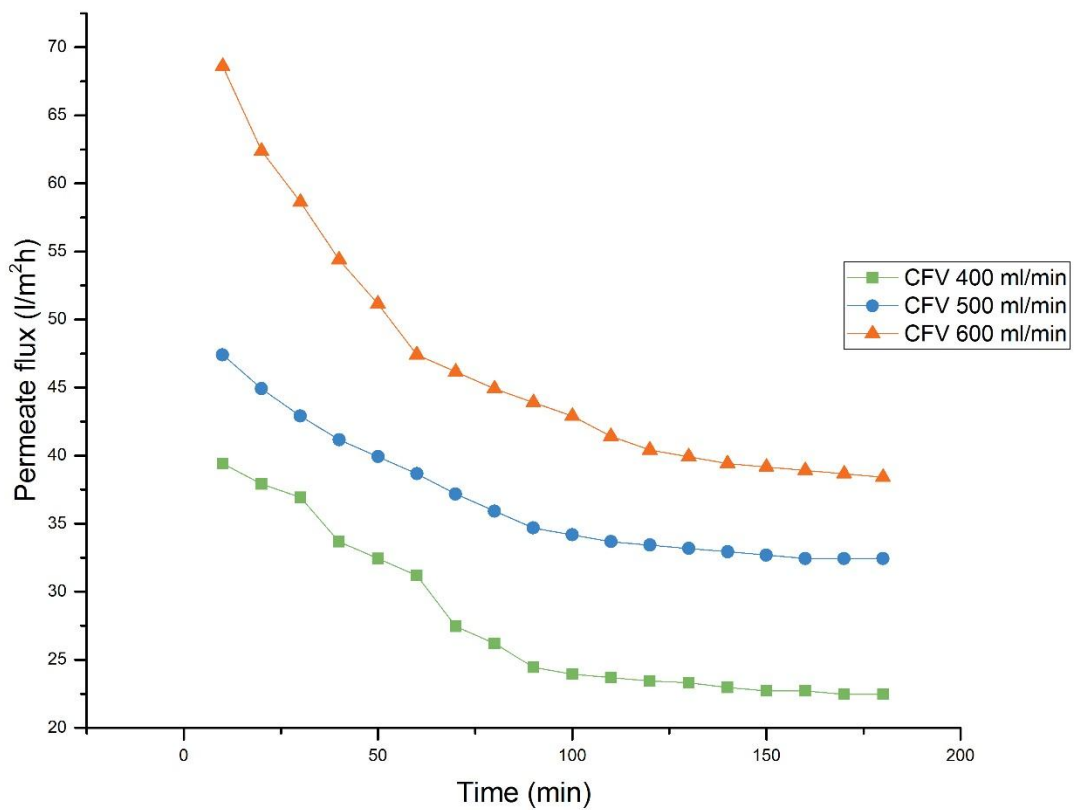
Increasing initial oil concentration decreases permeate flux due to higher oil droplets clogging membrane pores (Mohammadi and Esmaelifar, 2004). With the high oil concentration, the steady state permeate flux decreases, while concentration polarization and the ratio of oil retention increases (Ong et al., 2014, Yang et al., 2011). Based on experimental results showed in Figure 4.4, it is evident that permeate flux decreases regularly with time until it reaches steady state permeate flux condition with the onset of saturated cake formation.



**Figure 4.4** Effect of initial oil concentration on permeation flux using synthetic oil in water emulsion (pH: 3, T: 25 °C, CFV: 400 mL/min, TMP: 1 bar)

#### 4.3.4 Effect of cross flow velocity (CFV) on permeate flux

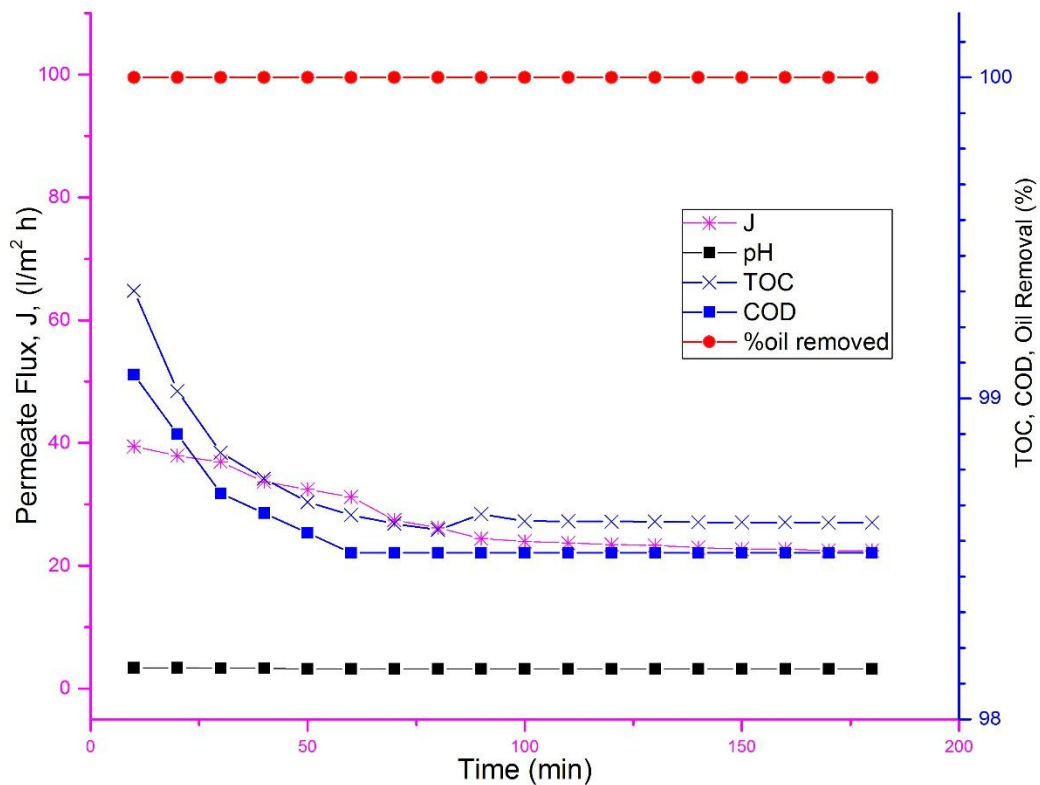
The experimental results of the effect of CFV shown in Figure 4.5 indicate that, for all CFV values, 400 to 600 mL/min, the flux reduction is linear with time. The flux reduction is nearly steady state after 180 min. Meanwhile, the permeate flux increases with the increase of CFV resulting in an increase in shear rate on membrane and decrease in the thickness of fouling layer. Increasing CFV helps to retard flux decline caused by concentration polarization and improves the washing away accumulated dissolved solid (Bourgeois et al., 2001).



**Figure 4.5** Effect of CFV on permeation flux using synthetic oil in water emulsion (Initial oil concentration: 0.3 g/L, pH: 3, T: 25 °C, CFV: 400 mL/min, TMP: 1 bar)

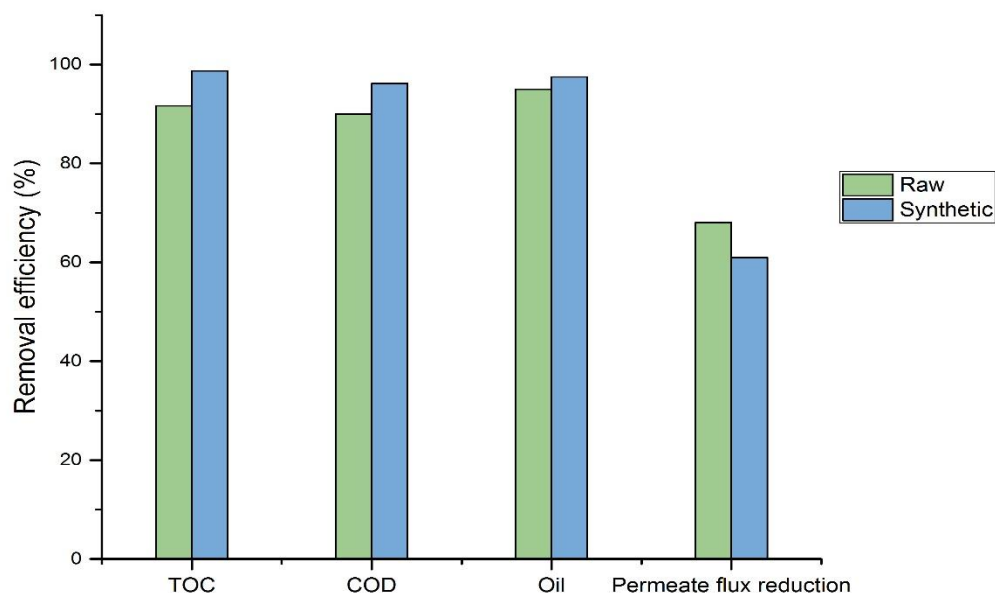
#### 4.3.5 Polymeric UF membrane for oily wastewater treatment

To understand the performance of the UF membrane for oily wastewater treatment, typical experiment was conducted to treat synthetic oil in water emulsion. The results presented in Figure 4.6 show the removal efficiency of TOC, COD, oil content and permeate flux reduction. The perfect performance of the UF membrane for TOC, COD and oil content removal was evident from the sustain high removal efficiency of 99 %, 98 % and 100 % for TOC, COD and oil content, respectively. However the permeate flux was reduced about 45 % from 40 L/m<sup>2</sup>h to 24 L/m<sup>2</sup>h, that could be attributed to cake gel layer formation.



**Figure 4.6** Effect of filtration time on permeate flux, pH and removal percentage of TOC, COD, oil concentration (Initial oil concentration: 0.3 g/L, pH: 3, Temperature: 25 °C, TMP: 1 bar, CFV: 400 mL/min)

To determine the effect of raw and synthetic oily wastewater on the removal efficiency of TOC, COD, oil content and permeate flux reduction. Experiments were conducted under the same conditions using different oily wastewater quality (Figure 4.7)

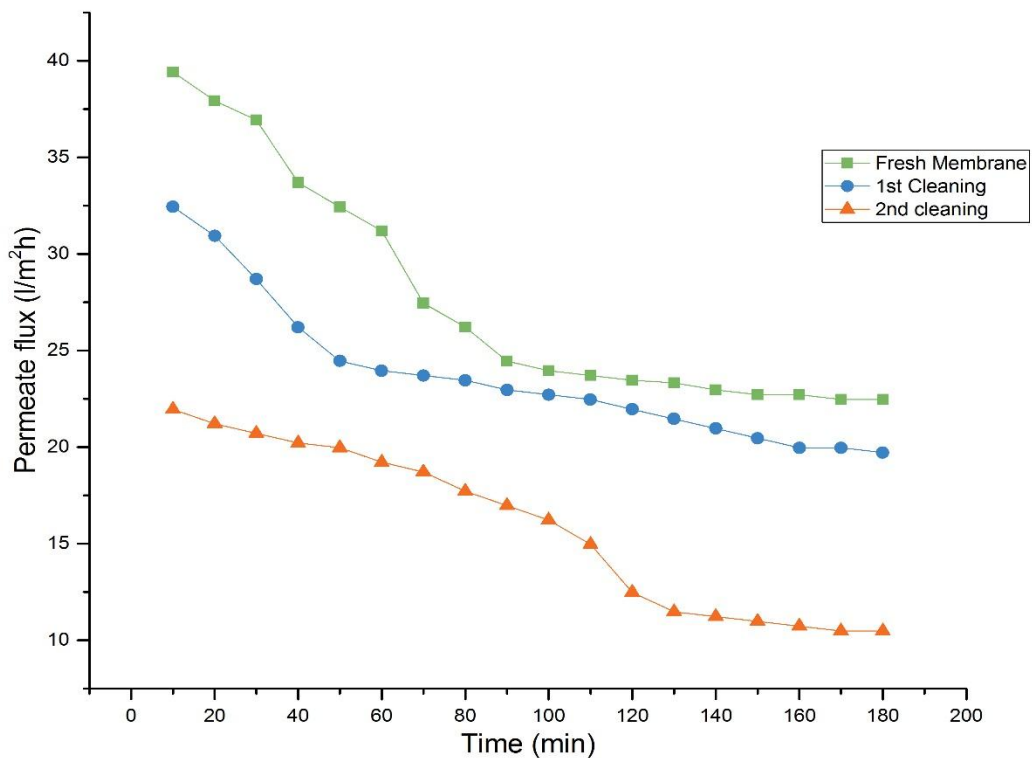


**Figure 4.7** Removal efficiency of TOC, COD, oil and permeate flux reduction of raw restaurant oily wastewater and synthetic oil in water emulsion (Oil concentration: 2 g/L, TMP: 1 bar, CFV: 400 mL/min, pH: 3, t: 180 min and T: 25 °C)

The removal efficiency values of TOC, COD and oil content of synthetic oily wastewater are higher than raw oily wastewater. Meanwhile, it is observed that the permeate flux reduction of synthetic oily wastewater is lower than that of raw wastewater. This can be attributed to the complex nature of the raw wastewater contents that were generated from many restaurant activities such as cooking various food and washing kitchen utensils. The results showed that the performance of the UF membrane was much better for treating synthetic oily wastewater than raw oily restaurant wastewater.

#### 4.3.6 Effect of membrane cleaning on permeate flux

Membrane cleaning purpose is to recovery the permeate flux decline due to clogging in membrane pores and on membrane surface (Lee et al., 1984, Mugnier et al., 2000). In order to investigate the effect of chemical cleaning on permeate flux recovery and fouling reduction, three experimental runs were conducted using synthetic oily wastewater. Fresh UF membrane was used as first run. Thereafter, the UF membrane was chemically cleaned and applied in the second run (first cleaning run) under similar operating conditions as before. Similarly, the third run was conducted after the second chemical cleaning run. According to the results which are presented in Figure 4.8, it is obvious that cleaning the membrane considerably increase permeate flux in its further usage by rinsing reversible fouling formation on the surface and in the pores of UF membrane (Hermia, 1985, Madaeni et al., 2012, Zulaikha et al., 2014).

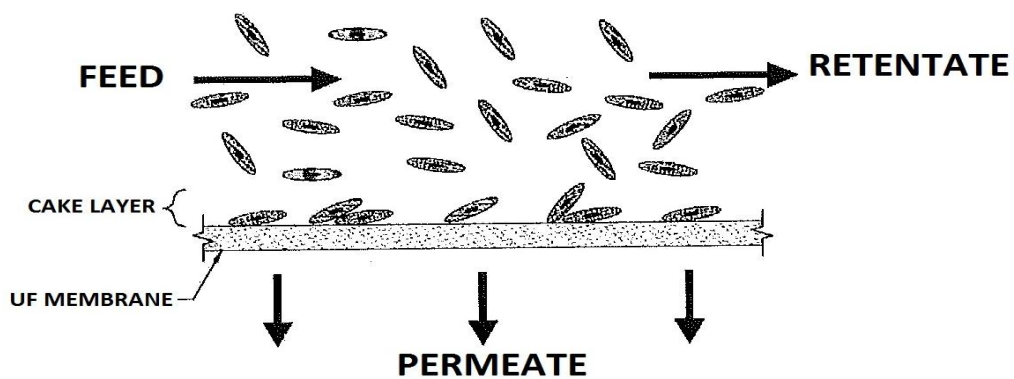


**Figure 4.8** Effect of chemical cleaning on permeate flux (Oil concentration: 0.3 g/L, pH: 3, T: 25 °C, CFV: 400 mL/min, TMP: 1 bar)

#### 4.3.7 Fouling mechanism analysis

In this section, the interpretation of the fouling mechanism occurring in the UF membrane was analyzed using Hermia's models. The models consist of four types, namely intermediate pore blocking model, standard pore blocking model, complete pore blocking and cake filtration model (Salahi et al., 2010b).

As can be seen in Table 4.2, Hermia's models which are widely recognized as a tool to characterize fouling mechanisms by fitting experimental data (Sarfaraz et al., 2012) show the tendency of fouling mechanism to cake filtration model (Figure 4.9). This model is able to predict the results perfectly with the highest  $R^2$  (Table 4.2).



**Figure 4.9** The mechanism of cake filtration model

Cake filtration model indicates that during the filtration process, particle arrives to the membrane surface and deposits on the previous pollutant particle forming a cake layer. This layer will thicken with time due to particle position (Salahi et al., 2010b, Decloux et al., 2007, Kong and Li, 1999).

**Table 4.2**  $R^2$  obtained for various initial feed oil concentration in terms of four types of Hermia's models

Feed oil concentration (g/L)	$R^2$			
	Complete pore blocking model	Standard pore blocking model	Intermediate pore blocking model	Cake filtration model
0.3	0.872	0.885	0.896	0.916
0.5	0.944	0.960	0.972	0.985
1	0.902	0.967	0.951	0.974

#### 4.4 Summary

The application of polymeric UF membrane for the treatment of oily wastewater generated from restaurant industry and oil in water emulsion proved to be one of the feasible options. Based on the experimental results, TOC, COD and oil content removal achieved were higher than 91%, 90% and 95%, respectively. The performance of the UF membrane for synthetic oily wastewater treatment was better than treating the raw wastewater one. This can be attributed to the complex compounds such as fat and grease in the raw restaurant oily wastewater. Chemical cleaning application can increase UF membrane flux by rinsing fouling layer on the surface and in the pores of membrane. Hermia's models can be used to describe fouling mechanism during filtration process. Cake filtration model tends to be considerable due to its higher correlation coefficient value. This model indicates that during filtration, the oil pollutant arriving to the membrane surface deposits on other oil pollutant forming a cake layer and thickens with time.

## **CHAPTER 5**

### **The Efficiency of Photo-Fenton Process for TOC and COD Removal from Industrial Oily Wastewater**



## 5.1 Introduction

In this chapter, the application of photo-Fenton process for oily wastewater purification including the effect of different operating conditions and kinetic modelling were studied. Although photocatalytic investigations based on Fenton reaction have been widely reported, there are only a few studies that focus on the investigation of Fenton's reagent consisting of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  decomposition during photocatalytic reaction and use of different light irradiation sources with almost no study on raw canola oil wastewater (COW). This COW was chosen as oily wastewater sample due to its large production in Australia.

Canola oil has several applications such as basic material for candles, inks, medicine application, biodiesel and cooking oil (Jenab et al., 2014). Similar to other edible oil industries, the COW production processes include crushing, degumming, neutralization, deodorization and refining. These steps can be the sources of oily wastewater discharge containing organic pollutant matter. Several treatment methods have been applied for oily wastewater such as adsorption, chemical, biological and filtration (Lucas and Peres, 2009). Unfortunately, some disadvantages of these techniques such as the phase transference of pollutant that needed a post-treatment, reaction time and the requirement of specific space need to be solved by applying more effective and efficient ways.

Recently, advanced oxidation processes (AOPs) are the preferred alternative treatment due to its capability for organic compounds mineralization. AOPs mostly characterized by hydroxyl radicals production that are responsible for degrading the organic pollutants to water, carbon dioxide and other harmless products. Fenton ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  or  $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ ), electrochemical oxidation, photo-Fenton

( $\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{Fe}^{3+}/\text{UV}$ ), electrochemical and photocatalysis ( $\text{TiO}_2/\text{O}_2$ ,  $\text{O}_3/\text{H}_2\text{O}_2$ ,  $\text{O}_3/\text{UV}$ ,  $\text{H}_2\text{O}_2/\text{UV}$ ) are examples of AOPs used in various industrial wastewater (Andreozzi et al., 1999). These AOPs (electrochemical, catalytic oxidation, solar photo-Fenton, catalytic wet oxidation and photocatalytic degradation) are also effective and efficient methods to treat oily wastewater including petroleum refinery and oil in water emulsion (Saien and Nejati, 2007, Pariente et al., 2010). The AOPs offer several advantages such as the complete mineralization of the organic contaminants (Salaices et al. 2004). Among the AOPs, the photocatalytic degradation using Fenton and photo-Fenton has been applied for mineralizing organic contaminants presented in the oily wastewater due to their simple method and high efficiency in pollutant removal without significant drawbacks except the cost of energy (Oppenländer, 2007, Pignatello et al., 1999, Torrades and García-Montaña, 2014, Elmorsi et al., 2010). The use of natural solar light can effectively reduce the operating cost. Related to Fenton's based reaction, most of the published studies were conducted using UV light as a source of irradiance for different industrial wastewater treatment. For instance, the treatment of the oily wastewater generated from palm oil refinery that was conducted using UV light irradiation - Fenton technique (Leong and Bashah, 2012). This study concluded that more than 70 % COD removal efficiency can be achieved under various temperatures. Other authors (Ahmed et al., 2011) applied UV light - Fenton to treat oily wastewater from olive oil plant. They reported that after 3 h of photo-Fenton reaction, almost complete color and aroma removals were achieved at optimum condition;  $\text{H}_2\text{O}_2$  3 g/L,  $\text{Fe}^{2+}$  30 mg/L, pH 3 and temperature 26 °C. For the comparison of Fenton and photo Fenton efficiency, an investigation has been conducted and revealed that photo-Fenton was more efficient than Fenton reaction stand-alone due to more hydroxyl radicals production (Torrades and García-Montaña, 2014).

Photo-Fenton achieved higher COD removal of 76.3 % compared to of 62.9 % achieved by Fenton. Furthermore, the application of UV-Fenton and ferrioxalate/peroxide/sunlight for dyes wastewater treatment found that decolourization and TOC removal were over 90 % and 29 %, respectively (Lucas and Peres, 2007). The examination of photo-Fenton ability to treat dark brown colored coffee wastewater showed that decolourization using natural solar irradiation was comparable to that using UV light irradiation (Tokumura et al., 2008). Oily lubricant wastewater was also treated by using photo-Fenton (Philippopoulos and Pouloupoulos, 2003). The study reported that the COD removal of over 40 % was achieved.

Although increasing interest has been devoted to photocatalytic degradation, the treatment of raw agro-oily wastewater by using photo-Fenton and the study of Fenton's reagent decomposition need to be further investigated. Therefore, the aims of this work are to: (i) Investigate the photo Fenton treatment of the raw canola oil wastewater under different operating conditions. (ii) Study the profiles of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and ferrous ion ( $\text{Fe}^{2+}$ ) decomposition during the light irradiation. (iii) Evaluate the influence of different light sources, natural solar light and artificial lights, which are still limited in the literature. The performance of the photo-Fenton method will be assisted through monitoring TOC and COD reductions.

## **5.2 Materials**

### ***5.2.1 Canola oil wastewater (COW)***

Oily wastewater sample, Canola oil wastewater (COW), was collected from Australian edible oil factory, located in Perth, Western Australia. The COW sample was filtered through a sieve to remove solid particles of millimeter size. Filtered oily wastewater sample was characterized for pH, TOC, COD and oil content concentration.

Then, it was stored at 4 °C for further experiment. The characterization of the wastewater is presented in Table 5.1.

**Table 5.1** Characteristics of canola oil wastewater (COW)

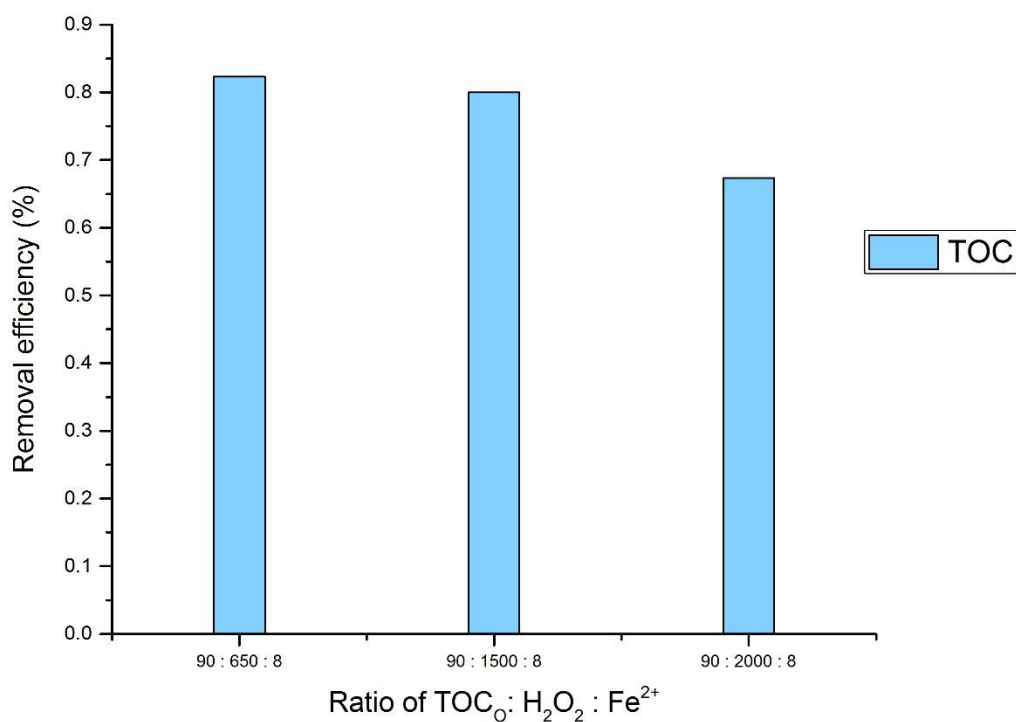
<b>Parameter</b>	<b>Value</b>
COD (mg/L)	330
TOC (mg/L)	90
Oil (mg/L)	250
pH	9

More detail of experimental set up and analytic procedure can be seen in Chapter 3.

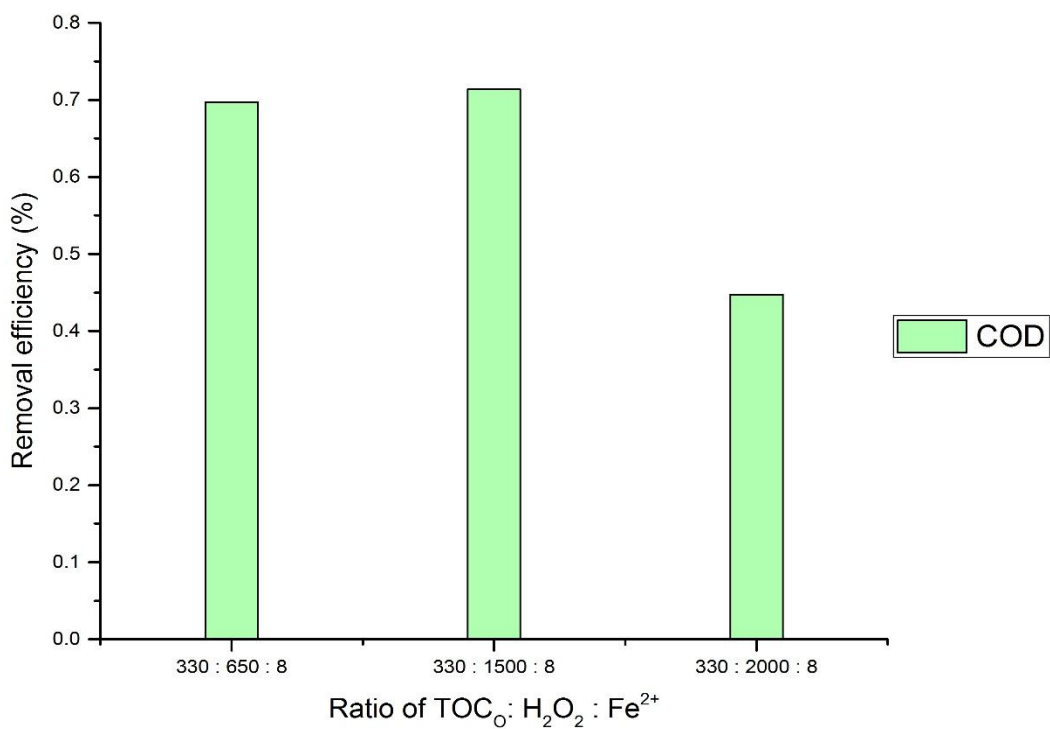
## **5.3 Results and discussion**

### **5.3.1 Effect of H<sub>2</sub>O<sub>2</sub> concentration**

The concentration of oxidant has significant influence on the rate of photocatalytic oxidation. This primary oxidant is responsible for highly reactive hydroxyl radical production that dictates the overall efficiency of degradation (Babuponnusami and Muthukumar, 2014). To evaluate the effect of H<sub>2</sub>O<sub>2</sub> on the oily wastewater treatment, experiments were performed at different H<sub>2</sub>O<sub>2</sub> concentrations, 650 mg/L, 1500 mg/L and 2000 mg/L. The operating conditions that include 8 mg/L of Fe<sup>2+</sup> concentration using natural solar light irradiation for 100 min were kept constant. The obtained results are demonstrated in Figures 5.1 – 5.2. These figures clearly show the influence of H<sub>2</sub>O<sub>2</sub> on the removal efficiency of both TOC and COD of the canola oil wastewater.



**Figure 5.1** Effect of  $\text{H}_2\text{O}_2$  concentration on TOC removal using natural solar light irradiation (pH: 3,  $\text{Fe}^{2+}$  : 8 mg/L, t: 100 min)



**Figure 5.2** Effect of  $\text{H}_2\text{O}_2$  concentration on COD removal using natural solar light irradiation (pH: 3,  $\text{Fe}^{2+}$  : 8 mg/L, t: 100 min)

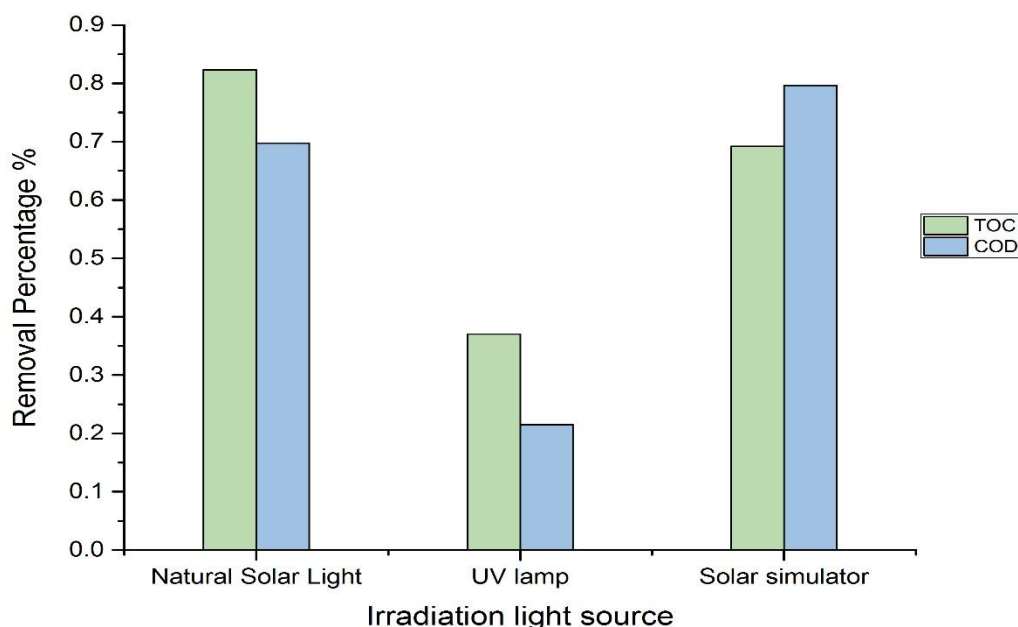
Increasing H<sub>2</sub>O<sub>2</sub> concentration from 650 to 1500 mg/L has no significant effect on the removal efficiency of both TOC and COD. However, further increase of the H<sub>2</sub>O<sub>2</sub> concentration to 2000 mg/L have reduced the removal efficiency to 67.33 % and 44.72 % for both TOC and COD, respectively. However, others reported higher pollutant degradation with higher H<sub>2</sub>O<sub>2</sub> dosage (Lin and Lo, 1997, Kang and Hwang, 2000). Excessive peroxide dosage can contribute to the scavenging of generated hydroxyl radicals causing negative impact (Ito et al., 1998). The unused portion of oxidant can also cause hydroxyl radicals to be in competition with other organic contaminants decreasing the oxidation efficiency (Elmorsi et al., 2010, Kallel et al., 2009, de Souza et al., 2006, Schrank et al., 2005, Bianco et al., 2011). Therefore, H<sub>2</sub>O<sub>2</sub> concentration should be considered for the highest degradation results. Hydroxyl radicals which are available in the system could be consumed by the excess H<sub>2</sub>O<sub>2</sub> (Nitoi et al., 2013), as follows:



According to the experimental results, the highest rate of TOC and COD reduction occurred in the first 10 min. This is caused by the sufficient amount of peroxide which reacted with Fe<sup>2+</sup> ion to mineralize pollutant. Meanwhile, for longer irradiance time, some oxidant has decomposed causing less TOC and COD reduction (Ebrahiem et al., 2013).

### 5.3.2 Effect of light source

Effect of different light sources on TOC and COD removal efficiency was investigated using natural solar light (intensity  $1450 \mu\text{moles}/\text{m}^2/\text{s}$ ), solar simulator (light intensity  $80 \mu\text{moles}/\text{m}^2/\text{s}$ ) and UV light (light intensity  $45 \mu\text{moles}/\text{m}^2/\text{s}$ ). The operating conditions of Fenton's reagent concentration were  $8 \text{ mg}/\text{L}$  and  $650 \text{ mg}/\text{L}$  for  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$ , respectively. As seen in Figure 5.3, the TOC removal efficiency of raw COW irradiated by natural solar light on a clear day condition is higher than that of both solar simulator and UV lamp irradiation. Meanwhile, the COD removal efficiency of raw COW irradiated by natural solar light is comparable to that of solar simulator and higher than that of UV lamp irradiation. This is caused by higher accumulated energy produced at higher light intensity. Increasing light intensity will increase the catalyst capability to adsorb more photons that can generate more hydroxyl radicals (Lucas and Peres, 2007, Tokumura et al., 2008, Ghaly et al., 2001).



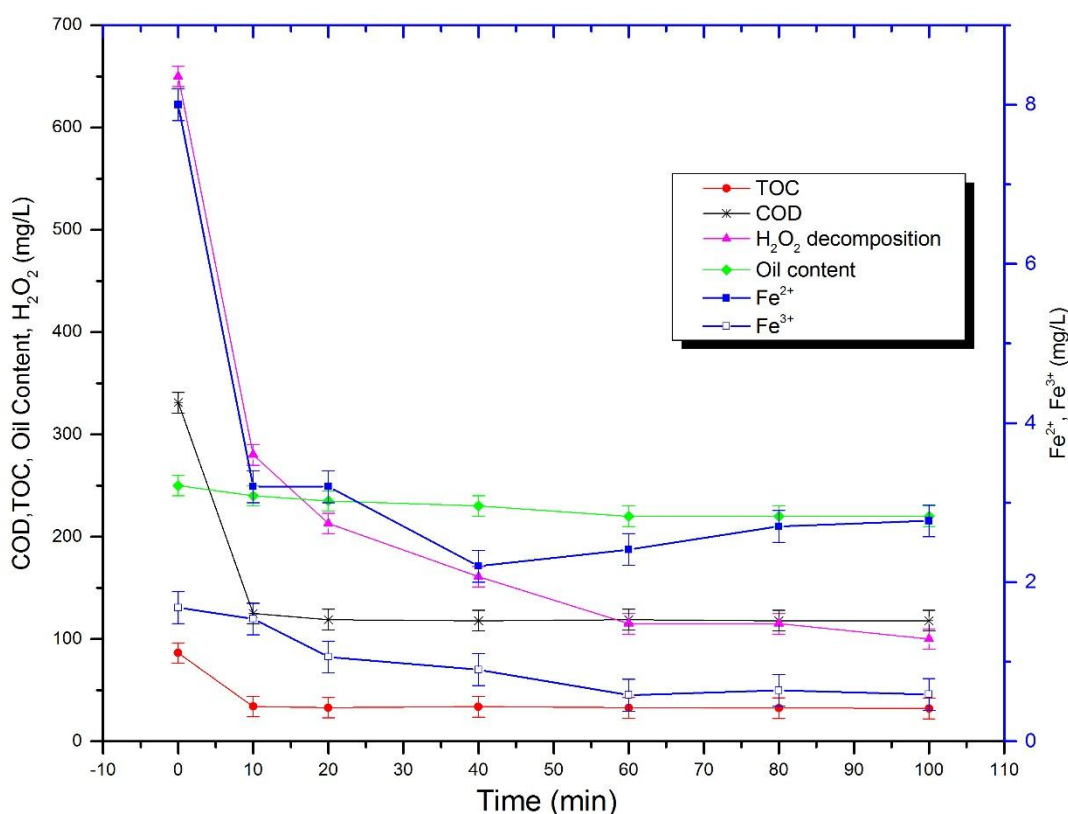
**Figure 5.3** Effect of light source on TOC and COD removal percentage ( $\text{Fe}^{2+}$ :  $8 \text{ mg}/\text{L}$ ,  $\text{H}_2\text{O}_2$ :  $650 \text{ mg}/\text{L}$ , t: 100 min)

The natural solar light consists of radiant energy that is approximately 50 % in the infrared region, 40 % in the visible region and 10 % in the UV region. In addition, the use of sunlight as an irradiation source for photo-Fenton process offers more beneficial cost value than artificial light such as UV and solar simulator that may consume more than 60 % of the total operational cost (Ebrahiem et al., 2013).

### 5.3.3 Typical photo-Fenton oxidation

In order to investigate the photo-Fenton oxidation of the COW, a typical experiment was conducted at  $\text{Fe}^{2+}$  8 mg/L and  $\text{H}_2\text{O}_2$  650 mg/L under natural solar light irradiation.

The experimental results are presented in Figure 5.4.



**Figure 5.4** Photocatalytic degradation profiles of COW using natural solar light and pH 3



According to the Figure 5.4, the highest reduction of TOC and COD occurred in the first 10 min with over 60 % and 58 %, respectively. Then, the removals level off with longer irradiation time. However, photo-Fenton has no significant effect on oil content degradation with only 12 % oil removal. This can be caused by the lack of effectiveness of Fenton reagent to break the strong bond of dissolved oil compound. The use of raw industrial oily wastewater contaminated by various unknown pollutants has also contributed to this low efficiency of oil reduction. Based on the experimental results, 75 % of H<sub>2</sub>O<sub>2</sub> was consumed with more than 50 % in the first 10 min. It means that most of this oxidant was consumed to produce hydroxyl radicals in the system resulting in outstanding performance in reducing organic matter even though it is used at low concentration (Philippopoulos and Pouloupoulos, 2003).

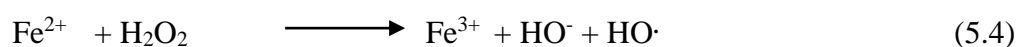
The reaction of peroxide decomposition into oxygen and water can be described by following reaction (Ebrahiem et al., 2013):



On the other hand, as a function of the reaction time, the significant decomposition of Fe<sup>2+</sup> takes place during the first 60 min of irradiation time. This result is caused by the change of Fe<sup>2+</sup> which become ferric ion (Fe<sup>3+</sup>) as a catalyst (Xu et al., 2007).

## 5.4 Reaction mechanism

The mechanism of generating OH radicals with the addition of peroxide has been suggested in several studies and can be described as follow (Guedes et al., 2003, Feng et al., 2003, Lucas and Peres, 2009) :



A range of competitive reactions may possible occur relating the components like ferrous ion ( $\text{Fe}^{2+}$ ), ferric ion ( $\text{Fe}^{3+}$ ),  $\text{H}_2\text{O}_2$ , super oxide and hydroxyl radicals.



Reactive hydroxyl radicals can oxidize the organic substrates (RH) and generate new radical:



The new radical ( $\text{R}^\bullet$ ) will be oxidized by  $\text{Fe}^{3+}$  generating carbon dioxide and water.

This reaction will also reproduce  $\text{Fe}^{2+}$  to warrant the sequence of the chain reaction:



## 5.5 Kinetic modelling

Detailed kinetic study of different individual reactions that occurred during photochemical oxidation is difficult due to the complexity of chemical compounds produced as intermediates. For this particular study, the kinetic modelling is based on the changes in TOC or COD. Fenton based reaction of organic matter can be represented by the following equation (Nieto et al., 2011) :

$$\frac{d[A]}{dt} = -k[A]^n \quad (5.10)$$

Where  $A$  represents TOC or COD,  $n$  is the order of the reaction,  $k$  is the reaction rate COW coefficient and  $t$  is the reaction time. For first- order reaction, the above equation can be rewritten as:

$$\frac{d[A]}{dt} = -k[A] \quad (5.11)$$

The linearized form is,

$$\ln(A_0) - \ln(A) = -kt \quad (5.12)$$

$$\ln\left(\frac{A_0}{A}\right) = -kt \quad (5.13)$$

In this study, both TOC and COD will be treated individually as the pollutant concentration.

For TOC:

$$\ln\left(\frac{TOC_0}{TOC}\right) = -kt \quad (5.14)$$

And for COD:

$$\ln\left(\frac{COD_0}{COD}\right) = -kt \quad (5.15)$$

Furthermore, the integration of the second order reaction is presented as following:

$$\frac{d[A]}{dt} = -k[A]^2 \quad (5.16)$$

Then linearized equation form yields:

$$-\frac{1}{[A]} = \frac{1}{[A]_0} + kt \quad (5.17)$$

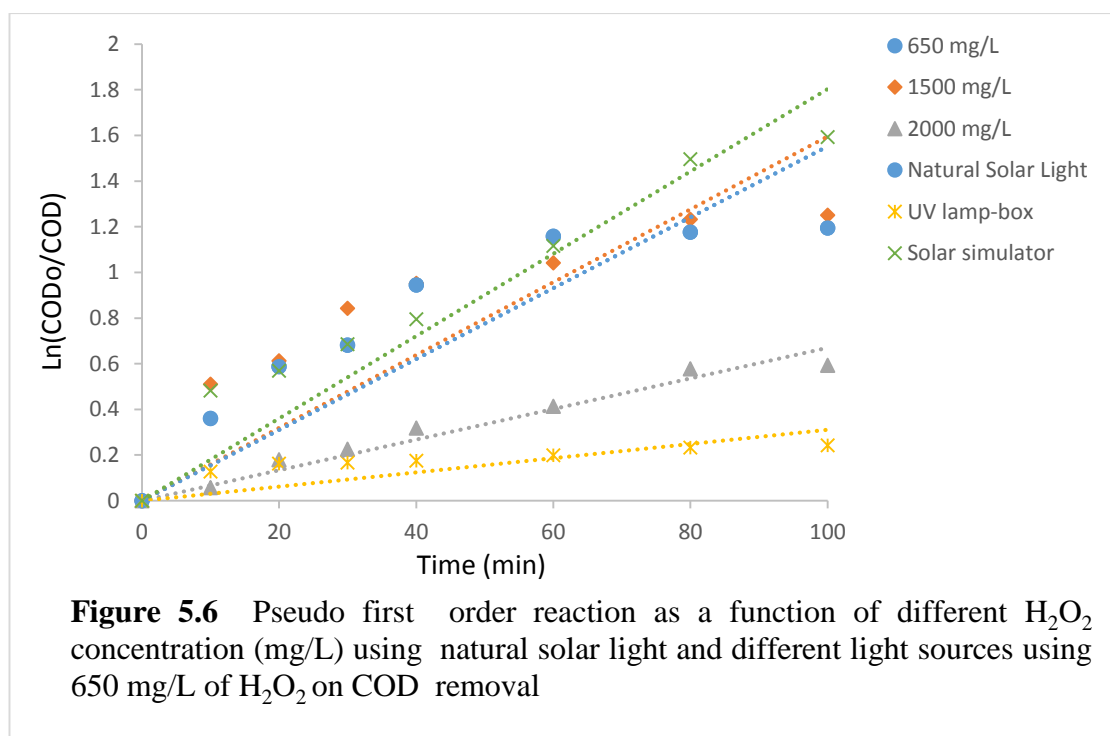
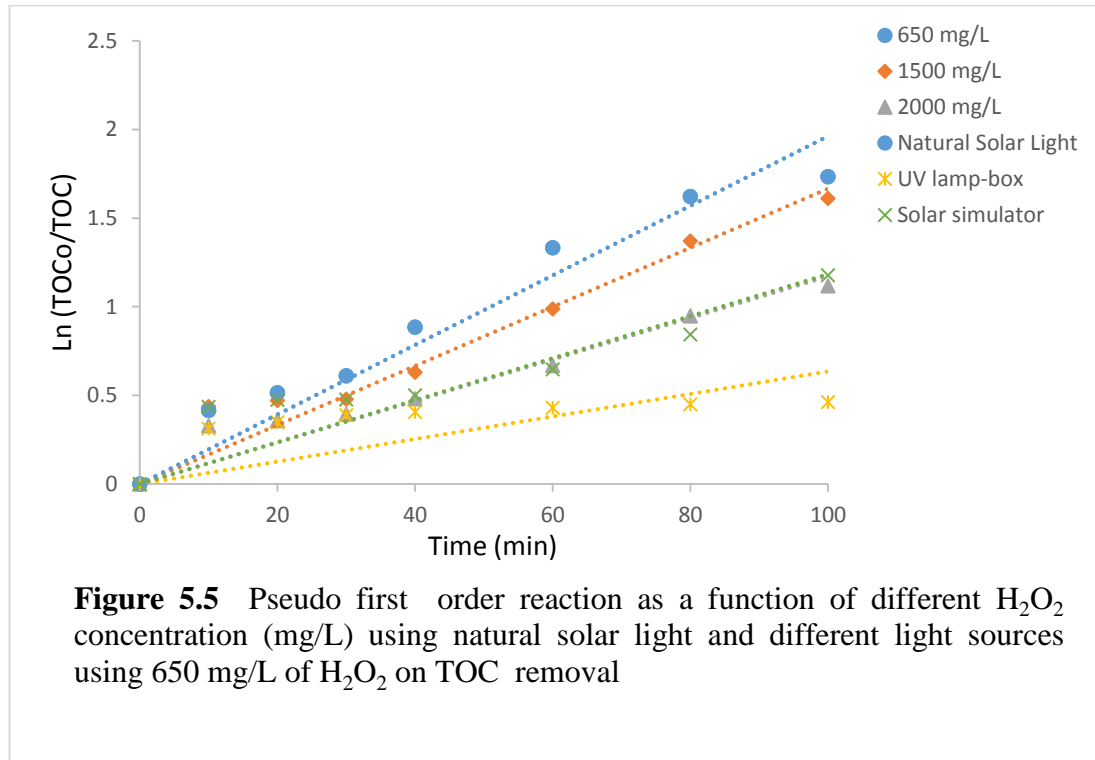
In terms of TOC, COD and the integration between  $t = 0$  and  $t = t$ , equation (5.17)

becomes 5.18 and 5.19, respectively:

$$\frac{1}{COD} - \frac{1}{COD_0} = kt \quad (5.18)$$

$$\frac{1}{TOC} - \frac{1}{TOC_0} = kt \quad (5.19)$$

These linearized forms were used to design the graphs of order reaction as showed in Figures 5.5 – 5.10. Then, the calculation of  $R^2$  and  $k$  values (Table 5.2 – 5.5) can be obtained.

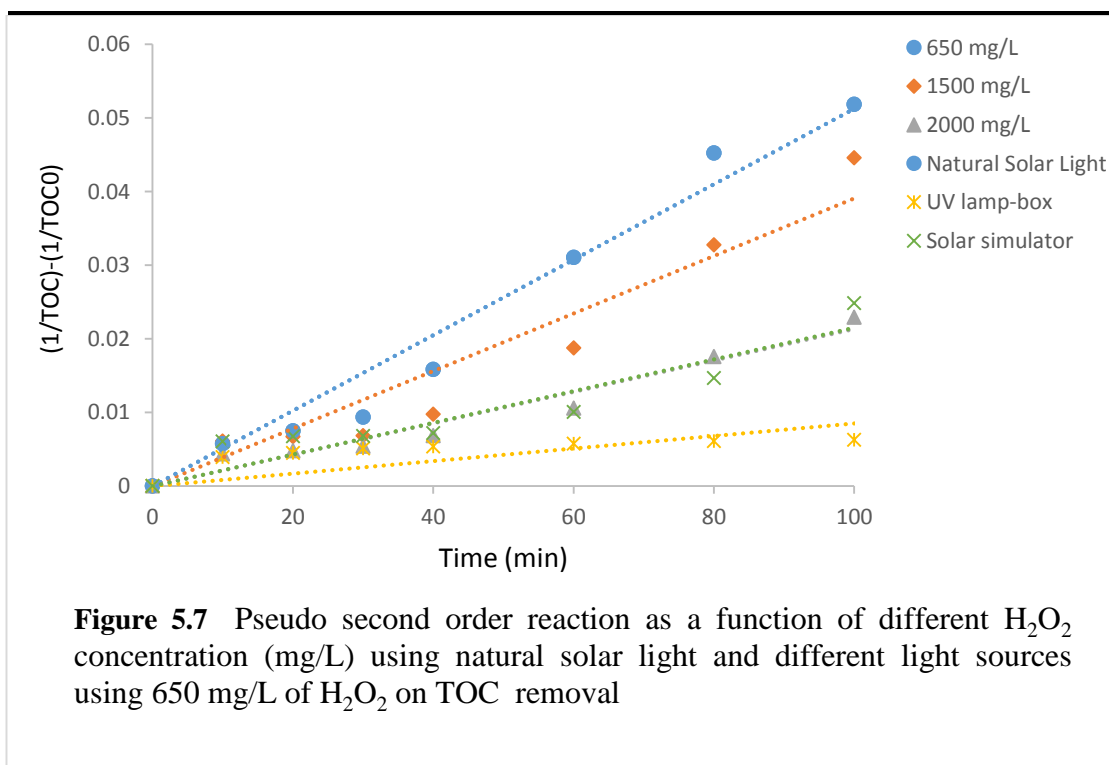


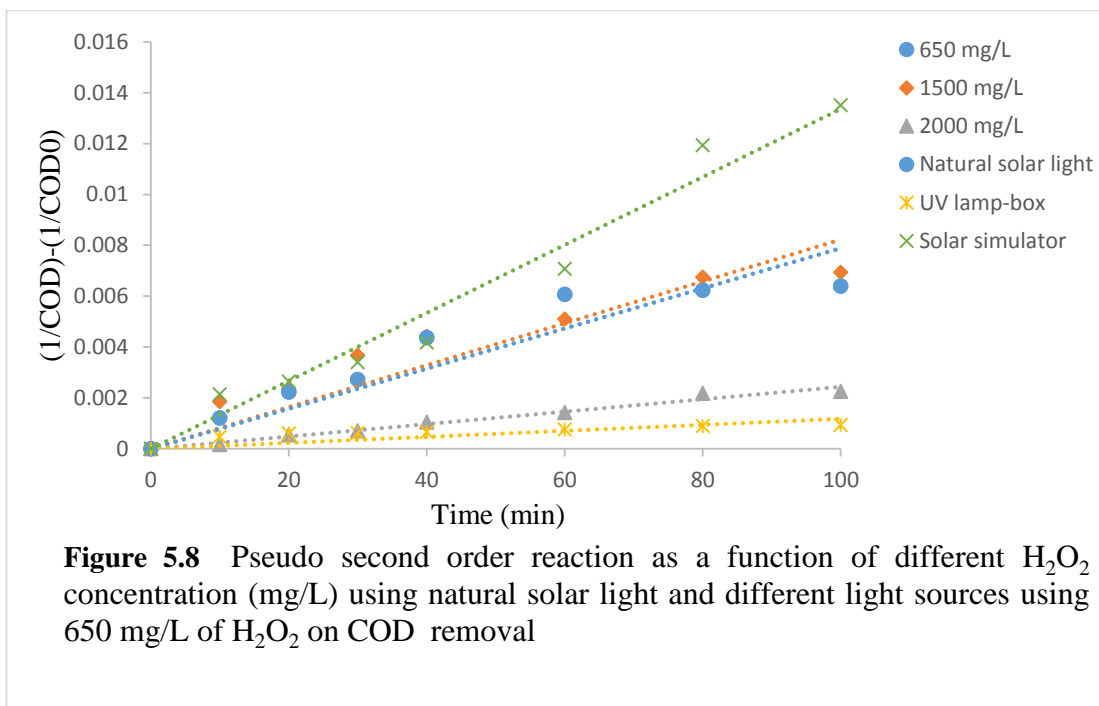
**Table 5.2** First order constant ( $k$ ) and least squares regression ( $R^2$ ) for different  $H_2O_2$  concentrations

Parameter		TOC		COD	
Light source	$H_2O_2$ concentrations (mg/L)	$k$ value (1/mg/L.min)	$R^2$	$k$ value (1/mg/L.min)	$R^2$
Natural solar light	650	$1.96 \times 10^{-2}$	0.942	$1.55 \times 10^{-2}$	0.657
	1500	$1.67 \times 10^{-2}$	0.950	$1.60 \times 10^{-2}$	0.538
	2000	$1.18 \times 10^{-2}$	0.768	$6.70 \times 10^{-3}$	0.962

**Table 5.3** First order constant ( $k$ ) and least squares regression ( $R^2$ ) for different light sources

Parameter		TOC		COD	
$H_2O_2$ concentration (mg/L)	Light source	$k$ value (1/mg/L.min)	$R^2$	$k$ value (1/mg/L.min)	$R^2$
650	Natural solar light	$1.96 \times 10^{-2}$	0.942	$1.55 \times 10^{-2}$	0.657
	UV light	$6.3 \times 10^{-3}$	0.329	$3.10 \times 10^{-3}$	0.200
	Solar simulator	$1.17 \times 10^{-2}$	0.927	$1.8 \times 10^{-3}$	0.895





**Table 5.4** Second order constant ( $k$ ) and least squares regression ( $R^2$ ) for different H<sub>2</sub>O<sub>2</sub> concentrations

Parameter		TOC		COD	
Light source	H <sub>2</sub> O <sub>2</sub> concentrations (mg/L)	$k$ value (1/mg/L.min)	$R^2$	$k$ value (1/mg/L.min)	$R^2$
Natural solar light	650	$5 \times 10^{-4}$	0.968	$8 \times 10^{-5}$	0.855
	1500	$4 \times 10^{-4}$	0.982	$8 \times 10^{-5}$	0.853
	2000	$2 \times 10^{-4}$	0.959	$2 \times 10^{-5}$	0.980

**Table 5.5** Second order constant ( $k$ ) and least squares regression ( $R^2$ ) for different light sources

Parameter		TOC		COD	
H <sub>2</sub> O <sub>2</sub> concentration (mg/L)	Light source	$k$ value (1/mg/L.min)	$R^2$	$k$ value (1/mg/L.min)	$R^2$
650	Natural solar light	$5 \times 10^{-4}$	0.968	$8 \times 10^{-5}$	0.855
	UV light	$8 \times 10^{-5}$	0.354	$1 \times 10^{-5}$	0.303
	Solar simulator	$2 \times 10^{-4}$	0.975	$1 \times 10^{-4}$	0.970

In the view of the results, for both parameters analyzed, H<sub>2</sub>O<sub>2</sub> concentration and light source, the second order kinetic model which is determined by the concentration of two chemical reactants involved or the concentration square of one chemical reactant has better correlation COV coefficient ( $R^2$ ) than the first order kinetic model. This assumes that the rate limiting step might be due to the chemical adsorption or reaction. Therefore, the kinetic model of this photocatalytic process follows the second order reaction.

## 5.6 Summary

In this work, the efficiency of photo-Fenton process was investigated for canola oil wastewater treatment under different operating conditions of H<sub>2</sub>O<sub>2</sub> concentration and light source. Experimental results showed that this method is effective and efficient to treat raw canola oil wastewater, especially for TOC and COD removal. TOC and COD removal percentage can achieve more than 82 % and 70 %, respectively, after 80 min irradiance of natural solar light, pH 3, H<sub>2</sub>O<sub>2</sub> 650 mg/L and Fe<sup>2+</sup> 8 mg/L. The kinetic experiment analysis proved that this process follows second order reaction. The result showed that 50 % of H<sub>2</sub>O<sub>2</sub> was consumed in the first 10 min then increased to 75 % at the end of the experiment (100 min). The results also showed that only 12 % of oil content removal can be achieved under the above conditions which make the photo-Fenton process better candidate as a pretreatment process for integrated membrane system.

## **CHAPTER 6**

# **Eucalyptus Bark as an Efficient and Cost Effective Biosorbent for Oily Wastewater Treatment**



## 6.1 Introduction

This chapter will investigate the effectiveness of the biosorption for oil content removal from the restaurant oily wastewater (ROW). Different organic waste materials, such as eucalyptus bark, watermelon shell, and chicken bone, will be applied in this study for the first time for oily wastewater treatment. ROW usually generated from several restaurant activities such as cleaning and cooking food, washing dishes and kitchen utensils (Kang et al., 2011, Zulaikha et al., 2014).

Oils can be categorized into two types, free oils and emulsified oils. Free oil is easily removed from water using a suitable physical treatment such as BAF (bubble air floatation) and skimming. However, removing the emulsified oil is a great challenge due to its stability in the aqueous phase (Angelova et al., 2011). In order to remove the emulsified oil from oily wastewater, adsorption process using biomaterials has been conducted due to several advantages such as simplicity, relatively lower processing cost, highly biodegradable and good removal percentage (Ibrahim et al., 2009, Ahmad et al., 2005). Different cost effective materials have also been applied for oil content removal from oily wastewaters (Table 6.1) such as cotton grass fiber (Suni et al., 2004), sago bark (Wahi et al., 2014), barley straw (Ibrahim et al., 2010), natural wool fibers (Rajakovic et al., 2007), walnut shell (Srinivasan and Viraraghavan, 2008), chitosan (Ahmad et al., 2005), silkworm cocoon waste (Moriwaki et al., 2009) sugarcane bagasse (Sun et al., 2004) and palm shell (Ngarmkam et al., 2011).

**Table 6.1** Different adsorbent materials for oil content removal from oily wastewater

<b>Adsorbent</b>	<b>Oily wastewater type</b>	<b>Results</b>	<b>Reference</b>
Modified Barley straw	Canola oil	Adsorption capacity: 44 mg/g, Adsorbent dosage: 1.3 g/L, Oil removal efficiency: 94 %, Sorption time: 60 min, pH: 6.0–8.0	(Ibrahim et al., 2010)
Natural wool fibers	Diesel oil	Adsorption capacity: 430 mg/g, Adsorbent dosage: 0.04 g/L, Oil removal efficiency: 95 %, Sorption time: 30 min, pH: 8.0	(Rajakovic et al., 2007)
Sugarcane bagasse	Emulsified machine oil	Adsorption capacity: 680 mg/g, Sorption time: 60 min	(Sun et al., 2004)
Walnut shell	Standard mineral oil	Adsorption capacity: 560 mg/g, Sorption time: 60 min	(Srinivasan and Viraraghavan, 2008)
Walnut shell	vegetable oil	Adsorption capacity: 0.58 g/g, Sorption time: 60 min	(Srinivasan and Viraraghavan, 2008)
Chitosan (flake)	Palm oil mill wastewater	Adsorbent dosage: 2 g/L, Sorption time: 30 min, Oil removal efficiency: 99 %, Mixing rate: 100 rpm, pH: 4.0–5.0	(Ahmad et al., 2005)
Cotton grass fiber	Refinery wastewater	Adsorption capacity: 1700 mg/g, Adsorbent dosage: 1 g/L, Oil removal efficiency: 89 %, Sorption time: 120 min	(Suni et al., 2004)
Chitosan (powder)	Palm oil mill wastewater	Adsorbent dosage: 0.5 g/L, Sorption time: 30 min, Oil removal efficiency: 99 % pH: 4.0–5.0	(Ahmad et al., 2005)
Palm shell activated carbon	Palm oil mill wastewater	Adsorption capacity: 33 mg/g Adsorbent dosage: 80 g/L Sorption time: 24 h, Oil removal efficiency: 85 % pH: 4.5	(Ngarmkam et al., 2011)
Palm shell carbon magnetic composite	Palm oil mill wastewater	Adsorption capacity: 100 mg/g, Adsorbent dosage: 80 g/L, Oil removal efficiency: 90 %, Sorption time: 24 h,	(Ngarmkam et al., 2011)
Sago bark	Palm oil mill wastewater	Adsorbent dosage: 17.5 g/L, Sorption time: 30 min, Oil removal efficiency: 45 % Mixing rate: 125 rpm, pH: 4	(Wahi et al., 2014)
Bentonite	Palm oil mill wastewater	Adsorbent dosage: 10 g/L, Sorption time: 30 min, Oil removal efficiency: 90 %, pH: 4.0–5.0	(Ahmad et al., 2005)
Silkworm cocoon	Vegetable oil	Adsorption capacity: 1500 m g/g, Sorption time: 10 min, Oil removal efficiency: 54 %	(Moriwaki et al., 2009)

However, it is worthy to introduce and investigate other agro waste materials such as eucalyptus bark and watermelon shell or animal waste material such as chicken bone as efficient and cost effective biosorbents for oil content removal from oily wastewater. To date, eucalyptus bark, watermelon shell and chicken bone have been applied as efficient biosorbents for dyes and heavy metals removal (Morais et al., 1999, Ghodbane et al., 2008, Sarin and Pant, 2006, Afroze et al., 2015, Znad and Frangeskides, 2014). However, their application for oil content removal from oily wastewater are still very scarce.

Therefore, this research work was undertaken to explore the potential use of eucalyptus bark (EB), watermelon shell (WS) and chicken bone (CB) as a cost effective and efficient biosorbent for oil removal from raw restaurant oily wastewater. The most effective biosorbent material will be further investigated and characterized under different operating conditions.

## **6.2 Materials and adsorption models**

### ***6.2.1 Restaurant oily wastewater (ROW)***

Raw ROW used was collected from Asian restaurants located in Perth, Western Australia. The sample was filtered through a sieve to remove solid particles of millimeter size. The filtered oily wastewater sample was analyzed for its COD, pH, TDS and oil content concentration (Table 6.2). The sample was stored at 4°C before use in order to minimize sample deterioration.

**Table 6.2** Characteristics of restaurant oily wastewater

Parameters	Values
COD (mg/L)	1100
Oil content (mg/L)	3000
TDS (mg/L)	300
pH	8

More detail of experimental set up and analytic procedure can be seen in Chapter 3.

### 6.2.2 Adsorption isotherm models

In this study, different isotherm models will be applied, including:

#### a. *Freudlich isotherm model.*

This model assumes that the adsorption process occurs on the heterogeneous surface.

It can be formulated with the following equation (Dawood et al., 2013):

$$\ln q_e = \ln k_f + \frac{1}{n} (\ln C_e) \quad (6.1)$$

Where  $q_e$ ,  $C_e$ ,  $k_f$  and  $n$  are the amount of oil adsorbed per unit of adsorbent at equilibrium time (mg/g), the equilibrium oil content concentration in the solution (mg/L), isotherm constant and the adsorption intensity, respectively.

#### b. *Langmuir isotherm model.*

This model assumes that the adsorption takes place onto an ideal homogeneous uniform surface with all sites on the adsorbent surface being equivalent. The linearized form of general Langmuir equation can be expressed as:

$$\frac{C_e}{q_e} = \left( \frac{1}{K_L q_m} \right) + \frac{C_e}{q_m} \quad (6.2)$$

Where  $q_m$  and  $K_L$  are the maximum adsorption capacity (mg/g) and Langmuir constant value related to adsorption energy (L/mg) which are predicted by plotting  $\frac{C_e}{q_e}$  vs  $C_e$ .

**c. Dubinin-Radushkevich model**

This model can be used to describe the adsorption mechanism related to Gaussian energy distribution onto a heterogeneous surface. The linearized form of this model is expressed as (Dubinin and Radushkevich, 1966):

$$\ln q_e = \ln q_m - \beta \epsilon^2 \tag{6.3}$$

Where  $q_e$ ,  $q_m$ ,  $\beta$  and  $\epsilon$  are the amount of oil adsorbed per gram adsorbent at equilibrium (mg/g), the maximum adsorption capacity (mg/g), a constant related to adsorption energy and the Polanyi potential related to the equilibrium concentration, respectively. The value of  $\epsilon$  can be obtained by the following equation:

$$\epsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \tag{6.4}$$

Where R is the gas constant (8.314 J/mol K) and T is the absolute temperature (K).

**6.2.3 Adsorption kinetic models**

To understand the adsorption mechanism, the pseudo first order, pseudo second order and intra particle diffusion models are used and evaluated as explained below.

**a. Pseudo first order and pseudo second order kinetic models.**

Pseudo–first order kinetic model can be linearized in an integral form shown by Equation 6.5 (Lagergren, 1898, Nandi et al., 2009):

$$\log (q_e - q_t) = \log (q_e) - \frac{K_1}{2.303} t \quad (6.5)$$

Where  $q_e$ ,  $q_t$ ,  $K_1$  and  $t$  are the amount of oil adsorbed at equilibrium time (mg/g), oil adsorbed at specific time (mg/g), equilibrium rate constant of pseudo first order adsorption ( $\text{min}^{-1}$ ) and time (min), respectively. The adsorption rate constants  $K_1$  can be calculated from the plot of  $\log (q_e - q_t)$  vs  $t$ .

The pseudo second order kinetic model can be linearized as in Equation 6.6 (Sen and Sarzali, 2008):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (6.6)$$

Where  $K_2$  is the pseudo second order rate constant (g/mg min) that can be estimated by plotting  $\frac{t}{q_t}$  vs  $t$ . Thus, the constant  $K_2$  can be used to obtain the initial sorption rate,  $h$ , at  $t=0$ , as follows:

$$h = k_2 q_e^2 \quad (6.7)$$

The rate constant ( $k_2$ ), initial adsorption rate ( $h$ ) and predicted amount of oil adsorbed at equilibrium time ( $q_e$ ) can be calculated by the plot of  $t/q$  vs  $t$  using Equation (6.6).

#### ***b. Intra particle diffusion model***

This model is generally used for adsorption mechanism identification for design purpose (Sen et al., 2011). For most adsorption process, the uptake varies proportionally with  $t^{1/2}$  rather than with contact time as represented by the following equation (Dawood et al., 2013, Weber and Beck, 1973):

$$q_t = K_{id} t^{0.5} \quad (6.8)$$

Where  $q_t$  (mg/g) is the adsorption capacity at time  $t$ ,  $K_{id}$  (mg/g.min<sup>0.5</sup>) is the rate constant of intra-particle diffusion, and  $t^{0.5}$  (min) is the square root of time. Plotting  $q_t$  vs  $t^{0.5}$  gives a linear relationship and  $K_{id}$  can be decided from the slope of the plot.

**c. Liquid Film Diffusion Model**

In liquid and solid adsorption system, the rate of accumulated solute in the solid phase is equal to that of solute transfer and can be written as follows (Boyd et al., 1947) :

$$\ln\left(1 - \frac{q_t}{q_e}\right) = -K_{fd}t \quad (6.9)$$

Where  $\ln\left(1 - \frac{q_t}{q_e}\right)$  is the fractional attainment of equilibrium and  $K_{fd}$  is the film diffusion rate constant. By plotting  $\ln\left(1 - \frac{q_t}{q_e}\right)$  vs  $t$ , it gives a linear relationship, then,  $K_{fd}$  can be obtained from the slope of the plot.

**d. Double-Exponential Model**

A double exponential function model can be written as follows (Wilczak and Keinath, 1993):

$$q_t - q_e = \exp(-k_1t) - \exp(-k_2t) \quad (6.10)$$

If  $k_1 \gg k_2$ , it means that the rapid process can be assumed to be negligible on the overall kinetics and the linearized form of the equation is:

$$\ln(q_e - q_t) = -k_2t \quad (6.11)$$

Where  $q_t$  and  $q_e$  (mg/g) are adsorption capacity at time  $t$  and at equilibrium respectively,  $K_1$  (min<sup>-1</sup>) is diffusion parameters of the rapid step and  $K_2$  for the slow step. Plotting  $\ln(q_e - q_t)$  vs  $t$  gives a linear relationship,  $K_2$  can be obtained from the slope of the plot.

#### 6.2.4 Thermodynamic study

To study the feasibility of adsorption process with respect to the temperature, thermodynamic analysis can be applied to determine parameters such as Gibb's free energy ( $\Delta G^o$ ), enthalpy change ( $\Delta H^o$ ) and entropy change ( $\Delta S^o$ ) using the following equation:

$$\Delta G^o = -RT \ln K_d \quad (6.12)$$

Where,

$$K_d = \frac{q_e}{c_e} \quad (6.13)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (6.14)$$

Combining Equations 6.12 and 6.14 resulted in:

$$\ln k_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (6.15)$$

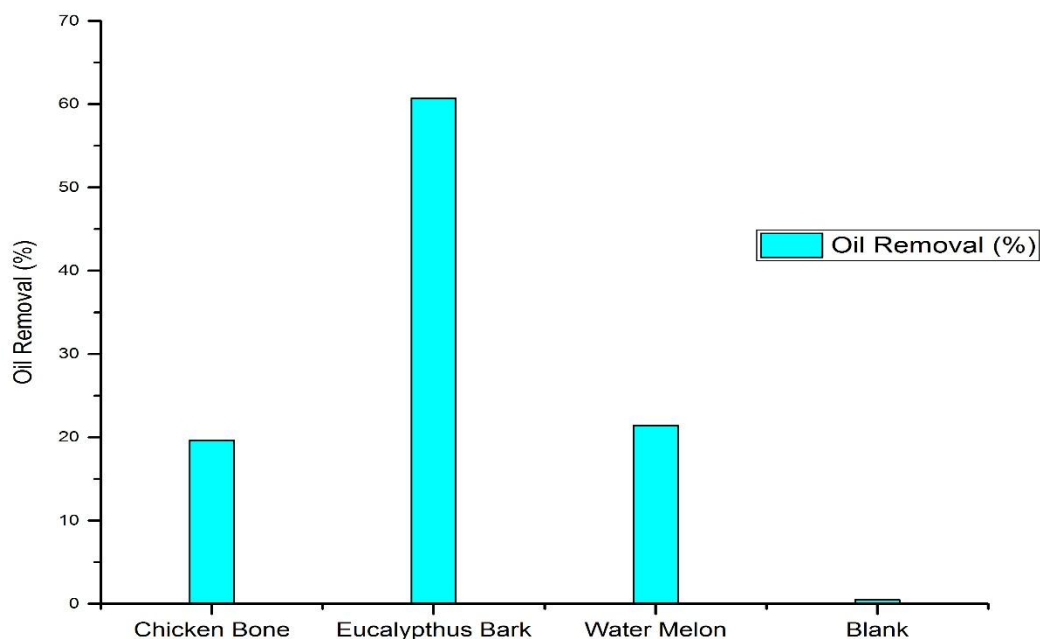
Where  $q_e$ ,  $C_e$ ,  $T$ , and  $R$  are the adsorption capacity at equilibrium (mg/g), equilibrium concentration (mg/L), temperature (K) and gas constant (8.314 J/mol K), respectively. The intercept and slope from the plot of  $\log (q_e/C_e)$  vs  $1/T$  resulted in entropy change ( $\Delta S^o$ ) and enthalpy change ( $\Delta H^o$ ). Gibb's free energy can be used to calculate the maximum work performed in the thermodynamic system. Entropy change applies whether the process is reversible or irreversible. Meanwhile, enthalpy change describes the amount of heat evolved or absorbed in a reaction system carried out at constant pressure.



## 6.3 Results and discussion

### 6.3.1 Preliminary experiment

To investigate the effectiveness of different agro waste materials, such as eucalyptus bark (EB), watermelon shell (WS), and chicken bone (CB), as a cost effective biosorbent for oil content removal from ROW, preliminary experiments were conducted in a batch wise at temperature 30 °C, pH 9, contact time 80 min, biosorbent dosage 12.5 g/L and agitation speed of 200 rpm. As can be seen in Figure 6.1, EB shows the best performance by achieving more than 60 % of oil removal percentage, while WS and CB only reach 21 % and 19.5 %, respectively. Therefore, the following sections will focus on EB as biosorbent for oil removal.

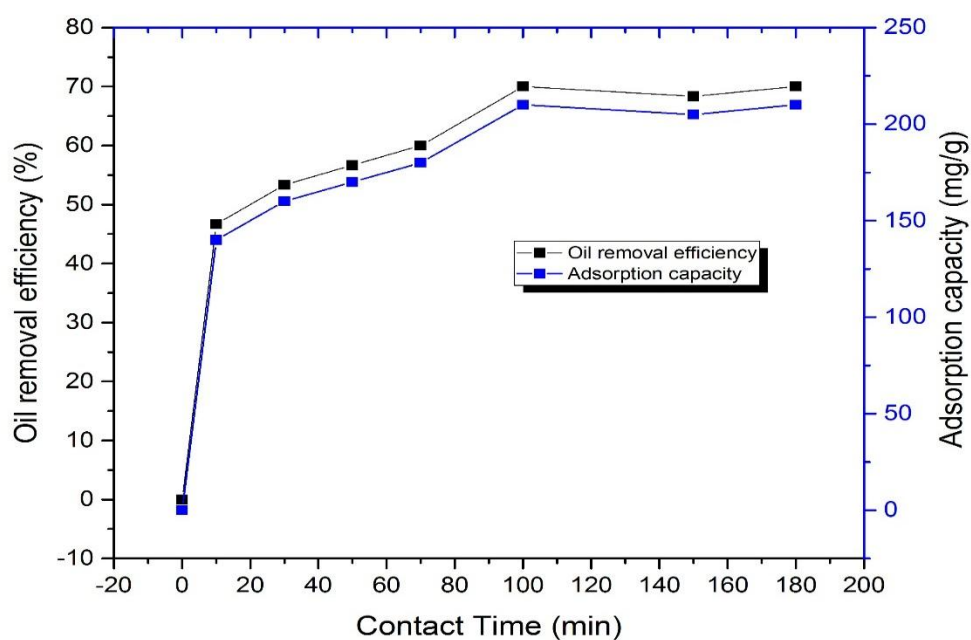


**Figure 6.1** The effectiveness of different waste materials for oil content removal from ROW (pH 9, adsorbent dosage: 12.5 g/L, contact time: 80 min, agitation speed: 200 rpm, T: 30 °C)

### 6.3.2 Effect of contact time

The effect of contact time on oil content removal efficiency and adsorption capacity of EB was investigated under the conditions of pH 3, temperature 30 °C, agitation

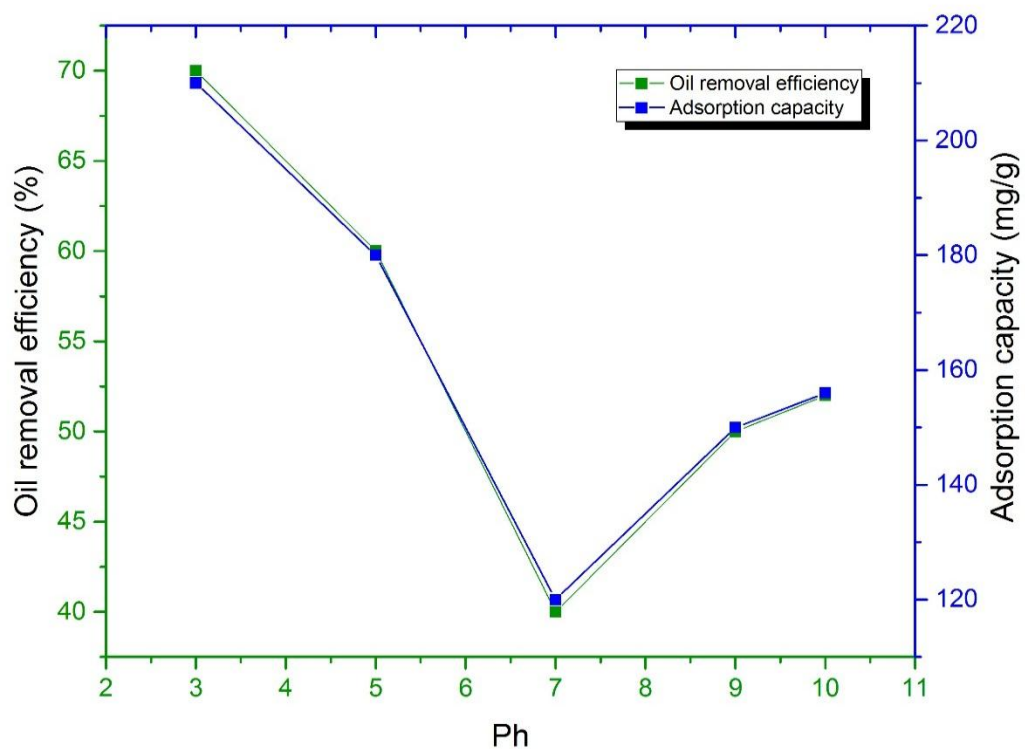
speed 200 rpm and 10 g/L adsorbent dosage. According to the experimental results that are depicted in Figure 6.2, oil removal efficiency and adsorption capacity increase with contact time. More than 45 % of oil was removed in the first 10 min due to the large availability of free binding biosorbent sites (Ahmad et al., 2005, Dąbrowski, 2001, Sen et al., 2011). This condition creates more chance of the oil molecules and biosorbent particles to interact with each other. Then, the adsorption process reaches equilibrium level gradually after 100 min. At the equilibrium, the adsorption capacity levelled off at about 215 mg/g and 70 % of oil content removal due to very limited surface available for oil entrapment (Wahi et al., 2014, Srinivasan and Viraraghavan, 2008).



**Figure 6.2** Effect of contact time on oil content removal efficiency and adsorption capacity (EB dosage: 10 g/L, pH: 3, agitation speed: 200 rpm, Temperature: 30 °C)

### 6.3.3 Effect of pH

The solution pH is important parameter because the pH influences surface properties, emulsion breaking, and binding site of biosorbent and wettability behavior (Ibrahim et al., 2009, Sokker et al., 2011). The effect of pH on oil content removal efficiency and adsorption capacity on EB biomass was also investigated at different pH of 3, 5, 7, 9 and 10 and keeping other conditions constant (temperature 30 °C, contact time 100 min, agitation speed 200 rpm and biosorbent dosage 10 g/L). The results are demonstrated in Figure 6.3.

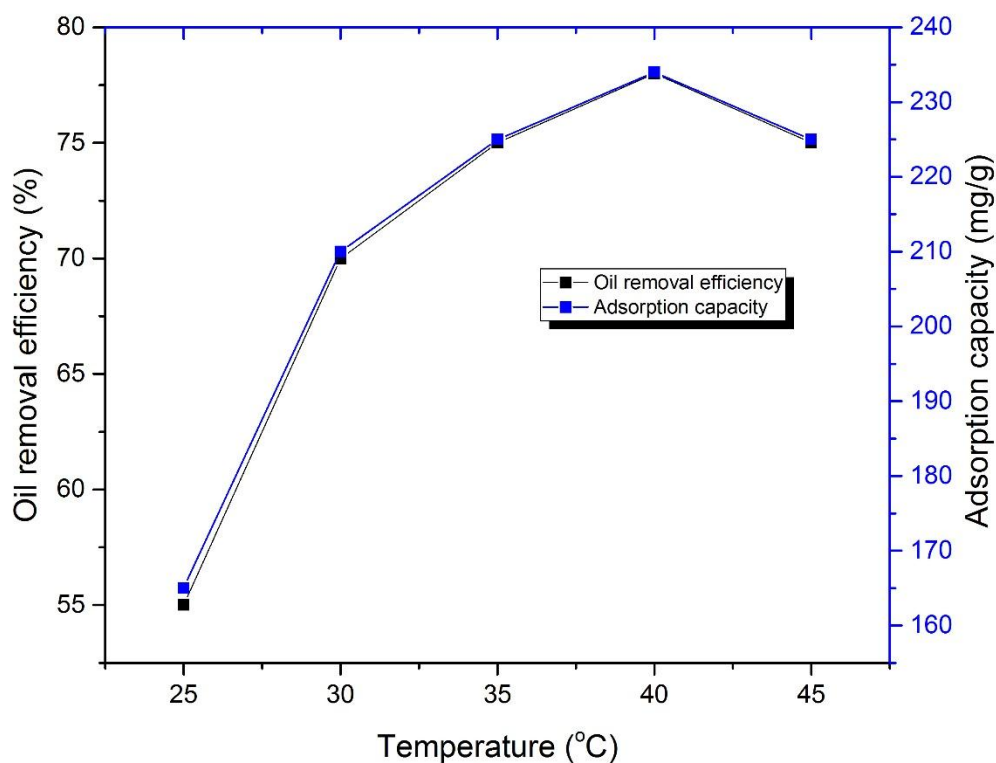


**Figure 6.3** Effect of solution pH on oil content removal efficiency and adsorption capacity (EB dosage: 10 g/L, contact time: 100 min, agitation speed: 200 rpm, Temperature: 30 °C)

In this study, the highest oil content removal and adsorption capacity were observed at pH 3 then decreased with increasing the pH. Acidic pH environment contributes to the process of oil droplets destabilization causing de-emulsification and larger oil droplets formation that enhance oil adsorption onto the adsorbent surface. At the basic pH, 9 and 10, there is the saponification process that will be dominant whereby oil hydrolysis in adsorbate occurs causing lower oil content removal efficiency (Ahmad et al., 2005). On the other hand, near neutral pH, 5 and 7, the values of oil removal and adsorption capacity are lower than acidic or basic solution pH. This can be attributed to the destabilization of biosorbent at neutral pH environment (Rajaković-Ognjanović et al., 2008). By knowing pH influence, the efficiency of adsorbent process can be enhanced. However, there is no need to search for zeta potential and zero point because both of them are more suitable for interfacial double layer adsorption process.

#### ***6.3.4 Effect of temperature***

In order to evaluate the effect of temperature on oil content removal and adsorption capacity, experiments were conducted at different temperatures of 25 °C, 30 °C, 35 °C, 40 °C and 45 °C. The other conditions were set at pH 3, contact time 100 min, agitation speed 200 rpm and EB dosage of 10 g/L. The results are shown in Figure 6.4.

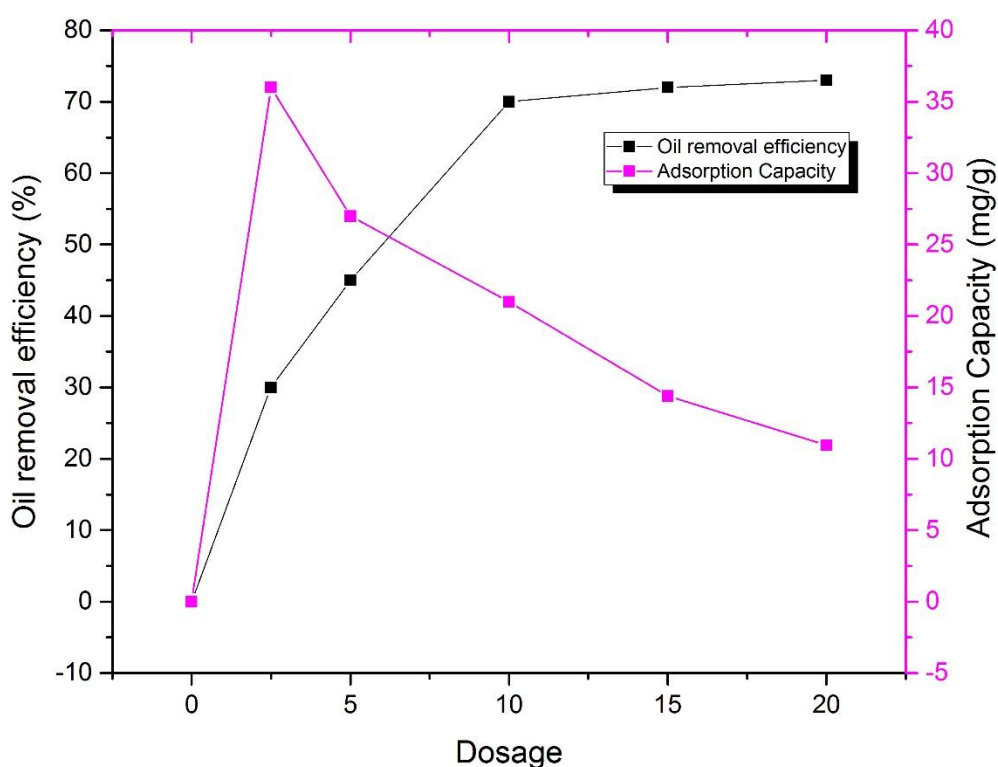


**Figure 6.4** Effect of temperature on oil content removal efficiency and adsorption capacity (EB dosage: 10 g/L, contact time: 100 min, pH: 3, agitation speed: 200 rpm)

It can be seen that increasing temperature increases the performance of EB. At elevated temperatures ( $\geq 30$  °C), there are more than 70 % of oil removal and 240 mg/g of adsorption capacity attained. While at lower temperature (25 °C), there is only less than 60 % of oil removal obtained. At higher temperatures, the interaction during adsorption process can be more effective and intense due to the higher diffusion rate of the adsorbate molecules across the adsorbent surface (Ibrahim et al., 2010, Rajaković-Ognjanović et al., 2008). This can also be considered that the adsorption is physical nature type due to no chemical reaction occurring during the process. Similar results of other low cost biosorbents used for oil removal such as barley straw and chitosan were reported in the literature (Ibrahim et al., 2009, Ahmad et al., 2005).

### 6.3.5 Effect of biosorbent dosage

The effect of biosorbent dosage on the adsorption process was investigated at different EB dosages; 2.5 g/L, 5 g/L, 10 g/L, 15 g/L and 20 g/L. The operating conditions were set up at temperature 30 °C, pH 3, contact time 100 min and agitation speed 200 rpm. The results are shown in Figure 6.5. According to the experimental results, increasing the EB dosage up to 10 g/L significantly enhanced the oil content removal efficiency up to 70 % due to the high availability of the active sites for biosorbent potential binding (Ahmad et al., 2005, Arief et al., 2008). The zero EB dosage represents the blank experiment (experiment without any EB). However, further increasing the EB dosage (> 10 g/L) will level off the oil removal efficiency due to the saturated pores or active sites onto the biosorbent surface (Nghah and Hanafiah, 2008).



**Figure 6.5** Effect of EB dosage on oil content removal efficiency and adsorption capacity (Initial oil concentration: 3 g/L, contact time: 100 min, pH: 3, agitation speed: 200 rpm, temperature: 30 °C)

Experimental results also show that adding more EB (> 2.5 g/L) will reduce the oil adsorption capacity from about 35 mg/g to 10 mg /g. This results was expected for constant oil content concentration (3 g/L) and more biosorbent dosage (2.5 g/L– 20 g/L of EB dosage).

### 6.3.6 Biosorbent characterization

Since EB showed higher performance for oil removal from ROW, its physicochemical characterization was further investigated to get more information regarding the EB specific area, average pore size, functional group, composition and spectrometric surface morphology. The analysis results which are obtained by both of experimental work and literature review are presented in Table 6.3.

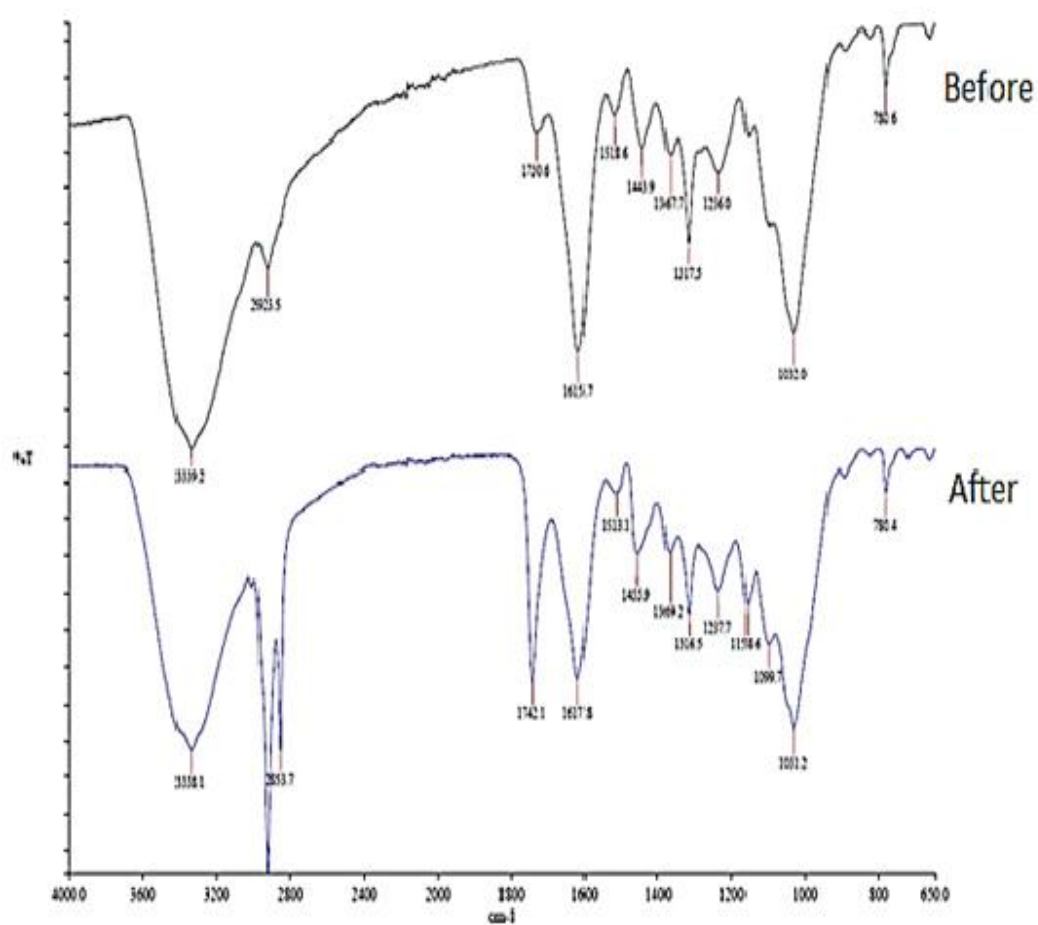
**Table 6.3** Physical-chemical properties of eucalyptus bark (Afroze et al., 2015, Gao et al., 2016)

Parameters	Values
BET surface area (m <sup>2</sup> /g)	6.1178
Total pore volume (cm <sup>3</sup> /g)	0.00355
Average pore size (A°)	18
Nitrogen, N (%)	0.063
Carbon, C (%)	40 - 45
Hydrogen, H (%)	5 – 6
Oxygen, O (%)	35 - 48

This data shows that EB has a good potential use as biosorbent. Elemental analyzer that was applied to determine adsorbent composition proved that the majority elements

of EB are carbon and oxygen, then followed by hydrogen and nitrogen, respectively. This is common in biosorbent materials due to its organic content (Afroze et al., 2015, Dawood et al., 2013).

FTIR analysis which is used to analyze the functional groups on the biosorbent surface was employed before and after adsorption process and the result is presented in Figure 6.6.



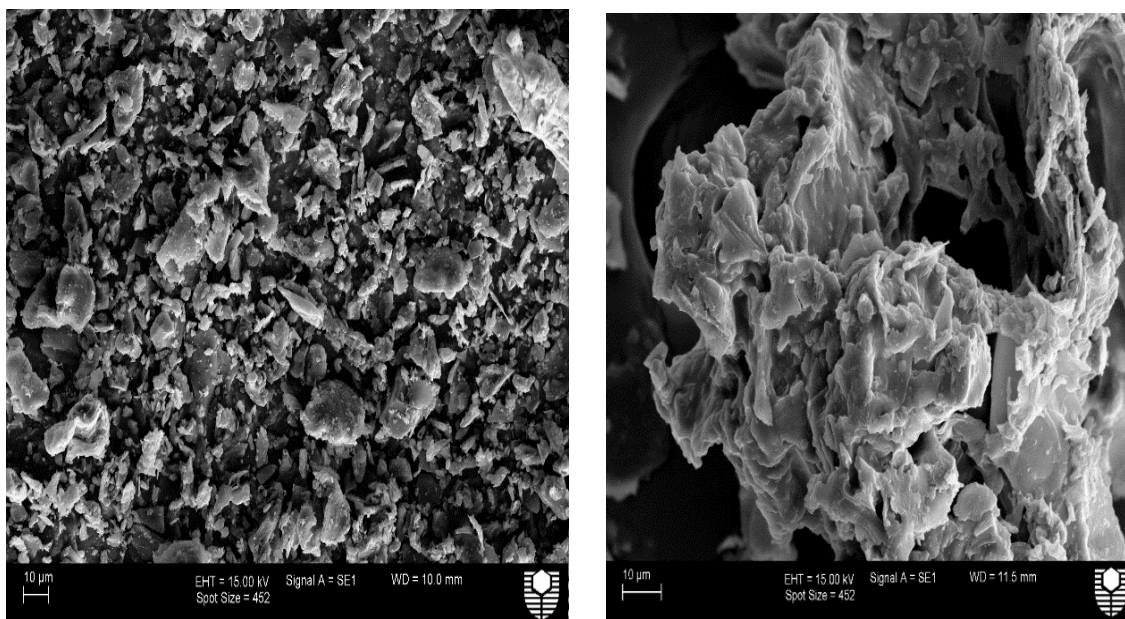
**Figure 6.6** FTIR spectra for eucalyptus bark (EB) before and after adsorption

For raw EB, several peaks were observed such as at  $3339.2\text{ cm}^{-1}$ ,  $2923.5\text{ cm}^{-1}$  and  $1730.6\text{ cm}^{-1}$  that are assigned to N – H  $\text{cm}^{-1}$ , C – H  $\text{cm}^{-1}$  and C = O  $\text{cm}^{-1}$  stretching, respectively (Absorptions, 1985). Peak at  $1615.7\text{ cm}^{-1}$  is due to N – H bending



vibration. The strong asymmetric stretching N – O is shown at  $1518.6\text{ cm}^{-1}$ . The peaks at  $1443.9\text{ cm}^{-1}$  and  $1367.7\text{ cm}^{-1}$  are attributed to C – H bending vibration of alkenas. Then, the peaks at  $1307.5\text{ cm}^{-1}$ ,  $1236\text{ cm}^{-1}$  and  $780.6\text{ cm}^{-1}$  correspond to C – O, C – N and C – Cl stretching (Groups, 1875), respectively. Furthermore, in general, the FTIR spectrum of used eucalyptus bark (after adsorption) shows approximately similar characteristics as raw EB (before adsorption) but with slight difference in the intensity. In used EB spectrum, there are also found two new peaks at  $1742.1\text{ cm}^{-1}$  and  $1158.6\text{ cm}^{-1}$  indicating C = O stretching and C – H bending vibration of alkyl halides, respectively (Absorptions, 1985).

To study the morphology of EB, scanning electron micrograph (SEM) before and after adsorption process is applied and shown in Figure 6.7 (a) and (b), respectively.



**Figure 6.7** SEM analysis of EB adsorbent (a) Fresh EB, (b) used EB

EB has pores that are amorphous carbon with non-crystalline structure. Then, after oil adsorption process, the surface and pores of EB appear as sticky and blurred material that can be assumed as the influence of adsorbed or trapped oil from the oily wastewater.

### 6.3.7 Adsorption isotherm

In this study, three isotherm models were employed namely Langmuir, Freudlich and Dubinin-Radushkevich isotherm models (Table 6.4) to understand the mechanism of oil removal by adsorption process. The correlation coefficient,  $R^2$ , is used as a parameter of isotherm model applicability. According to Table 6.4, Dubinin-Radushkevich isotherm model is found to be the best fitting for the adsorption of oil onto EB surface with  $R^2$  value of 0.87. Meanwhile, Langmuir and Freudlich isotherm models expressed lower linear regression coefficient. Dubinin-Radushkevich isotherm that has often successfully fitted high solute activities is generally applied to represent the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface (Dada et al., 2012). The maximum adsorption capacity ( $q_m$ ) was found to be 401 mg/g.

**Table 6.4** Langmuir, Freudlich and Dubinin-Radushkevich isotherm constant

<i>Langmuir</i>	
$K_L$ (L/mg)	$4.77806 \cdot 10^{-5}$
$q_m$ (mg/g)	3333.3333
$R^2$	0.7511
<i>Freudlich</i>	
$K_f$	0.187645638
$N$	1.012248203
$R^2$	0.8312
<i>Dubinin-Radushkevich</i>	
$q_m$ (mg/g)	401.0154679
$\beta$	0.1187
$R^2$	0.8693

### 6.3.8 Adsorption kinetic modelling

To analyze biosorbent performance in this study, different kinetic models including pseudo first order, pseudo second order, intra particle diffusion, liquid film diffusion and double exponential models (Table 6.5) were applied.

**Table 6.5** Adsorption kinetic models

<i>Pseudo first order model</i>	
$Q_e$ experimental (mg/g)	210
$Q_e$ calculated (mg/g)	130.11
$K_1$ ( $\text{min}^{-1}$ )	-0,053
$R^2$	0.791
<i>Pseudo second order model</i>	
$Q_e$ calculated (mg/g)	222.22
$K_2$ (mg/gmin)	0.0004
$R^2$	0.995
$h$ (mg/gmin)	20.491
<i>Intra-particle diffusion model</i>	
$K_{id}$ ( $\text{min}^{-1}$ )	7.161
$R^2$	0.914
<i>Liquid film diffusion model</i>	
$K_{fd}$ ( $\text{min}^{-1}$ )	-0.019
$R^2$	0.984
<i>Double exponential model</i>	
$K_2$ ( $\text{min}^{-1}$ )	-0.019
$R^2$	0.984

The results were presented in Figures 6.8 – 6.12. These models were tested at operating conditions; solution pH 3, temperature 30 °C, agitation speed 200 rpm and EB dosage 10 g/L. The equilibrium adsorption of pseudo second order which is confirmed by performing the regression and analysis on experimental data seems to be better in the kinetics modelling for the whole process of adsorption. Therefore, the adsorption of oil onto EB is consistent with the second-order reaction.

### 6.3.9 Thermodynamics analysis

Thermodynamic parameters such as  $\Delta G^o$ ,  $\Delta H^o$ , and  $\Delta S^o$  were used to test the feasibility of the adsorption process regarding the temperature influence and the results were illustrated in Table 6.6 at different temperatures 298, 303, 308, 313 and 318 K.

**Table 6.6** Thermodynamic parameters for oil adsorption onto EB at different temperatures

	$\Delta H^o$ (KJ/mol)	$\Delta S^o$ (J/molK)	$\Delta G^o$ (KJ/mol)					$R^2$
			298 K	303 K	308 K	313 K	318 K	
EB	-510.9	1.491	5.207	3.666	3.083	2.698	3.183	0.7134

Temperature has a significant effect on the adsorption capacity of the biosorbent. In general, increasing solution temperature will result in increasing removal efficiency because kinetic energy of the molecules in the system becomes higher (Znad and Frangeskides, 2014). The negative value of  $\Delta H^o$  indicates the exothermic nature of oil adsorption and the reaction is found to be nonspontaneous as  $\Delta G^o$  is  $> 1$ . The positive

value of  $\Delta S^\circ$  indicates increased randomness at solid/liquid interface during oil adsorption onto EB adsorbent.

## 6.4 Summary

The preliminary experiments revealed that out of all three biosorbents tested, eucalyptus bark (EB) had the best performance for removing oil. Therefore, EB was selected as a potential biosorbent for oil removal from ROW. Based on the experimental results, oil adsorption onto eucalyptus bark increases with the increase of adsorbent dosage, contact time and temperature while, it reaches best performance at acid condition (pH 3). The adsorption isotherms were analyzed by using Langmuir, Freundlich and Dubinin-Radushkevich isotherm models where Dubinin-Radushkevich model is found to be the best model with  $R^2$  value of 0.8695. The analysis proved that the adsorption kinetic follows the second-order reaction model with highest  $R^2$  value of 0.995. Thermodynamic analysis showed that adsorption process is nonspontaneous, exothermic and reversible.

## **CHAPTER 7**

### **Integrated UF Membrane Unit for Efficient Petroleum Refinery Wastewater Treatment (A Case Study)**

## 7.1 Introduction

Petroleum refineries usually need large quantities of water, from 0.4-1.6 times the amount of oil processed (Coelho et al., 2006). The oily wastewater from refineries, known as petroleum refinery wastewater (PRW), contains highly toxic compounds, such as aliphatic and aromatic petroleum hydrocarbons. Discharging PRW to water bodies without treatment results in serious environmental problems for both aquatic life and human health. For instance, the presence of chlorophenolic compounds (the main contaminants in refinery wastewaters) in drinking water can negatively affect the human central nervous system and has been linked to carcinogenic diseases at higher doses. Different treatment methods have been applied to remove pollutants and improve the quality of wastewater before its discharge into the environment. Conventional treatment methods, such as coagulation, dissolved air flotation (DAF) and the skimming method, have been applied extensively and are effective in removing free oil from wastewater (Salahi et al., 2010b). However, these techniques have some disadvantages, such as the need for post-treatment, low separation efficiency, long processing times, and large space requirements (Salahi et al., 2015, Salahi et al., 2010b). Other methods to treat wastewater include advanced oxidation processes, such as the Fenton process which uses iron ions and hydrogen peroxide. However, the Fenton process can be economically infeasible due to the high cost of chemicals. Membrane technology is also used to treat oily wastewater (Padaki et al., 2015). The use of this technology has become more widespread due to its superior permeate quality (Xia et al., 2004), its ability to separate particles of manageable size with high removal of bacterial and toxic residues (Ahmad and Chan, 2009) and its more simple equipment (Madaeni et al., 2012). However, the use of membrane technology can be affected by membrane fouling, where solutes or particles deposit onto the membrane

surface or into membrane pores, thereby reducing the membrane's ability to filter. Membrane fouling can be reversible or irreversible. Reversible fouling can be solved by physical or chemical cleaning, while irreversible fouling permanently damages the membrane and prevents further usage. Generally, fouling leads to permeate flux reduction. There is a rapid permeate flux decrease during the early period of filtration, which is followed by a long and gradual flux decline towards a steady or nearly steady state.

In order to reduce membrane fouling, oily wastewater should be pre-treated before it passes through the membrane system. Ultrafiltration (UF) and nanofiltration (NF) membrane technologies could be used to treat oily restaurant wastewater and achieve more than 90% chemical oxygen demand (COD) and turbidity removal. Then, a subsequent cleaning process could recover the flux percentage less than 40% (Zulaikha et al., 2014). Another study on oily wastewater treatment using a nanoporous membrane (NPM) and a nanoporous membrane-powdered activated carbon (NPM-PAC) integrated system, showed that NPM was significantly less effective for reducing both the COD and TOC when compared to the integrated NPM-PAC system (Sarfaraz et al., 2012). Mohammadi et al. investigated the performance of UF and combined UF-PAC for treating oily wastewater generated from a vegetable oil. The permeate of wastewater treated by UF-PAC showed high permeate flux with 91, 87, 100, 85 and 40 % removal of COD, TOC, total suspended solids (TSS),  $[\text{PO}_4^{3-}]$  and Cl, respectively (Mohammadi and Esmaelifar, 2004). Zhong et al. treated oily wastewater using ceramic membrane with flocculation as pre-treatment process and reported that the permeate flux increased when the wastewater was pre-treated (Zhong et al., 2003). Pulido et al. applied Fenton-like reaction, flocculation-sedimentation, and filtration by filters packed with sand and olive stones as pre-treatment processes for



oily wastewater prior to nanofiltration membrane treatment. They reported that the pre-treatment process significantly reduced the membrane fouling and enhanced the permeate flux (Pulido et al., 2015).

Previous studies have not examined the use of polymeric UF membrane performance in conjunction with pre-treatment system upstream of the membrane step. This study investigates the use of a polymeric UF membrane for PRW treatment in two different operating modes: the UF membrane-only mode (no pre-treatment) and the integrated mode, which includes Fenton-flocculation as pre-treatment stage to the membrane system. The foulant characteristics and fouling mechanism were analysed using FTIR, SEM, EDS and Hermia's model.

## 7.2 The characterizations of petroleum refinery wastewater (PRW)

The characterizations of PRW collected from the British Petroleum Kwinana Oil Refinery, Western Australia, are shown in Table 7.1.

**Table 7.1** Characteristic of raw PRW

Parameter	Raw PRW
TDS (mg/L)	1.67
TSS (mg/L)	2486
Oil (mg/L)	682
COD (mg/L)	850
pH	9.5
EC (mS)	2.3
Viscosity (mPas)	2.60

The oily wastewater was collected from the outlet of the dissolved air flotation (DAF) unit system before sending it to the biological treatment unit (BTU). The sample was characterized immediately and placed in the laboratory fridge at a temperature under

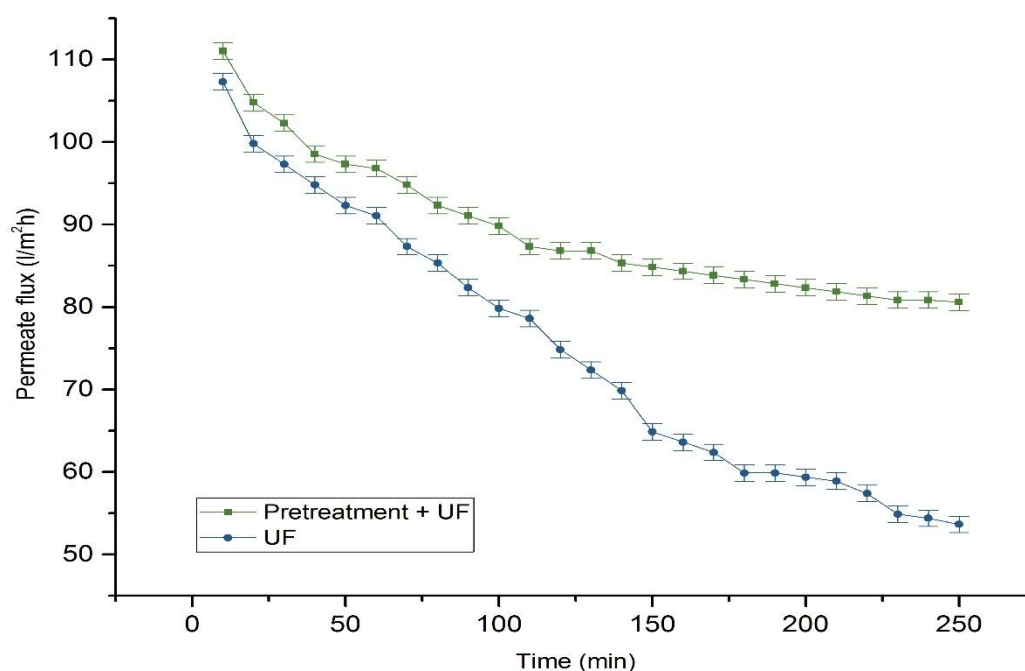
4 °C to minimize biological activity. The temperature of feed solution in feed tank was controlled by a thermally controlled magnetic stirrer at 25 °C.

More detail of experimental set up and analytic procedure can be seen in Chapter 3.

## 7.3 Results and discussion

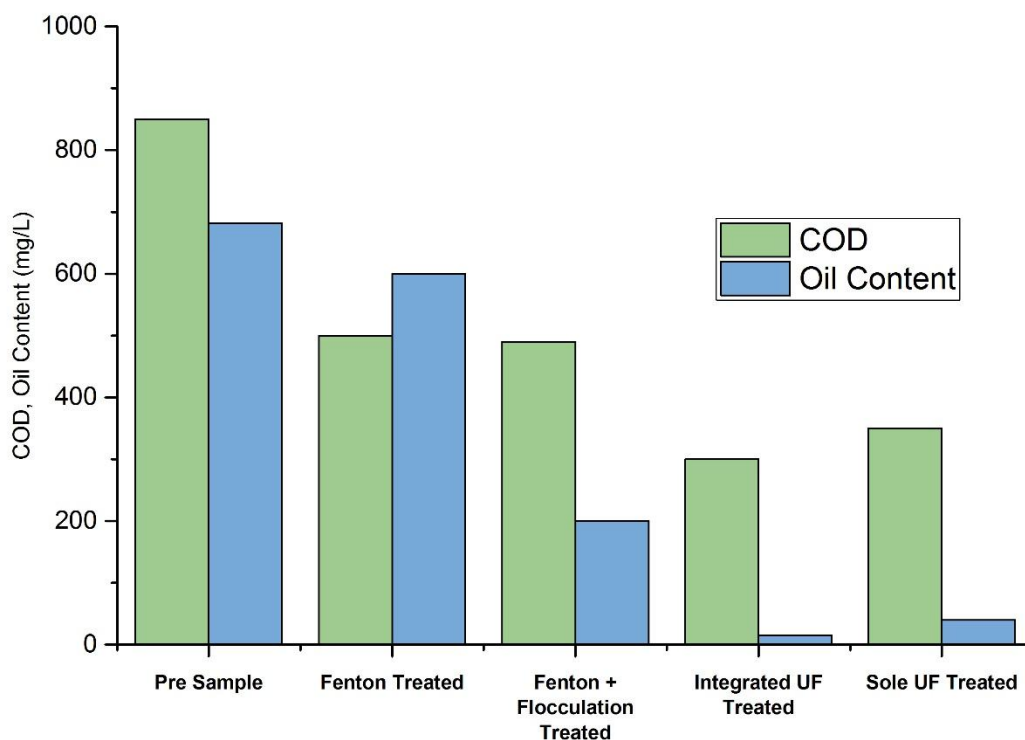
### 7.3.1 Effect of pre-treatment process on permeate flux

While the flux declined for both the untreated and pre-treated PRW samples, applying pretreatment process significantly increased the permeate flux and reduced the fouling (Figure 7.1). The permeate flux of the untreated samples (sole UF membrane) declined 51 % of their initial value (107 L/m<sup>2</sup>h), while for the pre-treated samples (Fenton with flocculation integrated-UF membrane), the flux decline was 28 % of their initial value (111 L/m<sup>2</sup>h). Additionally, the permeate flux increased 1.5 fold when applying the pre-treatment process, which indicates reduced fouling opportunity.



**Figure 7.1** The effect of pre-treatment (Fenton – flocculation) on UF membrane permeation flux (pH: 9.5, T: 25 °C, CFV: 600 mL/min, TMP: 1 bar)

Integrating the UF membrane with a pre-treatment process not only improved the permeate flux and reduced the fouling, but also enhanced the permeate quality. The values of COD and oil removal efficiencies of the PRW samples increased from 42 to 65% and from 94 to 98%, respectively (Figure 7.2).

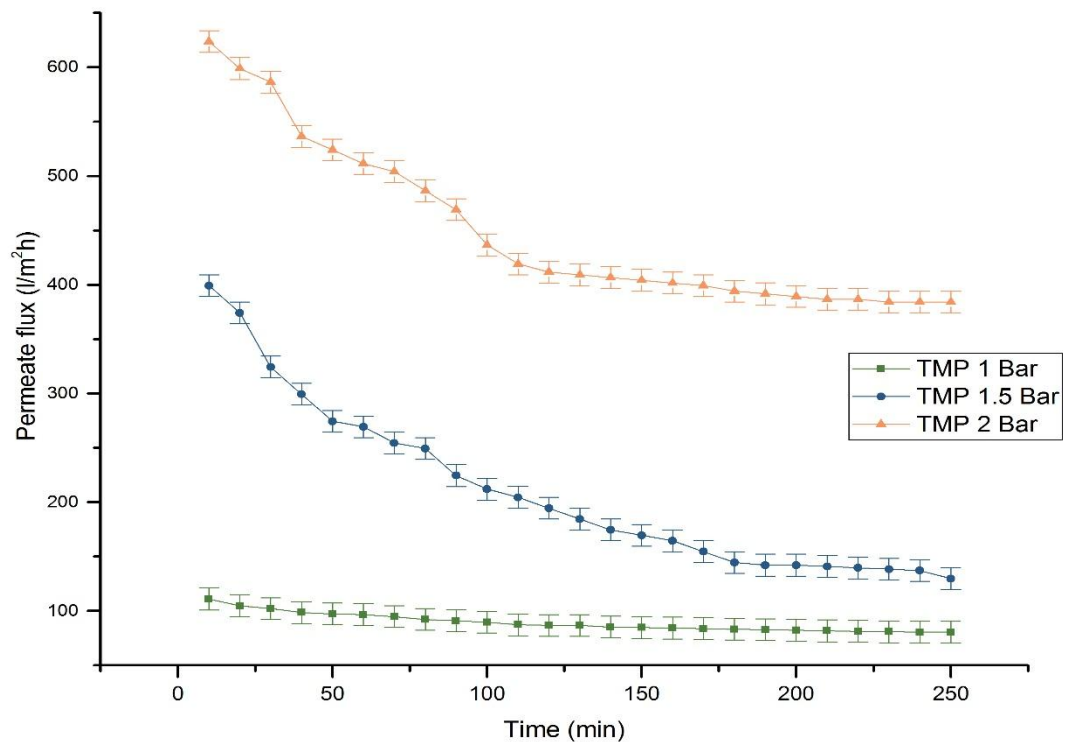


**Figure 7.2** The values of COD and oil concentrations for different treatment processes (sole and the integrated - UF membrane system)

### 7.3.2 Effect of TMP

As shown in Figure 7.3, increasing the TMP (from 1.5 to 2 bar) at a constant CFV (600 mL/min) resulted in an initial sharp decline in the permeate flux against over the first 100 min, before the flux becomes steadier over the remaining filtration time. A steady flux was achieved after 20 min at a TMP of 1 bar. The higher TMP enabled both solvent and solute droplets to pass through the membrane pores more rapidly. However, the higher TMP also caused the membrane to foul more easily due to the

accumulation of more oil droplets, both on the membrane surface and in the membrane pores (Hua et al., 2007). Increasing TMP had a positive effect on permeate flux but a negative effect on the quality of the permeate. Increasing the TMP from 1 bar to 2 bars reduced the COD removal efficiency from 68 to 62%, as, at a higher TMP, droplets will pass more quickly through the membrane pores (Mohammadi and Esmaelifar, 2004, Mutamim et al., 2012).



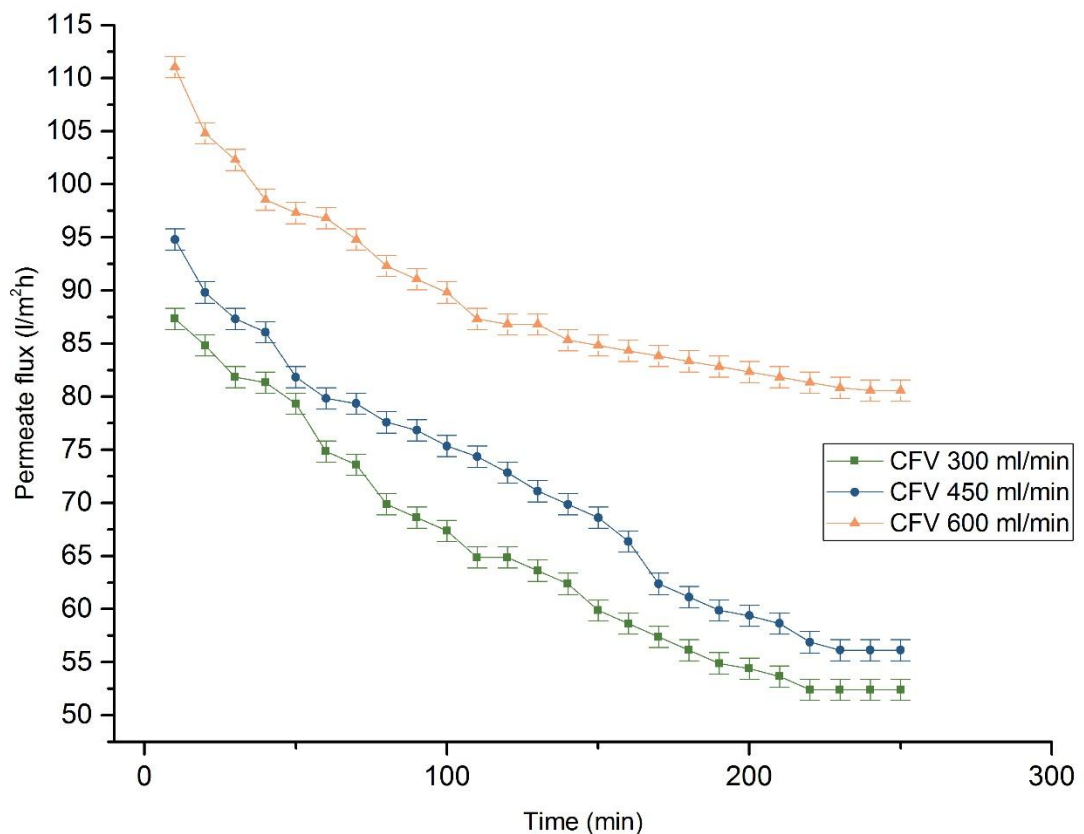
**Figure 7.3** The effect of TMP on permeate flux in the integrated UF membrane system (pH: 9.5, T: 25 °C, CFV: 600 mL/min)

### 7.3.3 Effect of CFV

Figure 7.4 illustrates the effect of CFV on permeate flux. A steep flux decline was observed in the first 100 min; a 23, 20 and 20% reduction from their initial values for CFVs of 300, 450 and 600 mL/min, respectively. Increasing CFV increases the initial and steady state flux. The initial flux increased by 28% when the CFV doubled from 300 to 600 mL/min. This reflects the higher turbulence and improved mass transfer of

rejected solutes back to the bulk solution, and the prevention of the fouling and gel layer concentration which would reduce the concentration polarization (Lobo et al., 2006).

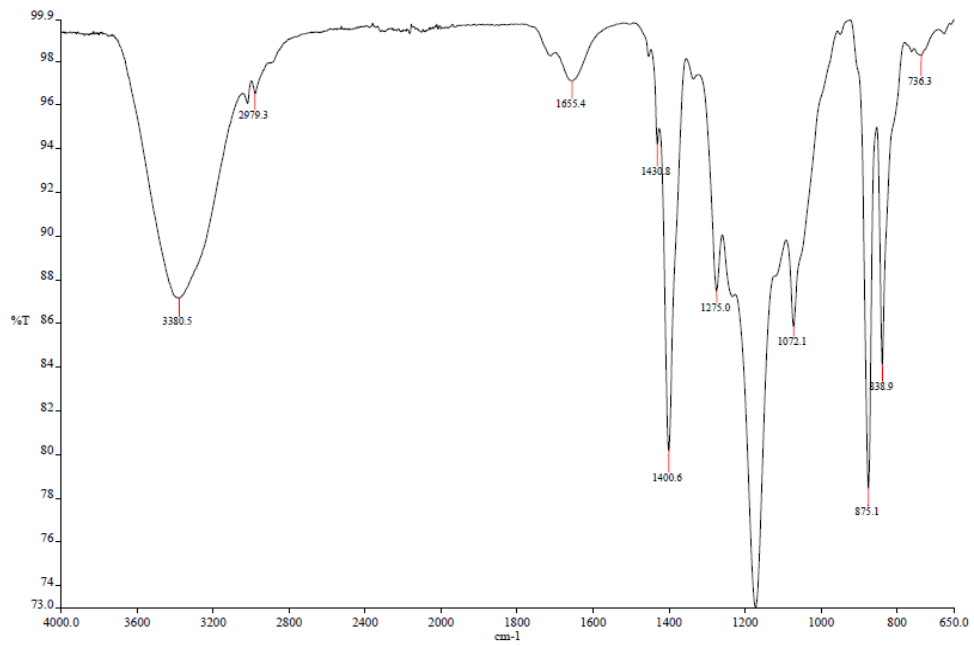
At a constant TMP (1 bar), the higher CFV was critical in achieving significantly higher permeate flux rates. The CFV also influenced the permeate quality, as it has in other studies (Ahmad et al., 2005a, Lobo et al., 2006). The COD removal efficiency increased from 63 to 67% when the CFV doubled from 300 to 600 mL/min. Clarke and Heath found that increasing the CFV leads to an increase in mass transfer coefficient or a reduction in boundary layer resistance, which would result in an increase in permeate flux (Ahmad et al., 2005a, Lobo et al., 2006).



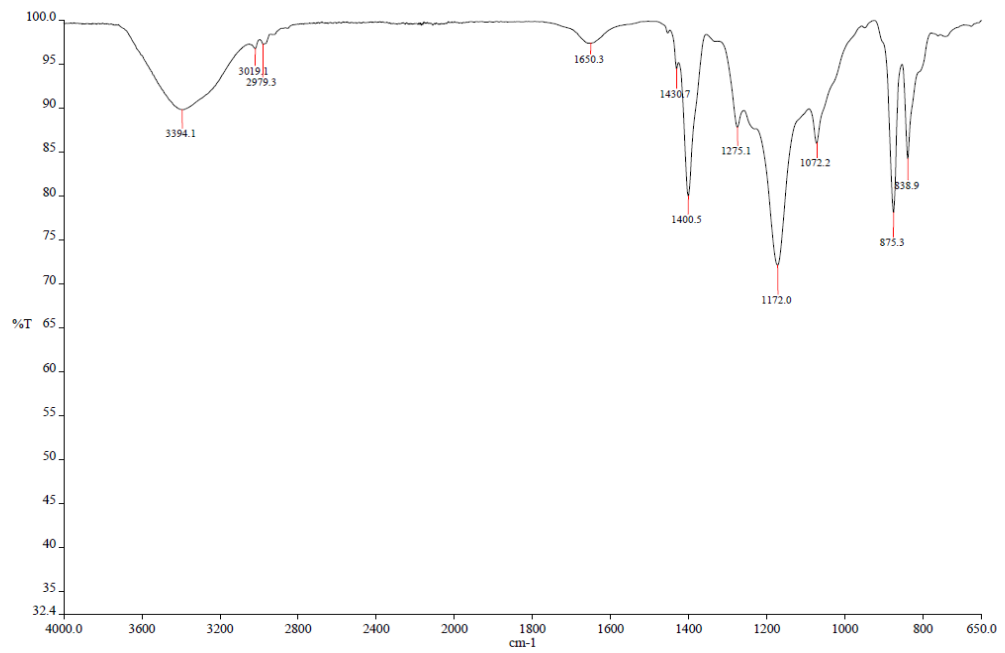
**Figure 7.4** The effect of CFV on permeate flux (pH: 9.5, T: 25 °C, TMP: 1 bar, samples collected every 10 min)

### 7.3.4 Membrane fouling analysis

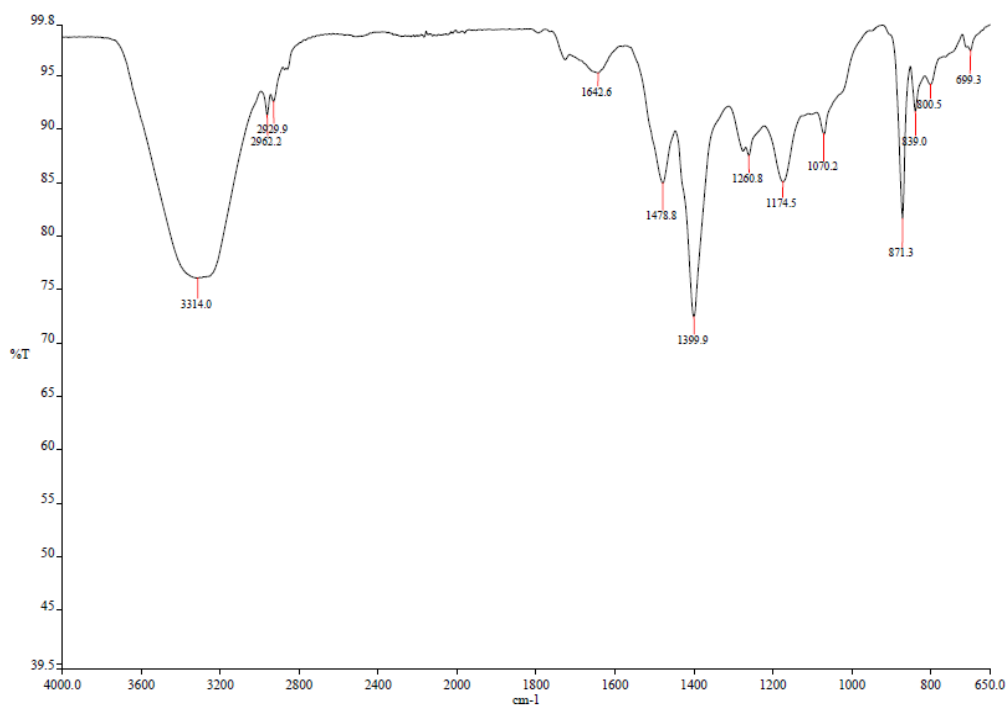
To characterize membrane fouling, the application of FTIR, SEM and EDS analysis had been applied. The FTIR spectra of membranes surface are shown in Figure 7.5. Fresh membrane (Figure 7.5a) showed some broad absorptions such as at  $3380.5 - 2979.3 \text{ cm}^{-1}$ , which are interpreted as hydrogen-bonded O-H stretching and at  $1400 - 1430 \text{ cm}^{-1}$  as H-C-H bend (Shariati et al., 2011). The C=O stretching or C-C=C symmetric stretching can also be seen at a broad absorption of  $1655.4 \text{ cm}^{-1}$  (Affam and Chaudhuri, 2013).  $\text{CF}_2$  function is shown at  $1275 \text{ cm}^{-1}$  and C-O vibration is at  $1072 \text{ cm}^{-1}$ . For fouled membrane (using untreated PRW sample as the feed solution) (Figure 7.5b), the FTIR spectrum contains several peaks relating to functional groups such as amines/amides N-H bend at  $3394.1 \text{ cm}^{-1}$ , and aromatic compounds which can be indicated at  $3019, 1430, 1400.5, 1275.1$  and  $875.3 \text{ cm}^{-1}$  (1875). Then C-C=C symmetric stretching of alkenes can be seen at  $1650 \text{ cm}^{-1}$ . The fouled integrated UF membrane spectrum (using treated PRW sample as the feed solution) (Figure 7.5c) shows a series of peaks from  $2962$  to  $2929 \text{ cm}^{-1}$  with shoulders that can be associated with C-H stretching in the methyl or methylene group and the vibration of C-O or  $\text{SiO}_2$  at  $1070 \text{ cm}^{-1}$  (Ibrahim et al., 2010). The C-C=C symmetric stretching shown at  $1478 \text{ cm}^{-1}$  (Affam and Chaudhuri, 2013) with bands at  $1642$  to  $1650 \text{ cm}^{-1}$  most likely corresponds to the presence of alkenes in term of C-C=C symmetric stretch. The peak at  $1399 \text{ cm}^{-1}$  could be interpreted as N=O bend (1985) or C-H bend vibration of the methylene group (Lingbo et al., 2005). Peaks near  $800 \text{ cm}^{-1}$  can be associated with C-Cl stretch alkyl halides (1875), silicate mineral (Lingbo et al., 2005) or phenyl attached to C=O (Moslehyani et al., 2015). Additionally, several peaks in the range of with range from  $1000$  to  $1300 \text{ cm}^{-1}$  show the presence of esters and ethers with C-O stretch (Groups, 1875).



**Figure 7.5a** FTIR spectrum of fresh UF membrane



**Figure 7.5b** FTIR spectrum of fouled UF membrane without pre-treatment

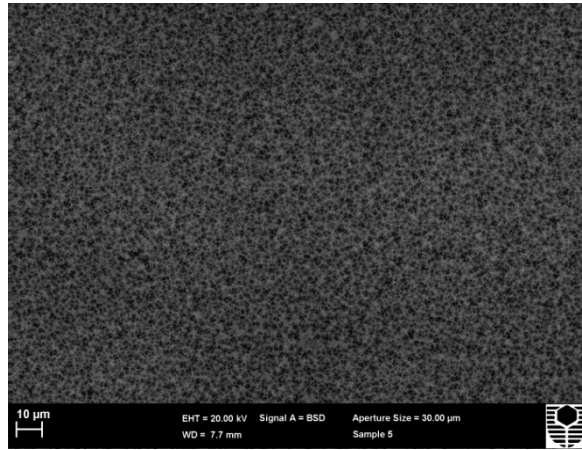


**Figure 7.5c** FTIR spectrum of fouled UF membrane with pre-treatment

To further examine membrane fouling by trapped foulants, SEM and EDS analyses were used to observe the composition and distribution of fouling layer on a membrane surface. Figure 7.6a shows a fresh membrane surface layer where the surface is free of foulant particles. Its nano-network surface can filter organic and inorganic matter as well as finite contaminants.

Figure 7.6b illustrates the fouled membrane for a pre-treated PRW sample, showing trapped micro particles forming gel layer. This membrane is brighter colour than a fresh membrane and has irregularly distributed micro particles and oil droplets on its surface and pores caused by foulant movement across the membrane's valleys and crests (Canizares et al., 2007). Figure 7.6c that shows the fouled membrane for untreated PRW sample illustrates more dominant fouling area containing foulant materials than that of membrane with pre-treated PRW sample.

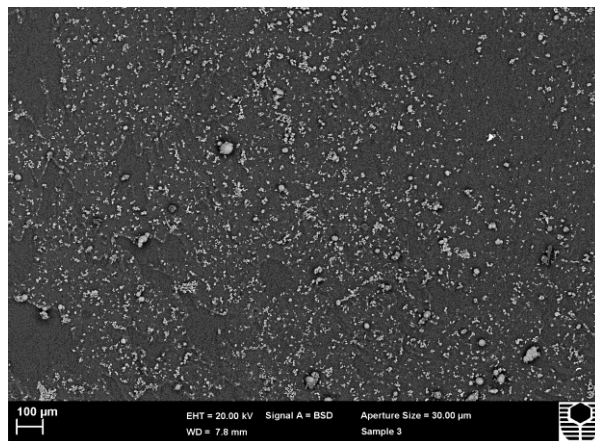




(a)



(b)



(c)

**Figure 7.6** SEM of the UF membrane (a) Fresh membrane (b) fouled membrane treating pre-treated PRW sample (integrated UF membrane), (c) fouled membrane treating untreated PRW sample (sole UF membrane)

EDS analysis can be used to investigate the chemical components of the foulant formed on membrane pores and surface (Pendashteh et al., 2011). Table 7.2 presents the EDS analysis of fresh membranes containing F and C as the main PVDF membrane material. The EDS results show the fouled membrane with a pre-treated feed solution that has more elemental or chemical components than that of a fresh surface.

As shown in Table 7.2, a layer on a fouled membrane surface consisted of C, O, F, Na, Mg, Si, S, Cl, Ca and Fe. This demonstrates that some contaminants remain in PRW samples after the pre-treatment stage. Unlike the organic material, the presence of metal elements could inhibit the performance of membranes even after chemical cleaning (You et al., 2006). This is believed to be one of the most important factors leading to flux reduction.

**Table 7.2** EDS analysis of UF membrane

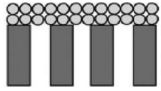
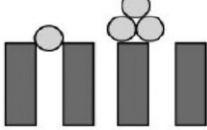
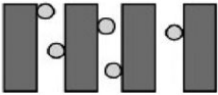
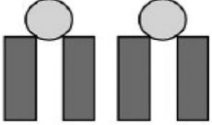
	UF membrane		
	Fresh	Fouled by raw PRW	Fouled by pre-treated PRW
Chemical components	C, F	C, F, O, Si, S, Cl, Cr, Fe, Mg	C, F, Ca, O, Na, S, Si, Cl, Mg

### ***7.3.5 Modelling of permeate flux decline***

Membrane fouling mechanism, which is responsible for permeate flux reduction, can be analyzed by fitting the experimental data obtained with Hermia's models, (intermediate pore blocking, standard pore blocking, complete pore blocking, and cake filtration), as described in Table 7.3. Furthermore, the estimated correlation coefficient based on Hermia's models analysis applied for the integrated-UF membrane system

operating under different conditions of TMP (1, 1.5 and 2 bars) and CFV (300, 450, and 600 mL/min) are shown in Table 7.4.

**Table 7.3** Hermia's models and blocking mechanism

<b>Blocking mechanism</b>	<b>n - value</b>	<b>Schematic representation</b>	<b>Hermia's models</b>
Cake layer formation	0		$\frac{1}{J^2} = \frac{1}{J_0^2} + K t$ (7.1)
Intermediate pore blocking	1		$\frac{1}{J} = \frac{1}{J_0} + K A t$ (7.2)
Standard pore blocking	1.5		$\frac{1}{J^{0.5}} = \frac{1}{J_0^{0.5}} + K t$ (7.3)
Complete pore blocking	2		$\ln(J) = \ln(J_0) - K t$ (7.4)

**Table 7.4** Estimated correlation coefficients ( $R^2$ ) of permeate flux predicted by Hermia's models

Operational condition		$R^2$ value			
TMP (bar)	CFV (mL/min)	Complete pore blocking	Standard pore blocking	Intermediate blocking	Cake filtration
1	600	0.903	0.914	0.925	0.944
1.5	600	0.949	0.971	0.981	0.982
2	600	0.857	0.871	0.884	0.906
1	300	0.974	0.981	0.986	0.990
1	450	0.986	0.986	0.984	0.974

The  $R^2$ -values indicate that cake filtration is the dominant mechanism; the cake filtration model provides a better fit to the experimental results than other models, as is evident from the highest  $R^2$ -values for all the applied conditions. The cake filtration model mechanism explains that during filtration, particles from the feed solution (pre-treated PRW) arrives to the membrane surface, deposits on other particles, and makes a cake layer which is then thickened with time (Salahi et al., 2010a, Abbasi and Mowla, 2014). As the  $R^2$  shows that the cake layer formation is the dominant fouling mechanism for all the TMP and CFV applied; changing the TMP (1–2 bar) and the CFV (300–600 mL/min) will not change the mechanism of the membrane fouling.

The deviation between the experimental and predicted data was observed in the complete and standard pore blocking models. For the complete pore blocking model, the deviation may be caused by the hydrophobicity of the oil molecule contained in the feed solution, which blocks all the membrane pores, while for the standard

blocking model, it might be due to the strong hydrogen bonding presence preventing the adsorptive fouling (Corbatón-Báguena et al., 2015, Amin et al., 2010).

## **7.4 Summary**

The integrated Fenton/flocculation-UF membrane system suggested in this study is an effective system for PRW treatment. The pre-treatment stage (Fenton/flocculation) increased permeate flux 1.5 fold and reduced the permeate flux decline (51 % decline from the initial value for UF membrane-only compared to 28% decline from the initial value for the integrated UF membrane). The pre-treatment stage also improved oil content, COD and TSS removal efficiencies to 98%, 65%, and 100%, respectively.

Based on Hermia's models, the cake layer formation was the dominant fouling mechanism for all the TMP (1–2 bar) and CFV (300–600 mL/min) applied in this study. Hydrocarbons, organic and inorganic compounds were the main components of the fouling cake layer, as shown by FTIR and EDS analysis. SEM analysis showed that the fouled membrane was dominated by a dense cake layer and irregularly distributed microparticles or oil droplets on the membrane surface and its pores. This study finds that TMP should be optimized in order to achieve high permeate quality and flux. Increasing the TMP from 1 to 2 bars reduced the COD removal efficiency from 68 to 62% but increased the permeate flux 4.5 fold. Future studies should further examine TMP optimization and the testing of other oily wastewater.

# **CHAPTER 8**

## **Conclusions and Recommendations**

## **8.1 Introduction**

This chapter introduces the conclusions drawn from the present study and also the suggested recommendations for further research. Different treatment technologies have been applied and investigated thoroughly under different conditions for oily wastewater treatment. The polymeric UF membrane was the main treatment method adopted in this work, other methods such as photo-Fenton, adsorption and flocculation were also investigated individually or combined with UF membrane. In order to make the study more useful and applicable, different raw oily wastewaters (canola oil wastewater, petroleum refinery wastewater and restaurant wastewater) and synthetic oily wastewater have been used as model pollutants.

## **8.2 Conclusions**

This thesis investigates the effectiveness of several treatment technologies including UF membrane, photo-Fenton, adsorption and integrated UF membrane for oily wastewater treatment. The following conclusions can be drawn:

### ***Oily wastewater treatment by UF membrane filtration***

The application of UF membrane for the purification of raw restaurant oily wastewater and synthetic oil in water emulsion was investigated. The influence of different TMP and initial oil concentrations on the membrane performance was studied through the measurement of permeate flux, TOC, COD and oil content concentration. In addition, chemical cleaning effect and membrane fouling mechanism were also analyzed. The experimental results showed that TMP significantly affects permeate flux since increasing TMP increases permeate flux. This is due to more driving force for solute particles or oil droplets to pass through the membrane pores. Then, increasing initial

oil concentration decreases permeate flux due to higher amount of oil droplets clogging membrane pores and membrane surface. The TOC, COD and oil removals of raw oily wastewater were slightly lower than synthetic oily wastewater, while the decline of raw oily flux was higher than the synthetic one due to the more complex organic and inorganic compounds in the raw oily wastewater. Furthermore, chemical cleaning applied can increase permeate flux in its further usage due to rinsing fouling layer on the surface and in the pores of membrane. In this study, Hermia's models (intermediate pore blocking model, standard pore blocking model, complete pore blocking and cake filtration model) used to analyze membrane fouling mechanism presented that cake filtration model was the best fit. This model indicates that during the filtration process, pollutant molecule arriving at the membrane surface deposits on other molecule forming a cake layer and thickens with time.

#### ***Oily wastewater treatment by photo-Fenton***

This research shows the findings of the study on the feasibility and enhancement of photo-Fenton process as an effective method to remove organic pollutants from raw canola oil wastewater. According to the experimental results, H<sub>2</sub>O<sub>2</sub> concentration influences the removal of TOC and COD. H<sub>2</sub>O<sub>2</sub> concentration which ranged 650 mg/L, 1500 mg/L and 2000 mg/L yields TOC reductions of 82.33 %, 80.01 % and 67.33 %, respectively. The corresponding COD reductions are 69.72 %, 71.11 % and 44.72 %, respectively. In photo-Fenton, irradiation time is important for organic pollutants removal. During 100 min of irradiation time, the highest TOC and COD reduction percentages occurred in the first 10 min, followed by more gradual degradation to reach a constant value. Natural solar light was found as the best light source of artificial light sources (UV light and solar simulator) due to getting higher



TOC and COD removals efficiency. By using natural solar light, TOC and COD concentration showed more than 82 % and 70 % removal efficiency, respectively, after 80 min irradiance with optimum conditions set of; pH 3, H<sub>2</sub>O<sub>2</sub> 650 mg/L, and Fe<sup>2+</sup> 8 mg/L. Then, kinetic experimental analysis demonstrated that this process follows second order reaction.

### ***Oily wastewater treatment by adsorption***

Several low cost biosorbents, eucalyptus bark (EB), watermelon shell (WS) and chicken bone (CB), were tested for oil removal from raw restaurant oily wastewater. Since EB was found to be the best for adsorbing oil, it was further characterized for subsequent studies under different operating conditions. Oil content removal efficiency and adsorption capacity increased with the increase of contact time where the rate of oil removal reached its highest percentage, more than 45 %, in the first 10 min. Then, the highest oil removal occurred at pH 3. This acidic pH environment can enhance the reaction efficiency that contributes to the process of oil droplets destabilization causing de-emulsification and larger oil droplets formation. At higher temperatures, ( $\geq 25$  °C), the removal of oil content increased due to higher diffusion rate of the adsorbate molecules crossed the adsorbent surface. EB dosage also affects oil removal since increasing EB dosage increases oil removal efficiency. Furthermore, the adsorption isotherms analyzed by Langmuir, Freundlich and Dubinin-Radushkevich isotherm models showed that Dubinin-Radushkevich model is fit best with  $R^2$  value of 0.869. The adsorption kinetic mechanisms analyzed using pseudo-first order, pseudo-second order, intra-particle diffusion, liquid film diffusion and double exponential models presented that the kinetic mechanism follows second-order reaction model with the highest  $R^2$  value (0.995).

### ***Oily wastewater treatment by integrated UF membrane***

Integrated UF membrane consisting of pre-treatment by Fenton/flocculation followed by UF membrane separation has improved permeate flux, reduced membrane fouling and enhanced permeate quality. By applying integrated UF membrane, COD and oil removal efficiencies of the refinery wastewater increased from 42 to 65% and 94 to 98% respectively. Increasing TMP increases permeate flux. However, increasing TMP affects the permeate quality by slight reducing of the COD removal efficiency from 68 to 62 %. This can be attributed to the fact that higher TMP will allow droplets to pass quickly through the membrane pores. Increasing CFV also increases permeate flux. The initial permeate flux increased by 28% when the CFV was doubled from 300 to 600 mL/min. The FTIR analysis shows the presence of hydrocarbons, organic and inorganic materials. Then, SEM images show different morphologies of the fresh and fouled membrane where the fouled one was dominant by dense cake layer and irregularly distributed micro molecules or oil droplets on membrane surface and pores. The EDS analysis also illustrates the cake layer on fouled membrane surface that consisted of C, O, F, Na, Mg, Si, S, Cl, Ca and Fe.

### **8.3 Recommendations for future directions**

The applicability of different technologies such as UF membrane, photo-Fenton, adsorption and integrated membrane for oily wastewater treatment was thoroughly presented and discussed in this thesis. The results indicate the effectiveness of these methods for improving oily wastewater quality. However, there are several issues that need to be further addressed to improve the present results before actual industrial application in wider industrial sectors.

Based on the results obtained, the following future directions are recommended:

- In order to be reliable for real industrial purpose, the next research has to scale up the processes to the pilot project.
- The integration of membrane filtration with other biosorbent materials or other type of AOPs can be investigated.
- For Fenton and photo-Fenton process, the alternative iron ( $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ) sources such as clay, soil and other organic materials should be investigated to minimize chemical cost used.
- In order to improve the adsorption efficiency to oil and other organic constituents from oily wastewater, the biosorbent (EB) can be modified chemically or physically.
- The application of other raw oily wastewater should be investigated.
- Other polymeric UF membrane materials such as polysulfone, polypropylene, cellulose acetate and polylactic acid need to be compared and investigated.

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# **APPENDIX A**

**Raw data for ultrafiltration membrane**

## A1. Effect of TMP on Permeation flux (Synthetic oily wastewater)

Fixed conditions:

pH=	3
Oil concentration=	2 g/L
T=	25 C
V=	400 ml/minute
A=	0.024 m <sup>2</sup>
t=	0.167 h
Emulsifier =	0.1 g/L

Time (min)	TMP 1 bar		TMP 2 bar		TMP 3 bar	
	V (l)	J (l/m <sup>2</sup> .h)	V (l)	J (l/m <sup>2</sup> .h)	V (l)	J (l/m <sup>2</sup> .h)
0		0	0	0	0	0
10	0.105	26.1976	0.72	179.6407	1.6	399.2016
20	0.097	24.2016	0.68	169.6607	1.5	374.2515
30	0.09	22.45509	0.65	162.1756	1.4	349.3014
40	0.088	21.95609	0.64	159.6806	1.4	349.3014
50	0.085	21.20758	0.63	157.1856	1.38	344.3114
60	0.082	20.45908	0.622	155.1896	1.35	336.8263
70	0.08	19.96008	0.55	137.2255	1.33	331.8363
80	0.08	19.96008	0.48	119.7605	1.3	324.3513
90	0.072	17.96407	0.4	99.8004	1.29	321.8563
100	0.065	16.21756	0.38	94.81038	1.28	319.3613
110	0.06	14.97006	0.35	87.32535	1.25	311.8762
120	0.055	13.72255	0.3	74.8503	1.24	309.3812
130	0.05	12.47505	0.3	74.8503	1.22	304.3912
140	0.044	10.97804	0.28	69.86028	1.2	299.4012
150	0.041	10.22954	0.28	69.86028	1.18	294.4112
160	0.041	10.22954	0.28	69.86028	1.15	286.9261
170	0.041	10.22954	0.28	69.86028	1.1	274.4511
180	0.041	10.22954	0.28	69.86028	1.1	274.4511

## A2. Effect of TMP on Permeation flux (Real oily wastewater)

Fixed conditions:

pH= 8.5  
oil  
concentration = 2 g/L  
T= 25 C  
V= 400 ml/min  
A= 0.024 m<sup>2</sup>  
t= 0.167 h

Time (min)	TMP 1 bar		TMP 2 bar		TMP 3 bar	
	V (L)	J (l/m <sup>2</sup> .h)	V (L)	J (l/m <sup>2</sup> .h)	V(L)	J (l/m <sup>2</sup> .h)
0		0	0	0	0	0
10	0.1	24.9500998	0.49	122.255489	1.67	416.6666667
20	0.092	22.95409182	0.32	79.84031936	1.48	369.261477
30	0.09	22.45508982	0.25	62.3752495	1.35	336.8263473
40	0.075	18.71257485	0.22	54.89021956	1.25	311.8762475
50	0.07	17.46506986	0.2	49.9001996	1.15	286.9261477
60	0.068	16.96606786	0.19	47.40518962	1.05	261.9760479
70	0.054	13.47305389	0.18	44.91017964	0.97	242.0159681
80	0.052	12.9740519	0.162	40.41916168	0.92	229.5409182
90	0.05	12.4750499	0.152	37.9241517	0.85	212.0758483
100	0.05	12.4750499	0.148	36.9261477	0.8	199.6007984
110	0.048	11.9760479	0.14	34.93013972	0.78	194.6107784
120	0.049	12.2255489	0.135	33.68263473	0.76	189.6207585
130	0.048	11.9760479	0.13	32.43512974	0.75	187.1257485
140	0.04	9.98003992	0.128	31.93612774	0.74	184.6307385
150	0.038	9.481037924	0.128	31.93612774	0.73	182.1357285
160	0.035	8.73253493	0.128	31.93612774	0.73	182.1357285
170	0.035	8.73253493	0.127	31.68662675	0.72	179.6407186
180	0.032	7.984031936	0.127	31.68662675	0.72	179.6407186

### A3. Effect of TMP on membrane permeability

Fixed conditions:

pH = 3    A = 0.024 m<sup>2</sup>  
 V = 400 ml/min                                      T = 0.167 h  
 T = 25 °C  
 t = 0.167 h

Pressure (Bar)	DI water volume (L)			DI water flux (L/M2H)		
	V <sub>wi</sub>	V <sub>ww</sub>	V <sub>wc</sub>	J <sub>wi</sub>	J <sub>ww</sub>	J <sub>wc</sub>
1	0.4	0.185	0.3	99.8003992	46.15768463	74.8502994
2	0.91	0.25	0.42	227.0459082	62.3752495	104.7904192
3	1.36	0.32	0.6	339.3213573	79.84031936	149.7005988

#### A4. Effect of initial oil concentration on permeation flux

Fixed conditions:

pH= 3  
P = 1 Bar  
T= 25 °C  
V= 400 ml/min  
A= 0.024 m<sup>2</sup>  
t= 0.167 h

Time (min)	Oil concentration (g/L)					
	0.3		0.5		1	
	V (L)	J (L/M <sup>2</sup> H)	V (L)	J (L/M <sup>2</sup> H)	V (L)	J (L/M <sup>2</sup> H)
0						
10	0.158	39.42115768	0.146	36.42714571	0.105	26.197605
20	0.152	37.9241517	0.14	34.93013972	0.098	24.451098
30	0.148	36.9261477	0.132	32.93413174	0.095	23.702595
40	0.135	33.68263473	0.128	31.93612774	0.08	19.96008
50	0.13	32.43512974	0.122	30.43912176	0.078	19.461078
60	0.125	31.18762475	0.11	27.44510978	0.076	18.962076
70	0.11	27.44510978	0.095	23.70259481	0.074	18.463074
80	0.105	26.19760479	0.09	22.45508982	0.072	17.964072
90	0.098	24.4510978	0.085	21.20758483	0.07	17.46507
100	0.096	23.95209581	0.083	20.70858283	0.067	16.716567
110	0.095	23.70259481	0.081	20.20958084	0.065	16.217565
120	0.094	23.45309381	0.079	19.71057884	0.062	15.469062
130	0.0935	23.32834331	0.075	18.71257485	0.058	14.471058
140	0.092	22.95409182	0.073	18.21357285	0.054	13.473054
150	0.091	22.70459082	0.071	17.71457086	0.049	12.225549
160	0.091	22.70459082	0.069	17.21556886	0.045	11.227545
170	0.09	22.45508982	0.068	16.96606786	0.044	10.978044
180	0.09	22.45508982	0.067	16.71656687	0.044	10.978044

## A5. Effect of filtration time on flux, TOC , COD, pH and oil rejection

Fixed conditions:

Oil conc. =	0.3	g/L
Emulsifier =	0.1	g/L
pH=	3	
T=	25	C
P=	1	Bar
A=	0.024	m <sup>2</sup>
t=	0.167	h
v=	400	ml/min

Time (min)	V (L)	J (L/M <sup>2</sup> H)	pH	TOC (mg/L)	COD (mg/L)	Oil conc. (mg/L)
0			3	390.3	1620	300
10	0.158	39.42115768	3.4	2.594	15	0
20	0.152	37.9241517	3.4	3.814	18	0
30	0.148	36.9261477	3.3	4.561	21	0
40	0.135	33.68263473	3.3	4.879	22	0
50	0.13	32.43512974	3.2	5.163	23	0
60	0.125	31.18762475	3.2	5.321	24	0
70	0.11	27.44510978	3.2	5.427	24	0
80	0.105	26.19760479	3.2	5.502	24	0
90	0.098	24.4510978	3.2	5.312	24	0
100	0.096	23.95209581	3.2	5.396	24	0
110	0.095	23.70259481	3.2	5.399	24	0
120	0.094	23.45309381	3.2	5.4	24	0
130	0.0935	23.32834331	3.2	5.402	24	0
140	0.092	22.95409182	3.2	5.41	24	0
150	0.091	22.70459082	3.2	5.411	24	0
160	0.091	22.70459082	3.2	5.411	24	0
170	0.09	22.45508982	3.2	5.413	24	0
180	0.09	22.45508982	3.2	5.412	24	0

## A6. Effect of membrane cleaning on permeate flux

Fixed conditions:

pH = 3  
P = 1 Bar  
V = 400 ml/min  
T = 25 C  
Oil Conc.= 0.3 g/L  
A = 0.024 m<sup>2</sup>  
t = 0.167 h

Time (min)	V based on cleansing number (L)			Flux (L/M <sup>2</sup> H)		
	0	1	2	Fresh Membrane	1st Cleaning	2nd cleaning
0	0	0	0	0	0	0
10	158	130	88	39.42115768	32.4351297	21.95608782
20	152	124	85	37.9241517	30.9381238	21.20758483
30	148	115	83	36.9261477	28.6926148	20.70858283
40	135	105	81	33.68263473	26.1976048	20.20958084
50	130	98	80	32.43512974	24.4510978	19.96007984
60	125	96	77	31.18762475	23.9520958	19.21157685
70	110	95	75	27.44510978	23.7025948	18.71257485
80	105	94	71	26.19760479	23.4530938	17.71457086
90	98	92	68	24.4510978	22.9540918	16.96606786
100	96	91	65	23.95209581	22.7045908	16.21756487
110	95	90	60	23.70259481	22.4550898	14.97005988
120	94	88	50	23.45309381	21.9560878	12.4750499
130	93.5	86	46	23.32834331	21.4570858	11.47704591
140	92	84	45	22.95409182	20.9580838	11.22754491
150	91	82	44	22.70459082	20.4590818	10.97804391
160	91	80	43	22.70459082	19.9600798	10.72854291
170	90	80	42	22.45508982	19.9600798	10.47904192
180	90	79	42	22.45508982	19.7105788	10.47904192

## **APPENDIX B**

### **Raw data for photo Fenton Process**



### **B1. Effect of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) concentration on TOC removal**

(H<sub>2</sub>O<sub>2</sub> concentrations; 650 mg/L, 1500 mg/L and 2000 mg/L., FeSO<sub>4</sub>.7H<sub>2</sub>O: 8 mg/L, sun light irradiation for 100 minutes).

Time (min)	TOC (mg/L)		
	H <sub>2</sub> O <sub>2</sub> concentration (mg/L)		
	650	1500	2000
0	89.88	89.88	89.88
10	59.29	58.02	64.65
20	53.67	56.09	62.88
30	48.81	55.68	60.59
40	37.11	47.87	55.62
60	23.7	33.46	46.06
80	17.74	22.8	34.83
100	15.88	17.96	29.36

### **B2. Effect of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) concentration on COD removal**

(H<sub>2</sub>O<sub>2</sub> concentrations; 650 mg/L, 1500 mg/L and 2000 mg/L., FeSO<sub>4</sub>.7H<sub>2</sub>O: 8 mg/L, sun light irradiation for 100 minutes).

Time (min)	COD (mg/L)		
	H <sub>2</sub> O <sub>2</sub> concentration (mg/L)		
	650	1500	2000
0	360	360	360
10	251	216	340
20	200	195	301
30	182	155	287
40	140	139	262
60	113	127	238
80	111	105	202
100	109	103	199

### **B3. Effect of light source on TOC removal**

(H<sub>2</sub>O<sub>2</sub> concentrations; 650 mg/L, FeSO<sub>4</sub>.7H<sub>2</sub>O: 8 mg/L, sun light irradiation for 100 minutes)

Time (min)	Light sources		
	sunlight	UV lamp-box	Solar simulator
0	89.88	93.51	90.42
10	59.29	68.39	58.45
20	53.67	65.97	56.19
30	48.81	63.42	56.08
40	37.11	62.26	54.78
60	23.7	60.86	47.38
80	17.74	59.64	38.91
100	15.88	58.88	27.86

### **B4. Effect of light source on COD removal**

Time (min)	Light sources		
	Natural Solar Light	UV-box	Solar Simulator
0	360	293	290
10	251	258	179
20	200	249	164
30	182	248	146
40	140	246	131
60	113	240	95
80	111	232	65
100	109	230	59

## **B5. Typical experiment : Fenton's reagent, TOC, COD and Oil decomposition**

(H<sub>2</sub>O<sub>2</sub> concentrations; 650 mg/L, FeSO<sub>4</sub>.7H<sub>2</sub>O: 8 mg/L, sun light irradiation, pH 3)

Ferrous (mg/L)

Time (min)	Ferrous ion (mg/L)
0	1.68
10	1.54
20	1.06
40	0.9
60	0.58
80	0.64
100	0.59

H<sub>2</sub>O<sub>2</sub> decomposition

Time (min)	H <sub>2</sub> O <sub>2</sub> (mg/L)
0	650
10	280
20	213
40	160.95
60	115
80	115
100	100

Oil removal

Time (min)	Oil (mg/L)
0	250
10	240
20	235
40	230
60	220
80	220
100	220

### TOC removal

Time (min)	TOC (mg/L)
0	86.41
10	34.08
20	32.9
40	33.87
60	32.81
80	32.5
100	32.1

### COD removal

Time (min)	COD (mg/L)
0	331
10	125
20	119
40	118
60	119
80	118
100	118

# **APPENDIX C**

## **Raw data for adsorption process**

### **C1. Preliminary experiment for biosorbent investigation**

(pH 9, adsorbent dosage: 12.5 g/L, contact time: 80 min, agitation speed: 200 rpm, T: 30 °C,

$C_0$ : 2.8 g/L)

$C_0$  = Initial oil concentration (g/L)

$C_1$  = Oil concentration after adsorption (g/L)

Chicken bone (CB)		Eucalyptus bark (EB)		Watermelon shell (WS)	
$C_1$	% oil removal	$C_1$	% oil removal	$C_1$	% oil removal
2.25	19.64285714	1.1	60.71428571	2.2	21.4285714

### **C2. Effect of contact time on oil removal**

(EB dosage: 10 g/L, pH: 3, agitation speed: 200 rpm, Temperature: 30 °C,  $C_0$ : 3 g/L)

$C_0$  = Initial oil concentration (g/L)

$C_1$  = Oil concentration after adsorption (g/L)

Contact Time (min)	$C_1$ (g/L)
10	1.6
30	1.4
50	1.3
70	1.2
100	0.9
150	0.95
180	0.9

### **C3. Effect of pH**

(EB dosage: 10 g/L, contact time: 100 min, agitation speed: 200 rpm, Temperature: 30 °C,

$C_0$ : 3 g/L)

$C_0$  = Initial oil concentration (g/L)

$C_1$  = Oil concentration after adsorption (g/L)

pH	$C_1$ (g/L)
3	0.9
5	1.2
7	1.8
9	1.5
10	1.44

### **C4. Effect of temperature**

(EB dosage: 10 g/L, contact time: 100 min, pH: 3, agitation speed: 200 rpm)

$C_0$  = Initial oil concentration (g/L)

$C_1$  = Oil concentration after adsorption (g/L)

Temperature (°C)	$C_1$ (g/L)
25	1.35
30	0.9
35	0.75
40	0.66
45	0.75

### C5. Effect of EB adsorbent dosage

(contact time: 100 min, pH: 3, agitation speed: 200 rpm, temperature: 30 °C, C<sub>0</sub>: 3 g/L)

C<sub>0</sub> = Initial oil concentration (g/L)

C<sub>1</sub> = Oil concentration after adsorption (g/L)

EB adsorbent dosage (g/L)	C1 (g/L)
2.5	2.1
5	1.65
10	0.9
15	0.84
20	0.81



## **APPENDIX D**

### **Raw data for integrated Fenton – UF membrane**

### D1. Effect of pretreatment process on permeate flux

T = 25 °C  
 v = 600 ml/min  
 TMP = 1 bar  
 pH = 9.5  
 A = 0.024 m<sup>2</sup>  
 t = 0.167 h

Time (min)	Pretreatment + UF		UF	
	V (L)	J (L/m <sup>2</sup> h)	V (L)	J (L/m <sup>2</sup> h)
0	0.445	111.0279441	0.43	107.2854291
10	0.42	104.7904192	0.4	99.8003992
20	0.41	102.2954092	0.39	97.30538922
30	0.395	98.55289421	0.38	94.81037924
40	0.39	97.30538922	0.37	92.31536926
50	0.388	96.80638723	0.365	91.06786427
60	0.38	94.81037924	0.35	87.3253493
70	0.37	92.31536926	0.342	85.32934132
80	0.365	91.06786427	0.33	82.33532934
90	0.36	89.82035928	0.32	79.84031936
100	0.35	87.3253493	0.315	78.59281437
110	0.348	86.82634731	0.3	74.8502994
120	0.348	86.82634731	0.29	72.35528942
130	0.342	85.32934132	0.28	69.86027944
140	0.34	84.83033932	0.26	64.87025948
150	0.338	84.33133733	0.255	63.62275449
160	0.336	83.83233533	0.25	62.3752495
170	0.334	83.33333333	0.24	59.88023952
180	0.332	82.83433134	0.24	59.88023952
190	0.33	82.33532934	0.238	59.38123752
200	0.328	81.83632735	0.236	58.88223553
210	0.326	81.33732535	0.23	57.38522954
220	0.324	80.83832335	0.22	54.89021956
230	0.324	80.83832335	0.218	54.39121756
240	0.323	80.58882236	0.215	53.64271457
250	0.323	80.58882236	0.215	53.64271457

## D2. Effect of Trans membrane pressure TMP

T = 25 °C  
 v = 600 mL/min  
 pH = 9.5  
 A = 0.024 m<sup>2</sup>  
 t = 0.167 h

Time (min)	(Bar)					
	1		1.5		2	
	V (L)	J (L/m <sup>2</sup> h)	V (L)	J (L/m <sup>2</sup> h)	V (L)	J (L/m <sup>2</sup> h)
10	0.445	111.0279441	1.6	399.2015968	2.5	623.752495
20	0.42	104.7904192	1.5	374.251497	2.4	598.8023952
30	0.41	102.2954092	1.3	324.3512974	2.35	586.3273453
40	0.395	98.55289421	1.2	299.4011976	2.15	536.4271457
50	0.39	97.30538922	1.1	274.4510978	2.1	523.9520958
60	0.388	96.80638723	1.08	269.4610778	2.05	511.4770459
70	0.38	94.81037924	1.02	254.491018	2.02	503.992016
80	0.37	92.31536926	1	249.500998	1.95	486.5269461
90	0.365	91.06786427	0.9	224.5508982	1.88	469.0618762
100	0.36	89.82035928	0.85	212.0758483	1.75	436.6267465
110	0.35	87.3253493	0.82	204.5908184	1.68	419.1616766
120	0.348	86.82634731	0.78	194.6107784	1.65	411.6766467
130	0.348	86.82634731	0.74	184.6307385	1.64	409.1816367
140	0.342	85.32934132	0.7	174.6506986	1.63	406.6866267
150	0.34	84.83033932	0.68	169.6606786	1.62	404.1916168
160	0.338	84.33133733	0.66	164.6706587	1.61	401.6966068
170	0.336	83.83233533	0.62	154.6906188	1.6	399.2015968
180	0.334	83.33333333	0.58	144.7105788	1.58	394.2115768
190	0.332	82.83433134	0.57	142.2155689	1.57	391.7165669
200	0.33	82.33532934	0.57	142.2155689	1.56	389.2215569
210	0.328	81.83632735	0.565	140.9680639	1.55	386.7265469
220	0.326	81.33732535	0.56	139.7205589	1.55	386.7265469
230	0.324	80.83832335	0.555	138.4730539	1.54	384.2315369
240	0.323	80.58882236	0.55	137.2255489	1.54	384.2315369
250	0.323	80.58882236	0.52	129.740519	1.54	384.2315369

### D3. Effect of Cross Flow Velocity (CFV)

T = 25 °C  
 TMP = 1 bar  
 pH = 9.5  
 A = 0.024 m<sup>2</sup>  
 t = 0.167 h

Time (min)	CFV (mL/min)					
	300		450		600	
	V (L)	J (L/m <sup>2</sup> h)	V (L)	J (L/m <sup>2</sup> h)	V (L)	J (L/m <sup>2</sup> h)
10	0.32	79.84031936	0.37	92.31536926	0.445	111.0279441
20	0.31	77.34530938	0.36	89.82035928	0.42	104.7904192
30	0.305	76.09780439	0.35	87.3253493	0.41	102.2954092
40	0.302	75.3493014	0.345	86.07784431	0.395	98.55289421
50	0.299	74.6007984	0.328	81.83632735	0.39	97.30538922
60	0.297	74.10179641	0.32	79.84031936	0.388	96.80638723
70	0.295	73.60279441	0.318	79.34131737	0.38	94.81037924
80	0.28	69.86027944	0.311	77.59481038	0.37	92.31536926
90	0.275	68.61277445	0.308	76.84630739	0.365	91.06786427
100	0.27	67.36526946	0.306	76.34730539	0.36	89.82035928
110	0.26	64.87025948	0.304	75.84830339	0.35	87.3253493
120	0.26	64.87025948	0.3	74.8502994	0.348	86.82634731
130	0.255	63.62275449	0.287	71.60678643	0.348	86.82634731
140	0.25	62.3752495	0.285	71.10778443	0.342	85.32934132
150	0.24	59.88023952	0.279	69.61077844	0.34	84.83033932
160	0.235	58.63273453	0.271	67.61477046	0.338	84.33133733
170	0.23	57.38522954	0.268	66.86626747	0.336	83.83233533
180	0.225	56.13772455	0.258	64.37125749	0.334	83.33333333
190	0.22	54.89021956	0.254	63.37325349	0.332	82.83433134
200	0.218	54.39121756	0.25	62.3752495	0.33	82.33532934
210	0.215	53.64271457	0.245	61.12774451	0.328	81.83632735
220	0.21	52.39520958	0.238	59.38123752	0.326	81.33732535
230	0.21	52.39520958	0.235	58.63273453	0.324	80.83832335
240	0.21	52.39520958	0.23	57.38522954	0.323	80.58882236
250	0.21	52.39520958	0.23	57.38522954	0.323	80.58882236

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