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TREATMENT OF LUBRICANT OILY EMULSION WASTEWATER BY COMBINING FLOTATION AND COAGULATION PROCESS

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Environmental Management
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Field of Study	Environmental Management
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งานวิจัยนี้ได้ทำการศึกษาประสิทธิภาพการบำบัดน้ำเสียปนเปื้อนน้ำมันเครื่องร่วมกับสารลดแรงตึงผิวชนิดประจุบวก (SDS) ประจุลบ (CTAB) และไม่มีประจุ (Tween20) ที่ทำการเตรียมค่าความเข้มข้นเท่ากับ 1 ซีเอ็มซี โดยประยุกต์ใช้กระบวนการโคแอกกูเลชันร่วมกับกระบวนการอินดิวซ์แอร์โฟลเทชัน (Modified Induce Air Flotation, MIAF) เปรียบเทียบกับกระบวนการอินดิวซ์แอร์โฟลเทชัน (IAF) และ กระบวนการโคแอกกูเลชัน (Coagulation) โดยปัจจัยที่ทำการศึกษาในส่วนของกระบวนการโคแอกกูเลชัน ได้แก่ ค่าพีเอช และปริมาณความเข้มข้นของสารโคแอกกูแลนท์ (สารส้ม) ในขณะที่ปัจจัยที่ทำการศึกษาในส่วนของกระบวนการ IAF และ MIAF ได้แก่ อัตราการไหลอากาศ ระยะเวลาในการเติมอากาศ และผลกระทบจากความเข้มข้นของสารโคแอกกูลแลนท์

จากการทดลองพบว่าประสิทธิภาพของการบำบัดซึ่งวัดในรูปของค่าซีโอดี ขึ้นอยู่กับปริมาณความเข้มข้นของสารโคแอกกูแลนท์ ค่าพีเอช และอัตราการไหลอากาศที่เหมาะสม สำหรับการประยุกต์ใช้กระบวนการ IAF สภาวะที่เหมาะสมในการบำบัดน้ำเสียปนเปื้อนน้ำมันร่วมกับสารลดแรงตึงผิวชนิด SDS, CTAB และ Tween20 อยู่ที่เวลาการเติมอากาศ 30 นาทีและอัตราการไหลของอากาศเท่ากับ 0.3, 0.3 และ 0.5 ลิตร/นาที โดยให้ประสิทธิภาพในการบำบัด 33.33%, 74.44%, และ 25.00% ตามลำดับ ในขณะที่กระบวนการโคแอกกูเลชันประสิทธิภาพสูงสุดในการบำบัดน้ำเสียปนเปื้อนสารลดแรงตึงผิวชนิด SDS, CTAB และTween20 เท่ากับ 61.82%, 59.77% และ 37.66% ซึ่งได้จากพีเอช 8 และความเข้มข้นของสารส้มเท่ากับ 400, 200 และ 150 มิลลิกรัม/ลิตร ตามลำดับ ทั้งนี้ ปริมาณสารลดแรงตึงผิวที่ใช้ในการเตรียมน้ำเสียตัวอย่าง ขนาดอนุภาคน้ำมันและประจุที่เกิดขึ้นบนผิวนั้น เป็นตัวแปรสำคัญที่ส่งผลต่อค่าประสิทธิภาพการบำบัดที่แตกต่างกัน นอกจากนี้ เมื่อพิจารณากระบวนการ MIAF ซึ่งมีความเหมาะสมสำหรับบำบัดน้ำเสียปนเปื้อนสารลดแรงตึงผิวชนิด SDS ในงานทดลองนี้พบว่าความเข้มข้นของสารส้มที่เหมาะสมเท่ากับ 300 มิลลิกรัม/ลิตร อัตราการไหลของอากาศเท่ากับ 0.3 ลิตร/นาที และเวลาการเติมอากาศ 30 นาที โดยสามารถลดค่าซีโอดีได้สูงสุด 75% ทั้งนี้ เมื่อวิเคราะห์จลนศาสตร์ของการบำบัดดังกล่าว ค่าคงที่ของปฏิกิริยา (log k) และ ค่าของลำดับปฏิกิริยา (n) ซึ่งสามารถคำนวณได้จากสมการอัตราการเกิดปฏิกิริยา (Reaction rate equation) นั้น สามารถนำมาวิเคราะห์หาปริมาณโคแอกกูแลนท์ที่เหมาะสมสำหรับกระบวนการ MIAF และสร้างสมการความสัมพันธ์เพื่อทำนายค่าประสิทธิภาพการบำบัดโดยให้ค่าความคลาดเคลื่อนในช่วง ± 25% นอกจากนี้ ค่าสัดส่วนระหว่างพื้นที่ผิวสัมผัสจำเพาะของฟองอากาศ (Interfacial area, a) และความเร็วเกรเดียน (Velocity Gradient, G) หรือค่าสัดส่วน a/G จัดเป็นพารามิเตอร์ที่สำคัญสำหรับควบคุมประสิทธิภาพของกระบวนการทำให้ลอย ในด้านการสัมผัสระหว่างฟองอากาศและอนุภาคน้ำมัน รวมไปถึงความปั่นป่วนที่เกิดขึ้นภายในระบบบำบัด ซึ่งค่า a/G มีความสัมพันธ์ในรูปแบบของสมการเส้นตรงกับประสิทธิภาพบำบัด ซึ่งมีความเป็นได้ที่จะประยุกต์ใช้เพื่อควบคุมสภาพการดำเนินงานที่เหมาะสมของกระบวนการต่อไป

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต สิริพร เลิศจินตนาการ

ปีการศึกษา 2551 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก

5087547820 : MAJOR ENVIRONMENTAL MANAGEMANT
KEYWORDS: OILY EMULSION WASTEWATER / SURFACTANT/ COAGULATION / MODIFIED INDUCE AIR FLOTATION / REACTION RATE CONSTANT.

SIRIPORN LERSJINTANAKARN: TREATMENT OF LUBRICANT OILY EMULSION WASTEWATER BY COMBINING FLOTATION AND COAGULATION PROCESS. THESIS ADVISOR: PISUT PAINMANAKUL, Ph.D., 151 pp.

The objective of this work is to study the treatment of stabilized lubricant oily emulsion wastewater containing with anionic (SDS), cationic (CTAB), and nonionic (Tween20) surfactants at concentration equal to 1 CMC (Critical Micelle Concentration). The Modified Induced Air Flotation process (MIAF), which is the combined process between the Induced Air Flotation (IAF) process and the coagulation process, were applied and also compared with those obtained with the IAF and coagulation processes.

The study has shown that the removal efficiencies were related with the alum dosage, pH value and air flow rate. For the IAF process, optimal treatment conditions for oil emulsion with SDS, CTAB, and Tween20 were obtained at 30 s of aeration time and at 0.3, 0.3, and 0.5 l/min of air flow rate: these provide the treatment efficiencies equal to 33.33%, 74.44% and 25.00%, respectively. Due to the coagulation process, the highest removal efficiencies from oily-emulsion wastewaters with SDS, CTAB, and Tween20 equal to 61.82%, 59.77% and 37.66% were achieved at pH 8 and at alum concentration 400, 200, and 150 mg/l. respectively. The concentration of surfactant used for preparing oil-emulsion, size of oil droplets and surface charge of oil droplets were proven to be the important parameters. For the MIAF process, the highest treatment efficiencies were obtained with the oily-emulsion wastewater with SDS: this was chosen in order to study, in detail, in term of kinetic and bubble hydrodynamic characteristics. The optimal operating conditions were 300 mg/l of alum concentration, 0.3 l/min of air flow rate, and 30 minutes of aeration time and thus 75% of treatment efficiencies can be obtained. The reaction rate constant (log k) and reaction order (n) related with coagulant concentration can be applied for proposing the simple model for predicting the treatment efficiency with average difference about ± 25%. Moreover, the ratio between interfacial area and the velocity gradient (a/G) have been proven to be the important parameter for controlling the flotation process efficiency in term of collision/attachment and of chemical mixing condition. The linear equation of treatment efficiencies and a/G ratio can be possibly applied as the important parameter for well controlling floatation process.

Field of Study: Environmental Management Student's Signature:..ศิริพร...เลิศจินตนากร
Academic Year: 2008 Advisor's Signature:.....Pisut P......

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LIST OF ABBREVIATIONS

Alum	Aluminium sulfate
CMC	Critical Micell Concentration
COD	Chemical Oxygen Demand
Cps	Centipoises
CTAB	Lauryl dimethyl benzyl ammonium bromine
DAF	Dissolve Air Flotation
Eff%	Removal Efficiency
IAF	Induce Air Flotaion
L/min	Liter per minute
m	Meter
MIAF	Modified Induce Air Flotation
mg/l	milligram per liter
mol/l	mole per liter
SDS	Sodium laurylsulfate
SFT	Surface Tension
Tween20	nonionic surfactant

CHAPTER I

INTRODUCTION

1.1 Statement of problem

Oily wastewater is one of the most concerned pollution sources that cause various severe effects on both human being and environments. There are many kinds of oily wastewaters that come from variety of sources, such as crude oil production, oil refinery, petrochemical industry, metal processing, car washing, lubricant and cooling agents. Normally, the oily wastewater is considered as hazardous industrial wastewater because it can contain toxic substances, like Phenols, Petroleum hydrocarbons, PolyAromatic Hydrocarbons (PAHs), that are inhibitory to plant and animal growth and also are mutagenic and carcinogenic to human being (Tri, 2002). Moreover, it can be noted that, even very low oil concentrations are toxic for microorganisms responsible for biodegradation in conventional sewage processes. Therefore, it can be stated that removal of the oil phase is essential before effluent disposal.

In practice, oily wastewater depends on the source related with the activities and production processes. The different oily wastewater types can be divided as follows:

- Oily wastewaters from palm oil mills are mostly contained with palm oil: the most generated from leaking of fruit bunch sterilization process. The concentration of palm oil contaminate in wastewater is 1,000-3,000 mg/l (Peachpibul, 2007).
- Oily wastewaters from metal industries (cutting oil) that are widely used in metal industries, such as rolling mill, forges, and metal workshops. It can be stated that this oil type can disperse and thus form the stabilized emulsion (100 to 5,000 mg/l) that difficulty to eliminate (Chooklin, 2004; Yang, 2007).
- Oily wastewaters obtained from gas/pump service station are mostly contained with petroleum oil and lubricant or motor oil (0.5 to 368 mg/l) (Numchaiwong, 1999) and wastewater generated with an average of 20 m^3 per day (Khondee, 2007). This wastewater generated by various activities (car

washing, cafeteria, lubricant changing or floor cleaning) can be considered as a part of the environmental problem (Sahairaksa, 1999).

Due to the increase of population and thus oil consumption, it can be stated that oily wastewater from gas/pump service station will become one of the important pollution issues in urban area. Generally, this type of oily wastewater will be present in from of emulsion with surfactants: these are the major constituent in car washing agents used in service station. The surfactant has contaminated surface water with an objectionable foaming property. Moreover, depending on their chemical structure, some emulsifiers are resistant to chemical attack that causes a higher COD in wastewater. (Langlais *et al*., 1991). Because of oily wastewater from car-washing activities are emulsion with surfactants; it is very difficult to treat by using classical method. Therefore, in this research was interest to study this type of oily wastewater.

Generally, oily wastewater is relatively difficult to be biodegraded, thus, it becomes clear that the use of the biological treatment is not the economical and suitable methods. Besides, there are possibilities to reuse or recover the hydrocarbons in the wastewater. Then treatment processes studied in this laboratory were based on separation processes (physical and physico-chemical techniques) in order to separate oil from water. Flotation is one of the advanced separation processes that used extensively in the removal of stable oily emulsion (Da Rosa and Rubio, 2005). This process operated by increasing the density differences between continuous phase and dispersed phase. This is accomplished by mean of adding gas or air into the oily wastewater to promote formation of air-solids or air-oil agglomerates (Aurelle, 1985). Normally, floatation can be divided into Dissolved Air Flotation (DAF) and Induced Air Flotation (IAF). In general, the DAF process that relates with the very small bubble sizes generated (30–100 μm in diameter) can provide the highest treatment efficiency (Rachu, 2005). However, DAF process has some limitations, i.e., high investment cost, complex operations and large equipment size. Therefore, IAF process is an attractive alternative and chosen for this study. Note that, in this IAF system, the bubbles (700–1500 μm in diameter) are mechanically formed by a combination of a high-speed mechanical agitator or an air injection system (Jameson, 1999).

Concerning to the treatment of oily wastewaters obtained from gas/pump service station, it can be noted that this oily wastewater contains with surfactant and forms stabilized emulsion. Therefore, it is very difficult to separate and treat by decantation process and biological process because of the small mean droplet size and chemical stabilization. Stabilized emulsion required the setting time was up to 26 hour in the setting tank and affect to biological treatment by oil interfere oxygen used of microorganism (Deng *et al*., 2005). From da Rosa and Rubio, 2005, the different flotation processes have been used extensively in the removal of stable oily emulsions or fine particles suspensions. Moreover, Reay and Ratcliff have shown that gas flotation is most effective when the oil droplets have diameters between 3 and 100 mm. Moreover, the obtained efficiencies are not greatly affected by bubble size, whereas by bubble number density. Thus, they suggest that it is better to have oil drops as large as possible (larger collision area) and bubble size as small as possible (longer residence times) (Moosai and Dawe, 2003). In order to enhance the treatment efficiency of oily wastewater with surfactants, the chemical treatment should be applied in order to “breaking” the emulsion to allow the micro droplet to coalesce and make it possible to separate by the physical processes (Shamrani *et al*., 2002). Chemical process for oily wastewater treatment is mainly destabilization process for destabilizing of stable emulsion. It consists of 2 main mechanisms, i.e. destabilization of oil droplets (Coagulation) and coalescence of destabilized oils (Flocculation). Therefore, it can be stated that this process is necessary when the wastewater to be treated contains stable or stabilized emulsion: it can not be treated by STOKES law-based processes. Destabilization chemicals (salts, acids, and polyelectrolyte) and coagulants (aluminum sulphate and ferric chloride) are the most widely used. This is because of their effectiveness, cheap, easy to handle and availability (Ahmad *et al*., 2006). In order to well manage the oily wastewater in real operation condition, the overview of various treatment processes for oily wastewater can be thus summarized and shown in Figure 1.1

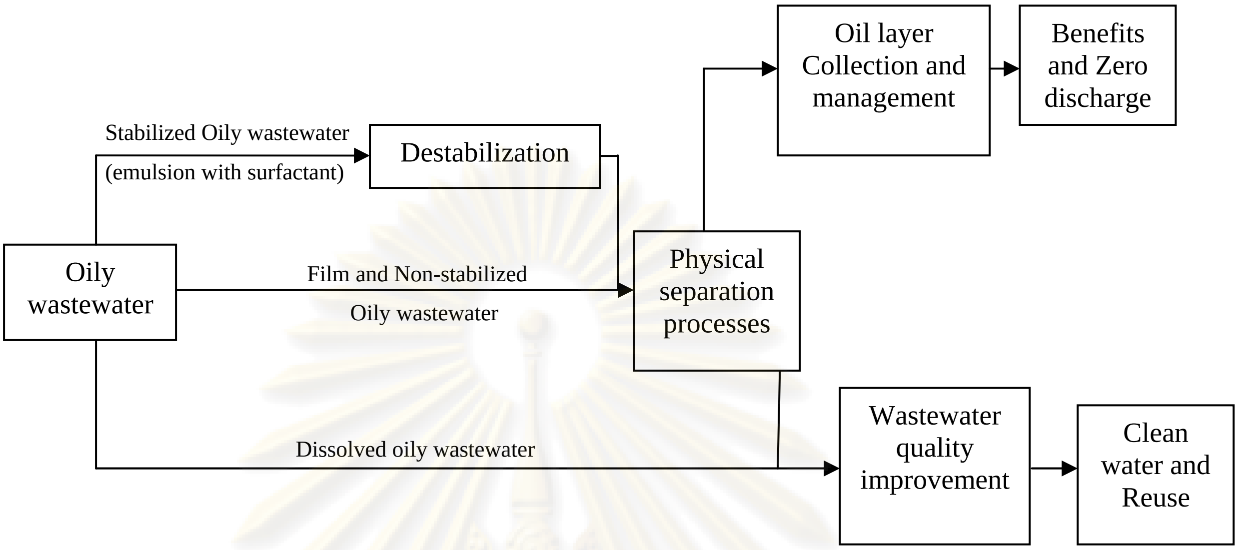


Figure 1.1 Treatment process for different type of oil

Up to now, a few studies have been focused on the relation between the bubble hydrodynamic conditions and the oily wastewater treatment efficiency by using Induce Air Flotation (IAF) process. Noted that the parameters, like bubble diameter, bubble rising velocity, bubble formation frequency and interfacial area, should be considered in order to study and compare the bubble hydrodynamic conditions obtained with different gas diffusers (Pisut *et al.*, 2005). Due to the oily wastewater from service station used as liquid phases under test in this study, it can be stated that these are the combination of different chemical agents (lubricant oil, surfactants and demulsifier dosages). Therefore, these complex liquid phases can affect the bubble hydrodynamic parameters, the interaction between oil droplet and bubble and thus efficiency in the flotation process. Therefore, in this research, the local method for determining the bubble hydrodynamic parameters were applied. Moreover, this study can be probably applied to consider the relation of the interfacial area obtained with generated bubbles and also their chemical mixing capacity onto the treatment efficiencies obtained with chemical processes, Induce Air Flotation (IAF) process and also the IAF process, together with the chemical process called Modified Induced Air Flotation (MIAF).

1.2 Objective

The main objective of this work is to study the treatment mechanism of lubricant oily emulsion containing with different types of surfactants by using the Induce Air Flotation (IAF) process, together with the coagulation process called Modified Induced Air Flotation (MIAF). The specific objectives can be expressed as follows:

1. To study the treatment efficiency of lubricant oily emulsion wastewater containing with anionic (SDS), cationic (CTAB), and nonionic (Tween20) surfactants by using the Modified Induced Air Flotation process (MIAF) compared with the IAF and coagulation processes.
2. To study the bubble hydrodynamic parameters and analyze the role of bubbles generated and chemical dosage in terms of oil droplet collision/attachment and of chemical mixing condition obtained with IAF and MIAF process.
3. To propose the simple model for predicting the overall treatment efficiency from the reaction rate constant (log k) and reaction order (n) and from relationship between bubble hydrodynamic parameters.

1.3 Hypothesis

1. There are the differences in removal efficiencies of the lubricant oily emulsion containing with different types of surfactants
2. Treatment efficiency of the lubricant oil emulsion containing surfactant will be depended on the choosing of treatment methods and also can be increased when used combined processes.

1.4 Scopes of the study

The research is divided into 6 steps including:

First step: Synthesis of oil in water emulsion with three type of surfactants

The aim of this step is to create the stabilized oil droplets as presented in term of oil-in-water emulsion with different types of surfactants (anionic, cationic and non ionic). Moreover, the different parameters will be investigated, for example, surface tension and the Critical Micelle Concentration (CMC) of synthesis oily wastewater.

Second step: Treatment of oily emulsion wastewater by coagulation process

The objective of this step is study (in jar test) to determine the optimal pH and concentration of Aluminium sulfate ($Al_2(SO_4)_3$) in order to treatment the lubricant oil emulsion containing with anionic, cationic and non ionic surfactants.

Third step: Treatment of oily emulsion wastewater by IAF process

The objective of this step is to study (in column flotation) for determining the optimal air flow rate and aeration time in order to treatment the lubricant oil emulsion containing with anionic, cationic and non ionic surfactants.

Forth step: treatment of oily emulsion wastewater by MIAF process

The objective of this step is to study (in column flotation) for determining the optimal air flow rate, aeration time and optimal concentration of alum in order to treatment the lubricant oil emulsion containing with anionic, cationic and non ionic surfactants.

Fifth step: Determination of bubble hydrodynamic parameters

In order to provide a better understanding on the obtained treatment efficiency, the bubble hydrodynamic parameters will be determined in this part. The bubble sizes (D_B) and their rising velocities (U_B), the bubble formation frequencies (f_B) will be experimentally analyzed. Moreover, the interfacial areas (a) will be calculated from the previous parameters

Six step: Proposition of the simple model for predicting the overall treatment efficiency.

CHAPTER II

THEORETICAL BACKGROUND AND LETERATURE REVIEW

2.1 Type of oily wastes

Oily waste materials are often measured in terms of their hexane solubility, for purposes of pollution evaluation (Supawimol, 2002). Types of oily wastes are as follows:

- Light hydrocarbons includes light fuels such as gasoline, kerosene and jet fuel, and miscellaneous solvents used for industrial processing, degreasing or cleaning purposes. The presence of waste light hydrocarbons may make the removal of other heavier oily waste more difficult.
- Heavy hydrocarbons, fuels and tars includes the crude oils, diesel oils, residual oils, slop oil, asphalt and road tar.
- Lubricants and Cutting fluids-oil lubricants generally fall into two classes;
  - Non-emulsifiable oils such as lubricating oils, cutting oils and drawing compounds.
  - Emulsifiable oils may contain fat, soap, or various other additives.
- Fat and fatty oils, these materials originate primarily from processing of foods and natural product. Fats result from plant products. Quantities of these oils result from processing soybeans, cottonseed, linseed and corn.

2.2 Sources of Oily Wastes by lubricant oil

2.2.1 Metal industry

In the metal industry, the two major sources of oily wastes are steel manufacture and metalworking. Oily wastes include both emulsified and non-emulsified or floating oils. In steel manufacture, steel ingots are rolled into desired shapes in either hot or cold rolling mills. Oily wastes from hot rolling mills contain primarily lubricating and hydraulic pressure fluids. In cold strip rolling, however, the steel ingot is usually oiled prior to rolling, to lubricate and to reduce rusting. Additional oil-water emulsions are sprayed during rolling to act as coolants.

Metalworking produces shaper metal pieces such pistons and other machine parts. Oily wastewater from metal working processes containing grinding oils, cutting oils, and lubrication fluids (Supawimol, 2002).

2.2.2 Pollutants from Gas station

Activities at gas station are not only fueling but also car washing, cafeteria, lubricant changing, floor cleaning, etc. Wastewater from car washing operations contains suspended solid, emulsifier and oily wastewater. Oily wastewater, not only presents in free oil form, but also in oil-in-water emulsion formed by admixture of automotive oil such as lubricant oil with emulsifier and wash water (Panpanit *et al.*,2001).

- **Pollutant in car wash wastewater**

Wastewater from gas station is generated from various activities. Generally, high volume of wastewater are generated from car washing operation. Mixed lubricating oils and emulsifier (various types of surfactants) are always found in car wash wastewater. Thus, car wash wastewater is considered as hazardous industrial wastewater because it contains petroleum hydrocarbons, plasticizers, and washing agents. The example of car wash wastewater characteristics are in Table 2.1

  - **Organic pollutant**

    Source of organic pollutant in gas station are cleaning chemical, fuel and vehicle exhaust, vehicle fluids, and oil and grease. Oil and grease or hydrocarbon concentrations in runoff depend on land use. It can present in wastewater many different forms including dissolved oil, free oil, and emulsified oil. These contaminants, which come from used lubricant oil, fuel oil and vehicle exhaust, contain many different compounds. Lubricant oil contains varieties of organic matter such as additive chemical, aliphatic and aromatic compounds (Ratpakdi, 2005).

- **Inorganic pollutant**

Heavy metals are mostly released by motor vehicles. Automobile fluid, deterioration parts and vehicle exhaust are the sources of heavy metals found in gas station runoff. Lubricant oil contains copper, lead, nickel, and zinc, especially high levels of zinc. Moreover, for nutrients, sources of nutrients in gas station runoff come from phosphates containing soap or detergent which are used in car washing and others cleaning processes.

Table 2.1 Wastewater characteristic of car washing and other facilities in gas stations (Khondee, 2007)

Parameter	Car washing (Thailand)	Commercial parking lot (USA)	Radiator repair shop (USA)	Gas station (Thailand)
	Mean(SD)	Mean(SD)	Pretreated	Mean(SD)
pH	5.67 (1.13)	6.4 (0.4)	-	7.78 (0.18)
BOD (mg/l)	229.50 (79.54)	-	192	87.10 (8.22)
COD (mg/l)	497.75 (174.55)	171.7 (205.0)	-	193.2(84.57)
DOC (mg/l)	-	40.1 (57.1)	-	-
TOC (mg/l)	-	-	-	-
Hydrocarbons (mg/l)	-	-	-	-
Oil & Grease (mg/l)	37.0 (16.82)	7.4 (10.3)	17	22.13 (7.23)
TSS (mg/l)	79.0 (19.97)	55.1 (71.6)	160	84.23 (59.06)
VSS (mg/l)	-	38.6 (60.5)	-	-
Total P (mg/l)	6.62 (0.98)	-	-	-
NO_3^-(as NO_3^- N)(mg/l)	-	1.0 (0.2)	-	-
Aluminium	-	2235	-	-
Cadmium	-	-	-	-
Chromium	-	-	-	-
Copper	-	103	192	-
Lead	-	45	287	-
Nickel	-	75	-	-
Zinc	-	2601	232	-

2.3 Categories of oily wastewater

Type of oil found in oily wastewater can include fats, lubricants, cutting fluids, heavy hydrocarbon such as tars, grease, crude oil, diesel oils; and light hydrocarbons such as kerosene, jet fuel, and gasoline. The oily impurities in the wastewater from refineries and other oil processing operation can be present in four groups, in accordance with its droplet size (Rachu, 2005).

- Free oil is oil in form of film on the surface of wastewater, or oil in form of big oil drops in the waste water, is usually more than 95% of oil droplet in the mixture of the water and the free oil is larger than 40 mm in size. It can rise to the surface of the water in which it is contained and is the most economically removed in an oil/water separator utilizing corrugated plates (Supawimol, 2002).
- Emulsion without surfactants is the free oil and water mixture to sewer turbulence will break up into very small droplets or particles ranging in size from 10 to 40 mm in size and which are more or less stable (Supawimol, 2002).
- Emulsion with surfactants is the wastewater that contains oil, water and surface-active agent, which may consists of only one surfactant or both surfactant and co-surfactant. Presence of these surface active substances cause decrease in interfacial tension between oil and water, thus make the oil disperse into very fine droplets, down to micron size. Their rising velocity is then very small. So this type of emulsion is stable, as it is called, and not prone to decant naturally (Rachu, 2005).
- Dissolved oil, all oil is soluble to certain extent, in general, if we consider oil of the same series:
  - The solubility increases as the molecular weight decreases. The volatility evolves, therefore, in the same direction and the lighter hydrocarbons are the most soluble and the most volatile;
  - The solubility increase with unsaturation.

Dissolved oil is not present in the form of discrete particle; therefore, it can not be removed from the flow stream with a classical oil/water separator (Vijay *et al*., 1995). Dissolved oil present in quantities sufficient to warrant removal, the use of activated carbon adsorption columns or biological treatment may both be considered.

2.4 Surfactant

Surface-active agents, or surfactants, are molecules which are able to modify the properties of an interface, e.g. liquid/air or liquid/liquid by lowering the surface or interfacial tension (Moosai and Dawe, 2003), molecules are soluble both in oil and water. They usually localize themselves and form a layer (generally, monomolecular layer) at the surfaces or interfaces. This phenomenon is called surface activity. Chemically, they always comprise of large polar functional groups. One end of the molecules that is soluble in oils is usually a long chain of aliphatic or aromatic or both forms of organic groups with 8 to 18 carbon atoms. Being a long chain, this hydrophobic part is usually called “tail” of the surfactants. Another end, which is water soluble or hydrophilic, is usually called “head” of the surfactant (Rachu, 2005). Thus the symbol of surface-active agents is usually drawn as a circle with long tail as shown in Figure 2.1

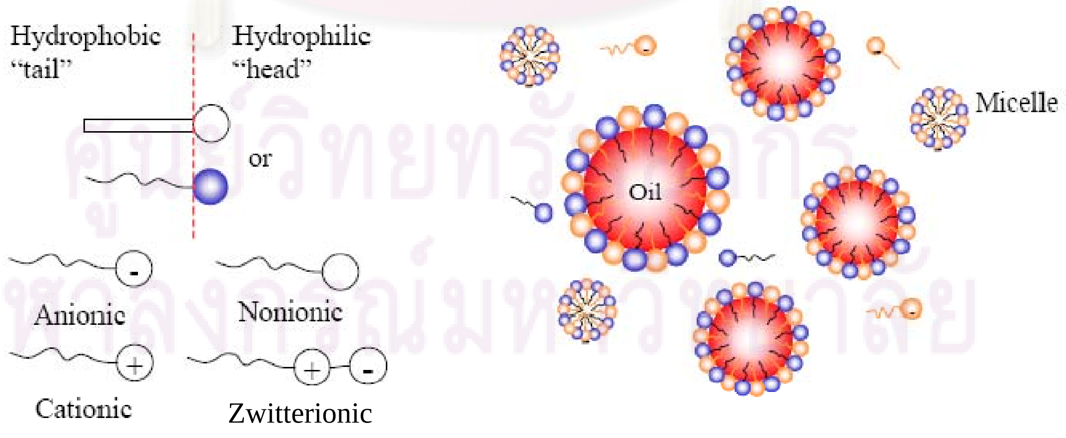


Figure 2.1 Symbols of surface active agent and its localization at oil/water interfaces (Rachu, 2005).

2.4.1 General classification of surfactant

A classification is simply based on the nature of the hydrophilic group. Four main classes can be distinguished and called anionic, cationic, nonionic and zwitterionic (Rachu, 2005).

- **Anionic surfactant**

The surfactant that the surface-active portion contains negative charge and tends to adsorb onto the positive charge hydrophilic surface. This type of surfactant is the most widely used in industrial application because of their low cost of manufacturer. Common anionic surfactants are:

  - **Soaps** are usually sodium or potassium salt, derived from fats and oils by saponification (hydrolysis with presence of alkaline agent) with sodium hydroxide.
  - **Sulfate surfactants** are salts of sulfated alcohol, such as dodecyl or lauryl alcohol. General formula of these surfactants is in the form of R-OSO3-M^+,where M^+ represent positive-charge ion, such as sodium or potassium.
  - **Sulfonate surfactants** are sulfonated compound, mainly derived from esters, amides and alkylbenzenes. An example of these surfactants is sodium alkylbenzene sulfonate. General formula is R-SO3-M^+.

- **Cationic surfactant**

The surfactant that the surface-active portion contains positive charge and tends to adsorb onto the negative charge hydrophilic surface. There are several researches that utilized this surfactant to do site remediation because of its unique property to be strongly absorbed onto most surfaces. The most common cationic surfactant is the quaternary ammonium compounds.

- **Nonionic surfactant**

The surfactant that the surface-active portion contains no charge and be able to adsorb onto either hydrophilic and hydrophobic surface and oriented toward the surface depending on the nature of surface. The most common nonionic surfactant is based on ethylene oxide or could be referred as ethoxylated surfactants.

- **Zwitterionic surfactant**

The surfactant that the surface active portion contains both positive and negative apparent without changing the charge of surface significantly.

2.4.2 Effect of surfactants presence in oily wastewater

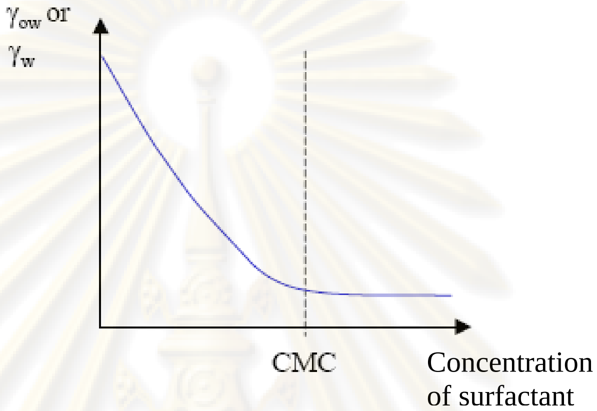


Figure 2.2 Diagram of the electrical double layer (Rachu, 2005).

Normally, surfactants lower the oil/water interfacial tension. Relation between interfacial tension and concentration of surfactant is as shown in Figure 2.2. From the graph, interfacial tension decreases rapidly at the beginning. Then, the rate of decrease lowers until the concentration of surfactant reached a certain value, called “Critical Micelle Concentration” (CMC). After that, the tension remains relatively constant. This can be explained by the formation of groups of surfactant molecules called “micelle” (Figure 2.1). These surfactants will no longer localize at the surface of droplets, so they have no effect on the tension (Rachu, 2005).

2.5 Oily wastewater treatment processes

For oily wastewater treatment processes, each process has its own characteristic or limitation so it can be used to separate some certain ranges of oil droplet. The treatment processes covered the entire range of the oily wastewater can be summarized as follow;

2.5.1 Physical treatment process

The physical treatment processes covered the entire range of the oily wastewater can be summarized as follow (Rachu, 2005);

- Decanting is an oil separation process that depends purely on Stoke's law. The oil droplets in wastewater will allow to decant (or rise) naturally to the surface of water. It is very simple and proven to be very good process for separation of free oil. However, in case of very small droplets, it may take too long time for the droplets to reach the surface or it may need so large tank to become economical.
- Skimmer is the device designed to remove oil film from the water surface.
- Coaleser is a modified Stoke's law-based separation process by increasing the size of oil droplet. Since rising velocity is proportional to square of droplet size, theoretically, coalescer can enhance oil separation efficiency more rapidly than other process that work on other parameters. Coalescer performance with stabilized emulsion is not so good since the droplets are very stable and unlikely to coalesce with each other.
- Hydrocyclone is a modified Stoke's law-based separation process by increasing the acceleration of the system. Hydrocyclone replaces gravity acceleration (g) with centrifugal acceleration, which can reach several hundreds times of g. Thus it is very compact separation process. It must also be noted that hydrocyclone is actually a concentrator. It can not separate water-free oil. Separated oil usually contains some water. Thus it need to be further treated by other process.
- Flotation is a modified Stoke's law-based separation process by decreasing density difference between oil and water. It can be obtained by addition of gas or air bubble to wastewater to form agglomerates with oil droplets. Since air or gas has low density the agglomerates, then has lower density than oil drops, resulting in higher rising velocity. Normally, flotation can be divided into Dissolved Air Flotation (DAF) and Induced Air Flotation (IAF).

2.5.2 Thermal processes

Thermal processes is the separation process based on thermodynamic properties of oil/water mixture that involve changing of phases of the materials to be separated. Since the processes involve phase changing, they inevitably consume high energy.

This is the reason why they are scarcely used for general wastewater treatment. However, it may become economical alternative if the product from the treatment can be recycled or relative easier for ultimate disposal.

2.5.3 Chemical process

For oily wastewater treatment is mainly destabilization process for destabilizing of stable emulsion. It consists of 2 main mechanisms, i.e. destabilization of oil droplets and coalescence or flocculation of destabilized oils. This process is necessary when the wastewater to be treated contains stable or stabilized emulsion.

2.5.4 Finishing processes

To meet the effluent standards, effluent from aforementioned processes may need further treatment before discharge to receiving water body. The most widely used processes for finishing propose are biological treatment and adsorption (by activated carbons).

2.6 Chemical treatment processes

Chemical treatment in oil/water separation process, normally refer to chemical destabilization, coagulation and flocculation (Shamrani *et al*., 2002). The process, then, does not “destroy” oil. Its major role is to transform the oil into the form that facilitates oil/water separation (Rachu, 2005). Normally, chemical treatment will be required when oil or hydrocarbon is present in the form of very stable emulsion, which will not be naturally coalesced. So it is very difficult to separate them by mean of physical process alone (Rachu, 2005; Shamrani *et al*., 2002).

Coagulation and flocculation method is widely used in water and wastewater treatments. In conventional wastewater treatment systems, coagulants such as aluminum chloride, ferrous sulphate, aluminum sulphate, ferric chloride and hydrated lime are the most widely used: this is because of their effectiveness, cheap, easy to handle and availability (Ahmad *et al*., 2006).

2.6.1 Important properties of stable emulsion

- **Thermodynamic stability**

Normally, interfacial tension of oil is positive. To increase the stability of oil droplets, the interfacial tension should be lowered to increase the area, thus decrease the diameter of the droplets. Addition of surfactant can lower the interfacial tension by its localization at the droplet surface. The surfactant will try to stretch or increase the surface of oil droplets as much as possible in order to locate itself at the surfaces. It results in virtual force (p) that tries to stretch the surface, countering to the interfacial tension ($\gamma_{o/w}$) that tries to contract the surface, as shown in Figure 2.3.

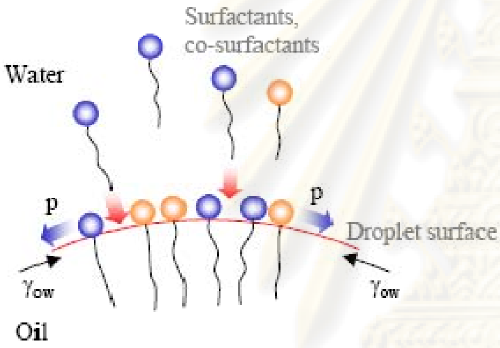


Figure 2.3 Interfacial of oil and water with the presence of surfactants (Rachu,2005)

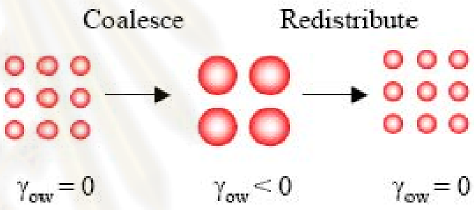


Figure 2.4 Coalescence and redistribution of droplets in thermodynamically stabilized emulsion (Rachu, 2005)

If the surfactant concentration is high enough, it will lower the tension until it becomes zero. At thermodynamic equilibrium condition, the system of these small droplets has zero energy. When they coalesce, the sum of surface area will decrease so the equilibrium is disturbed. The energy, thus the tension, will become negative. So they will spontaneous redistribute to their original small diameters to maintain the equilibrium, as shown in Figure 2.4

- **Dynamic stability**

This stability comes from 2 equally important factors or resistance, i.e. electrical and mechanical resistances or barriers.

1. Electrical barrier

Electrical characteristic of charged particles can be explained by the double layer theory, as shown in Figure 2.5. The original charge of oil droplet is normally negative, acquired by negative ion adsorption. From its electrical charge, the oil droplet can attract ions of the opposite charges (counter ions) to surround it. However, the counter ions, in this case, are positively charged ions, which are usually surrounded by molecule of water. So they can come close to the oil droplet only at a certain distance called "Stern layer thickness" (Ω). The stern layer is the inner layer of the double layer, according to the theories. Other counter ions that locate outside the stern layer will more dense near the surface and then will thin out until their concentration are equal to that in bulk liquids. This outer layer is called the diffused layer. Outside the diffuse layer, the effect from droplet charge is negligible.

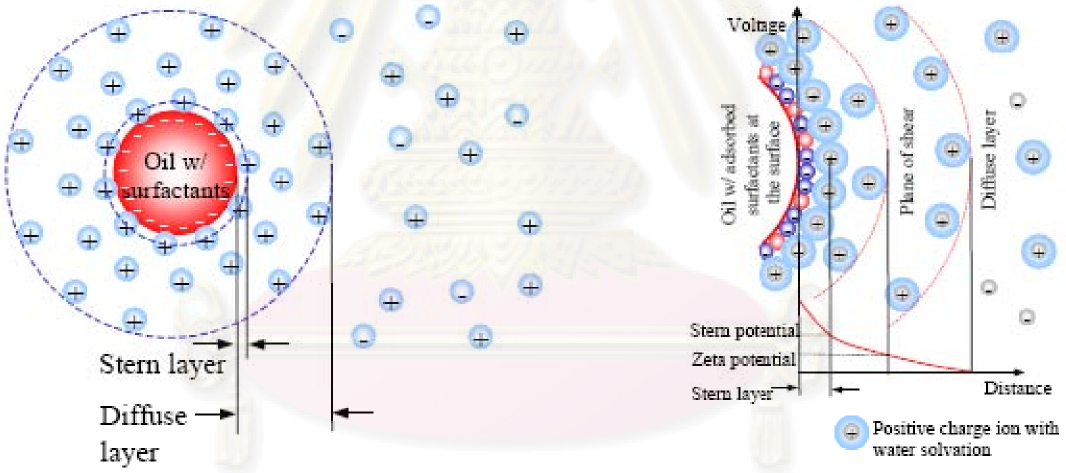


Figure 2.5 Diagram of the electrical double layer (Rachu, 2005).

Electric force from the charge of the droplet can be measured by its movement when it is placed in electrical field. For the negatively charged particle, it will move toward anode. The movement can be transformed to the value of electrical voltage. This voltage is called Zeta potential (Z). The higher value, the greater its force to repulse co-ions. So the droplets can not come close to each other.

2. Dynamic barriers

Due to the dynamic barriers, some systems of low Z are also found very stable. This can be explained the presence of dynamic barriers. The film of surfactants on the surface of droplets is relatively rigid. Even the droplets collide; the film will not rapture and can prevent coalescence. To increase the rigidity of film, Non-ionic co-surfactants are added so their molecules can locate tightly among charged surfactants, resulting in a rigid film. This is the reason why the co-surfactants or multi-surfactants are used in production of cutting oil emulsion.

2.6.2 Destabilization of stabilized emulsion

To destabilize the stabilized emulsion, the properties of the stable emulsion must be eliminated or minimize by applying various methods:

- Increase of interfacial tension to eliminate thermodynamic stability
- Minimize or elimination of surfactant films around the droplets
- Reduction of charge of the droplets to eliminate or minimize electrical barriers. When the droplets can come close to each other at some certain distance. Attractive force between molecules (called “Van Der Waal force”) overcomes repulsive force from electrical charges. So the net force will be attractive (Figure 2.6) and the droplets move toward each other and have a chance to coalesce.

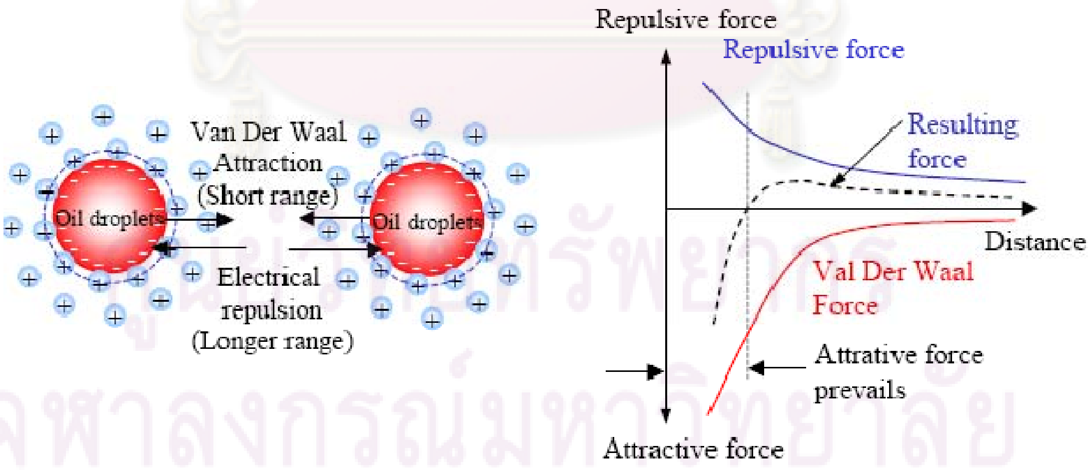


Figure 2.6 Force diagrams of oil droplets and relation of repulsive, attractive and resulting force with the distance between oil droplets (Rachu, 2005).

2.6.3 Destabilization (Coagulation) processes

- **Types of Destabilization methods**

In order to destabilize the stable oily wastewater, different types of destabilization processes can be applied as follows:

- **Reduction of diffuse layer thickness**

When counter-ions are added into the wastewater, these ions will be attracted by the droplet charges. Thus they will surround more tightly near the droplets and reduce the diffused layer thickness. This effect results in reduction of Zeta potential. So the droplets can come closer to each other and have a chance to coalesce. For general oily wastewater and cutting oil wastewater, droplets have negative charges. So, the counter ions in these cases are positive charges, e.g. Na^+, H^+ in the forms of NaCl or H_2SO_4, etc. The counter-ions can be added until the system reaches iso-electric condition (potential = 0). However, this mechanism cannot reverse the droplet charges, no matter how many ions are added.

- **Sweep coagulation**

Some metal salts can form complexes with other ions in the water, such as hydroxide. These complexes can trap the oil droplets, thus the droplets can be separated from the emulsion. These types of chemicals are normally multivalent metal salts, such as alum.

- **Adsorption and charge neutralization**

Addition of surfactants that have the opposite charges to those used in the emulsion may result in destabilization of oil droplets by adsorption of the new surfactants and neutralization of the existing charges. But it must be noted that, if overdose, this mechanism will cause reversal and re-stabilization of emulsion.

- **Bridging**

There are several commercial chemical products that can be used to destabilize the emulsion. From their molecule structure and properties, they may trap the oil droplets by their bridging properties or adsorb the oil droplets and from scum or sludge.

- **Precipitation of surfactants**

Since emulsion stability is based on presence of surfactants, precipitation of surfactants can certainly destabilize the emulsion. Addition of some chemicals can react with the surfactants, resulting in complexes of no surfactant property. Bivalent or multivalent salts are used to precipitate the surfactants, such as $CaCl_2$, $MgCl_2$, $MgSO_4$, Alum (aluminium sulfate) or ferric chloride. Generally, the higher the valence, the better the efficiency to precipitate the surfactants and the smaller dosage of the salts required. However, precipitation efficiency also depends on the types of salts and surfactants used in the emulsion, which should be verified by jar test. Efficient salt for one surfactant may ineffective for other types of surfactants.

Note that these different methods of destabilization can act individually or interparticles with one another, but all require adding counter ions or charges to coagulate. The greater ionic strength of the counter ions, the greater the destabilization effectiveness.

- **Chemicals (coagulant) used for the destabilization processes**

Chemicals generally used to achive the destabilization mechanisms described above include:

- **Monovalent electrolytes**

Examples of this type of salt are NaCl and H_2SO_4. Main destabilization mechanism is reduction of diffuse layer. Thus required dosage is quite high in order to provide sufficient concentration of positive ions in the entire emulsion to destabilize the droplets. For certain types of surfactants, e.g. soaps, acid can cause destabilization be neutralization of saponification process that gives rise to the soaps. In this case, required concentration is much lower.

- **Bivalent electrolytes**

Examples of this type of chemicals are $CaCl_2$, $MgSO_4$ and $MgCl_2$. Main destabilization mechanism is precipitation of surfactants. Free surfactants in water will react with Ca or Mg ions and form complexes. Equilibrium between adsorbed, ionized surfactants on the droplet surfaces and free surfactants is shifted. So ionized surfactants will reverse into free surfactants thus, reduce the stability of droplets. This effect is practically governed by solubility product of the surfactants. Required dosage in this case is lower than that of monovalent ones.

- **Multivalent electrolytes**

Examples of this type of chemical are ferric chloride ($FeCl_3$) and alum. They are generally more effective in destabilization than the previous two chemicals. But it may not be used with some surfactants, such as certain types of soaps. Main destabilization mechanisms are combination between precipitation of surfactants as well as sweep coagulation. So the actual dosage is lower than that calculated from solubility product alone and usually lowest among the first three electrolytes

- **Surfactants of opposite charge**

Examples of cationic surfactants that may be used for emulsion destabilization are N-cetylpyridinium chloride and salts of quaternary ammonium hydroxide. Main destabilization mechanism is adsorption and charge neutralization. Overdose must be avoided to prevent charge reversal and re-stabilization.

- **Rapid Mixing mechanism for the destabilization processes**

Rapid mixing is designed to provide complete mixing between wastewater and destabilization chemicals. There are 2 main types of mixing methods, i.e. hydraulic (weir, flume, static mixer) and mechanical (pumping, mechanical mixer). Main design criterion is described in the form of velocity gradient (G) as shown in equation 2.1 (Raynolds and Richards, 1996).

$$G = \left(\frac{P}{\mu . V}\right)^{0.5} \qquad (2.1)$$

Where G = Velocity gradient (normally in second $^{-1}$)
μ = Dynamic viscosity of wastewater, normally same as water
P = Mixing power (normally in watt)
V = volume of the mixing tank

- **Study of the Destabilization (coagulation) processes (Jar test)**

There are several factors that affect coagulation. Some of the more critical factors include: pH, mixing affects, zeta potential, coagulant dosage, anions or cations in solution, and temperature (Alley, 2000). It is necessary to determine the ideal range for each of these factors, if chemical coagulation is to be used in treatment of the wastewater. The most commonly used method for coagulation control is the jar test which is used in order to determine:

  - Type of coagulant
  - Coagulant dosage, if a coagulant aid is required and the dosage of such an aid
  - Determination of the optimum pH
  - Determination of point of addition of pH adjustment chemicals and coagulant aids
  - Determination of the dilution of coagulant
  - Optimization of mixing energy and time for rapid mixing and slow mixing

In practice, the irrespective of what coagulant or coagulant aid are used, the optimum dose and pH are determined by jar test as follow:

  - rapidly mixing at 100 rpm the coagulant and the wastewater in a large beaker or jar for 1 minute
  - then slowly mixing at 30 rpm the solution for 30 minutes
  - then allowing the flocs to settle for 30 minutes
  - The beginning parameter and final parameter (COD, TSS, Turbidity, etc.) can be measured or visual inspection can be used to determine effectiveness.

2.6.4 Chemical reaction of Alum used in Coagulation processes

In Coagulation-Flocculation processes, alum used in water and wastewater treatment is $Al_2(SO_4)_3{\cdot}14H_2O$. (The ‘14’ actually varies from 13 to 18.) For brevity, this will simply be written without the water of hydration as $Al_2(SO_4)_3$. When alum is dissolved in water, it dissociates according to the following equation (Sincero, 2003).

$$Al_2(SO_4)_3 \longrightarrow 2Al^{3+} + 3SO_4^{2-} \qquad (2.2)$$

By rapid mixing, the ions must be rapidly dispersed throughout the tank in order to affect the complete coagulation process. Because the water molecule is polar, it attracts Al^{3+} forming a complex ion according to the following:

$$Al^{3+} + 6\,H_2O \longrightarrow Al(H_2O)_6^{3+} \qquad (2.3)$$

In fact, further reaction with the water molecule involves hydrolysis of the water molecule and exchanging of the resulting OH^- ion with the H_2O ligand inside the coordination sphere. Some of the hydrolysis products of the ligand exchange reaction are mononuclear, which means that only one central atom of aluminum is in the complex and some are polynuclear, which means that more than one central atom of aluminum exists in the complex. The complex ligand exchange reactions as following:

$$Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H^+ \qquad (2.4)$$

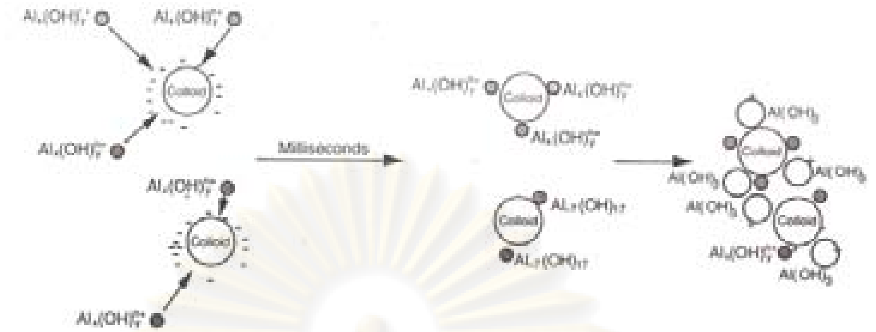
$$Al^{3+} + 2H_2O \rightleftharpoons Al(OH)_2^{+} + 2H^+ \qquad (2.5)$$

$$7Al^{3+} + 17H_2O \rightleftharpoons Al_7(OH)_{17}^{4+} + 17H^+ \qquad (2.6)$$

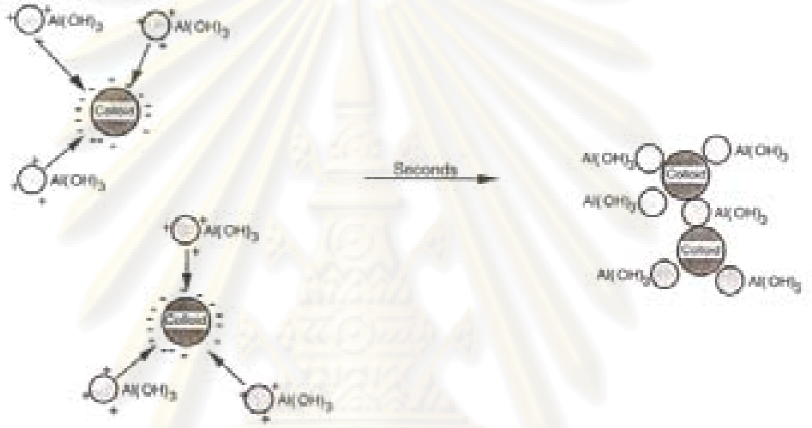
In coagulation treatment of water, conditions must be adjusted to allow maximum precipitation of the solid represented by $Al(OH)_{3(s)}$ following reaction:

$$Al^{3+} + 3H_2O \longrightarrow Al(OH)_{3(s)} + 3H^+ \qquad (2.7)$$

To allow for this maximum precipitation, the concentrations of the complex ions must be held to a minimum. Figure 2.7 depicts sweep floc coagulation in that the positively charged aluminum hydroxide reacts with the colloid to both bonds with it and also perhaps enmesh it.



(a) Ractant: soluble hydrolysis species and colloids Destabilized particles Floc



(b) Reactants: aluminum hydroxide sols and colloids Enmeshed colloids

Figure 2.7 Adsorption destabilization and sweep coagulation models of coagulation. (a) Adsorption destabilization. (b) Sweep floc coagulation (Hendricks, 2006).

In practice, the above reactions actually produce minimum oxyhydroxo complexes, or microflocs that crowd the colloids. These microflocs are positively charged, and they neutralize the charge in colloids and attract negatively charge colloids. Moreover, the optimum pH for alum coagulation is 5 to 7. This optimum is lower for soft, colored water and higher for hard waters. Alum naturally lower the pH of the water to which it is added, depending upon how much alkalinity is initially present. With the production of CO_2, the pH drops as CO_2 is converted to H_2CO_3, carbonic acid. An acid or lime may have to be added to maintain the optimum pH range. If the solution has high alkalinity, such $Ca(HCO_3)_2$, the pH adjustment probably will not be necessary, otherwise, lime or a base should be added to keep the pH around 6 (Alley, 2000).

2.6.5 Chemical reaction of ferric chloride used in Coagulation processes

The ferric chloride used in water and wastewater treatment is $FeCl_3.6H_2O$ or $FeCl_3$ anhydrous. For brevity, this will simply be written without the water of hydration as $FeCl_3$. When ferric chloride is dissolved in water, it dissociates according to the following equation (Sincero, 2003).

$$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^- \qquad (2.8)$$

As in any coagulation process, these ions must be rapidly dispersed throughout the tank in order to effect the complete coagulation process. The solid precipitate $Fe(OH)_{3(S)}$ and complexes are then formed. The reactions, together with the respective equilibrium constants at 25 ºC, are as follows:

$$Fe(OH)_{3(S)} \rightleftharpoons Fe^{3+} + 3OH^- \qquad (2.9)$$

$$Fe(OH)_{3(S)} \rightleftharpoons FeOH^{2+} + 2OH^- \qquad (2.10)$$

$$Fe(OH)_{3(S)} \rightleftharpoons Fe(OH)_2^+ + OH^- \qquad (2.11)$$

$$Fe(OH)_{3(S)} + OH^- \rightleftharpoons Fe(OH)_4^- \qquad (2.12)$$

$$2Fe(OH)_{3(S)} \rightleftharpoons Fe(OH)_2^{4+} + 4OH^- \qquad (2.13)$$

The complexes are $FeOH^{2+}$, $Fe(OH)_2^+$, $Fe(OH)_4^-$, and $Fe(OH)_2^{4+}$. Also note that the OH^- ion is a participant in these reactions. This means that the concentrations of each of these complex ions are determined by the pH of the solution.

In the application of the above equations in an actual coagulation treatment of water as in all applications of coagulations, conditions must be adjusted to allow maximum precipitation of the solid represented by $Fe(OH)_{3(S)}$ following reaction:

$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_{3(s)} + 3HCl \qquad (2.14)$$

To allow for this maximum precipitation, the concentrations of the complex ions must be held to a minimum.

2.6.6 Flocculation process

The purpose of flocculation is to bring particles together to form well settling flocculation. The rate of aggregation is dependent upon the rate of interparticle collisions. When particles aggregate, hydrodynamic shear forces in the water can cause the aggregation to break-up. Aggregation and break-up can occur simultaneously. Normally, the particle collision can occur through three different mechanisms consist of brownian diffusion, differential settling, and fluid shear (Alley, 2000).

- **Brownian diffusion or perikinetic flocculation** is the random motion of particles caused by contact with water molecules. The thermal energy of the water is the driving force behind this mechanism.
- **Differential settling** is based on particle settling caused by gravity. As particles settle, they collect other particles and agglomerate to further enhance settling and particle contact.
- **Fluid shear or orthokinetic flocculation** is particle contact caused by fluid movement in currents. The particle follows fluid flow and subsequently contacts other particles also following the flow of the fluid. The fluid motion can be described by the velocity gradient, which is the change in velocity over a corresponding distance, and is expressed in unit of inverse time (1/time).

Each of these mechanisms plays a role in flocculation. Brownian diffusion and differential settling are based on the thermal energy of the fluid and gravity/quiescent conditions, respectively. Because the thermal energy of water cannot be changed, Brownian diffusion cannot be designed, and because differential settling is not a significant factor in flocculation, completely quiescent conditions are not beneficial. Fluid shear can be induced, however. Fluid motion fields can be generated to produce orthokinetic flocculation.

2.7 Flotation process

Flotation is the separation process accomplished by the attachment of air bubbles to the solid or liquid particles to be removed. The particles with attached air bubbles then become buoyant and rise to the surface where they may be removed by skimmer blades. The elements of the flotation process are; (1) generation of air bubbles, (2) contact between the air bubbles and the particles to be removed, (3) flotation of particles by the buoyant force created, and (4) removal by skimming (Hendricks, 2006). Normally, The flotation process has been used extensively in the removal of stable oily emulsions or fine particles suspensions are Dissolved Air Flotation, DAF and Induced Air Flotation, IAF (Da Rosa and Rubio, 2005).

- **Dissolved Air Flotation (DAF)**

A stream of treated wastewater is saturated with air at elevated pressures up to 4-5 atm. Small bubbles are formed by a reduction in pressure of the water pre-saturated with air at pressures higher than atmospheric. The supersaturated water is forced trough needle valves or special orifices, and clouds of small bubbles, 30–70 µm in diameter, are produced just down-stream of the constriction (Da Rosa and Rubio, 2005). As the small air bubbles rise, they attach and adhere to the oil globules. The resulting bubble and oil complex form rises to the liquid surface due to differential gravity. Consequently, Free oil form is easily be skimmed off by skimmer (Panpanit, 2001).

- **Induce Air Flotation (IAF)**

The air could be induced from the atmosphere without the need to provide blowers or compressors (Jameson, 1999). Bubbles are mechanically formed by a combination of a high-speed mechanical agitator and an air injection system. The technology makes use of the centrifugal force developed. The gas, introduced at the top, and the liquid become fully intermingled and, after passing through a disperser outside the impeller, form a multitude of bubbles sizing from 700–1500 µm diameter. This method, well known in mineral processing, is utilized also in the petrochemical industry, for oil–water separation (Rubio *et al*, 2002).

2.7.1 Flotation of oily wastewater

Small bubbles and oil drops must be contacted, and then attached, for flotation to be occurred. As oil and air are both less dense than water, they will both rise if placed in water. The effectiveness of flotation of oily wastewater depends on the traditional gravity separation parameters within Stokes equation of liquid density difference, oil droplet size and distribution, oil-bubble contacts, oil-air bubble hydrodynamics, the interfacial properties between the oil, air and water, temperature, viscosity, and chemical content of the wastewater and the oil (Moosai and Dawe, 2003).

- **Stokes equation**

A major factor in flotation is the droplet rise velocity. Solution of the Navier Stokes equation for the terminal rise velocity, for rigid spheres under the relevant conditions for flotation gives Stokes equation (Rachu, 2005),

$$V = \frac{\Delta\rho . g . d_E^2}{18 . \mu_C} \tag{2.15}$$

Where V = Rising or settling velocity (based on density of the 2 phases)

$\Delta\rho$ = Difference between density of dispersed and continuous phases

d_E = Diameter of dispersed phase

μ_C = Dynamic viscosity of continuous phase

In case of oily wastewater, the dispersed phase is hydrocarbon or oil and the continuous phase is water. Because the density of hydrocarbons in wastewater is normally lower than water’s. It is prone to rise to surface of the water.

Flotation units make use of the size and density parameters in Stokes equation. Stokes equation states that the rise velocity is dependent on bubble/droplet diameter and density difference. Oil droplet size is therefore very important; small droplets the rise velocity was slow. Attaching bubble to oil reduces the oil density thereby increasing the density difference between the oil agglomerates and water and increases the agglomerate diameter thereby producing a faster rise rate. (Moosai and Dawe, 2003).

- **Oil droplet size**

The oil in oilfield wastewater is often mainly stabilized oil-in-water emulsion with the droplets in the range 3- 20 μm. Estimates using Stokes equation predict setting time that it will take around 50 s for a 70 µm, 600 s for 20 µm and 3000 s for 10 µm diameter oil drop for oily wastewater does not containing surfactant (Moosai and Dawe, 2003). And for oily wastewater containing surfactant with the droplets in the range 3- 5 µm required the setting time was up to 26 hour to reduce oil concentration less than 100 mg/l (Deng *et al*, 2005).

- **Oil-bubble contacts**

Bubbles are generally larger than oil drops, often being >50 µm. Due to this larger bubble size and the larger density difference between the air and water about 0.9 g/cm^3 compared to oil and water about 0.1 g/cm^3, bubbles will generally rise some 10-100 times faster compared to oil drops of similar. A range of bubbles is beneficial because the smaller bubbles can capture the smaller oil droplets and the larger ones the larger droplets. Naturally too, the longer the residence time of the gas bubbles in the flotation tanks, the greater the number of bubble-oil droplet collisions, the greater the quantity of the oil that ought to be removed (Moosai and Dawe, 2003).

- **Oil-gas bubble hydrodynamics**

The bubble rising velocities depend on the bubble size, increasing of bubble size make the velocity of bubbles increased, until the size of bubble more than 1 mm the velocity of bubbles remain constants (Jameson,1999) as shown in Figure 2.8

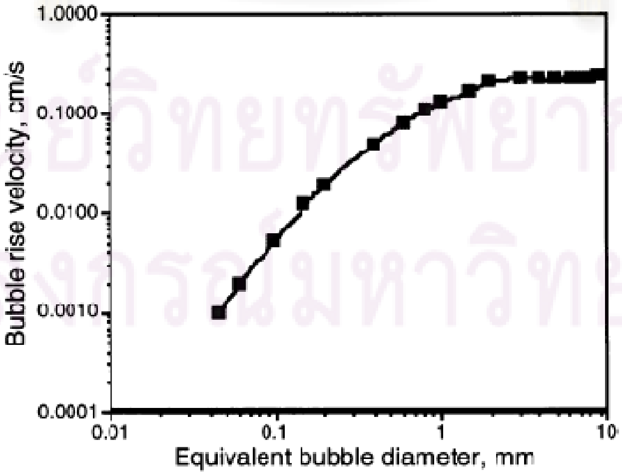


Figure 2.8 The bubble rising velocities in tap water as a function of the equivalent bubble diameter (Jameson, 1999).

The bubble and oil droplet must firstly come into close proximity so that their mutual trajectories lead to collide. The motion normally observed within the flotation chamber is erratic and has a complex flow pattern, with complicated flow streamlines of the oil droplets and gas bubbles. Note that many of the oil drops deflect past the gas bubbles rather than make the desired collision and attachment. The gas bubbles and oil droplets contact as shown in Figure 2.9, 2.10 and 2.11. It can be stated that this collision frequency is very difficult to estimate. Such calculations are made, even more difficult, because the bubbles grow as they ascend due to a reduction of hydrostatic pressure during bubble rise about 0.3% for a 100 µm rise and also because air can diffuse into the bubble from the water if the water is supersaturated with air.

Hydrodynamic theories of the collision between particles and bubbles have been developed, with that by Reay and Ratcliff (1975). They have showed that gas flotation is most effective when the oil droplets have diameters between 3 and 100 µm and that the efficiency is not greatly affected by bubble size. Whereas, this obtained performance is significantly affected by bubble number density. Moreover, large oil droplet and small bubble size has higher efficiency than small oil droplet and large bubble size because large oil droplet has larger collision area and small bubble size has longer residence times (Moosai and Dawe, 2003).

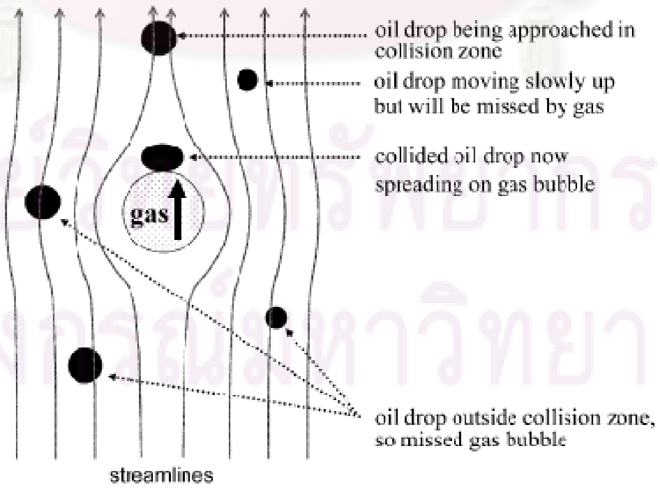


Figure 2.9 The oil/ gas bubble rise hydrodynamics (Moosai and Dawe, 2003).

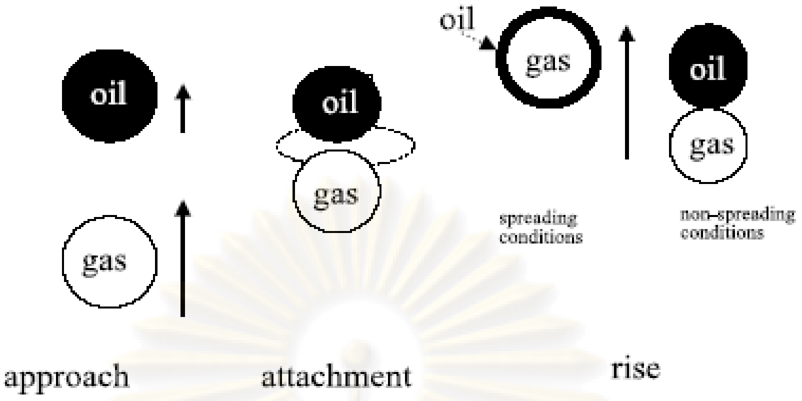


Figure 2.10 The attachment process (Grattoni *et al*., 2003).

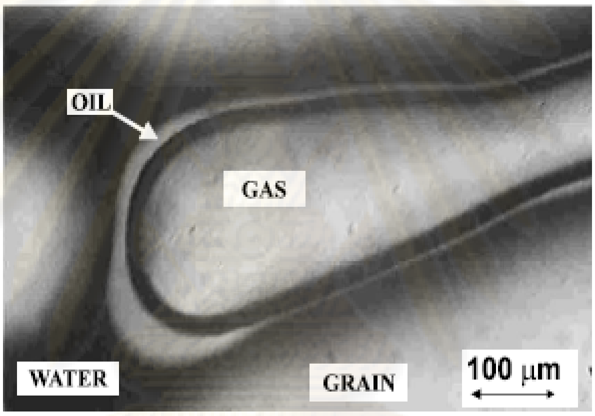


Figure 2.11 The gas bubbles and oil droplets contact (Grattoni *et al*., 2003).

2.7.2 Bubble hydrodynamic parameters

Due to the collision between oil droplet and bubble occurred in flotation process, bubble hydrodynamic parameters are thus the important factors that can affect the treatment efficiency obtained with flotation process. Therefore, this section will describe the determination of different bubble hydrodynamic parameters based on experimental and prediction methods. Note that these obtained values can be then applied to calculate finally the associated interfacial area.

- **Bubble diameter (D_B)**

The measurement of bubble diameter at any flow rate (Q_g) can be performed by Image analysis techniques. In this study, the 200-300 bubbles at any gas flow rates were captured and then analyzed by using the high speed camera and image analysis program, respectively. Note that, in this research, the average diameter (d_{avg}) will be calculated by equation (2.16).

$$d_{avg} = \frac{\sum_{i=1}^{N} d_i}{N} \tag{2.16}$$

Moreover, the bubble diameter can also be determined by using the mathematical model as shown in Table 2.2

Table 2.2 Mathematical model for determining the bubble diameters (Painmanakul and Jamnongwong, 2007)

No.	Correlation for predicting bubble size	Conditions
1	$d_B = \left(\frac{6 d_0 \sigma g_c}{g \Delta\rho}\right)^{1/3}$	$Q_{go} < \left[\frac{20(\sigma d_o g_c)^5}{(g\Delta\rho)^2 \rho_L^3}\right]^{1/6}$
2	$d_B = 0.0287 d_0^{1/2} \mathrm{Re}^{1/3}$	Re < 2100
3	$d_B = \left(\frac{72\rho_L}{\pi^2 g \Delta\rho}\right)^{1/5} Q_{go}^{0.4}$	
4	$d_B = 7.1\times10^{-4} \Delta P^{0.328}$	
5	$d_B = 15.73\times10^{-3} D_c^{0.32} \left(\frac{Q_g}{A_{or}}\right)^{0.16}$	
6	$d_B = 1.56\,\mathrm{Re}^{0.058} \left(\frac{d_0^2 \sigma}{\Delta\rho g}\right)^{1/4}$ $d_B = 0.32\,\mathrm{Re}^{0.425} \left(\frac{d_0^2 \sigma}{\Delta\rho g}\right)^{1/4}$	1 < Re < 10 10 < Re < 21000
7	$\frac{g \rho_L d_B^2}{\sigma} = 8.8 \left(\frac{u_G \mu_L}{\sigma}\right)^{-0.04} \left(\frac{\sigma^3 \rho_L}{g \mu_L^4}\right)^{-0.12} \left(\frac{\rho_L}{\rho_G}\right)^{0.22}$	

- **Bubble rising velocity (U_B)**

From Painmanakul *et al.*, 2005, the bubble rising velocities have been calculated by using the image analysis technique. In this study, the generated bubbles will be captured, in reactor, in order to analyze the rising distance between two frames (ΔD) at any acquisition time frame (t_{frame}). Thus, the bubble rising velocity can be calculated by equation (2.17)

$$U_B = \frac{\Delta D}{t_{frame}} \tag{2.17}$$

Where U_B = Bubble rising velocity, m/s
ΔD = Distance between two frames, m
t_{frame} = Acquisition time frame, s

In addition, the bubble rising velocity can be also obtained from the experimental results between bubble rising velocities and bubble diameters in clean and contaminated water (Grace and Wairegi, 1986). Moreover, the different correlation can also be applied to calculate the bubble rising velocities, as shown in Table 2.3

Table 2.3 Determination of bubble rising velocity (Painmanakul and Jamnongwong, 2007)

No.	Correlation for predicting bubble rising velocity	Conditions
1	$U_B = \frac{g\Delta\rho d_B^2}{12\mu_L}$	$\mathrm{Re} < 250, \frac{\mu_G}{\mu_L} = 0$
2	$U_B = \frac{g\Delta\rho d_B^2}{18\mu_L}$	$\mathrm{Re} < 250, \frac{\mu_G}{\mu_L} \to \infty$
3	$U_B = \frac{\mu_L}{\rho_L d_B}\left(J - 0.857\right)M_o^{-0.149}$	250 < Re<6000
4	$U_B = \left(\frac{2}{d_B r} + 0.5 d_B g\right)^{0.5}$	$0.2 \le d_B \le 8cm$
5	Experimental curve for predicting the bubble rising velocity	

- **Bubble formation frequency: f_B**

Bubble formation frequency is the number of bubble generated within one second. From Painmanakul *et al.*, 2005, it can be calculated from the number of orifice multiply with gas flow rate of each orifices, then divided by volume of bubble as shown in equation (2.18)

$$f_B = \frac{N_{OR} \times q}{V_B} \tag{2.18}$$

Where
f_B = Bubble formation frequency, s^{-1}
N_{OR} = Number of orifices
q = Gas flow rate through the orifice, m^3/s
V_B = Bubble volume, m^3

- **Interfacial area: a**

The interfacial area is defined as the ratio between the bubble surfaces (S_B) and the total volume in reactor (V_{Total}). The number of bubbles (N_B) is deduced from the terminal rising bubble velocities (U_B) and the bubble formation frequency (f_B) as:

$$N_B = f_B \times \frac{H_L}{U_B} \tag{2.19}$$

Then, the interfacial area can be calculated from equation (2.20)

$$a = N_B \times \frac{S_B}{V_{total}} = f_B \times \frac{H_L}{U_B} \times \frac{\pi D_B^2}{AH_L + N_B V_B} \tag{2.20}$$

Where
a = Interfacial area, m^{-1}
N_B = Number of bubbles generated
S_B = Total bubble surface, m^2
V_{total} = Total volume in reactor, m^3
f_B = Bubble formation frequency, s^{-1}
H_L = Liquid height, m
U_B = Bubble rising velocity, m/s
D_B = Bubble diameter, m
A = Cross-sectional area of reactor, m^2
V_B = Bubble volume, m^3

2.7.3 Factors affecting treatment efficiency obtained with Flotation process

Flotation is achieved by enabling oil drops to attach themselves to bubbles, so that the increased density differential makes the oil rise faster to the surface of the wastewater. Flotation is dependent on various factors as follows: (Moosai and Dawe, 2003):

- Hydrodynamic forces e.g. the movements of the bubbles, drops and continuous phase;
- Thermodynamic forces e.g. interfacial interactions;
- Physicochemical aspects e.g. chemical interactions affecting the interfacial interactions.

The efficiency of separation can be increased by coalescence of oil drops, which may be aided by surfactants and/or chemical demulsifiers. The attachment of oil drops to bubbles and the formation of a stable bubble drop aggregate are rate-controlling steps, the important step for flotation process can occur as follows:

- Demulsification of oily wastewater and increase of oil droplet size by coalescence;
- Approach of oil drops and bubbles;
- Drainage and rupture of the interstitial film;
- Attachment of gas bubbles to the oil , for successful flotation, spreading of oil drops onto bubbles. Clearly during this short period , the surface forces that give attachment and the drainage of the liquid film must be complete;
- Rise of the coalesced phases to the surface for it to be skimmed off.

2.7.4 Modified Induce Air Flotation (MIAF)

Modified Induce Air Flotation (MIAF) is the process which combines between the de-emulsification (addition of chemicals that destroy the protective action of the emulsifying agent) and flotation in order to improve efficiency of oily wastewater treatment. Normally, the oil droplets presences in wastewater are usually very small (below 10 µm in diameter) and often locate within the colloidal range. Due to the electrostatic repulsion forces which protected from spontaneous coalescence into larger ones, it is very difficult to separate by using the simple gravity separation (decantation or Floatation) (Zouboulis and Avranas, 2000). In order to augment the mean oil droplet size and thus increase the rate of collection by the air bubbles, the destabilized agents (coagulant) are necessary to maximize the rate of flotation or minimize the zeta potential of the colloid system (Al-Shamrani *et al.*, 2002 and Jameson, 1999). The combined separation process includes two steps:

1. The first step is the destabilization (demulsification) and flocculation processes. The chemical agents will be added to the oily wastewater to cause the demulsifying and flocculating oil droplets. Note that this increases the size of oil droplet flocs and also forms the stable hydrophobic droplets.
2. The second step is separation by flotation process. In the column, micro-bubbles and oil droplet flocs will collide and then attach to each other, in order to form the air-floc particles agglomeration. Then these air-floc particles will be raised to the surface of the liquid, driven by their lower density. Therefore, the oil droplets can be separated from the wastewater.

Note that the optimal operating condition concerning to chemical dosage and gas flow rate are important to reach the collision/attachment mechanism between oil droplet and generated bubble, thus to obtain the highest treatment efficiency. Meyssami and Kasaeian (2005) have studied on the destabilization of olive oil wastewater by using IAF with chitosan. From Figure 2.12, the results have been shown that the increasing aeration rate, the air-floc particles are broken and then oil droplet start resuspending in the wastewater. Conversely, at higher chitosan concentration, higher aeration rates could be used. Due to this study, the optimum aeration rate of 3 l/min was required for the chitosan concentration of 100 gm/l. Moreover, the aeration time of 45 s and pH 6 correspond to the reduction of more than 90% of the initial concentration.

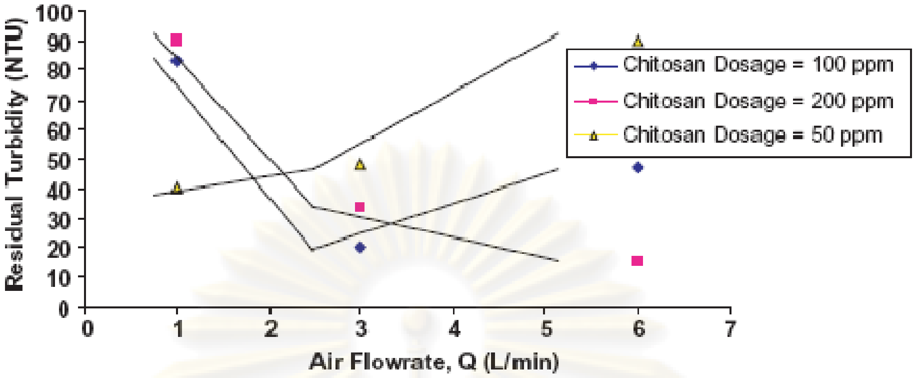


Figure 2.12 Effect of chitosan concentration and air flow rate on residual turbidity of olive oil/water emulsions (Meyssami and Kasaeian, 2005).

2.8 Literature reviews

Deng *et al*. (2005) have studied on the destabilization of oil droplets in produced water from ASP flooding: difficult to treat due to large quantities of residual chemicals (alkali, surfactant and polymer). Surfactant was mainly the responsible for stabling of oil droplets, decreasing oil–water interfacial tension and also zeta potential on the surface of the oil droplets. The results have showed that anionic and nonionic polyacrylamide, used in this work, provide the deprived oil–water separation and also increase the final oil concentration in the wastewater. However, PAC and cationic polyacrylamide were found to be very effective in the oil–water separation. Due to the initial oil concentration of 2000 mg/l, it can be found that PAC dosage of 600 mg/L, and cationic polyacrylamide dosage of 400 mg/L can reduce the oil concentrations after 4 hours operation time to 97 and 95 mg/L, respectively.

Al-Shamrani *et al*. (2002) have studied on the destabilization of oil–water emulsions containing with nonionic surfactant (Span 20). They found that, by using aluminium sulphate and ferric sulphate, the treatment efficiencies up to 99.3% and 99.94% can be obtained at pH 8 and pH 7, respectively. Moreover, the rapid mixing times for 120 s and flocculation times ranging from 15 to 20 min should be applied for DAF separation process.

Da Rosa and Rubio (2004) have reviewed and also described the FF (flocculation–flotation) processes which are developed for the separation of aerated polymeric flocs. This study has presented that the remove of emulsified oil and solids from water were more than 90% removal efficiencies. Moreover, the colloidal suspensions [$Fe(OH)_3$] from water can facilitate the overall separation. The polymer flocs obtained in this study were well structured, big size with elongated (string like) format. The FF appears to have some advantages, for example, an adequate turbulence, low area required, absence of mobile parts, simple design, and low mechanical and electrical energy required.

Zouboulis and Avranas (2000) have studied on the treatment of oil-in-water emulsions containing nonionic surfactant (Tween 80) by combining coagulation and Dissolved Air Flotation (DAF) processes. The results have shown that the use of polyelectrolytes (organic flocculants of cationic or anionic type) was not able to effectively treat these chosen stabilized emulsions. While the addition of ferric chloride and the subsequent application of Dissolved Air Flotation was found very efficient. The optimum experimental conditions can be summarized at recycle ratio 30%, pH 6, Fe^{3+} 100 mg/l and sodium oleate 50 mg/1. Due to this condition, more than 95% of the emulsified oil was effectively separated from the initial concentration of 500 mg/1.

Meyssami and Kasaeian (2005) have studied on the using of the combination of the coagulation and Induce Air Flotation (IAF) process in the treatment of olive oil wastewater. The studies have found that, in the jar experiments, chitosan and alum were the most effective coagulating agents. At pH 6, the chitosan and alum used together at concentrations of 15 and 25 ppm, respectively, can provide the lowest turbidity values. In IAF experiments, the chitosan concentration of 100 ppm, aeration rate of 3 l/min, aeration time of 45 s, temperature of 20 ºC and pH 6 can produced highest treatment efficiency. Moreover, the 95% COD values measured were reduced.

Chooklin (2004) has studied on the removal of stabilized oil in wastewater emulsion by induce air flotation. They found that the optimum condition for soluble cutting oil removal depended on types of surfactant and a quantity of electrolyte, such as 1 CMC

Tween 80 and 160 mg/l $Al_2(SO_4)_3$, 0.25 CMC CTAB and 480 mg/l $Al_2(SO_4)_3$, 0.25 CMC SDS and 280 mg/l $Al_2(SO_4)_3$. Moreover, an appropriate pH was at 7, exception in case of using SDS was at pH 4. The higher oil removal was obtained when employing 8 ml/sec in air flow rate, 615-688 µm in air bubble size and 20 minutes in flotation time. Aluminium cation can effectively destabilize the wastewater emulsion and thus more than 99 % of stabilized soluble cutting oil emulsion removed.

CHAPTER III

METHODOLOGY

3.1 Research overview

The research is divided into 6 steps including: synthesis of oil in water emulsion with three type of surfactant, treatment of synthetic oily emulsion wastewater by coagulation process (jar test), by Induced Air Flotation (IAF) and by Modified Induced Air Flotation (MIAF), determination of bubble hydrodynamic parameters, and proposition of the simple model for predicting the overall treatment efficiency from the reaction rate constant (log k) and reaction order (n) and from relationship between bubble hydrodynamic parameters. Therefore, the research flowchart can be illustrated in Figure 3.1

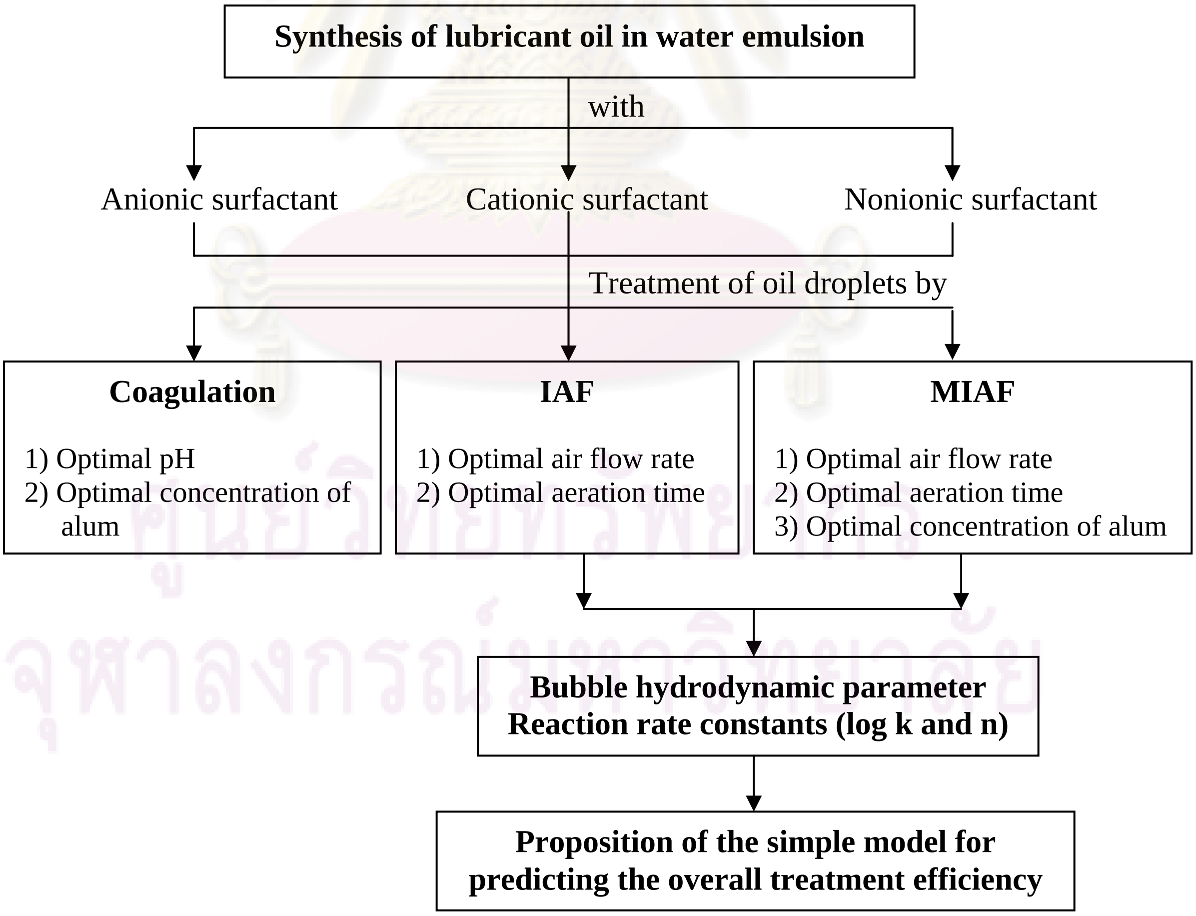


Figure 3.1 Flowchart of the research

3.2 Experimental Set-up

3.2.1 Chemical agents used in this study

1. Sodium Hydroxide ($NaOH$) was purchased from J.T. Baker Chemical Co.
2. Alum ($Al_2(SO_4)_3 .18H_2O$) was purchased from Ajax Finechem Ptl Ltd.
3. Sodium laurylsulfate (SDS), anionic surfactant was purchased from Carlo ERBA Chemical Co.
4. Tween 20, nonionic surfactant was purchased from Ajax Finechem Ptl Ltd.
5. Lauryl dimethyl benzyl ammonium bromine (CTAB), cationic surfactant was purchased from Asia Pacific Specialty Chemicals Limited.
6. Potassium Dichromate Digestion ($K_2Cr_2O_7$) was purchased from Ajax Finechem Ptl Ltd.
7. Ferrous Ammonium Sulfate ($Fe(NH_4)_2(SO_4)_26H_2O$) was purchased from Ajax Finechem Ptl Ltd.
8. Sulfuric acid (H_2SO_4) was purchased from Volchem Chemical Co.
9. Silver sulfate (Ag_2SO_4) was purchased from Merck Chemical Co.
10. 1-10 phenantroline was purchased from Ajax Finechem Ptl Ltd.
11. Ferrous Sulfate ($FeSO_4{\cdot}7H_2O$) was purchased from Ajax Finechem Ptl Ltd.
12. Lubricant oil, PTT V-120 manufactured by Petroleum Authority of Thailand (PTT).

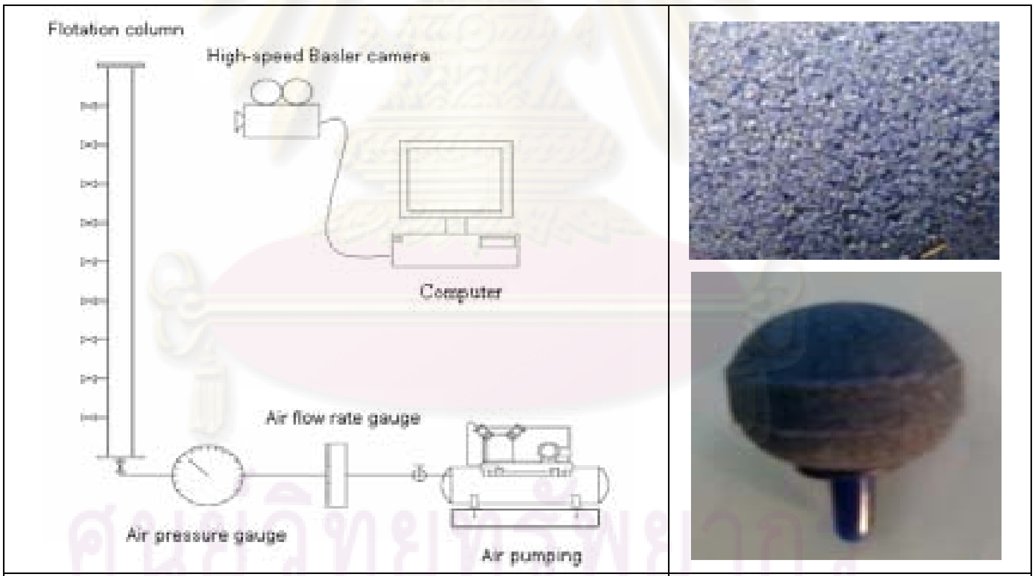
3.2.2 Equipments

1. Agitator
2. Tensiometer K10T, Kruss, Germany.
3. pH meter CG 840, Scientific Promotion, Thailand.
4. Motor stirrer, IKA, Becthai, Thailand.
5. Jar test, JR 6 A Brand, M-LAB, Thailand.
6. Air Pump, Puma, Thailand.
7. Optical Microscope, BX50, Olympus
8. Flow monitor, TS11500, SIKA, Switzerland.
9. Electronic manometer, Nuova Fima

10. Equipment set of COD test
    - Tube size 16 x 150 mm
    - Hot air oven 600, Memmert, Germany.
    - Volumetric flask
    - Cylinder
    - Pipet
11. Bubble column with 0.05 m. in diameter and 2 m. in height
12. Rigid Orifice
13. Basler camera (high speed camera (100 images/s))

3.2.3 Construction of column flotation system

The schematic diagram of wastewater flow through the column flotation system was shown in Figure 3.2



(a) (b)

Figure 3.2 The schematic diagram of experimental floatation system

The flotation process, used in this study, consisting of: Air compressor, Air flow meter, Electronic manometer, Rigid orifice air diffuser (Figure 3.2 (b)), Flotation column with 0.05 m. in diameter and 2 m in height (loading with oily waste water 2.7 liters per batch), High-speed camera and set of computer for acquiring and analyzing the bubble hydrodynamic parameters (Pylon Store and Bubble Measuring Program).

The chemical solutions (coagulant) are injected directly at the bottom of the flotation column. The operating conditions were as follows: room temperature, liquid height H_L= 1.6 m and the sampling point located at 0.2 m above the air diffuser.

3.3 Experimental procedures

3.3.1 Synthesis of oil-in-water emulsion

The aim of this part is to create the stabilized oil droplets as presented in term of oil-in-water emulsion with different types of surfactants (anionic, cationic and non ionic). Moreover, the different parameters were investigated, for example, surface tension and the Critical Micelle Concentration (CMC) of synthesis oil emulsion wastewater. Note that the surface tension decreases when stability of oil droplet increases.

Experiment

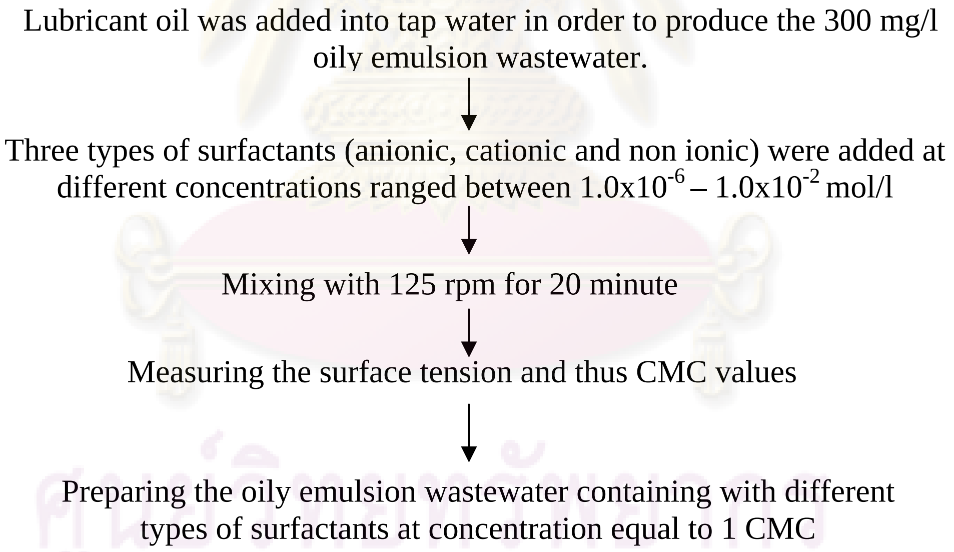


Figure 3.3 Preparation of synthetic lubricant oily wastewater.

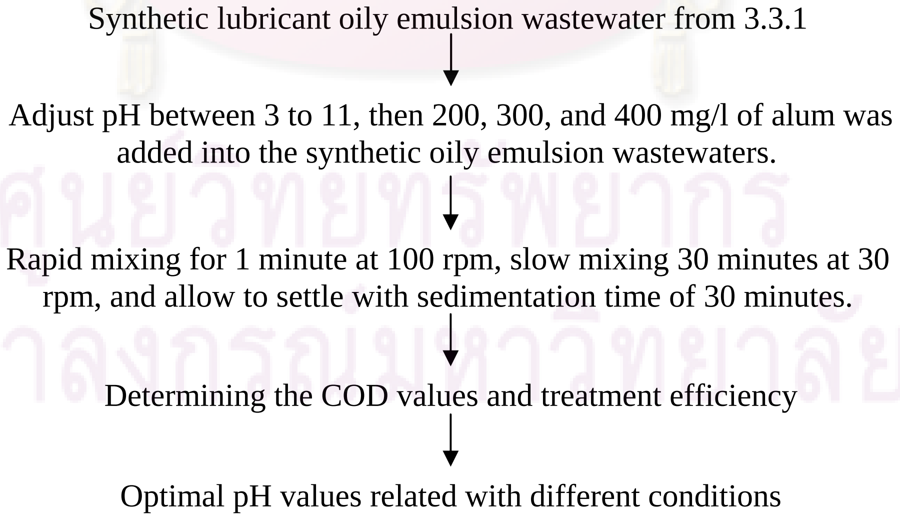
Table 3.1 Variable for measured the surface tension and the CMC values of oily emulsion with surfactants

Fixed Variables	**Parameter**
Concentration of emulsion	300 mg/l
Temperature	Room temperature
Mixed rate	125 rpm for 20 minutes
Independent Variables	**Parameter**
3 types of surfactant concentration	$1.0\times10^{-6} - 6.0\times10^{-2}$ mol/l
Dependent Variables	**Parameter**
Surface tension	Value depend on tensiometer CMC

3.3.2 Treatment of synthetic oily emulsion wastewater by coagulation process

The objective of this section is to study (in jar test) in order to determine the optimal pH and concentration of Aluminium sulfate ($Al_2(SO_4)_3$). Note that, this chemical agent was used for destabilizing the oily emulsion wastewater containing anionic, cationic and non ionic surfactants.

Experiment: determination of optimal pH values



Synthetic lubricant oily emulsion wastewater from 3.3.1

Adjust pH between 3 to 11, then 200, 300, and 400 mg/l of alum was added into the synthetic oily emulsion wastewaters.

Rapid mixing for 1 minute at 100 rpm, slow mixing 30 minutes at 30 rpm, and allow to settle with sedimentation time of 30 minutes.

Determining the COD values and treatment efficiency

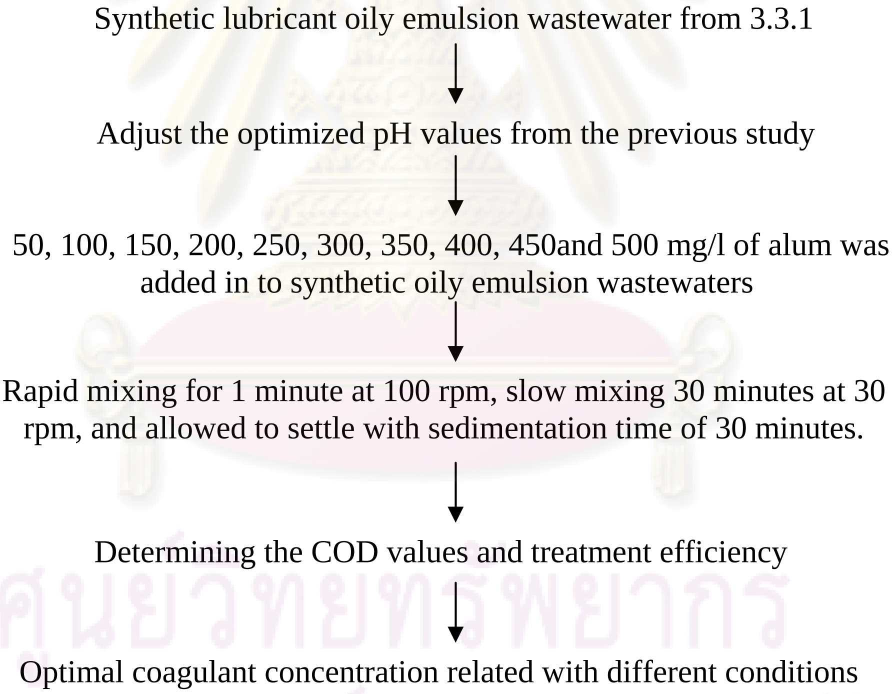
Optimal pH values related with different conditions

Figure 3.4 Determination of the optimal pH values by using $Al_2(SO_4)_3$ as Coagulant.

Table 3.2 Variable of study the optimal pH values by using $Al_2(SO_4)_3$ as Coagulant

Fixed Variables	**Parameter**
Synthetic lubricant oil emulsion wastewater	From 3.3.1
Independent Variables	**Parameter**
Coagulant concentration ($Al_2(SO_4)_3$)	200, 300, and 400 mg/l
pH values	pH range 3-11
Dependent Variables	**Parameter**
Residual oil concentration	COD

Experiment: Determination of optimal concentration of alum



Synthetic lubricant oily emulsion wastewater from 3.3.1

Adjust the optimized pH values from the previous study

50, 100, 150, 200, 250, 300, 350, 400, 450and 500 mg/l of alum was added in to synthetic oily emulsion wastewaters

Rapid mixing for 1 minute at 100 rpm, slow mixing 30 minutes at 30 rpm, and allowed to settle with sedimentation time of 30 minutes.

Determining the COD values and treatment efficiency

Optimal coagulant concentration related with different conditions

Figure 3.5 Diagram of determining the optimal concentration of Aluminium sulfate ($Al_2(SO_4)_3$) .

Table 3.3 Variable of study the optimal concentration of Aluminium sulfate ($Al_2(SO_4)_3$)

Fixed Variables	**Parameter**
Synthetic lubricant oil emulsion wastewater	From 3.3.1
pH values	pH from the previous study
Independent Variables	**Parameter**
Coagulant concentration ($Al_2(SO_4)_3$)	50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mg/l
Dependent Variables	**Parameter**
Residual oil concentration	COD

3.3.3 Treatment of synthetic oily emulsion wastewater by Induced Air Floatation (IAF)

The goal of this part is to analyze (in column flotation) to determine the optimal air flow rate and also aeration time for treatment the prepared oily emulsion wastewater containing anionic, cationic and non ionic surfactants. Note that, the reaction rate constant in reaction rate equation can be calculated by the variation of COD with time obtained experimentally in this work.

$$\frac{dC}{dt} = R = -K.C^n \qquad (3.1)$$

R is the reaction rate calculated by the variation of C (COD) with time. Logk and n are the reaction rate constant and reaction order, respectively.

<u>**Experiment: Determination of optimal air flow rate and aeration time**</u>

Synthetic lubricant oily emulsion wastewater from 3.3.1

↓

Air injecting at different flow rate 0.025, 0.1, 0.3, 0.5, and 0.7 l/min
for 80 minutes overall aeration time

↓

Sampling the effluents at 0, 1, 2, 4, 6, 8, 10, 20, 30, 40, 50 ,60 ,70 and 80 minutes.

↓

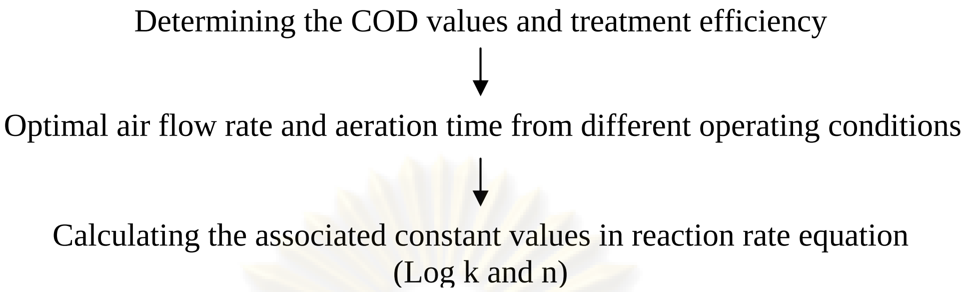


Figure 3.6 Determination of the optimal air flow rate and aeration time for IAF process.

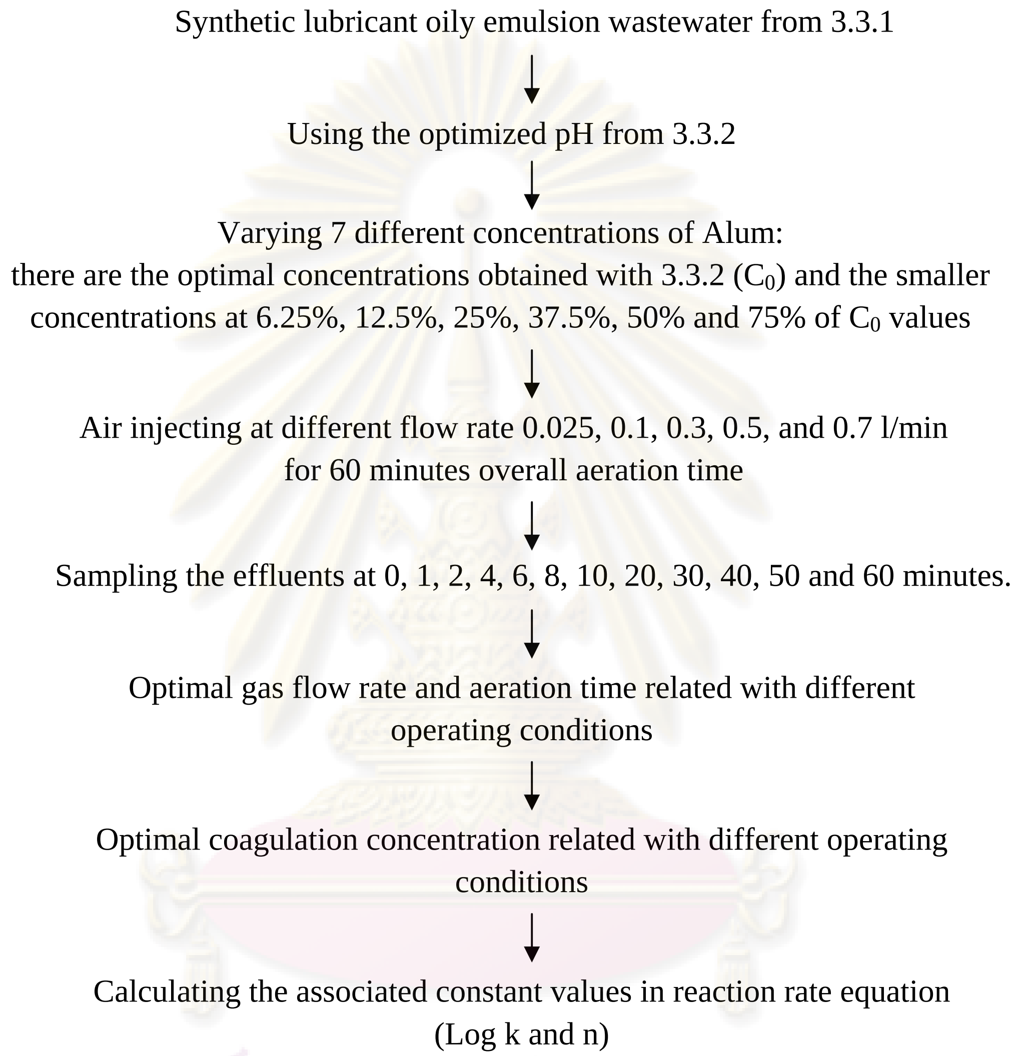
Table 3.4 Variable of study the optimal air flow rate and aeration time for IAF process.

Fixed Variables	**Parameter**
Synthetic lubricant oil emulsion wastewater	From 3.3.1
Volume of oil emulsion wastewater	2.7 liters per batch
Rigid orifices	As in figure 3.2 (b)
Independent Variables	**Parameter**
Air flow rates	0.025, 0.1, 0.3, 0.5, and 0.7 l/min
Aeration time	0, 1, 2, 4, 6, 8, 10, 20, 30, 40, 50, 60, 70 and 80 minutes
Dependent Variables	**Parameter**
Residual oil concentration	COD
Reaction rate equation	Log k and n
Bubble hydrodynamic parameters	a, D_B, f_B, U_B

3.3.4 Treatment of synthetic oily emulsion wastewater by Modified Induced Air Floatation (MIAF)

The objective of this part is to study (in column flotation) for determining the optimal air flow rate, aeration time and optimal concentration of alum in order to treatment the oily emulsion wastewater containing with anionic, cationic and non ionic surfactants.

Experiment: Determination of optimal air flow rate, aeration time and optimal concentration of alum



Synthetic lubricant oily emulsion wastewater from 3.3.1

↓

Using the optimized pH from 3.3.2

↓

Varying 7 different concentrations of Alum:
there are the optimal concentrations obtained with 3.3.2 (C_0) and the smaller concentrations at 6.25%, 12.5%, 25%, 37.5%, 50% and 75% of C_0 values

↓

Air injecting at different flow rate 0.025, 0.1, 0.3, 0.5, and 0.7 l/min for 60 minutes overall aeration time

↓

Sampling the effluents at 0, 1, 2, 4, 6, 8, 10, 20, 30, 40, 50 and 60 minutes.

↓

Optimal gas flow rate and aeration time related with different operating conditions

↓

Optimal coagulation concentration related with different operating conditions

↓

Calculating the associated constant values in reaction rate equation (Log k and n)

Figure 3.7 Determination of the optimal air flow rate, aeration time and optimal concentration of alum and ferric chloride for MIAF process.

Table 3.5 Variable of study the optimal air flow rate, aeration time and optimal concentration of alum for MIAF process.

Fixed Variables	**Parameter**
Synthetic lubricant oil emulsion wastewater	From 3.3.1
Volume of oil emulsion wastewater	2.7 liters per batch
Rigid orifices	As in figure 3.2 (b)
pH	pH from 3.3.2
Independent Variables	**Parameter**
Air flow rates	0.025, 0.1, 0.3, 0.5, and 0.7 l/min
Aeration time	0, 1, 2, 4, 6, 8, 10, 20, 30, 40, 50 and 60 minutes
Coagulant concentration ($Al_2(SO_4)_3$)	The optimal concentrations obtained with 3.3.2 (C_0) and the smaller concentrations at 6.25%, 12.5%, 25%, 37.5%, 50% and 75% of C_0 values
Dependent Variables	**Parameter**
Residual oil concentration	COD
Reaction rate equation	Log k and n
Bubble hydrodynamic parameters	a, D_B, f_B, U_B

3.3.5 Determination of bubble hydrodynamic parameters

In order to provide a better understanding on the obtained treatment efficiency, the bubble hydrodynamic parameters were determined in this part. The bubble sizes (D_B) and their rising velocities (U_B), the bubble formation frequencies (f_B) were experimentally analyzed. Moreover, the interfacial areas (a) were calculated from the previous parameters, as shown in equation 3.1:

$$a = N_B \times \frac{S_B}{V_{total}} = f_B \times \frac{H_L}{U_B} \times \frac{\pi D_B^2}{AH_L + N_B V_B} \qquad (3.2)$$

Experiment: Determination of bubble hydrodynamic parameters

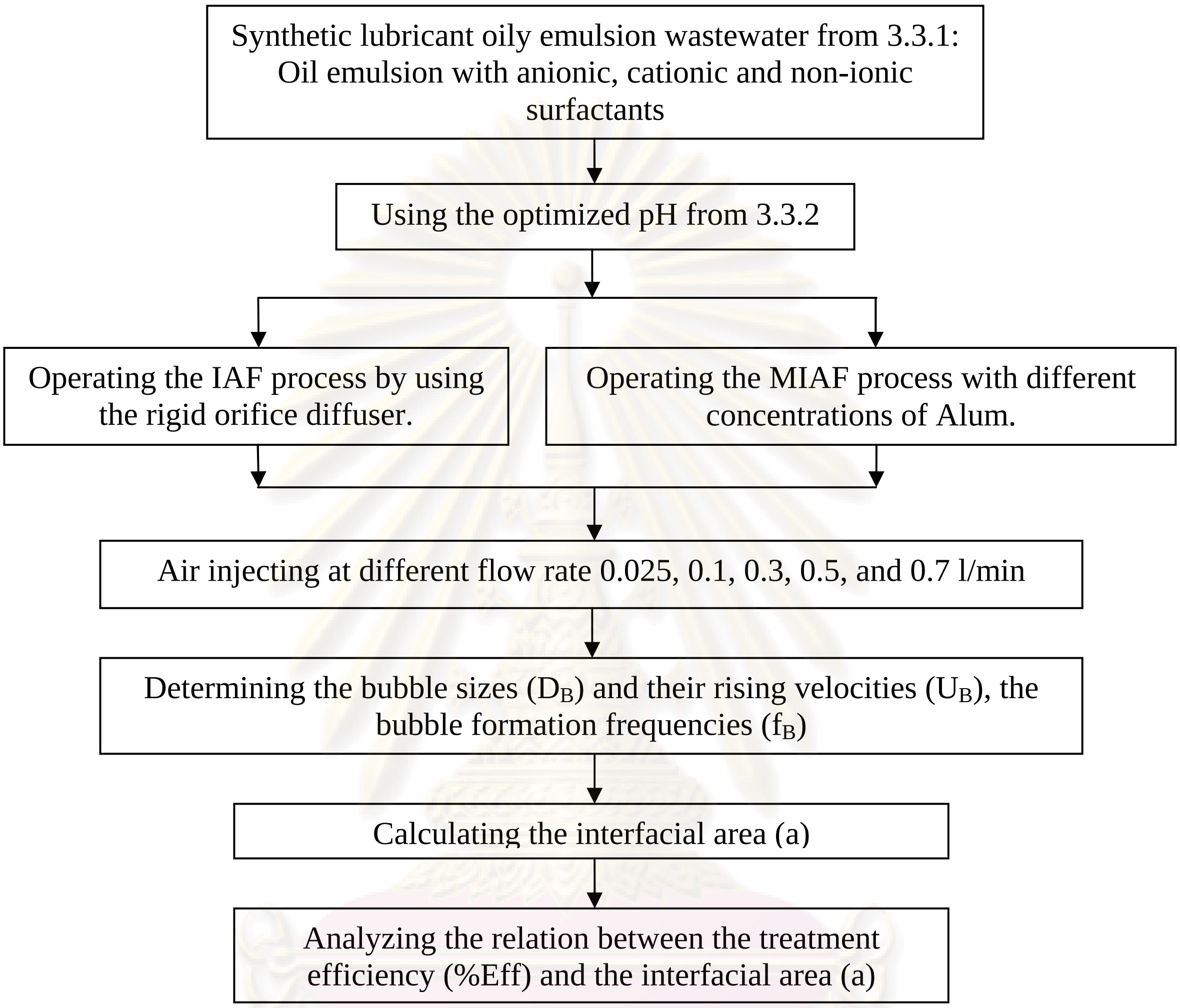


Figure 3.8 Determination of bubble hydrodynamic parameter for IAF and MIAF process.

3.3.6 Proposition of the simple model for predicting the overall treatment efficiency

In this part, the simple model for predicting the overall treatment efficiency were proposed based on the relationship between treatment efficiency (%Eff) and interfacial area (a). Moreover, the reaction constants (log k and n) obtained experimentally were applied in order to proposed simple model also. Finally, the treatment efficiencies obtained with the proposed model were compared with those obtained experimentally.

3.4 Analytical methods

The analytical methods for determining the different parameters are summarized as shown in Table 3.6

Table 3.6 The analytical methods for determining the different parameters

Parameter		Analytical method
Oil Concentration	COD	Closed-reflux method
Critical Micelle Concentration	Surface tension	Tensio meter
Bubble hydrodynamic parameters	- Bubble size	High speed camera (100 images/s)
	- Bubble rising velocity	
	- Bubble formation frequency	
	- Air flow rate	Flow monitor (SIKA)
	Interfacial area	
Reaction rate constants	$\frac{dC}{dt} = R = -K.C^n$	
Removal efficiency	$\%Eff = \frac{COD_{in} - COD_{out}}{COD_{in}}$	

CHAPTER IV

RESULTS AND DISCUSSION

The results presented in this chapter were based on the series of experiments conducted during the course of this study. The test results could be provided into six parts. The first part dealt with properties of synthetic lubricant oily emulsion wastewater. The second, the third, and the fourth part concerned with treatment of oily emulsion wastewater by Induce Air Flotation (IAF), coagulation, and Modify Induce Air Flotation (MIAF) process respectively. The fifth part was to determination of reaction rate constant (log k) and reaction order (n). Subsequently, the final part was conducted to bubble hydrodynamic and mixing parameter for IAF and MIAF process.

4.1 Properties of synthetic lubricant oily emulsion wastewater

4.1.1 The Critical Micelle Concentration (CMC)

In this study, the synthetic lubricant oily emulsion wastewater was prepared by the addition of surfactants including anionic (SDS), cationic (CTAB) and non ionic (Tween20). The concentration of oily emulsion wastewaters was 300 mg/l. Moreover, the prepared oily emulsion wastewater was measured in term of the surface tension in range $0.0005 x10^{-2}$ to $0.6x10^{-2}$ mol/l of surfactant concentration in order to investigate the stabilized oil droplets, at critical micelle concentration (1 CMC) as shown in Figure 4.1

From the results, it can be found that surface tension decreases rapidly at the beginning stage when concentrations of SDS, CTAB and Tween20 increasing in range between 0.01 - 0.2 x 10^{-2} mol/l, 0.0005 - 0.01 x 10^{-2} mol/l and 0.001 - 0.05 x 10^{-2} mol/l, respectively. Due to the decreasing of surface tension between water and oil droplets, the oil droplets still have the available surface area in order to be adsorbed by surfactant molecules. Then, the decreasing rates were lowers until the concentration of SDS, CTAB and Tween20 reached a certain value in range between

(0.2-0.6, 0.01-0.6, 0.05-0.6) x 10^{-2} mol/l respectively, called “Critical Micelle Concentration” (CMC). After that, the measured surface tensions remain relatively constant. This can be explained by the formation of groups of surfactant molecules called “micelle” (Rachu, 2005). Note that, these prepared oily emulsion wastewaters have more electric charge on the surface due to the type of surfactant applied. Thus, the smaller oil droplet size will be obtained and then turned into the stabilized oily-emulsion presence in wastewater: it is very difficult to treat by using classical physical method.

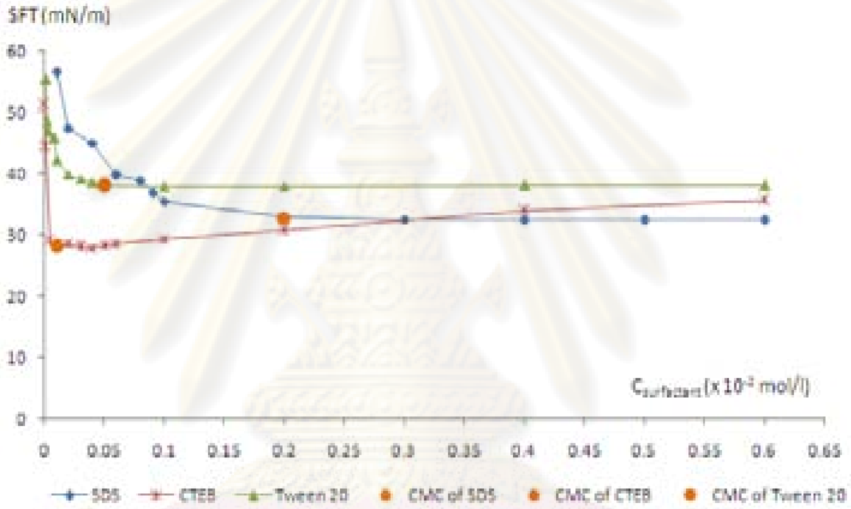


Figure 4.1 Surface tension versus concentration of surfactant for different types of surfactants

Therefore, the 300 mg/l of oily-emulsion wastewater with SDS, CTAB and Tween20 at CMC concentration (0.2, 0.01 and 0.05) x 10^{-2}mol/l, respectively were applied to prepare the stabilized oily emulsion wastewater, in this research.

4.1.2 Size of oil droplet, Viscosity and COD

In this part, Light Microscope with Contrast Condenser, BX50, Olympus was used to measured the size distribution of oil droplets of the synthetic wastewaters as shown in Figure 4.2. Moreover, the photograph of oil droplets containing with 3 types of surfactants can be shown as in Figure 4.3. Note that, Brookfield Digital Rheometer (DV-III) was applied to measure the wastewater viscosity and the close reflux method was used to measured COD values. The experimental results obtained were summarized in Table 4.1.

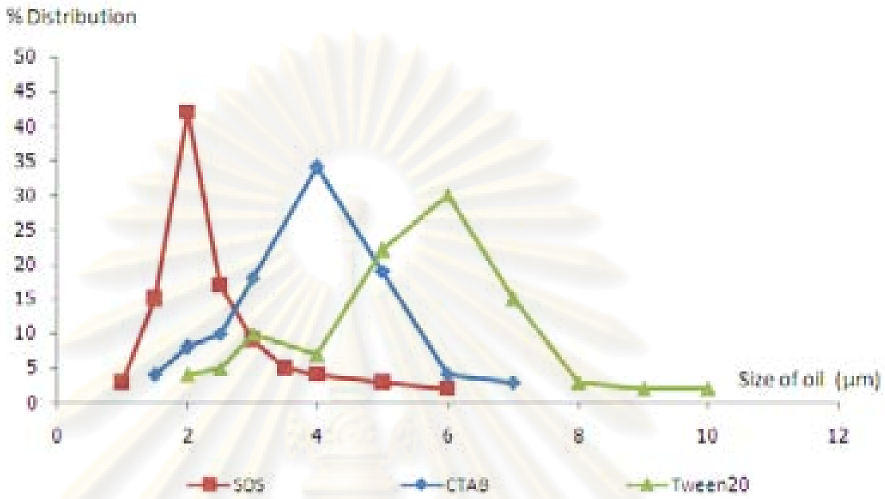


Figure 4.2 Size Distribution of oil droplets of the emulsion with 3 types of surfactants.

According to Figure 4.2, it can be found that the highest % distribution values of oil droplets presence in synthetic wastewater with SDS, CTAB and Tween20 were obtained with the oil droplet size equal to 2, 4 and 6 μm, respectively. Note that, these size obtained are smaller than those obtained with oily emulsion without surfactant (≈10 μm). Moreover, the difference in oil droplet sizes correspond with the molecular weight of surfactant. The results can be concluded as follows:

Molecular weight:	Tween20 > CTAB > SDS
Size of oil droplet:	Tween20 > CTAB > SDS

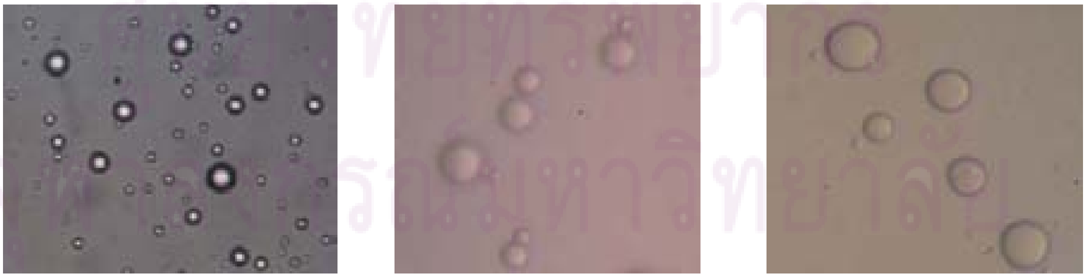

(A) (B) (C)

Figure 4.3 Size of oil droplets of oily emulsion wastewater with SDS (A), CTAB (B) and Tween20 (C) capture from Light Microscope (40x)

Table 4.1 Properties of oily emulsion wastewater containing with 3 types of surfactants (anionic (SDS), cationic (CTAB) and non ionic (Tween20))

Surfactant	MW (g/mol)	CMC (mol/l)	CMC (g/l)	COD (mg/l)	μ_L (cps)	D_{oil} (μm)
Anionic surfactant	288.80	0.002	0.575	1010	19.8	2
Cationic surfactant	364.45	0.0001	0.037	360	19.5	4
Nonionic surfactant	1227.54	0.0005	0.614	940	18.9	6

As presented in Table 4.1, the COD values of oily emulsions with SDS, CTAB and Tween20 were 1010, 360 and 940 mg/l, respectively. From the obtained results, it can be note that COD values depend on the applied surfactant concentrations in order to prepare the oily emulsion wastewater samples: the highest concentration used is SDS (0.002 mol/l) obtained the highest COD value, next is Tween20 (0.0005 mol/l), and finally is CTAB (0.0001 mol/l) obtained the lowest COD value. For viscosity value of oily emulsion wastewater with SDS, CTAB and Tween20 were 19.7, 19.3 and 18.9 Centipoises (cps), respectively: it can be note that viscosity values of 3 type of oily emulsion wastewater were not different in values. Thus, small effect of liquid viscosity on different types of surfactants can be obtained in this study.

4.1.3 Effect of aeration (generated bubbles) on surfactants and coagulants

In this study, the COD values were applied in order to analyze the oil concentration and thus calculate the treatment efficiency. However, in stabilized oily emulsion wastewater prepared in this work, the different types of surfactants (SDS, CTAB and Tween20) and coagulant (alum) were used and thus represented in the measured COD values. Therefore, in order to well define the treatment efficiency in terms of oil droplet separation, the COD test experiments for a given contaminant presences in liquid phase were operated in this work.

In practice, the prepared oily-emulsion wastewater without surfactant and coagulant concentrations was firstly analyzed in terms of COD values. Moreover, the COD values obtained with the solution with different surfactants (1 CMC) and alum concentration (= 300 mg/L) were measured and compared with those obtained at the 30 minute of aeration time. The summarized results can be presented in Figure 4.4.

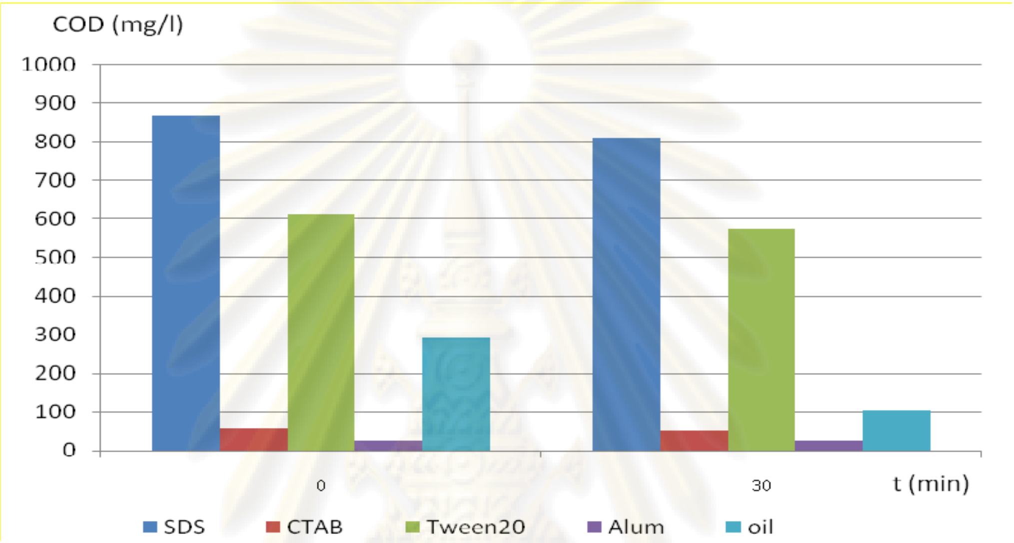


Figure 4.4 COD test experiments for a given contaminant presences in liquid phase

According to Figure 4.4, the COD values obtained with the synthetic stabilized oily emulsion wastewater (tap water, lubricant oil, and different types of surfactants) as presented in Table 4.1 are closed to those obtained with the sum of the COD values of lubricant oil and surfactant (Figure 4.4). The COD values of prepared lubricant oil wastewater (≈ 292 mg/L) are closed to the applied of lubricant oil concentrations used in this study. Moreover, by using the flotation process at 0.3 l/min of air flow rate, the treatment efficiencies considered in term of COD value, about 68% can be observed. This result corresponds to the non-stabilized oil droplet (not mixed with surfactants), and it can be thus separated or treated more easily than in the case of stabilized ones. Note that, the amounts of alum presence in reactor were not affected by the bubbles generated. Moreover, it can be found that the aeration provides the small effect on the reduction of surfactant concentrations (COD) for the negative, positive and non-ionic charged surfactants. In addition, the associated decreasing effect relates with surfactant concentration applied for preparing the stabilized oily emulsion wastewater in this study: significant change were observed in the case of anionic (SDS) and non-ionic (Tween20) surfactants. Therefore, it can be concluded that the COD values are possible to be used in order to analyze the oil concentration and thus calculate the removal efficiency. Because, the bubbles generated in flotation process have been proven to comprise the slightly effect on the concentrations of surfactants and coagulants presence in reactor.

4.2 Treatment of oily emulsion wastewater by Induce Air Flotation (IAF) process

The objective of this part is to study the mechanism of IAF process (in column flotation) in order to determine the optimal air flow rate and aeration time for treatment of oily emulsion wastewaters containing with SDS, CTAB and Tween20. Note that, air flow rate 0.025-0.7 l/min and aeration time 0-80 minutes were applied in this part.

4.2.1 Optimal air flow rate and aeration time for oily emulsion containing SDS

Figure 4.5 presents the treatment efficiency of oily emulsion wastewater containing with anionic surfactant (SDS) by the IAF process as a function of time, for different air flow rates.

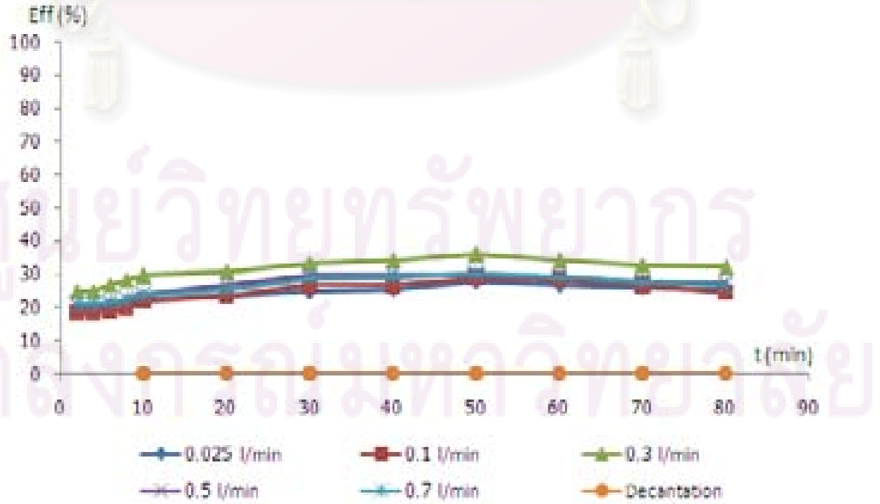


Figure 4.5 Treatment efficiency of oily emulsion with SDS as a function of time for different air flow rates

According to Figure 4.5, it can be firstly found that the treatment efficiency obtained with the IAF processes (36%) are greater than those obtained with the decantation process (≈ 0%) for 80 minutes operation time. These results confirm that the generated bubbles interact with the oil droplets and act like “rising parachutes” for oil droplets. The medium treatment efficiency (≈ 33%) obtained in this result can be explained by the smallest size of oil droplets affecting to oil-bubble collision/attachment mechanism and by the 0.575 g/l of SDS applied for preparing the synthetic wastewater. The maximum efficiencies were achieved at 0.3 l/min for air flow rate and at 50 minutes operation times. However, there is a little effect of air flow rates and time on the Eff% values. Therefore, in practice, the optimal operating conditions should be functioned at 0.3 l/min for air flow rates and at 30 minutes operations times because this condition obtained high efficiency (33%) and used less operation time.

4.2.2 Optimal air flow rate and aeration time for oily emulsion containing CTAB

Figure 4.6 presents the treatment efficiency of oily emulsion wastewater containing with cationic surfactant (CTAB) by the IAF process as a function of time, for different air flow rates.

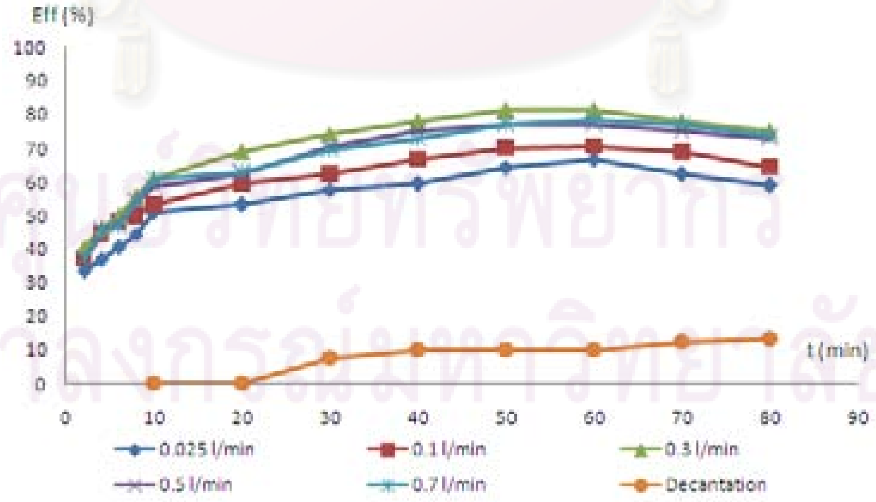


Figure 4.6 Treatment efficiency of oily emulsion with CTAB as a function of time for different air flow rates

As shown in Figure 4.6, it can be found that the treatment efficiency obtained with the IAF processes (40-80%) are greater than those obtained with the decantation process (about 16%). The highest treatment efficiencies (≈ 80%) obtained in this result were based on the size of oil droplet that is larger than obtained with SDS (4 µm > 2 µm), the small chemical dosage (CTAB = 0.037 g/l) and the positive charge on the surface of oil droplets enhancing the oil-bubble collision/attachment phenomena. Moreover, the maximum efficiencies (80%) was achieved at 0.3 l/min for air flow rate and at 50 minutes operation times, and then the efficiencies decreased with increasing time. Although, the maximum efficiencies was achieved at 0.3 l/min for air flow rate and at 50 minutes operation times. In this work, the optimal conditions should be operated at 0.3 l/min for air flow rate and at 30 minutes operations times because this condition obtained high efficiency (75%) and used less operation time. In this study, for any air flow rates, three zones can be found on the variation of the treatment efficiency with operating time.

1. Free surface zone: In this zone, the oil droplets have the available free surfaces for interacting with the generated bubbles. Therefore, there is a little effect of air flow rate and also the aeration time in this zone. The treatment efficiencies are about 40-60% for all air flow rate.

2. Attachment zone: In this second zone, the highest efficiencies were observed. The treatment efficiencies obtained depend on the air flow rates used in this experiment. The largest and smallest treatment efficiencies were obtained with the air flow rates at 0.3 l/min and 0.025 l/min, respectively: turbulent nature (energy) of bubble generation phenomena is probably responsible for reducing the contact time between oil droplets and generated bubbles and thus the treatment efficiency. Therefore, it can be expressed that the coalesced or attachment mechanism becomes the important factor, in this zone, in order to remove the oil droplets to the surface of water.

3. Breaking zone: In this last zone, the treatment efficiencies obtained experimentally started to decrease due to the breaking phenomena of the oil/bubble aggregates formed in the attachment zone at the surface of

floatation column (Meyssami and Kasaeian, 2005). Therefore, it is not necessary, in practice, to operate the IAF process with the very high air flow rate and also for elongated aeration time.

4.2.3 Optimal air flow rate and aeration time for oily emulsion containing Tween20

Figure 4.7 presents the treatment efficiency of oily emulsion wastewater containing with nonionic surfactant (Tween20) by the IAF process as a function of time, for different air flow rates.

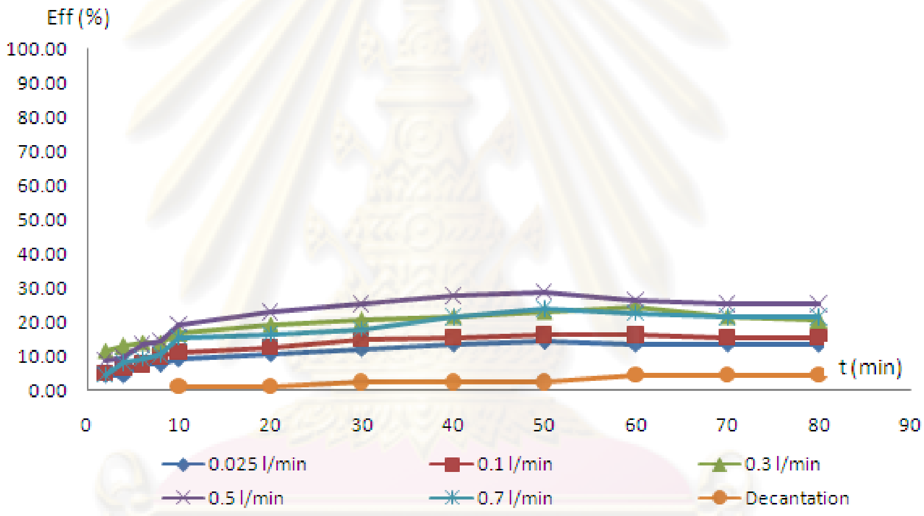


Figure 4.7 Treatment efficiency of oily emulsion with Tween20 as a function of time for different air flow rates

As shown in Figure 4.7, it can be found that the treatment efficiency obtained with the IAF processes (10-28%) are greater than those obtained with the decantation process (about 4%). Moreover, the maximum efficiencies (28%) were obtained at 0.5 l/min for air flow rate and at 50 minutes operation times, and then the efficiencies decreased with increasing time. In this work, the optimal conditions should be operated at 0.5 l/min for air flow rate and at 30 minutes operations times for the same reason as previously described in terms of energy consumption and operation time. The lowest treatment efficiency (≈ 25%) obtained in this case corresponds probably with the non-ionic charge around the oil droplet surface from the non-ionic surfactant (Tween20) used in this work: the largest oil droplet size (≈ 6μm) obtained with this wastewater cannot provide the highest values of %Eff. Moreover, the high concentration and molecular weight of Tween20, which are equal to 0.614 g/l and g/mol respectively, were also the responsible for these results.

In conclusion, the comparison of the optimal air flow rates and aeration time for treating and destabilizing the oily emulsion containing SDS, CTAB and Tween20, can be shown in Table 4.2.

Table 4.2 The optimal operation for oily-emulsion with 3 type of surfactant by IAF

Surfactant	Air flow rate (l/min)	Time (min)	Treatment efficiency (%)
Anionic surfactant	0.3	30	33
Cationic surfactant	0.3	30	75
Nonionic surfactant	0.5	30	25

From the result, it can be seen that: % Eff $_{CTAB}$ > % Eff $_{SDS}$ > %Eff $_{TWEEN20}$. Note that, the application of IAF process of oily emulsion wastewaters containing with anionic, cationic and non-ionic surfactants can provide only 33%, 75% and 25% treatment efficiencies, respectively. However, shorter operation times (< 10 minutes) than those obtained with the decantation process can be observed. Then, the other processes have to be considered and applied in order to enhance the treatment efficiency. Moreover, the oil droplet sizes and their relative charges on oil surface are proved to be the important factors controlling the treatment efficiencies. Therefore, in next part, the other processes will be considered and applied in order to enhance the treatment efficiency: the chemical coagulation process is necessary to be applied along with the IAF process, as the combined process.

4.3 Treatment of oily emulsion wastewater by coagulation process

The objective of this section is to determine (in jar test) the optimal pH and concentration of Aluminium sulfate ($Al_2(SO_4)_3$) for treating and destabilizing the oily emulsion wastewater containing with SDS, CTAB and Tween20. Note that, the range of pH values of 3-11 and of alum concentration 50-500 mg/l were applied in this part.

4.3.1 Optimal pH and concentration of alum for oily emulsion containing SDS

4.3.1.1 Optimal pH for oily emulsion containing SDS

Figure 4.8 presents the variation of treatment efficiency of oily emulsion with SDS by the coagulation process with pH values at different concentrations of alum.

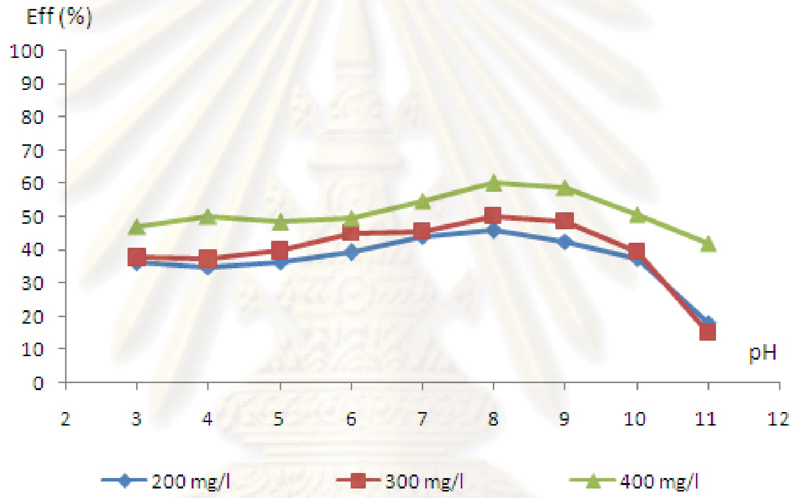


Figure 4.8 Treatment efficiency of oily emulsion with SDS versus pH values for different alum concentration

As shown in Figure 4.8, at pH values 8, it can be found that the maximum efficiencies (Eff_{max}) 45 % was achieved at 200 mg/l of alum concentration, the Eff_{max} values of 50% was achieved at 300 mg/l of alum concentration, the Eff_{max} values of 60 % was achieved at 400 mg/l of alum concentration, respectively. Note that, there are two important factors that affect to the obtained removal efficiencies.

- Alum concentration: it can be found that the treatment efficiencies increase with the alum concentrations. These high concentrations of alum (300 – 400 mg/l) required in this experiment, can be explained based on the destabilized mechanism like and charge neutralization and sweep floc coagulation.

Moreover, alum, applied in this study, has a relatively low charge density compared to the other coagulants such as Chitosan (Ahmad et al., 2006).

- pH value: it can be observed that the treatment efficiencies increase with the range of pH (3-8). However, for the pH higher than 8, there is a decrease in the treatment efficiency. These results indicate that, at acid and neutral pH values, the generated alum floc was presented in term of positive charge as Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_3$: these can be destabilize of oil droplets particle (negative charge surface) and also form the bigger floc size, thus higher treatment efficiencies. On the other hand, at high pH values, the negative charge of (OH^-) was adsorbed on surface of oil droplets and soluble in liquid phase under test. For this reason, there is not enough the alum concentration for destabilization of oil droplets and thus lower efficiency obtained at higher pH value.

4.3.1.2 Optimal concentration of alum for oily emulsion containing SDS

Figure 4.9 presents the treatment efficiency of oily emulsion wastewater containing with anionic surfactant (SDS) by the coagulation process with the alum concentration at pH 8.

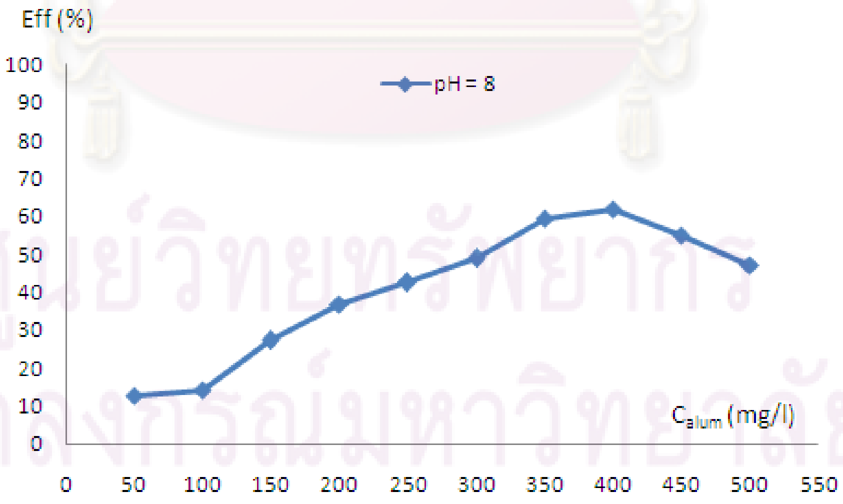


Figure 4.9 Treatment efficiency of oily emulsion wastewater with SDS versus alum concentration for pH 8

From the results presented in Figure 4.9, it was observed that the highest treatment efficiency (61.82%) was obtained at pH 8 and 400 mg/l of alum concentration. Note that, in this study, two stages can be found on the variation of the treatment efficiency with concentration of alum:

- First step: the treatment efficiencies increase with the alum concentrations. The highest %Eff values was observed at pH 8 and at a concentration 400 mg/l of alum, as shown in Figure 4.8
- Second step: for the concentrations higher than 400 mg/l, there is a decrease in the treatment efficiency indicating that the charge reversal phenomenon occurred with over alum concentration injected in the oily wastewater. This observation was also reported in the work of Meyssami, B. and Kasaeian, 2005.

4.3.2 Optimal pH and concentration of alum for oily emulsion containing CTAB

Figure 4.10 and 4.11 presents the treatment efficiency of oily emulsion with CTAB by the coagulation process with different pH values and alum concentrations, respectively.

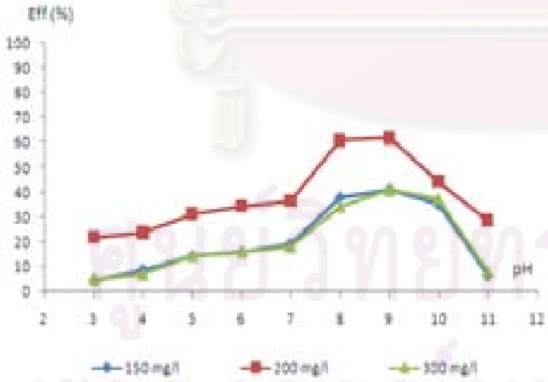


Figure 4.10 Treatment efficiency versus pH values for different alum concentrations

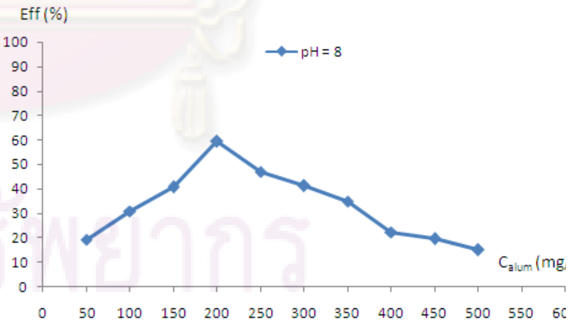


Figure 4.11 Treatment efficiency versus alum concentration for optimal value (pH 8)

As shown in Figure 4.10, it can be found that the optimal pH value equal to 9 and this was applied in order to determine the optimal alum concentration in next part. The maximum efficiencies equal to 62%, 41% and 40% were obtained with the alum concentration at 150, 200 and 300 mg/l, respectively. Note that, in this work, the optimal pH should be operated at pH 8 for all concentration of alum because this condition can also provide the high efficiency 61%, 38% and 35% for 150, 200 and 300 mg/l of alum concentration, respectively: lower sodium hydroxide dosage is thus required. Moreover, there are two factors affecting the treatment efficiency:

- pH value: it can be found that the treatment efficiencies increase with the pH (3-9). Note that, higher pH values can provide more anionic ion and thus destabilize the oil droplet surface with cationic surfactant (CTAB). However, for pH higher than 9, there is a decrease in the treatment efficiency: the restabilized mechanism has been obtained with negative-charged oil droplet. Therefore, the alum concentration injected in liquid phase was inadequate in order to destabilize those oil droplets.
- Alum concentrations: it can be found that the treatment efficiencies increase with the alum concentrations. The highest treatment efficiency was observed at pH 8 and 200 mg/l of alum concentration (as shown in Figure 4.11). However, there is a decrease in the treatment efficiency for the concentrations higher than 200 mg/l. It can be found that, even the repulsion electrical force between the positive charge from oil droplet and alum used as coagulant, the acceptable treatment efficiency (≈ 60%) were obtained. The large oil droplet size (4 µm) and the small amount of cationic surfactant (CTAB) added for preparing the stabilized oily-emulsion at 1 CMC should be the main explanation for the sweep floc coagulation mechanism from 200 mg/L of alum injected in this case. Note that, there is not enough alum concentration for operating the previous mechanism at lower concentration (< 200 mg/l). Moreover, at higher concentration (> 200 mg/l), more significant effect of repulsion force can be occurred and thus decrease the associated treatment efficiency.

4.3.3 Optimal pH and concentration of alum for oily emulsion containing Tween20

Figure 4.12 and 4.13 presents the treatment efficiency of oily-emulsion with Tween20 by the coagulation process with different pH values and alum concentration

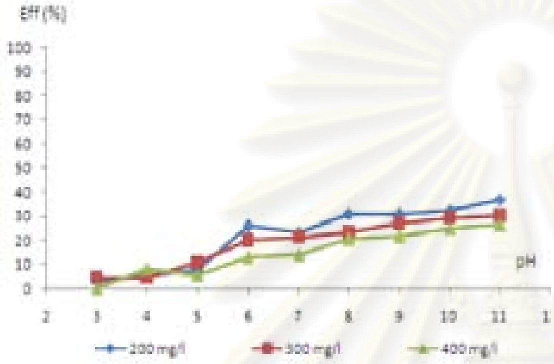


Figure 4.12 Treatment efficiency versus pH values for different alum concentrations

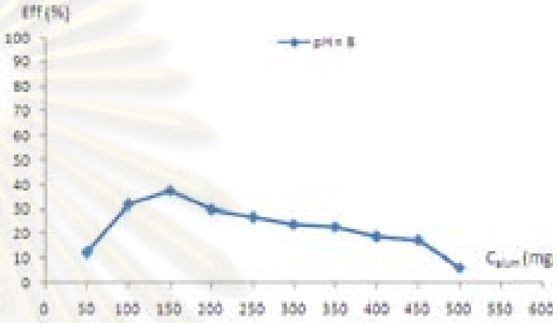


Figure 4.13 Treatment efficiency versus alum concentration for optimal value (pH 8)

As shown in Figure 4.12, it can be found that the maximum efficiencies 36 % was achieved at pH 11 for concentration 200 mg/l of alum, 30 % was achieved at pH 11 for concentration 300 mg/l of alum and 26 % was achieved at pH 11 for concentration 400 mg/l of alum, respectively. Although, the maximum efficiencies were achieved at pH 11 for all concentration of alum. In this work, the optimal pH should be operated at pH 8 for all concentration of alum because this condition obtained high efficiency 31%, 23% and 20% respectively and used lower sodium hydroxide dosage than pH 11. Note that, there are two factors that effect to treatment efficiency.

- pH value: it can be found that the treatment efficiencies increase with the pH indicating that, at low pH (acid condition), the positive charge of (H^+) was absorb on surface of oil droplets and soluble in solution. For this reason, the oil droplets become more stable and thus difficult to be destabilized by applied alum as coagulant. However, for higher pH values (base condition), the negative charge of (OH^-) can be adsorbed on surface of oil droplets: these condition can facilitate the destabilization of oil droplets by added alum, the formation of bigger floc size and thus the augmentation of treatment efficiencies.

- Alum concentrations: it can be found that the treatment efficiencies increase with the alum concentrations. The high treatment efficiency was observed at pH 8 and at a concentration 150 mg/l of alum, as shown in Figure 4.13. Whereas, for the concentrations higher than 150 mg/l, there is a decrease in the treatment efficiencies indicating that the solution has gone through the point of net electrical charge and the added alum has increased the positive charge of the emulsions (Charge reversal).

In this study, the comparison of the optimal values of pH and alum concentration for destabilizing the oily emulsion containing with different surfactants (SDS, CTAB and Tween20) by coagulation process can be shown in Table 4.3

Table 4.3 The optimal operation for oily emulsion wastewater with 3 type of surfactant by coagulation process

Surfactant	Size	Alum (mg/l)	pH	Removal efficiency (%)
Anionic surfactant	2	400	8	62
Cationic surfactant	4	200	8	60
Nonionic surfactant	6	150	8	38

As presented in Table 4.3, it can be noted that found that the optimal pH value were observed at pH 8 for whatever the liquid phases. Moreover, the treatment efficiency was related with the ionic charge presence on the oily-emulsion surface: the values of %Eff obtained with the positive charge and negative charge based on the use of anionic (SDS) and cationic (CTAB) surfactants, respectively were greater than those obtained with non-ionic charge from non-ionic surfactant (Tween20). Therefore, it can be stated that non-ionic surfactant contaminated in lubricant oily emulsion wastewater can produce more stable oily emulsion and thus difficult to be separated or treated by the coagulation-flocculation process. In conclusion, the size of oil droplets and chemical dosage should be taken into account as the important parameters for enhancing the overall treatment efficiency.

Due to the comparison of the performance obtained with IAF process (Table 4.2) and the coagulation-flocculation process in jar test (Table 4.3), it can be observed that the treatment efficiencies obtained with coagulation process are greater than those obtained with the IAF process, except oily emulsion wastewater with cationic surfactant. However, the disadvantage of the chemical process is that long operation times (rapid/slow mixing and sedimentation) are needed, in addition, with the optimum dosage of alum and pH value. Therefore, in the next part, the treatment of lubricant oily emulsion containing with surfactants by using the Induce Air Floatation (IAF) process, together with the coagulation process called Modified Induced Air Floatation (MIAF) will be studied.

4.4 Treatment of oily emulsion wastewater by Modify Induce Air Floatation process (MIAF)

The objective of this part is to study MIAF process (in column floatation) for determine the optimal air flow rate, aeration time and optimal concentration of alum, in order to treatment the oily-emulsion wastewater containing with different surfactants (SDS, CTAB and Tween20). Note that, air flow rate 0.025-0.7 l/min and aeration time 0-60 minutes were applied in this part.

4.4.1 Optimal air flow rate and aeration time for oily emulsion containing SDS, CTAB and Tween20 by MIAF

Figure 4.14 - 4.20 presents the treatment efficiency of oily emulsion with SDS by the MIAF process as a function of time, for different air flow rates at alum concentration 25, 50, 100, 150, 200, 300 and 400 mg/l, respectively.

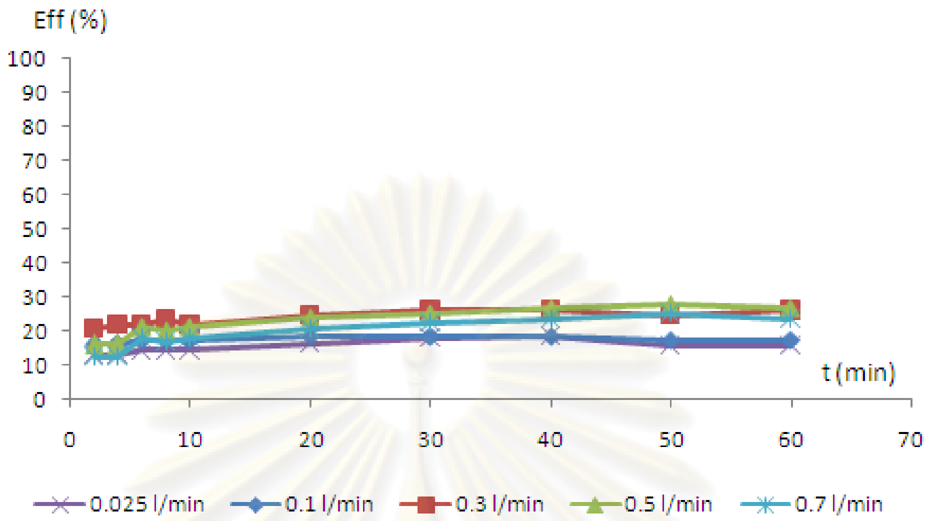


Figure 4.14 Treatment efficiency of oily emulsion with SDS as a function of time for different air flow rates at alum concentration 25 mg/l

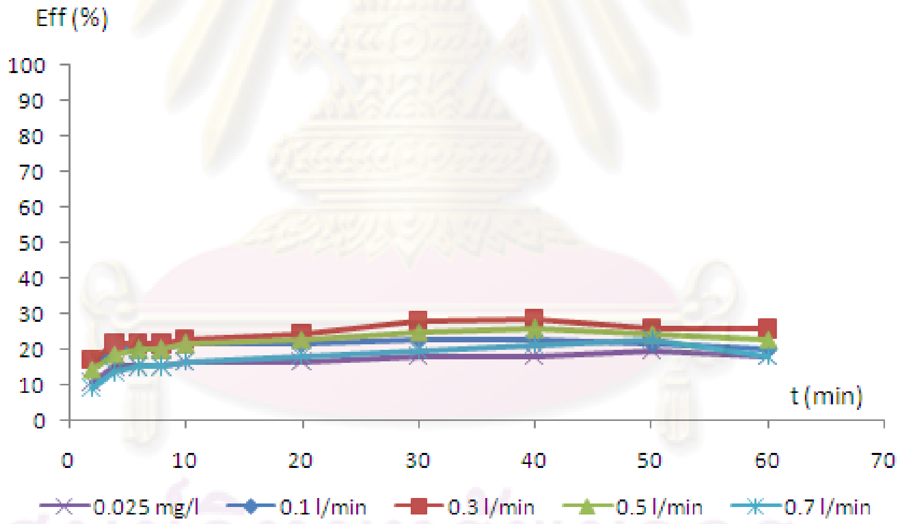


Figure 4.15 Treatment efficiency of oily emulsion with SDS as a function of time for different air flow rates at alum concentration 50 mg/l

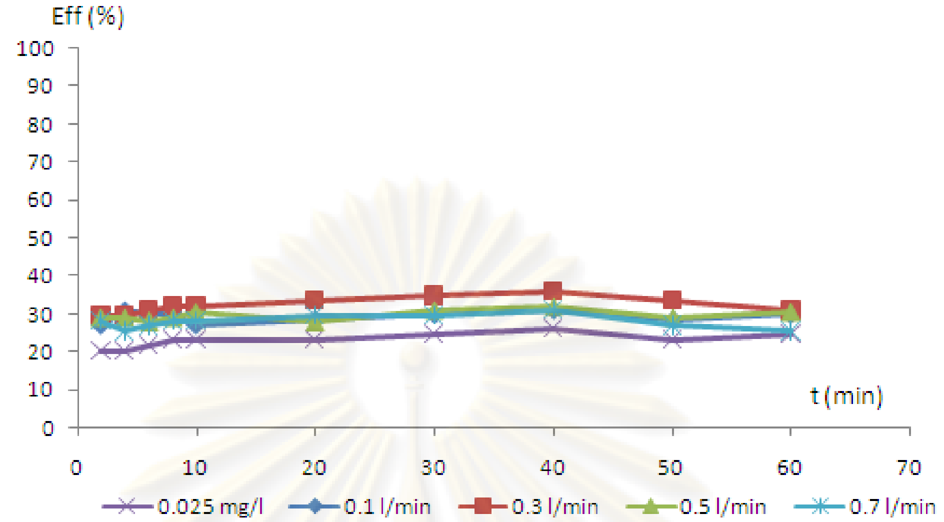


Figure 4.16 Treatment efficiency of oily emulsion with SDS as a function of time for different air flow rates at alum concentration 100 mg/l

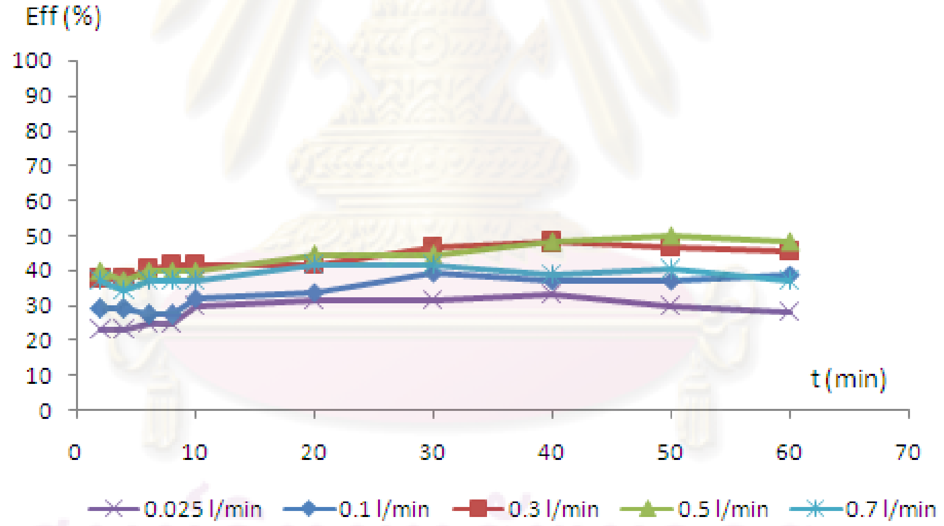


Figure 4.17 Treatment efficiency of oily emulsion with SDS as a function of time for different air flow rates at alum concentration 150 mg/l

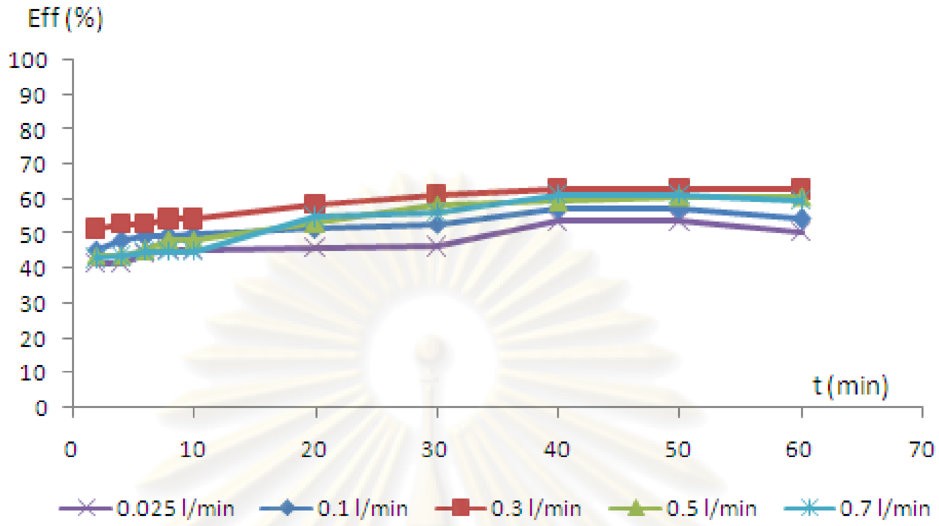


Figure 4.18 Treatment efficiency of oily emulsion with SDS as a function of time for different air flow rates at alum concentration 200 mg/l

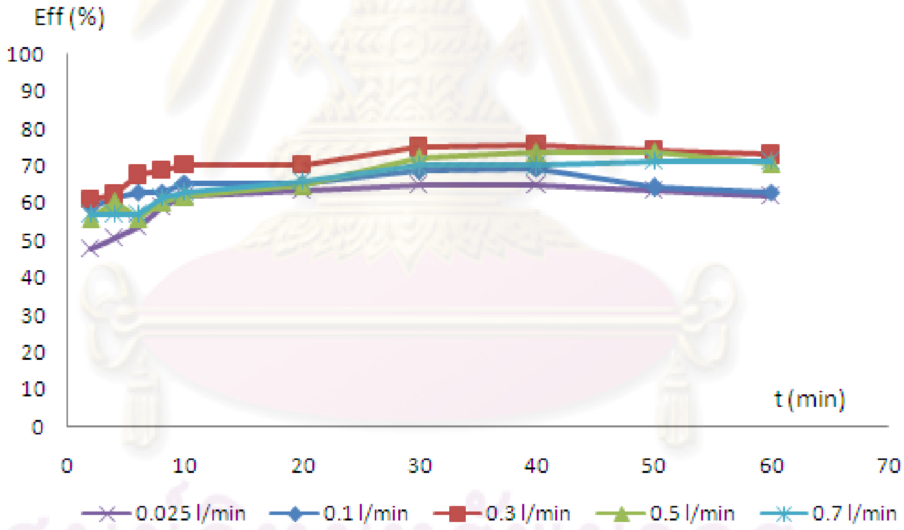


Figure 4.19 Removal efficiency of oily emulsion with SDS as a function of time for different air flow rates at alum concentration 300 mg/l

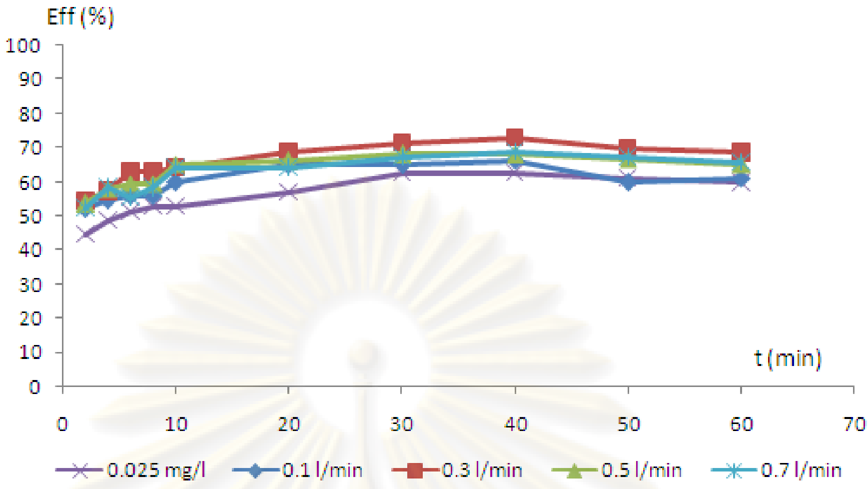


Figure 4.20 Treatment efficiency of oily emulsion with SDS as a function of time for different air flow rates at alum concentration 400 mg/l

According to Figure 4.14 - 4.20, it can be found that the highest treatment efficiencies were obtained with the MIAF processes at alum concentration 25, 50, 100, 150, 200, 300 and 400 mg/l were 26%, 28%, 36%,48%, 63%, 76% and 73%, respectively. Note that, the optimal air flow rate (0.3 l/min) and aeration time (30 minutes) can be observed for whatever the MIAF experiments. Therefore, the treatment efficiencies of oily emulsion wastewater with anionic surfactant (SDS) obtained with the optimal air flow rate (0.3 l/min) as function of aeration time, for different alum concentrations, were presented as shown in Figure 4.21.

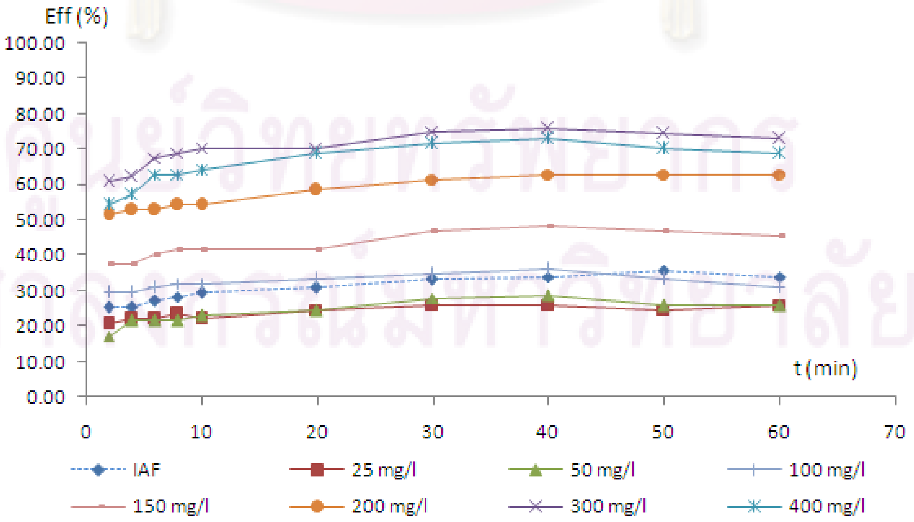


Figure 4.21 Treatment efficiency of oily emulsion with SDS as a function of time for 0.3 l/min air flow rates at all alum concentration

From the result, it can be explained that the treatment efficiencies were based on three factors as follow:

- Air flow rate: it can be found that the treatment efficiencies increase with the flow rate ranged between 0.025 and 0.3 l/min: this corresponds with the number of bubble generate increased with air flow rate. Note that, there are not only high interacting opportunity of surface between oil droplets and bubbles, but also the proper mixing condition between generated bubbles that can be obtained in this operation condition. However, for higher air flow rate (0.3 - 0.7 l/min), the treatment efficiencies start decreasing. It can be stated that the high Q_G values can affect the interacting opportunity between oil droplets and generated bubbles by inducing the turbulent mixing condition and also by reducing the retention time of bubble in floatation column.
- Aeration time: it can be found that the treatment efficiencies increase with time (0 - 40 min), and then decrease with increasing aeration time. The breaking phenomena of the oil/bubble aggregates at top of flotation column can be possibly responsible for this result (Meyssami and Kasaeian, 2005).
- Coagulant dosage: it can be found that the treatment efficiencies increase with alum concentrations. These high concentrations of alum required in this experiment can be explained based on the destabilized mechanism (sweep floc coagulation).

The comparison between the treatment efficiencies obtained with the coagulation-flocculation in jar test experiment and with MIAF process at the optimal operation condition (air flow rate 0.3 l/min and aeration time 30 minutes) can be presented in Table 4.4. Note that, the velocity gradient (G) were determined and applied in order to analyze the mixing condition occurred in both treatment processes.

Table 4.4: Comparison of treatment efficiency and velocity gradient (G) between MIAF at 0.3 l/min for air flow rate and at 30 minutes operation times and jar test for oilyemulsion wastewater containing with anionic surfactant (SDS)

Coagulant	Dosage (mg/l)	Treatment efficiency (%) MIAF	G (s^{-1})	Treatment efficiency (%) jar test	G (s^{-1})
Alum	25	26	174.59	10	30.52-185.78
	50	28	174.59	12	30.52-185.78
	100	35	174.59	14	30.52-185.78
	150	47	174.59	27	30.52-185.78
	200	62	174.59	37	30.52-185.78
	300	75	174.59	49	30.52-185.78
	400	72	174.59	62	30.52-185.78

According to Table 4.4, it can be concluded that:

- For any given alum dosages added in liquid phase, the treatment efficiencies obtained with MIAF process are greater than those obtained with the coagulation process (14-26%);
- Operation time for treating the oily emulsion wastewater containing with anionic surfactant (SDS) by MIAF process (30 min) are lesser than that used by the coagulation-flocculation process in jar test (60 min);
- The G values obtained with MIAF process (0.3 l/min) were equal to 174.59 and range between those obtained with and jar test experiments (31 - 185.78 s^{-1} for slow and rapid mixing condition, respectively). Therefore, it can be expressed that bubble generated by air diffuser can be applied, not only for separating the oil droplets to the surface, but also for producing the chemical mixing condition in the MIAF process.

Figure 4.22 and 4.23 presents the treatment efficiency of oily emulsion wastewater containing with cationic surfactant (CTAB) by the MIAF process as a function of time, for different air flow rates and alum concentrations (25 and 200 mg/l).

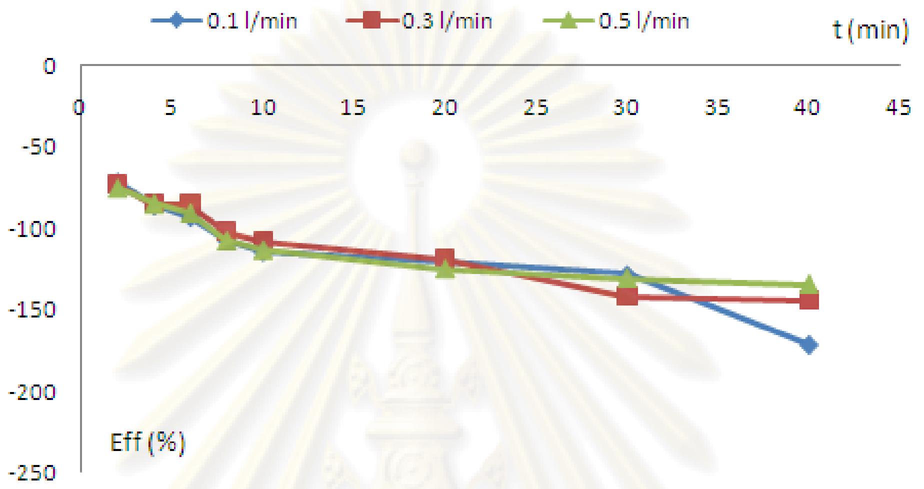


Figure 4.22 Treatment efficiency of oily emulsion with CTAB as a function of time for different air flow rates at alum concentration 25 mg/l

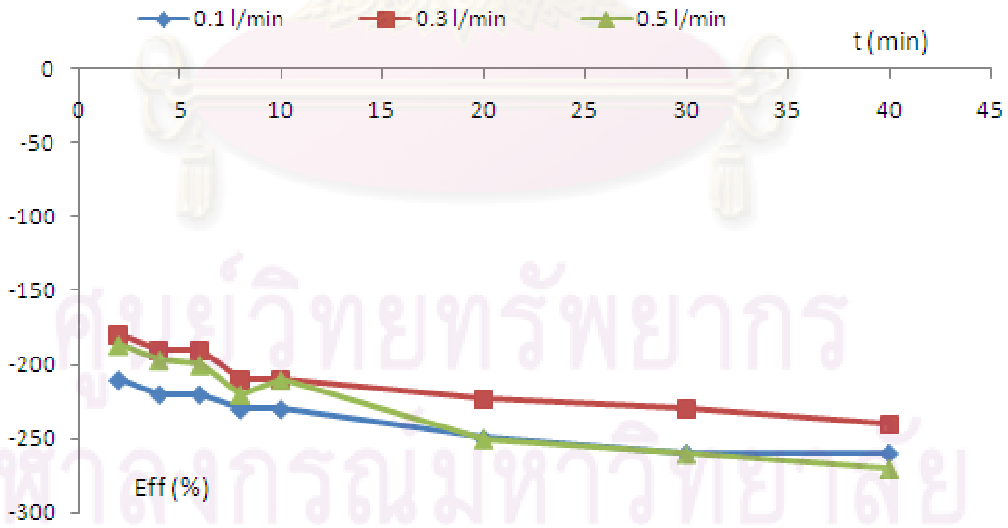


Figure 4.23 Treatment efficiency of oily emulsion with CTAB as a function of time for different air flow rates at alum concentration 200 mg/l

As shown in Figure 4.22 – 4.23, the treatment efficiency obtained with MIAF process are negative values: this indicates that the MIAF process should not be used in the case of oily emulsion with CTAB surfactant. Note that, due to treatment of oily emulsion with CTAB by alum, the positive charge of alum was difficultly adsorbed on the surface of oil droplets with cationic surfactant (positive charge). These results can be described due to the highest separation efficiency obtained with the 4μm oil droplet size as previously presented in Figure 4.6. Therefore, the small amount of oil droplets particle were remained in oily emulsion phase. This phenomenon can thus decrease the available targets for sweep floc coagulation which is the main mechanism for the treatment of this oily emulsion by coagulation-flocculation process. Moreover, concerning to lowest or negative values of Eff% compared with both IAF and coagulation processes; the remained alum dosage in the system is conscientious for these results. Note that, the values of Eff% obtained with 25 mg/l of alum are lesser than those obtained with 200 mg/l of alum: this confirms the proposed hypothesis.

Figure 4.24 and 4.25 presents the treatment efficiency of oily emulsion wastewater containing with non-ionic surfactant (Tween20) by the MIAF process as a function of time, for different air flow rates and alum concentrations (25 and 150 mg/l).

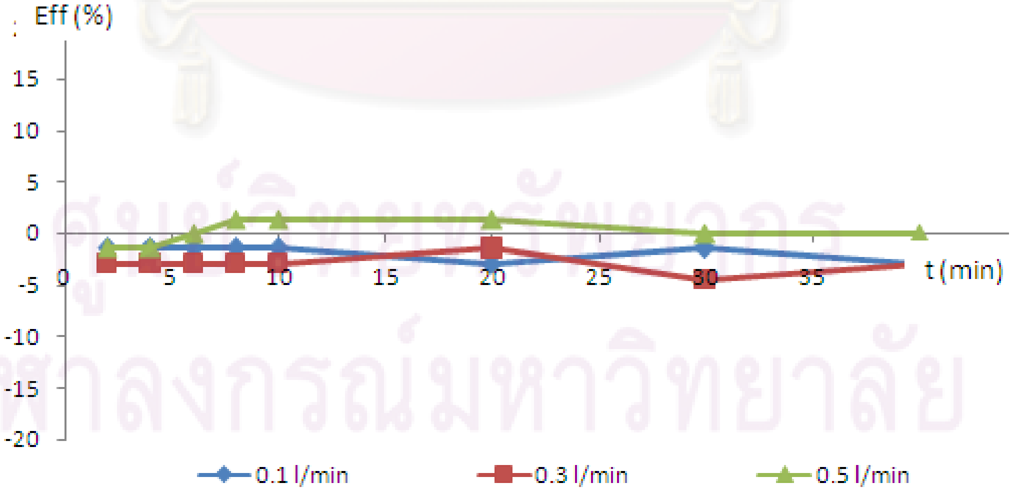


Figure 4.24 Treatment efficiency of oily emulsion with Tween20 as a function of time for different air flow rates at alum concentration 25 mg/l

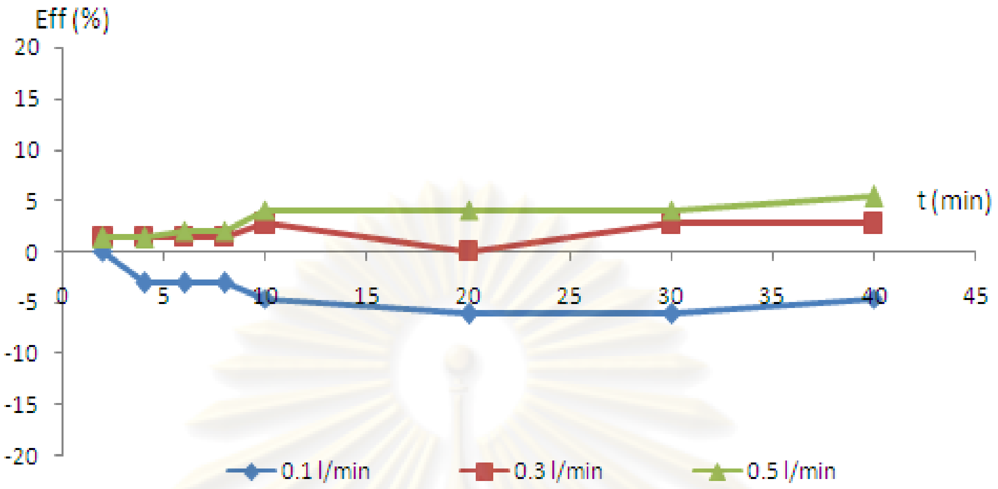


Figure 4.25 Treatment efficiency of oily emulsion with Tween20 as a function of time for different air flow rates at alum concentration 150 mg/l

According to Figure 4.24 and 4.25, it can be noted that the treatment efficiency obtained with the MIAF process are lower than those obtained with the IAF (26 %) and chemical processes (31 %). Moreover, small effect of chemical dosage (25 and 150 mg/L) can be observed: this confirms the unmatched coagulant (alum) used in this study. The drawback results obtained with the MIAF process can be explained that the biggest size of oil droplets in this case (6 µm) was separated by interacting with the generated bubble. Thus, the available targets for sweep floc coagulation mechanism were reduced and thus treatment efficiency obtained with MIAF process. Note that, the negative effect in this case is less pronounced than in the case of oily emulsion wastewater with cationic surfactant (CTAB): more targets or oil droplets remained in liquid phase due to their non-ionic charged surface and thus difficulty for oil/bubble interaction is probably responsible for these results. Moreover, from the lowest values of %Eff obtained with the MIAF process, the limitation on the treatment of this type of oily wastewater, in terms of oil/bubble attachment in flotation process and of charge destabilization in coagulation process, has to be studied and also improved.

4.4.2 Study of kinetic condition for treatment the oily emulsion wastewater containing with different surfactants (SDS, CTAB and Tween20) by the MIAF process

The goal of this part is to study the kinetic condition for treatment the oily emulsion wastewater containing with different surfactants (SDS, CTAB and Tween20) by the MIAF process. Note that, for oily emulsion with SDS was analyzed at 0 - 30 minutes for operation times, at 0.3 l/min for air flow rate (from experiment 4.4.1), and at different alum concentrations (25, 50, 100, 150, 200, 300, and 400 mg/l). Moreover, for oily emulsion wastewater with CTAB and Tween20, these studies were at 0-40 minutes for operation times, at 0.3 l/min for air flow rate, and at different alum concentrations (200 and 150 mg/l).

Figure 4.26 presents the COD values of oily emulsion with SDS by the MIAF process as a function of time at 0.3 l/min for air flow rate, for different alum concentrations.

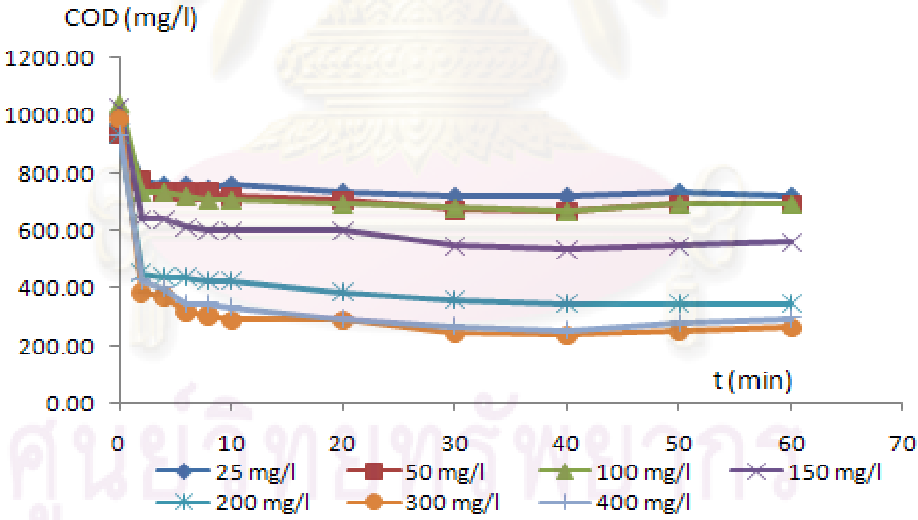


Figure 4.26 COD values of oily emulsion with SDS as a function of time for different alum concentration at 0.3 l/min for air flow rate

As shown in Figure 4.26, for whatever the alum concentrations applied in this study, three zones can be found on the variation of the treatment efficiency with operating time:

1. First zone: In this zone, it can be found that COD value decreases rapidly at the beginning stage (0-10 min) of all alum concentrations. This corresponds with the oil droplets having the available free surfaces for interacting with the generated bubbles.
2. Second zone: In this zone, the treatment efficiencies decrease slowly at 10-40 min of operation time for all alum concentrations.
3. Third zone: In this last zone, the COD values obtained experimentally started increasing due to the breaking phenomena of the oil/bubble aggregates located at the surface for long aeration time of flotation column. Therefore, it is not necessary, in practice, to operate the MIAF process with the very long aeration time: this confirm with those obtained with the IAF process.

Figure 4.27 and 4.28 presents the COD values of oily emulsion containing with CTAB and Tween20 surfactants by the MIAF process as a function of time, respectively. The air flow rate (0.3 l/min) and different alum concentrations (25, 50, 100, 150 and 200 mg/l) were applied in this part.

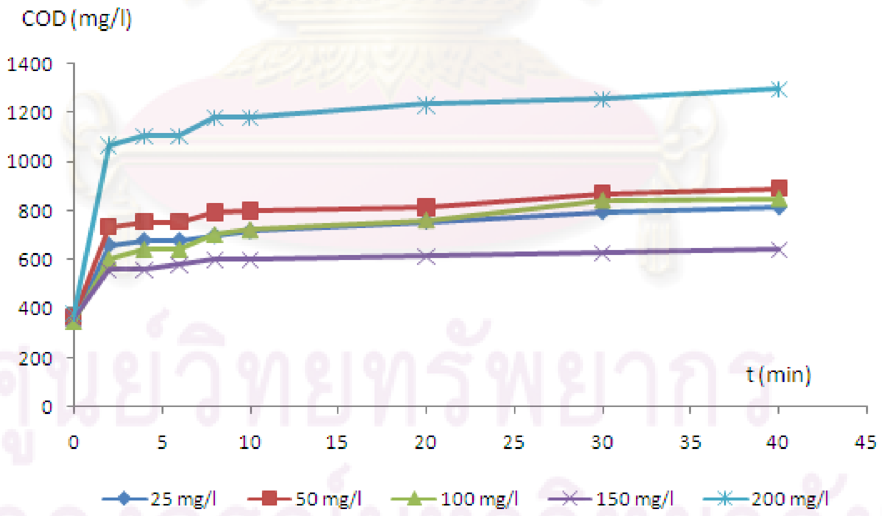


Figure 4.27 COD values of oily emulsion with CTAB as a function of time at 0.3 l/min for air flow rate, for different alum concentrations

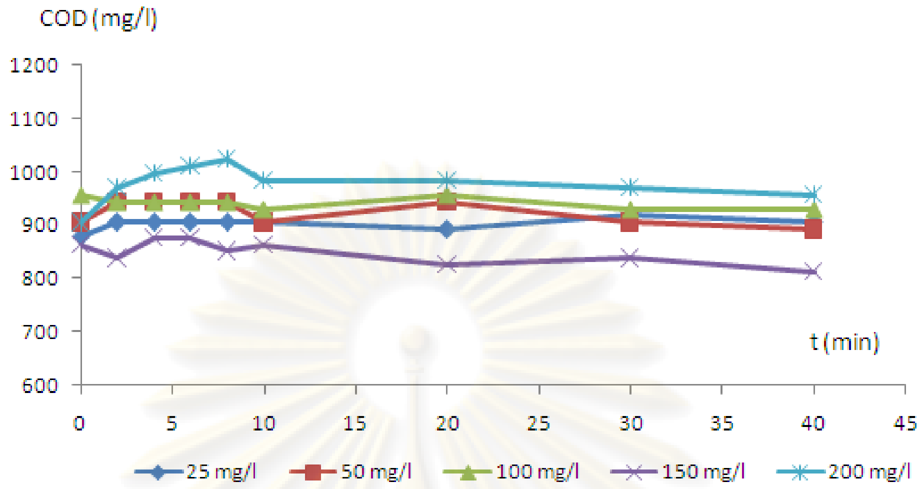


Figure 4.28 COD values of oily emulsion with Tween20 as a function of time at 0.3 l/min for air flow rate, for different alum concentrations

According to Figure 4.27, it can be noted that, whatever the alum concentrations, the COD values increase with time in the case of oily emulsion with CTAB. The reduction of oil droplet due to the flotation mechanism and thus of target for sweep floc coagulation in chemical treatment are responsible for these results as previously described. Concerning to oily emulsion with Tween 20 as shown in Figure 4.28, the indistinguishable variation of the treatment efficiencies with time can be observed: this corresponds with non-ionic surfactant chosen in this study that is quite difficult to be treated by the IAF, Coagulation-flocculation and also MIAF processes.

In order to compare the kinetic conditions obtained with different treatment methods (IAF, Coagulation-flocculation and MIAF), the experimental results in terms of COD reduction in function of time were considered. Figure 4.29 – 4.31 present the variation of COD values with time obtained with oily emulsion wastewater containing with anionic surfactant (SDS), cationic surfactant (CTAB) and non-ionic surfactant (Tween20) by the MIAF, IAF and Coagulation-flocculation processes, respectively.

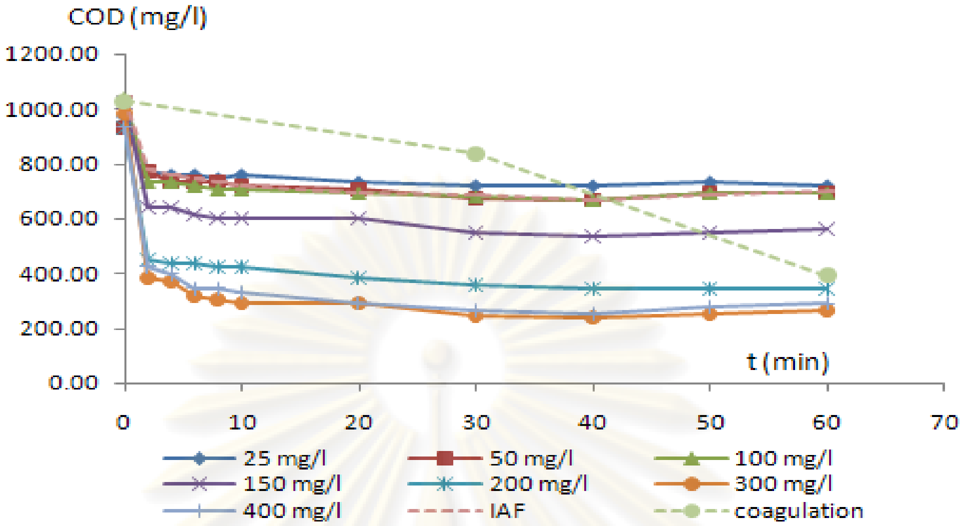


Figure 4.29 COD values of oily emulsion with SDS as a function of time for MIAF, IAF and Coagulation process

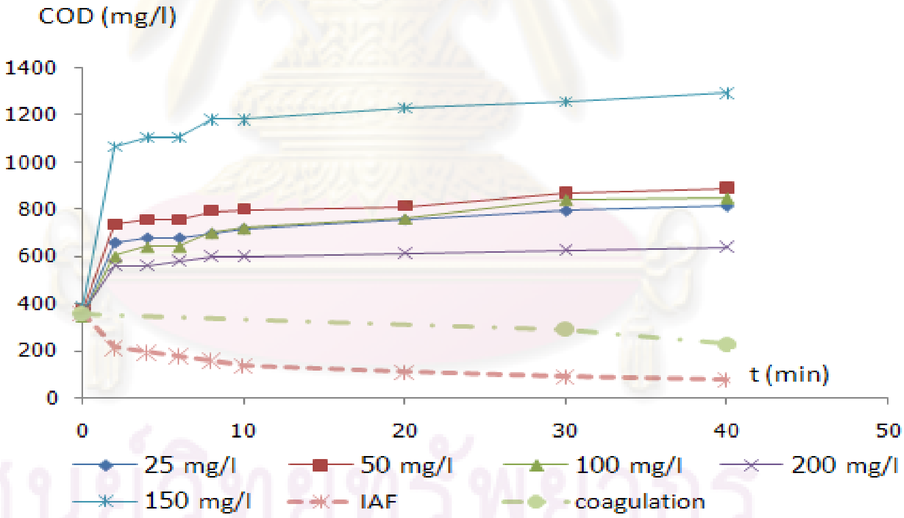


Figure 4.30 COD values of oily emulsion with CTAB as a function of time for MIAF, IAF and coagulation process

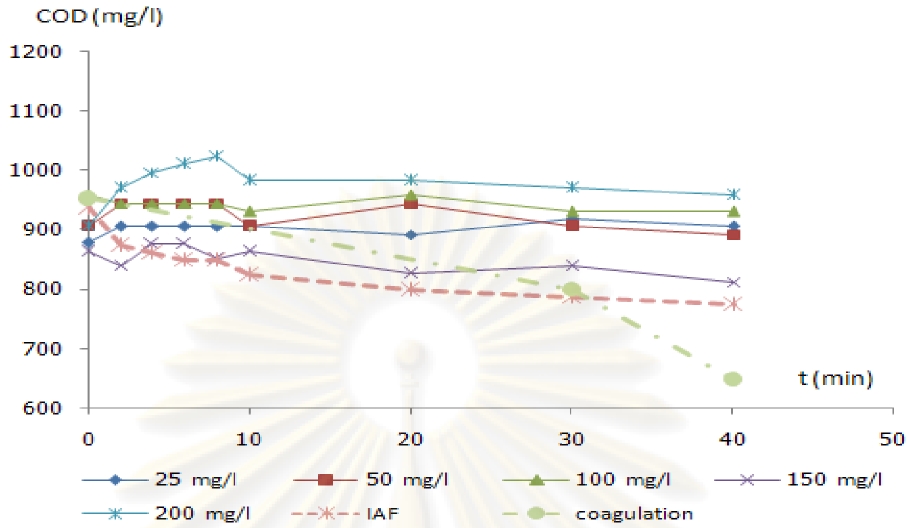


Figure 4.31 COD values of oily emulsion wastewater with Tween20 as a function of time for MIAF, IAF and coagulation process

According to obtained results as in Figure 4.29 – 4.31, it can be noted that, only in the case of anionic surfactant (SDS), the reduction of COD values with time can be clearly found due to different treatment methods applied in this study. Therefore, the analyze of kinetic for destabilizing and separating the oily emulsion wastewater by MIAF process were considered in the case of oily emulsion wastewater with SDS. Then, the reaction rate constant (log k) and reaction order (n) were determined in order to provide a better understanding on the effect of chemical dosage injected in the MIAF process. Moreover, the role of alum concentration for treating the oily emulsion with SDS by MIAF process was also analyzed in term of bubble hydrodynamic parameters and of mixing condition. Note that, the simple model can be possibly proposed for predicting the treatment efficiency obtained with MIAF process.

4.5 Determination of reaction rate constant (log k) and reaction order (n)

In this part, the reaction rate constant (log k) and reaction rate order (n) were determined in order to provide a better understanding on the effect of chemical dosages on treatment efficiencies obtained with the MIAF process. Note that, the values of log k and n can be calculated by using the Differentials method as described in Equation 4.1 and 4.2.

$$-r_A = -\frac{dC_A}{dt} = k(C)^n \tag{4.1}$$

Then, take log to both sides of equation (4.1), can be rewritten as

$$\log_{10}\left(-\frac{dC_A}{dt}\right) = \log_{10} k + n\log_{10} C_A \tag{4.2}$$

Figure 4.32 and 4.33 showed the example for determining the values of n and log k in the case of oily emulsion wastewater containing with anionic surfactant (SDS) at 0.3 l/min for IAF process. Firstly, the value of $-\frac{dC}{dt}$ or slope from graph of the variation of COD with time was determined as shown in Figure 4.32.

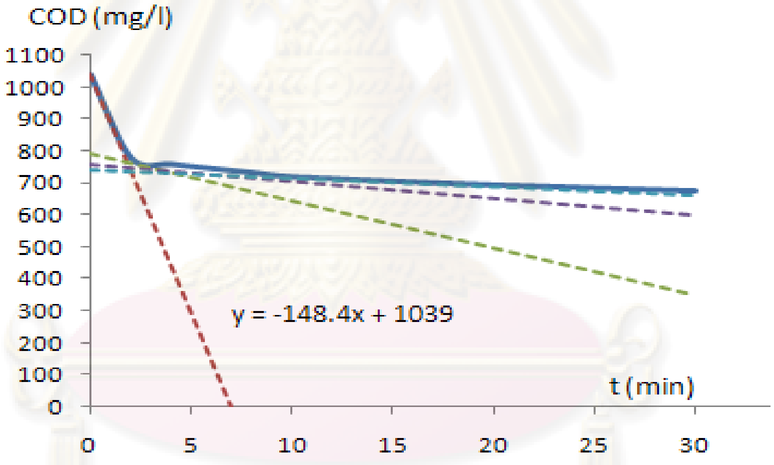


Figure 4.32 An example to find $-\frac{dC}{dt}$ (slope) for treatment oily emulsion wastewater with SDS at 0.3 l/min for air flowrate of IAF process

From Figure 4.32 obtained linear equation y=-148.4x +1039, we can know that $-\frac{dC}{dt}$ = -148.4. Then, take log to $-\frac{dC}{dt}$ follow as equation 4.2 and plot graph between log $-\frac{dC}{dt}$ and log C for determining the values of n and log k related with the slope and intersection, respectively, as shown in Figure 4.33.

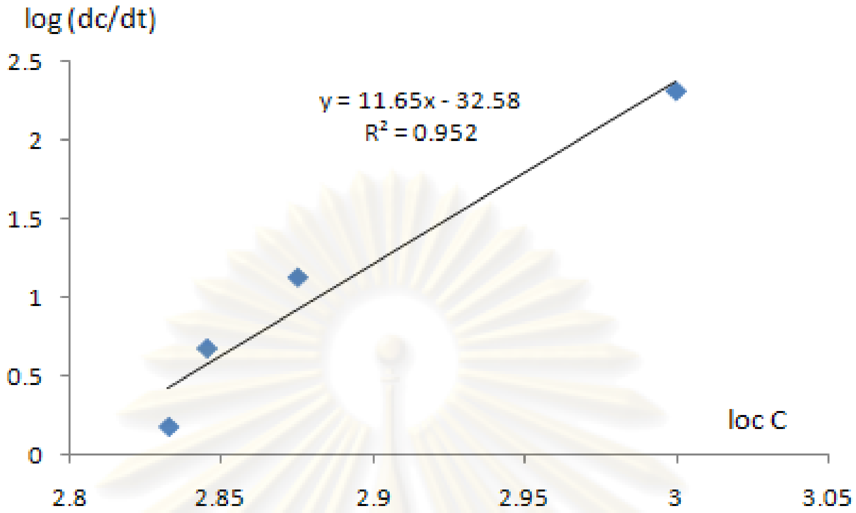


Figure 4.33 An example to find n and log k for treatment oily emulsion wastewater with SDS at 0.3 l/min for air flowrate of IAF process

From Figure 4.33, the obtained linear equation (y = 11.65x – 32.58) can provide the values of n = 11.65 and log k = - 32.58. Note that, this differential method were applied for different operating conditions of the MIAF process. The calculated n and log k values were presented as in Figure 4.34 and 4.35, respectively. Figure 4.34 shows the relation between the reaction rate order (n) and the alum concentrations obtained with the IAF and MIAF processes, for different gas flow rates (0.025, 0.1, 0.3, 0.5 and 0.7 l/min).

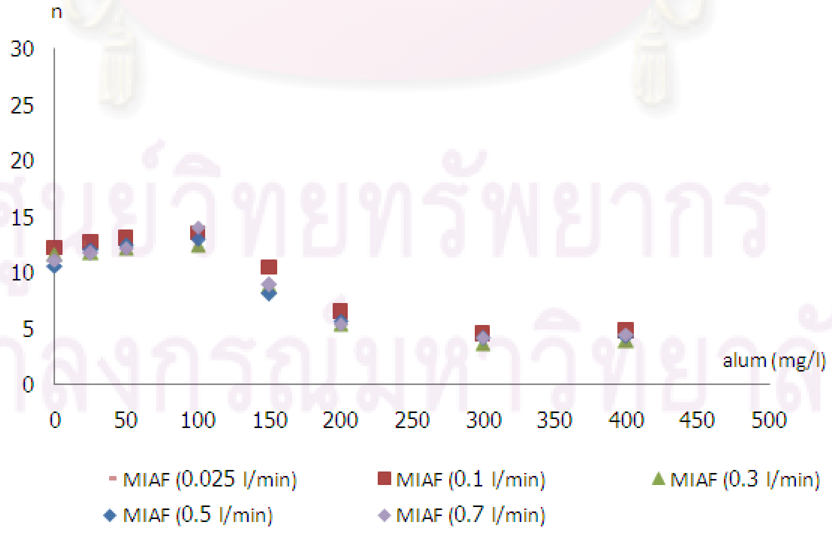


Figure 4.34 Reaction rate order (n) versus concentration of alum for IAF and MIAF processes

As shown in Figure 4.34, the reaction rate order (n) varied between 4 and 14 while concentration of alum ranged between 0 and 400 mg/l. It can be found that the values of n were increased at low concentration of alum (0 - 100 mg/l) and then decreased at higher alum concentration (100 – 300 mg/l), and finally remained roughly constant at alum concentrations greater than 300 mg/l for whatever the air flow rates applied in the MIAF process. Moreover, there is a little effect of air flow rate for n value: it can be stated that the variation of this n value should be depend only on the alum concentration applied. Due to the comparison between the values of n and Eff%, it can be noted that the increase of n value can reduce the treatment efficiency. Therefore, the application of chemical dosage and air flow rate in order to obtain the highest n value, it should not be the proper method for improving the reaction rate (R) as in equation 4.1 for treatment oily emulsion wastewater by MIAF process.

Figure 4.35 shows the relation between the reaction rate constant (log k) and the alum concentrations obtained with the IAF and MIAF processes, for different air flow rates (0.025, 0.1, 0.3, 0.5 and 0.7 l/min).

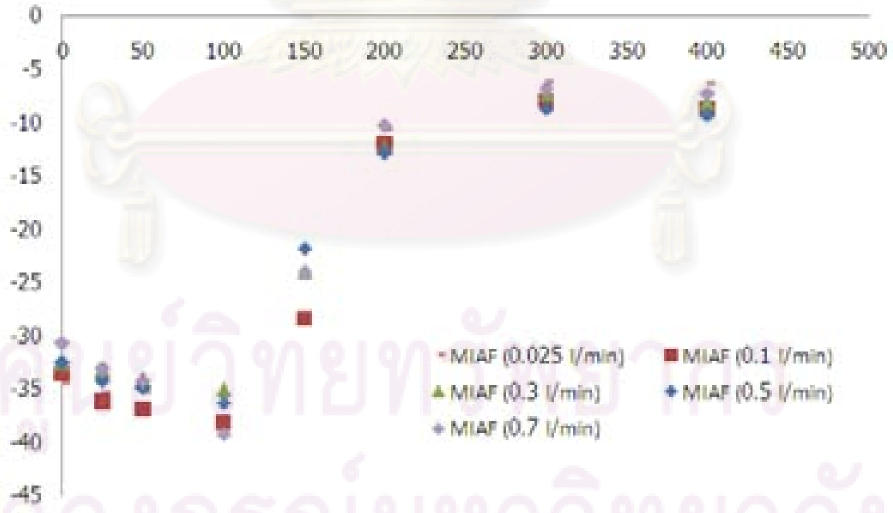


Figure 4.35 Reaction rate constant (log k) versus concentration of alum for IAF and MIAF processes

According to Figure 4.35, the reaction rate constants (log k) vary between -35 and -6 while alum concentrations range between 0 and 400 mg/l. It can be found that the reaction rate constant (log k) were decreased at low concentration of alum (0 - 100 mg/l) and then increased at higher alum concentration (100 – 300 mg/l), and finally remained roughly constant at alum concentrations greater than 300 mg/l, for whatever the air flow rates. From the obtained results, the log k values correspond with the treatment efficiency as presented in Figure 4.21 (highest log k values can provide the maximum Eff% value). Moreover, the effect of air flow rate injected in the flotation column on the log k values is more pronounced than that on the n value. Thus, it can be note that the reaction rate constant (log k) was related with the air flow rate applied for MIAF process for chemical mixing and oil phase separating from wastewater.

In fact, it can be found that the variation of log k values with alum concentrations was opposite as compared with those obtained with the n values (Figure 4.34). Moreover, due to the increase of alum concentration, the values of n and log k seem to be compensated with each other. Therefore, the suitable chemical dosage that provides the proper n and log k values are necessary to obtain the highest removal efficiency. The comparison of reaction rate order (n), reaction rate constant (log k) and treatment efficiency for treating the oily emulsion wastewater containing with anionic surfactant (SDS) by MIAF process can be summarized as in Table 4.5

Table 4.5 Reaction rate order (n), Reaction rate constant (log k) and Treatment efficiency of oily emulsion wastewater with SDS by MIAF process

Surfactant	Alum dosage (mg/l)	Treatment Efficiency (%)	N	Log k
Anionic surfactant	25	26	11.81	-33.27
	50	28	12.19	-34.15
	100	35	12.51	-35.12
	150	47	8.82	-21.00
	200	62	5.38	-10.43
	300	75	3.64	-6.36
	400	72	3.94	-6.20

4.5.1 Proposed model for predicting the treatment efficiency obtained with MIAF process

Regarding their importance, the reaction rate constant (log k) and the reaction rate order (n) were chosen, in this work, in order to propose the simple model for predicting the treatment efficiency obtained with MIAF process. The following correlation can be expressed as:

$$\%Eff_{Model} = \frac{\overline{n}}{\overline{K}} \times \%Eff_{IAF} = \frac{n_{MIAF} / n_{IAF}}{\log k_{MIAF} / \log k_{IAF}} \times \%Eff_{IAF} \qquad (4.3)$$

Where: $\%Eff_{model}$ = Treatment efficiency of MIAF process from calculation (%)
$\%Eff_{IAF}$ = Treatment efficiency of IAF process from experiment (%)
$\overline{n}$ = Ratio between n obtained with MIAF and IAF process
$\overline{K}$ = Ratio between log k obtained with MIAF and IAF process

Note that, the values of n_{IAF}, log k_{IAF} and $\%Eff_{IAF}$ were applied in this proposed prediction model in order to take into account the results obtained experimentally with the IAF process, as the basic values without the effect of chemical dosage.

In Figure 4.36, the treatment efficiencies calculated by the predicting correlation (Eff_{mod}) are compared with those obtained with the experimental method (Eff_{exp}) for the MIAF process with different air flow rates (0.025, 0.1, 0.3, 0.5 and 0.7 l/min) and alum concentrations (25, 50,100, 150, 200, 300 and 400 mg/L).

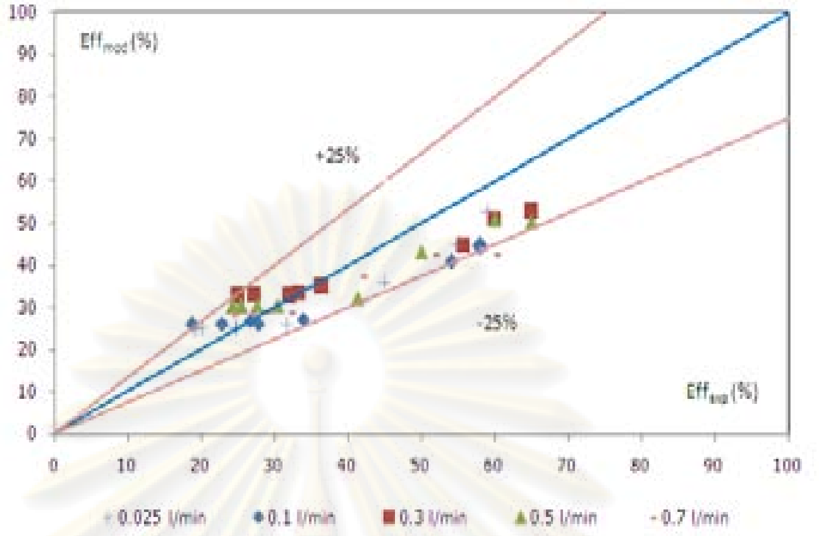


Figure 4.36 Comparison of experimental and predicted the treatment efficiencies

Concerning to Figure 4.36, the relatively good agreement between the experimental and the predicted treatment efficiencies by using MIAF process for the lubricant oily emulsion wastewater containing with anionic surfactant (SDS) is obtained (average difference about ±25%). However, more experimental data are necessary to accurately propose and also validate these correlations. In the future, different types of coagulants and diffusers should be tested to extend the operating condition ranges. Moreover, this simple correlation can be possibly used as the tools in order to choose the proper chemical dosage required in MIAF process.

A comparison between experimental and the predicted treatment efficiency (%) of oil emulsion wastewater with SDS can be summarized as in Table 4.6.

From the result known that, there is the effect of air flow rate to treatment of oily emulsion both with IAF and MIAF process, and also effect to reaction rate (log k). Therefore, to provide the better understanding and chosen the optimal air flow rate (Q_g) for treatment of oily emulsion by flotation process. Next part, the bubble hydrodynamic parameters (bubble size, bubble formation frequency and their rising velocity and interfacial area) and also the mixing parameters (velocity gradient) are thus the important factors were studied.

Table 4.6 Experimental and the prediction removal efficiency (%) of oily emulsion wastewater with SDS by IAF and MIAF process

Surfactant	Alum dosage (mg/l)	Experimental Removal Efficiency (%)	Prediction Removal Efficiency (%)	Difference (%)
SDS	0 (IAF)	33.33	33.33	0
	25	26.03	33.08	-7.05
	50	27.86	33.27	-5.41
	100	34.62	33.20	1.41
	150	46.75	39.18	7.56
	200	61.43	48.08	13.34
	300	75.00	53.40	21.59
	400	71.42	59.32	11.67

4.6 Bubble Hydrodynamic and Mixing Parameters for IAF and MIAF process

In this part, the bubble hydrodynamic parameters (bubble size, bubble formation frequency and their rising velocity and interfacial area) and also the mixing parameters (velocity gradient) were studied in order to provide the better understanding on the variation of treatment efficiencies obtained with different air flow rates and chemical dosage in the IAF and MIAF processes.

4.6.1 Bubble diameter (D_B)

Figure 4.37 shows the relation between the generated bubble diameter (D_B) and the air flow rate obtained with the IAF process for treating the oily emulsion wastewaters containing with different surfactants (SDS, CTAB and Tween20).

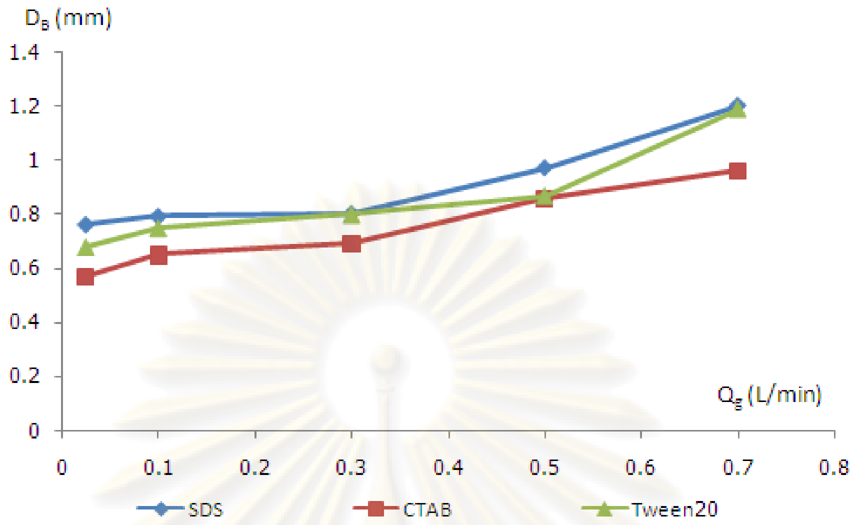


Figure 4.37 Bubble size versus air flow rate for the IAF processes

As shown in Figure 4.37, the bubble diameters varied between 0.5 and 1.2 mm while air flow rates were changed between 0.025 and 0.7 ml/s. Moreover, the bubble sizes were roughly constant at low air flow rate and then increase at high air flow rates applied in the IAF processes. As proposed by Painmananakul *et al.* (2005), the differences in terms of bubble diameters are directly linked to static surface tension ($\sigma_{L\ CTAB} < \sigma_{L\ NON} \approx \sigma_{L\ SDS}$) as previously presented in Figure 4.1. However, at higher air flow rate, the bubble diameter is no longer controlled by the forced balance at detachment, but rather by the power dissipated in the liquid, conditioning the bubble break up and coalescence phenomena. Moreover, the variation of bubble diameter (D_B) and the air flow rate obtained with different alum concentrations for the MIAF processes will be then shown in Figure 4.38. Note that, only oily emulsion wastewaters containing with anionic surfactant (SDS) were reported, in this stage, because high treatment efficiencies obtained with MIAF process can be observed. Therefore, it is interesting to study, not only the effect of chemical dosage as in previous part, but also the effect of bubble hydrodynamic parameters related with different air flow rates.

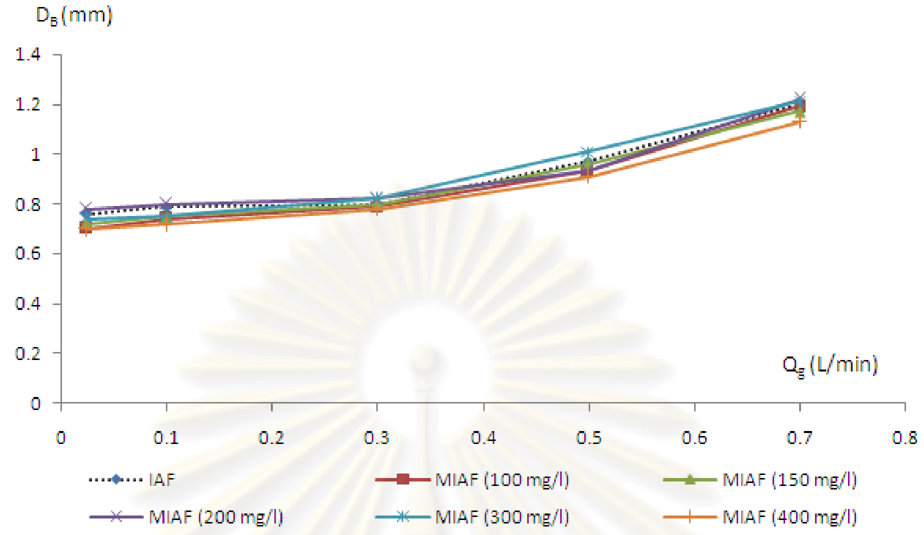


Figure 4.38 Bubble size versus air flow rate of the IAF and MIAF processes for treatment oily emulsion wastewater with SDS

As shown in Figure 4.38, it can be stated that the bubble sizes obtained with the treatment oily emulsion with SDS by MIAF process, which contains the liquid phase contaminated with different alum concentrations, are closed to those obtained with IAF process. Moreover, in presence of different alum concentrations, even in the large quantities, there is little effect on the bubble size generated in the flotation process: the surfactant presence in liquid phase is probably responsible for these results.

4.6.2 Interfacial Area (a) and Velocity Gradient (G)

Over this bubble diameter range, the terminal rising bubble velocities (obtained experimentally) varied between 5.5 and 10.5 cm.s^{-1} and were within the range of the U_B values of Grace and Wairegi (1986) corresponding to the contaminated systems. Moreover, whatever the operating conditions, the bubble formation frequencies vary inversely with the bubble diameters. The values of f_B obtained vary between 1600 and 25000 s^{-1}for air flow rates varying between 0.025 – 0.7 l/min.

By using the experimental results of the bubble sizes (D_B), the bubble formation frequencies (f_B), and their rising velocities (U_B), the local interfacial area (a) can be determined as shown in equation 4.4. Figure 4.39 shows the relation between the interfacial area (a) and the air flow rate for the IAF.

$$a = N_B \times \frac{S_B}{V_{total}} = f_B \times \frac{H_L}{U_B} \times \frac{\pi D_B^2}{AH_L + N_B V_B} \tag{4.4}$$

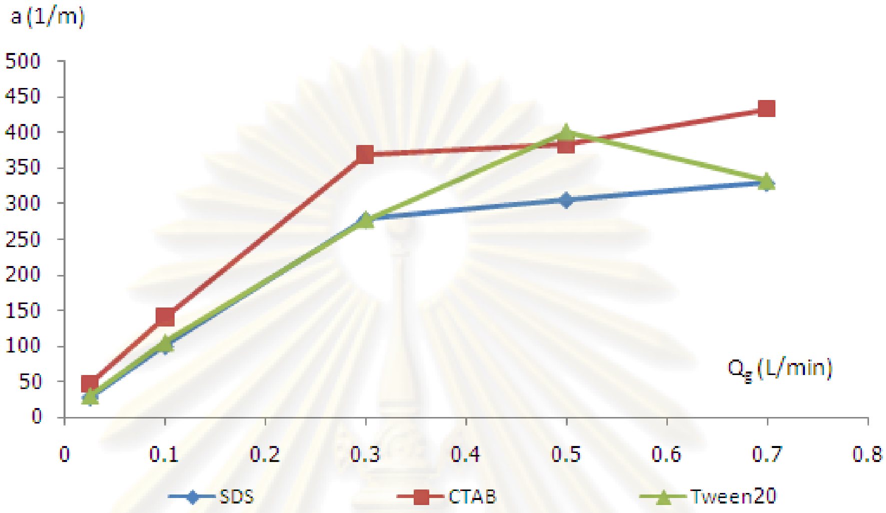


Figure 4.39 Interfacial area versus air flow rate for the IAF processes

As shown in Figure 4.39, the interfacial areas (a) vary between 30 and 430 m^{-1} while air flow rates can alter between 0.025 and 0.7 l/min. It can be noted that the obtained values are corresponded with the number of bubbles generated and thus the available bubble surface for interacting with oil droplets presence in the liquid phase. Therefore, these values of a roughly increase with the air flow rate injected into the flotation column and then reach to the approximate constant values. Except in the case of Tween20, the obtained a value was start decreasing at Q_G = 0.5 l/min due to the large bubble size generated, and thus small bubble formation frequency obtained in this zone. These results confirm that it is not necessary to operate the flotation process at high Q_G values for augmenting the interaction between bubbles and oil droplets. In the case of MIAF process applied in these experiments, the relation between the interfacial area (a) and the air flow rate with different alum dosage for treatment oily emulsion wastewater with SDS can be shown as in Figure 4.40.

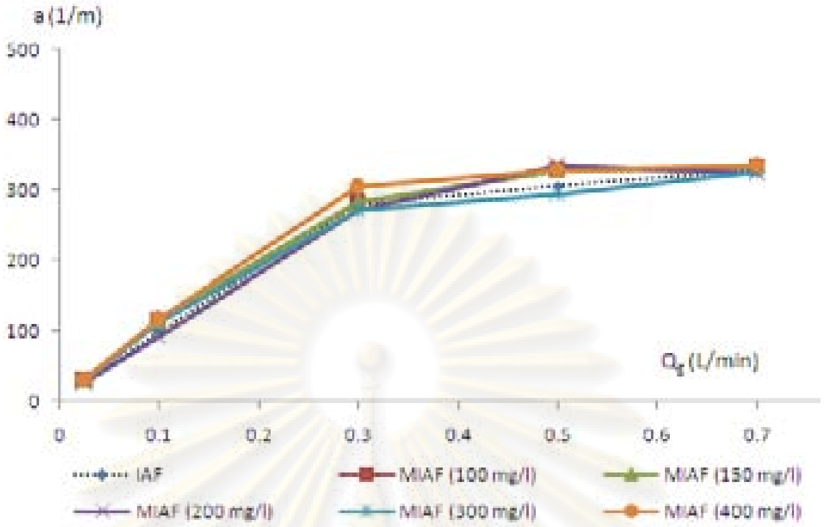


Figure 4.40 Interfacial area versus air flow rate of the IAF and MIAF processes for treatment oily emulsion wastewater with SDS

According to Figure 4.40, it can be stated that the interfacial area obtained with the MIAF process are close to those obtained with the IAF process. There is small effect of alum concentrations on the interfacial areas as same as observed previously in the case of bubble sizes. Note that, the values of (a) are directly linked to the bubble diameters, bubble rising velocities and their formation frequencies. Therefore, the addition of alum as coagulant, in this study, cannot provide some modification of bubble hydrodynamic parameters obtained in floatation column: the difference in treatment efficiencies should be mostly related with the chemical dosage technique applied.

Moreover, it can be expressed that not only the interfacial area (a) have been proven to be the important parameter for controlling the flotation process efficiency and operation cost, but also the velocity gradient (G) should be taken into account in order to analyze the mixing condition related with the air flow rate injected in flotation column. Note that, the calculation of velocity gradient (G) with air flow rate can be presented in Equation 4.5 and 4.6 (Reynolds and Richards, 1996) and was shown in Figure 4.41.

$$P = C_1 Q_g \log\left[\frac{(h+C_2)}{C_2}\right] \tag{4.5}$$

$$G = \left[\frac{P}{uV}\right]^{\frac{1}{2}} \tag{4.6}$$

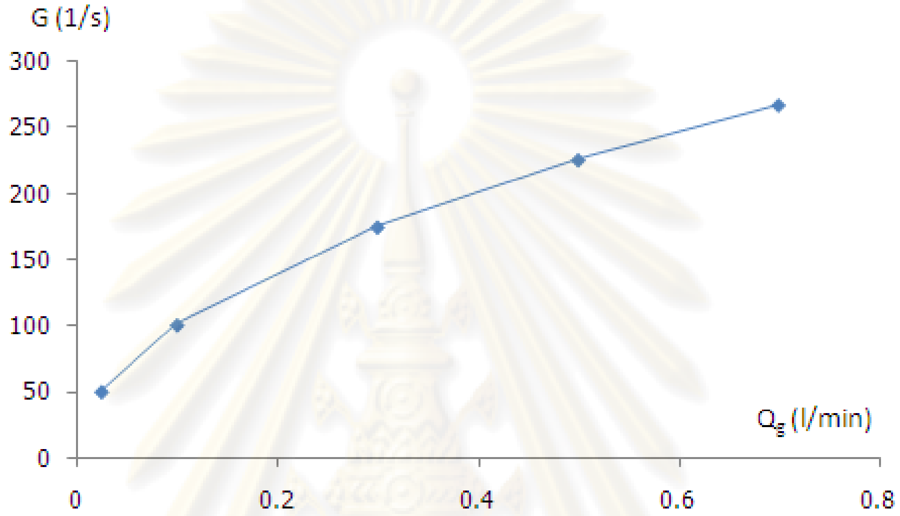


Figure 4.41 Velocity gradient versus air flow rate of the IAF and MIAF processes

Concerning to Figure 4.41, whatever the flotation system (IAF and MIAF), the values of G increase linearly with the air flow rate. Their values vary between 50 and 267s^{-1} whereas the air flow rates change between 0.025 and 0.7 l/min: more turbulent mixing condition occurs at higher air flow rate. Therefore, these results confirm the drawback due to the operation of flotation process at high Q_G values: reduction of available bubble surface for interacting with oil droplets and also more turbulent condition that destroyed the oil-bubble aggregates can be achieved.

In order to take into account the available bubble surface and also the mixing condition occurred in the flotation process, the ratio of interfacial area (a) to velocity gradient (G) was determined and presented in Figure 4.42 and 4.43 for IAF and MIAF for the treatment oily emulsion wastewater containing with anionic surfactant (SDS), respectively.

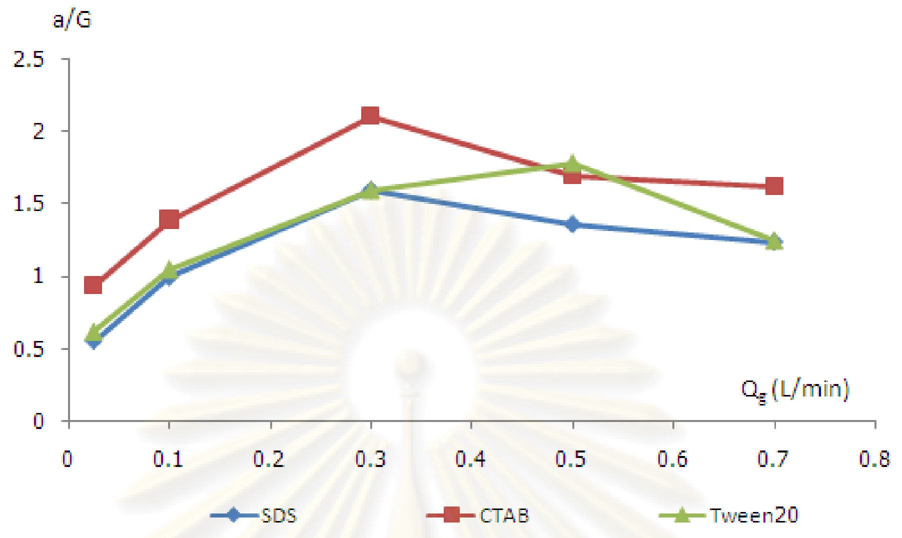


Figure 4.42 Ratio of interfacial area to velocity gradient (a/G) versus air flow rate for treating the oily emulsion wastewater with SDS by IAF and MIAF processes

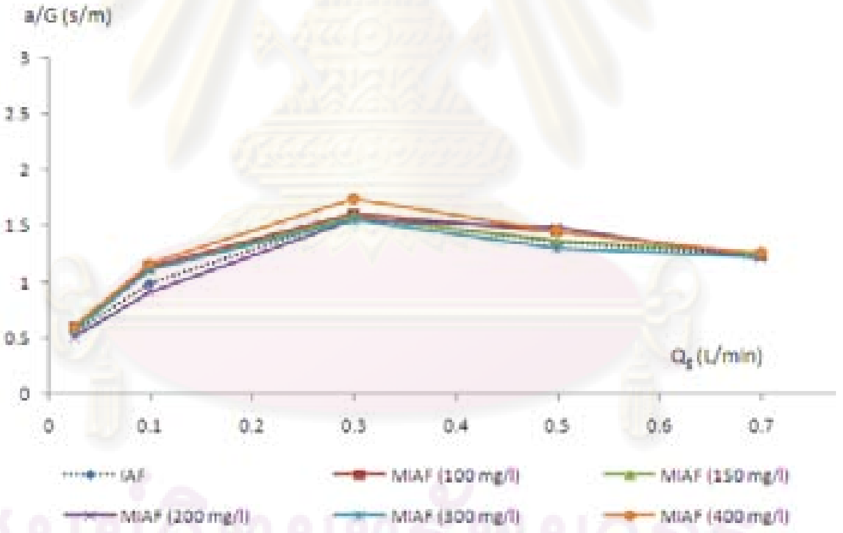


Figure 4.43 Ratio of interfacial area to velocity gradient (a/G) versus air flow rate for treating the oily emulsion wastewater with SDS by IAF and MIAF processes

As shown in Figure 4.42 and 4.43, the ratios of interfacial area to velocity gradient vary between 0.5 and 2.1 s^{-1} while air flow rates can change between 0.025 and 0.7 l/min. Moreover, it can be found that the maximum of the a/G values can be found at the air flow rate equal to 0.3 l/min for oily emulsion with SDS and CTAB and at the air flow rate equal to 0.5 l/min for oily emulsion with Tween20 which correspond to the Q_g values that provide the highest treatment efficiency obtained with both IAF and MIAF processes

Therefore, the a/G ratio can be used in order to select the optimal operating condition of the flotation process. Note that, the optimal chosen a/G ratio will relate to the air flow rates that generate, not only high interacting opportunity/surface between oil droplets and bubbles, but also proper mixing condition between generated bubbles, oil droplets and applied chemical agents in the flotation processes (IAF and MIAF), and thus the highest oily emulsion wastewater treatment efficiency.

4.6.3 Effect of the a/G ratio on the treatment efficiency

In this part, the relation between the treatment efficiency (%Eff) and the ratio of interfacial area to velocity gradient (a/G) for treatment of oily emulsion wastewater by IAF process and also of oily emulsion wastewater containing with SDS by MIAF process are shown in Figure 4.44 and 4.45, respectively.

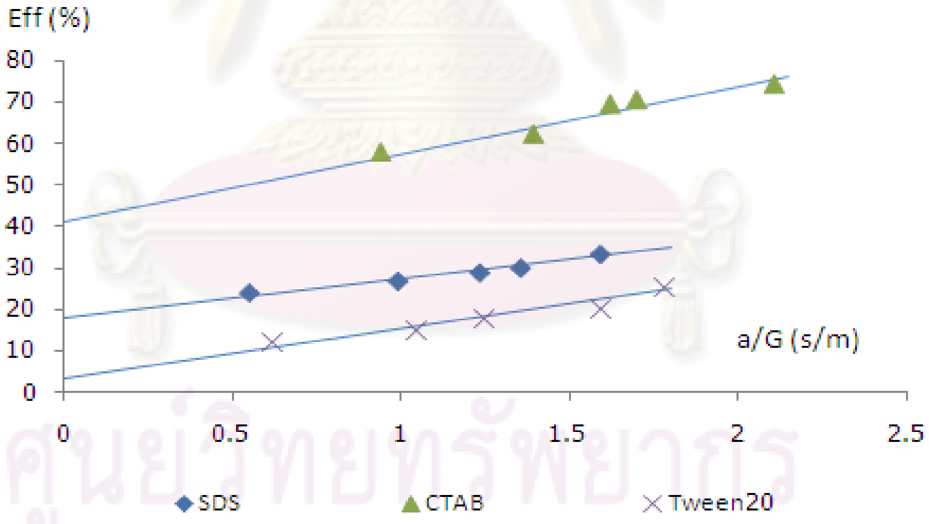


Figure 4.44 Treatment efficiency versus ratio of interfacial area to velocity gradient for the IAF processes

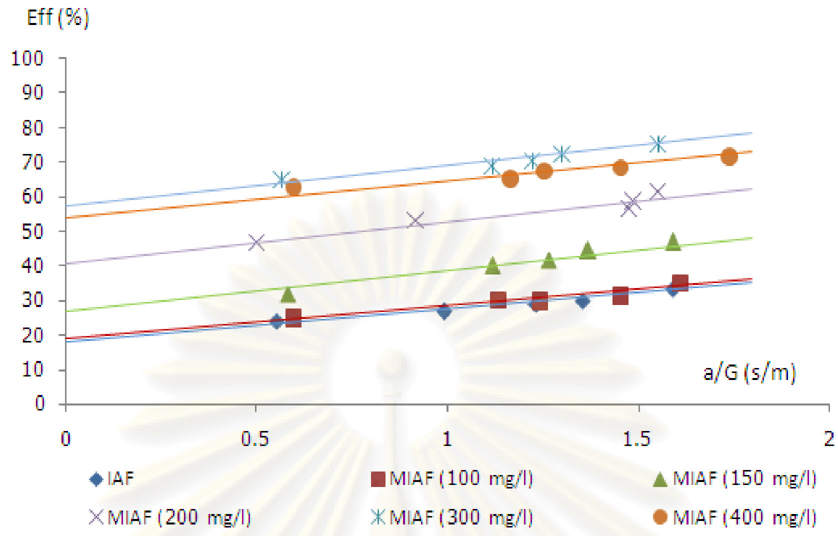


Figure 4.45 Treatment efficiency versus ratio of interfacial area to velocity gradient for the IAF and MIAF processes for treatment oily emulsion wastewater with SDS

As presented in Figure 4.44 and 4.45, it can be found that the treatment efficiencies obtained with IAF and MIAF processes increase linearly with the a/G values. However, at the same a/G value, the differences of treatment efficiencies obtained with the IAF and MIAF processes can be observed. These confirm that, not only the interacting and mixing phenomena control the overall treatment efficiency, but also the chemical dosages applied in the MIAF process can affect the associated performances. Moreover, the values of slope, intersection and R-squared related with these linear equations obtained with the IAF and MIAF processes can be summarized as in Table 4.7.

According to Table 4.7, the treatment efficiencies relate with the values of slope (S) for different oily wastewaters: highest treatment efficiencies (75%) can be obtained with the highest S values (15.27) in the case of IAF process for oily emulsion with CTAB. These correspond with the suitable operating conditions in terms of oil droplet size, of charge interaction between bubble and oil droplet and of amount of added surfactant concentration as previously described. Therefore, even the similar bubble hydrodynamic and mixing condition (a/G values) applied in flotation column; the difference of %Eff can be obtained due to the unmatched bubble and oil droplet mechanism occurred.

Table 4.7 Constants obtained with linear equation for the IAF and MIAF processes

Oily emulsion wastewater	**Flotation System**	**Eff (%)**	**Slope (S)**	**Intersection (I)**	**R^2**	**Decantation (%)**
SDS	IAF	33	8.816	18.42	0.929	0
	MIAF (100 mg/l)	35	8.940	19.09	0.928	14.18
	MIAF (150 mg/l)	47	9.150	22.84	0.936	27.2
	MIAF (200 mg/l)	62	10.700	40.79	0.939	36.8
	MIAF (300 mg/l)	75	11.360	58.35	0.961	48.8
	MIAF (400 mg/l)	72	11.100	57.25	0.992	61.8
CTAB	IAF	75	15.270	43.24	0.942	7.78
Tween20	IAF	25	10.590	4.54	0.939	2.12

For the MIAF process for treating the oily emulsion wastewater with anionic surfactant (SDS), the values of slope (S) obtained increase with the alum concentration and were greater than those obtained with the IAF process. Note that, these values are then closed to each other at high alum concentration applied in process: small effect of alum concentrations, as shown previously in terms of bubble hydrodynamic parameters and interfacial area, can be observed in this zone. Thus, it can be stated that, in order to obtain the elevated influence of chemical dosages added into the MIAF process, the suitable chemical dosage and also a/G value should be chosen. This corresponds with the suitable mixing condition required for destabilizing the stabilized oily emulsion and forming the larger oil droplets in the coagulation-flocculation processes, and finally separating the generated aggregates to the top of column in flotation process. Moreover, the values of intersection points (I), obtained with the linear equations for IAF and MIAF processes, are closed to the treatment efficiencies obtained with the decantation process with adding the chemical agents: the average difference about ± 10% were observed. Concerning to the these results, it can be noted that the chemical dosage method into the decantation process (without mixing or flowing condition) can be possibly applied in order to firstly investigate the chemical treatment ability for applying in the MIAF process. Because, due to the linear equation, the high treatment efficiencies were based on the slope values (S) and also the optimal intersection points (I).

In conclusion, the appropriate a/G ratio and chemical dosage have been proven to be very important parameter for acquiring the superlative treatment efficiency from the MIAF process. The effect of a/G ratio and chemical dosage can be related with the slope (S) and the intersection points (I), respectively. Moreover, regarding their importance, the linear relation between the treatment efficiency and the a/G ratio obtained experimentally with IAF and MIAF processes, are applied in order to predict the overall treatment efficiencies. The following correlation can be expressed as:

$$\%Eff = \frac{a}{G}(slope) + b \qquad (4.7)$$

In addition, based on the proposed prediction model for predicting the treatment efficiency as in equation 4.3, the effect of chemical dosage has been taken into account. Therefore, it is interesting to combine these two equations as:

$$\%Eff_{MIAF} = \left(\frac{\bar{n}}{\bar{K}}\right) \times \left(\frac{a}{G}(slope) + b\right)_{IAF} \qquad (4.8)$$

Note that, this equation can be used to propose the prediction model for predicting, not only the effect of chemical dosage in terms of reaction rate constant (Log k) and order (n), but also the effect of bubble hydrodynamic parameters related with different air flow rates in term of the ratio of interfacial area and velocity gradient (a/G). In future, more experimental data are necessary to accurately propose and also validate these correlations. The different types of coagulants and air diffusers should be studied to extend the operating condition ranges.

4.7 Power consumption and Cost Analysis

The objective of this part is to analyze the power consumption and also the associated operation cost required for the flotation (IAF and MIAF) processes. Note that, in the case of a air–liquid reactor equipped with air diffuser, the total specific power consumption (P_G) can be related to the total gas pressure drop according to the following equation (Bouaifi *et al.*, 2001);

$$P_G = Q \times (\rho_L g H_L + \Delta P) \tag{4.9}$$

Where: Q_G and V_L are the applied air flow rate at operating temperature and pressure (m^3/s) and liquid phase volume (m^3), respectively. ρ_L is liquid density (kg/m^3) and g is acceleration due to gravity (m/s^2). Moreover, H_L is liquid height (m), and ΔP is pressure drop measured experimentally in this study (Pa). Moreover, in the case of rapid and slow mixing mechanism in jar test experiments, the power consumption (P) is given by the following equation (Reynold and Richard, 1996):

$$P = K_T n^3 D_i^5 \rho \tag{4.10}$$

Where: K_T and D_i are the impeller constants (2.25) and the impeller diameter (0.075 m), respectively, n is the rotational speed equal to 1.67 rps for rapid mixing and to 0.5 rps for slow mixing. Moreover, is. Therefore, by using the above equations, the power consumption related with different oily wastewater treatment techniques can be calculated and summarized as in Table 4.8.

Table 4.8 Power consumption required for IAF, MIAF, and coagulation processes.

Process	Qg (L/min)	ΔP (pa)	P_G (Watt)
IAF and MIAF	0.025	18500	0.01424
	0.1	19000	0.05780
	0.3	20000	0.17842
	0.5	20750	0.30362
	0.7	21000	0.42799
Process	**P for Rapid Mixing (Watt)**		**P for Slow Mixing (Watt)**
Coagulation	0.02470		0.00067

According to Table 4.8, concerning to the IAF and MIAF processes, the power consumptions were increased with air flow rate. These values are greater than those required for the rapid and slow mixing in coagulation-flocculation process, even at the best operating air flow rate (Q_G = 0.3 l/min). Therefore, the selection of suitable air flow rate and thus a/G ratio is essential to be applied in order to achieve the high treatment efficiency and also save the related energy consumption. Based on the calculated power consumption, the associated operation cost obtained with different treatment techniques (IAF, MIAF and coagulation processes) can be summarized as in Table 4.9. Note that, the best operating conditions related with different were applied with the electric power cost (3.6246 Baht/Unit) in this calculation (PEA, 2009). Moreover, the chemical cost (alum) used in this work is 1000 Baht/kg.

Table 4.9 Operation cost from IAF, MIAF and coagulation processes

Process	Efficiency %	Cost of Power (Baht) per m^3	Cost of Chemical (Baht) per m^3	Total Cost (Baht) per m^3
IAF process for treating the oily emulsion wastewater				
SDS	33.33	0.129343464	-	0.129343464
CTAB	74.44	0.129343464	-	0.129343464
Tween20	25.00	0.220103189	-	0.220103189
Coagulation-flocculation process for treating the oily emulsion wastewater				
SDS (400 mg/L)	61.82	0.00339376	400	400.0034
CTAB (200 mg/L)	59.77	0.00339376	200	200.0034
Tween20 (150 mg/L)	37.66	0.00339376	150	150.0034
MIAF process for treating the oily emulsion wastewater with anionic surfactant (SDS)				
150 mg/l of Alum	46.75	0.129343464	150	150.1293
200 mg/l of Alum	61.43	0.129343464	200	200.1293
300 mg/l of Alum	75.00	0.129343464	300	300.1293
400 mg/l of Alum	71.43	0.129343464	400	400.1293

According to Table 4.9, the operation costs associated to IAF process are significant lower than those associated to the other process. In the case of oily emulsion with CTAB, the IAF process should be applied because of the suitable sizes between oil droplets (4 µm) and generated bubble (0.69 mm) and thus high treatment efficiency. Regarding to overall operation cost, it can be expressed that the chemical cost is the most important factor controlling the overall cost. Moreover, the chemical cost required in the coagulation-flocculation process can be summarized as: $Cost_{SDS} > Cost_{CTAB} > Cost_{Tween20}$. The stabilized oil droplet size and charge due to different surfactants applied were the key parameter that controls the amount of chemical dosage, and thus their cost. Note that, the cost for mixing equipments and rapid / slow mixing and sedimentation tank have to be additionally considered in this chemical treatment method. Therefore, the alternative treatment method that can reduce the chemical dosage should be considered, like the MIAF process. As concluded previously about the treatment of oily emulsion, especially with SDS by MIAF process, it can be noted that the cost reduction (100 Baht per m^3) can be obtained due to the application of 300 mg/L instead of 400 mg/L as in chemical process. In conclusion, more researches about the bubble hydrodynamic parameters and also about the suitable design of flotation process in order to obtain the highest a/G values is necessary for providing, not only the high treatment efficiency, but also reducing the required chemical dosage.

CHAPTER V

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The objective of this work is to study treatment mechanism of 300 mg/L of lubricant oily emulsion wastewater containing with anionic surfactant (SDS), cationic surfactant (CTAB), and nonionic surfactant (Tween20) by IAF, coagulation, and MIAF processes. Base on the results obtained in this study, the following conclusion can be presented:

5.1.1 Treatment of oily emulsion wastewater by Induce Air Flotation (IAF)

- Whatever the treatment efficiencies obtained with the IAF processes are greater than those obtained with the decantation process, and there is a little effect of different air flow rates and aeration time;
- The optimal operating conditions for oily emulsion wastewater with SDS, CTAB, and Tween20 were aeration time at 30 minute and air flow rate between 0.3 and 0.5 l/min: these can provide the treatment efficiencies equal to 33.33%, 74.44%, and 25.00%, respectively;
- The oil droplet sizes and their relative charges on oil surface have been proved to be the important factors controlling the treatment efficiencies.

5.1.2 Treatment of oily emulsion wastewater by coagulation process

- At optimal pH 8, the highest treatment efficiency obtained with oily emulsion wastewater with SDS, CTAB, and Tween20 were 61.82%, 59.77%, and 37.66% with the associated alum concentration at 400, 200, and 150 mg/l, respectively;
- Surfactant concentrations used for preparing the synthetic wastewater, oil droplet sizes and their ionic charge have been proved to be the important parameters controlling the treatment efficiencies;

- Non-ionic surfactant contaminated in lubricant oily emulsion wastewater can produce more stable oily emulsion and thus difficult to be separated or treated by the coagulation-flocculation process.

5.1.3 Treatment of oily emulsion wastewater by Modify Induce Air Flotation (MIAF) process

- Concerning to the oily emulsion wastewater with SDS, the treatment efficiencies obtained with MIAF process are greater than those obtained with the coagulation process for a given alum concentration in liquid phase;
- The bubble generated by air diffuser can be applied, not only for separating the oil droplets to the surface, but also for producing the chemical mixing condition in the MIAF process.
- In case of oily emulsion wastewater with CTAB and Tween20, the negative effect was observed: the limitation in terms of oil/bubble attachment and charge destabilization were possibly responsible for these results;
- Based on the kinetic study, three zones can be found, especially in the case of SDS, on the variation of the treatment efficiency with operating time: oil free surface, attachment and breaking zones;
- By using the differential method, the reaction rate constant (log k) and the reaction rate order (n) can be determined in order to provide a better understanding on the effect of chemical dosage on MIAF process;
- The simple model for predicting the treatment efficiency obtained with MIAF process were proposed from the values of n and log k and expressed as:

$$\%Eff_{Model} = \frac{\bar{n}}{\bar{K}} \times \%Eff_{IAF}$$

- Relatively good agreement between the experimental and the predicted treatment efficiencies by using MIAF process for the lubricant oily emulsion wastewater containing with anionic surfactant (SDS) is obtained (average difference about ± 25%).

5.1.4 Bubble hydrodynamic parameter

- The experimental method for analyzing the bubble hydrodynamic parameters (bubble size, bubble formation frequency and their rising velocity) were applied in order to finally obtained the interfacial area;
- Due to the IAF process, the differences in terms of bubble size ($D_{B\ CTAB} < D_{B\ NON} \approx D_{B\ SDS}$) are directly linked to static surface tension obtained with 3 types of synthetic wastewater ($\sigma_{L\ CTAB} < \sigma_{L\ NON} \approx \sigma_{L\ SDS}$);
- Small effect of the alum concentration was observed on the bubble hydrodynamic parameters obtained with MIAF processes.
- The optimal chosen a/G ratio will relate to the air flow rates that generate, not only high interacting opportunity/surface between oil droplets and bubbles, but also proper mixing condition between generated bubbles, oil droplets and applied chemical agents in the flotation processes (IAF and MIAF), and thus the highest oily emulsion wastewater treatment efficiency;
- The linear relation between the treatment efficiency and the a/G ratio obtained experimentally with IAF and MIAF processes, were applied in order to predict the overall treatment efficiencies as following equation:

$$\%Eff = \frac{a}{G}(slope) + b$$

5.2 Recommendations

In the future, it is interesting to study the different types of oily emulsion wastewater produced from various types of oils and surfactants. It is essential to continue studying with different types of chemical agents and air diffusers in order to extend the operating condition ranges and to validate the correlation proposed in this study. Moreover, it is obvious that the results observed in our small bubble column volume have to be validated into a tall bubble column and at higher air flow rates.

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APPENDICES

APPENDIX A

1. Synthetic lubricant oil emulsion wastewater

Table A-1 Surface Tension Value of oil emulsion with SDS

Concentration of surfactant (x10-2 mol/l)	Surface Tension, SFT (mN/m)
0.01	56.493
0.02	47.387
0.04	44.962
0.06	39.650
0.08	38.758
0.09	36.848
0.10	35.454
0.20	32.830
0.30	32.549
0.40	32.435
0.50	32.400
0.60	32.360

Table A-2 Surface Tension Value of oil emulsion with CTAB

Concentration of surfactant (x10-2 mol/l)	Surface Tension, SFT (mN/m)
0.0005	51.147
0.001	44.426
0.005	28.970
0.01	28.110
0.02	28.591
0.03	27.989
0.04	27.926
0.05	28.353
0.06	28.635
0.10	29.353
0.20	30.755
0.40	33.790
0.60	35.520

Table A-3 Surface Tension Value of oil emulsion with Tween20

Concentration of surfactant (x10-2 mol/l)	Surface Tension, SFT (mN/m)
0.001	55.347
0.002	48.439
0.004	46.828
0.008	45.740
0.01	42.147
0.02	39.806
0.03	39.090
0.04	38.608
0.05	37.990
0.10	37.790
0.20	37.890
0.40	37.930
0.60	38.000

2. Optimal oil emulsion treatment condition by coagulation

2.1 Optimal pH value

Table A-4a Optimal pH value for treatment of oil emulsion containing SDS

Concentration (mg/l)	Alum					
	200		300		400	
pH	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %
3	644.85	36.15	629.31	37.69	534.71	47.06
4	659.76	34.68	635.32	37.10	505.00	50.00
5	641.27	36.51	609.21	39.68	521.65	48.35
6	614.78	39.13	556.23	44.93	510.55	49.45
7	566.21	43.94	550.91	45.45	457.87	54.67
8	547.08	45.83	505.00	50.00	404.00	60.00
9	582.69	42.31	517.95	48.72	415.07	58.90
10	632.64	37.36	610.44	39.56	498.08	50.68
11	827.87	18.03	860.98	14.75	584.74	42.11

Table A-4b Optimal pH value for treatment of oil emulsion containing CTAB

Concentration (mg/l)	Alum					
	150		200		300	
pH	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %
3	963.02	4.65	789.87	21.79	963.56	4.60
4	927.79	8.14	776.92	23.08	934.54	7.47
5	863.20	14.53	692.76	31.41	859.08	14.94
6	845.58	16.28	660.38	34.62	847.47	16.09
7	810.35	19.77	621.54	38.46	824.25	18.39
8	634.19	37.21	401.41	60.26	661.72	34.48
9	598.95	40.70	388.46	61.54	603.68	40.23
10	669.42	33.72	543.85	46.15	638.51	36.78
11	939.53	6.98	725.13	28.21	928.74	8.05

Table A-4c Optimal pH value for treatment of oil emulsion containing Tween20

Concentration (mg/l)	Alum					
	200		300		400	
pH	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %
3	978.92	3.08	965.44	4.41	978.92	3.08
4	954.66	5.48	965.44	4.41	925.83	8.33
5	929.66	7.95	902.27	10.67	952.61	5.68
6	748.59	25.88	808.00	20.00	879.29	12.94
7	775.12	23.26	796.62	21.13	869.07	13.95
8	695.78	31.11	775.80	23.19	803.41	20.45
9	699.23	30.77	738.08	26.92	791.62	21.62
10	681.16	32.56	713.73	29.33	757.50	25.00
11	637.89	36.84	705.78	30.12	744.21	26.32

2.2 Optimal concentration of alum

Table A-5 Optimal concentration of alum for treatment of oil emulsion containing SDS, CTEB, and Tween20

Sample	SDS		CTAB		Tween20	
Alum Dosage (mg/l)	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %
50	881.06	12.77	289.66	19.54	826.06	12.12
100	866.74	14.18	250.34	30.46	640.91	31.82
150	735.28	27.20	215.17	40.23	585.97	37.66
200	638.32	36.80	144.83	59.77	659.22	29.87
250	580.55	42.52	186.21	48.28	688.45	26.76
300	516.93	48.82	211.03	41.38	714.93	23.94
350	410.12	59.39	231.72	35.63	725.14	22.86
400	385.64	61.82	277.24	22.99	765.43	18.57
450	453.31	55.12	289.66	19.54	778.44	17.19
500	532.83	47.24	297.93	17.24	881.25	6.25

3. Optimal oil emulsion treatment condition by IAF

Table A-6a Flow rate and aeration time for treatment of oil emulsion containing SDS

Flow Rate (l/min)	0.025		0.1		0.3		0.5		0.7	
Time (min)	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %
0	1016.84	-	827.37	-	1039.78	-	1026.70	-	904.07	-
2	814.74	19.88	675.79	18.32	778.20	25.16	810.90	20.38	715.45	20.86
4	808.42	19.88	669.47	18.32	758.58	25.16	810.90	21.02	708.94	20.86
6	795.79	20.50	663.16	19.08	745.50	27.04	797.82	21.02	702.44	21.58
8	789.47	21.74	644.21	19.85	732.43	28.30	778.20	22.29	689.43	22.30
10	776.84	22.36	631.58	22.14	719.35	29.56	752.04	24.20	673.17	23.74
20	764.21	23.60	606.32	23.66	693.19	30.82	719.35	26.75	643.90	25.54
30	757.89	24.84	606.32	26.72	686.65	33.33	719.35	29.94	637.40	28.78
40	732.63	25.47	587.37	26.72	667.03	33.96	719.35	29.94	630.89	29.50
50	745.26	27.95	593.68	29.01	686.65	35.85	725.89	29.94	637.40	30.22
60	751.58	26.71	606.32	28.24	699.73	33.96	738.96	29.30	650.41	29.50
70	751.58	26.09	606.32	26.72	699.73	32.70	738.96	28.03	650.41	28.06
80	757.89	25.47	625.26	24.43	706.27	32.08	745.50	27.39	663.41	26.62

Table A-6b Flow rate and aeration time for treatment of oil emulsion containing CTAB

Flow Rate (l/min)	0.025		0.1		0.3		0.5		0.7	
Time (min)	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %
0	360.00	-	360.00	-	360.00	-	368.00	-	368.00	-
2	240.00	33.33	226.80	37.00	213.60	40.67	230.00	37.50	232.00	36.96
4	226.72	37.02	200.00	44.44	194.00	46.11	200.00	45.65	200.00	45.65
6	214.00	40.56	186.00	48.33	180.00	50.00	192.00	47.83	196.00	46.74
8	200.00	44.44	180.00	50.00	160.00	55.56	168.00	54.35	168.00	54.35
10	176.00	51.11	168.00	53.33	140.00	61.11	152.00	58.70	144.00	60.87
20	168.00	53.33	146.00	59.44	112.00	68.89	138.00	62.50	136.00	63.04
30	152.00	57.78	136.00	62.22	92.00	74.44	108.00	70.65	112.00	69.57
40	146.00	59.44	120.00	66.67	80.00	77.78	92.00	75.00	100.00	72.83
50	128.00	64.44	108.00	70.00	68.00	81.11	84.00	77.17	84.00	77.17
60	120.00	66.67	106.00	70.56	68.00	81.11	84.00	77.17	80.00	78.26
70	136.00	62.22	112.00	68.89	80.00	77.78	92.00	75.00	84.00	77.17
80	148.00	58.89	128.00	64.44	90.00	75.00	100.00	72.83	96.00	73.91

Table A-6c Flow rate and aeration time for treatment of oil emulsion containing Tween20

Flow Rate (l/min)	0.025		0.1		0.3		0.5		0.7	
Time (min)	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %
0	837.50	-	1012.50	-	987.50	-	1050.00	-	1031.25	
2	800.00	4.48	962.50	4.94	875.00	11.39	962.50	8.33	987.50	4.24
4	800.00	4.48	950.00	6.17	862.50	12.66	950.00	9.52	950.00	7.88
6	775.00	7.46	937.50	7.41	850.00	13.92	912.50	13.10	937.50	9.09
8	775.00	7.46	912.50	9.88	850.00	13.92	900.00	14.29	925.00	10.30
10	762.50	8.96	900.00	11.11	825.00	16.46	850.00	19.05	875.00	15.15
20	750.00	10.45	887.50	12.35	800.00	18.99	812.50	22.62	862.50	16.36
30	737.50	11.94	862.50	14.81	787.50	20.25	787.50	25.00	850.00	17.58
40	725.00	13.43	856.25	15.43	775.00	21.52	762.50	27.38	812.50	21.21
50	718.75	14.18	850.00	16.05	762.50	22.78	750.00	28.57	787.50	23.64
60	725.00	13.43	850.00	16.05	750.00	24.05	775.00	26.19	800.00	22.42
70	725.00	13.43	856.25	15.43	775.00	21.52	787.50	25.00	812.50	21.21
80	725.00	13.43	856.25	15.43	787.50	20.25	787.50	25.00	812.50	21.21

4. Optimal oil emulsion treatment condition by MIAF

Table A-7a Flow rate and aeration time for treatment of oil emulsion containing SDS at alum 25 mg/l

Flow Rate (l/min)	0.025		0.1		0.3		0.5		0.7	
Time (min)	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %
0	933.33	-	1000.00	-	973.33	-	1000.00	-	960.00	-
2	813.33	12.86	840.00	16.00	773.33	20.55	840.00	16.00	840.00	12.50
4	813.33	12.86	840.00	16.00	760.00	21.92	840.00	16.00	840.00	12.50
6	800.00	14.29	826.67	17.33	760.00	21.92	786.67	21.33	786.67	18.06
8	800.00	14.29	826.67	17.33	746.67	23.29	800.00	20.00	800.00	16.67
10	800.00	14.29	826.67	17.33	760.00	21.92	786.67	21.33	786.67	18.06
20	780.00	16.43	813.33	18.67	733.33	24.66	760.00	24.00	760.00	20.83
30	766.67	17.86	813.33	18.67	733.33	26.03	746.67	25.33	746.67	22.22
40	760.00	18.57	813.33	18.67	720.00	26.03	733.33	26.67	733.33	23.61
50	786.67	15.71	826.67	17.33	733.33	24.66	720.00	28.00	720.00	25.00
60	786.67	15.71	826.67	17.33	720.00	26.03	733.33	26.67	733.33	23.61

Table A-7b Flow rate and aeration time for treatment of oil emulsion containing SDS at alum 50 mg/l

Flow Rate (l/min)	0.025		0.1		0.3		0.5		0.7	
Time (min)	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %
0	880.00	-	933.33	-	933.33	-	933.33	-	880.00	-
2	786.67	10.61	786.67	15.71	773.33	17.14	800.00	14.29	800.00	9.09
4	746.67	15.15	746.67	20.00	733.33	21.43	760.00	18.57	760.00	13.64
6	746.67	15.15	746.67	20.00	733.33	21.43	746.67	20.00	746.67	15.15
8	746.67	15.15	746.67	20.00	733.33	21.43	746.67	20.00	746.67	15.15
10	733.33	16.67	733.33	21.43	720.00	22.86	733.33	21.43	733.33	16.67
20	733.33	16.67	733.33	21.43	706.67	24.29	720.00	22.86	720.00	18.18
30	720.00	18.18	720.00	22.86	680.00	27.86	700.00	25.00	706.67	19.70
40	720.00	18.18	720.00	22.86	666.67	28.57	693.33	25.71	693.33	21.21
50	706.67	19.70	733.33	21.43	693.33	25.71	706.67	24.29	680.00	22.73
60	720.00	18.18	746.67	20.00	693.33	25.71	720.00	22.86	720.00	18.18

Table A-7c Flow rate and aeration time for treatment of oil emulsion containing SDS at alum 100 mg/l

Flow Rate (l/min)	0.025		0.1		0.3		0.5		0.7	
Time (min)	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %
0	920.00	-	986.67	-	1040.00	-	960.00	-	946.67	-
2	733.33	20.29	720.00	27.03	733.33	29.49	680.00	29.17	680.00	28.17
4	733.33	20.29	680.00	31.08	733.33	29.49	680.00	29.17	706.67	25.35
6	720.00	21.74	693.33	29.73	720.00	30.77	693.33	27.78	693.33	26.76
8	706.67	23.19	693.33	29.73	706.67	32.05	680.00	29.17	680.00	28.17
10	706.67	23.19	720.00	27.03	706.67	32.05	666.67	30.56	680.00	28.17
20	706.67	23.19	706.67	28.38	693.33	33.33	693.33	27.78	666.67	29.58
30	693.33	24.64	693.33	29.73	680.00	34.62	662.67	30.97	666.67	29.58
40	680.00	26.09	680.00	31.08	666.67	35.90	653.33	31.94	653.33	30.99
50	706.67	23.19	706.67	28.38	693.33	33.33	680.00	29.17	693.33	26.76
60	693.33	24.64	693.33	29.73	693.33	30.77	666.67	30.56	706.67	25.35

Table A-7d Flow rate and aeration time for treatment of oil emulsion containing SDS at alum 150 mg/l

Flow Rate (l/min)	0.025		0.1		0.3		0.5		0.7	
Time (min)	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %
0	800.00	-	826.67	-	1026.67	-	933.33	-	893.33	-
2	613.33	23.33	586.67	29.03	640.00	37.66	560.00	40.00	560.00	37.31
4	613.33	23.33	586.67	29.03	640.00	37.66	586.67	37.14	586.67	34.33
6	600.00	25.00	600.00	27.42	613.33	40.26	560.00	40.00	560.00	37.31
8	600.00	25.00	600.00	27.42	600.00	41.56	560.00	40.00	560.00	37.31
10	560.00	30.00	560.00	32.26	600.00	41.56	560.00	40.00	560.00	37.31
20	546.67	31.67	546.67	33.87	600.00	41.56	520.00	44.29	520.00	41.79
30	546.67	31.67	500.00	39.52	546.67	46.75	520.00	44.29	520.00	41.79
40	533.33	33.33	520.00	37.10	533.33	48.05	480.00	48.57	546.67	38.81
50	560.00	30.00	520.00	37.10	546.67	46.75	466.67	50.00	533.33	40.30
60	573.33	28.33	506.67	38.71	560.00	45.45	480.00	48.57	560.00	37.31

Table A-7e Flow rate and aeration time for treatment of oil emulsion containing SDS at alum 200 mg/l

Flow Rate (l/min)	0.025		0.1		0.3		0.5		0.7	
Time (min)	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %
0	866.67	-	933.33	-	933.33	-	853.33	-	826.67	-
2	506.67	41.54	506.67	45.71	453.33	51.43	480.00	43.75	470.67	43.06
4	506.67	41.54	480.00	48.57	440.00	52.86	480.00	43.75	466.67	43.55
6	480.00	44.62	473.33	49.29	440.00	52.86	466.67	45.31	453.33	45.16
8	473.33	45.38	473.33	49.29	426.67	54.29	440.00	48.44	453.33	45.16
10	472.00	45.54	466.67	50.00	426.67	54.29	440.00	48.44	453.33	45.16
20	466.00	46.23	453.33	51.43	386.67	58.57	400.00	53.13	373.33	54.84
30	464.00	46.46	440.00	52.86	380.00	61.43	353.33	58.59	360.00	56.45
40	400.00	53.85	400.00	57.14	346.67	62.86	346.67	59.38	320.00	61.29
50	400.00	53.85	400.00	57.14	346.67	62.86	333.33	60.94	320.00	61.29
60	430.00	50.77	426.67	54.29	346.67	62.86	333.33	60.94	333.33	59.68

Table A-7f Flow rate and aeration time for treatment of oil emulsion containing SDS at alum 300 mg/l

Flow Rate (l/min)	0.025		0.1		0.3		0.5		0.7	
Time (min)	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %
0	946.67	-	1040.00	-	986.67	-	906.67	-	933.33	-
2	493.33	47.89	426.67	58.97	386.67	60.81	400.00	55.88	400.00	57.14
4	466.67	50.70	400.00	61.54	373.33	62.16	360.00	60.29	400.00	57.14
6	440.00	53.52	386.67	62.82	320.00	67.57	400.00	55.88	400.00	57.14
8	386.67	59.15	386.67	62.82	306.67	68.92	360.00	60.29	360.00	61.43
10	360.00	61.97	360.00	65.38	293.33	70.27	346.67	61.76	346.67	62.86
20	346.67	63.38	360.00	65.38	293.33	70.27	320.00	64.71	320.00	65.71
30	333.33	64.79	326.67	68.59	246.67	75.00	253.33	72.06	280.00	70.00
40	333.33	64.79	320.00	69.23	240.00	75.68	240.00	73.53	280.00	70.00
50	346.67	63.38	373.33	64.10	253.33	74.32	240.00	73.53	266.67	71.43
60	360.00	61.97	386.67	62.82	266.67	72.97	266.67	70.59	266.67	71.43

Table A-7g Flow rate and aeration time for treatment of oil emulsion containing SDS at alum 400 mg/l

Flow Rate (l/min)	0.025		0.1		0.3		0.5		0.7	
Time (min)	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %
0	960.00	0.00	1026.67		933.33	0.00	920.00	0.00	893.33	0.00
2	533.33	44.44	493.33	51.95	426.67	54.29	426.67	53.62	426.67	52.24
4	493.33	48.61	466.67	54.55	400.00	57.14	386.67	57.97	373.33	58.21
6	466.67	51.39	453.33	55.84	346.67	62.86	373.33	59.42	400.00	55.22
8	453.33	52.78	453.33	55.84	346.67	62.86	373.33	59.42	373.33	58.21
10	453.33	52.78	413.33	59.74	333.33	64.29	320.00	65.22	320.00	64.18
20	413.33	56.94	360.00	64.94	293.33	68.57	313.33	65.94	320.00	64.18
30	360.00	62.50	360.00	64.94	280.00	71.43	293.33	68.12	293.33	67.16
40	360.00	62.50	346.67	66.23	253.33	72.86	293.33	68.12	280.00	68.66
50	373.33	61.11	413.33	59.74	280.00	70.00	306.67	66.67	293.33	67.16
60	386.67	59.72	400.00	61.04	293.33	68.57	320.00	65.22	306.67	65.67

Table A-8a Flow rate and aeration time for treatment of oil emulsion containing CTAB at alum 25 mg/l

Flow Rate (l/min)	0.1		0.3		0.5	
Time (min)	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %
0	348.39	-	348.39	-	348.39	-
2	716.13	-105.56	658.06	-88.89	716.13	-105.56
4	735.48	-111.11	677.42	-94.44	735.48	-111.11
6	735.48	-111.11	677.42	-94.44	735.48	-111.11
8	754.84	-116.67	696.77	-100.00	754.84	-116.67
10	754.84	-116.67	716.13	-105.56	793.55	-127.78
20	793.55	-127.78	754.84	-116.67	793.55	-127.78
30	793.55	-127.78	793.55	-127.78	812.90	-133.33
40	832.26	-138.89	812.90	-133.33	851.61	-144.44

Table A-8b Flow rate and aeration time for treatment of oil emulsion containing CTAB at alum 200 mg/l

Flow Rate (l/min)	0.1		0.3		0.5	
Time (min)	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %
0	380.95	0.00	380.95	0.00	380.95	0.00
2	1180.95	-210.00	1066.67	-180.00	1092.06	-186.67
4	1219.05	-220.00	1104.76	-190.00	1130.16	-196.67
6	1219.05	-220.00	1104.76	-190.00	1142.86	-200.00
8	1257.14	-230.00	1180.95	-210.00	1219.05	-220.00
10	1257.14	-230.00	1180.95	-210.00	1180.95	-210.00
20	1333.33	-250.00	1231.75	-223.33	1333.33	-250.00
30	1371.43	-260.00	1257.14	-230.00	1371.43	-260.00
40	1371.43	-260.00	1295.24	-240.00	1409.52	-270.00

Table A-9a Flow rate and aeration time for treatment of oil emulsion containing Tween20 at alum 25 mg/l

Flow Rate (l/min)	0.1		0.3		0.5	
Time (min)	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %
0	891.80	-	878.69	-	931.15	-
2	904.92	-1.47	904.92	-2.99	944.26	-1.41
4	904.92	-1.47	904.92	-2.99	944.26	-1.41
6	904.92	-1.47	904.92	-2.99	931.15	0.00
8	904.92	-1.47	904.92	-2.99	918.03	1.41
10	904.92	-1.47	904.92	-2.99	918.03	1.41
20	918.03	-2.94	891.80	-1.49	918.03	1.41
30	904.92	-1.47	918.03	-4.48	931.15	0.00
40	918.03	-2.94	904.92	-2.99	931.15	0.00

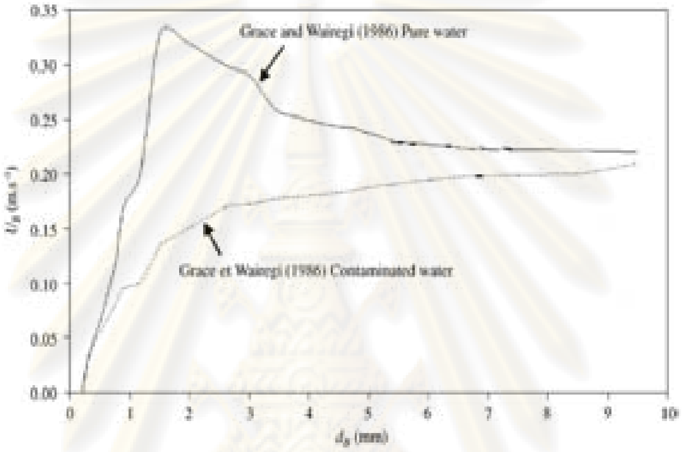
Table A-9b Flow rate and aeration time for treatment of oil emulsion containing Tween20 at alum 150 mg/l

Flow Rate (l/min)	0.1		0.3		0.5	
Time (min)	COD (mg/l)	Removal %	COD (mg/l)	Removal %	COD (mg/l)	Removal %
0	926.98	-	863.49	-	888.89	-
2	952.38	-2.74	838.10	2.94	838.10	5.71
4	939.68	-1.37	876.19	-1.47	850.79	4.29
6	952.38	-2.74	876.19	-1.47	825.40	7.14
8	926.98	0.00	850.79	1.47	838.10	5.71
10	914.29	1.37	863.49	0.00	825.40	7.14
20	914.29	1.37	825.40	4.41	825.40	7.14
30	907.94	2.05	838.10	2.94	812.70	8.57
40	901.59	2.74	812.70	5.88	812.70	8.57

APPENDIX B

1. Bubble Hydrodynamic

Figure B-1 The relationship between velocity of bubble (U_B) and size of bubble (d_B) for determine velocity of bubble values (U_B) by Grace and Wairegi (1986) corresponding to the contaminated water.



2 Analyzed n and log k for treatment oil emulsion with SDS by IAF

Figure B-2a Analyzed n and log k for treatment oil emulsion with SDS at 0.025 l/min for gas flow rate

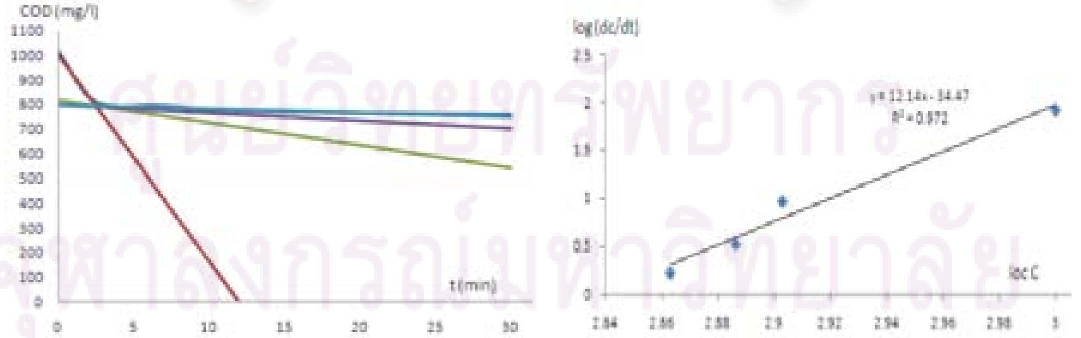


Figure B-2b Analyzed n and log k for treatment oil emulsion with SDS at 0.1 l/min for gas flow rate

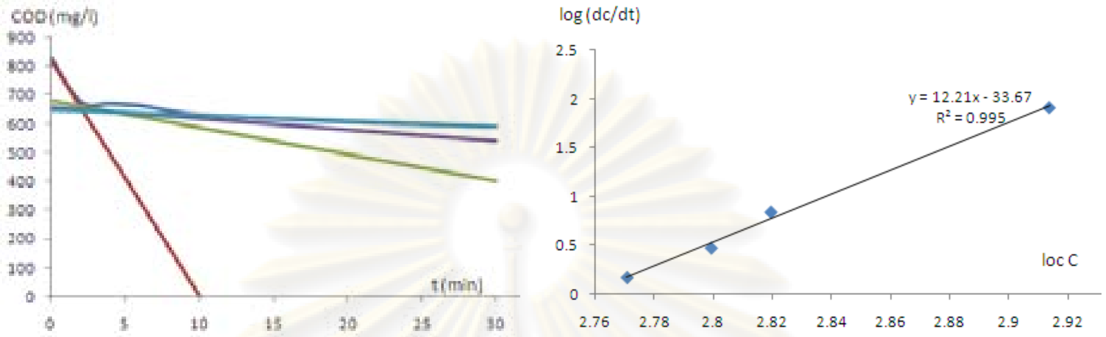


Figure B-2c Analyzed n and log k for treatment oil emulsion with SDS at 0.3 l/min for gas flow rate

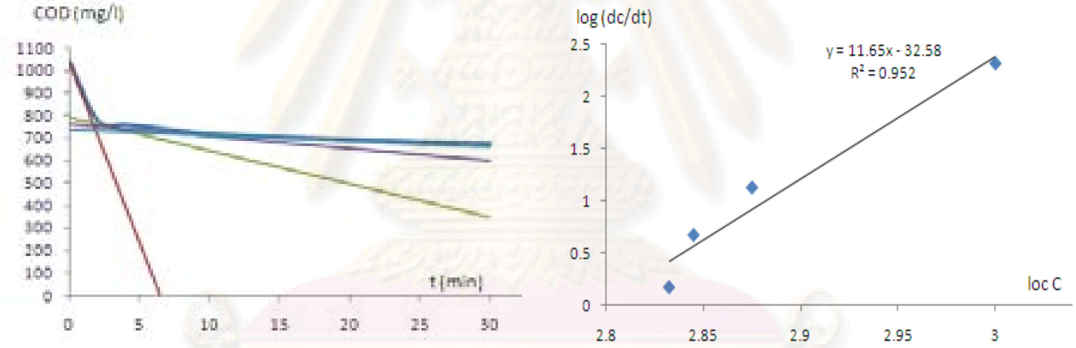


Figure B-2d Analyzed n and log k for treatment oil emulsion with SDS at 0.5 l/min for gas flow rate

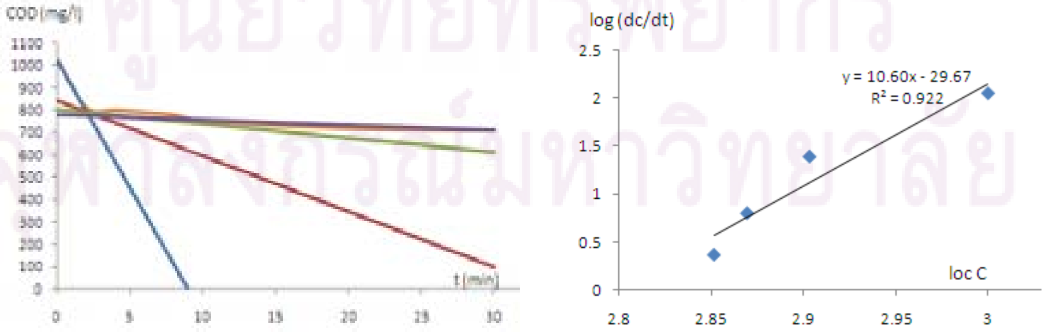
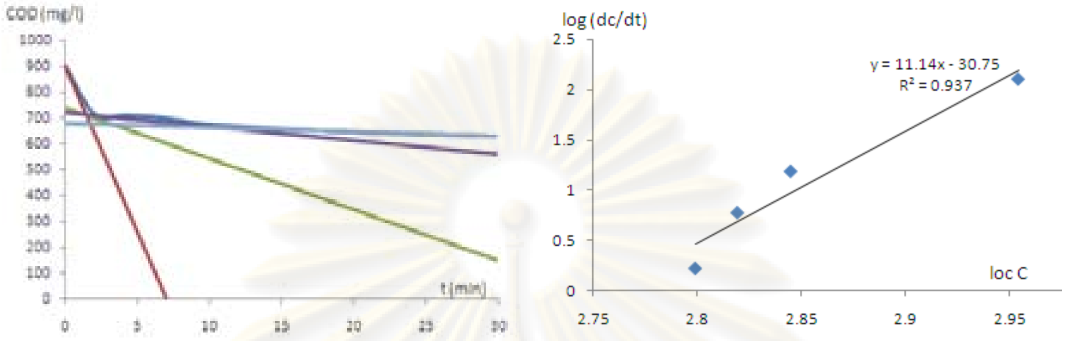


Figure B-2e Analyzed n and log k for treatment oil emulsion with SDS at 0.7 l/min for gas flow rate



3 Analyzed n and log k for treatment oil emulsion with SDS by MIAF

3.1 Analyzed n and log k for treatment oil emulsion with SDS at 0.1 l/min for gas flow rate at different alum concentration

Figure B-3a Analyzed n and log k for treatment oil emulsion with SDS at 25 mg/l of alum

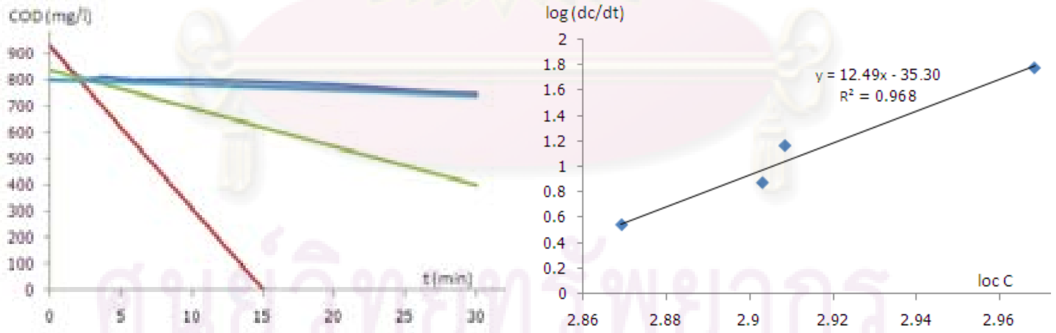


Figure B-3b Analyzed n and log k for treatment oil emulsion with SDS at 50 mg/l of alum

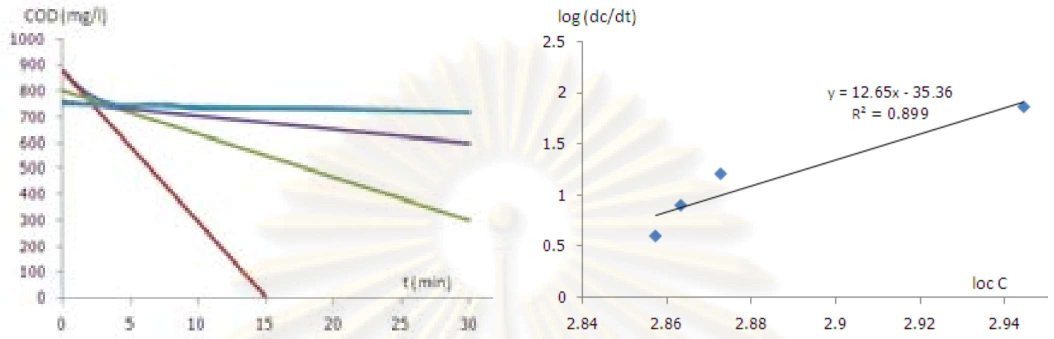


Figure B-3c Analyzed n and log k for treatment oil emulsion with SDS at 100 mg/l of alum

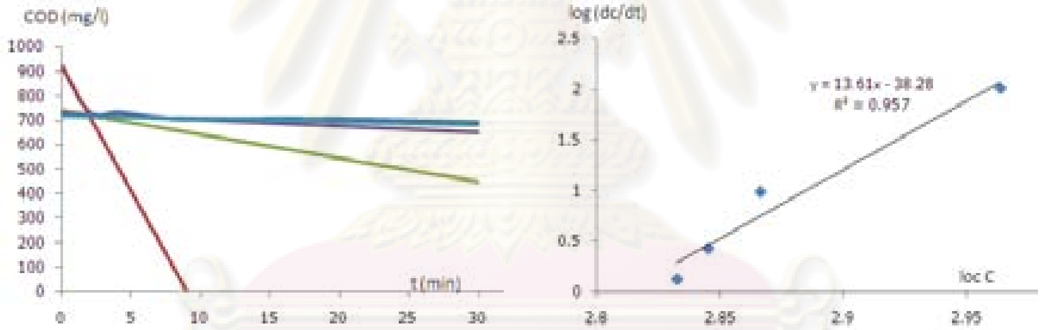


Figure B-3d Analyzed n and log k for treatment oil emulsion with SDS at 150 mg/l of alum

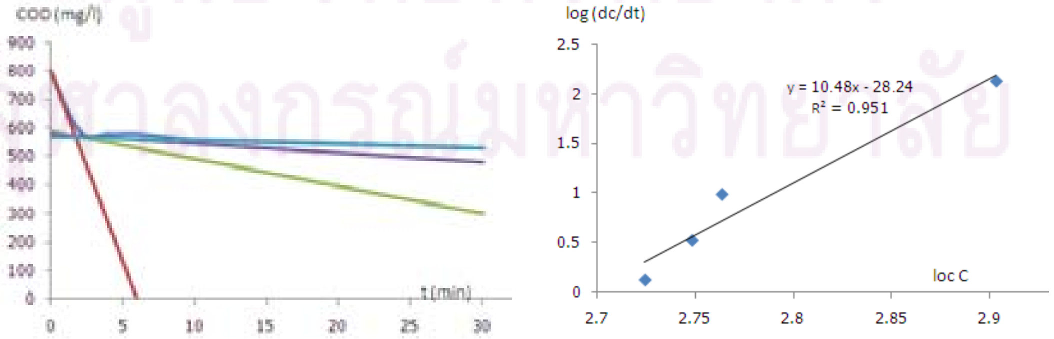


Figure B-3e Analyzed n and log k for treatment oil emulsion with SDS at 200 mg/l of alum

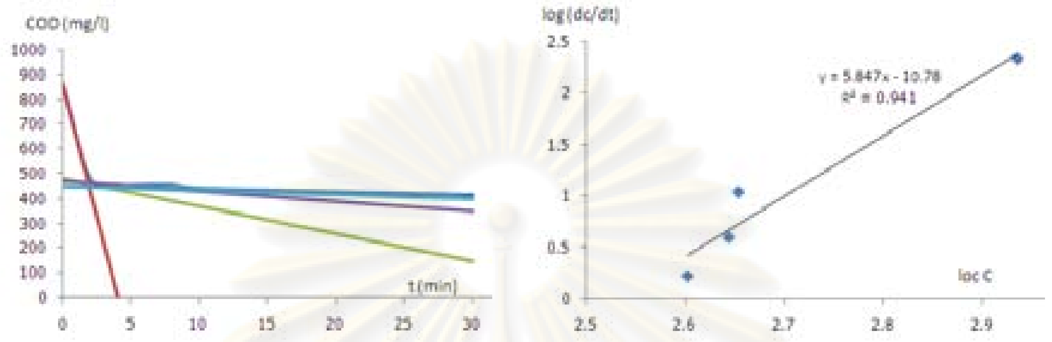


Figure B-3f Analyzed n and log k for treatment oil emulsion with SDS at 300 mg/l of alum

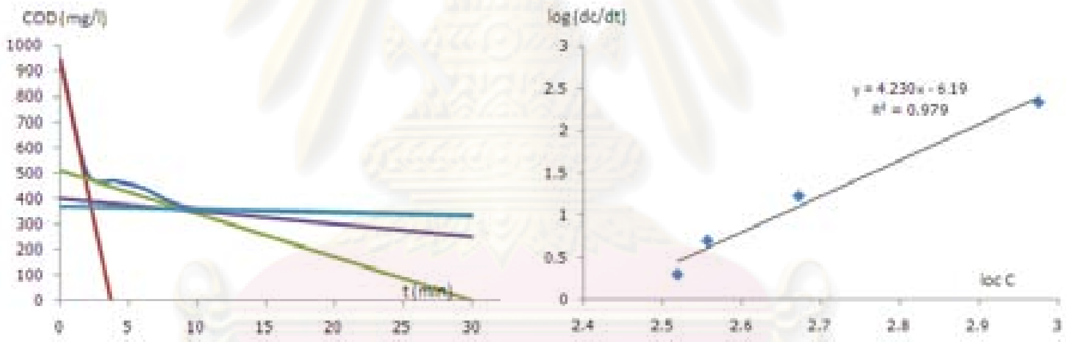
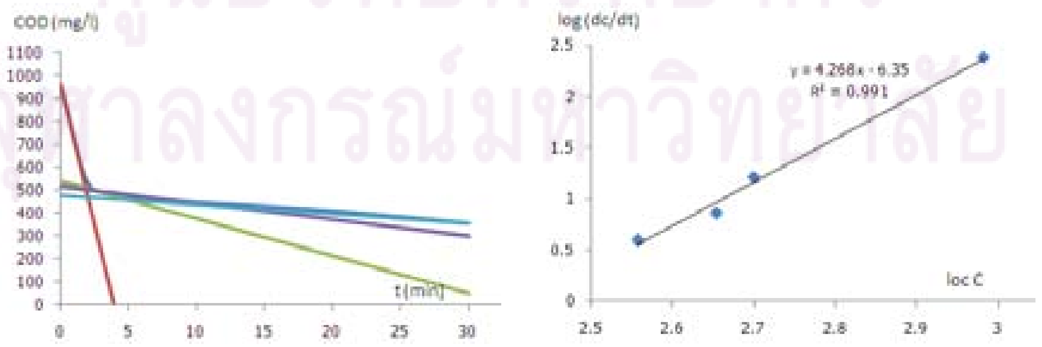


Figure B-3g Analyzed n and log k for treatment oil emulsion with SDS at 400 mg/l of alum



3.2 Analyzed n and log k for treatment oil emulsion with SDS at 0.1 l/min for gas flow rate at different alum concentration

Figure B-4a Analyzed n and log k for treatment oil emulsion with SDS at 25 mg/l of alum

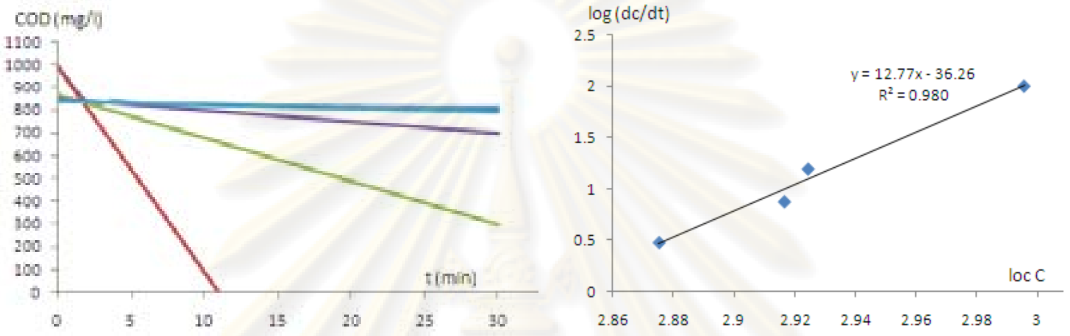


Figure B-4b Analyzed n and log k for treatment oil emulsion with SDS at 50 mg/l of alum

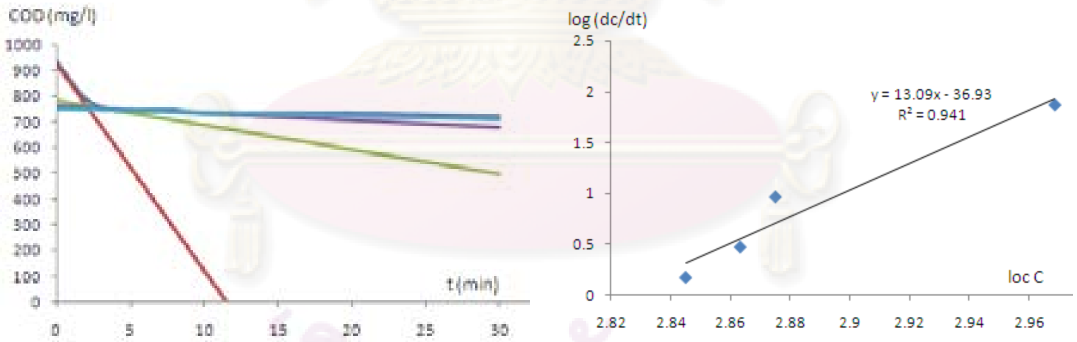


Figure B-4c Analyzed n and log k for treatment oil emulsion with SDS at 100 mg/l of alum

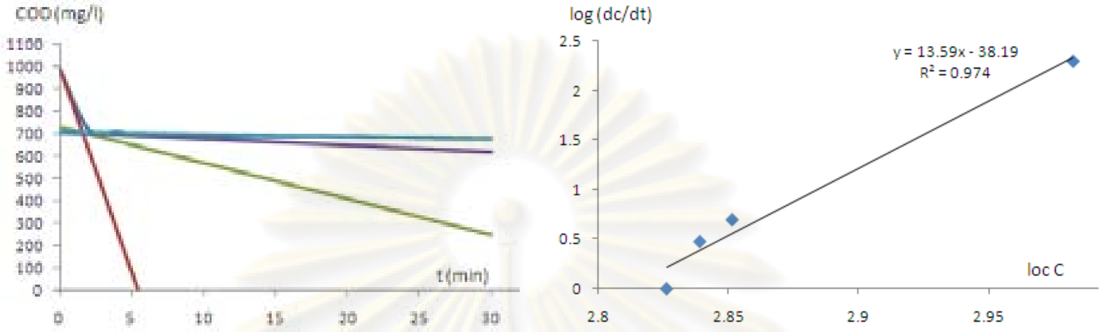


Figure B-4d Analyzed n and log k for treatment oil emulsion with SDS at 150 mg/l of alum

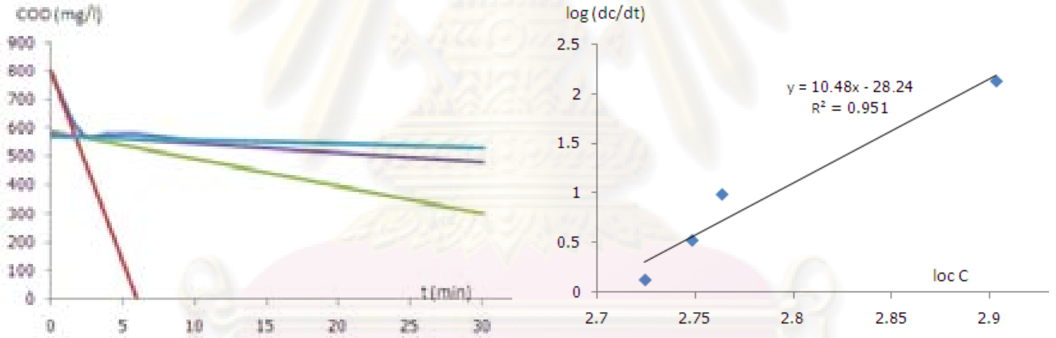


Figure B-4e Analyzed n and log k for treatment oil emulsion with SDS at 200 mg/l of alum

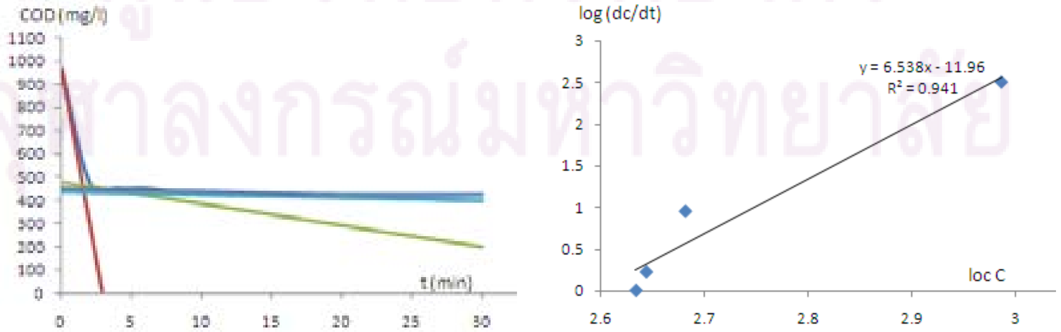


Figure B-4f Analyzed n and log k for treatment oil emulsion with SDS at 300 mg/l of alum

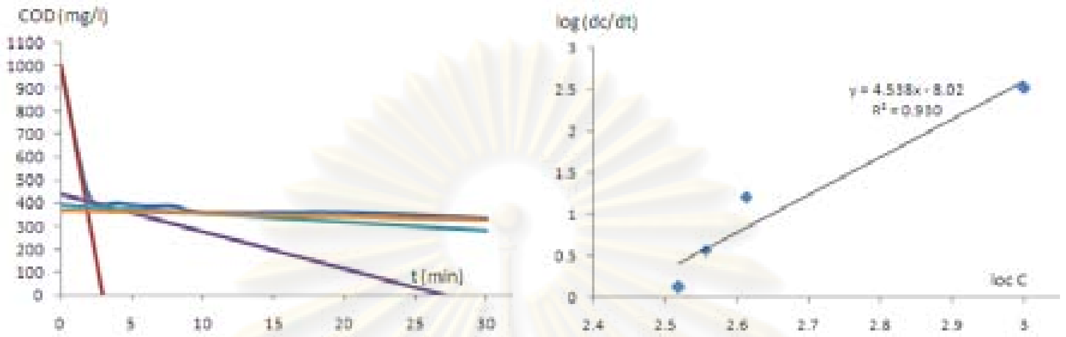
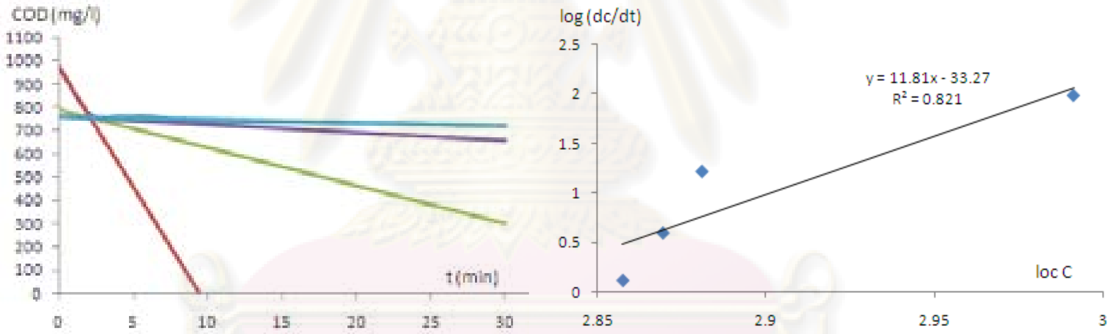


Figure B-4g Analyzed n and log k for treatment oil emulsion with SDS at 400 mg/l of alum



3.3 Analyzed n and log k for treatment oil emulsion with SDS at 0.3 l/min for gas flow rate at different alum concentration

Figure B-5a Analyzed n and log k for treatment oil emulsion with SDS at 25 mg/l of alum

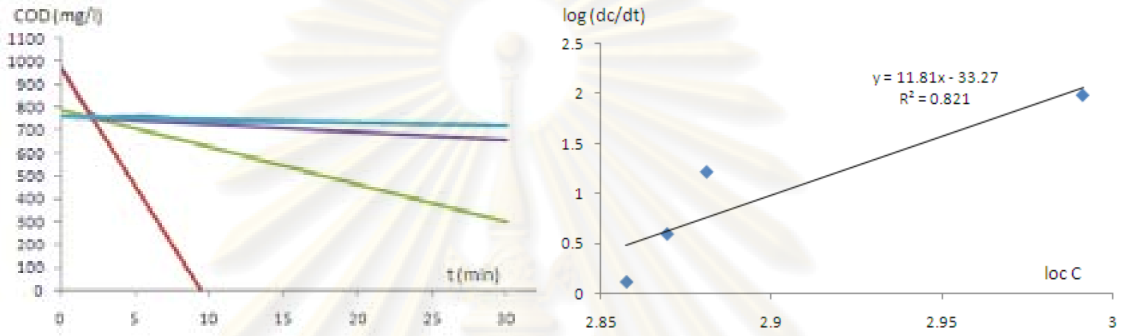


Figure B-5b Analyzed n and log k for treatment oil emulsion with SDS at 50 mg/l of alum

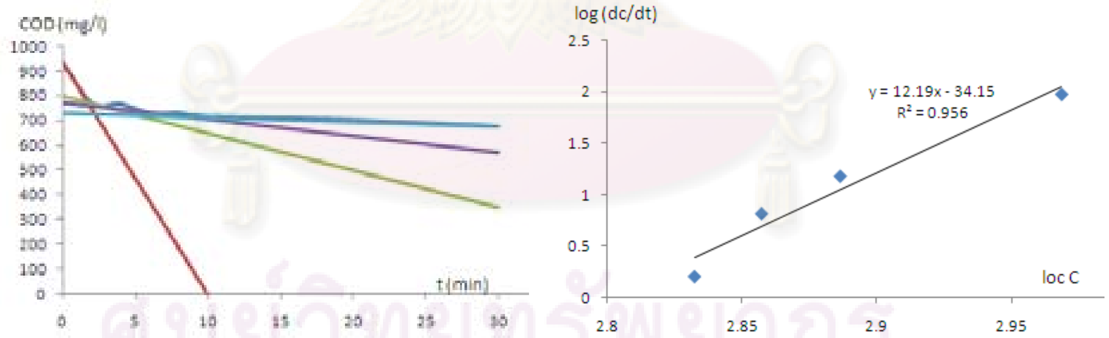


Figure B-5c Analyzed n and log k for treatment oil emulsion with SDS at 100 mg/l of alum

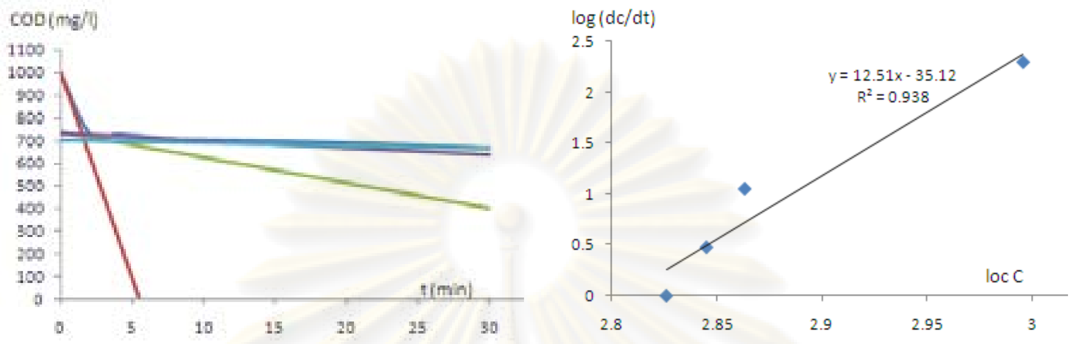


Figure B-4d Analyzed n and log k for treatment oil emulsion with SDS at 150 mg/l of alum

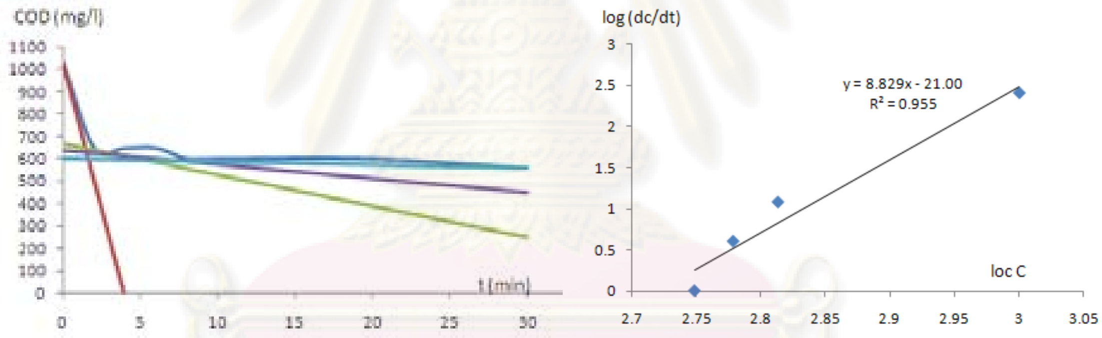


Figure B-5e Analyzed n and log k for treatment oil emulsion with SDS at 200 mg/l of alum

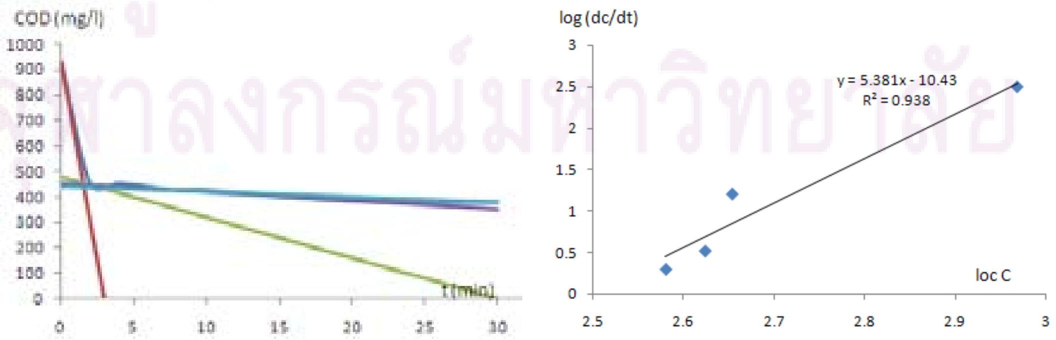


Figure B-5f Analyzed n and log k for treatment oil emulsion with SDS at 300 mg/l of alum

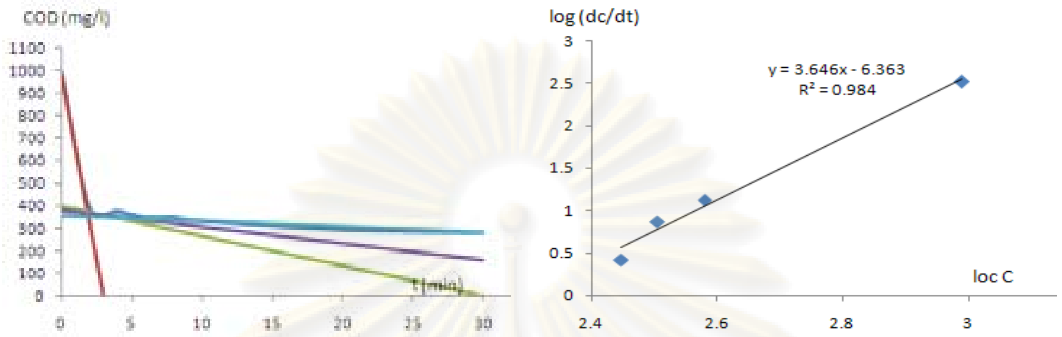
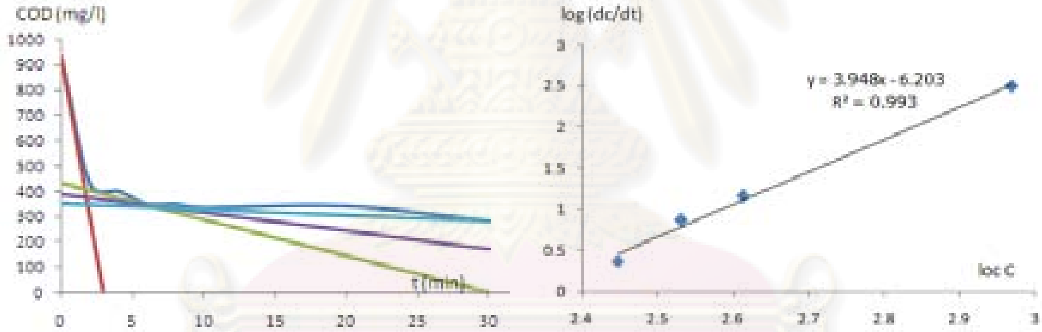


Figure B-5g Analyzed n and log k for treatment oil emulsion with SDS at 400 mg/l of alum



3.4 Analyzed n and log k for treatment oil emulsion with SDS at 0.5 l/min for gas flow rate at different alum concentration

Figure B-6a Analyzed n and log k for treatment oil emulsion with SDS at 25 mg/l of alum

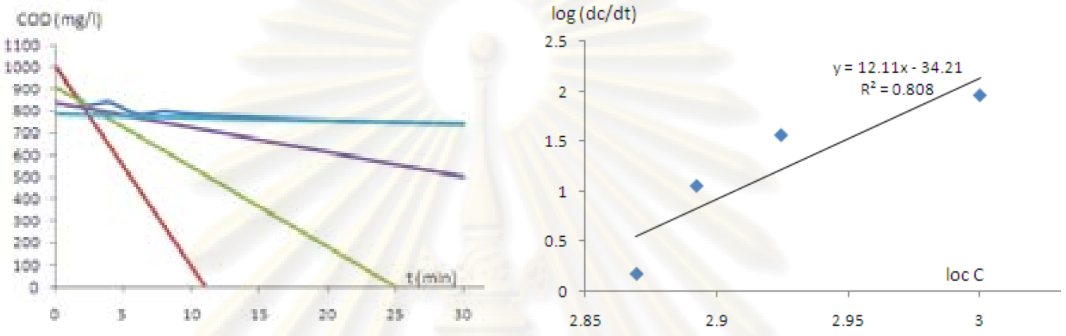


Figure B-6b Analyzed n and log k for treatment oil emulsion with SDS at 50 mg/l of alum

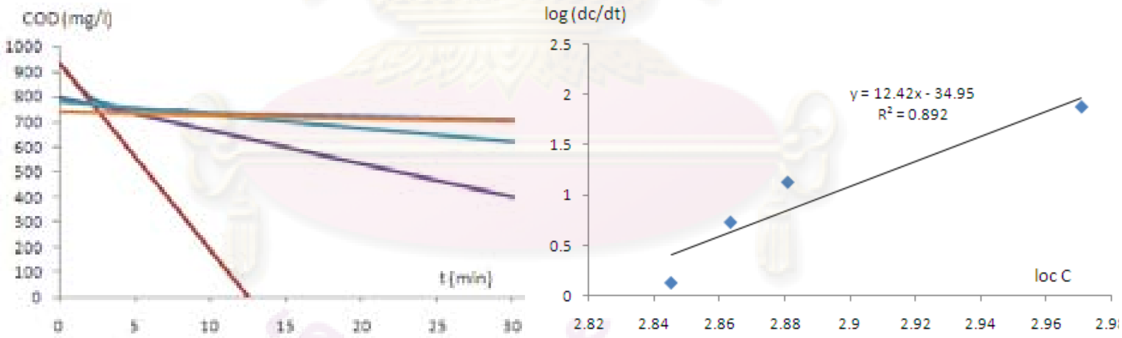


Figure B-6c Analyzed n and log k for treatment oil emulsion with SDS at 100 mg/l of alum

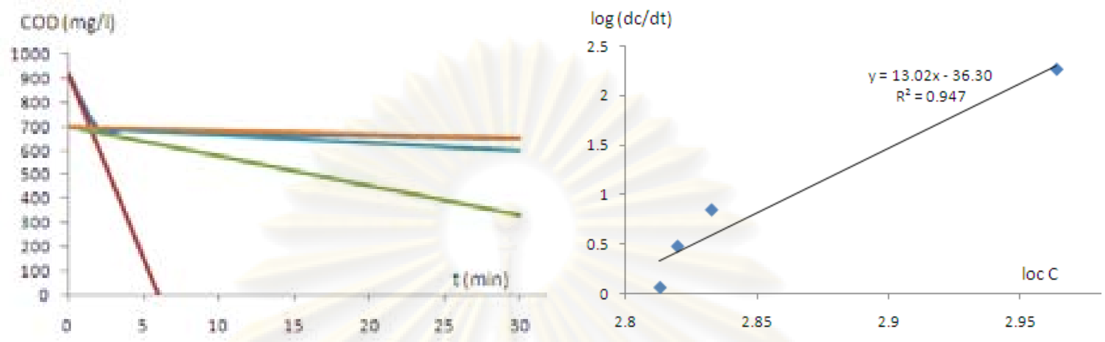


Figure B-6d Analyzed n and log k for treatment oil emulsion with SDS at 150 mg/l of alum

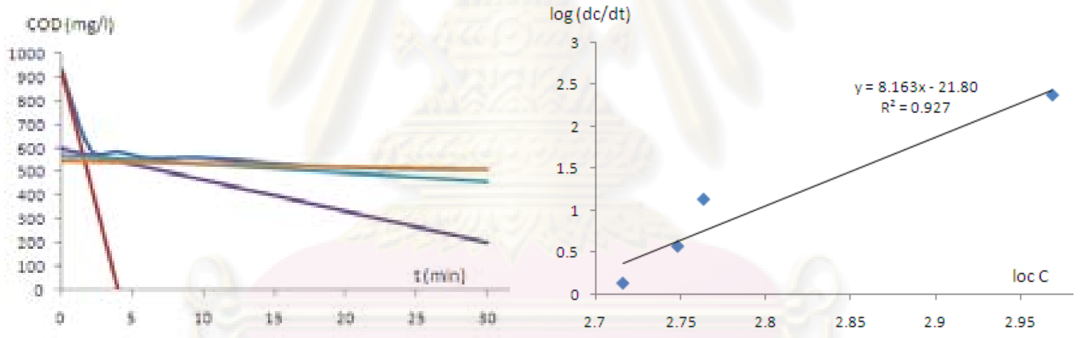


Figure B-6e Analyzed n and log k for treatment oil emulsion with SDS at 200 mg/l of alum

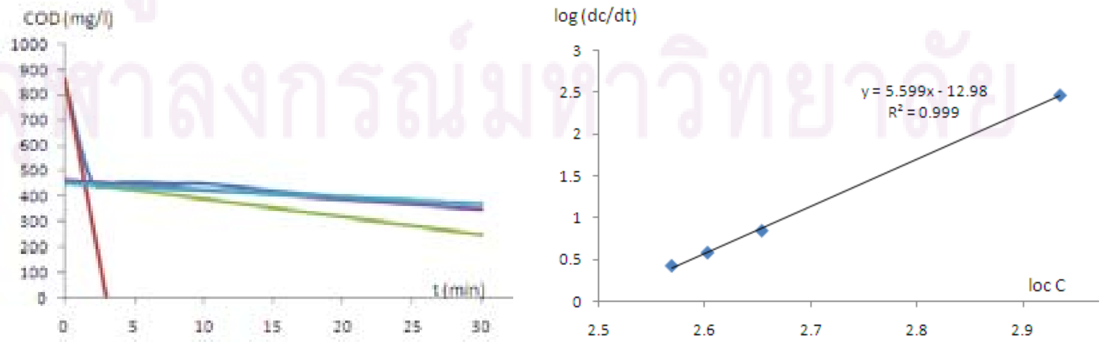


Figure B-6f Analyzed n and log k for treatment oil emulsion with SDS at 300 mg/l of alum

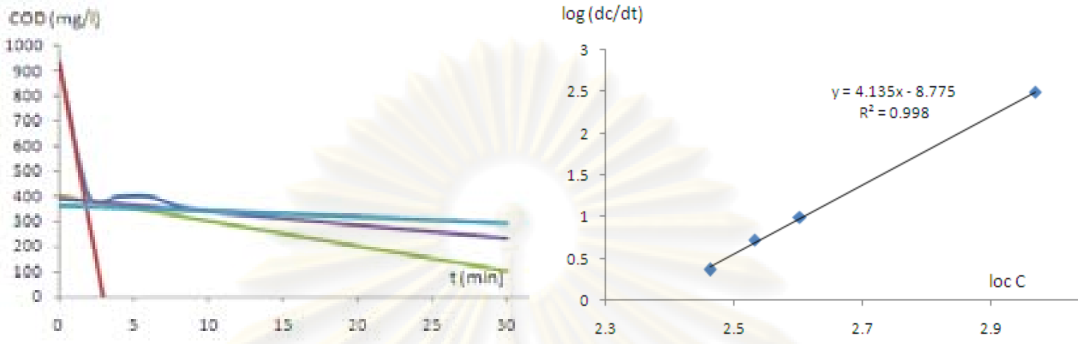
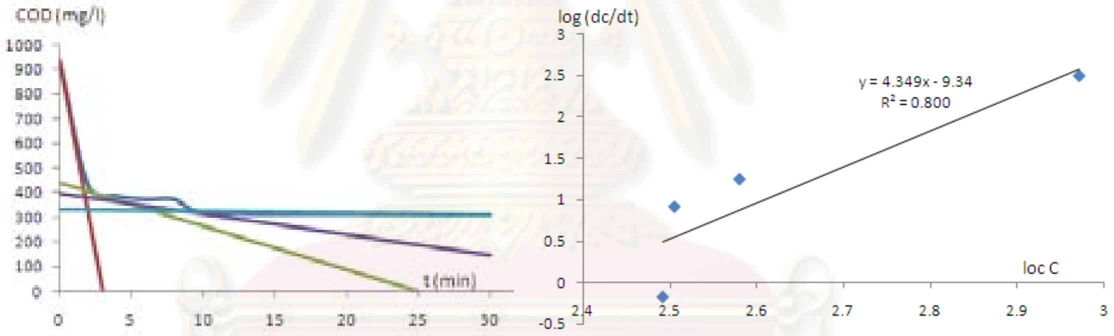


Figure B-6g Analyzed n and log k for treatment oil emulsion with SDS at 400 mg/l of alum



3.5 Analyzed n and log k for treatment oil emulsion with SDS at 0.7 l/min for gas flow rate at different alum concentration

Figure B-7a Analyzed n and log k for treatment oil emulsion with SDS at 25 mg/l of alum

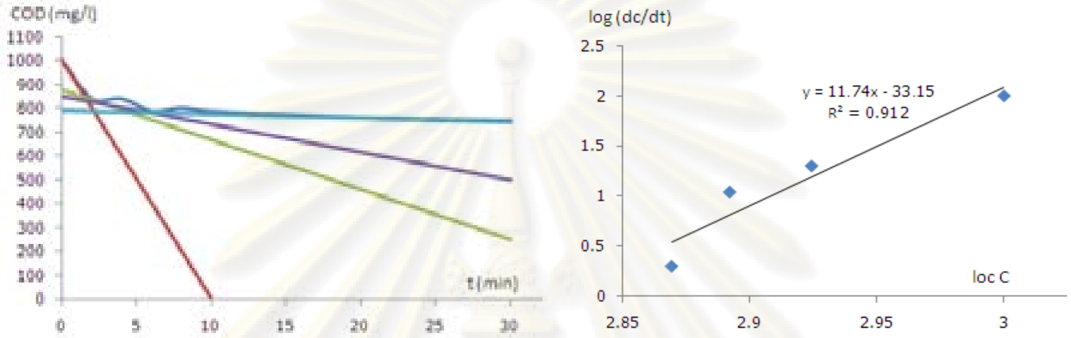


Figure B-7b Analyzed n and log k for treatment oil emulsion with SDS at 50 mg/l of alum

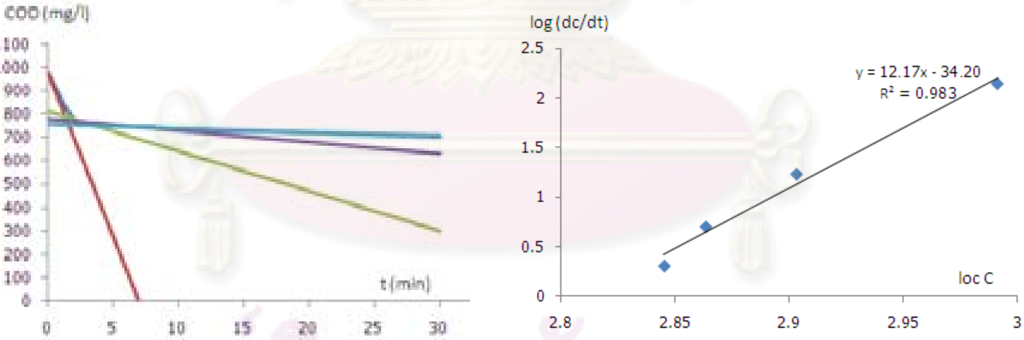


Figure B-7c Analyzed n and log k for treatment oil emulsion with SDS at 100 mg/l of alum

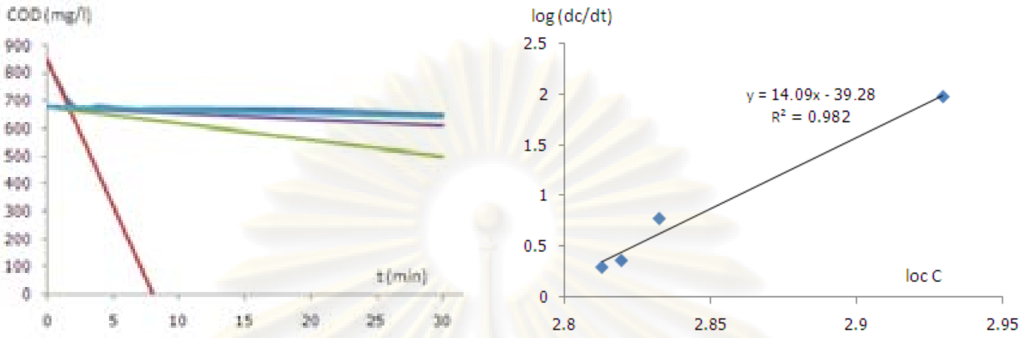


Figure B-7d Analyzed n and log k for treatment oil emulsion with SDS at 150 mg/l of alum

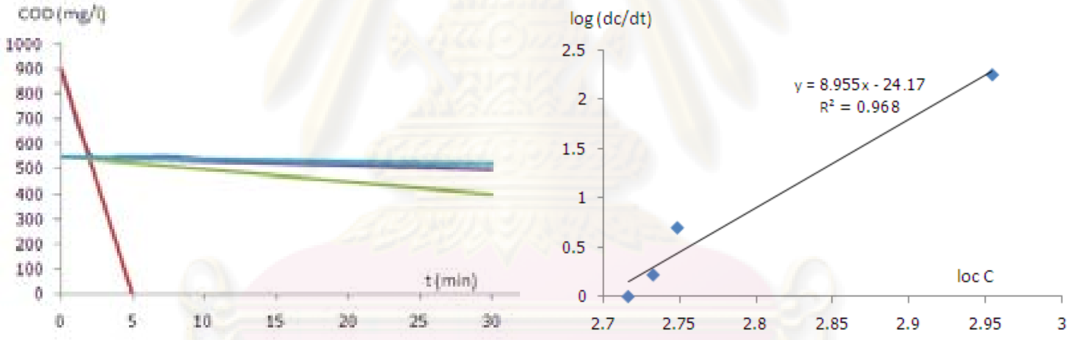


Figure B-7e Analyzed n and log k for treatment oil emulsion with SDS at 200 mg/l of alum

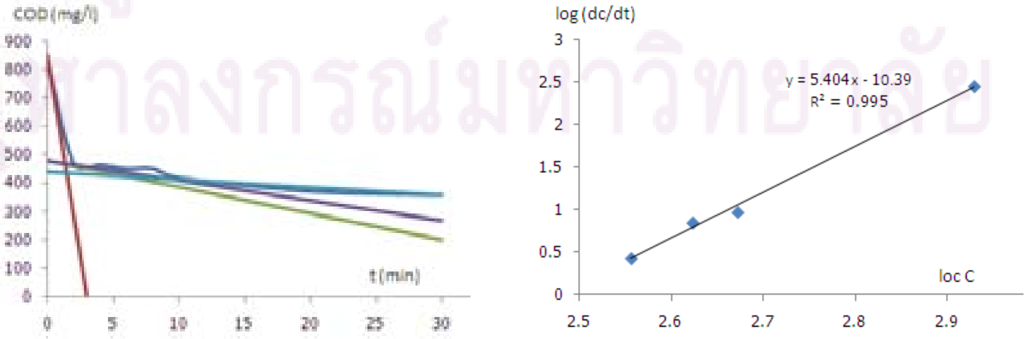


Figure B-7f Analyzed n and log k for treatment oil emulsion with SDS at 300 mg/l of alum

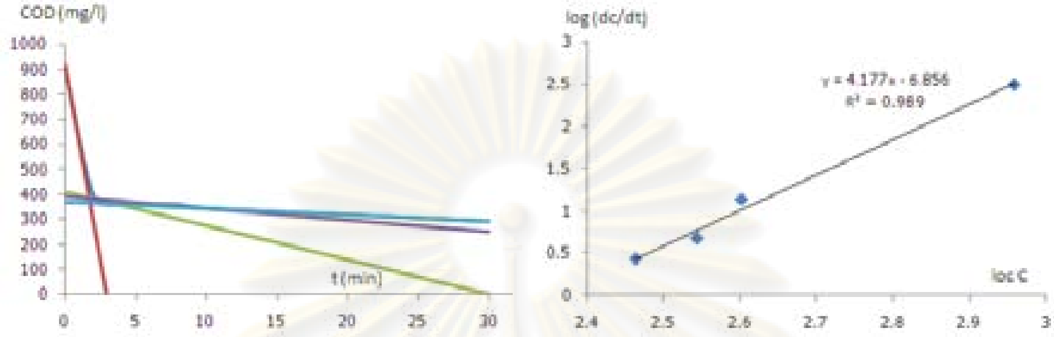
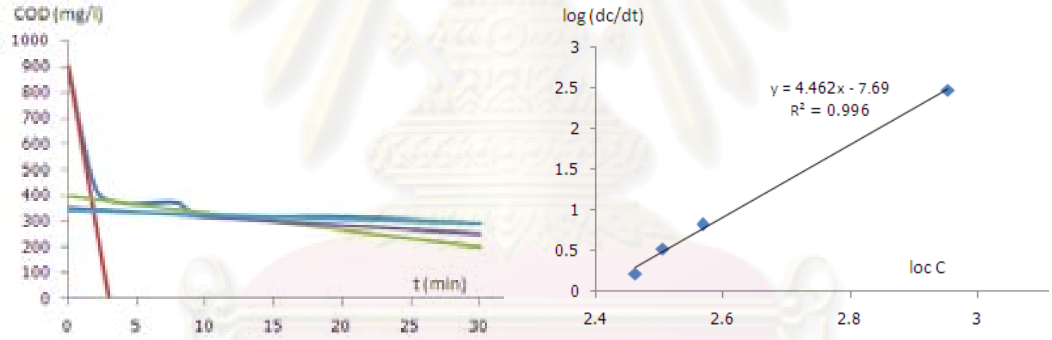


Figure B-7g Analyzed n and log k for treatment oil emulsion with SDS at 400 mg/l of alum



APPENDIX C

1. Bubble Hydrodynamic Parameter

Table C-1 The relationship between Size of bubble (D_B) and Flow rate for IAF

Flow Rate (L/min)	D_B (mm)		
	Sample		
	SDS	CTAB	Tween 20
0.025	0.76	0.57	0.68
0.1	0.79	0.65	0.75
0.3	0.80	0.69	0.80
0.5	0.97	0.86	0.87
0.7	1.20	0.96	1.19

Table C-2 The relationship between Size of bubble (D_B) and Flow rate for MIAF of oil emulsion with SDS

Flow Rate (L/min)	D_B (mm)				
	Alum concentration (mg/l)				
	100	150	200	300	400
0.025	0.70	0.72	0.78	0.74	0.70
0.1	0.74	0.75	0.80	0.75	0.72
0.3	0.79	0.80	0.82	0.82	0.78
0.5	0.95	0.96	0.93	1.01	0.95
0.7	1.19	1.17	1.22	1.21	1.18

Table C-3 The relationship between Bubble velocity (U_B) and Flow rate for IAF

Flow Rate (L/min)	U_B (cm/sec)		
	Sample		
	SDS	CTAB	Tween 20
0.025	7.0	5.5	7.0
0.1	7.5	6.5	7.5
0.3	8.0	7.0	8.0
0.5	10.0	9.0	8.5
0.7	10.5	10.0	10.5

Table C-4 The relationship between Bubble velocity (U_B) and Flow rate for MIAF of oil emulsion with SDS

Flow Rate (L/min)	U_B (cm/sec)				
	Alum concentration (mg/l)				
	100	150	200	300	400
0.025	7.0	7.0	7.5	7.0	7.0
0.1	7.0	7.0	8.0	7.0	7.0
0.3	8.0	8.0	8.0	8.0	7.5
0.5	9.5	10.0	9.5	10.0	9.5
0.7	10.5	10.5	10.5	10.5	10.5

Table C-5 The relationship between Interfacial area (a) and Flow rate for IAF

Flow Rate (L/min)	a (m^{-1})		
	Sample		
	SDS	CTAB	Tween 20
0.025	27.847	47.256	31.123
0.1	100.015	140.258	105.349
0.3	277.777	368.069	277.777
0.5	305.460	382.811	400.671
0.7	329.218	432.098	331.984

Table C-6 The relationship between Interfacial area (a) and Flow rate for MIAF of oil emulsion with SDS

Flow Rate (L/min)	a (m^{-1})				
	Alum concentration (mg/l)				
	100	150	200	300	400
0.025	30.234	29.394	25.324	28.600	30.234
0.1	114.400	112.874	92.592	112.874	117.577
0.3	281.294	277.777	271.002	271.002	303.893
0.5	328.306	308.642	335.366	293.362	328.306
0.7	331.984	337.659	323.821	326.497	334.798

Table C-7 The relationship between Velocity gradient (G) and Flow rate for IAF and MIAF

Flow Rate (L/min)	Velocity gradient (s^{-1})
0.025	50.39
0.1	100.79
0.3	174.58
0.5	225.39
0.7	266.68

Table C-8 The relationship between Interfacial area per Velocity gradient (a/G ratio) and Flow rate for IAF

Flow Rate (L/min)	a/G (m/s)		
	Sample		
	SDS	CTAB	Tween 20
0.025	0.552	0.937	0.617
0.1	0.992	1.391	1.045
0.3	1.591	2.108	1.591
0.5	1.355	1.698	1.777
0.7	1.234	1.620	1.244

Table C-9 The relationship between Interfacial area per Velocity gradient (a/G ratio) and Flow rate for MIAF of oil emulsion with SDS

Flow Rate (L/min)	a/G (m/s)				
	Alum concentration (mg/l)				
	100	150	200	300	400
0.025	0.599	0.583	0.502	0.567	0.599
0.1	1.134	1.119	0.918	1.119	1.166
0.3	1.611	1.591	1.552	1.552	1.740
0.5	1.456	1.369	1.487	1.301	1.456
0.7	1.244	1.266	1.214	1.224	1.255

BIOGRAPHY

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Siriporn Lersjintanakarn and Pisut Painmanakul. *Treatment of lubricant oily wastewater containing surfactants by combining the flotation and coagulation processes*. The Proceedings of 8th National Environmental Conference, March 25 -27, 2009, at Suranaree University, Nakhon Ratchasima, Thailand, Organized by the Environmental Engineering Association of Thailand.