Doctoral Dissertation

APPLICATION OF MICROBUBBLE IN OIL REMOVAL FROM OIL-IN-WATER EMULSIONS

(水中油滴エマルジョンからの油分除去へのマイクロバブルの適用)

LE VAN TUAN

Division of Environmental Science & Engineering
Graduate School of Science and Engineering
Yamaguchi University, Japan

March 2014

博士論文

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A dissertation submitted to the Division of Environmental Science and Engineering of Yamaguchi University in partial fulfillment of the requirements for the degree of Doctor of Engineering (Dr. Eng.)

Advisor: Professor Dr. Tsuyoshi IMAI
Department of Environmental Science and Engineering,
Yamaguchi University

Committee Members:
Professor Dr. Tsuyoshi IMAI
Professor Dr. Masahiko SEKINE
Professor Dr. Masakazu NIINAE
Assoc. Professor Dr. Takaya HIGUCHI
Assoc. Professor Dr. Takashi SAEKI

山口大学大学院理工学研究科環境共生系専攻
Division of Environmental Science & Engineering
Graduate School of Science and Engineering
Yamaguchi University, Japan

ABSTRACT

The development of flotation techniques for oil-in-water emulsions in wastewater effluents has attracted the attention of many researchers. This is essential for ensuring the compliance of water reuse and oil recovery with environmental policies. This dissertation presents the results of using tiny microbubbles and/or microbubbles combined with cyclone bubbles for the treatment of oily wastewater by three modified flotation processes.

The first, a modified column flotation with high rate of induced microbubbles (MBs) was used to separate synthetic emulsified palm oil (EO, d < 16 μm), with using polyaluminium chloride (PAC) as a coagulant and cetyltrimethylammonium chloride (CTAC) as a cationic surfactant. Using MB treatment process alone showed less impact on EO reduction compared to MB–PAC or MB–CTAC. However, MBs presented significant removal EO in acidic water condition. The high concentration of emulsified palm oil (~1000 mg L^{-1}) was successful separated approximately 90% by MB(2.5 min)–PAC(50 mg L^{-1}) from pH 3 to 7 and more than 82% by MB(2.5 min)–CTAC(0.5 mg L^{-1}) with pH between 5 and 7. These data indicated that the good efficiency of EO removal by using the small dosage of CTAC (0.5 mg L^{-1}) with 100 times smaller than using PAC dosage (50 mg L^{-1}) was a meaningful result for further studies that focus on developing flotation system in order to achieve high treatment efficiency and economic.

The second, flotation process presents the results of using tiny microbubbles (MBs, diameter range: 1–16 μm) and MBs combined with "normal cyclone bubbles" (NBs) for the separation of finely emulsified palm oil (EO, d < 16 μm). Treatment by a combination of MB/NB was more efficient for EO separation than was treatment by MB alone. For instance, at an EO concentration of 1009 mg L^{-1} and under identical treatment conditions (treatment time: 60 min, pH: 7.0, temperature: 36.5 ± 0.5 °C, and salinity: 0.0 mg L^{-1}), treatment by MB and MB/NB combination (NBs flow rate: 2.5 L min^{-1}) yielded high EO removal efficiencies of 73% and 86%, respectively. The performance of this flotation technique for EO removal was improved in the presence of NaCl (< 30 mg L^{-1}) and at low temperatures (< 40 °C) or low pH (< 7). These promising results indicate the potential application of this approach for oil field treatment, because of the simple design, reduced floated product, and enhanced oil recovery.

The third, flotation process reveals the results of using MBs (dissolution type) and cyclone MBs (ejector type) for the treatment of real palm oil mill effluent (POME) under batch and continuous operations. This modified flotation method was designed to be a potential approach for reducing the floated product and enhancing oil recovery in POME. Here, POME was collected and treated after decanters processing at the palm oil mill (Synn Palm Oil Company), in Simpang province, Malaysia. According to the analysis results (n = 9), this POME is hot (74.9 ± 4.6 °C), low pH (4.9 ± 0.1) and possesses high fluctuation of oil and grease (O&G: 13,167 ± 4,105 mg L^{-1}), total solid (TS: 60,844 ± 7,194 mg L^{-1}), and chemical oxygen demand (COD: 98,697 ± 10,723 mg L^{-1}). The rapid assessment pollutants loading rate estimated about 7.9 tons O&G, 36.5 tons TS, and 59.2 tons COD were generated in the milling process per day. The separation of these contaminants was well achieved by batch mode operation in a long retention time (i.e. influent O&G: 5,800 mg L^{-1}, removal efficiency more than 60%, at 60-min). For continuous modes, low efficiency of O&G, TS, and COD removal were observed.

学位論文要旨

パームオイルを生産する際に排出される廃水中には油分がエマルジョンの状態で含まれている。このパームオイル含有廃水（エマルジョン）からの油分除去に関して、浮上濃縮法は有効な方法であり、多くの研究者が研究開発を行ってきた。環境保全のために、水の再利用を考慮に入れたオイルの回収を行うことは非常に重要である。本研究では微細なマイクロバブルと通常の旋回流式ノーマルバブルを組み合わせた油水分離技術を開発した。

まず、上述のパームオイル廃水の模擬廃水（パームオイルを用いた模擬エマルジョン廃水：平均オイル径が 16μm 以下）を対象に、既存の技術である凝集沈澱法とマイクロバブルとの組合せによる効率改善を図った。マイクロバブルのみの処理では、ポリアルミニウムクロライド（PAC）＋マイクロバブルあるいはセチルトリメチルアンモニウム塩（CTAC）＋マイクロバブルの処理より低い除去率であった。しかしながら、マイクロバブルのみの処理でも模擬廃水の pH が低い（酸性）場合は、良好な除去率を示した。模擬廃水が高い濃度の場合（～1000 mg L^{-1}）には、PAC（50 mg L^{-1}）＋マイクロバブル処理（2.5 min）により約 90％の除去率が得られ、CTAC（0.5 mg L^{-1}）＋マイクロバブル処理（2.5 min）により 82％以上の除去率が得られた。これらの結果から、CTAC は極めて少量の添加で良好な除去率が得られたことから、CTAC を凝集剤としてマイクロバブルとの組合せによる油分除去の有効性が明らかとなった。

次に、分離回収した油分を再利用することを念頭に、凝集剤を用いないマイクロ及びノーマルバブルを組み合わせた油水分離技術を開発した。マイクロバブル（粒径が 1～16μm）に旋回流式ノーマルバブルを組み合わせることで、マイクロバブルのみの処理に比べて除去効率が向上した。すなわち、エマルジョン濃度が 1009 mg L^{-1} の場合に、マイクロバブルのみの処理（処理時間 60 min）に比べてマイクロ＋ノーマルバブル処理（処理時間 60 min、ノーマルバブルの流量 2.5 L min^{-1}）の方が 73％から 86％に向上した。このマイクロ＋ノーマルバブル処理は塩分の存在（< 30 mg L^{-1}）、40℃以下の水温、そして低 pH（<7）の場合にその処理効率が向上することが確認された。以上の結果から、マイクロバブルに旋回流式ノーマルバブルを組み合わせることで、その浮上速度を上昇させ、油水分離効率の向上が可能であることが明らかとなった。

最後に、実際のパームオイル廃水を対象にマレーシアの現地パームオイル生産工場（Synn Palm Oil Company, in Simpang province, Malaysia）でパイロットプラント（溶解方式のマイクロバブル発生器とエジェクター方式のマイクロバブル発生器との組み合わせ）を製作し、実廃水（Palm Oil Mill Effluent (POME)）からのパームオイルの除去に関する現地実験（回分実験と連続実験）を行った。実 POME は、高温（74.9 ± 4.6 ℃）で低 pH（4.9 ± 0.1）、高い濃度変動（oil and grease: 13,167 ± 4,105 mg L^{-1}, Total Solids: 60,840 ± 7,190 mg L^{-1}, COD: 98,700 ± 10,700 mg L^{-1}）であった。この分析結果から、このパームオイル生産工場からおよそ 7.9 トンの oil and grease、36.5 トンの Total Solids、59.2 トンの COD が 1日に排出されていると推算された。実験結果から、回分運転条件（60 min）において、この実 POME から 60％以上の油分除去が可能であることが明らかとなり、本法の有効性が示されたと考えられる。

ACKNOWLEDGEMENTS

To turn my wishes into practice, I appreciate many good things that my family, teachers and colleagues have given me to finish a long doctor course time at Yamaguchi University. This dissertation would not have been done without the education of my academic supervisors, the funding of the Vietnam Ministry of Education and Training, the funding of Yamaguchi University, and uncountable support from my family and friends.

First of all, I would like to appreciate very much to my advisor: Professor Tsuyoshi Imai for all his kindness to me, expert suggestions on my researches, and warmly encourage for my life in Japan.

It is an honor for me to express my sincere gratitude to academic staffs in Division of Environmental Science and Engineering, Yamaguchi University: Prof. Masahiko Sekine, Assoc. Prof. Takaya Higuchi, Assoc. Prof. Koichi Yamamoto, Assistant Prof. Ariyo Kanno and Ms. Toshimi Yamamoto for their expert and meaningful advices, as well as for their kind attention in many aspects.

I would like to thank all of my research colleagues: Jantima Teeka, Vo Thanh Huy, Emma Yuliani, Gatot Eko Susilo, Wei Jie, Sun Xiaofeng, Cheng Xuehang, Novi Arfarita, Akhmad Rivai, Evi Kurniati, Kanthima Phummala, Rina Febrina, Yatnanta Padma Devia, Riyanto Haribowo, MDM Manesa, and other friends in Japan for their kindly helps, valuable comments, and colorful friendship.

A special thanks to Mr. Masaki Hisadomi, Mr. Tetsuya Sawada, Mr. Ryosuke Doi, Mr. Ng Hsien Wan, and Mr. Daisuke Ayukawa for their valuable helps and support to me during the experiments in Malaysia.

At all times in my life, I would like to express my heartfelt gratitude to my happy family, especially my parents, my wife, my lovely daughters, my brothers and my sisters, for their uncountable love and care.

Le Van Tuan

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CHAPTER 1

INTRODUCTION

1.1 General

Practically, oil-in-water emulsions separation from wastewater effluents is a significant work to improve water quality, oil recovery, water reuse, protection of downstream facilities and environmental permit compliance (Bande *et al.*, 2008; Santander *et al.*, 2011). Common pollutants found in the effluents of many industries are oil and grease, and their concentration in wastewater varies from a few mg L^{-1} to as high as 5% – 10% by volume (Frank, 1988; Lawrence *et al.,* 2006). For instance, the concentration of oil and grease in palm oil mill effluent (POME) normally varies from 130 to 18,000 mg L^{-1} and approximately 2000 mg L^{-1} is present in the form of emulsified oil (EO) (Ahmad *et al.,* 2006; Lam and Lee, 2011).

EO is a colloidal suspension of a liquid with droplet sizes of less than 20 µm, and thus, they can pass through the primary separator (Lawrence *et al.,* 2006). In addition, EO remains stable over time as a result of a combination of some physical and chemical mechanisms (Frank, 1988). Therefore, the removal of very fine oil droplets (2–30 µm) is difficult and very limited (Da Rosa and Rubio, 2005; Lawrence *et al.,* 2006; Le *et al.,* 2013). In reality, various methods are suggested for oil-in-water emulsions treatment, such as adsorption, coagulation, membrane filtration, biological treatment, flotation, hydrocyclone methods, electro-coagulation, and electro-coflotation (Zouboulis and Avranas, 2000; Lawrence *et al.,* 2006; Bande *et al.,* 2008).

Among these methods, the microbubble flotation has attracted attention from many researchers. Thus, a microbubble (MB) is defined as a tiny bubble, whose diameter is less than several hundred micrometers, and normally between 10 and 60 µm. MB has various useful characteristics, including a high solubility in the liquid, a large gas–liquid interfacial area, high inner pressure, and long residence time (Terasaka *et al.,* 2011). For separation of oil-in-water emulsions, the MB technologies have been shown valuable application due to high treatment efficiency, handling high-shock loads, enhancing oil recovery, low capital investment costs, and low operational costs (Rubio *et al.* 2002; Li *et al.,* 2007; Bande *et al.,* 2008; Le *et al.,* 2013). Moreover, MB flotation can be operated as a primary treatment for reducing the cost of aerobic digestion (i.e. bio-oxidation ponds) because of high dissolved oxygen concentration in effluents (Rubio *et al.* 2002).

1.2 Significance

MBs in water and EO carry negative charges, thus hindering the attachment without coagulation (Lawrence *et al.,* 2006). Consequently, the combination of coagulation and flotation has usually selected for the separation of EO (Le *et al.*, 2012). However, the complex operation steps in the coagulation process, including flash mixing and slow mixing, as well as the long retention time (for sedimentation and flotation) are the main demerits of this method. Furthermore, a large amount of sludge produced with metal hydroxides (aluminium or iron) or organic de-emulsifiers leads to difficulties in dewatering of the sludge and efficient oil recovery (Frank, 1988). Besides coagulants, cationic surfactants are added to make the MBs positively charged (Henderson *et al.,* 2008; Edzwald, 2010). Although cationic-surfactant-treated absorption materials such as organoclay, wheat straw, and barley straw have been used to separate EO (Ibrahim *et al.,* 2009), the performance of the combination of cationic surfactants and MBs in the separation has not been studied widely.

On the other hand, theoretical and practical implications of the flotation method showed that oil-bubble collection efficiency increases with decreasing bubble size (Moosai and Dawe, 2003). Unfortunately, the high energy required for producing MBs has a significant effect on the operating costs (Edzwald, 2010). Because of the low rising velocities of MBs, EO droplets, and oil-gas agglomerates, a long residence time is normally required. Additionally, MBs lead to high water content in the floated product (Miettinen *et al.*, 2010). Therefore, this study using a variety of gas bubble sizes (MBs in combination with "normal cyclone bubbles", NBs) is expected to increase the hydrodynamic forces and decrease the residence time in the flotation method. This latter technique has developed for separation of oil from real POME.

1.3 Objectives

The main objectives of this research were to:

1. Evaluate and compare the effectiveness of fine EO separation by a modified flotation process under three process conditions: MBs treatment only, MBs treatment with polyaluminium chloride (PAC) as a coagulant (MBs–PAC), and MBs treatment with cetyltrimethylammonium chloride (CTAC) as a cationic surfactant (MBs–CTAC).

2. Develop a new column flotation and investigate the effectiveness of fine EO treatment by MBs only and treatment by MBs in combination with NBs.

3. Develop a new flotation process and apply to treatment of a real POME under batch and continuous operations.

1.4 Structure of dissertation

CHAPTER 1	Introduction
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CHAPTER 4	Performance of tiny microbubbles enhanced with "normal cyclone bubbles" in separation of fine oil-in-water emulsions
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CHAPTER 6	Conclusions and future works

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CHAPTER 2

LITERATURE REVIEW

2.1 Oil and grease (O&G)

2.1.1 Overview

Oil and grease (O&G) are common pollutants found in the effluents of many industries. The term of O&G contains a wide range of contaminants, such as fatty acids, surfactants, petroleum hydrocarbons, phenolic compounds, animal oils, vegetable oils, etc. (Lawrence *et al.,* 2006). Components of oily wastewater include mainly n-alkanes, alkenes, alkynes, aromatics (benzenes, phenols), poly-nuclear aromatics (humus, polycyclic aromatic hydrocarbons), and other complex hydrocarbon compounds (Zhao *et al.,* 2006). According to US Environmental Protection Agency, O&G concentrations are not determine as the present of specific compounds but are defined as substances that can be extracted by a particular solvent, such as hexane or Freon (carbon tetrachloride chloroform, or fluorocarbons) (Frank, 1988; Lawrence *et al.,* 2006).

Depending on droplet size of O&G presents in water/wastewater. O&G could be counted in the several forms, free oil (macro-emulsions) (>150 μm), emulsified oil (micro-emulsions) (<20 μm) and dissolved oil (mini-emulsions) (<5 μm) (Bande *et al.,* 2008). In addition, O&G can be classified depend on its density and water density. Oil will float if the ratio of the density of oil to receiving water is larger than 1.0 and opposite (Figure 2.1) (Lawrence *et al.,* 2006).

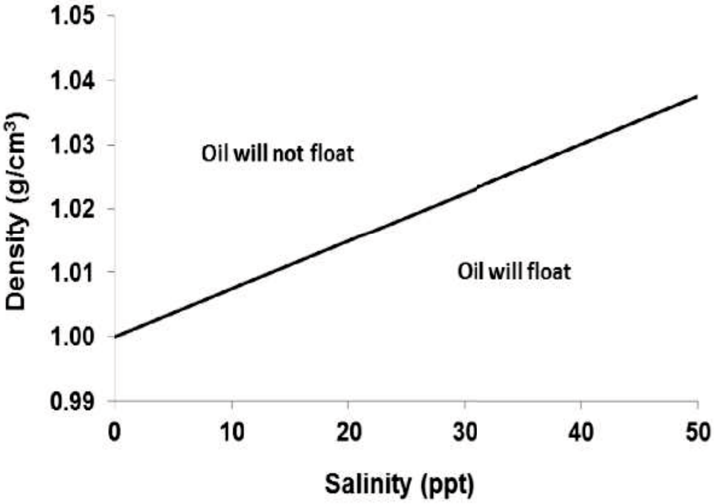

Figure 2.1 The relationship between density and salinity effect on the floatable characteristic of oil. Temperature: 15 °C. (Lawrence *et al.,* 2006)

Figure 2.1 shows the relationship of density and salinity effect on the floatable characteristic of oil. In oily wastewater treatment, two types of oil are needed to separate, free oil and emulsified oil. Because of lower specific gravity than water, free oil can rapidly rise to the surface, thus it is called floatable oil. Emulsified oils are often resistant to being separated from water because the droplets are either resistant to rising to the surface and/or they rise so slowly that they cannot be removed effectively with most of oil-water gravity separators.

2.1.2 O&G in wastewater of selected industrial effluents

O&G in wastewater effluents come from many industries sources such as petroleum refineries, metal finishing, iron and steel plants, aluminum forming, military maintenance, food processing, soap manufacturing, paper de-inking operations, mill waste, chemical processing, manufacturing plants, and others (Gu and Chiang, 1999). Oily wastewater comes from numerous sources including floor washes, machine coolants, alkaline and/or acid cleaners, spills from manufacturing process, etc. (Lawrence *et al.,* 2006). Oil-contaminated wastewater is a very common occurrence. The oil concentration varies greatly from several mg L^{-1} to as high as 5–10% by volume (Frank, 1988) and it normally ranges between 100 and 1000 mg L^{-1} (Bande *et al.,* 2008; Santander *et al.,* 2011). The main sources of oily wastes from industries are shown in Table 2.1 and some reviews of the O&G concentrations in selected industrial effluents are listed in Table 2.2.

Table 2.1 The main sources of oily wastes from industrial effluents (modified from Lawrence *et al.,* 2006)

Source	Industries	Characteristic
Floor washing	All industries	Mixture of many types of oils from spill of hydraulic fluids; oil mists from spraying/coating, etc.; may present in free and emulsified forms; can be stabilized by dirt, debris and solvents.
Vegetable and animals fats splitting, refining	Edible oil, fish processing, detergent manufacture, tank car washing, textile, leather	Both free and emulsified oils; Difficulty for treatment process
Petroleum oils	Petroleum refining, drilling	Both free and emulsified oils; Difficulty for treatment process
Machine coolants	Metals manufacturing machining	Normally emulsified oils; Difficulty for treatment process
Acid and alkaline cleaning	Metal fabrication, iron and steel, metal finishing, industrial laundries	Normally emulsified oils; Difficulty for treatment process

Table 2.2 Some reviews of the O&G concentrations in selected industrial effluents

Effluent	O&G (mg L^{-1})	Effluent	O&G (mg L^{-1})
Palm oil industry(*)	130 – 18,000	Aluminum rolling	5,000 – 50,000
Food processing	3,000 – 4,000	Can forming	~ 200,000
Mining operation	3,000 – 23,000	Petroleum refining	16 – 3,200
Metal finishing	100 – 5,000	Oil drilling	7 – 1,300
Steel-rolling mill	~ 7,200	Crude oil tank ballast	3 – 72

(*)Adapted from (Lam and Lee, 2011); others adapted from (Lawrence et al., 2006)

2.1.3 Impacts of O&G

Naturally, oil has been part of the environment for millions of years (Kingston, 2002) and oil spills may cause of nature or human activities. In term of human activities, for instance, each year the petroleum industrial is transport about 5 million tons of petroleum across the seas around the world, and thus putting the marine ecosystem in a dire risk (Al-Majed *et al.,* 2012). Numerous industrial effluents discharge high concentration oily wastes (Lawrence *et al.,* 2006). Without treatment, oil discharged into the water environment may cause many serious effects on the aquatic life (i.e. long-term impacts on fishes, benthic organism, seabirds), odor and color pollution, as well as reduce natural water purification (Kingston, 2002; Abid *et al.,* 2003; Bande *et al.*, 2008). Bathing in contaminated oily water and/or consumption sea foods affected by toxic oils could be harmful for human health even causes cancer. Oil can be covering to filter surface area that lead to decrease the filtration efficiency. Oil layers can be preventing the transfer of oxygen and nutrients to microorganisms in the biological wastewater treatment process (Bande *et al.*, 2008).

Oil spills into the sea surface might effected by many factors such as sea conditions, wind velocity and direction, current and tides, temperature and atmospheric conditions (Kingston, 2002; Al-Majed *et al.,* 2012). Although as a slick of few millimeters thick, however, various physical, chemical and biological processes simultaneously undertakes after oil spills on the sea surface (Figure 2.2), such as spreading, evaporation, emulsification, photo-oxidation (photolysis), dispersion, sinking, resurfacing, tar balls formation, and biodegradation (Al-Majed *et al.,* 2012).

The sinks of oil spillage in the seawater can be summarized as follows: after oil spills on the sea surface, the volatile compounds in crude oil rapidly evaporate. This contains most of the toxic components. In addition, atmospheric oxidation (UV radiation in sunlight) can oxidize some of the constituents present in oil. The oxidation products may contain some of acidic and phenolic compounds, which may be more toxic than the original hydrocarbons. Furthermore, some hydrocarbons can dissolve into the water phase. As well, oil droplet is broken by sea-wave actions into small size 0.01–1 mm and is stabilized in the water column until degraded by bacterial action. Moreover, adsorption with other substances (clay or sand) in the water column may transfer oil to the seabed. Last but not less, accumulations processes can also cause tar balls to sink into the seabed (Kingston, 2002).

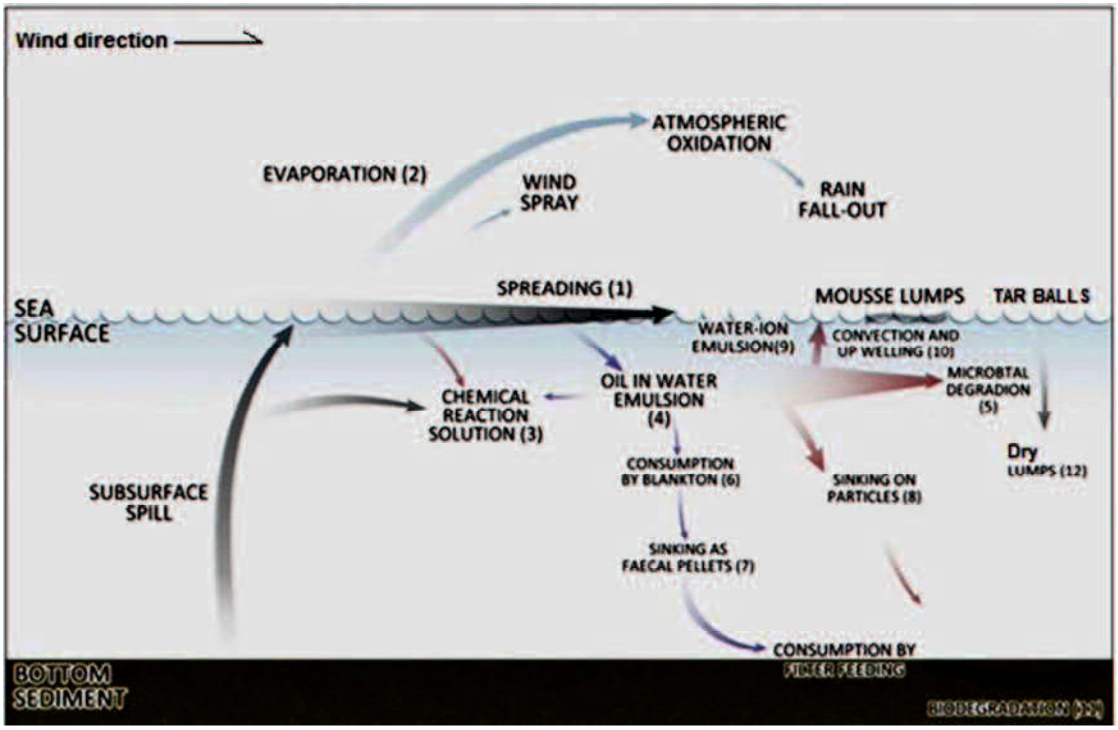

Figure 2.2 Physical, chemical and biological processes changing properties of oil spilled into the sea (modified from Al-Majed *et al.,* 2012)

2.2 Oil-in-water emulsions

2.2.1 Formation and characteristic of emulsified oil

Oil-in-water emulsion is as a colloidal system, in which oil (droplet size, d < 20 µm) is dispersed in the water phase. Oily emulsion concentration in the wastewater may range from a few mg L^{-1} to as much as 5–10% by volume (Frank, 1988). Taking palm oil mill effluent (POME) for instance, the concentration of O&G in widely varies from 130 to 18,000 mg L^{-1} (Lam and Lee 2011), and approximately 2,000 mg L^{-1} is present in the form of emulsified oil (EO) (Ahmad *et al.,* 2006).

EO is formed by several ways as follows (Frank, 1988; Lawrence *et al.,* 2006; Hempoonsert *et al.,* 2010):

- Energy (i.e. pumping, mixing): violent mixing and shearing actions of oily wastewater in transfer pumps; other activities of adding energy may count by accidentally, mechanically emulsify oil.
- Emulsifiers: adding certain organic chemicals such as soaps and detergents can form emulsions.
- Heat: some organic compounds can be formed emulsions at low or high temperature.

Oil-in-water emulsion stability is preserved by a combination of complex physical and chemical mechanisms (Frank, 1988; Beeby and Nicol, 1993). Normally, an emulsifier is a complex molecule, often having a hydrophilic (water-loving) group and lipophilic (oil-loving) group (Figure 2.3 a). In the water phase, the emulsifier has an affinity characteristic for both water and oil that leads them to gain the natural forces of coalescence. On the other hand, EO usually has high surface negative charges, which provide stability to the emulsion systems. Especially, the common existence of surface-active agents, such as organic materials or cleaners, these chemicals and EO molecules usually carry an electric charge (i.e. COO^-, OH^-) and seek out the oil/water interface. Thus, static electric chargers accumulated by friction between the oil and water phases enhance the stability of oil-in-water emulsions. Additionally, fine-solid particles may stabilize an emulsion by adsorbed at the oil/water interface. This interfacial film tends to prevent the coalescent of the dispersed droplets (Figure 2.3b).

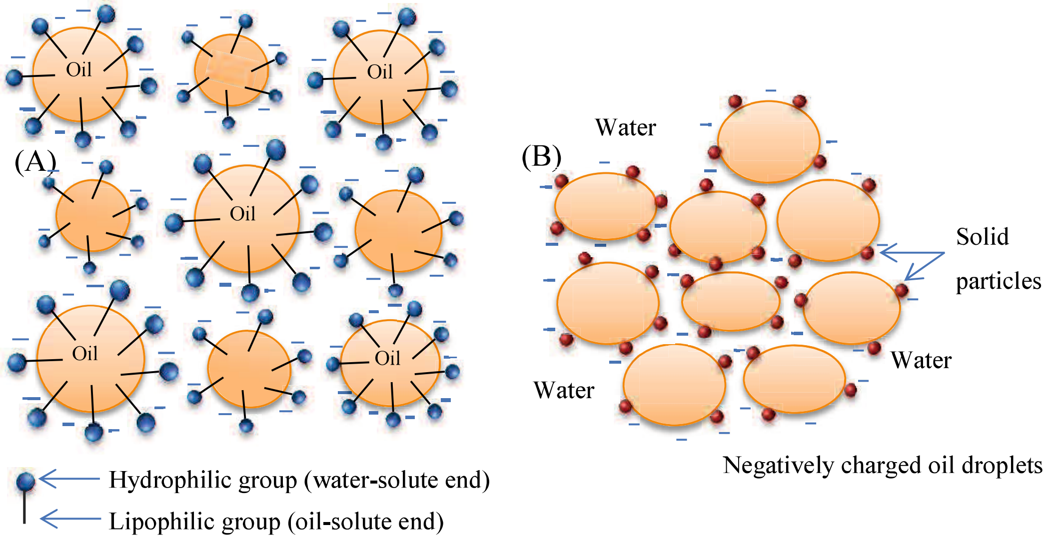

Figure 2.3 Oil-in-water emulsions by $^{(a)}$ chemical and $^{(b)}$ physical stabilization (modified from Frank, 1988)

2.2.2 The importance of EO separation

Separation of oil-in-water emulsion from wastewater effluents is important for improving the water quality, oil recovery, and water re-use, for protecting downstream facilities, and for ensuring compliance with environmental policies. The US Environmental Protection Agency limited the O&G content of industrial wastewater effluents was lower than 40 mg L^{-1} (Gu and Chiang, 1999). In palm oil industry, the government of Malaysia (from 1984), Thailand (from 1996) and Indonesia (from 2002) manage the palm oil mill effluents used for O&G concentrations discharge standards are lower than 50 mg L^{-1}, 25 mg L^{-1} and 25 mg L^{-1}, respectively. Moreover, the high performance of using emulsifying oils with water for apply in spray combustors have been attracted many researchers to re-use oils in oily wastewater (Fu *et al.,* 2003).

Thus, oil properties play important roles for oil and water separation. EO becomes stable over time by its physical and chemical mechanisms (Frank, 1988). Therefore, the removal of oil-in-water emulsions, especially in heavy crude oils (where the oil density is close to the water density) is difficult and very limited (Moosai and Dawe, 2003; Da Rosa and Rubio, 2005; Bande *et al.*, 2008). In addition, the extent of oily treatment problem can be dependent on the grade of emulsion stability (Beeby and Nicol, 1993). Consequently, we can classify into two types of oily wastewater treatment, primary and secondary treatment systems. The primary system is engaged to separate floatable oil (lower specific density than water) from water and EO, in which, skimmer and gravity separation are the main treatment methods. So far, the purpose of secondary treatment system is continued to remove oil –in – water emulsions.

2.3 Microbubble (MB)

2.3.1 Properties of MB

A microbubble (MB) is defined as a tiny bubble, whose diameter is less than several hundred micrometers, and normally between 10 and 60 μm (Terasaka *et al.,* 2011). MBs have various useful characteristics, including a high solubility in the liquid, a large gas–liquid interfacial area and long residence time. Therefore, they can enhance to dissolve the oxygen gas into water (Rubio et al. 2002; Kawahara *et al.,* 2009; Terasaka *et al.,* 2011; Le *et al.*, 2013).

The importance factors for understanding the properties of MBs are MB size (diameter), rising velocity, type of gas and surface charge. Thus, MB diameter (sizes of several 100 μm and less) rise as rigid spheres (Edzwald, 2010) and this MB size can be used to calculate its rising velocity (i.e. via Stokes equation, which is covered later) (Moosai and Dawe, 2003). Some MBs are too small even below visible size and have color similar to snow. Hence, it can reflect light in all directions; this explains why the MBs are seemed slowly rising in water. Sometime, MBs cloud is called “white-water” or “milk-water” (Rodrigues and Rubio, 2007; Edzwald, 2010). In flotation techniques, MB size is key factor effects on the efficiency of collisions and attachment between particles and MBs (Edzwald, 2010). Practically, air gas is widely used in water treatment facilities, the gases (mainly N_2 and O_2) are non-polar molecules, and therefore these molecules have a weakest intermolecular force interaction (Edzwald, 2010). Air bubbles in waters exert a negative surface charge under wide range of pH. Many researchers have identified this characteristic by negative zeta (ζ) potential measurement. Theoretical, the negative zeta potentials are commonly used for assessment of the accumulation of negatively charged surfactants or aquatic humic substances that concentrate at the bubble-water interface (Edzwald, 2010). However, even in distilled water MB zeta potential can be easily measured about -35 mV (Agarwal *et al.,* 2011). This could be caused by smaller anions (i.e. HCO_3^-, d ~ 4 A°) that reside at the bubble–water interface more than larger hydrated cations (i.e. H_3O^+, d ~ 9 A°) (Edzwald, 2010). The charge at bubble surfaces can be re-charged (positive) with addition of cationic surfactants or polyelectrolytes for various water applications.

2.3.2 MB generation techniques

MBs formation, growth and collapse in a solution can be termed as cavitation. Cavitation phenomenon is also classified into four categories depended on the method of generation, including hydrodynamic, acoustic, optic and particle (Gogate, 2008). The hydrodynamic cavitation is produced as a result of the pressure in the liquid systems (i.e. pumps, turbines, nozzles, etc.) drops below the saturated vapor pressure. While the cavitation refers to the nucleation, growth and collapse of bubbles under ultrasonic waves is called acoustic cavitation. The optic cavitation produces when the medium is radiated and broken down forming bubbles by high-intensity laser pulses under extreme conditions. Besides the photons in the optic cavitation, other elementary particles (e.g. protons; neutrons) can also be generated bubbles when these high-energy particles pass the mediums. As a result, amount of mediums will be ionized and rapidly heated, resulting in tiny bubbles (Gogate, 2008; Agarwal *et al.,* 2011). In reality, many techniques have been developed for the generation of MBs (Terasaka *et al.,* 2011), of which the hydrodynamic cavitation method is widely used in term of water treatment application (Agarwal *et al.,* 2011). In this part, we mainly focus on the principle of this typical method.

From hydrodynamic cavitation, most all MB generators involve mechanical parts (e.g. a pump, a nozzle) where strong shears force impacts on a liquid (Terasaka *et al.,* 2011). MBs can be created from the pressure drop (decompression) in the nozzle/injection devices or gas–water circulation (Edzwald, 2010; Terasaka *et al.,* 2011; Agarwal *et al.,* 2011). Zhou *et al.,* 2009 was fully discussed the factors affecting bubble formation by hydrodynamic cavitation. It can be named as nozzle properties (size, length), water temperature, the existence of tiny particles (i.e. hydrophobic particles) in water, etc. Some reviews of MB generators are demonstrated as below:

(1). Pressurized dissolution (decompression) type

A typical pressurized dissolution type MB generator is shown in the Figure 2.4. At high pressure (300–600 kPa), the mixture of liquid and gas is pressurized in the dissolution tank. Unstable supersaturated gas is eventually escapes out from the water resulting in a large number of MBs (normally diameter: 30–100 µm) (Rodrigues and Rubio, 2007; Terasaka *et al.*, 2011; Agarwal *et al.*, 2011).

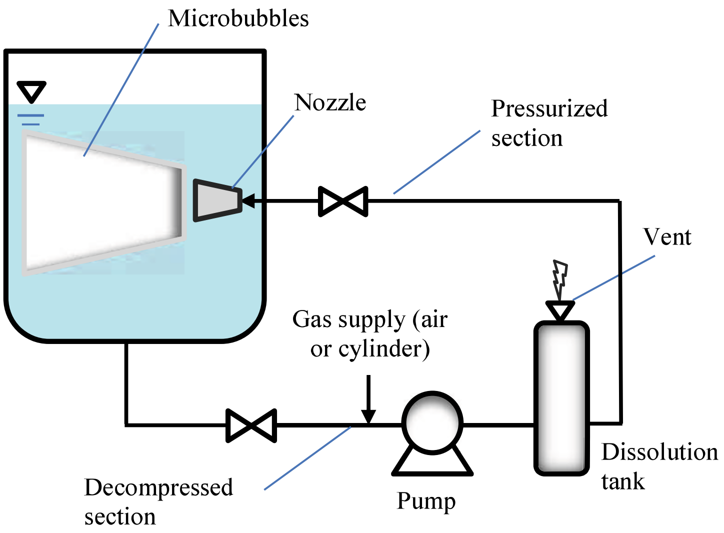

Figure 2.4 MB generator: pressurized dissolution (decompression) type (Terasaka *et al.*, 2011)

(2). Venturi type

Similar to pressurized dissolution type, the venturi type aerator (Figure 2.5) has also been commonly used. This is because of the advantages of compact size, low pump power (about 80–105 kPa) and high-density generation of MBs (diameter < 1mm, with a mean diameter below 100 µm) (Xu *et al.,* 1996; Agarwal *et al.,* 2011). A recirculation stream entrances the inlet of a venturi nozzle may contain milli-bubbles is feed with water/wastewater stream. MBs are formed due to decrease in static pressure when the liquid-gas phase flow is accelerated through the throat of the venturi tube (Terasaka *et al.,* 2011).

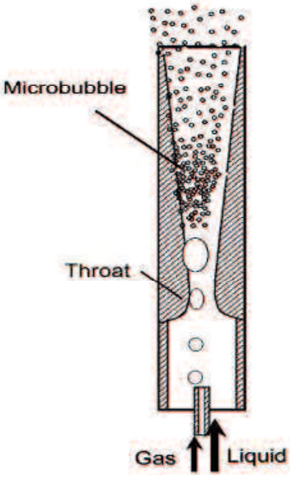

Figure 2.5 MB generator: Venturi type (Xu *et al.,* 1996)

(3). Ejector type

Figure 2.6 shows an ejector type MB generator. Basically, ejector technique uses the venturi effect by using a converging-diverging nozzle to change the pressure energy from liquid to velocity energy (Parmar and Majumder, 2013). A low-pressure zone will formed and enhanced a suction gas to entrance from the most reduced pressure points (Terasaka *et al.,* 2011). After passing through the throat of the ejector, the reducing of gas-liquid velocity can be created the number of MBs with diameter 40–50 µm (Parmar and Majumder, 2013).

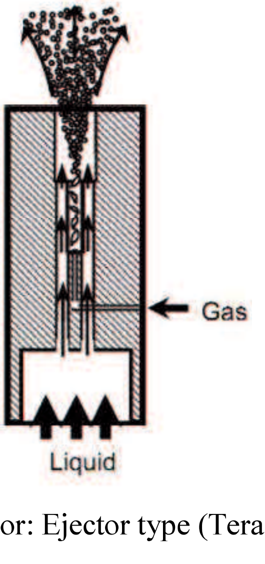

Figure 2.6 MB generator: Ejector type (Terasaka *et al.,* 2011)

(4). Gas–water circulation (or rotary liquid flow) type

For gas–water circulation type generator (Figure 2.7), pressurized water is pumped to create a cyclone liquid, as the same time the gas is introduced into the water vortex. The high smashed and sheared gas-liquid mixture (gas: liquid ratio ranges from 1:7 to 1:15) can produce MBs of diameter 10 to 50 µm (Terasaka *et al.,* 2011; Parmar and Majumder, 2013).

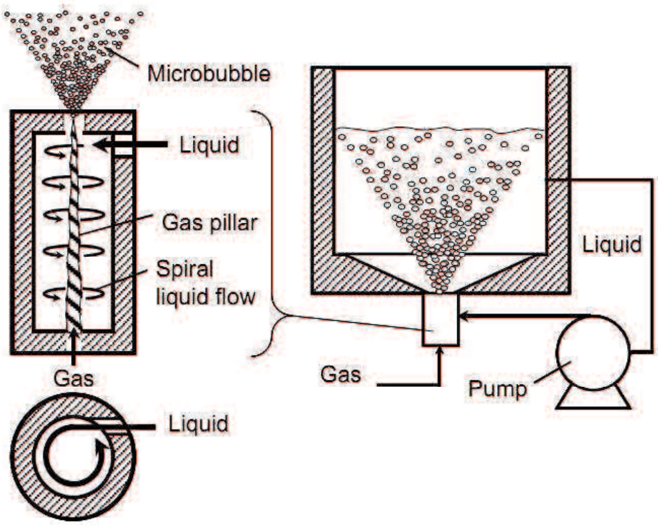

Figure 2.7 MB generator: Gas–water circulation type (Terasaka *et al.,* 2011)

2.3.3 Water clean-up by MB technology

Practically, there are many applications of MBs for water treatment, especially applied the MB flotation technologies (Terasaka *et al.*, 2011). Numerous flotation technologies (dissolved air flotation, induced flotation, electro-flotation, column flotation, etc.) are demonstrated in the section 2.4.

Additionally, in the past few years, MBs and nanobubbles have been widely used as a water clean-up technique for degradation of organic pollutants, disinfection, cleaning and de-fouling of solid surfaces on membranes (Agarwal *et al.*, 2011). This is because the fine bubbles may be able to generate highly reactive free radicals (*OH) without the use of any toxic chemical (Agarwal *et al.*, 2011). Various organic compounds (i.e. alachlor herbicide, p-nitrophenol, rhodamine B) are degraded by MBs and nanobubbles technique. Catalyze chemical reactions and detoxification water efficiencies are improved by ozonation or UV irradiations of MBs/nanobubbles (Agarwal *et al.*, 2011).

In this context, we would like mainly focus on oil-in-water treatment by gas flotation technique.

2.4 Separation of oil-in-water emulsion by bubble treatment

2.4.1 Bubble and floc-bubble aggregate rise velocity base on Stokes' equation

Droplet rise velocity plays an important role in gas flotation method. The rise velocity equations for bubble and floc-bubble aggregate in a column of water has attracted many researchers (Moosai and Dawe, 2003; Edzwald, 2010). Without turbulence (quiescent condition), the Stokes' law can be used to calculate the fine bubble ($d < 130$ μm) and floc-bubble aggregate ($d < 200$ μm) rise rate (Letterman, 1999; Moosai and Dawe, 2003; Edzwald, 2010).

Stokes' equation:

$$v = \frac{g(\rho_w - \rho_o)d^2}{18\mu_w} \qquad (2.1)$$

Where v = rate of flotation, cm/s

d = droplet diameter (oil or gas), cm

g = gravitational acceleration, 980 cm/s^2

$\rho_w - \rho_o$ = difference in density between continuous (water) and droplet phase (oil or gas), g/cm^3

μ_w = dynamic viscosity of continuous (water) phase, g/cm.s

The Stokes equation (2.1) shows that the rise velocity is dependent on droplet diameter and the difference in density between continuous and droplet phase. Therefore, in separation oil-in-water emulsions by gas flotation, the identifying of oil droplet size and bubbles size are very important. The smaller droplets get slower the rise velocity. In addition, oil-bubble and/or floc-bubble aggregate may reduce the oil density thereby increasing the differential density and enhancing a faster flotation rate (Moosai and Dawe, 2003; Grattoni *et al.*, 2003). However, it should be noted that Stokes equation holds well practically for solid spheres in the range of 10 to 200 μm (Moosai and Dawe, 2003).

Practically, it should be achieved a rise velocity of oil-bubble agglomerate in reasonable residence time (< 30 min) for a commonly separation unit with 2 m in height (Moosai and Dawe, 2003). In oil field wastewater, EO is well known as a suspension of droplet sizes less than 20 μm (Lawrence *et al.*, 2006). Using Stokes equation predict EO (size = 20 μm, $\rho_w - \rho_o = 0.1$ g/cm^3) rise velocity for 1.0 cm results in flotation time 600 s, equivalent to the velocity 1.67×10^{-3} cm s^{-1}. Consequently, the oil-bubble agglomerate diameter is required bigger than 60 μm to achieve the flotation time (Moosai and Dawe, 2003). On the other hand, gas bubbles, normal flotation techniques are normally produce the bubbles (diameter > 50 μm) larger than oil drops. Due to the bigger size and significantly different of density between water (~ 1.0 g/cm^3) and gas (~ 0.1 g/cm^3), gas bubbles may rise faster than oil droplet in same size from 10 to 100 times (Moosai and Dawe, 2003). It estimated that the rise rate for a 100 μm bubble is about 5.56×10^{-1} cm s^{-1} at temperature 20 ^{o}C (Edzwald, 2010). Using a variety of gas bubble sizes is expected to increase the hydrodynamic forces (Moosai and Dawe, 2003), decrease in the overall density of the phase, and consequently decrease the residence time in the flotation method (Bai *et al.*, 2011). Moreover, small and large MBs can capture small and large oil droplets, respectively (Moosai and Dawe, 2003).

2.4.2 Oil-bubble interaction

Gas bubble rises faster than oil. Oil-bubble interaction can be understand as an entrapment of gas bubbles with oil drops, in that case the oil can rise quickly than without the gas (Moosai and Dawe, 2003; Grattoni *et al.*, 2003). Figure 2.8 shows the oil-bubble rise hydrodynamic (Figure 2.8 a) and the attachment (Figure 2.8 b) between them. At first, the oil drop and the bubble must come into close enough to collision. If oil drops are outside the collision zone, they will miss the gas bubble. The interaction efficiency between oil and gas bubble are effect by number factors as a flow pattern around the oil drops (Grattoni *et al.*, 2003), oil and gas bubble properties, hydrodynamic forces, thermodynamic, and physicochemical aspects (Moosai and Dawe, 2003; Lawrence *et al.*, 2006). This will be discussed later in the section 2.4.3.

Although the attachment of gas bubbles and oil droplets mechanisms are complicated, but the spreading oil on gas has been observed and presented (Grattoni *et al.*, 2003; Moosai and Dawe, 2003). There was an evidence of oil over gas spreading and non-spreading (Figure 2.9) depending on a spreading coefficient of a fluid (S) (Grattoni *et al.*, 2003). In the oil-gas-water system, the oil spreading coefficient can identified as equation:

$$S_o = \gamma_{wg} - \gamma_{ow} - \gamma_{og} \qquad (2.2)$$

Where γ_{wg}, γ_{ow} and γ_{og} are water – gas, oil – water, and oil – gas surface tension (dynes cm^{-1}), respectively. If $S_o > 0$ (positive, $\gamma_{wg} > \gamma_{ow} + \gamma_{og}$, spreading), the total spreading of oil layer onto water – gas interface (Figure 2.9 a). The spreading phenomenon is essential for the oil to rise faster and for the oil-gas continue attaches during the movement to the surface. And if $S_o < 0$ (negative, $\gamma_{wg} < \gamma_{ow} + \gamma_{og}$, non-spreading), there is a definite contact angle between the oil and the gas – water interface (Figure 2.9 b) (Grattoni *et al.*, 2003).

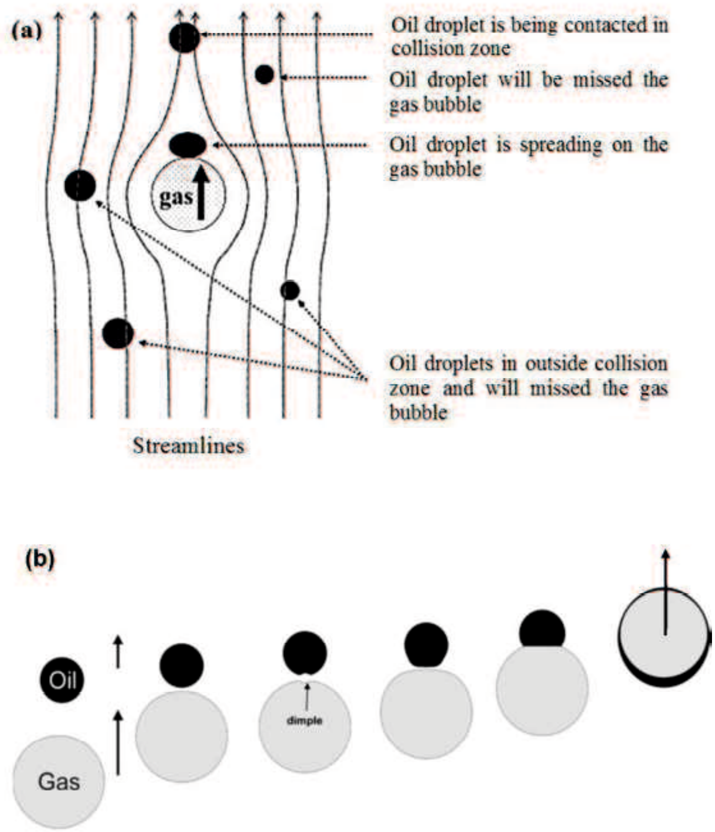

Figure 2.8 $^{(a)}$ The oil-bubble rise hydrodynamic and $^{(b)}$ the oil-bubble attachment (modified from Moosai and Dawe, 2003)

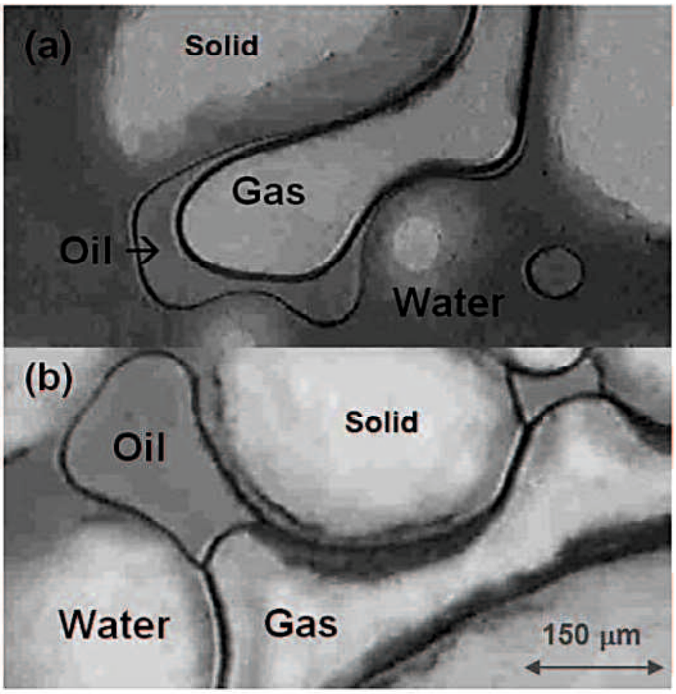

Figure 2.9 The oil-gas-water system: oil spreading $^{(a)}$ and non-spreading $^{(b)}$ conditions (modified from Grattoni *et al.*, 2003)

2.4.3 Factors affecting on oil-gas bubble contacts

The efficiency of flotation process is strongly dependent on the attachment of gas bubbles to the dispersed oil droplets (Moosai and Dawe, 2003). This attachment relies on:

- Characteristics of oil droplets (diameter, viscosity, density)
- Characteristics of bubbles (diameter, density)
- Hydrodynamic forces (i.e. the movements of bubbles, drops and continuous phase)
- Thermodynamic forces (i.e. interfacial interactions)
- Physicochemical aspects (i.e. chemical interactions)

Principally, the movement of bubble and fine oil drop is complex in oily wastewater. Thus it is not obviously defined which processes, oil-bubble (and bubble-bubble) collision, interaction and detachment are directly affected on the flotation efficiency (Painmanakul *et al.*, 2010). Due to the numerous well-design experiments and computational models have been submitted, it is noted that the bubble-bubble (and oil-bubble) interactions and forces can be described theoretically, including Van der Waals, electrostatic, hydrophobic interaction, and hydrodynamic repulsion (Painmanakul *et al.*, 2010; Edzwald, 2010). However, the quantification of the forces is difficult in some cases (Edzwald, 2010).

In practice, gas bubbles play an important role in the separation of oil droplets from the liquid phase (Moosai and Dawe, 2003; Santander *et al.*, 2011). It is commonly understood that a decrease in the gas bubble size results in improved fine particle separation and oil droplet recovery, because of the large air-bubble surface area. On the other hand, the oil droplets (or fine particles) and gas bubbles are carry the negative charge on the surface, thus hindering the attachment between them (Edzwald, 2010). Therefore, the oil droplets (i.e. emulsified oil) should be increased the size and re-charged the interface by coalescence or using cationic surfactants before attempting to flotation (Grattoni *et al.*, 2003; Edzwald, 2010). For oily wastewater treatment, many different chemical agents (i.e. coagulants, flocculants, and polymers) have been investigated the optimum dosage, pH and treatment time for an application on flotation process (Ahmad *et al.*, 2006; Painmanakul *et al.*, 2010; Le *et al.*, 2012). Furthermore, the vital factors for this hybrid method including gas flow rate, bubble size, viscosity of water phase, equipment or reactor design and chemical agents using have also been attracted many researches (El-Kayar *et al.*, 1993; Da Rosa and Rubio, 2005; Painmanakul *et al.*, 2010; Le *et al.*, 2013). Normally, the essential steps in the oily wastewater flotation process are oil emulsion breaking (increase the size), approach of oil and bubble, attachment of bubble to the oil, oil-bubble aggregates rise to the surface for it to be skimmed off (Grattoni *et al.*, 2003).

2.4.4 Types of flotation processes

In general, flotation can be described as a gravity separation process in which gas bubbles attach to fine particles to cause the apparent density of the bubble-particle agglomerates to be less than the water density, thereby allowing the agglomerate to rise up the surface (Letterman, 1999). Particularly, a good flotation for oily wastewater separation is combination of an effective chemical program (emulsified oil breaking), a well introduced gas bubbles into the water system, and an efficient skimming floated product in the surface (Frank, 1988).

The emulsion destabilization can be maintained by chemical treatment (the section 2.5). Here, the key design factors for a flotation setup are the flotation space where the bubbles are formed and where the oil-gas interaction occurs (Moosai and Dawe, 2002). Thus, there are number of methods to produce MBs that has mentioned before (the section 2.3). Consequently, variety types of flotation processes have been developed (Letterman, 1999; Rubio *et al.*, 2002). Practically, induced air flotation (IAF) and dissolved air flotation (DAF) are two common techniques used for oily wastewater clean-up (Frank, 1988; Moosai and Dawe, 2002). Recent developments in flotation techniques such as electro-flotation, column flotation, centrifugal flotation, etc. are also revealed in this section.

(1). Induced air flotation

In IAF technique (Figure 2.10), the gas is mechanically introduced into the mixing area by a combination of a high-speed mechanical agitator or an air injection system (Rubio *et al.*, 2002; Painmanakul *et al.*, 2010). For oily wastewater treatment, the mechanical force agitates the oily water and shears the gas into bubbles (100–1000 μm) (Moosai and Dawe, 2002) or the air diffuser may formed the larger bubbles (700–1500 μm) (Painmanakul *et al.*, 2010). Thus, many IAF units have been designed and even developed with centrifugal force (Rubio *et al.*, 2002; Moosai and Dawe, 2002). IAF can be designed to operate in low retention time (about 4 min) and high hydraulic loading due to the larger bubbles rise faster. Additionally, the installed costs per unit of IAF are usually lower than DAF (Frank, 1988; Moosai and Dawe, 2002). However, in numerous applications where separating a high concentration of fine particles (solids) and oil is the major target, IAF shows a low of effluent clarity and floated product density than DAF (Frank, 1988; Moosai and Dawe, 2002). In case a combination of chemical treatment, the chemicals are normally chosen and added to the influent focusing on bubble-water interface reactions (fast reactions allow floc-forming) (Frank, 1988).

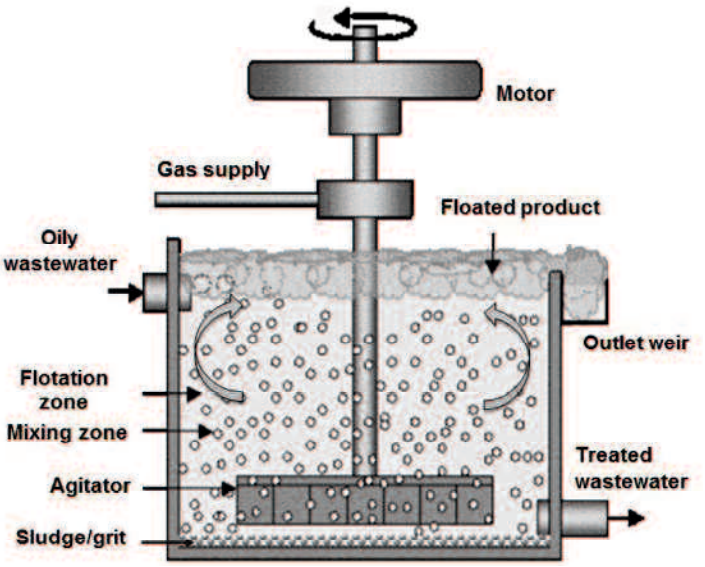

Figure 2.10 Oily wastewater clean-up by induced air flotation (modified from Moosai and Dawe, 2002).

(2). Dissolved air flotation

In DAF, the gas bubbles are produced in a different way by a reduction in pressure of water stream saturated with air at pressures higher than atmospheric (Letterman, 1999; Rubio *et al.*, 2002). There are three main types of DAF, named as vacuum flotation, micro-flotation, and pressure flotation of which pressure flotation is the most widely used (Letterman, 1999). There are three basic pressure DAF processes, including: (a) full-flow (total pressurization of feed-wastewater) (b) split-flow (partial pressurization of inlet wastewater), and (c) recycle pressurization (Letterman, 1999; Rubio *et al.*, 2002; Al-Shamrani *et al.*, 2002; Moosai and Dawe, 2002).

The latter mode is the most appropriate system for oily wastewater treatment (Figure 2.11) (Letterman, 1999; Al-Shamrani *et al.*, 2002). Here, the recycle water (consisting of 20–50% of treated effluent flow) is being recycled (by a recycle pump), pressurized (by a saturation vessel) and mixed with the flocculated wastewater. When water is released in the flotation cell at atmospheric pressure, the MBs (10–100 μm) are formed and these bubbles attach to the solids (floc and/or oil) and float them to the surface (Letterman, 1999; Al-Shamrani *et al.*, 2002; Lawrence *et al.,* 2006; Edzwald, 2010). Flocculation time and hydraulic loading are two key design factors of this technological development. Practical, the flocculation time should be designed in a short time (< 10 min) and hydraulic loading rate may be considered at 5–15 m^3/m^2 h or higher (Edzwald, 2010). Although, the producing of pressurized MBs is ensured for an efficient separation process (Al-Shamrani *et al.*, 2002). However, due to the long retention time requirement the DAF unit might be inefficient to treat huge volume and high flow rates effluents (i.e. POME) (Lawrence *et al.,* 2006; Wu *et al.*, 2010). Table 2.3 shows the main difference between IAF and DAF systems.

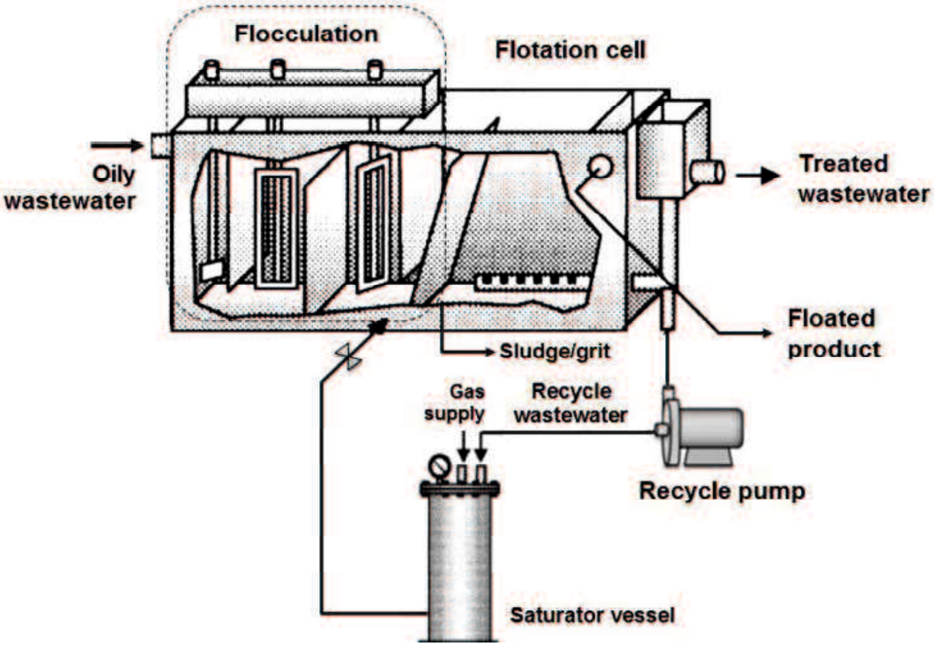

Figure 2.11 Oily wastewater clean-up by dissolved air flotation (modified from Moosai and Dawe, 2002).

Table 2.3 Comparison of IAF and DAF systems (modified from Frank, 1988)

Induced air flotation	Dissolved air flotation
Bubbles are formed mechanically mixed or injection system. Need high-energy mixing	Bubbles are formed by reduction pressure. Need saturation equipment
Surface interaction at air-water interface	Bubbles trapped into flocs of solids and oil
Bubbles size: 100–1000 μm Rapid rise rate	Bubbles size: 10–100 μm Slow rise rate
Shorter retention time	Longer retention time
High turbulence	Low turbulence
Chemical program focuses on air-water interface reactions	Chemical program focuses on coagulant and flocculation
Lower density of floated product	Higher density of floated product

(3). Other flotation techniques

Other conventional flotation techniques (electro-flotation, column flotation, and centrifugal flotation) are shortly summarized to show their main features.

Electro-flotation is an alternative to float pollutants to the surface by MBs (average diameter ~ 20 μm) formation through the electrolysis of water, producing oxygen and hydrogen gases at the surface of electrodes (normally aluminum or iron) (Rubio *et al.*, 2002; Lawrence *et al.*, 2006; Bande *et al.*, 2008). This technique has the principal benefits include creating fine bubbles and producing varying bubble concentrations (Bande *et al.*, 2008). Therefore, this process is the clarity of treated wastewater; however, the disadvantages are electrode costs and maintenance costs, the emission of H_2 gas and a large amount of sludge produced (Lawrence *et al.*, 2006).

Column flotation is one of interest technique for mineral processing as well as oily wastewater separation (El-Kayar *et al.*, 1999; Rubio *et al.*, 2002; Li *et al.*, 2007). Figure 2.12 shows the Microcel flotation column. Here, MBs is generated by pressured water, added air and sheared through a sparger. Feed wastewater entrances in the top and treated effluent discharges in the bottom of column (Rubio *et al.*, 2002).

Centrifugal flotation has been applied in wastewater clean-up by using centrifugal force to increase mixing of bubbles and particles with chemicals and enhance solid-liquid separation. A bubble accelerated flotation (BAF) system is successfully operated in applications to remove O&G, BOD, etc. (Rubio *et al.*, 2002; Colic *et al.*, 2007). This technique can be operated with numerous bubble generations such as induced air (Induce Air BAF), vacuum (Vacuum BAF), and electro-flotation (Electro-flotation BAF) (Rubio *et al.*, 2002; Colic *et al.*, 2007).

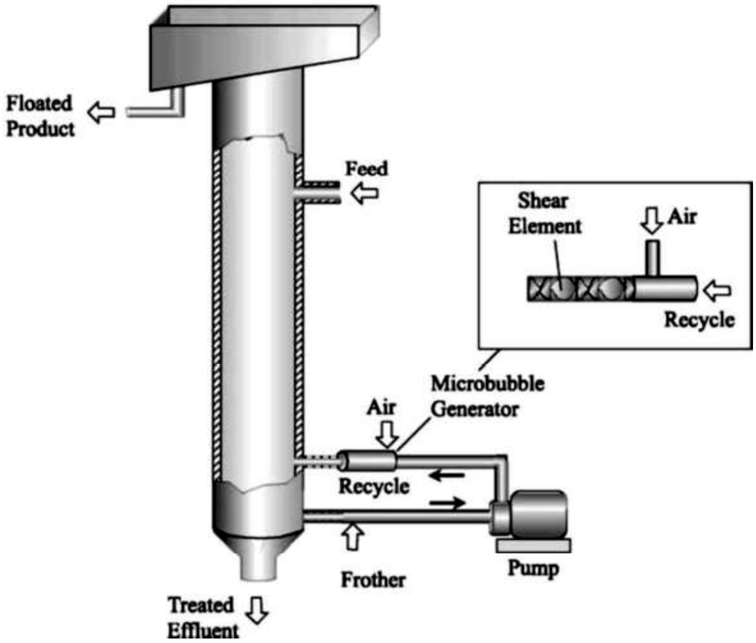

Figure 2.12 The Microcel flotation column (Rubio *et al.*, 2002)

2.5 Chemical emulsion breakers

Chemicals are commonly used to break colloidal particles as a whole and EO as particular (Lawrence *et al.,* 2006). Chemicals are also applied to improve of mechanical treatment efficiency (Frank, 1988). In breaking oil-emulsions, the selected chemicals must be neutralized of the charged oil droplets to coalesce as the first stage and followed by the separate of oil-agglomerate as a second stage. In fact, oil-in-water emulsion usually has high surface negative charges; therefore, to destabilize an EO, a cationic (positive charge) emulsion breaker is normally used (Figure 2.13) (Lawrence *et al.,* 2006; Frank, 1988). Traditionally, strong acidic solutions i.e. H_2SO_4 (Bande *et al.*, 2008; Le *et al.*, 2012), HCl (Ahmad *et al.*, 2006), or HNO_3 (Kuo and Lee, 2010) has been applied as the first step in the de-emulsification of oily wastewater in treatment plants. The strong acidic conditions may cause the protonation of the carboxylate ion in EO droplets to the carboxylic acid, allowing the oil droplets to agglomerate (Frank, 1988). Inorganic de-emulsifiers (i.e. salts of aluminum or iron) are widely used in oily wastewater clean-up due to effective in wide pH range and inexpensive (Takahide, 1999). The use of organic emulsion breakers (i.e. polyamines, polyacrylates and their substituted copolymers) are more effective than inorganic demulsifies because of the higher ionic valences and the excellent charge neutralizing abilities (Frank, 1988; Takahide, 1999). Consequently, organic emulsion breakers often require lower dosages than inorganic demulsifies, and reduce the amount of sludge generated in a treatment program by as much as 50 to 75% (Frank, 1988; Takahide, 1999).

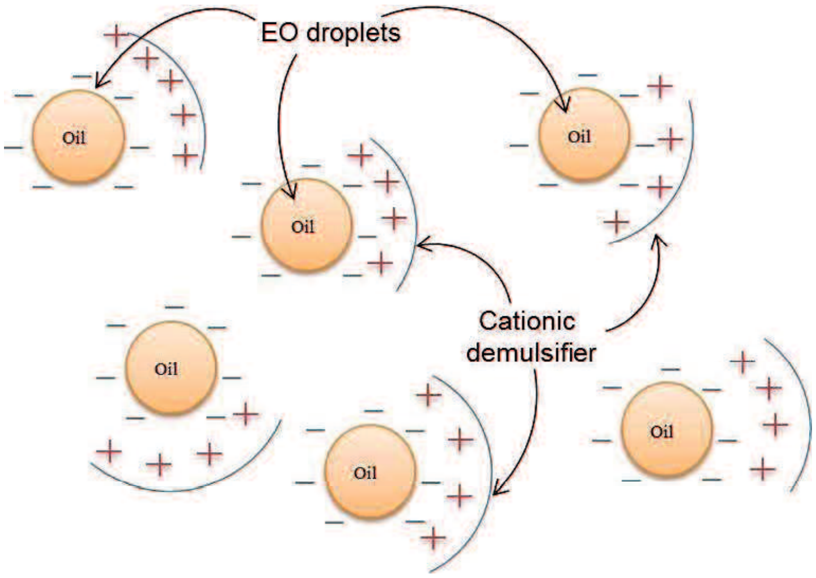

Figure 2.13 The action of a cationic emulsion breaker in neutralization EO surface charges (modified from Frank, 1988)

2.6 Other techniques for oil-in-water emulsions treatment

Practically, the flotation processes have been shown valuable application in oil-in-water emulsions treatment due to high treatment efficiency, handling high-shock loads, enhancing oil recovery, low capital investment costs, and low operational costs (Rubio *et al.* 2002; Li *et al.*, 2007; Bande *et al.*, 2008; Le *et al.*, 2013). Therefore, it has been widely applied and continuous attracting many scholar researchers.

On the other hand, various separate and combined physical, chemical, and biological methods have also suggested for oil-in-water emulsions treatment (Ahmaduna *et al.*, 2009). Here, we can named as adsorption (Viraraghavan and Mathavan, 1988; Solisio *et al.*, 2002; Li Xiaobing *et al.*, 2010), coagulation (Rios *et al.*, 1998; Hempoonsert *et al.*, 2010), electro-coagulation (Bensadok *et al.*, 2008), membrane filtration (Lawrence *et al.*, 2006; Ahmaduna *et al.*, 2009), biological treatment (Zhao *et al.*, 2006; Jeganathan *et al.*, 2007), advanced oxidation (Kang *et al.*, 2011), microwave irradiation (Kuo and Lee, 2010), hydrocyclone (Beeby and Nicol, 1993; Bai *et al.*, 2011). Some reviews of main advantage and disadvantage of oily wastewater treatment processes are listed in the Table 2.4.

Table 2.4 Advantage and disadvantage of oily wastewater treatment processes

Process	Advantages	Disadvantages
Air flotation	Handle high-shock loads, low cost	Sludge disposal problems Require chemicals
Electro-flotation	High efficiency, low cost Remove dissolved oils	Replacement of aluminum or iron electrode
Electro-coagulation	High efficiency, low cost Remove dissolved oils	Replacement of aluminum or iron electrode
Filtration	Handle high-shock loads	Require back washing
Membrane process	Remove dissolved oils	Low flux rates Membranes fouling
Biological treatment	Remove dissolved oils	Pre-treatment requires Long retention time
Carbon adsorption	Remove dissolved oils	Regeneration requirement, High cost
Advanced oxidation	Remove dissolved oils No-recontamination	Require chemicals High cost
Hydrocyclone	Ease of control, low cost	Low efficiency

The application of these techniques has been limited for both technical and economic reasons. Take adsorption method for example, adsorption process is one of the interesting methods for removing oil-in-water emulsions, and activated carbon is normally used. However, the regeneration is required because of the high cost of activated carbon. Alternatively, the replacement by inexpensive materials (i.e. charcoal, barley straw, fly ash, clays, etc.) and treated with chemicals (i.e. metal oxides, surfactants) are needed (Solisio *et al.*, 2002; Li Xiaobing *et al.*, 2010). Nevertheless, a few applications of the replacement adsorbents have been reported (Ibrahim *et al.*, 2010).

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CHAPTER 3

SEPARATION OF OIL-IN-WATER EMULSIONS BY MICROBUBBLE TREATMENT AND THE EFFECT OF ADDING COAGULANT OR CATIONIC SURFACTANT ON REMOVAL EFFICIENCY

3.1 Introduction

Separation of oil-in-water emulsion from wastewater effluents is important for improving the water quality, oil recovery, and water re-use, for protecting downstream facilities, and for ensuring compliance with environmental policies. Common pollutants found in the effluents of many industries are oil and grease, and their concentration in wastewater varies from a few mg L^{-1} to as high as 5%–10% by volume (Frank, 1988; Lawrence *et al.,* 2006). For instance, the concentration of oil and grease in palm oil mill effluent (POME) normally varies from 130 to 18,000 mg L^{-1}, and approximately 2000 mg L^{-1} is present in the form of emulsified oil (EO) (Lam and Lee, 2011; Ahmad *et al.,* 2006).

EO is a colloidal suspension of a liquid with droplet sizes of less than 20 μm, and thus, they can pass through the primary separator (Lawrence *et al.,* 2006). In addition, EO remains stable over time as a result of a combination of some physical and chemical mechanisms (Frank, 1988). Therefore, the removal of very fine oil droplets (2–30 μm) is difficult and very limited (Da Rosa and Rubio, 2005; Lawrence *et al.,* 2006). In practice, the emulsion can be separated by methods such as adsorption, coagulation, electro-coagulation, membrane filtration, biological treatment, flotation, and electro-coflotation (Lawrence *et al.,* 2006; Bande *et al.,* 2008). Among these methods, the combination of coagulation and flotation for the separation of EO has attracted attention from many researchers. Some reviews of the de-emulsification of oil-in-water emulsion by flotation methods are listed in Table 3.1.

In a flotation tank, the number of microbubbles that can attach to a floc (~100 μm) is limited. Therefore, to produce large floc particles, coagulants are added and the detention time is adjusted such that microbubbles (MBs) can attach to the floc particles (Edzwald, 2010). MBs in water and EO carry negative charges, thus hindering the attachment without coagulation (Edzwald, 2010). Therefore, besides coagulants, cationic surfactants are added to make the MBs positively charged (Henderson *et al.,* 2008; Edzwald, 2010). Although cationic-surfactant-treated absorption materials such as organoclay, wheat straw, and barley straw have been used to separate EO (Ibrahim *et al.,* 2009), the performance of the combination of cationic surfactants and MBs in the separation has not been studied widely.

The main objective of this research was to evaluate and compare the effectiveness of EO separation by the flotation process under three process conditions: MB treatment only, MB treatment with polyaluminium chloride (PAC) as a coagulant (MB–PAC), and MB treatment with cetyltrimethylammonium chloride (CTAC) as a cationic surfactant (MB–CTAC). The experiments were conducted in batch mode to observe the effect of MBs, flotation time, PAC dosage, CTAC dosage, and pH on the flotation method.

3.2 Materials and Methods

3.2.1 Oil-in-water emulsion samples

EO with a concentration of ~1000 mg L^{-1} was prepared from warm tap water (~40 °C) and palm oil product (Z67, Japan). The samples were mixed using a food mixer (volume 1.8 L). Batches of 1.0 L of sample were prepared. Samples of 20 mL were taken from 20 s to 30 min, and the EO particle size was determined using Olympus light microscope and Thoma hemocytometer (1/10 mm depth, 1/400 mm^2).

3.2.2 Experimental setup

A conventional jar test system with six beakers was used to investigate the optimum dose of PAC to coagulate the EO sample (~1000 mg L^{-1}). 500 mL of the sample was added to each beaker. The coagulant (PAC) was added with different dosages and the samples were rapidly mixed at 110 rpm for 2 min and then slowly mixed at 30 rpm for 10 min. After 10-min sedimentation time, 10 mL of the solutions was centrifuged at 1250 rpm for 5 min and analyzed for the concentration of EO. The remaining samples were used to predict the volume of floated produce after 4-h sedimentation time by using 500-mL cylinders.

The laboratory setup for the flotation column used in this study (Figure 3.1) is modified from the Microcel flotation column (Rubio *et al.,* 2002). The main components of the unit were a flotation tank, a stirrer, a thermometer, a pump, and an MB generator with an MB diffuser (egg-shaped BT-50 nozzle). The reactor was a columnar plastic tank with a working volume of 2.5 L (10.7 cm in diameter and 28 cm in height). The MB generator with the BT-50 nozzle has a high flow rate (~180 mL S^{-1}) and can produce MBs with sizes ranging from a few micrometers to a hundred of micrometers. For each batch mode operation, 9-L samples were prepared, of which 6 L was used to restart the system twice. The pH of the samples was adjusted using 5.0N H_2SO_4 and 1.0N NaOH and measured by a pH meter (D-13 Horiba). After adding the coagulant (PAC, 10 g L^{-1}, type 30% $Al_2(SO_4)_3$) or cationic surfactant (CTAC, 1 g L^{-1} or 10 g L^{-1}, $CH_3(CH_2)_{15}CH_2\text{-}N(CH_3)_3Cl$), the samples were mixed using a stirrer (Elela, type z-2200) and then the MB generator was turned on. Treated water was taken from the bottom of the reactor.

Table 3.1 Some reviews of the de-emulsification of oil-in-water emulsion by flotation methods

Process	Application	Emulsified oil		Microbubbles		Optimum conditions	Oil concentration		Reference
		Method	Size, μm	Method	Size, μm		Influent mg L^{-1}	Removal %	
Coagulation and dissolved air flotation	Emulsion oil contain n-octane, non-ionic surfactant Tween 80	Ultrasonic	2 – 6	Pressure	30 – 120	pH 6 Ferric chloride 100 mg L^{-1} Sodium oleate 50 mg L^{-1}	500	95	Zouboulis and Avranas 2000
Coagulation and dissolved air flotation	Non-ionic surfactant (Span 20) 0.3%, oil and deionized water	Mixing	–	Pressure	–	pH 8 Aluminium sulphate 100 mg L^{-1} pH 7 Ferric sulphate 120 mg L^{-1}	1,630	>90	Al-Shamrani *et al.*, 2002
Coagulation and dissolved air flotation	Mixing lubricating oil, cooking oil, ghee and mixture of all	Mixing	–	Pressure	–	pH 5–6 Alum 2.5 g L^{-1} Polymer 1.25 g L^{-1}	50-500	85	Abid Baig *et al.*, 2003
Flocculation and electro-flotation	Cutting oil (80% mineral oil, 10% surfactants, 10% others)	–	–	Electric DC	–	pH 8.6 Aluminium sulphate 200 mg L^{-1} or Ferric sulphate 200 mg L^{-1}	10,000 – 40,000	99	Mostefa and Tir 2004
On-line flocculation–flotation	Synthetic emulsion oil	–	~10	Pressure	–	pH 6 Polyacrylamide 2 mg L^{-1} Ferric hydroxide 50 mg-Fe L^{-1}	695	>90	Da Rosa and Rubio 2005
Dissolved air flotation	Synthetic emulsion oil from dehydrated and degassed crude oil	Mixing	0.4 – 100	Pressure	–	pH 6–9 Sodium dodecyl sulfonate 10mg L^{-1} Polyaluminium chloride 30 mg L^{-1} Polyacrylamide 15 mg L^{-1}	100	>90	Li *et al.*, 2007
Electro-flotation	Crude oil	Mixing	–	Electric DC	–	pH 4.72 Salinity 4 mg L^{-1}	50	94	Bande *et al.*, 2008
Coagulation and modified induced air flotation	Synthetic emulsion from palm oil, tap water and anionic surfactant	Mixing	–	Pressure	–	pH 8 Alum: 800 – 1400 mg L^{-1}	10,000	94 – 97	Painmanakul *et al.*, 2010

Several methods can be used to analyze oil-in-water emulsions, such as n-hexane extraction, chemical oxygen demand (COD) analysis, spectrophotometric analysis, zeta-potential determination, and turbidity measurements. However, the most effective and simplest method is COD measurement (Painmanakul *et al.,* 2010). In this research, the concentration of EO was measured by analyzing COD following the standard procedure (5220D, APHA 1998).

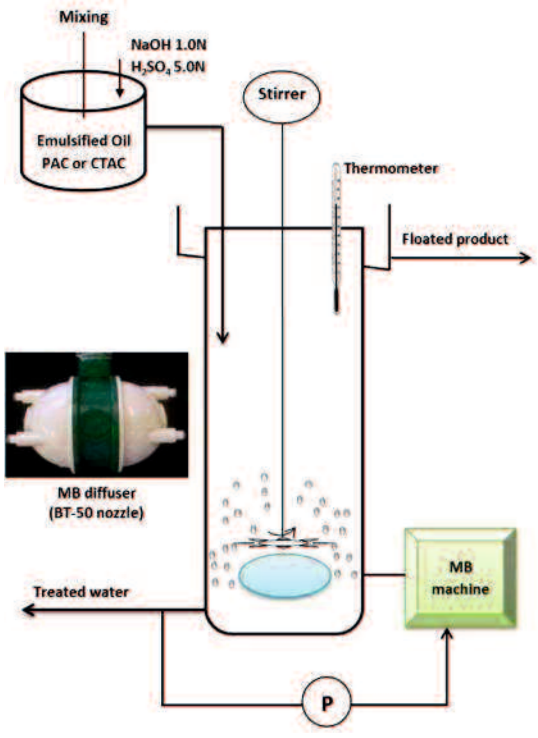


Figure 3.1 Experimental setup

3.3 Results and Discussion

3.3.1 EO preparation

The results showed that most of the free oil was transferred to EO (d < 20 μm) after 4 min of mixing (Figure 3.2 a). In addition, UV spectrophotometry results obtained at an EO concentration of 1012 mg L^{-1} (mixing time: 4 min) showed two peaks at wavelengths of 278 nm and 284 nm. The absorbance values of the samples were determined at these wavelengths. A significant increase in the absorbance value at these two wavelengths was observed from 20 s to 4 min, after which no change was observed in the absorbance values (Figure 3.2 b). Therefore, a mixing time of 4 min was chosen to prepare the EO in this research.

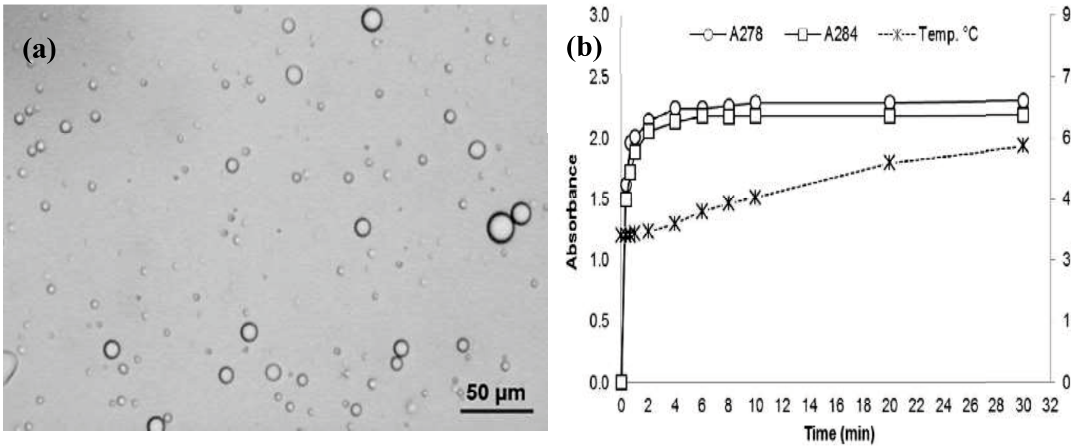


Figure 3.2 (a) EO droplet sizes after mixing for 4 min. (b) Variation in temperature and absorbance at wavelengths of 278 nm and 284 nm. EO concentration: 1012 mg L^{-1}.

3.3.2 Effect of PAC dosage

The effect of PAC dosage on the separation of EO concentration of 1007 mg L^{-1} (COD: ~3138 mg L^{-1}) was investigated by batch coagulation tests (Figure 3.3). An increase in PAC concentration from 10–50 mg L^{-1} resulted in a significantly higher percentage of EO removal. It was noticed that at a coagulant concentration of 50 mg L^{-1} a 97% removal of EO was reached, creating about 40 ml L^{-1} of floated product.

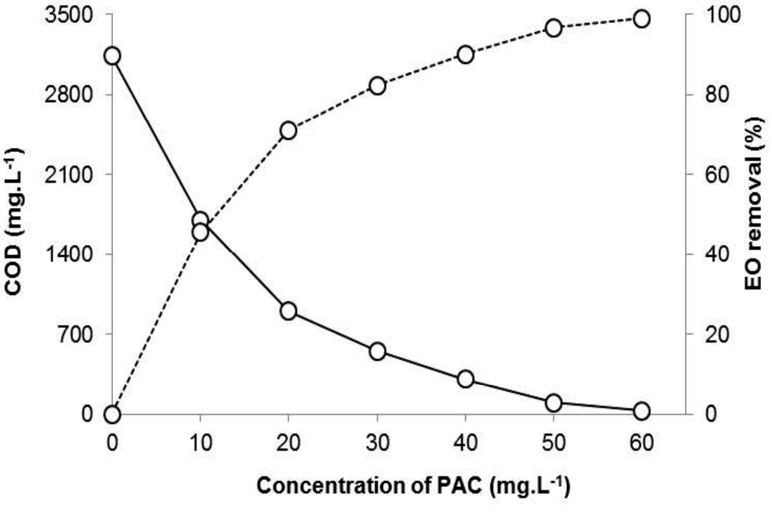


Figure 3.3 Effect of PAC dosage on EO removal efficiency.
EO concentration: 1007 mg L^{-1} (COD: ~3138 mg L^{-1}), pH: 7.0. Treatment conditions: rapid mixing at 110 rpm for 2 min, slow mixing at 30 rpm for 10 min. Sedimentation time: 10 min. Centrifugation speed: 1250 rpm. Centrifugation time: 5 min

In fact, the conventional coagulation method showed a high efficiency of EO removal at low PAC concentrations. These results can be explained by the high charge density of both PAC and EO in water (Ahmad *et al.,* 2006). PAC is not only able to neutralize the negative charge of EO droplets, but also forms aluminium hydroxide flocs which plays an important role for a better coagulation (Takahide, 1999). Still, the complex operation steps of the coagulation process, including flash mixing, slow mixing, and a long sedimentation time are a main weakness of this method. A PAC dosage of 50 mg L^{-1} was selected to study other factors, which influenced the flotation method.

3.3.3 Effect of CTAC dosage

The effect of CTAC dosage on the removal of EO was investigated by changing the CTAC dosage from 0.001 mg L^{-1} to 10 mg L^{-1}. Here an EO concentration of 1005 ± 1 mg L^{-1} (corresponding to a COD of 3116 ± 30 mg L^{-1}) was used, MB time was 2.5 min, pH was 7.0 and the flotation time ranged from 2.5–27.5 min (Figure 3.4). The use of CTAC was shown to be same effective as the use of PAC in the separation of EO with the highest percentage of EO removal recorded being 87 ± 2.0% and 81 ± 1.5% at a CTAC concentration of 0.5 and 1.0 mg L^{-1}, respectively. At higher CTAC concentrations a sharp decrease of EO removal efficiency was observed and only 7 ± 0.9% of EO was separated at a concentration of 10 mg L^{-1} CTAC.

Remarkably, by using a low concentration of CTAC as the cationic surfactant a large amount of EO can be removed. This research indicated that this concentration is about 100 times smaller than the used PAC dosage (50 mg L^{-1}). Furthermore, a concentration of 0.5 mg L^{-1} CTAC is also lower than the concentrations used for other inorganic and/or organic emulsion breakers reported in previous studies (Table 3.1). For example, it required a concentration of Fe^{3+}: 100 mg L^{-1} and sodium oleate: 50 mg L^{-1} to separate 95% of the EO with initial concentration of 500 mg L^{-1} (Zouboulis and Avranas, 2000). As well, in order to remove an influent EO concentration of 100 mg L^{-1} to less than 10 mg L^{-1}, a combination between two coagulation reagents (cationic polyacrylamide: 15 mg L^{-1} and PAC: 30 mg L^{-1}) was done (Li *et al.,* 2007), etc. This can be explained by the fact that CTAC has a low molecular weight (MW = 320) and carries a residual positive charge. Therefore, CTAC is not only able to reduce the negative charges present on the surface of the oil droplets, but also adsorbs on the oil droplets to create macro-flocs (Moosai and Dawe, 2003). On the other hand, CTAC could make the MB positively charged, leading to a higher chance of MB attaching to the EO and/or flocs, thereby increasing the oil-gas-floc size (Henderson *et al.,* 2008).

The use of an excess concentration of CTAC was shown previously to decrease the flotation efficiency. Such a trend was also documented by Li *et al* for their investigation on the effect of the feed concentration of the anionic surfactant sodium dodecyl sulfonate (Li *et al.,* 2007). This is because the effectiveness of the surfactant strongly depends on the critical concentration that is required to form aggregates. Above this concentration, micelles will be formed (Moosai and Dawe, 2003). For that reason, in case of field operations it is suggested to monitor wastewater characteristics as well as surfactant dosages frequently.

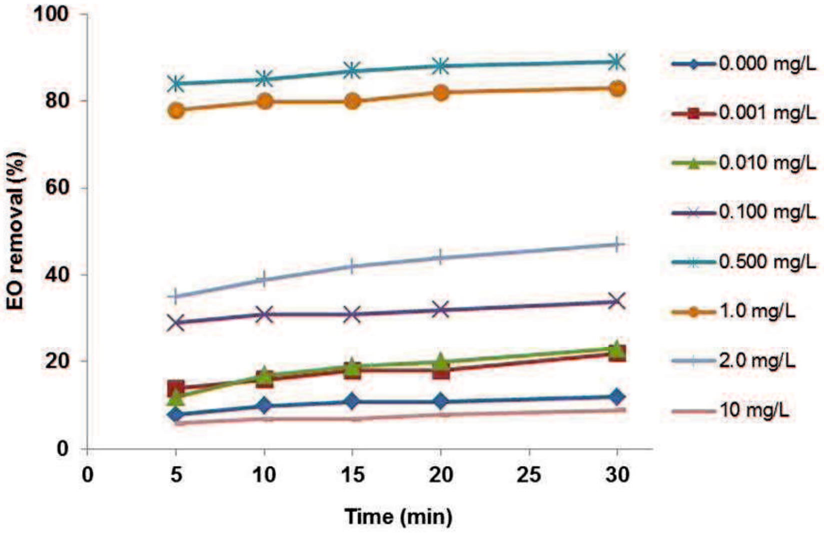
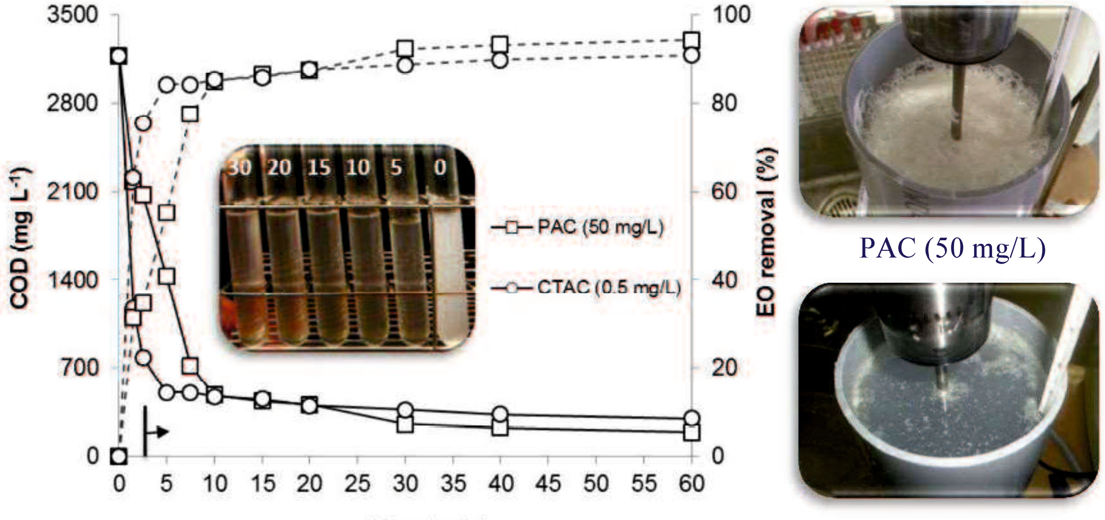


Figure 3.4 Effect of CTAC dosages on EO removal efficiency.
EO: 1005 ± 1 mg L^{-1} (mean ± SD, n = 8) (COD: ~3116 ± 30 mg L^{-1}). pH: 7.0.
MB generation time: 2.5 min.

3.3.4 Effect of flotation time

Flotation time plays an important role on the efficiency of flotation methods. In practice, a detention time from 1.5 to 2.5 min is usually selected to replicate flow conditions in the contact zone of the dissolved air flotation (DAF) process (Edzwald, 2010). To investigate the effect of flotation time on EO removal, in this study an operation time of 2.5 min for the MB generator was selected. After 30 min flotation time, both using PAC (50 mg L^{-1}) and CTAC (0.5 mg L^{-1}) a high efficiency of EO removal was achieved of 92% and 89%, respectively (Figure 3.5). Application of CTAC revealed to be more effective than PAC in terms of flotation time as well as dosage. While a dosage of 0.5 mg L^{-1} of CTAC displayed a high EO removal efficiency within a short flotation time (2.5–5 min) and in addition created only a small amount of floated product, PAC (50 mg L^{-1}) required over 10 min flotation time and produced more floated sludge.

It should be noted that the number of MBs that can attach to a floc (~100 µm) is very limited (Edzwald, 2010). For this reason, at the same flotation column volume, a change in the surface area (diameter) or height of the reactor could improve the efficiency of the treatment method. In addition, the mixing rate is an important factor that influences MB attachment to EO and/or flocs. Thus, besides affecting the separation of EO and/or floc particles, MBs generated by the diffuser produce the right chemical mixing condition. In the case of PAC (50 mg L^{-1}), the mixing procedure (rapid mixing at 300 rpm for 2 min, slow mixing at 30 rpm for 10 min) mostly transferred the EO to flocs. Therefore, the MBs mainly supported the separation between the two phases, i.e., water and solid (floc particles). In contrast, in the case of CTAC (0.5 mg L^{-1}), the MBs played the main role of mixing CTAC with the EO. The high efficiency of EO removal of the MB treatment with CTAC as compared to the MB treatment with PAC provides an important result for the development of a high efficiency and economic flotation system, especially because it does not require a complex mixing procedure.



PAC (50 mg/L)

CTAC (0.5 mg/L)

Figure 3.5 Effect of flotation time on EO removal efficiency. EO: 1009 mg L^{-1} (~ COD 3173 mg L^{-1}); pH 7.0; Temp. 40 ± 0.5°C. CTAC (0.5 mg L^{-1}): rapid mixing 300 rpm, 2 min; MB time 2.5 min. PAC (50 mg L^{-1}): rapid mixing 300 rpm, 2 min; slow mixing 30 rpm, 10 min; MB time: 2.5 min).

3.3.5 Effect of pH

The pH value of a sample significantly enhances the efficiency of the EO breaking process through its impact on the surface charge of MB, oil droplets, and the resulting flocs (Zouboulis and Avranas, 2000; Ahmad *et al.,* 2006; Li *et al.,* 2007). In this study, the effect of pH was studied by varying the pH from 3 to 8. The optimum concentrations of PAC (50 mg L^{-1}) and CTAC (0.5 mg L^{-1}) were used and MB time was 2.5 min (Figure 3.6). The treatment methods were named MB–PAC (50 mg L^{-1}) and MB–CTAC (0.5 mg L^{-1}). After adjustment of the pH and adding PAC or CTAC, the samples from MB–PAC (50 mg L^{-1}) treatment were rapidly mixed at 300 rpm for 2 min and slow mixed at 30 rpm for 10 min. For the two other methods, the samples were simply mixed rapidly at 300 rpm for 2 min. During the flotation stage, five samples for each method taken at 2.5, 7.5, 12.5, 17.5, and 27.5 min.

Among the inorganic coagulants, PAC is well known to be a good candidate for the separation of EO within a wide pH range (5–7.5) (Takahide *et al.,* 1999; Ahmad *et al.,* 2006). For the MB–PAC (50 mg L^{-1}), this research showed steady EO removal efficiencies of 86 ± 2.8%, 88 ± 3.2%, 87 ± 5.9%, 85 ± 6.9%, and 81 ± 13.4% when going from pH 3 to 7. The significant difference in standard deviations between the treatment methods can be explained by the effect of flotation time. Again, when comparing MB or MB–CTAC (0.5 mg L^{-1}) with MB–PAC (50 mg L^{-1}), MB–PAC (50 mg L^{-1}) generated the highest amount of floated product. With this high amount of floated product, it could take more time for all the floc-bubble-aggregates and/or floc-aggregates to reach the surface. Consequently, 2.5 to 5 min flotation time was needed for MB and MB–CTAC (0.5 mg L^{-1}) to reach the highest percentage of EO removal. In contrast, more than 10 min flotation time was needed for MB–PAC (50 mg L^{-1}).

MB–CTAC (0.5 mg L^{-1}) showed a high EO removal efficiency of 80 ± 2.0%, 81 ± 2.6% and 86 ± 1.6 % when going from pH 5 to pH 7. Using a DAF column, Li *et al.,* (2007) also indicated that the pH value should be adjusted from 5 to 9 when separating oil from wastewater (with initial EO concentration: 100 mg L^{-1}, PAC: 20 mg L^{-1}, sodium dodecyl sulfonate: 5.0 mg L^{-1}, EO removal efficiency: approximately 77%). However, the reduced pH (pH 3–4) of the samples could have led to ionization of the EO droplets and, therefore, the addition of CTAC might have resulted in a reduction in EO separation efficiency (Ibrahim *et al.,* 2009). According to the present results, a pH around neutrality gave the same EO separation efficiency for MB–PAC (50 mg L^{-1}) and MB–CTAC (0.5 mg L^{-1}).

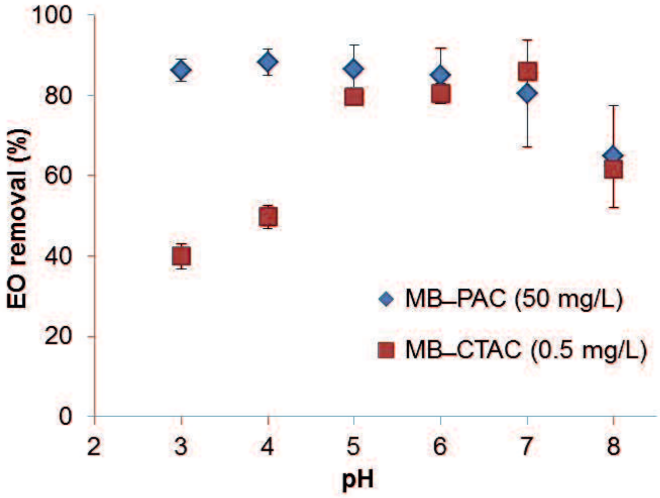


Figure 3.6 Effect of pH on EO removal efficiency.
EO: 1007 ± 2 mg L^{-1} (COD: ~3068 ± 64 mg L^{-1}). MB generation time: 2.5 min.

3.3.6 Effect of MBs

In the batch mode of the flotation method, the effect of MBs was investigated at EO concentrations of 105 mg L^{-1} (COD: ~303 mg L^{-1}), 508 mg L^{-1} (COD: ~1482 mg L^{-1}), and 1007 mg L^{-1} (COD: ~3138 mg L^{-1}), while the MB generator was operated during 60 min at pH 7.0 (Figure 3.7 a). During this period, a steady rise in temperature was recorded from 38–74 °C with an average increase of 0.6 °C per minute. For all three concentrations of influents, a slight decrease in EO concentration with time was observed. After 60 min of MB generation at EO influent concentrations of 105 mg L^{-1}, 508 mg L^{-1} and 1007 mg L^{-1}, the percentage of EO removal was 48%, 41%, and 29%, respectively. This low EO removal efficiency indicates that the interaction between the MBs and EO was weak. In addition, the operation of the MB generator for a long time and the increase in the temperature caused the MBs to rise fast to the surface.

Nevertheless, the effect of pH on EO removal efficiency by using MB only was found to increase dramatically from 10 ± 1.1% at a slightly alkaline pH of 8, to 70 ± 1.7% under acidic conditions (pH 3) (Figure 3.7 b). Traditionally, sulfuric acid has been applied as the first step in the emulsion breaking of oily wastewater in treatment plants. The strong acidic conditions may cause the protonation of the carboxylate ion in EO droplets to the carboxylic acid, allowing the oil droplets to agglomerate (Frank, 1988). As a result, MBs have a higher chance to attach to the agglomerates' surface. At pH 4, an EO removal efficiency of 69 ± 2.0% was reached. Without PAC or CTAC, this result shows that it may be worthwhile to investigate the effect of MBs on the separation of acidic oily wastewater sources such as POME (pH 3.4–5.2) (Lam and Lee, 2011), especially for enhanced oil recovery. Consequently, in the next research, some of vital factors i.e. reactor design; gas flow rate; bubble size; pH and temperature of liquid will studied to improve the attachment between gas bubbles and oil droplets.

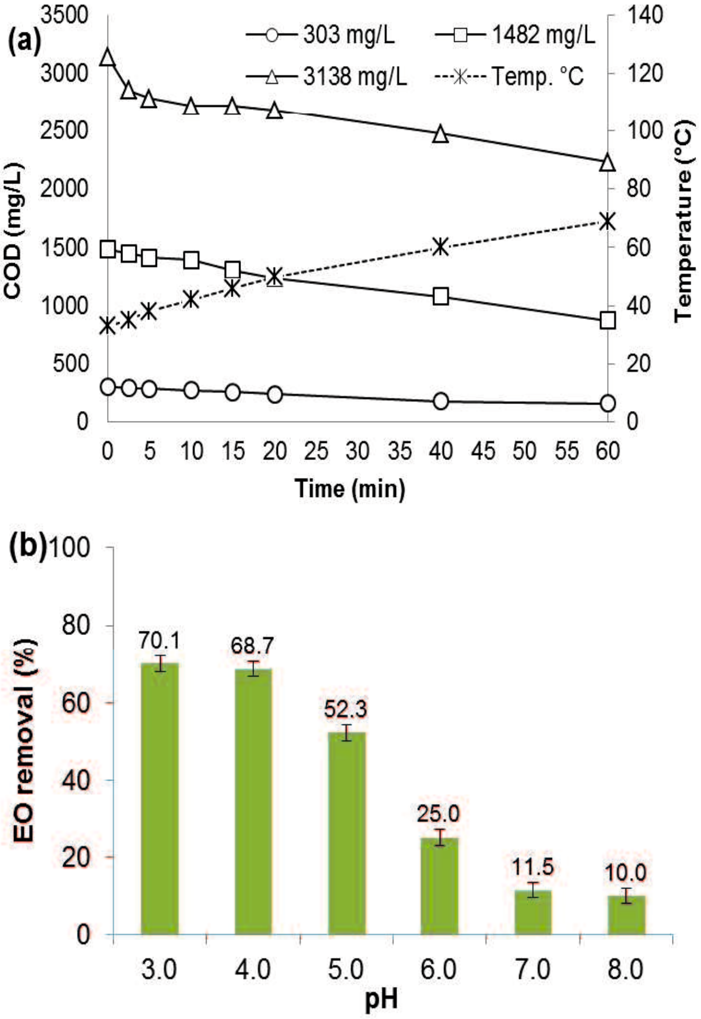


Figure 3.7 (a) Effect of MB generation time on EO removal efficiency at pH 7. EO: 105 mg L^{-1} (COD: ~303 mg L^{-1}), EO: 508 mg L^{-1} (COD: ~1482 mg L^{-1}) and EO: 1007 mg L^{-1} (COD: ~3138 mg L^{-1}). (b) Effect of pH on EO removal efficiency by using MB only. EO: 1007 ± 2 mg L^{-1} (COD: 3068 ± 64 mg L^{-1}). MB generation time: 2.5 min.

3.4 Conclusions

This study evaluated the efficiency of MB treatment alone, MB treatment with PAC as the coagulant, and MB treatment with CTAC as the cationic surfactant in the separation of EO by modified column flotation under a high MB flow rate.

The separation of oil-in-water emulsions is successfully achieved by the combination of MB–PAC or MB–CTAC. A high concentration of emulsified palm oil (~1000 mg L^{-1}) was successfully separated with an efficiency of approximately 90% by MB treatment with PAC (MB generation time: 2.5 min, PAC: 50 mg L^{-1}, pH: 3–7) and with an efficiency of more than 82% by MB treatment with CTAC (MB generation time: 2.5 min, CTAC: 0.5 mg L^{-1}, pH: 5–7). The data indicate a good EO removal efficiency at a low concentration of CTAC (0.5 mg L^{-1}), which was 100 times less than that of PAC dosage (50 mg L^{-1}).

Although the use of MB treatment alone showed less impact on the EO removal efficiency than MB–PAC or MB–CTAC at pH around neutrality, however, MB treatment exhibited a significant EO removal efficiency (~70%) in acidic water. This result is interesting to consider the development of efficiency and economical flotation systems for separation of oil from acidic oily wastewater sources such as POME (pH 3.4–5.2).

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CHAPTER 4

PERFORMANCE OF TINY MICROBUBBLES ENHANCED WITH "NORMAL CYCLONE BUBBLES" IN SEPARATION OF FINE OIL-IN-WATER EMULSIONS

4. 1 Introduction

In oil field wastewater, the oil concentration varies greatly from a few mg L^{-1} to as high as 5–10% by volume (Frank, 1988; Lawrence *et al.*, 2006) and it normally ranges between 100 and 1000 mg L^{-1} (Bande *et al.*, 2008; Santander *et al.*, 2011). Emulsified oil (EO) is well known as a suspension of droplet sizes less than 20 μm (Moosai and Dawe, 2003; Lawrence *et al.*, 2006), and it becomes stable over time by its physical and chemical mechanisms (Frank, 1988). Therefore, the removal of oil-in-water emulsions, especially in heavy crude oils (where the oil density is close to the water density) is difficult and not widely used (Moosai and Dawe, 2003; Da Rosa and Rubio, 2005; Bande *et al.*, 2008). Consequently, the development of separation techniques for oil-in-water emulsions in wastewater effluents has attracted the attention of many researchers. This is essential for ensuring the compliance of water reuse and oil recovery with environmental policies (Bande *et al.*, 2008; Santander *et al.*, 2011).

Numerous methods can be applied for the separation of oil-in-water emulsions, such as adsorption, coagulation, membrane filtration, biological treatment, flotation, hydrocyclone methods, electro-coagulation, and electro-coflotation (Zouboulis and Avranas, 2000; Lawrence *et al.*, 2006; Bande *et al.*, 2008). Among these processes, the combination of coagulation and flotation has shown valuable applications in the separation of different EO concentrations. However, the complex operation steps in the coagulation process, including flash mixing and slow mixing, as well as the long retention time (for sedimentation and flotation) are the main demerits of this method. Furthermore, a large amount of sludge produced with metal hydroxides (aluminium or iron) or organic de-emulsifiers leads to difficulties in dewatering of the sludge and efficient oil recovery (Frank, 1988).

Theoretical and practical implications of the flotation method showed that gas bubble size and density are the key factors influencing the gas flotation efficiency (Letterman, 1999). Oil-bubble collection efficiency increases with decreasing bubble size (Moosai and Dawe, 2003). Unfortunately, there are several disadvantages in using only microbubbles (MBs) in the flotation process. First, MBs and EO carry negative charges in water, which hinders their attachment to each other (Lawrence *et al.*, 2006). The high energy required for producing MBs has a significant effect on the operating costs (Edzwald, 2010). Because of the low rising velocities of MBs, EO droplets, and oil-gas agglomerates, a very long residence time is required. Furthermore, MBs lead to high water content in the floated product (Miettinen *et al.*, 2010). Hence, using a variety of gas bubble sizes is expected to increase the hydrodynamic forces and decrease the residence time in the flotation method.

Considering the use of gas bubbles as a potential approach in the separation of EO for reducing the floated product and for oil recovery, a simple method for an oil-wastewater treatment plant has been developed. The main objective of this research was to evaluate and compare the effectiveness of fine EO separation by a modified flotation process under two process conditions: treatment by tiny MBs only and treatment by MBs in combination with "normal cyclone bubbles" (NBs). The experiments were conducted in batch mode to observe the effects of treatment time, NB flow rate, initial EO concentration, temperature, pH, and salinity on the flotation method.

4.2 Materials and methods

4.2.1 Oil-in-water emulsion samples

The materials used for preparing the EO samples were palm oil (Z67_Japan, density: 0.850 g mL^{-1} at 35 ^{o}C) and warm tap water. EO samples with varying concentrations of 100–1000 mg L^{-1} were prepared by a mixing method using a common food mixer. During the preparation of EO (20 s to 30 min), samples of 20 mL were withdrawn, and the EO droplet size was determined by using an Olympus light microscope with Thoma hemocytometer (1/10 mm depth, 1/400 mm^2) and a laser light scattering particle size distribution analyser (Horiba LA–920). The latter instrument was also used for investigating the MB size in water. Here, the mean of EO or MB diameter was calculated following the equation of the Sauter diameter (D_{32}), which is defined as:

$$D_{32} = \frac{\sum_i^n n_i d_i^3}{\sum_i^n n_i d_i^2}$$

Where d_i is the EO or MB diameter and n_i is the number of EO or MB.

4.2.2 Experimental setup

The main components of the designed experimental setup (Figure 4.1) are a flotation tank, an air pump, an air flow meter, two NB diffusers, a recycling pump, a MB generator with a MB diffuser (BT–50 nozzle), and an oxygen meter–thermometer (DO meter – OM51). The flotation tank was a columnar clear acrylic plastic tank (working volume: ~10 L, 108 mm in diameter and 1090 mm in height). The MB generator is a pressurized dissolution type. At high pressure, the mixture of liquid and gas (air) is pressurized in the dissolution tank. Unstable supersaturated solution of gas in liquid is eventually escapes out from the water resulting in a large number of MBs (Terasaka *et al.*, 2011). The MB generator with an MB nozzle used in this study can produce a high flow rate (10.8 L min^{-1}) and tiny MBs (d < 16 µm) at room temperature. The MB nozzle was fixed inside the reactor at a height of about one-fifth of the total height from the top of the reactor. The NB flow rate was changed by an air valve pump and measured by an air flow meter. Two NB nozzles were placed at the bottom of the reactor at vertical angles of 30° and 45° for spreading the NBs (d: 0.5 ~ 20 mm) and for generating cyclone air flow inside the separator. Overall, the flotation column is long and narrow, and using a wide range of gas bubble sizes can produce a swirling flow inside the column.

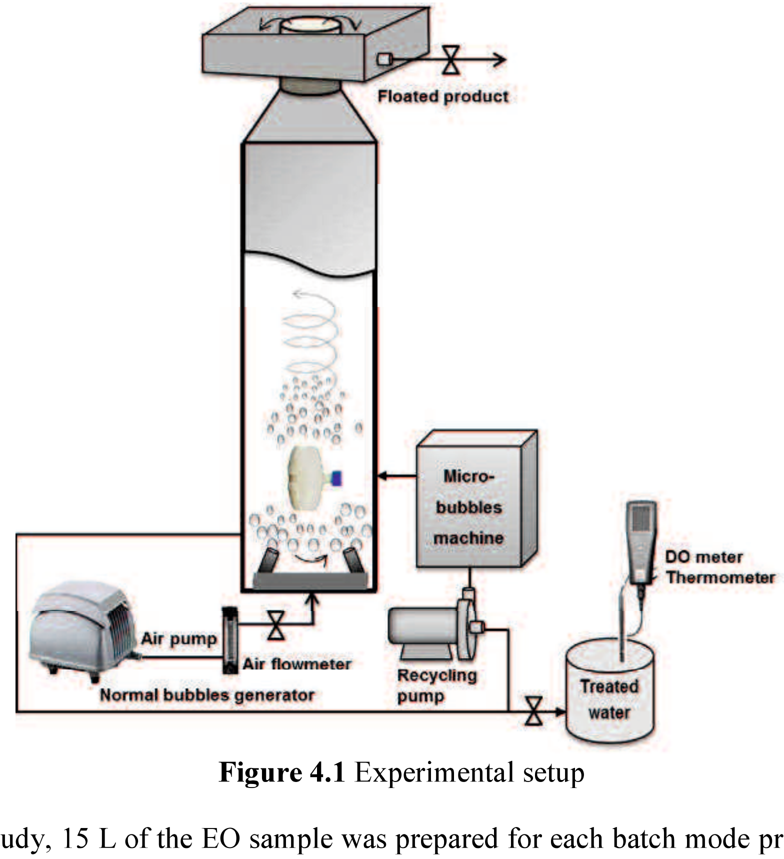

Figure 4.1 Experimental setup

In the study, 15 L of the EO sample was prepared for each batch mode process, and ~4.0 L of this volume was used to restart the system. Solutions of H_2SO_4 (5.0 N) and NaOH (1.0 N) were used to adjust the pH of the oil-in-water emulsion influents. A 100 mL sample of treated water was withdrawn from the bottom of the flotation tank during the treatment time for analysing the EO removal efficiency, EO droplet size, dissolved oxygen (DO), and temperature. In this research, the chemical oxygen demand (COD) method (5220D, APHA 1998) was used to analyse the concentration of EO (Painmanakul *et al.*, 2010).

4.3 Results and discussion

4.3.1 EO preparation

According to the results, 100% of free palm oil was transferred to a fine EO (d < 16 µm, the Sauter EO diameter: 6.31 µm) after 4 min of mixing (Figure 4.2 (a–d)). The mixture showed a uniform milk-white colour. UV spectrophotometry results obtained for the EO concentration of 1012 mg L^{-1} (mixing time: 4 min) showed the highest peak at a wavelength of 278 nm. This wavelength was used to determine the absorbance values of the EO samples (115 mg L^{-1}, 501 mg L^{-1}, and 1012 mg L^{-1}). There was a significant increase in absorbance at mixing times between 20 s and 4 min, after which no change was observed (Figure 4.2 e). Therefore, in this research, all the EO samples were prepared using a mixing time of 4 min.

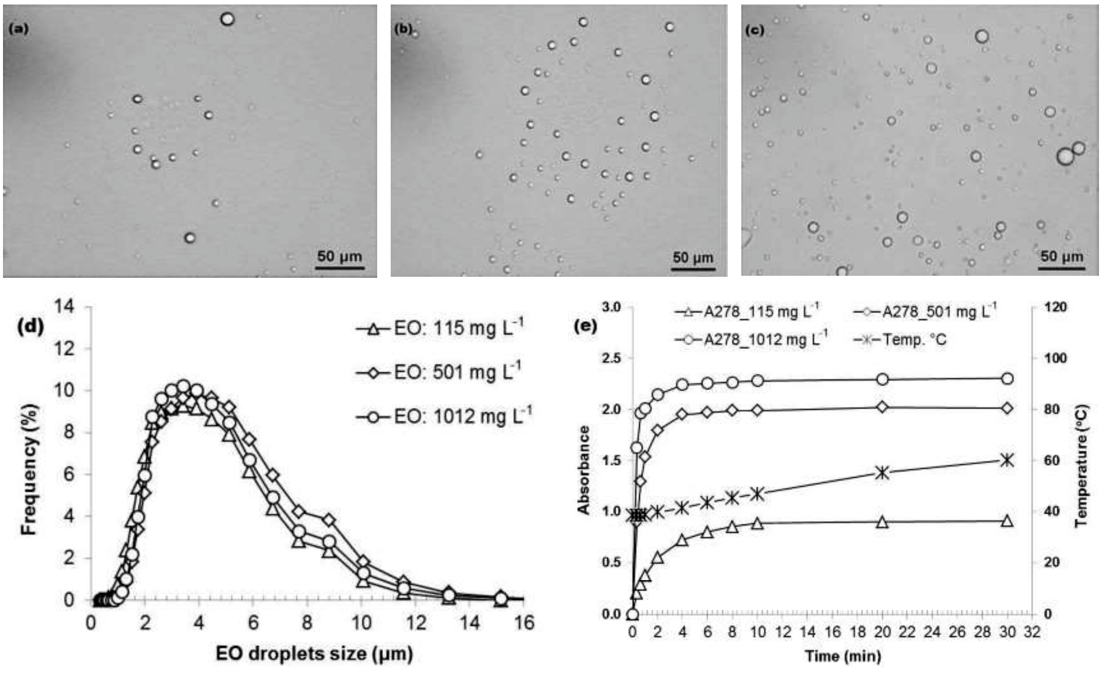

Figure 4.2 EO droplets (mixing time: 4 min), EO concentration: (a) 115 mg L^{-1}, (b) 501 mg L^{-1}, (c) 1012 mg L^{-1}. (d) Distribution of EO droplet sizes. (e) Variation in temperature (38–60 °C) and absorbance at the wavelength of 278 nm as a function of time.

4.3.2 Characteristics of MBs and MBs combined with NBs

MB size plays an important role in determining the efficiency of flotation methods. White water collector modelling by Edzwald indicated that smaller bubbles increase the performance of the flotation process (Edzwald, 2010). In this research, the MB size and flow rate were controlled primarily by the pressure (~1.0 MPa) across a BT–50 nozzle. An MB generator operation time of 10 min was selected to identify the MB size and the rise velocity. The results of MB size distribution analyses (Figure 4.3 a) indicated white water due to the formation of 1–16 μm MBs at room temperature (~23 °C). Here, the Sauter MB diameter was 6.59 ± 0.23 μm, which was the same as the EO droplet size (Figure 4.2 d). The MB rise velocity was recorded directly in the flotation tank by a digital camera and calculated from the relationship between the flotation time and the float height (Liu *et al.*, 2010). In fact, treatment with NBs increased the rise velocity of the MBs. Laminar flow conditions were found in the case of MBs as well as MBs combined with NBs (NBs flow rate: 2.5 L min^{-1}) (Figure 4.3 b) and the average MB rise velocities were 0.087 and 0.164 cm s^{-1}, respectively.

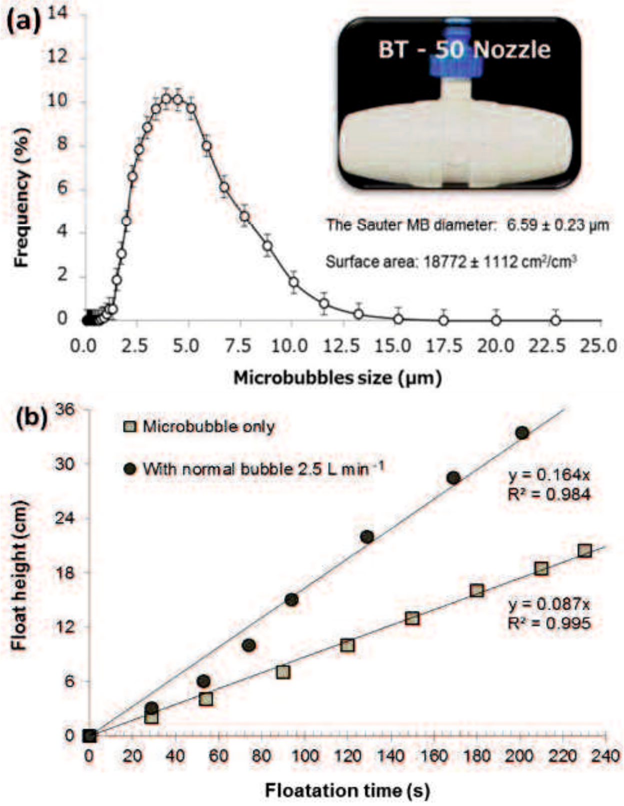

Figure 4.3 (a) MB size distribution in water. (b) Float height and flotation time of MBs and MBs combined with NBs in water. MB generator time: 10 min. Temperature: ~23 °C.

4.3.3 Effect of NB flow rate

The effect of NB flow rate on the removal of EO (Figure 4.4 a) was studied by changing the NB flow rates from 0 to 7.5 L min^{-1}. The MB generator was operated continuously at a constant flow rate (10.8 L min^{-1}). An EO concentration of 1009 ± 1 mg L^{-1} (equivalent to a COD of 3173 ± 30 mg L^{-1}) was used under identical treatment conditions (pH: 7.0 ± 0.1 and temperature: 36.5 ± 0.5 °C). In addition, the value of DO in water was measured during the treatment time of 0–60 min.

Applying the flotation method for the separation of very fine EO droplet sizes ($d < 10$ μm) was very challenging (Da Rosa and Rubio, 2005), and thus, even upon treatment with high-flow-rate MBs, the oil-bubble contact was not good. Nevertheless, it was interesting to note that the combination of MBs and NBs significantly improved the separation of oil-in-water emulsions. Without NBs, considering only the effect of tiny MBs, the separation of fine EO proceeded rapidly from 2.5 min (9%) to 30 min (59%) and slowed down thereafter. The highest percentages of EO removal recorded at the NB flow rate of 2.5 $Lmin^{-1}$ were 77% and 86%, after 30 and 60 min, respectively. The dissolved oxygen concentrations in the effluents were steady and saturated (~9.0 mg L^{-1}) for all gas flow rates. This result showed that it may be meaningful to investigate the combination of flotation and aerobic treatment for the EO removal.

The application of a wide range of gas bubble sizes in the flotation process was shown to be beneficial for the EO removal. This can be explained by an increase in the bubble volume (Letterman, 1999); small and large MBs can capture small and large oil droplets, respectively (Moosai and Dawe, 2003). Furthermore, the attachment of MBs to the EO could increase the differential density (Moosai and Dawe, 2003) and reduce the viscosity of the liquid (Bai *et al.*, 2011). Here, this flotation technique could be classified as a centrifugal flotation unit. Naturally, the NB velocity swirl flow of the liquid phase and cause the centrifugal forces inside the separator. This force may be able to improve the separation efficiency of bubbles/oil aggregates, increase the gas transfer rates, which result in decrease the residence time in the flotation method (Rubio *et al.,* 2002; Colic *et al.,* 2007).

However, increasing the NB flow rate from 5.0 to 7.0 L min^{-1} was shown slightly decrease the EO removal efficiency. Such a trend was also reported by Painmanakul *et al.*, who investigated the effect of different gas flow rates in the separation of oily wastewater by induced air flotation (flotation column: 50 mm × 2000 mm). The turbulent energy created at high NB flow rates could reduce the efficiency of contact between the EO and the gas bubbles (Painmanakul *et al.*, 2010). A higher NB flow rate also yields a higher air-liquid ratio, and the excessive NBs may disturb the hydrocyclone flow in the flotation process (Bai *et al.*, 2011).

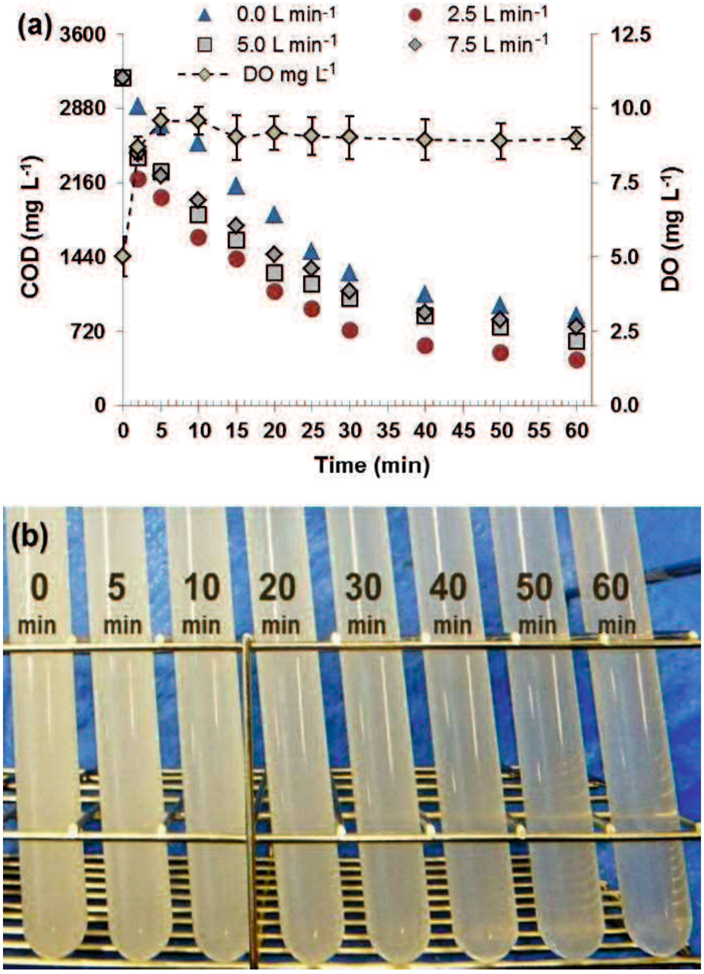

Figure 4.4 (a) Effect of NB flow rate on the EO removal efficiency determined by chemical oxygen demand (COD) and variation of dissolved oxygen (DO) during the treatment time. EO: 1009 ± 1 mg L^{-1} (COD: 3173 ± 30 mg L^{-1}). pH: 7.0 ± 0.1. Temperature: 36.5 ± 0.5 ^{o}C. (b) Oil-in-water emulsions before and after treatment by MBs combined with NBs. NB flow rate: 2.5 L min^{-1}.

4.3.4 Effect of initial EO concentration

The performance upon changing the initial EO concentration was investigated over a range of EO concentrations of 103 mg L^{-1} (~COD: 328 mg L^{-1}), 501 mg L^{-1} (~COD: 1464 mg L^{-1}), and 1009 mg L^{-1} (~COD: 3173 mg L^{-1}). The MB and NB generators (NB flow rate: 2.5 L

min^{-1}) were operated for 0–60 min at an initial pH of 7.0 ± 0.1 and temperature 36.5 ± 0.5 °C (Figure 4.5 a). During this period, there was a steady rise in temperature from 36.5 to 46.0 (± 0.5) °C. At the EO concentrations of 103, 501, and 1009 mg L^{-1}, the EO removal efficiency increased sharply to 67%, 68%, and 77%, respectively, after 30 min of treatment. This indicated that the performance of the modified flotation method is effective even under a high shock load of EO in the influent. On the other hand, at an EO concentration of 1009 mg L^{-1}, the size of fine EO droplets in the influent (EO diameter: 6.31 μm) decreased rapidly during the first 5 min (to 5.79 μm) and gradually up to a treatment time of 60 min (Figure 4.5 b). Thus, the results showed that larger EO droplets are easier to separate than are the smaller ones. In addition, there was a significant increase in the proportion of EO droplets smaller than 2 μm.

In general, the efficiency of the flotation process is strongly dependent on the attachment of gas bubbles to fine particles (Edzwald, 2010). In the oil field wastewater treatment by a flotation method, oil-bubble attachment relies on the properties of the oil (diameter, concentration, viscosity) and gas bubbles (type of gas, diameter, density), hydrodynamic and thermodynamic forces, and physicochemical aspects (Moosai and Dawe, 2003; Lawrence *et al.*, 2006). In particular, gas bubbles play an important role in the separation of oil droplets from the liquid phase of the emulsion (Santander *et al.*, 2011). It is commonly understood that a decrease in the gas bubble size results in improved fine particle separation and oil droplet recovery, because of the large air-bubble surface area. In reality, the MB size in dissolved air flotation ranges from a few tens to several hundreds of microns, with a median of 40 μm (Letterman, 1999), and larger bubbles may be as big as 1–10 mm (Edzwald, 2010). For instance, in a conventional jet cell process (Santander *et al.*, 2011), where MBs (100–800 μm) were applied, the EO removal was approximately at 80% under identical treatment conditions (EO concentration 50–400 mg L^{-1}, poly(vinyl alcohol) concentration 3 mg L^{-1}, DSS concentration 27 mg L^{-1}, air flow rate 3 L min^{-1}, temperature 27–35 °C, average EO droplet size 23 μm, and pH 6.5). However, the oil separation efficiency decreased when the EO droplet size was smaller than 10 μm, because of the Brownian motion of the EO droplets when the size is sufficiently small (< 5 μm) (Painmanakul *et al.*, 2010). In this study, the combination of tiny high-flow-rate MBs and cyclone NBs shows good potential for the separation of oil-in-water emulsions. This new method enables the effective separation of the

EO (> 2 μm) over a wide range of concentrations (100–1000 mg L^{-1}) and affords less floated products, without the need for chemicals for de-emulsification. Nevertheless, the disadvantage of this process is the need for producing tiny MBs, which requires a much higher pressure (~1.0 MPa) as compared to that (0.4–0.6 MPa) for dissolved air flotation.

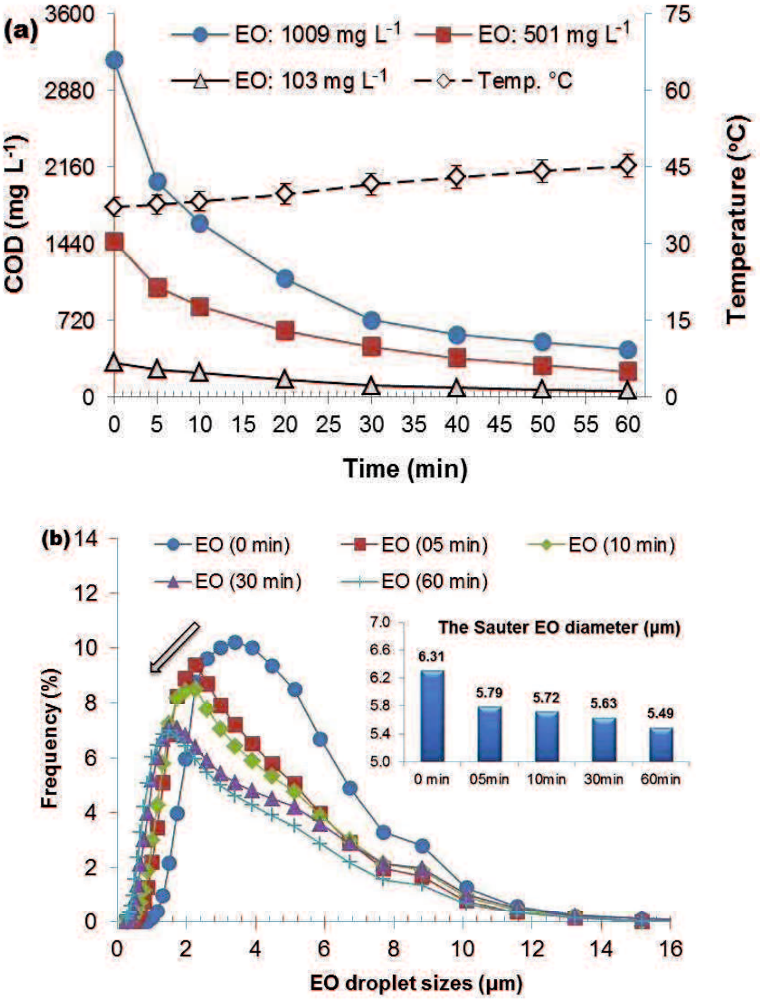

Figure 4.5 (a) Removal efficiency at different initial EO concentrations, determined by chemical oxygen demand (COD), and the variation in temperature during the treatment time. NB flow rate: 2.5 L min^{-1}. pH: 7.0 ± 0.1. Temperature: 36.5 ± 0.5 °C. (b) EO droplet size distributions in water before and after the treatment by MBs combined with NBs. Initial EO concentration: 1009 mg L^{-1}.

4.3.5 Effect of temperature

The effect of temperature on the EO removal efficiency is shown in Figure 4.6. In the initial temperature range 36–45 °C, the EO removal efficiency decreased notably with an increase in temperature. Theoretically, the temperature of water enhances the bubble rise velocity through its effect on the bubble diameter and dynamic viscosity (Letterman, 1999). The increase in temperature is observed through an increase in the volume of gas bubbles or decrease in the bubble surface area, which results in reduced solubility of the gas bubbles and rapid rise of the bubbles to the water surface (Pérez-Garibay *et al.*, 2012). In practice, it is very difficult for the designer and plant operator to control the bubble rise velocity in the flotation process (Edzwald, 2010), because of the fluctuation of the influent temperature. Operating at high temperatures is especially required for the treatment of oil field wastewaters such as palm oil mill effluent (POME) (Lam and Lee, 2011). According to the current results, even temperatures lower than 40 °C yield good EO separation efficiency.

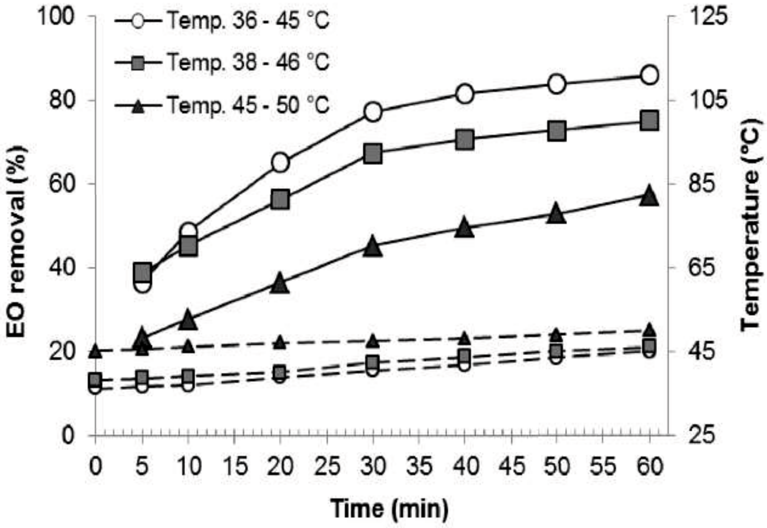

Figure 4.6 Effect of temperature on the EO removal efficiency.
EO: 1009 ± 1 mg L^{-1} (COD: 3173 ± 30 mg L^{-1}). pH: 7.0 ± 0.1. NB flow rate: 2.5 L min^{-1}

4.3.6 Effect of pH

pH is an important factor influencing the emulsion breaking process. Strong acidic solutions have been applied to alter the pH levels before de-emulsification, such as H_2SO_4 (Bande *et al.*, 2008), HCl (Ahmad *et al.*, 2006), or HNO_3 (Kuo and Lee, 2010). In fact, MBs and EO carry negative charges. Strong acidic solutions may cause protonation of a carboxylate ion to afford a carboxylic acid (Frank, 1998) and reduce the negative zeta potential of the EO droplets (Al-Shamrani *et al.*, 2002; Kuo and Lee, 2010). As a result, EO droplets are more strongly agglomerated at low pH than under neutral and alkaline conditions; therefore, there is a greater possibility of the attachment of MBs to the agglomerate surface. As shown in Figure 4.7, the EO separation efficiency decreased slightly with an increase in pH from 3 to 7 and decreased rapidly at pH 7 to 9. Remarkably, a high EO separation efficiency of more than 67% was observed over a wide pH range (3–7) after a 30-min treatment. Hence, it may be worthwhile to investigate the performance of the flotation process in the separation of acidic oily wastewater, such as POME (pH 3.4–5.2) (Lam and Lee, 2011).

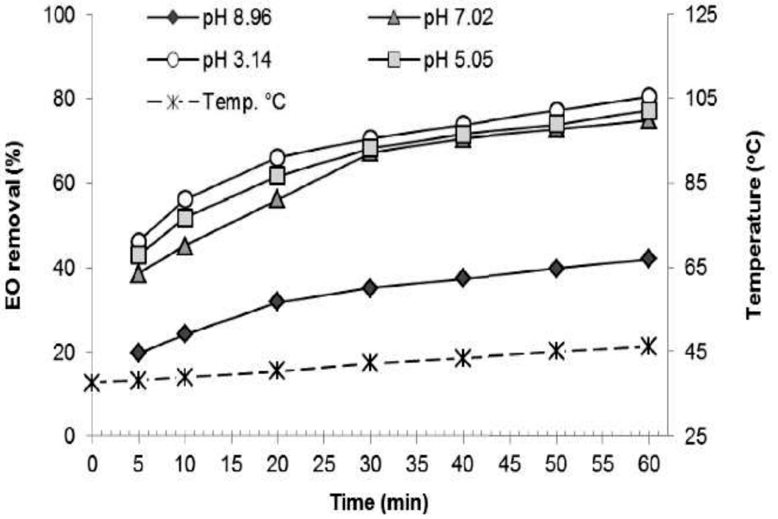

Figure 4.7 Effect of pH on the EO removal efficiency.
EO: 1009 ± 1 mg L^{-1}. Temperature: 38.0 ± 0.5 ^{o}C. NB flow rate: 2.5 L min^{-1}

4.3.7 Effect of sodium chloride

The changes in the EO treatment performance with the addition of different NaCl concentrations are shown in Figure 4.8. A significant increase in the EO removal efficiency was observed when the NaCl concentration was increased from 0 to 30 mg L^{-1}. Approximately 90% of the EO was removed within 60 min at a NaCl concentration of 30 mg L^{-1} and influent EO concentration of 1009 mg L^{-1}.

According to the literature, added salt enhances the flotation by modifying the surface charge of the gas bubbles and oil droplets (Moosai and Dawe, 2003) as well as by decreasing the gas bubble size (El-Kayar *et al.*, 1993). Consequently, it influences the flotation efficiency. However, further addition of NaCl (50 mg L^{-1}) rapidly reduced the efficiency of EO removal. Bande *et al.,* (2008) also reported this interesting phenomenon, following the application of electro-flotation for the removal of oil field effluent. Thus, ionic strength may affect bubble-bubble and bubble-particle interactions (Edzwald, 2010). In particular, the large volumes of oil field wastewater, i.e. petroleum waste, may contain NaCl (El-Kayar *et al.*, 1993). Therefore, further research on this phenomenon is necessary.

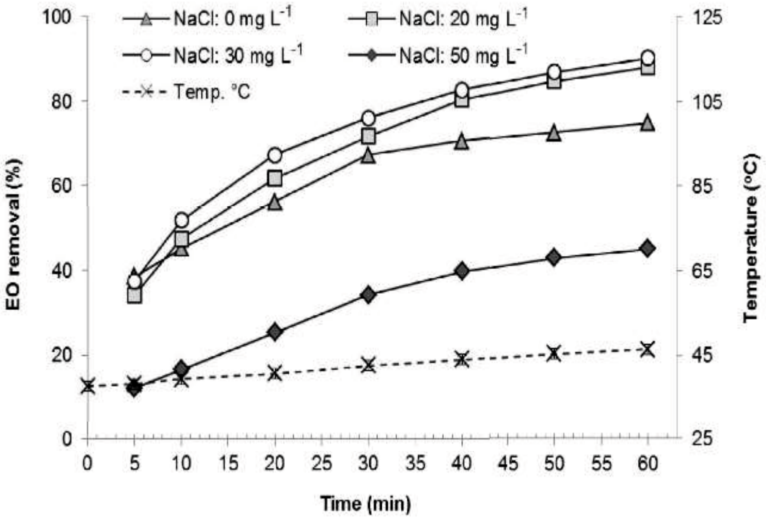

Figure 4.8 Effect of salt concentration on the EO removal efficiency.
EO: 1009 ± 1 mg L^{-1}. pH: 7.0 ± 0.1. Temperature: 38.0 ± 0.5 °C. NB flow rate: 2.5 L min^{-1}

4.4 Conclusions

The experimental setup allows for efficient flotation to remove oil-in-water emulsions without using any coagulant. Separation of fine EO emulsions (d < 16 μm) is successfully achieved by the combination of tiny high-flow-rate MBs and cyclone NBs, but there is little effect on EO droplets smaller than 2 μm. In the normal concentration range 100–1000 mg L^{-1}, clear EO separation was observed after 30 min, with a removal efficiency of more than 67%. The performance of this flotation technique for EO removal was improved in the presence of NaCl (< 30 mg L^{-1}) and at low temperatures (< 40 °C) or low pH (< 7). These promising results indicate the potential application of this approach for oil field treatment, because of the simple design, reduced floated product, and enhanced oil recovery.

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CHAPTER 5

TREATMENT OF PALM OIL MILL EFFLUENT BY FLOTATION TECHNIQUE CASE STUDY IN SYNN PALM OIL COMPANY, SIMPANG MALAYSIA

5.1 Introduction

Over the past few years, the Malaysian palm oil industry has grown rapidly and quickly becoming one of the world's largest producers and exporters of palm oil products (Wu *et al.*, 2009; Lam and Lee, 2011). This industry has been become an important contributor to Malaysia's GDP (i.e. the total export of palm oil products in 2008 raked up 20,268 million USD), as well as has significantly increased the standard living of its populations (Wu *et al.*, 2010). The number of palm oil mills in Malaysia has increased rapidly, i.e. from only 10 operated mills in 1960 to 410 mills in 2008 (Wu *et al.*, 2010). Nevertheless, the production of such large amounts of palm oil products (i.e. more than 17.7 million tons crude palm oil in 2008) results in a vast amount of palm oil mill effluent (POME) discharged to the environment. At least 44 million tons of POME was generated in Malaysia in 2008 and continued to rise there after (Wu *et al.*, 2010). Figure 5.1 shows the palm oil milling process (by wet method) and its products. Here, the crude palm oil and kernels are as primary products and biomass is as secondary product.

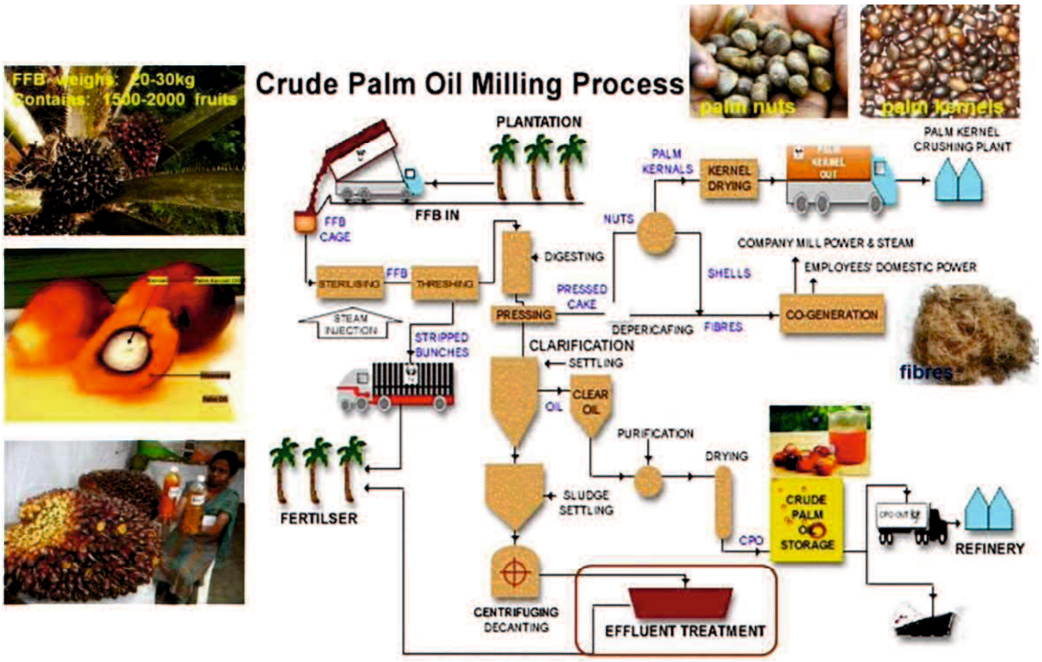

Figure 5.1 Crude palm oil milling process and its products.

It is estimated that 5–7.5 m^3 of water is required for producing each ton of crude palm oil, in which more than 50% of this water ends up as POME (Wu *et al.*, 2009). Raw POME has a thick brownish and as colloidal suspension containing 95–96% of water, 0.6–0.7% of O&G and 4–5% of total solids (TS) including 2–4% suspended solids (SS) (Ahmad *et al.*, 2003). Characteristics of POME and its discharge standards of selected countries (Malaysia, Thailand, and Indonesia) are listed in Table 5.1. Although POME is a non-toxic liquid waste, the direct discharge of POME into the environment is not encouraged due to the low pH, the high concentrations of COD, BOD, O&G, TS, SS, temperature, etc. (Lam and Lee, 2011). Consequently, treatment of POME is important for improving the water quality, oil recovery, protecting downstream facilities, and for ensuring compliance with environmental policies.

Table 5.1 Characteristics of POME and its discharge standards in Malaysia, Thailand, and Indonesia (Wu *et al.*, 2010; Lam and Lee, 2011)

	Characteristics of POME		POME discharge standards		
Parameters	Range (mg L^{-1})	Mean (mg L^{-1})	Malaysia (1984)	Thailand (1996)	Indonesia (2002)
pH	3.4 – 5.2	4.2	5 – 9	5 – 9	6 – 9
Temperature	–	–	< 45	< 40	–
BOD$_5$	10,250 – 43,750	25,000	< 100 $^{(*)}$	< 100	< 100
COD	15,000 – 100,000	51,000	–	< 1,000	< 350
TS	11,500 – 79,000	40,000	–	–	< 250
SS	5,000 – 54,000	18,000	< 400	< 150	–
O&G	130 – 18,000	6,000	< 50	< 25	< 25
TN	180 – 1,400	750	–	< 50	< 50

All parameters are in units of mg L^{-1} with the exception of pH and temperature (^{o}C).
$^{(*)}$The sample for BOD analysis is incubated at 30 ^{o}C for 3 days.

POME can be treated by numerous methods including biological treatment (facultative lagoons, open tank digester, ponds aeration, anaerobic baffled and up flow anaerobic sludge blanket, etc.) and physicochemical treatment (adsorption, solvent extraction, sedimentation, coagulation, flocculation, membrane filtration, flotation, etc.) (Poh and Chong, 2009; Foo and Hameed, 2010; Wu *et al.*, 2010). In Malaysia, more than 85% the POME mills have been applied the open ponding system for POME treatment due to low operating costs. However, disadvantages of this system are requirement of large land area, long retention time, and low treatment efficiency. Furthermore, with the rapid increasing the number of palm oil mills and the public's increased awareness of air and water pollution, these operation types fascinatingly converted into closed digesters (Ahmad *et al.*, 2005; Poh and Chong, 2009).

Physicochemical treatment technologies may provide a possible solution for the current POME management (Wu *et al.*, 2009). It is desired to combine an effluent treatment with the recovery of POME solids, O&G in which the recovered solids can be re-used as fertilizer or animal feed (Wu *et al.*, 2009). Numerous physicochemical methods based on the laboratory scale were proposed to treat POME. Coagulation, flocculation and adsorption could be applied together with membrane filtration process to produce good quality effluent (Ahmad *et al.*, 2003). However, a very large amount of coagulants and adsorbents are required and membranes are fouled that makes the overall treatment process unfeasible and uneconomical. The combination of coagulation and flotation has been shown valuable applications for POME treatment (Ng *et al.*, 1988; Wu *et al.*, 2010), but the numerous complex operation steps (flash mixing and slow mixing, long retention time) are needed. Moreover, sludge contaminated with metal hydroxides, polymers, or organic de-emulsifiers leads to difficulties in dewatering of the sludge and efficient oil recovery (Frank, 1988).

Overall, flotation can be described as a gravity separation process in which gas bubbles attach to fine particles to cause the apparent density of the bubble-particle agglomerates to be less than the water density, thereby allowing the agglomerate to rise up the surface (Letterman, 1999). Theoretically, the key design factors for a flotation setup are the flotation space where the bubbles are formed and where the oil-gas interaction occurs (Moosai and Dawe, 2003). The efficiency of flotation process is strongly dependent on the attachment of gas bubbles to the dispersed oil droplets (Moosai and Dawe, 2003). It is commonly understood that a decrease in the gas bubble size results in improved fine particle separation and oil droplet recovery, because of the large air-bubble surface area. Nowadays, there are number of methods to produce microbubbles (MBs) including hydrodynamic, acoustic, optic and particle (Gogate, 2008) of which the hydrodynamic cavitation method is widely used in term of water treatment application (Gogate, 2008; Agarwal *et al.,* 2011). From hydrodynamic cavitation, most all MB generators involve mechanical parts (e.g. a pump, a nozzle) where strong shears force impacts on a liquid (Terasaka *et al.*, 2011). MBs can be created from the pressure drop in the nozzle/injection devices or gas–water circulation (Terasaka *et al.*, 2011; Agarwal *et al.*, 2011). Consequently, variety types of flotation processes have been developed for oily water clean-up (Letterman, 1999; Rubio *et al.*, 2002). Furthermore, the vital factors for this hybrid method including gas flow rate, bubble size, viscosity of water phase, equipment or reactor design and chemical agents using have also been attracted many researches (El-Kayar *et al.*, 1993; Da Rosa and Rubio, 2005; Moosai and Dawe, 2003; Bayati *et al.*, 2011; Le *et al.*, 2013).

According to the promising results from the chapter 4, a new flotation method without using any coagulant has developed to investigate the treatment efficiencies of real POME under batch and continuous operations.

5.2 Materials and methods

5.2.1 Wastewater

In this study, POME was collected and treated after decanters processing of the palm oil mill – Synn Palm Oil (SPO) Company, Simpang province, Malaysia. It was estimated approximately 600 m^3 POME generated and discharged for daily operation in SPO Company (10 hours processing per day with the capacity of 100 tons of fresh fruit bunches per hour).

5.2.2 Experimental setup

The designed experimental setup (Figure 5.2) contains various components for this flotation. The main components of the unit (Table 5.2) were a POME received tank (sampling No.1; after decanters processing), a circulation tank (sampling No.2), a flotation tank (sampling No.3), an oil recovery tank (sampling No.4), pressure pumps (1–5), air pump, ejector MB generators (5 ejectors, in which 4 ejectors were set up in the flotation tank and 01 ejector was placed in the circulation tank), MB diffusers (BT-50 nozzle, 8 nozzles), "normal bubbles" nozzles, an air flow meter, pressure meters, valves, and shower spray nozzles.

All of the POME received tank, the circulation tank, the flotation tank and oil recovery tank were made by standard steel with working volume 1000 L, 960 L, 670 L, and 400 L, respectively. In the flotation tank, 4 out tubes (come from 4 ejectors MB generators) were sited at the bottom of the reactor at vertical angles of 45^o for spreading the MBs and for generating cyclone air flow inside the separator. The MB nozzles (8 nozzles) were fixed inside the reactor at a height of about one-fifth of the total height from the top of the reactor. As a typical pressurized dissolution MB generator, the mixture of liquid and gas was pressurized by the pump 3 (high POME flow rate: 80 L min^{-1}, at pressure: 200–250 kPa). Unstable supersaturated gas is eventually escapes out from the water resulting in a large number of MBs (Terasaka *et al.*, 2011; Agarwal *et al.*, 2011). POME after decanter processing was pumped to the circulation tank. Here, a part of total solids and O&G were separated by an ejector MB generator and “normal bubbles” nozzles from air pump. Subsequently, POME was feed to the flotation tank by pump 2, pump 3 or pump 4. Treated POME in the floatation tank was rotational flowed to the circulation tank; the wastewater after treatment was discharged from the bottom of the circulation tank to bio-oxidation ponds system of the company. Floated product was skimmed in the top of flotation tank and the top of circulation tank, transferred to the oil recovery tank, and pumped back to the factory by pump 5.

For each of samplings (No.1 to No.4), a 1000 mL sample was taken during the treatment time (3 – 4 times) for analysing the removal efficiency due to parameters: total COD, TS, and O&G. In this study, pH and temperature were measured directly by pH meter and thermometer; COD, TS, and O&G were analysed following standard methods (APHA, 2005).

Table 5.2 The main components of the experimental setup

Device	Main purposes
POME received tank	Receive POME after the decanters processing, mixing POME
Circulation tank	Receive POME by Pump 1; Supply POME to flotation tank by pump 2, pump 3 and pump 4; Enhance the flotation process
Flotation tank	Separation O&G, solids in POME
Oil recovery tank	Receive floated product from the top of flotation tank and circulation tank
Pump 1	Feeding POME from the received tank to the circulation tank
Pump 2	Feeding POME to the flotation tank through the ejectors to produce MBs
Pump 3	Feeding POME to the flotation tank through BT-50 nozzles to produce MBs
Pump 4	Feeding POME from the circulation tank to the flotation tank; Producing MBs via the ejector in circulation tank
Pump 5	Pumping the floated product back to the factory
Air pump	Supply gas bubbles in circulation tank and gas for producing MBs

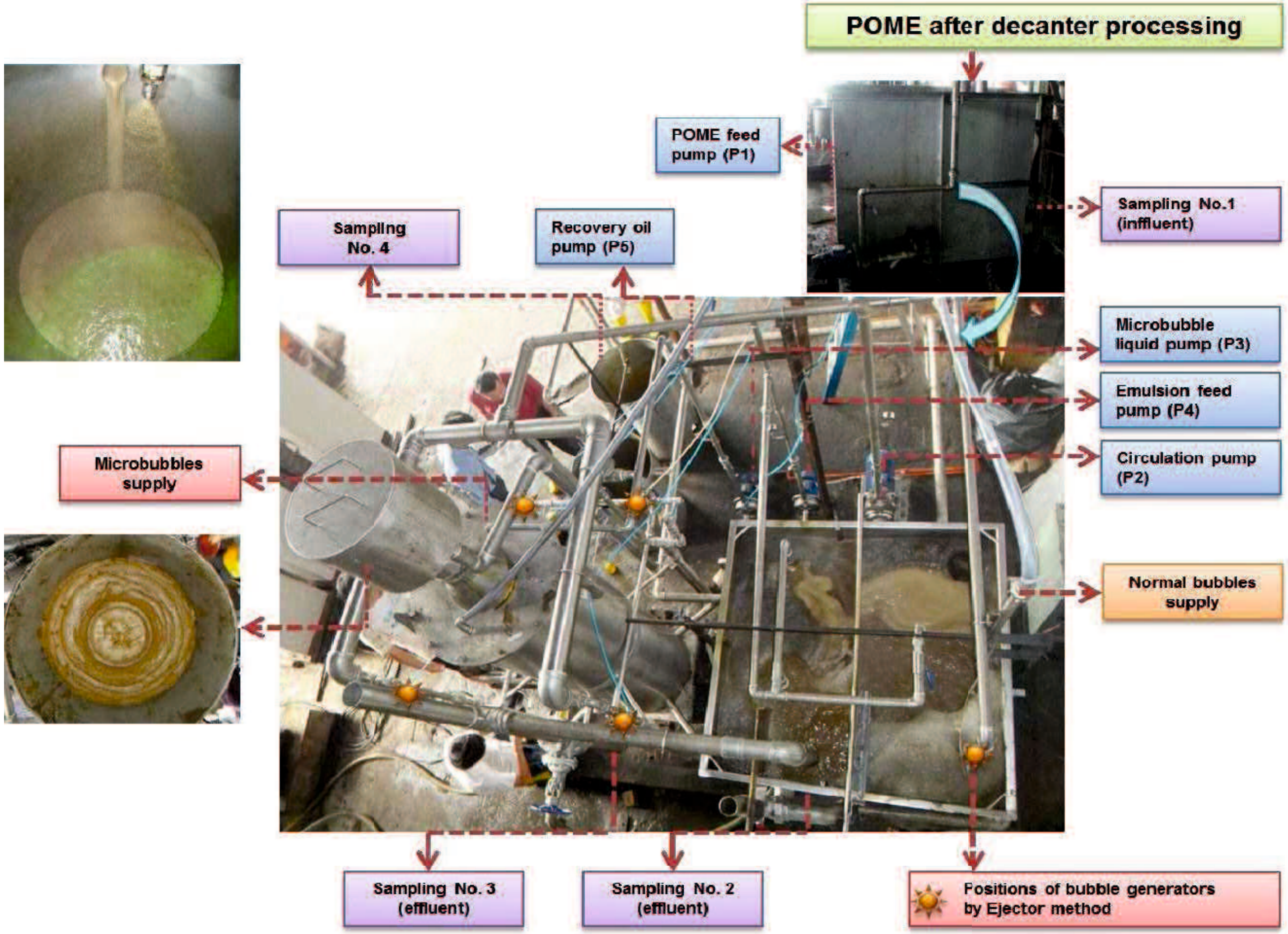

Figure 5.2 Experimental setup

5.3 Results and Discussion

5.3.1 Characteristics and rapid assessment of POME in SPO Company

In general, the oil droplets in POME are stable with very small size (emulsified oil) (Ahmad *et al.*, 2006). Furthermore, the high loading of COD, high temperature, low pH, and together with the colloidal nature of the suspended solids cause to treatment of POME by conventional methods is very difficult (Wu *et al.*, 2010). Table 5.3 shows the general characteristics of raw POME after decanter processing in SPO Company. According to the analysis results, this POME is hot (74.9 ± 4.6 ^{o}C), low pH (4.9 ± 0.1), and possesses high fluctuation of O&G: 13,167 ± 4,105 mg L^{-1}, TS: 60,844 ± 7,194 mg L^{-1}, and COD: 98,697 ± 10,723 mg L^{-1}. Here, the average concentration of COD and O&G are much higher than the mean of POME in two times.

Principally, the capacity of mills varies between 60 and 100 tons of fresh fruit bunches per hour. At the SPO Company, this mill processing is usually operating in high capacity (100 tons per hour) during 10 hours a day and generated about 600 m^3 d^{-1} of POME. The rapid assessment pollutants loading rate of the POME (Table 5.4) estimated approximately 7.9 tons of O&G, 36.5 tons TS, and 59.2 tons COD were generated in this milling process per day. Therefore, the development of separation technique is needed for enhancement of oil recovery and for wastewater treatment with environmental policies.

Table 5.3 Characteristics of POME after decanter processing in SPO Company

Characteristics of POME *(Wu et al., 2010; Lam and Lee, 2011)*			Characteristics of POME *(Our analysis results: 28/11 – 13/12/2012)*		
Parameters	Range (mg L^{-1})	Mean (mg L^{-1})	Parameters	Range (mg L^{-1})	Mean ± SD (n=9) (mg L^{-1})
pH	3.4 – 5.2	4.2	pH	4.8 – 5.1	4.9 ± 0.1
Temperature	–	–	Temperature	69 – 84	74.9 ± 4.6
O&G	130 – 18,000	6,000	O&G	8,500 – 18,900	13,167 ± 4,105
TS	11,500 – 79,000	40,000	TS	49,000 – 70,900	60,844 ± 7,194
COD	15,000 – 100,000	51,000	COD (total)	76,650 – 109,850	98,697 ± 10,723
All parameters are in units of mg L^{-1} with the exception of pH and temperature (^{o}C).					

Table 5.4 Rapid assessment pollutants loading rate of POME

Fresh fruit bunch (tons)	Average concentration of pollutants in POME		
	O&G (mg L^{-1})	TS (mg L^{-1})	COD (total) (mg L^{-1})
~ 1000	13,167 ± 4,105	60,844 ± 7,194	98,697 ± 10,723
POME flow rate (m^3 d^{-1})	Pollutant loading rate = Q (m^3 d^{-1}) × C (mg L^{-1}) × 10^{-3} = A (kg d^{-1})		
	O&G (kg d^{-1})	TS (kg d^{-1})	COD (total) (kg d^{-1})
~ 600	7,900	36,506	59,218

5.3.2 POME separation efficiency by batch mode operations

In this study, POME was stabilized overnight (~12 hours) in the circulation tank, and naturally temperature was gradually decreased to 39 ± 1°C. Two batch modes testing upon difference the initial O&G concentrations were operated and named as Test 1 (O&G: 15,100 mg L^{-1}) and Test 2 (O&G: 5,800 mg L^{-1}) (Figure 5.3). The ejector MB generators and the dissolution MB generator were worked for 0–120 min at POME flow rate 290 L min^{-1} of pump 2, 30 L min^{-1} of pump 4, and 80 L min^{-1} of pump 3. Here, POME treatment performance was calculated via the reducing concentration of O&G, COD and TS in the circulation tank (after stabilization, sampling No.2) and the flotation tank (after treatment, sampling No.3). Table 5.5 reveals of the operations apparatus.

Flotation time plays an important role on the efficiency of flotation methods, thus, there was a significant increase in removal O&G, COD and TS efficiencies during treatment time. At the concentrations of O&G: 15,100 mg L^{-1}, COD: 104,075 mg L^{-1}, and TS: 64,100 mg L^{-1}, the removal efficiencies increased gradually to 33.1%, 16.9%, and 8.4%, respectively, after 120 min of treatment (Figure 5.3 a). In case of lower O&G concentration (5,800 mg L^{-1}), a high separation efficiency of more than 60 % was observed after a 60-min treatment (Figure 5.3 b) and slowed down thereafter. It was seem to be the lower initial O&G concentration got higher the separation efficiency. However, in term of O&G loading the Test 1 removed about 1,675 g h^{-1} (5,000 mg L^{-1} × 670 L/2 hours); it was slightly higher than the operation Test 2 of which 1,340 g h^{-1} (4,000 mg L^{-1} × 670 L/2 hours) was separated.

According to the analysis results, the POME is hot and concentration of O&G in this POME is extremely fluctuating. Moreover, high concentration of O&G in POME is present in the form of emulsified oil (Ahmad *et al.*, 2006). Therefore, a long retention time is necessary to remove O&G from POME.

Table 5.5 Operations apparatus of two batch modes testing

Operation	Operating time (min)	POME flow rate (L min^{-1})				Air supply (L min^{-1})	
		Pump 1	Pump 2	Pump 3	Pump 4	*Ejector	**Dissolution
Test 1	120	0	290	80	30	2.5	1.5
Test 2	120	0	290	80	30	2.5	1.5

**Ejector: amount of air supply for each of ejector MB generator in flotation tank*

***Dissolution: amount of air supply for dissolution MB generator in flotation tank*

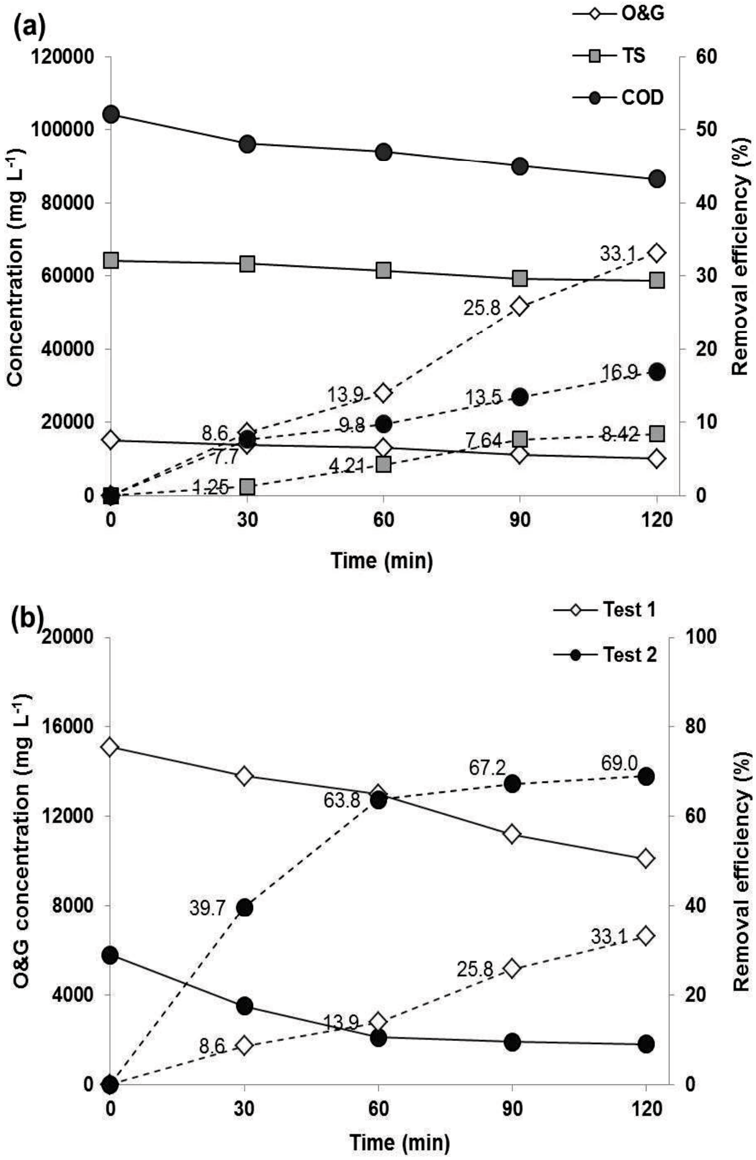

Figure 5.3 POME separation efficiencies by the batch mode operations.
Temperature: 39 ± 1 °C.

5.3.3 POME separation efficiency by continuous mode operations

Before each of operation, “old” POME in the flotation system was totally discharged and the system was washed. POME was feed into the system at flow rate 20 L min^{-1} (Test 3) and 30 L min^{-1} (Test 4). After full feeding POME into the circulation tank, POME was pumped to the flotation tank. For each of continuous mode operations, the three samplings: No.1 (POME after decanters processing), No.2 (in the bottom of the circulation tank) and No.4 (in the oil recovery tank) were withdrawn during the flotation time (at least 150 min to 360 min). Here, the POME separation efficiency (via the parameters O&G, TS and COD) was calculated using concentration of sampling No.1 and sampling No.2. The operations apparatus are listed in the Table 5.6 and the treatment efficiencies are showed in the Figure 5.4.

Thus, it was rather difficult for the assessment and for the determination of the most favorable operation due to the highly unstable of O&G, TS, and COD concentration and/or temperature parameter during the treatment time, as well as the difference of concentration ratio (i.e. O&G : TS; O&G : COD) between them. In general, the treatment efficiency of continuous mode was lower than the batch mode operation. An increase in POME feeding flow rate from 20 to 30 L min^{-1} resulted in a significantly lower percentage of O&G removal, 36 ± 9% and 25 ± 11%, respectively. The concentration of O&G in the oil recovery tank (Figure 5.4 a) was highly enriched from 2 – 3 times compared with POME. Nevertheless, these treatments were shown low effective in the separation of TS (average: 4%) (Figure 5.4 b) and COD (average: 5 – 9%) (Figure 5.4 c).

Principally, the higher recycle pressurization can produce of smaller MBs (Bayati *et al.*, 2011). For POME flow rates (Table 5.6) pumped from circulation tank to floatation tank, the air flow rates used for pressurized MB generator and ejector MB generators was adjusted and controlled at 1.5 L min^{-1} and 2.5 L min^{-1}, to keep the pressure values at 200–250 kPa. Consequently, the pressure value can be changed follow the POME recycle flowing rate. Hence, further research on the effect of recycle pressurization on this flotation is necessary. In addition, the effect of gas and solids ratio should be investigated.

Table 5.6 Operations apparatus of continuous modes testing

Operation	Operating time (min)	POME flow rate (L min^{-1})				Air supply (L min^{-1})		Hydraulic loading rate (m^3/m^2 h)		Floated product	
		Pump 1	Pump 2	Pump 3	Pump 4	Ejector	Dissolution	Flotation tank	Flotation & Circulation tank	Flow rate (L min^{-1})	Volume per hour (L)
Test 3 (n = 3)	150 – 330	20	290	80	30	2.5	1.5	3.62	0.75	~1.2	~72
Test 4 (n = 3)	300 – 360	30	290	80	30	2.5	1.5	5.43	1.12	~1.4	~84

Note: Hydraulic loading rate = POME feeding flow rate (Pump 1)/(Surface area of flotation tank or flotation and circulation tank)

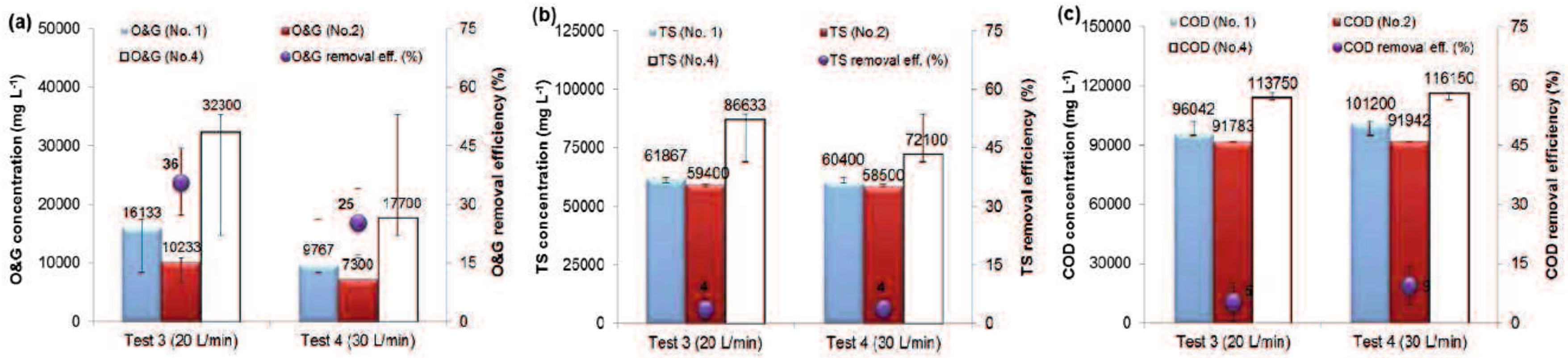

Figure 5.4 The concentrations of $^{(a)}$O&G, $^{(b)}$TS, $^{(c)}$COD in the influent (No.1), the effluent (No.2) and the oil recovery tank (No.4) of difference continuous POME feeding flow rates, 20 L min^{-1} and 30 L min^{-1}. Temperature: 74.9 ± 4.6 °C.

5.3.4 Economics of the MB technique

Principally, there are many types of costs involved in wastewater treatment plant, i.e. equipment purchase cost, operating cost, energy cost, chemicals cost, maintenance cost, installation cost, environmental cost, disposal cost, etc. In this part, the economics of the MB technique for treatment of POME would be evaluated within the estimated cost of energy input (electricity) and the value of palm oil recovery. Here, the average concentration of O&G: 13,200 mg L^{-1} (n = 9) in POME was selected. In addition, it was estimated that under continuous mode (i.e. POME flow rate: 20 L min^{-1}), the MB technique can be separated more than 36% O&G and the concentration of O&G in oil recovery tank can be enriched about 3 times, with the volume of floated product being ~72 L after 60-min treatment.

Actually, this MB technique requires about ~6.7 kWh (energy consumption) for the treatment of 1200 L of POME (to high as 5400 L, pump 1) (Table 5.7). However, the palm oil product can be recovered about 1.9 kg O&G [(3 × 13,200 mg L^{-1} - 13,200 mg L^{-1}) × 72 L× 10^{-6}] and the treatment process can be reduced more than 5.7 kg O&G (36% × 13,200 mg L^{-1} × 1200 L × 10^{-6}) to discharge to the ponds system.

Presently, industrial electricity cost per kWh in Malaysia varies from 0.045 to 0.083 USD and crude palm oil is around 800 USD/ton. Thus, the cost of total energy consumption 6.7 × 0.083 = 0.56 USD (to treat 1200 L of POME) was significantly lower than the cost of palm oil recovery 0.8 × 1.9 = 1.52 USD (from 1200 L of POME). In addition, we can continue improve the efficiency of MB technique.

Table 5.7 Total energy consumption of the MB technique

Unit	Q min – Q max (L min^{-1})	Q operation (L min^{-1})	Power (kW)	Time operation (min)	Energy (kWh)
Pump 1	20 – 90	20	0.68	60	0.68
Pump 2	200 – 700	290	4.10	60	4.10
Pump 3	50 – 180	80	0.95	60	0.95
Pump 4	20 – 90	30	0.68	60	0.68
Pump 5	20 – 90	20	0.68	3.6	0.04
Air pump	200	–	0.21	60	0.21
Total energy consumption for the treatment of 1200 L of POME					**6.66**

5.4 Conclusions

The POME was highly unstable in terms of O&G, TS, and COD concentration and temperature during the treatment time. The modified flotation method was shown to be a potential approach for reducing the floated product and enhancing oil recovery in POME. The separation of these contaminants was well achieved by batch mode operation in a long retention time (i.e. O&G: 5,800 mg L^{-1}, removal efficiency more than 60%, at 60-min retention time). Although low efficiency of O&G, TS, and COD removal were observed under continuous modes, however, the cost of total energy consumption was significantly lower than the value of palm oil recovery. Further researches on the effect of recycle pressurization, gas/solids ratio and how to manage the floated product after POME treatment are necessary.

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CHAPTER 6

CONCLUSIONS AND FUTURE WORKS

6.1 Conclusions

Principally, this dissertation has been shown three independent studies results in chapter 3 to chapter 5. However, it can be seen the development of flotation processes due to improve the treatment of oil-in-water emulsions efficiencies and enhance oil recovery from lab scale to field treatment. Some main comparisons between our studies: using of MB–PAC, MB–CTAC or MB–NB in treatment of EO, with traditional flotation technology (coagulation – flotation) in treatment of EO is shown in Table 6.1.

(1). Separation of oil-in-water emulsions by MB, MB–PAC and MB-CTAC

The separation of oil-in-water emulsions is successfully achieved by the combination of MB–PAC or MB–CTAC. A high concentration of emulsified palm oil (~1000 mg L^{-1}) was successfully separated with an efficiency of approximately 90% by MB treatment with PAC (MB generation time: 2.5 min, PAC: 50 mg L^{-1}, pH: 3–7) and with an efficiency of more than 82% by MB treatment with CTAC (MB generation time: 2.5 min, CTAC: 0.5 mg L^{-1}, pH: 5–7). The data indicate a good EO removal efficiency at a low concentration of CTAC (0.5 mg L^{-1}), which was 100 times less than that of PAC dosage (50 mg L^{-1}).

Although the use of MB treatment alone showed less impact on the EO removal efficiency than MB–PAC or MB–CTAC at pH around neutrality, however, MB treatment exhibited a significant EO removal efficiency (~70%) in acidic water. This result is interesting to consider the development of efficiency and economical flotation systems for separation of oil from acidic oily wastewater sources such as POME (pH 3.4–5.2).

(2). Separation of oil-in-water emulsions by the combination of MB and NB

The experimental setup allows for efficient flotation to remove oil-in-water emulsions without using any coagulant. Separation of fine EO emulsions (d < 16 μm) is successfully achieved by the combination of tiny high-flow-rate MBs and cyclone NBs, but there is little effect on EO droplets smaller than 2 μm.

In the normal concentration range 100–1000 mg L^{-1}, clear EO separation was observed after 30 min, with a removal efficiency of more than 67%. The performance of this flotation technique for EO removal was improved in the presence of NaCl (< 30 mgL^{-1}) and at low temperatures (< 40 ^{o}C) or low pH (< 7). These promising results indicate the potential application of this approach for oil field treatment, because of the simple design, reduced floated product, and enhanced oil recovery.

Table 6.1 Advantage and disadvantage of EO treatment processes: combination of coagulation – flotation, MB–PAC, MB–CTAC, and MB–NB

Treatment by	Advantages	Disadvantages
Coagulation and flotation (Some reviews of the de-emulsification of oil-in-water emulsion by flotation methods were listed in Table 3.1 (page 31).	• Handle high-shock loads; • High efficiency (85 – 99%); • Can remove dissolved oils.	• Require to adjust pH and high dosage of chemicals; • Chemical mixing program (flash mixing and slow mixing); • Long treatment time; • Sludge disposal problems (large amount of sludge produced with metal hydroxides (aluminium or iron) or organic de-emulsifiers); • Require sludge treatment.
MB–PAC (this study: chapter 3)	• Handle high-shock loads; • High efficiency (>90%, pH: 3-7); • Can remove dissolved oil.	• Require high dosage of PAC (50 mg/L for EO: 1000 mg/L); • Chemical mixing program (flash mixing and slow mixing); • Long treatment time; • Large amount of sludge produced with aluminum hydroxide (~40 mL/L); • Require sludge treatment.
MB–CTAC (this study: chapter 3)	• Handle high-shock loads; • High efficiency (>82%, pH: 5-7); • Can remove dissolved oil; • Does not require a complex mixing procedure; • Short treatment time; • Produce a small amount of sludge (a few mL/L).	• Require low dosage of CTAC (0.5 mg/L for EO: 1000 mg/L); • Require flash mixing; • Require sludge treatment.
MB–NB (this study: chapter 4)	• Handle high-shock loads; • Rather high efficiency (> 67%, pH: 3-7); • Can remove EO (d > 2 μm); • Does not require any chemicals and mixing procedure; • We can recover the oil for food.	• Long treatment time (> 30 min)

(3). Treatment of real POME by the MB technique

POME was collected and treated after decanters processing at the palm oil mill (Synn Palm Oil Company), in Simpang province, Malaysia. This POME is hot (74.9 ± 4.6 ^{o}C), low pH (4.9 ± 0.1) and possesses high fluctuation of O&G: 13,167 ± 4,105 mg L^{-1}, TS: 60,844 ± 7,194 mg L^{-1}, and COD: 98,697 ± 10,723 mg L^{-1}. The rapid assessment pollutants loading rate estimated about 7.9 tons O&G, 36.5 tons TS, and 59.2 tons COD were generated in the milling process per day.

The modified flotation method was shown to be a potential approach for reducing the floated product and enhancing oil recovery in POME. The separation of these contaminants was well achieved by batch mode operation in a long retention time (i.e. O&G: 5,800 mg L^{-1}, removal efficiency more than 60%, at 60-min retention time). Although low efficiency of O&G, TS, and COD removal were observed under continuous modes, however, the cost of total energy consumption was significantly lower than the value of palm oil recovery. In addition, we can continue improve the efficiency of this technique.

6.2 Future works

(1). Zeta potential should be measured for fully understanding the effects of MBs, pH, salinity, PAC, CTAC, etc. on the oil-in-water emulsions treatment.

(2). In fact, open ponding system (combination of anaerobic – facultative – aerobic) has normally selected for POME treatment because of low operation costs. However, disadvantages of this system are requirement of large land area, very long retention time, and low treatment efficiency. Due to long retention time of biodigestion (i.e. POME in the SPO company, HRT = 107 days), pH of POME was changed from acidic (pH: 4.4 ± 0.2) in the influent to slightly alkaline (pH: 8.0 ± 0.1) in the effluent.

According to the results in the chapter 3, at pH 5 – 7, MB-CTAC treatment gave a good EO removal efficiency at a low concentration of CTAC within a short flotation time. Furthermore, MB–CTAC treatment created only a small amount of floated sludge and might cause very high dissolved oxygen concentration in the effluent. Therefore, the combination of MB–CTAC or MB–NB–CTAC would be investigated for enhancement of the aerobic digestion. In addition, oil floated product should be studied and used as a potential energy (i.e. apply in spray combustors).

(3). For the POME flotation treatment system (chapter 5), further researches on the effect of recycle pressurization, gas and solids ratio and how to manage the floated waste after POME treatment are necessary.

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