การบำบัดน้ำเสียสังเคราะห์ที่ปนเปื้อนน้ำมันตัดด้วยกระบวนการทำให้ลอยด้วยอากาศร่วมกับกระบวนการโคแอกกูเลชัน และการประยุกต์ใช้ฟองอากาศเคลือบน้ำมัน

นางสาวสุรารักษ์ อวนญวน

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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TREATMENT OF SYNTHETIC CUTTING-OILY WASTEWATER BY INDUCED AIR FLOTATION COMBINED WITH COAGULATION PROCESS AND REACTIVE OIL CONCEPT

Miss Suraruk Uanyuan

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สุรารักษ์ อวนญวน : การบำบัดน้ำเสียสังเคราะห์ที่ปนเปื้อนน้ำมันตัดด้วยกระบวนการทำให้ลอยด้วยอากาศร่วมกับกระบวนการโคแอกูเลชัน และแนวคิดการใช้ฟองอากาศเคลือบน้ำมัน (TREATMENT OF SYNTHETIC CUTTING-OILY WASTEWATER BY INDUCED AIR FLOTATION COMBINED WITH COAGULATION PROCESS AND REACTIVE OIL CONCEPT) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: อ. ดร. พิสุทธิ์ เพียรมนกุล, 111 หน้า

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาประสิทธิภาพการบำบัดน้ำเสียสังเคราะห์ที่ปนเปื้อนน้ำมันหล่อลื่นแปรรูปโลหะด้วยกระบวนการทำให้ลอยแบบอินดิวแอร์โฟลเทชั่น (Induced Air Flotation: IAF) ร่วมกับกระบวนการโคแอกูเลชัน (Coagulation) เรียกว่ากระบวนการโมดิฟลายด์อินดิวแอร์โฟลเทชั่น (Modify Induced Air Flotation: MIAF) รวมถึงการประยุกต์ใช้แนวคิดการใช้ฟองอากาศเคลือบน้ำมัน โดยทำการศึกษาด้วยคอลัมน์ 2 ขนาดคือ ขนาดเล็กมีเส้นผ่านศูนย์กลาง 4.2 ซม. และขนาดใหญ่มีเส้นผ่านศูนย์กลาง 10 ซม. เพื่อวิเคราะห์หาสภาวะที่เหมาะสมในการเดินระบบบำบัดในด้านอัตราไหลอากาศ ปริมาณสารเคมี ตัวแปรทางอุทกพลศาสตร์ของฟองอากาศ และรูปแบบการกระจายของเวลากัก (Residence Time Distribution: RTD) โดยเดินระบบแบบทีละเท (Batch process) และแบบต่อเนื่อง (Continuous process)

จากการทดลองพบว่า ขนาดของน้ำมันหล่อลื่นแปรรูปโลหะที่มีขนาดหยดน้ำมันเฉลี่ยประมาณ 1.3 ไมครอน ซึ่งทำให้ไม่สามารถบำบัดได้ด้วยกระบวนการตกตะกอนตามปกติ และยังเป็นข้อจำกัดสำหรับกระบวนการ IAF และกระบวนการทำให้ลอยโดยใช้ฟองอากาศเคลือบเคโรซีน ในขณะที่ สภาวะที่เหมาะสมของกระบวนการโคแอกูเลชันที่ให้ประสิทธิภาพการบำบัดสูงสุดถึง 91.23% คือ ที่ค่า pH เริ่มต้น 7 โดยใช้สารส้ม 150 มก/ลิตร โดยสภาวะนี้จะนำไปใช้ในการศึกษากระบวนการ MIAF ต่อไป สำหรับกระบวนการ MIAF แบบทีละเท พบว่าสำหรับคอลัมน์ขนาดเล็กให้ประสิทธิภาพการบำบัด 94.96% โดยใช้ปริมาณสารส้ม 150 มก/ลิตร ที่อัตราไหลอากาศ 1.0 ลิตร/นาที ในขณะที่คอลัมน์ขนาดใหญ่ให้ประสิทธิภาพการบำบัด 82.97% โดยใช้ปริมาณสารส้ม 255 มก/ลิตร และที่อัตราไหลอากาศ 2.0 ลิตร/นาที นอกจากนี้ การบำบัดน้ำเสียปนเปื้อนน้ำมันหล่อลื่นแปรรูปโลหะ ไม่ขึ้นอยู่กับค่าอัตราส่วน a/G ซึ่งเป็นตัวแปรรวมทางอุทกพลศาสตร์ของฟองอากาศและทางกายภาพ (ความปั่นป่วน) ของระบบ เนื่องจากข้อจำกัดในการรวมตัวกันของหยดน้ำมันขนาดเล็กและฟองอากาศ แต่ขึ้นอยู่กับการทำลายเสถียรภาพทางเคมีของหยดน้ำมันเป็นหลัก สำหรับการเดินระบบของกระบวนการ MIAF แบบต่อเนื่องพบว่า ได้ประสิทธิภาพการบำบัดประมาณ 80% โดยประมาณที่อัตราน้ำเข้า 5 ลิตร/ชม และ 11 ลิตร/ชม สำหรับคอลัมน์เล็ก ในขณะที่การเดินระบบในคอลัมน์ใหญ่ที่ได้ประสิทธิภาพการบำบัดเพียง 40-50% ซึ่งเป็นผลจากการไหลวนของน้ำที่เป็นผลกระทบจากความแตกต่างของโมเมนตัม ซึ่งส่งผลเสียต่อการรวมตัวของฟล็อคที่เกิดขึ้น โดยผลกระทบดังกล่าวสอดคล้องกับผลการวิเคราะห์รูปแบบการกระจายของเวลากัก (RTD) กล่าวคือ ข้อมูล RTD จากการทดลองในคอลัมน์เล็กสามารถอธิบายได้โดยใช้รูปแบบการไหลแบบถังกวนต่ออนุกรมในทุกสภาวะทำการทดลอง (ให้อากาศและไม่ให้อากาศ) ในขณะที่ พบรูปแบบการไหลที่ใกล้เคียงถังกวนอุดมคติในการเดินระบบด้วยคอลัมน์ใหญ่ ซึ่งรูปแบบการไหลดังกล่าวสามารถส่งผลเสียต่อประสิทธิภาพการบำบัดโดยรวม ในอนาคต ปัญหาข้างต้นอาจสามารถแก้ไขได้โดยการเดินระบบ MIAF แบบต่อเนื่องร่วมกับขั้นตอนการตกตะกอน (Continuous-Settling) รวมถึงเดินระบบแบบเอสบีอาร์ (Sequencing Batch Reactor, SBR) เพื่อเพิ่มประสิทธิภาพการบำบัดโดยรวม

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต สุรารักษ์ อวนญวน
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5187599520 : MAJOR ENVIRONMENTAL MANAGEMANT
KEYWORDS: OILY WASTEWATER / COAGULATION / MODIFIED INDUCE AIR FLOTATION / BUBBLE HYDRODYNAMIC PARAMETERS / RESIDENCE TIME DISTRIBUTION

SURARUK UANYUAN: TREATMENT OF SYNTHETIC CUTTING-OILY WASTEWATER BY INDUCED AIR FLOTATION COMBINED WITH COAGULATION PROCESS AND REACTIVE OIL CONCEPT. THESIS ADVISOR: PISUT PAINMANAKUL, Ph.D., 111 pp.

The objective of this research was to study the treatment efficiency of cutting oily-wastewater by using Induced Air Flotation (IAF) process combined with coagulation process called as Modified Induced Air Flotation (MIAF) and also reactive oily bubble concept. The experiment was conducted in 2 flotation columns; small column with 4.2 cm diameter and large column with 10 cm diameter. The optimal operating condition (gas flow rate, chemical dosage, bubble hydrodynamic and residence time distribution, RTD) were investigated whereby the batch and continuous processes.

The results showed that cutting oil-droplet (average size approximately 1.3 μm) cannot be separated by decantation and also caused some limitation to IAF and reactive oily bubble coated with kerosene flotation processes. Concerning to the study of coagulation in jar test, the optimal condition was at an initial pH 7 and 150 mg/L of alum: highest removal efficiency was 91.23%. Note that this condition was then applied further in MIAF process. The treatment efficiencies obtained with small and large columns in batch MIAF process were 94.69% and 82.97%, respectively. The optimal conditions were 150 mg/L of alum dosage and 1.0 L/min of gas flow rate for the small column and 225 mg/L of alum and 2.0 L/min of gas flow rate for large column. Moreover, the treatment of cutting oily-wastewater was independent on a/G ratio related with bubble hydrodynamics and mixing parameters, and thus causes some limitation on oil droplet-bubbles agglomeration. In this work, the chemical destabilization was proven as the important treatment mechanism. Moreover, in continuous process, the treatment efficiencies obtained with small column (80%) were greater than those obtained with large column (25-45%): the difference in terms of momentum force, water recirculation and thus floc breaking phenomena occurred in large column should be responsible for these results. According to RTD experiments, tanks in series model were investigated with small column, while closely to ideal CSTR model were obtained with large column flotation: this can affect negatively the overall treatment efficiencies. In future, the continuous MIAF process with settling reactor or Sequencing Batch Reactors (SBR) should be applied in order to enhance the treatment of cutting oily-wastewater.

Field of Study: Environmental Management Student's Signature:..............................

Academic Year: 2009 Advisor's Signature:..............................

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LIST OF ABBREVIATIONS

Alum	Aluminum sulfate
COD	Chemical Oxygen Demand
Cps	Centipoises
% Remove	Removal Efficiency
IAF	Induce Air Flotation
L/min	Liter per minute
L/hr	Liter per hour
m	Meter
MIAF	Modified Induce Air Flotation
g/L	gram per liter
CSTR	Continuous Stirred Tank Reactor
RTD	Residence Time Distribution
Re	Renold Number
OH^-	Hydroxyl group
SBR	Sequencing Batch Reactor

NOMENCLATURES

D_B	Bubble diameter (m)
U_B	Bubble rising velocity (m/s)
f_b	Bubble formation frequency (s^{-1})
a	Bubble interfacial area (m^{-1})
G	Velocity gradient (s^{-1})
μ	Liquid Viscosity (Pa.s, kg/m.s)
ρ	Liquid density (kg/m^3)
σ^2	Variance
θ	Time dimensionless
$E(t)$	residence time distribution function
$E(\theta)$	dimensionless of residence time distribution function
$\varnothing$	Column diameter
τ	Theoretical residence time (min)
$\bar{t}$	Experimental residence time (min)
Q_G	gas flow rate (L/min)
Q_L	liquid flow rate (L/hr)
n	series of stir tank
d	column/pipe diameter (m)
v	velocity (m/s)

CHAPTER I

INTRODUCTION

1.1 Problem statement

Oily wastewater generated from various industries such as oil refinery, petrochemical plants and similar facilities have been produced wastewater containing various pollutants. This prevents oxygen dissolved into water and aquatic life lack of oxygen. In addition even very low concentration is toxic to microorganisms, so that biodegradation is eventually inhibited (Lersjintanakarn, 2008). In oily wastewater treatment, two types of oil, free oil and emulsified oil are needed to be removed. Emulsified oil category is generally found in wastewater effluent with concentration may be up to 1000 ppm and emulsified oil droplet size is 50 μm in diameter approximately. This causes the problem to conventional techniques. Thus two or more treatment approaches are necessary to combine.

Cutting oil which is also called soluble oil and rapid emulsification in water are intensively used in metalworking processes (e.g. as rolling, mills, and metal workshop) (Portela et al, 2001). Cutting oil is rapidly emulsified in water due to the basic composition of cutting oils consisted of mineral oils (40-80 wt %), emulsifiers, coupling agents, and disinfectants (20-60 wt %) (Ríos et al, 1998). The soluble cutting oils have both properties of lubrication and cooling and are rapidly emulsified in water becoming very stable emulsion (Li et al, 2007). However, it loses lubricating and cooling properties after used. It causes environmental problems due to their dissociation/ breakdown of cutting fluid at high temperature, water pollution and soil contamination during disposal (Xavior and Adithan, 2009). Moreover, cutting oil used in pipelines set up could contaminate drinking water as uncommon but possible (Rella et al, 2002).

Several alternative methods have been proposed to be mainly oily wastewater treatment system, for example, adsorption, flocculation, electrocoagulation, flotation (Zoiboulis and Avranas, 2000), ultrafiltration (Hu et al, 2002). The quantity of cutting oil containing in wastewater is very low concentration, incineration might not be the properly disposal approach (Portela et al, 2001). Consequently, salts containing cutting oils formula should be carefully considered as the cause of furnace lining corrosion (El Baradie, 1996)b. Gravity settler and cyclone approach are preferable to non-dissolved oil removal for many industries. Heavy crude oils, which have density nearly water, are difficult to treat by this method. The difference of density and buoyancy between two phases of oil and water is small and results in ineffective performance. Because they are tending to form stable emulsions with water; therefore, gas flotation becomes effective method (Moosai and Dawe, 2003).

Due to oil emulsion can be removed effectively whereby flotation process which generates bubble to attach suspended particles and float up to the surface (Lersjintanakarn, 2008). Therefore it has become crucial process in oily wastewater treatment with several advantages, for instance, great potency, compact size and low capital cost. To obtain a good performance, oil droplets dispersed in emulsion should be destabilized by coagulation before separated by flotation. Coagulation is the process that addition of chemical to reduce repulsion between dispersed particles and allows them agglomerate resulting in increasing size of floc, and effective approach to use together with induced air flotation (IAF) (Meyssami and Kasaeian, 2004).

Oily flotation is one of development of flotation process has been applied. It has been primary improved from gas flotation in order to increasing recovery product in processing ores and demonstrated the selective properties on target mineral particles by control surface properties from coating type of chemical. Oily flotation which is the usage of bubbles coated with oil (oily bubble) has been primary improved from gas flotation in order to increasing product recovery in processing ores. The previous study is reported that kerosene (reactive oil model) was successfully used in particles collection of bitumen extraction and showed shorter induction time of bubble-particles attachment (Li et al, 2006). Therefore, the concept of reactive oil-bubble is interested to be included in this study in order to improve oil droplet and bubble adhesion in the attachment step by their hydrophobicity interface.

1.2 Objectives

The main objective of this research was to study performance of induced air flotation (IAF) process combined with coagulation processes called modified induced air flotation (MIAF) on synthetic cutting oily-wastewater treatment. The specific objectives were:

1. To study feasibility of gas bubble coated with kerosene with IAF process on cutting oily wastewater treatment;
2. To determine the optimal operating conditions for coagulation and MIAF processes such as initial pH, chemical concentration, gas flow rate and bubble hydrodynamic parameter;
3. To extend operating condition and improve overall treatment efficiency of continuous MIAF process for cutting oily wastewater treatment;
4. To investigated the effect of liquid flow regime on treatment efficiency of continuous MIAF process by analyzing Residence Time Distribution (RTD).

1.3 Scope

This research was conducted in batch (IAF, coagulation and MIAF) and continuous processes (MIAF) for treating the cutting oily-wastewater at department of Environmental Engineering, Chulalongkorn University. The following details can be summarized:

1. This research was conducted by using concentrated cutting oil (Castrol cooled BI) mixed with tap water at concentration 1g/L as synthetic oily wastewater. The oil concentration was selected from intermediate value from Chooklin, 2004.
2. Two sizes of 2 m height column were used which diameter are 4.2 and 10 cm. These two columns equipped with different gas diffusers. Small column was equipped with rigid gas diffuser while large column equipped with flexible membrane diffuser. Sampling was performed at 20 cm and 90 cm above gas distributor for batch and continuous processes.
3. Kerosene (Shell) was used to generate reactive oily bubble and alum was used as coagulant in coagulation and MIAF processes.
4. Bubble hydrodynamic and mixing parameters will be investigated and presented in terms of ratio of interfacial area and velocity gradient (a/G).
5. Continuous MIAF process was conducted with different liquid flow rate (Q_L) and then analyzed liquid flow regime by RTD experiments.

CHAPTER II

THEORETICAL BACKGROUND

2.1 Physical characteristics of oily wastewater (Aurelle, 1985)

Selection of proper approach to treat oily wastewater depends upon characteristics of pollutant forms that possibly caused from various factors. Oily wastewater attribute can be defined in 4 different categories. The characteristics of oily waste from various industries are shown in **Table 2.1** which indicates that emulsified oil attribute is difficult to treat.

1. **Dissolved oils**

Hydrocarbons are not totally dissolved in water. The solubility depends on molecular weight and polarity, the solubility increases as the molecular weight decreases. Low molecular weight hydrocarbons which are easily volatized are also soluble hydrocarbons.

2. **Oils emulsions in absent of surfactants**

Wastewater effluents from industrial processes are frequently found in emulsion form which can be caused by centrifugal pump, venturi, and elbow joint. This oil in water (O/W) is produced by both of agitation to disperse hydrocarbons in water and during the phenomenon of biphasic condensation. These emulsions can be divided into primary and secondary emulsions.

Primary emulsions have droplet diameters more than 100 microns and the micro-droplet can be visible with naked eyes. Secondary emulsions have droplet diameters less than 20 microns and can be visible as milky trait.

3. **Oils emulsions in present of surfactants**

Emulsions of oil and water with the presence of surfactants are mostly found in industrial effluent, and their interaction (O/W and surfactants). The presence of surfactants results in decreasing of interfacial tension of oil in water emulsion. Under this condition (within stripped area), emulsion is very stable (stabilized emulsion), the oil phase presented in emulsion spontaneously.

4. **Film layer of oils**

Oily layer is usually floated on the oil-air interface and this form can be quickly separated gravity (Da Rosa and Rubio, 2005). Small amount of oil is sometimes covered wide spread of water surface as a monolayer film. Spontaneous monolayer of oil film can be created by small amount of oil. The densities of hydrocarbons that are lower than water make them easily collected at the surface.

Table 2.1 Characteristics of oily waste from industries (Adapted from Wang et al, 2004)

Source	**Industries**	**Characteristics**
Alkaline and acid cleaners	Metal fabrication, iron, and steel, metal finishing industrial	Normally highly emulsified due to surfactants; difficult to treat
Machine coolants	Metals manufacturing machining	Normally emulsified and difficult to treat
Vegetable and animal fats splitting, refining, rendering	Edible oil, detergent manufacture, fish processing, textile (wool scouring), tank car washing	Both free and emulsified oils; difficult to treat
Petroleum oils	Petroleum refining, Petroleum drilling	Both free and emulsified oils; difficult to treat

2.2 Cutting Fluids

Firstly, the cutting fluid actions are reported as coolants by Taylor in 1907 (Xavior and Adithan, 2009). Cutting fluids are the material used in machining process to improve tribological characteristics of work piece-tool-system (Sokovic and Mijanovic, 2001). Turning process, the mineral from the surface of rotating cylindrical workpiece is removed by cutting tool. Mineral removed is called “chip”. The sliding of chip on the tool surface affects in creation of high shear stress and friction coefficient during chip formation (Xavior and Adithan, 2009).

The cutting fluids can decrease heat at the cutting area by flooding over the tool chip and work piece. Cutting fluids act as cooling and lubricating agents at the cutting zone. During metal machining operation, the contact of interface between chip/workpiece and tool produce heat in every cutting speed caused by wear rate, shear strength and friction. These problems lead to machine materials corrosion and workpiece distortion. The high speed cutting required cooling effects whereas the lubricating action is more important at the lower speed. Coolant properties must be high thermal conductivity, high specific heat capacity and high heat of vaporization. Water, one of the best media known, can be composed of partly constituent to perform this requirement. However, water is not a good lubricant and can be corrosive to ferrous metal. Moreover, water tends to wash lubricant in rotating and sliding of machine and leads to machine corrosion. Sometimes, extreme pressure (EP) agents are added when used in severe machining operations. The mixture properties are combined cooling and anti-corrosion action. Cutting fluids have become desirable solution and provided more benefit for manufacturers. In case they have been used or selected in optimal manner, cutting fluids result in increasing of productivity, reducing costs by making higher cutting speeds, higher feed rates and more depths of cut possible. In addition cutting fluids can also increase tool life, reduce surface roughness, extend dimensional accuracy, and decrease energy consumed by mainly characteristic cooling and lubricating actions (El Baradie, 1996)a. However, environmental problems caused from cutting fluid applications may occur due to their dissociation/ breakdown of cutting fluid at high temperature, water pollution and soil contamination during disposal (Xavior and Adithan, 2009).

Classification of cutting fluids

The cutting fluids can be categorized according to various criteria. Herein the main group of cutting fluids is categorized according to its composition. Three categories are water-soluble fluids (water miscible), neat cutting oils and gasses. Classification of metalworking fluids and their composition before being dispersed in water is shown is **Figure 2.2**.

1. Water-soluble fluids (water miscible)

"Soluble oils" do not referred to dissolve in water but are mineral oils blended with emulsifier. Mixing blended in water disperse oil droplet in continuous phase of water and then become oil in water emulsion. The original applications of water soluble fluids are used for high speed cutting machining operation because they have better cooling capabilities in thermal reduction of tool parts. Water-soluble fluids are mixed with water to perform various dilutions that the proportions depend on type of operation. Classification of soluble cutting fluids **(Figure 2.1)** can be divided in 3 types; emulsifiable oils (soluble oil), chemical (synthetic) oils and semi-chemical (semi-synthetic) fluids. Types and general characteristics of them are shown in **Table 2.2.**

2. Neat Cutting Oils

Neat cutting oils are used in undiluted form. They do not have to be totally consisted of mineral oils, but they often include high percent of additives. These cutting fluids are very suitable for very high cutting pressure operation because they are notable in lubricating action. The major groups of neat cutting oils are mineral oils, fatty oils. Neat cutting oils formula can be blended and proportion with extreme pressure additives, sulphur and chlorine. Mineral oils consisted of mineral oils without additives, have poor lubricating properties but they are low cost. These oils are stable and suitable for light operations, for example, the machine operation of aluminum, magnesium, brass, and sulphurized or lead free machining steels. Fatty oils are obtained from lard and rape (seed of rape plant) oil. They are once widely used but they are difficult to gain today. Fatty oils are very polar, high "oiliness" anti friction performance, but they have poor anti weld characteristics. They are also easily oxidized and caused odors.

Table 2.2 Water Soluble (Water Miscible) Fluids (El Baradie, 1996a)

CLASS	TYPE	GENERAL CHARACTERISTICS
Emulsifiable Oils	1) General purpose soluble oils	➢ Used at dilutions between 1:10 and 1:40 to give a milky emulsion. ➢ Used for general purpose machining.
	2) Clear type soluble oils	➢ Used at dilutions between 1:50 and 1:100. ➢ Their high emulsifier content results in emulsions which vary from translucent to clear. ➢ Used for grinding or light duty machining.
	3) Fatty soluble oils	➢ Used at similar concentrations to 1) and of similar appearance. ➢ Their fat content makes them particularly good for general machining operations on nonferrous metals.
	4) EP soluble oils	➢ Generally contain sulphurized or chlorinated EP additives. ➢ Used at dilutions between 1:5 and 1:20 where a higher performance than that given by 1), 2) or 3) is required.
Chemical (Synthetic) fluids	1) True solutions	➢ Essentially solutions of chemical rust inhibitors in water. ➢ Used at dilutions between1:50 and 1:100 for grinding operations on iron and steel.
	2) Surface active chemical fluids	➢ Contain mainly water soluble rust inhibitors and surface active load carrying additives. ➢ Used at dilutions between 1:10 and 1:40 for cutting and at higher dilution for grinding. ➢ Most are suitable for both ferrous and nonferrous metals.
	3) EP surface active chemical fluids	➢ Similar in characteristics to 2) but containing EP additives to give higher machining performance when used with ferrous metals. ➢ Used at dilutions between 1:5 and 1:30.
Semi-chemical (Semi-synthetic) fluids		➢ Essentially a combination of a chemical fluid and a small amount of emulsifiable oil in water forming a translucent, stable emulsion of small droplet size. ➢ EP additives are usually included permitting their use for moderate and heavy duty machining and grinding applications.

3. Gasses

Air can be considered to be another cutting fluid and has attractive results in prolong tool life. Even gaseous lubricant does inefficiency to us as coolant due to its lower cooling capacity than liquids, there was report that employment of cool air promotes 400 percent increasing of tool life in milling operation. Gaseous that was considered to use as cutting fluids are carbon dioxide and nitrogen.

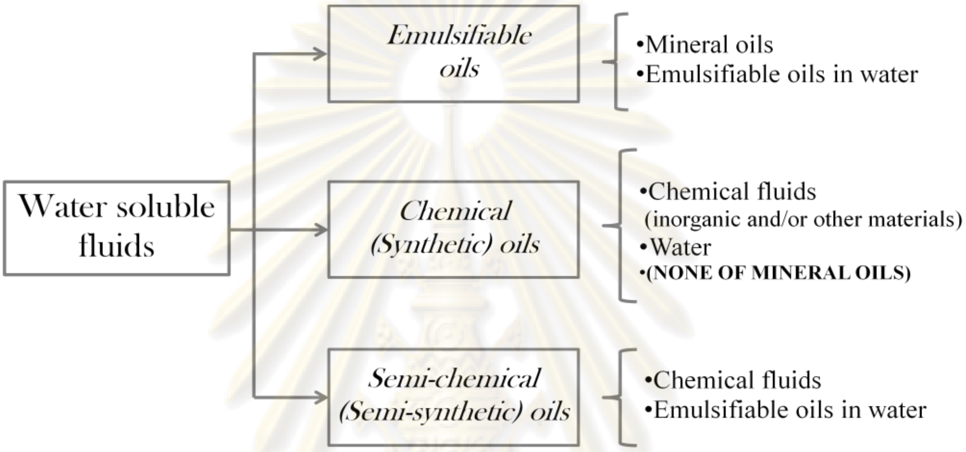


Figure 2.1 Classification of Water Soluble Fluids

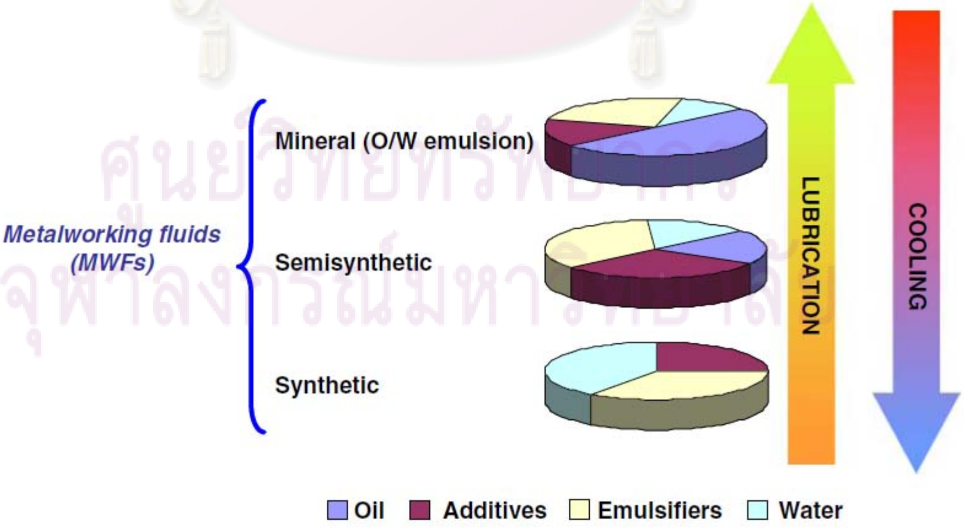


Figure 2.2 Classification of metalworking fluids and their composition before being dispersed in water (Benito et al, 2009)

2.3 Physico-chemical treatment of oily wastewater

Various oily treatment technologies have been reported based on physical and chemical processes. Due to biocides, for example, heterocyclic sulfur and nitrogen compounds, containing in cutting oils, biodegradation has become less important for oily wastewater treatment processes**,** whereas these chemicals prevent their degradability (Cañizares et al, 2008). However, physical cooperated with chemical treatments can provide a good performance for oily wastewater treatment. Chemicals are firsly used to destabilize colloid state of emulsion by reducing of repulsion between surface active and dispersing medium (Bensadok et al, 2007) and physical methods which are enabling to separate oil from water are gravitation, filtration, flotation and centrifugation.

The primary treatment of oily wastewater is normally removal of free oil by physical process. The secondary is dealing with breaking oil-water emulsion and soluble oil using chemicals process, and separation by physical process later. The tertiary treatment associates finishing process to complete oily wastewater treatment. Oily waste water treatment approach can be briefly summarized as follows (Lersjintanakarn, 2008).

Decantation: The floatable free oil rising up to water surface is natural phenomena and simple to handle at primary treatment of oily wastewater. This method separates free oil without modified original oil characteristic by means of stokes law application. Thus, decantation does not applicable to small oil droplets removal because small oil droplets take very long time to rise up to water surface causing the larger tank construction and uneconomical.

Coalescence: This method accelerates increasing size of oil droplets based on Strokes Law parameters. The rising velocity is proportional to droplets size square so that it affects on increasing of oily emulsion separation, the secondary treatment.

Flotation: This process applied stokes law by increasing different density between oil and water by injection of gas bubbles into water phase in order to pick up oil droplets dispersed in water and rise up together at the surface. The agglomeration of oil and gas bubbles rapidly rise up due to gas or air has lower density than water. There are two types of flotation in general classification, induced air flotation (IAF) and dissolved air flotation (DAF).

Chemical process: The purpose of chemical utilization is for destabilization of stable oil emulsion. This method is mainly used for stable emulsified oil containing wastewater. Chemicals destabilized oil droplet stability first, and then destabilized oil droplets tend to coalesce and floc formation. The fundamental of this process is based on knowledge of electrical properties at colloids surface, not stokes law.

2.4 Colloids and Stability

The term coagulation herein is referred to overall process of particle aggregation which is both particle destabilization and particles transport. Flocculation is applied for describe particle transport step (Weber, 1972) using external energy input to induce the floc formation.

2.4.1. Colloids

Turbidity in effluent wastewater is the result of dispersion of colloids which is very fine particles with a diameter between 10^{-9}-10^{-6} m. Colloid is a type of mixture which one substance is immiscible dispersed throughout another. Colloid system consists of 2 phases which are dispersed phase and continuous phase. The different property that distinguishes colloid from true solution is light scattering causing by the light beam passes through colloid and light is reflected by colloid unlike passing through true solution resulting in little light scattering. This phenomenon is known as Tyndall effect. Another the specific characteristic of colloids is the Brownian motion, which keep particles diffused in random fashion.

2.4.2. Stability of colloids

The stability of colloidal particles, which is the results of the interaction of electric surface charge between colloids, allows them dispersed in suspension or prevents them from aggregation. This electrical interaction may be attractive or repulsive forces depend upon type of charge positive or negative that colloids carry. Like charges repel each other. Mostly the particles dissolved in water have a negative charge repel each other and allow them disperse in water following with their turbidity present.

1) Electric double layer Theory

Due to their small size and mass, they cannot be settling by gravitational force and are difficult to separate from water. Its buoyancy and kinetic energy is very low to conquer the repulsive force. However, smaller size particles have high surfaces area and bring about to form double layer. The ions attract to unlike charges at the particle surface forming a first inner layer by accumulation of counter ions, stern layer. The next stern layer is diffused layer containing the opposite charges of surrounding colloidal particles accumulation. This layer cannot be regularly removed by external velocity gradient since it bound to the particles as the shear plane. Thus, diffused layer does not affected by fluid motion. The distribution charge of electric double layer is illustrated in **Figure 2.3**.

2) Zeta potential

The electrostatic potential generated from the accumulation of surrounding ion of colloidal particles is indicated by zeta potential. Zeta potential is an indirect measure the different electrical potential between shear plan and bulk fluids of solution. The electric potential around colloidal particles correlated with distance from particles surface is shown in **Figure 2.4**.

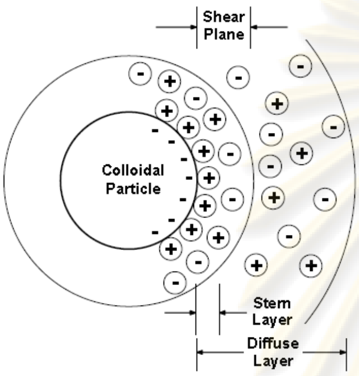


Figure 2.3 Electric double layer

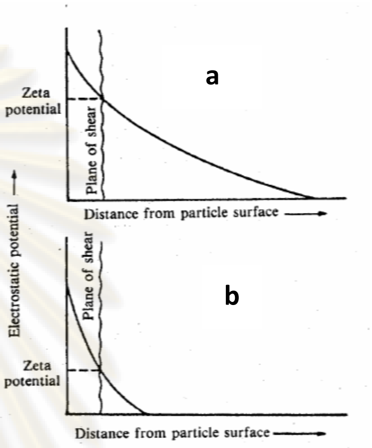


Figure 2.4 Intensity of zeta potential variation in different distance from particles surface (a) before and (b) after coagulants addition (Sastaravet, 2008)

2.5 Coagulation

Coagulation is the physicochemical destabilization process increasing size of floc formation from small suspended particles in water to separate from mixture up to the surface. The method link to elimination of this electrostatic barrier is coagulation-flocculation. The process destabilizes colloid charge by coagulants addition is chemical coagulation. Additionally, surfactant is used to alter its characteristics whereby absorb the surface of colloid. To separate colloids from water, destabilization of colloids charges is needed by neutralization of its charge first. When the charge layer is removed, these particles tend to be agglomerate, then settled and further disposed by other mechanisms. Alum and ferric chloride are generally used as mainly available in commercial coagulants in water supply and other industrial proceeding.

2.5.1 Destabilization of colloids mechanisms

Different chemical addition affects on different colloids destabilization mechanism. It is up to condition used, some materials function as coagulant or coagulant aids, and some can destabilize colloids more than one mechanism. The destabilization of colloids is carried out through four different methods: (1) Diffuse layer compression; (2) adsorption to produce charge neutralization; (3) enmeshment in a precipitate; and (4) adsorption to permit interparticle bridging.

1. Double layer compression

This mechanism is the purely electrostatic interaction between some coagulant species and colloidal particles. Ion of the opposite charge increases counter ions and results in diffuse layer is compressed when high concentration of electrolyte is introduced. The distances of repulsive interaction between similar colloidal particles are reduced. The effective of coagulation in wastewater treatment is determined in jar test which the coagulant dosage is varied and turbidity remained after appropriate stirring and settling (Weber, 1972).

Counter-ions addition (opposite charge ion to particle) into the wastewater reduces the diffused layer thickness. This effect results in reduction of Zeta potential. For general oily wastewater and cutting oil wastewater, droplets have negative charges. So, the counter ions in these cases are positive charges, for example, Al^+. 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 (Lersjintanakarn, 2008).

2. Sweep coagulation (Enmeshment in a precipitate)

Enmeshment of colloids in precipitation is generally called sweep coagulation. Metal hydroxide precipitates, $Al(OH)_3$, or $Fe(OH)_3$, will be generated when introduced alum ($Al_2(SO_4)_3$) and ferric chloride ($FeCl_3$) with high enough concentration interact with hydroxides (OH^-). The particles are then entrapped in precipitates formation (Wang et al, 2005). In case of colloidal particles dispersed in water present in low concentration (low turbidity), coagulation accomplishment requires large amount of coagulant more than water containing high content of colloids, whereas it is low possibility that coagulants can contact with colloids. Sweep coagulation is pertinent in this case whereby the excess coagulant is added into the water to enhance contact probability of coagulants and colloids, and form entrapped a sticky insoluble precipitate (Weber, 1972).

3. Adsorption and charge neutralization

Some chemical species that carry the opposite charge to colloids are capable of being adsorbed at the surface of colloidal particles. A destabilization phenomenon of colloids by chemical coagulation is combined of various mechanisms. Typically coagulants which function of adsorption and electrostatic neutralization are the long-chain organic amines. The positive charged of organic amine molecules (R-NH^{3+}) are rapidly attach negatively charged of colloids. The charge on particles is neutralized and the electric repulsion is eliminated or minimized causing destabilization and therefore agglomeration. The organic amines are hydrophobic since lacking of interaction between CH_2 containing in their R-chain and enclosing water. Consequently, these positive charged ions are driven out in water and coming close to absorbed on particle interface. However, an over dose of R-NH^{3+} counter ions bring about charge reversal from negative to positive and return to be dispersion (restabilization) system.

In cast using metal salts as coagulants, dissociated metallic ions undergo hydrolysis and form positively charged metallic hydroxyoxide complexes. Trivalent salts of aluminum and iron create various species due to hydrolysis products which tend to polymerize to give polynuclear metallic hydroxides. The over dose of metallic salts is the similar manner of organic amines in which results in charge reversal and restabilization of particles (Wang et al, 2005). Reduction of surface charge by adsorption is a much different mechanism than reduction by double layer compression.

1. The sorbable species are capable of destabilizing colloids is used at much lower dosage than the nonsorbable used in "double layer compressing" ions.
2. Destabilization by adsorption is stoichiometric. Thus, the required dosage of coagulant increases as the concentration of colloids increases.
3. It is possible to overdose a system with an adsorbable species and cause restabilization as a result of a charge reversal on the colloidal particle.

4. Adsorption to permit interparticle bridging

Macromolecules can be also used as destabilizing agents, for example, cellulose, starch including synthetic organic polymer. This high molecular weight polymer may be positive charge, negative charge or neutral. However, anionic polymer is noted that is the most economical in wastewater treatment although dispersed particles have negatively charged also. The chemical groups which located in polymer molecule interact with colloidal surface. Some of this group adsorb on surface of particle and leave extending molecule into the solution. If a second particle contacts the vacant site of this extended part, it will be attached (Weber, 1972). There are several commercial chemical products that can be used as destabilizing agents. Their molecule structure and properties may attach oil droplets by the extended remainder (Lersjintanakarn, 2008).

2.5.2. Influencing coagulation factors

Several factors affect significantly coagulation process and are present in the following discussion described below (Wang et al, 2005).

1. Colloid concentration

Colloid concentration is gather impact to either dosage required or coagulation efficiency. The required dosage in coagulation is stoichiometrically involving dispersed colloidal particle concentration in solution. The rate of coagulation is slow for dilute colloidal systems consist of low number of colloidal particles in suspension. In case of low colloids concentration present, improvement could be used coagulant aid or applied a large coagulant dose to suspension. However, applied overdose concentration could results in enhancing restabilization of colloids opportunity.

2. Coagulant dosage

The effect of aluminum and iron coagulant dose was studied and evaluated as the four relationships zone; first low dosage zone, increasing the dosage progressively to the highest dosage divided in zone four.

Zone 1: Insufficient coagulant dosage to destabilization of colloids
Zone 2: Sufficient coagulant has been introduced to allow coagulation occur
Zone 3: Excess coagulant leading to charge reversal and restabilization of particles
Zone 4: Oversaturation allow metal hydroxide precipitate entraps colloidal particles and create sweep coagulation efficiently

3. Zeta potential

Zeta potential is stand for the net charge of colloidal particles. Higher value of zeta potential is greater magnitude of repulsive force between colloids. Consequently, colloidal system stability is enhanced. The zeta potential is measured by electrophoretic of particle mobility in electric field.

4. Affinity of colloids for water

Hydrophilic (water-loving) colloids are very stable due to their hydration shell, chemicals cannot easily replace sorbed water molecules. Hence, they are difficult to destabilize by coagulation and remove from suspension. Hydrophobic stability depends upon their electrostatic charge and the more of their water-loving. The suspension containing such hydrophilic particles needs 10-20 times of coagulant when compared with normally dose for destabilization of hydrophobic particles. Conversely, hydrophobic (water-hating) the metal oxide can be easily destabilized or coagulated. The bulk colloidal particles of turbid water contain the mixture of hydrophilic and hydrophobic in suspension coming with the intermediate in the degree of their difficulty to coagulate.

5. pH value

pH value is represent of value measured of H^+ and OH^- ion concentration. Isoelectric point is referred to the pH value that charge is the most nearly neutralized. At high pH value above isoelectric point, the particles charge become more negative charge or less positive leading to reverse effect take place. The Isoelectric point of alum is generally about pH 8, but it varies in pH range 7 to 9. The greatest adsorption take place at the pH range provided the minimum solubility.

6. Anions in solution

The restriction of restabilization colloids and charge reversal is concerned when using alum and iron as coagulants. Nevertheless the behavior could be restrained in present of high concentration of anions like sulfate, silicate and phosphate. The ability to prevent restabilization is worked when $[SO_4^{2-}]$ is excess up to 10-14 mg/L. Using alum as coagulant causes several species of positively charged of aluminum hydroxyoxides. Aluminum hydroxide has lowest solubility at isoelectric point located on pH range 7-9. Increasing of alum while maintained this pH range initiates sweep coagulation take place and aluminum hydroxide precipitation. Conversely, at the lower pH range (5 - 7), increasing of alum dosage brings about promoting of positively charged alum species that can adsorbed on particles surface, and hence charge reversal and restabilization occurred. Moreover, this similar idea is able to adapt for iron coagulation.

7. Cations in solution

Divalent cations, for example, Ca^{2+} and Mg^{2+}, have been recommended in which helpful and necessary to coagulation of is negatively charged clay particles with the three effects.

(1) Double layer compression

(2) Minimization of repulsive force between negatively charged of colloids

(3) Reduction of repulsive barrier between adsorbed polymers

8. Temperature

Coagulation under the low temperature using metallic salts affects in converse effect. The suggestion of switch to iron salts is recommended when working under the low temperature. Enhancing the rate of coagulation at higher temperature can be done by the following:

(1) Increasing kinetic energy or molecule velocity

(2) Promote chemical reaction rates

(3) Reduction of flocculation time

(4) Decreasing water viscosity

(5) Modify floc formation into larger agglomeration

9. Gradient velocity (G)

In addition of known appropriate type and coagulant dosage, gradient velocity (G) is another important parameter indicating turbulent level process and energy consumption in coagulation. The approach developing to control this process except jar test could be zeta potential control, residual coagulant analysis. In case of velocity gradient occurred from aeration or pneumatic mixing, power could be determined by following equation (Sastaravet, 2008):

$$P = C_1 Q_G \log\left(\frac{h + C_2}{C_2}\right) \qquad \textbf{Eq. 2.1}$$

P = Power consumption (Nm/s)
C_1 = Constant = 3904
C_2 = Constant = 10.33
H = Dept of diffuser (m)
Q_G = Air flow rate (m^3/min)

2.6. Flocculation process

The complete design coagulation unit has to consider both particle destabilization and particle transport. Two step process involving chemical and physical aspects is based on colloids chemistry and fluid mechanics. Destabilization is evaluated in jar test to determine proper coagulant type and dosage. The particle transport on flocculation to produce inter particle contacts is the next considered. Flocculation is provided for interparticle contacts. The general contacts is performed by orthokinetic flocculation that is colloidal particles collide with each other caused from velocity gradients produced by fluid mechanical means. Design of flocculation unit is associated with velocity gradient selection, reactor configuration, detention time to produce aggregations of suitable size for removal in subsequent unit (Weber, 1972). The term coagulation herein is referred to overall process of particle aggregation which is both particle destabilization and particles transport. Flocculation is applied for describe particle transport step (Weber, 1972) using external energy input to induce the floc formation.

2.7 Flotation Process

The flotation is associated with surfaces chemistry of separated material which natural hydrophobic materials are mainly ideal material and this process involves several physical phenomena (Zoiboulis and Avranas, 2000). As theoretical predict, the collection efficiency is therefore depending on droplet size and bubble size (Zoiboulis and Avranas, 2000; Moosai and Dawe, 2003).

2.7.1. Flotation process category

The flotation processes frequently mentioned in wastewater treatment area are induced air flotation (IAF) and dissolved air flotation (DAF) according to different in air injection methods (Moosai and Dawe, 2003).

1) Induced air flotation (IAF)

Air injection into liquid is able to perform by both mechanical type which bubbles is relatively coarse in ranged 2-5 mm and blowing air through porous material by rotating impeller. This type of flotation can induce atmospheric air without requirement of blowers or compressors, which is why it has known as “induced air flotation” in water treatment industry (Jameson, 1999). The role of IAF for treatment of wastewater discharged from steel mills, dairy factories and remediation of soil contaminated with petroleum was demonstrated that IAF is successfully used for separation of algae and phosphorus compounds from sewage effluent plant. IAF process uses gas bubble size between 40-1000 μm and turbulent hydrodynamic conditions. The retention time is generally less than 5 min. (Rubio et al, 2002).

2) Dissolved air flotation (DAF)

The DAF process is much more commonly used in water treatment than IAF. Water stream saturated with air raised pressure up to 4 atm is injected into flotation tank. Small bubbles are produced while the pressured is decreased from value of pressurized to atmospheric pressure. For this reason, small bubbles produced via DAF make water treatment beneficial. Nevertheless, the residence time of small bubbles is relatively long causing large flotation cell construction (Jameson, 1999). The DAF process utilizes the microbubbles size between 30-100 μm and quiet. The retention time is longer than IAF process; therefore, DAF does not suitable for large volume effluent treatment. (Rubio et al, 2002)

2.7.2. Flotation efficiency

The flotation is associated with surfaces chemistry of separated material which natural hydrophobic materials are mainly ideal material and this process involves several physical phenomena (Zoiboulis and Avranas, 2000). The performance of flotation process is relied on capability of bubbles to collect particles and carried them to the surface where the sludge forms. The particles is transformed to hydrophobic or non-wetting first, and then attached to bubbles, this is called collection mechanism. As theoretical predict, the collection efficiency is therefore depending on droplet size and bubble size and distribution (Zoiboulis and Avranas, 2000; Moosai and Dawe, 2003), oil-bubble contacts, oil-air bubble hydrodynamics, interfacial properties between oil, air and water, temperature and viscosity (Moosai and Dawe, 2003).

2.8. Stokes Equation

The droplet rise velocity is the major factor in air flotation. The terminal rise velocity, U_B for rigid spheres under lamina flow is given in Stokes equation (**Eq.2.2**). The rising velocity is dependent on bubble/droplet diameter and density difference. Thus, oil droplet size is very important. Increasing density difference enhances rising rate of oil-water agglomerates. Stokes equation is describe reasonable well for the solid sphere in the rank $10 < d < 200$ μm, and for the similar size of gas bubbles when surfactant is present in water. The Stokes equation can be assumed that it is valid when applied with oily wastewater since the surfactant is normally present. The surfactants plays a role in rigidify gas bubble and water interface.

$$U_B = \frac{d^2 g \Delta\rho}{18\mu} \qquad \textbf{Eq.2.2}$$

where, U_B, terminal velocity (rising or settling) of particles, d; diameter of dispersed phase particles, g; gravitational acceleration, Δρ; difference in density between dispersed and continuous phase, μ; continuous phase viscosity.

2.9 Modified Induced Air Flotation (MIAF)

Modified Induce Air Flotation (MIAF) is the physicochemical process developed from combination of the use of chemicals to destabilize oil droplet and gas flotation process to remove destabilized oil out of water. MIAF is created for the purpose of improve oily wastewater treatment efficiency.

Soluble cutting oil is normally consisted of surfactants; therefore, oily wastewater polluted by cutting oil is very easily mixed and become very stable emulsion rapidly. In general, the diameter of oil droplets in presence of surfactants (oil-water emulsion) is less than 10 μm that cannot be treated by Stokes based processes. This size is classified into colloidal range which is very stable dispersed in the liquid phase affected by Brownian motion and electrostatic repulsion. The particles is very small size, the electrostatic force intensity is stronger effect than gravity force. Thus, colloidal particles cannot settle by gravity force and drain out through decantation. Even though this oil drops can be settling, it takes very long time.

For MIAF process, the solution for emulsified oil separation from water is needed to destabilize dispersed oil droplet first by elimination or minimization of repulsive barrier (diffused layer) that blocks oil droplet to coalesce. The latter step required is physical process to separate destabilized oil in form of floc such as flotation. So MIAF is classified in two major steps consisted of coagulation-flocculation and induced air flotation.

Step 1: The mainly approach to destabilize oil droplets present in stable emulsion (coagulation). Coalescence or aggregation of destabilized oil droplets (flocculation) is then occurred due to the repulsive barrier thickness is already removed or minimized.

Step 2: Flotation process has been become acceptable method to remove fine particles and applied with oily wastewater treatment present in form of stable emulsion. The gas bubbles, normally air, introduced by flotation process are entrapped within floc leading to increasing of density difference between floc and air.

2.10 Bubble hydrodynamic Parameters

1. Bubble diameter (D_B)

Bubble diameter is important parameter which determines gas hold up, rising velocity and air dispersion in flotation system. The bubble sizes is also related with particle removal potency and have strong affect for flotation rate constant (k) when it is described by the first order rate equation. However, for mechanical flotation cell and turbulent conditions, flotation constant is less dependent on bubble diameter (Grau and Heiskanen, 2005). Bubble diameter is determined by image analysis technique using high speed camera (100 images/s). The average diameter (d_{avg}) is measured from 150-200 bubbles and calculated by **Eq. 2.3**.

$$d_{avg} = \frac{\sum_{i=1}^{N} d_i}{N} \qquad \textbf{Eq.2.3}$$

2. Bubble rising velocity (U_B)

The bubble rising velocities have been calculated by using the image analysis technique. The terminal velocities of bubbles produced in most frequent diameter will be used to calculate by measuring distance between two frames and variation of **Eq. 2.3**. (Painmanakul et al., 2005).

$$U_B = \frac{\Delta D}{t_{frame}} \qquad \textbf{Eq.2.4}$$

Where U_B = Bubble rising velocity

ΔD = Distance between two frames

t_{frame} = Acquisition time frame

Additionally, bubble rising velocities can be determined by plot correlation between terminal rising velocities versus bubble diameter as obtained in experimental curved of Grace and Wairegi (Painmanakul et al, 2004).

3. Bubble formation frequency (f_B)

A number of bubbles generated through air diffuser per unit of time are referred to bubble bubbles formation frequency (f_B). It can be determined by **Eq. 2.5** (Painmanakul et al., 2004).

$$f_B = \frac{Q_G}{V_B}$$ **Eq. 2.5**

Where f_B = Bubble formation frequency, s^{-1}

Q_g = Gas flow rate (m^3/s)

V_B = Bubble volume, m^3

The relationship of bubble frequency and air flow rate is correspondingly when one of them is changed. In case of increased air flow rate influence on promoted bubble frequency, this brings about introduction of collision probability.

4. Interfacial area (a)

The interfacial area, a considerable parameter related with flotation efficiency, is defined as the ratio between the bubble surfaces (S_B) and the total volume in reactor (V_{Total}). The interfacial area is able to experimentally determine using the number of bubbles (N_B) which is calculated from the terminal rising bubble velocities (U_B) and the bubble formation frequency (f_B) as expressed in **Eq.2.6**.

$$N_B = f_B \times \frac{H_L}{U_B}$$ **Eq. 2.6**

Hence, the interfacial area can be calculated from the **Eq. 2.7** below

$$a = N_B \times \frac{S_B}{V_{total}} = f_B \times \frac{H_L}{U_B} \times \frac{\pi D_B^2}{AH_L + N_B V_B}$$ **Eq. 2.7**

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

D_B = Bubble diameter, m

A = Cross-sectional area of reactor, m^2

V_B = Bubble volume, m^3

2.11 The concept of reactive oily bubble

Reactive oily bubble herein is referred to bubbles covered by a thin layer of oil containing oil soluble collectors (surfactants) which are added into oil phase in order to turn particles into hydrophobic state. Reactive oily-bubble flotation was developed from the concept of oil flotation which is able to collected fine particles with small oil droplets instead of gas bubbles in flotation column due to small oil droplets are easier generated than air bubbles.

In conventional flotation, fine particles have small inertia in following the liquid stream line since their kinetics energy is insufficient for particle-bubble attachment mechanism. Large amount of fine bubbles were use as the flotation carrier to increase both of surface area flux and to enhance collision efficiency. However, generation of small bubbles to enhance much more carrying capacity is more difficult than making of small oil droplets. These small oil droplets with 0.5 to 50 µm in diameter can be produced by emulsification.

For conventional oil flotation, oil droplets were used as the carrier to collect particles. It has been demonstrated in the laboratory scale that it has capability for recovery the fine particles less than 10 µm. The fine particles are more easily collected at oil-water interface when compare with air-water interface due to strong attractive force of molecule interface. However, it has been considered as uneconomical for commercial scale because large amount of oils requirement in operation, oils recovery and recycling stage. This is the reason why the use of bulk oil carrier in hydrophobic particles collection could not be remained.

Collector is inferred to chemical reagents which make the target particles hydrophobic in liquid. Emulsification of oily collector enhances a number of oil droplet and oil droplet distributions and hence improves flotation kinetic. For reactive oily bubble flotation, the selectivity of particles can be controlled by type and concentration of additional collector in oil phase. The different oil-assisted flotation processes are illustrated in the **Figure 2.5**.

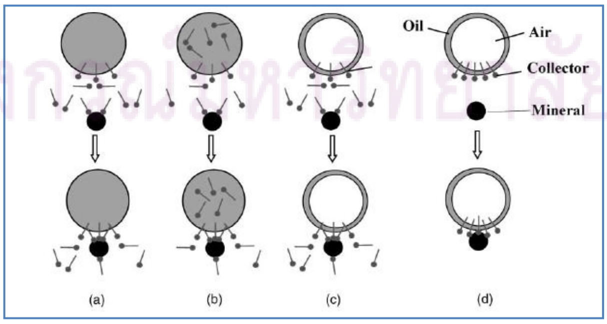


Figure 2.5 Reactive oily bubble flotation in comparison with oil-assisted flotation system: (a) conventional oil flotation where oil droplets are used to lift mineral and collectors are added in aqueous phase, (b) emulsion flotation which oil droplets are used to lift mineral but collector are added in oil phase, (c) oily bubble flotation which used air bubble covered

with thin oil film to lift mineral and collectors are added in aqueous phase, (d) reactive oily bubble flotation which is similar to (c) but collectors are added in oil phase and decrease oil amount (Liu et al, 2002).

The conventional oil flotation as shown in **Figure 2.5a**, collector is added into aqueous phase and present on mineral surface later. Without the direct contact between oil-water interfaces and particle surfaces, the attachment process would be retard. The modified oil flotation process as shown in **Figure 2.5b**, the collector is added in oil phase and also mentioned to emulsion flotation. This technique can carry out partly of conventional oil flotation. However, it is not only required large amount of oil and collector but led to face the problem of collector transfer into aqueous phase also. The conventional oily bubble flotation as shown in the **Figure 2.5c**, the drawback of conventional oil flotation process is remained but only small amount of collector is needed to add into aqueous phase. The reactive oily bubble as shown in **Figure 2.5d**, it has been developed from modified emulsion and conventional reactive oil flotation together to obtain a good beneficial from both approaches (small amount of oil and collector addition).

In conventional oil flotation practice, a collector is introduced into water phase, but reactive oily bubble flotation is the process that collector is introduced into oil phase and giving the following advantages:

(i) reduce additional collector and its distribution in aqueous phase, causing undesirable gangue particles activation,

(ii) avoid unnecessary interaction between collector frother and other chemicals present at the surface of mineral/water,

(iii) high collecting power from high concentration of collector at oil/water interface,

(iv) the specificity of reactive oily bubble will capture only target particles according to the use of specific chemical and interaction between collector and target mineral active site.

The chemicals addition to modified bubble or particles surfaces can be served as alternative tool to selective separation. Kerosene is also used in the same manner to modified bubble surface in order to improve collection efficiency emulsified oil droplets in this study. That is why the used of hydrophobic surface bubble collect dispersed oil droplets is likely to acquire a better performance in emulsified oily wastewater treatment (Liu et al, 2002).

2.12 Reactor design concept

The operation system of reactor can be roughly used to classify the reactor types in to three models; batch, and continuous (Roberts, 2009).

Batch operation: There is neither inflow nor outflow of reactants or products while reaction is occurred. It used for small scale operation, for testing new process (feasibility testing step), and for production of expensive products. The advantage of batch operation is high conversion by the reactants leaving in reactor for long time periods. However, the disadvantages are appeared as high labor costs per unit production, difficult to operate at large scale.

Continuous operation: The continuous stir tank reactor (CSTR) is commonly used in several industrial processes because it is suitable for large production scale. CSTR is usually operated at steady state and used for the well mixed requirement. The temperature and concentration in exit stream is the same as element elsewhere in the tank. It is easy to maintain temperature, conditions for production including less labor cost but it has lower conversion in comparison to batch operation. For ideal system, well-mixed model can be applied whereas the highly non-ideal flow, the modeling techniques such as residence time distribution is used instead.

2.13 Residence time distribution (RTD) (Fogler, 1992)

For continuous operation, the informative tool to acquire knowledge of fluid dynamics of the real reactors and it is used in the reactor design and scale-up to achieve the desired flow characteristics is the residence time distribution (RTD). The ideal CSTR concept is inferred to the composition of the effluent is similar to the composition in the reactor. In practice CSTR (or mixed reactor), the uniform content and the composition at the exit stream do not follow the ideal concept CSTR concept. The flow pattern regularly presents in the inter behavior between perfectly mixed and plug flow. RTD is also applied to find out how the flotation tank works and the results will be further used to improve its design and performance.

The residence time is how long the elements stay in the reactor once entering. In continuous process, the products are gradually with minimal interruptions through a series of operations. Products stream is continuously withdrawn from the reactor while some parts maybe remain in the reactor (stagnant region). The material stay at stagnant region spent more time than materials stay in other region or it can be said that elements use different time to stay in reactors. The incompletely mixed elements may leave out of reactor before react with other chemicals. This directly relates to the flow behavior and process efficiency.

Efficiency of dynamic process such a flotation is directly related to time material spends in the tank. The RTD function is best analysis tool for indication of the flow in vessel. The most important throughput from RTD experiments is determination of mean residence time. The relationship between experimental measured and expected mean residence time is the easiest-to- obtain the hydrodynamic of flotation vessel. However, only RTD measurement is insufficient in reactor design, other parameters should be additional considered case by case in particular reactor.

2.14 Literature review

1. Cutting oil toxicity

The metal workers are easily exposed the carcinogenic N-nitrosodiethanolamine (NDELA) containing in of synthetic cutting fluids at the working place. This chemical was considered as the genotoxic, the DNA damaged substance which the level of DNA damage depends on the concentration in the work places (Fuchs et al, 1995). Besides, cutting oil could be probably contaminated drinking water as uncommon from the misuse in pipelines set up. The unpleasant tasted and odors are the results of the volatile and semi volatile chemicals such as xylenes, diphenyl ether and bornyl acetate (Rella et al, 2002).

2. Destabilization oil droplet

Destabilization of commercial soluble cutting oil using $CaCl_2$ and $AlCl_3$ inorganic salts as coagulant was studied the effect of electrolytes on stability of aqueous emulsions. The major factor suggested in this treatment is soluble cutting oil formula. The destabilization rate is decreasing with time due to the reducing of number of droplets. However, the final turbidity remained in aqueous phase is between 100-200 NTU indicated that oil content is still high, but dispersed oil can be remove further by ultrafiltration (Rios et al, 1997).

3. Flotation

Induced air flotation (IAF) has a number of advantages when compared to dissolved air flotation (DAF) even larger bubble generated. IAF has been extensively used in wastewater treatment to removal fine particle and IAF can be provided a great potential when used corporate with optimal pH and flocculants. Moreover, IAF is successfully used for separation of algae and phosphorus compounds from sewage effluent plant. The smaller bubbles size (10-100μm) produced in DAF process (10-100μm) by pressurized saturated air in water. These small bubbles performed a good collection of fine particles but they also have small terminal velocities. Therefore, the equipment for this process has to be used in the larger size. The used of larger bubble is the reason is the reason why the IAF system can be developed in the compact size and surface chemistry are paid more attention (Jameson, 1999).

The previous study about MIAF was conducted for clean-up synthetic oily wastewater containing surfactants to determine optimal operating conditions. Palm oil and lubricants were selected as the oil model by Sastaravet and Lersjintanakarn respectively. The three different kind of surfactants used in oil emulsion preparation are SDS, CTAB, and Tween 20, alum ($Al_2(SO_4)_3$) and ferric chloride ($FeCl_3$) were used as coagulants. In coagulation process, the highest treatment efficiency was obtained when alum is applied for lubricant oily wastewater containing SDS (Lersjintanakarn, 2008). However, ferric chloride is more appropriate for wastewater synthesized from palm oil (Sastaravet, 2008). The IAF experiments investigated that the highest efficiency was obtained with using SDS surfactants for both of lubricant and palm oil treatment. Therefore, SDS was selected to study in MIAF for more details in term of kinetics and bubble hydrodynamics characteristics. The results of MIAF process revealed the better performance of oil removal efficiency when compared with IAF at operating conditions of 0.3 L/min air flow rate, 30 min aeration time. Additionally, the ratio of interfacial area (a) and gradient velocity (G) was justified as an important parameter applied to controlling flotation efficiency by using linear equations (Lersjintanakarn, 2008; Sastaravet, 2008).

4. Reactive oily flotation process

A newly concept of reactive oily bubble as the carrier in flotation was demonstrated by using kerosene as the model of reactive oil. The collectors (surfactant) which were introduced into the oil phase were anionic and cationic surfactants. The fine particles were agglomerated by the surface of reactive oily bubble and this thin film oil could be easily controlled by types and concentration of collectors. The selective attachment was carried out based on the characteristic of electrokinetic of kerosene droplet in aqueous collector solution. The surface charge is related the surface properties of oil droplet (Liu et al, 2002). Bitumen extraction was developed by using oily bubbles (bubble coated with oily thin film) in flotation stage. These oily bubbles affect on increasing contact angle leading to reducing of induction time for bubble-bitumen attachment due to the surface properties oily bubble is controlled. Kerosene coated oily bubbles was investigated as well improvement in bitumen recovery (Li et al, 2006).

5. Residence time distribution (RTD)

RTD data was used to roughly describe mixing conditions of columns. Materials which are reported to tailing and concentrate were traced by liquid radioactive tracer. Large and small tank-in-series and N perfect mixers in series were the best models to present the flow pattern of liquid transferred to tailing and concentrate, respectively. However, the presence of vertical baffles affect on mixing conditions of industrial columns was close to well mixed ones. Increasing gas flow rate affects increasing of mixing degree, whereas the mean residence times of liquid transferred to both tailing and concentrate streams were reduced at the same time (Massinaei et al, 2007).

The world wide annual usage of metalworking fluids is estimated to exceed 2×10^{9} L; however, the wastes could be up to ten times of spending since they have to be diluted before use (Cheng et al, 2005). A large amount of emulsified wastewater is discharged and cannot be treated by common method. Thus, it is required advance separation technologies to handle the treatment processes into appropriate manners for minimization of great impacts on human and environment. Advance separation processes raising up vertical velocity of oil droplets is flotation or it is also known as an alternative approach which treat oily wastewater based on the difference of density between bubbles and water phases in transferring bubble-oil droplet rising up. IAF process accelerates oil droplets velocity via blowing air at atmospheric pressure into oily wastewater. However, using IAF alone cannot treat effluent water meeting the standard since; the shortcomings of using flotation alone in water treatment field are not only low separation efficiency but also resources intensive from bubble generation. Therefore, hybrid process such induced air flotation (IAF) process combined with coagulation process called modified induced air flotation (MIAF) is studied in order to improved treatment efficiency in this study.

CHAPTER III

MATERIALS AND METHODS

3.1 Overview of research

This research mainly consists of 4 parts. The first part related with batch studies beginning with cutting oily-wastewater preparation and analysis. The second part studies the oily-wastewater treatment by IAF process, reactive oily flotation, coagulation process (Jar Test) and MIAF process. Moreover, in the third part, the effect of bubble hydrodynamic and mixing condition parameters on overall treatment efficiency was investigated and also applied in order to propose the prediction model. Note that the objectives of the first 3 parts were to obtain optimal condition and understanding about treatment mechanisms. The final parts aimed at extend operating condition from batch to continuous process including analysis of an influential flow behavior occurred in flotation column by using residence time distribution (RTD) diagnostic.

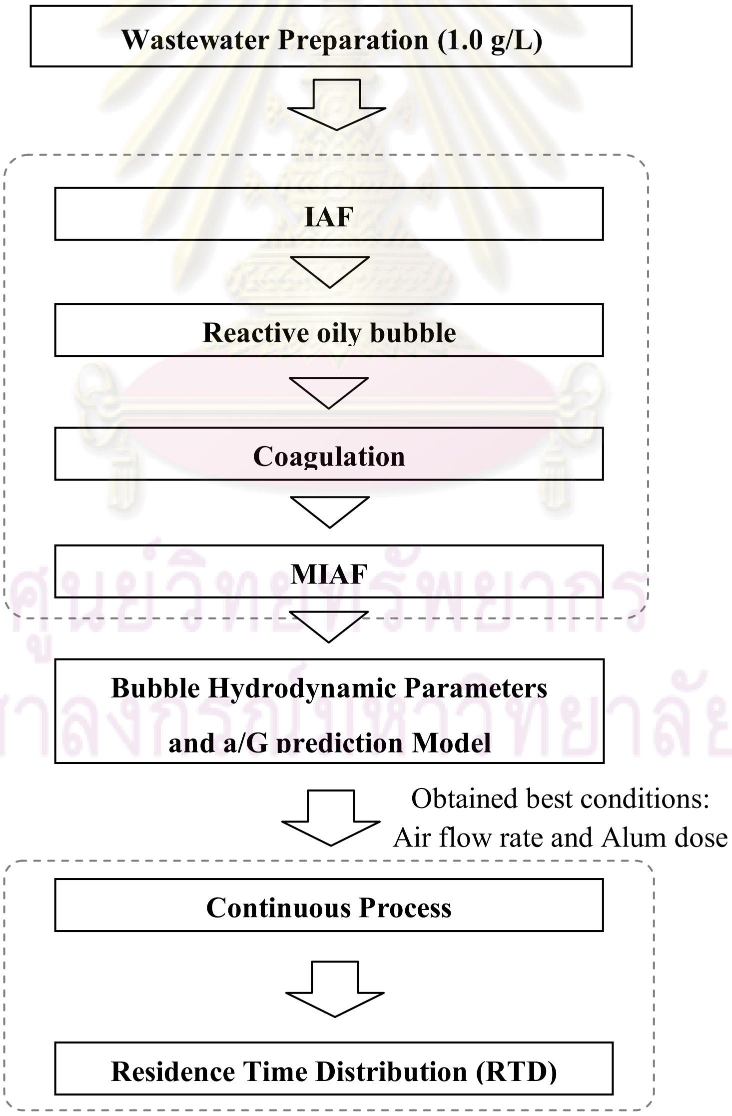
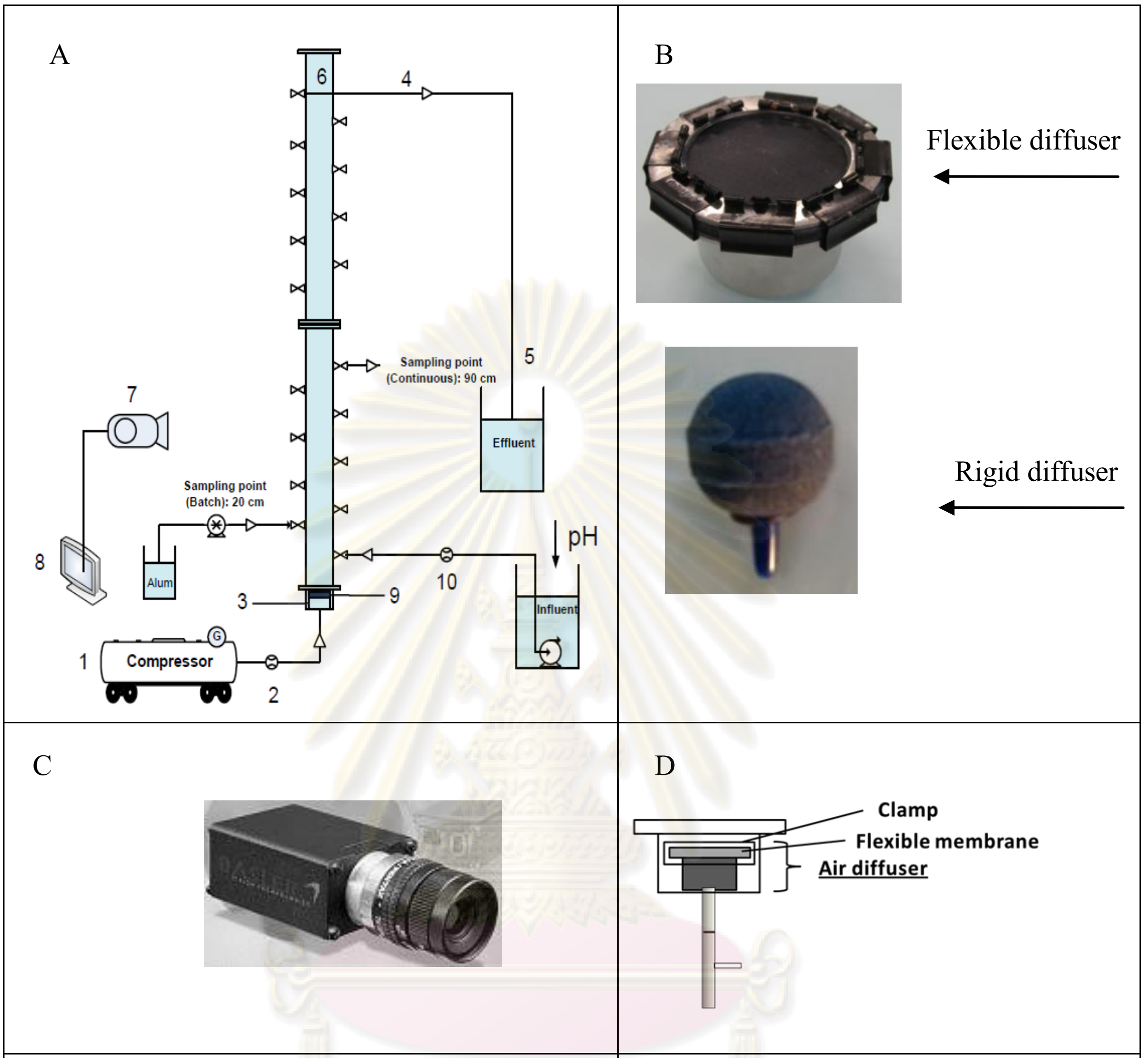


Figure 3.1 Overview of research

3.2 Experimental set-up



(A) Schematic of flotation apparatus

(B) Air diffuser: 2 types

(C) High speed camera

(series of continuous images)

(D) Reactive oil chamber

1 = Air compressor
2 = Air flow meter
3 = Reactive oil chamber (same with D)
4 = Water effluent point
5 = Effluent tank
6 = Floatation column
7 = High speed camera (Basler)
8 = Computer for data analysis
9 = Air diffuser
10= Water flow meter

Figure 3.2 Experimental set-up and components

Table 3.1 Description of small and large columns

PARAMETER	SMALL COLUMN	LARGE COLUMN
Inner diameter (cm)	4.2	10.0
Height (m)	2.0	2.0
Gas diffuser type	Rigid	Flexible membrane

The experiments set-up illustrated in the **Figure 3.2** were conducted by using two sizes of clear acrylic column (6), 0.042 m and 0.10 m in diameter and 2.0 m in height. The compressed air from air compressor (1) was regulated and measured by air flow meter (2), (0.2-2.0 L/min, New Flow), and then passed through rigid air diffuser (9) into the small column (6). For large column, modified industrial flexible membrane was used as air flexible diffuser. An air diffuser apparatus was shown in **Figure 3.2D**. Bubble configurations were photographed by high speed camera (7) (100 images/sec, Basler) as shown in **Figure 3.2C**, and analyzed by computer software (8). 2.7 L and 15 L of pre-adjusted pH of synthetic oily-wastewater were filled in small and large flotation column (6) in each batch. For continuous process, oily wastewater was injected into flotation tank via water pump and controlled feed rate by water flow meter (10) (2.5-25 L/hr; New Flow, and 10-100 L/hr; New Flow).

3.3 Chemical agents and equipments

Chemicals

1. Cutting oil Cooled BI: Castrol)
2. Alum ($Al_2(SO_4)_3.18H_2O$): Ajex Finchem Plt Ltd
3. Sodium Hydroxide (NaOH): J.T. Baker Chemical Co.
4. Potassium Dichromate Digestion ($K_2Cr_2O_7$): Ajax Finechem Ptl Ltd.
5. Ferrous Ammonium Sulfate ($Fe(NH4)_2(SO4)_26H_2O$) : Ajax Finechem Ptl Ltd.
6. Sulfuric acid (H_2SO_4): Merck Chemical Co.
7. Silver sulfate (Ag_2SO_4): Merck Chemical Co.
8. 1-10 phenantroline : Ajax Finechem Ptl Ltd.
10. Mercury (II) sulfate ($HgSO_4$): Merck Chemical Co.
11. Kerosene (Shell)

Equipments

1. JR-6D, M-LAB, Thailand.
2. Tensiometer K10T, Kruss, Germany.
3. pH meter, Extech
4. High speed camera, Basler, Germany
5. Water pump, Pioneer, Japan
6. Air Pump, Tiger, Thailand.
7. Optical Microscope, Nikon YS2-H
8. Flow monitor, New Flow
9. Clear acrylic cylindrical column: $\varnothing_{in}$ 4.2 cm, 2 m height
10. Clear acrylic cylindrical column: $\varnothing_{in}$ 10.0 cm, 2 m height
11. Peristaltic pump

3.4 Preparation of synthetic cutting oily wastewater

1g/L synthetic cutting-oily wastewater was prepared by addition of 1.1ml concentrated cutting oil into tap water and adjusts final volume of emulsion into 1L; homogeneous cutting oil emulsion was obtained by mixing under 125 rpm of mechanical stirring for 20 min as briefly shown in **Figure 3.3** (adapted from Leasjintanakarn, 2008). Samples were taken to measure oil droplets diameter, surface tension, and viscosity by optical microscope (Nikon YS2-H), Tensiometer, and viscometer (Brookfield) respectively.

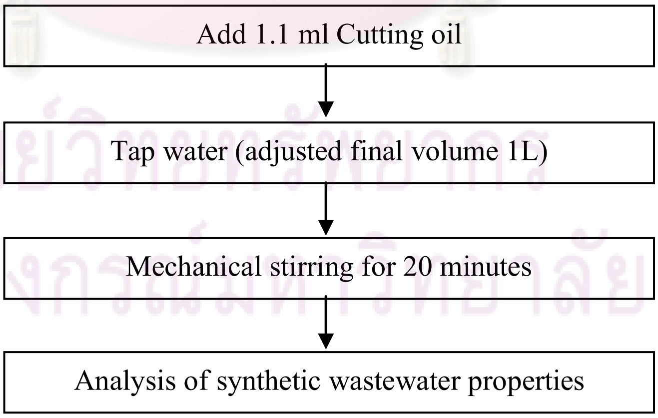


Figure 3.3 Wastewater Preparation

3.5 Batch induced air flotation (IAF) process

The IAF process was conducted in clear acrylic cylindrical column with 2 m height, 0.042 m diameter for small column and 0.10 m diameter for large column. The various air flow rate were regulated by flow meter in range 0.3-1.0 L/min and 0.3-2.0 L/min for small and large column respectively. The bubble configurations were captured by high speed camera (100 images/s; Basler). The samplings were performed at 20 cm above the top of diffuser at 0-40 min and 0-60 min for small and large column respectively. COD, bubble hydrodynamic parameters were analyzed.

Table 3.2 Variable of study the optimal air flow rate and aeration time of IAF process

Fixed Variables	**Parameter**
Volume of oily wastewater	2.7 L (Small column), 15 L (Large column)
pH	From jar test
Independent Variables	**Parameter**
Air flow rates:	0.3-1.0 L/min (Small column) 0.3-2.0 L/min (Large column)
Aeration time	0-40 min: small column, 0-60 min: large column
Dependent Variables	**Parameter**
Residual oil concentration	COD, turbidity
Bubble hydrodynamic parameters	a, D_B, f_B, U_B

3.6 Reactive oily bubble IAF

Reactive oily bubble concept was applied with conventional IAF by using kerosene as oil model and collector containing cutting oil formula is used instead of additional collector. Kerosene is fully filled into stainless steel bottom chamber as show in the **Figure 3.2B** before equipped with clear acrylic flotation tank, and then the experiment is similar conducted to IAF experiment in batch process as briefly shown in **Figure 3.4**. The Oily bubbles are generated by bubbling air through the air diffuser and oil phase respectively, then passing through a flexible membrane into wastewater. Eventually, air bubbles coated with thin oily film are obtained. The best air flow rate obtained from batch reactive oily bubble IAF will be further performed in continuous experiments.

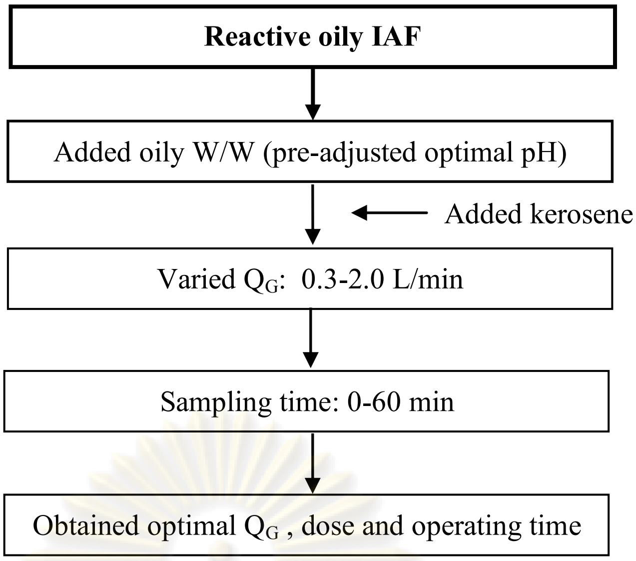


Figure 3.4 Reactive oily bubble IAF procedure

3.7 Determination of the optimal condition of coagulation process

The appropriate chemicals that should be used as coagulant for wastewater treatment can be determined by using results from jar tests. The jar test experiment was conducted 2 steps by jar test apparatus (**Figure 3.5**) to determine optimal pH and optimal dosage.

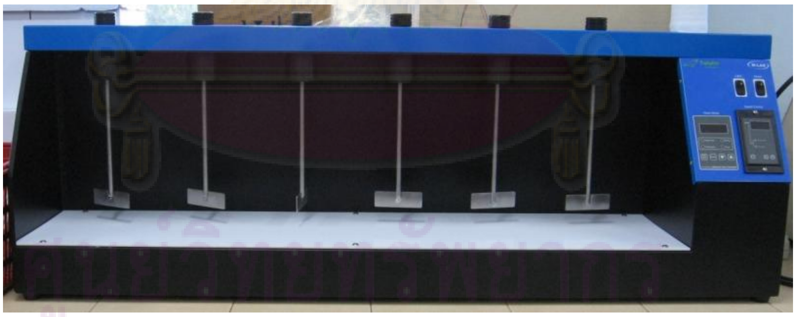


Figure 3.5 Jar Test apparatus (JR-6D, M-LAB)

<u>3.7.1 Determination of optimal pH</u>

The synthetic cutting-oily wastewater was used to determine optimal pH and dosage of coagulation. The initial pH of 1000 ml wastewater was adjusted by 1 N H_2SO_4 or 1 N NaOH solutions varied at 4, 6, 7, 8, 9, and 10. Alum ($Al_2(SO_4)_3.18H_2O$) was used as coagulant. The 50, 100, 150 mg/L coagulant concentration were added. Samples were stirred at 100 rpm (1 min) and 30 rpm (30 min). A 30 min of rest time were allowed for flocculation before taking samples to measure COD.

3.7.2 Determination of optimal coagulant dosage

The synthetic wastewater was adjusted at optimal pH and then Alum was introduced in 1000 ml with dosage 25, 50, 100, 150, 200, 250, 300, 350, 400, and 450 mg respectively. These samples were stirred at 100 rpm (1 min) and the 30 rpm (30 min) before taking samples to measure COD. Optimal dose was considered within 30 min of rest time.

Table 3.3 Variable of study the optimal pH values

Fixed Variables	**Parameter**
Synthetic cutting oily wastewater volume	1L
Independent Variables	**Parameter**
Coagulant dose ($Al_2(SO_4)_3$)	50, 100, and 150 mg/L
pH values	4,6,7,8,10
Dependent Variables	**Parameter**
Residual oil concentration	COD

Table 3.4 Variable of study the optimal concentration of Aluminum sulfate ($Al_2(SO_4)_3$)

Fixed Variables	**Parameter**
Synthetic cutting oily wastewater volume	1L
pH values	pH from the previous study
Independent Variables	**Parameter**
Coagulant dose ($Al_2(SO_4)_3$)	25-450 mg/L
Dependent Variables	**Parameter**
Residual oil concentration	COD, turbidity

3.8 Batch modified induced air flotation (MIAF) process

The experiment was similarly conducted to IAF. Coagulations are performed at the optimal conditions of pH and dose. Alum dosage was varied in range smaller and larger optimal dosage between 75-175 mg/L. Air flow rates were set at 0.1-2.0 L/min, optimal pH was adjusted; coagulant was added. The samplings were performed at 20 cm above the top of diffuser during 0-60 min. COD, bubble hydrodynamics, and turbidity was then analyzed. Batch IAF and MIAF experiments procedures were shown in **Figure 3.6**. The best air flow rate and coagulant concentration obtained from batch MIAF was further studied in continuous MIAF experiments.

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

Fixed Variables	**Parameter**
Volume of oily wastewater	2.7 L (Small column), 15 L (Large column)
pH	obtained from Jar test
Independent Variables	**Parameter**
Air flow rates	0.3-1.0 L/min (Small column) 0.3-2.0 L/min (Large column)
Aeration time	0-40 min: small column, 0-60 min: large column
Alum dose	75-175 mg/L: small column 100-225 mg/L: large column
Dependent Variables	**Parameter**
Residual oil concentration	COD
Bubble hydrodynamic parameters	a, D_B, f_B, U_B

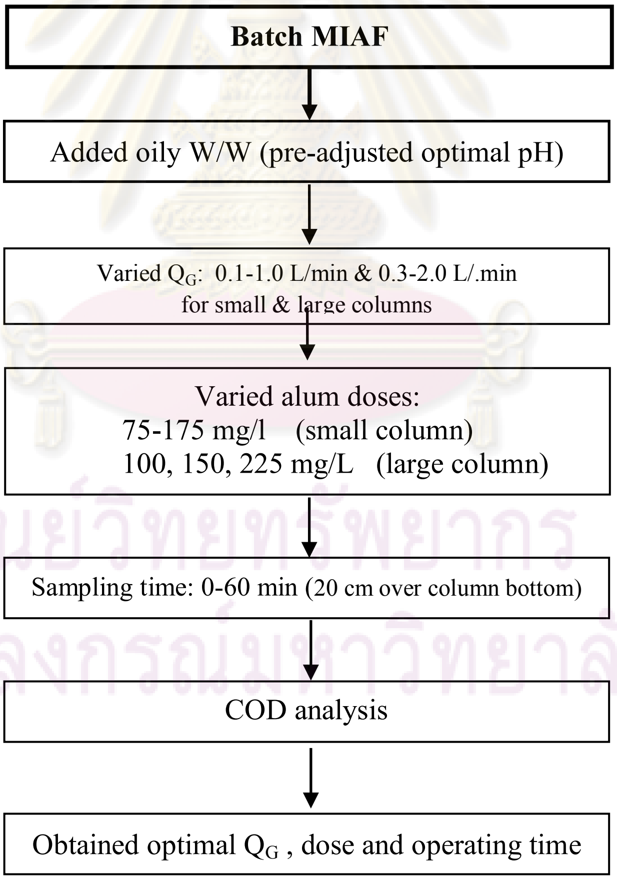


Figure 3.6 Batch MIAF experiments

3.9 Study the treatment of cutting oily-emulsion in continuous process

The continuous process study was divided into 3 parts as the following; (1) study performance at different feed rate (Q_L) in small and large column, (2) diagnose of residence time distribution (RTD) and (3) flocculation-settling study. Wastewater was fed continuously at desired flow rate (Q_L) which varied from 5 and 11 L/hr (low and high level) for small column and 15, 30 and 45 L/hr for large column. The applied feed rates were roughly considered by the proper operating time from batch process and head power of pump performance. Alum was also continuous entered into column by using peristaltic pump at the same time of wastewater, and then gas flow rate (used each optimal value from batch studies) was injected. Sampling was performed at sampling point located at the height that provided the lowest turbidity along the column at 0-60 min during operation. The particular study of RTD was separately described in next paragraph. After rapid mixing (continuous operation), the rest time was provided in flocculation-settling study for allowing floc formation. The brief of experimental procedures of continuous MIAF study are illustrated in the **Figure 3.7.**

Table 3.6 Variable of study the continuous MIAF process.

Fixed Variables	**Parameter**
Air flow rates	From batch MIAF
Initial pH of oily wastewater (optimal)	Obtained from Jar test
Independent Variables	**Parameter**
Feed rate (Q_L): small column	5, 11 L/hr
Sampling time: small column	0-60 min
Feed rate (Q_L): large column	15, 30, 45 L/hr
Sampling time: large column	0-60 min
Dependent Variables	**Parameter**
Residual oil concentration	Turbidity

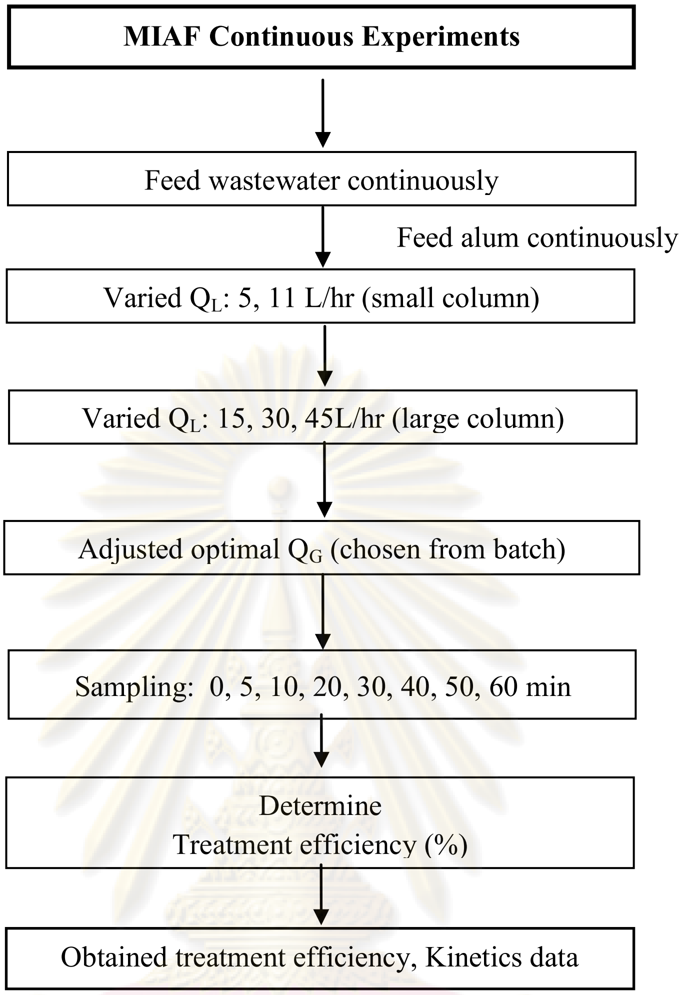


Figure 3.7 Continuous MIAF experiments procedure

3.10 Residence time distribution (RTD)

A real reactor may not have uniform flow patterns for each liquid flow rate which affect on liquid dynamics inside reactor. Thus, measurement of residence time distribution at whatever liquid flow rate assists in evaluation of the real flow characteristic in reactor. RTD was studied by tracer injection method by injection of tracer at the inlet system, and then sample from the outlet of system was taken to measure tracer concentration as a function of time.

After the air flow rate, feed rate were adjusted and system reach the steady state, 5 N NaOH, which was used as a tracer, was quickly injected by pulse injection method at the inlet of system (30 cm above column bottom). The outlet tracer concentration was measured in term of conductivity (mS). The residence time distribution function E(t),and mean residence time ($\bar{t}$) were analyzed. The brief of experimental procedure for RTD study was illustrated in the **Figure 3.8.**

Table 3.7 Variables of RTD diagnostic.

Fixed Variables	**Parameter**
Air flow rates	Best value from batch MIAF
Tracer	10 mL of 5 N NaOH
Independent Variables	**Parameter**
Feed rate (Q_L) : small column	5, 11 L/hr
Sampling time: small column	0-60 min
Feed rate (Q_L): large column	15, 30, 45 L/hr
Sampling time: large column	0-60 min
Dependent Variables	**Parameter**
NaOH concentration at outlet system	Conductivity (µS)

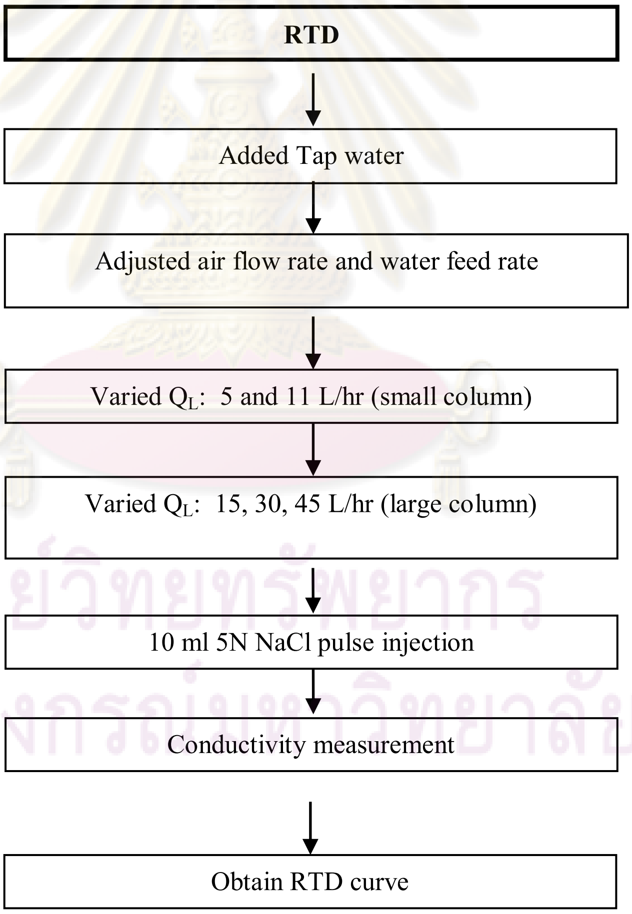


Figure 3.8 RTD experimental diagrams

3.11 Analytical parameter

- **COD**

  Initial and residual oil concentrations were analyzed in term of COD value by using standard close reflux-tritimetric method according to APHA, AWWA, and WEF, 1998.

- **Oil droplet diameter**

  Optical microscope model Nikon YS2-H equipped with digital camera was used to analyze oil droplet size. Average size of oil droplet was determined from measuring 100-150 oil droplets as representative samples.

- **Removal efficiency (%Eff)**:

  The efficiency of treatment process is determined by **Eq. 3.1**.

$$\%Eff = \frac{(COD_{in} - COD_{out})}{COD_{in}} \times 100 \qquad \textbf{Eq.3.1}$$

- **Velocity gradient**

  The power required for mixing can be either provided by mechanical and pneumatic means. The mixing level was indicated by velocity gradient, G, which is function of the power input into water. It could be said that velocity gradient (G) is another important parameter indicating turbulent level process and energy consumption in coagulation (Sastaravet, 2008). In case of velocity gradient of pneumatic mixing can be determined by equation **Eq. 2.1** (Reynolds and Richards 1996) while velocity gradient from mechanical mixing can be determined by **Eq.3.2** (Wang et al, 2005).

$$P = C_1 Q_G \log\left(\frac{h + C_2}{C_2}\right) \qquad \textbf{Eq. 2.1}$$

$$G = \sqrt{\frac{P}{\mu V}} \qquad \textbf{Eq. 3.2}$$

where

P = Power input (watt, J/s)
C_1 = Constant = 3904
C_2 = Constant = 10.33
h = Depth of diffuser (m)
Q_G = Air flow rate (m^3/min)
μ = dynamic (absolute) viscosity of water (N.m/s)
V = water volume (m^3)

- **Bubble hydrodynamic parameters**

  For bubble clusters analysis, the series of digital image were required. The camera was programmed at 100 images/s. Advantages of using high speed camera is that the bubbles dynamic can be observed entire the experiment. The bubble hydrodynamic parameters, from previous studies were determined for better understanding on bubble characteristic effect on obtained treatment efficiency. The bubble sizes (D_B), rising velocities (U_B), bubble formation frequencies (f_B) were experimental investigated and interfacial areas (a) was calculated from **Eq.2.7**. The schematic of bubble hydrodynamics analysis was illustrated in **Figure 3.9**. The measurement of the air bubble size distribution in the studied flotation column is carried out by photographic method. Images of the air bubbles were taken by using a high speed camera (Basler). One hundred images were taken at a time interval of 1 s. To obtain sufficiently representative bubble diameter, 100-150 bubbles were evaluated by the computer.

- **RTD**

  The residence time distribution (RTD) was determined by pulse injection method by using 10 ml of 5N NaOH (Analytical grade, Ajex) as a tracer. Tracer concentration at the outlet was measured as the function of time by using conductivity meter (Eutech Instruments, CON11&CON110).

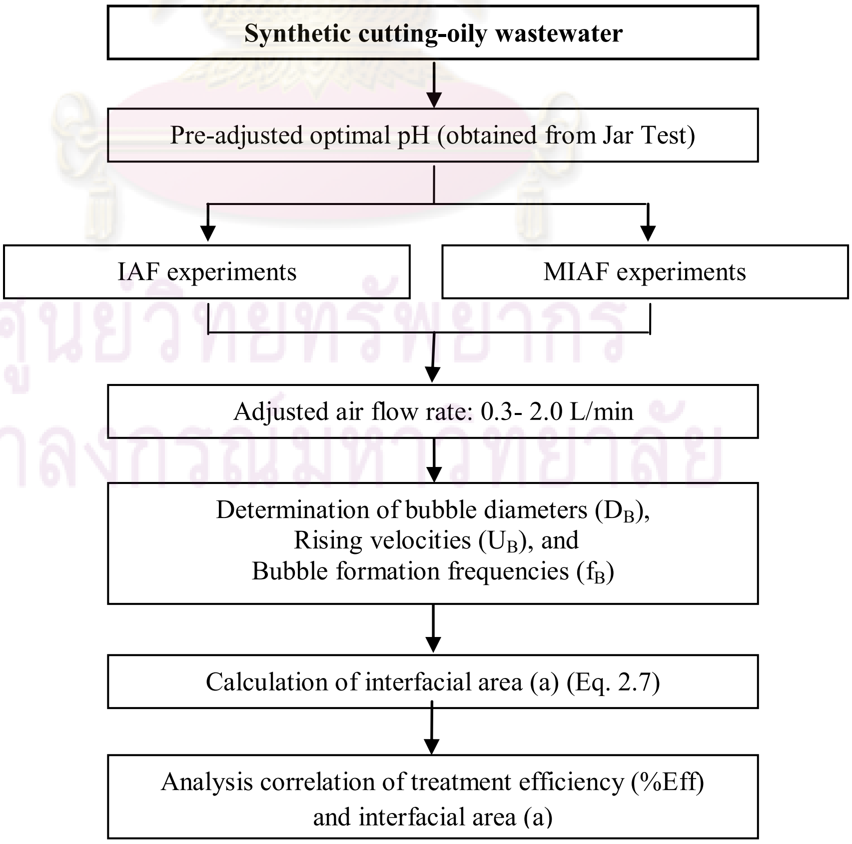


Figure 3.9 Analyzing methods for bubble hydrodynamic parameters.

The analytical methods determination was summarized in **Table 3.8**.

Table 3.8 Summary of analytical parameters and equations

Equations	**Parameters**
$\%Eff = \frac{(COD_{in} - COD_{out})}{COD_{in}} \times 100$	% EFF: treatment efficiency (%) COD_{in}: COD before treated COD_{out}: COD after treated
$G = \sqrt{\frac{P}{\mu V}}$	G: velocity gradient (s^{-1}) P: Power input (watt, J/s) μ: viscosity of water (N.m/s) V: water volume (m^3)
$P = C_1 Q_G \log\left(\frac{h + C_2}{C_2}\right)$	P : Power input (watt, J/s) C_1 = Constant = 3904 C_2 = Constant = 10.33 h = Depth of diffuser (m) Q_G = Air flow rate (m^3/min)
$a = N_B \times \frac{S_B}{V_{total}} = f_B \times \frac{H_L}{U_B} \times \frac{\pi D_B^2}{AH_L + N_B V_B}$	a: Interfacial area (m^{-1}), N_B: Number of bubbles generated, S_B**:** Total bubble surface (m^2), V_{total}: Total in reactor volume (m^3), f_B: Bubble formation frequency (s^{-1}), H_L: Liquid height (m), D_B: Bubble diameter (m), A: Cross-sectional area of reactor(m^2)
$f_B = \frac{Q_g}{V_B}$	f_B: Bubble formation frequency, s^{-1} Q_g: Gas flow rate (m^3/min) V_B: Bubble volume, m^3
$U_B = \frac{\Delta D}{t_{frame}}$	U_B: Bubble rising velocity ΔD: Distance between two frames t_{frame}: Acquisition time frame

CHAPTER IV

RESULTS AND DISCUSSIONS

The results and discussions obtained in this research were divided into 6 parts as the following; 1) oily wastewater analysis and Induced Air Flotation (IAF), 2) reactive oily bubble flotation, 3) treatment of oily wastewater by coagulation process (Jar Test), 4) IAF combined with coagulation processes called Modified Induced Air Flotation (MIAF), 5) bubble hydrodynamic parameters and prediction model and 6) the study of continuous MIAF process and residence time distribution (RTD) analysis.

4.1 Oily wastewater Analysis and IAF Process

The characteristic of cutting-oily emulsion prepared by mixing concentrated cutting oil with tap water was present in this part. The appearance of diluted cutting oil with tap water was shown in the **Figure 4.1** as milky emulsion and droplet size photograph was shown in **Figure 4.2**. For other properties of cutting-oily emulsion (viscosity and surface tension) including data comparison with other oily wastewaters were summarized in **Table 4.1**.

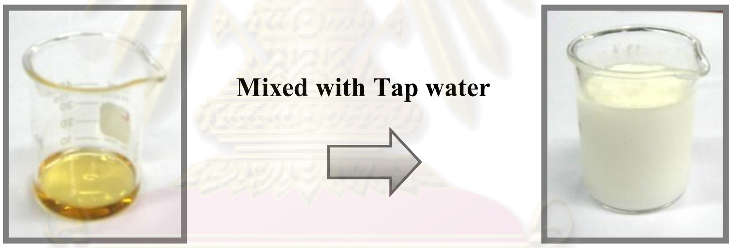


Figure 4.1 The appearance of concentrate and diluted cutting oil

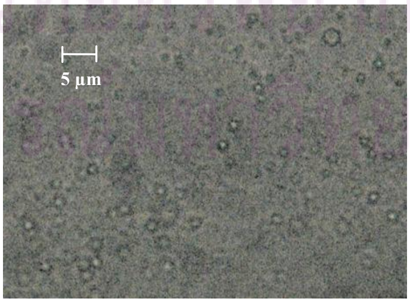


Figure 4.2 Droplet size of cutting-oily wastewater **(40X)**

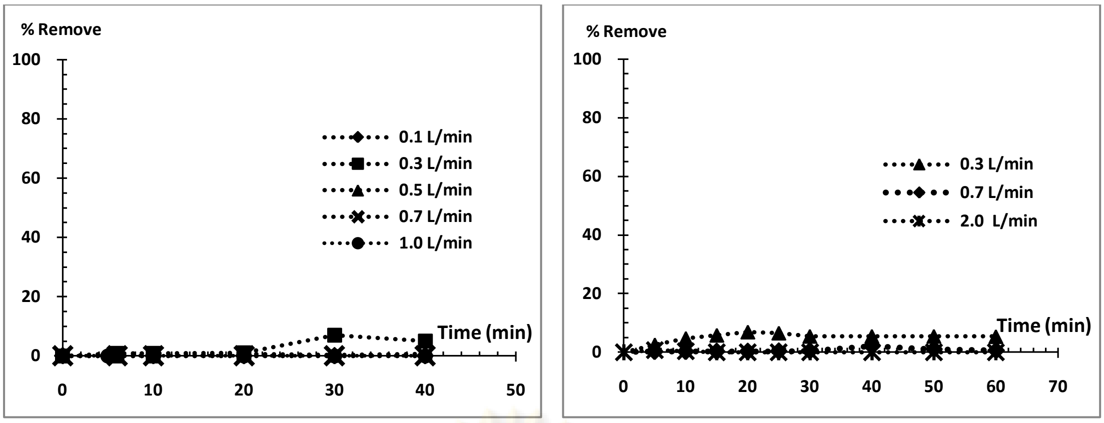
It can be noted that, very small droplet size of cutting oily-wastewater (≈ 1.3 µm as seen in **Figure 4.2**), the lowest removal efficiencies can be obtained from decantation due to this small size has very small effect by gravity force and this is also refers to small settling velocity. Even if it can be settled, it required very long time in comparison with the droplet size of lubricating and palm oil. Thus, the efficiencies obtained by decantation were to palm oil >> lubricating oil > cutting oil as in **Table 4.1**. Moreover, the droplet size can also affect the colloid density presence in liquid phase and thus turbidity condition of different wastewaters: highest turbidity was observed with cutting oily-wastewater. This corresponds to larger droplet size of lubricating and palm oily-wastewater which have 2 and 5 µm of oil droplet size, respectively (Lersrijintanakarn, 2008 and Sastaravet, 2008). Moreover, it can also be observed that surface tension and viscosity properties can affect to treatment performance: this will be described in more detail later. Therefore, in order to improve velocity of separation process, flotation, which is the process based on increasing density difference between oil and water and leading to promote oil rising velocity, should be applied as presented in **Figure 4.3**.

Table 4.1 Characteristics of 1.0 g/L synthetic cutting-oily wastewater

Parameter	Cutting oil	Lubricating oil*	Palm oil*
Oil concentrations (g/L)	1	0.3	5
Droplet size (µm)	1.3	2	5
COD (mg/L)	2,846	1,010	10,190
Turbidity (NTU)	1356	265	71.17
Viscosity (cps)	9.16	19.8	19.7
Surface tension (mN/m)	47.02	47.39	31.2
Decantation Efficiency (%)	0	3	31.25

* data was obtained from Sastravet, 2008 and Lersjintanakarn, 2008

Figure 4.3a and b present the study of cutting oily wastewater treatment by IAF process using gas flow rate varied between 0.3-1.0 L/min for small column and 0.3-2.0 L/min for large column. As compared with the removal efficiency from decantation process, the removal efficiencies obtained with IAF process were greater than those obtained from decantation one. These results confirmed that the generated bubbles interact with the oil droplets and act like "rising parachutes" for oil droplets (Painmanakul et al, 2009). The maximum removal efficiencies were achieved at 0.3 L/min gas flow rate equal to 7.0% at 30 min aeration time for small column and 5.4 % at 20 min for large column. However, the obtained treatment efficiencies from IAF process in both columns were very low when compared to other oily wastewaters. **Figure 4.4** presents the removal efficiency versus gas flow rates with IAF process for different types of oily wastewaters obtained with small column. It can be noted that, at 0.3 L/min gas flow rate, the highest removal efficiencies were again observed and equal to 7.0 %, 33.96%, and 69.28 % for cutting oil, lubricant and palm oil, respectively.



(a) small column (b) large column

Figure 4.3 Treatment efficiency of IAF process

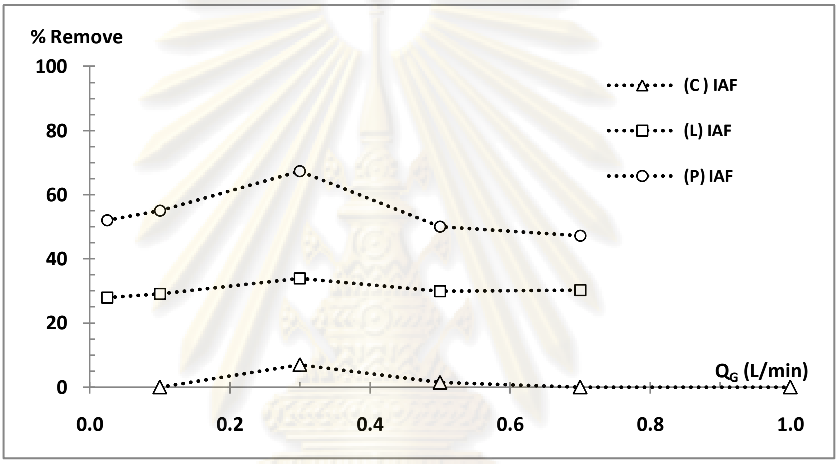


Figure 4.4 Removal efficiency of IAF process for different types of oily wastewater in small flotation column

By comparing the kinetic of removal efficiency obtained with different types of oily wastewater as in **Figure 4.5**, it can be stated that, especially in case of palm oily-wastewater, three kinetic zones (free surface, attachment and breaking zones) can be clearly found on the variation of the removal efficiency with operating time (Painmanakul et al, 2009). However, these kinetic studies indicated that lower oil/bubble aggregates formed in the attachment zone due to their oil-phase characteristics as in **Table 4.1** (very small droplet size of cutting-oily droplets) and thus the destabilization mechanism providing low amount of aggregated oil/bubble particle formation can be thus slightly affected by the breaking phenomena occurred at the surface of flotation column. Therefore, it is not necessary to operate at high gas flow rate and elongate operating time in practice. The steady-state of operating time at 30 min should be thus chosen in case of palm and lubricant oily-wastewater, whereas this cannot be clearly concluded in case of cutting oily-wastewater at present.

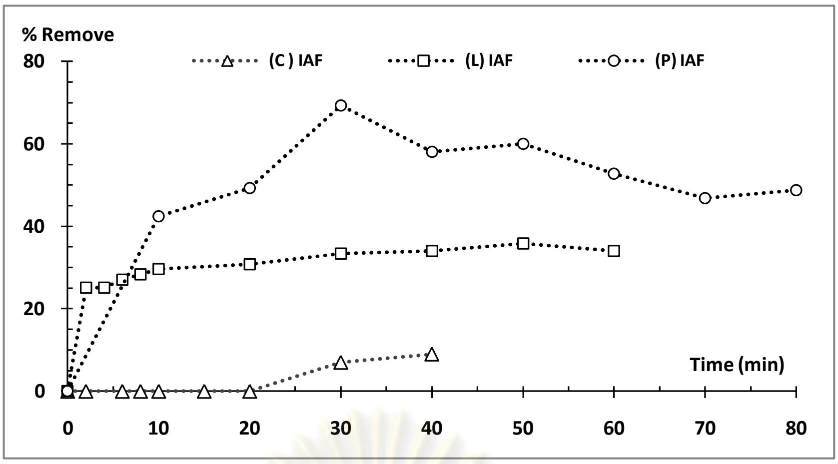


Figure 4.5 Variation of kinetic data of IAF processes for different oily wastewaters for small column

In conclusion, it can be stated that the removal efficiencies relate with the oil-droplet size presence individually of each types of oily wastewater: this cause some limitation on the application of IAF process, especially in case of cutting oily wastewater. Therefore, other additional techniques, such as reactive oily flotation, coagulation, should be employed in order to enhance the process performance.

4.2 Reactive oily bubble flotation

In this part, the reactive oily bubble concept was performed by using kerosene for generating the reactive oily bubbles in order to improve the IAF process of cutting oily-wastewater treatment. These experiments were conducted only in large flotation column due to the equipment installation (see **Figure 3.2**). The experiments were operated for 30 min and gas flow rate was varied at 0.3, 0.5, 1.0 and 2.0 L/min. Removal efficiency was determined by turbidity measurement instead COD due to kerosene was flammable chemical and can cause the experimental error based on COD measurement.

According to **Figure 4.6a**, oil removal can be observed at low gas flow rates. The low efficiency (3% approximately) were obtained with 0.3-0.5 L/min gas flow rate and similar to the experimental values obtained with conventional IAF process: this was related to the same bubble generation phenomena obtained with the IAF study. However, the removal efficiencies were decreased at the high gas flow rate ($Q_G > 0.5$ ml/s): this corresponds with the kerosene property that can be dissolved in organic solvent inducing the reduction of cutting-oily droplet size, and also the turbulent condition at the high gas flow rate that can break oil droplet into smaller size. Additionally, the aeration mixing aid kerosene partially mixed with cutting oily wastewater resulting in turbidity values increased. For residual kerosene, this was insoluble in cutting oily wastewater, it separately present in a layer over the water surface as shown in **Figure 4.6b**. Besides, low attractive performance, using of kerosene coated bubble also recovered shortcomings such as giving strong bad characteristic odor and rubber part destruction on equipment, like membrane sparger, pipeline for inlet and chemical feed. Note that, kerosene adsorbed on rubber membrane made this membrane surface more soft and flexible condition and thus easily broken during the operation. Therefore, other processes like chemical destabilization should be applied with IAF processes (called MIAF) to enhance cutting oily-wastewater treatment.

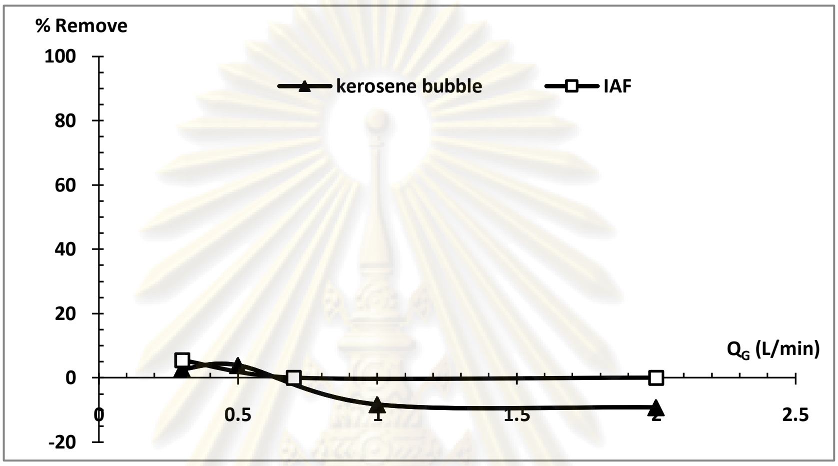


Figure 4.6 (a) Treatment efficiency of cutting oily wastewater by reactive oily bubble flotation process

Figure 4.6 (b) Kerosene layer at surface of reactive-oil flotation column

4.3 Treatment of oily wastewater by coagulation process (Jar Test)

As discussed previously, the cutting oily wastewater was unsuccessfully treated by decantation, IAF and also reactive oily bubble flotation. In order to achieve the attractive performance for treating the cutting oily wastewater, the combined IAF with coagulation processes (MIAF) was emphasized. However, the successful coagulation is attained by using optimal pH and suitable coagulant concentration. In accordance with the zeta potential of cutting oily droplet is negatively charged (Chooklin, 2004), alum was selected for effectively destabilization of cutting oily wastewater due to its highly positively charged and also inexpensive in this study.

Thus, the jar test was firstly required in order to determine the optimal conditions. In this work, the initial pH values (4-10) and coagulant dosages (Alum) 25 – 450 mg/L were investigated.

4.3.1 Optimal initial pH

Figure 4.7 presents the oil removal efficiency at different initial pH values. The highest removal efficiency 57.31%, 76.61% and 91.23% were remarkably obtained at pH 7 (neutral) by using 50, 100 and 150 mg/L alum, respectively. The positively charge alum floc Al $^{3+}$, Al(OH)$^{+2}$, Al(OH)$_3$ can be produced sufficiently at a neutral pH leading to neutralization of negatively charged cutting oil-droplet and increasing size of oil droplets in liquid phase. On the other hand, the negatively charged (OH$^-$) ion can be formed at higher pH (base) resulting in increasing of negatively charged species presented in waster. Consequently, the amount of positively charged from the low alum dosages (50 and 100 mg/L) were also used in order to react with this negatively charged, and thus not enough to destabilize the cutting oil-droplets compared with higher alum doses. This phenomenon can be confirmed due to the oil removed obtained with 150 mg/L were greater than those obtained with the lower dosages at high pH values (pH > 8).

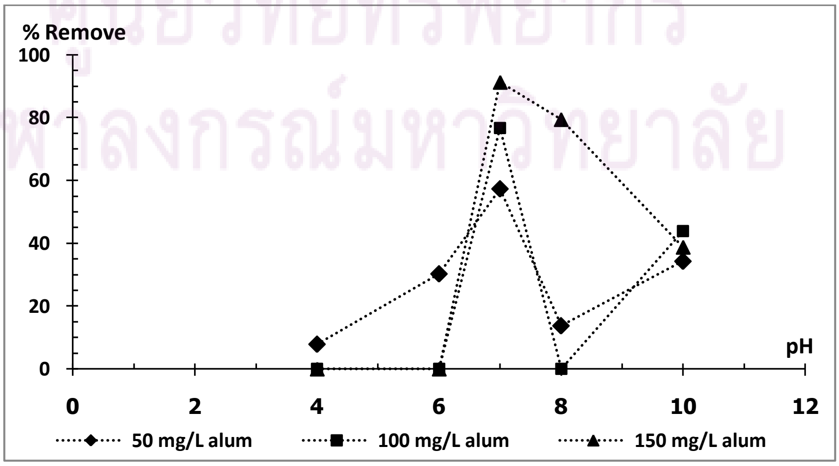


Figure 4.7 Treatment efficiency of coagulation by using alum at different initial pH

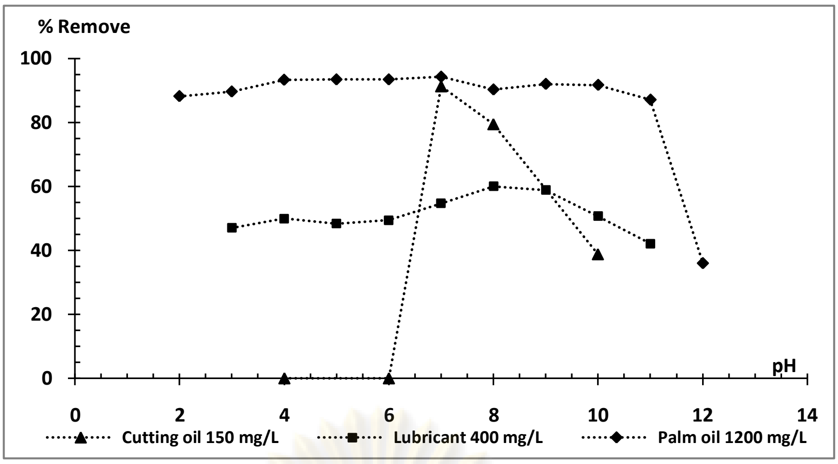


Figure 4.8 Removal efficiency versus pH values for different alum concentration

In comparison of coagulation of cutting oil to lubricating oil and palm oil results as shown in **Figure 4.8**. The highest removal efficiencies related with cutting oil, lubricating oil, and palm oil removal were 91.23%, 61.82%, and 89.7% at initial pH 7, 8 and 7, respectively. It can be stated that the influence of pH values was more pronounced in case of cutting oily wastewater compared with the others: very small droplet size (1.3 μm) and also various contaminants presence in this liquid phase should be responsible for these results.

4.3.2 Optimal coagulant dosage

As shown in **Figure 4.9,** the optimal alum concentration for 1.0 g/L cutting-oily wastewater coagulation was 150 mg/L with the removal efficiency equal to 91.23%. These high concentrations of alum (150 mg/L) required in this experiment, can be explained based on different destabilization mechanisms, like adsorption or charge neutralization, sweep floc coagulation, etc.

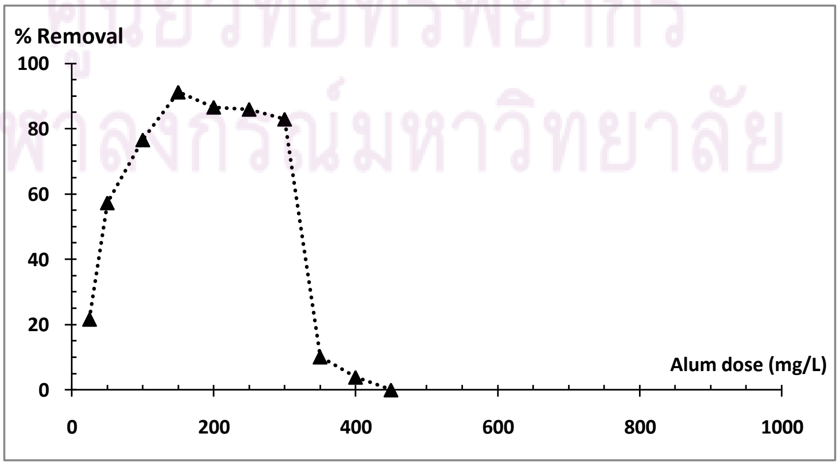


Figure 4.9 Treatment efficiency of coagulation process with different alum doses

In comparison of coagulation of cutting oil to lubricating oil and palm oil results as shown in **Figure 4.10**. At optimal pH value, the suitable alum concentration should be 150, 400, and 800 mg/L for cutting oil, lubricating oil, and palm oil, respectively. These results can be possibly related with the values of MW, droplet size, colloid density and thus turbidity as shown in **Table 4.1**. In addition, for the concentrations higher than suitable alum doses in case of cutting and lubricating oily wastewater, there is a significant decrease in the removal efficiency indicating that the solution has gone through the point of net electrical charge. Moreover, the added alum has increased the positive charge of the emulsions (Charge reversal); however, this was not clearly occurred in case of palm oil. Therefore, it can be concluded that the adsorption or charge neutralization was the main treatment mechanism for very small oil droplet (cutting oil and lubricating oil) and sweep-floc coagulation was the main treatment mechanism for palm oil respectively (Renault et al, 2009).

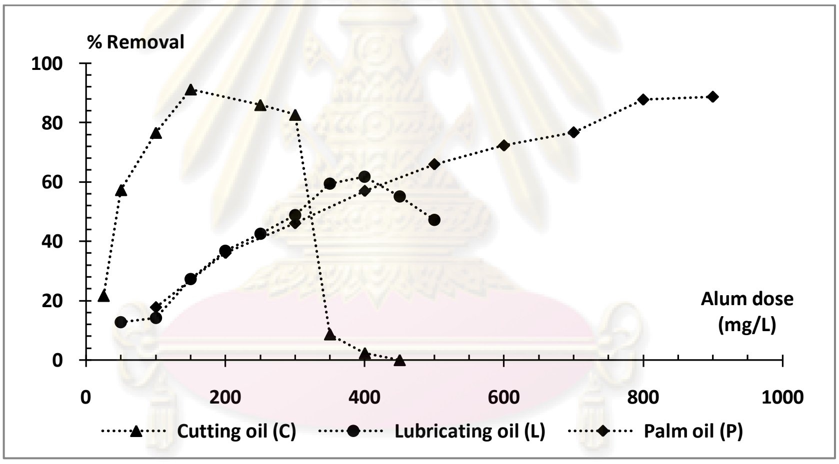


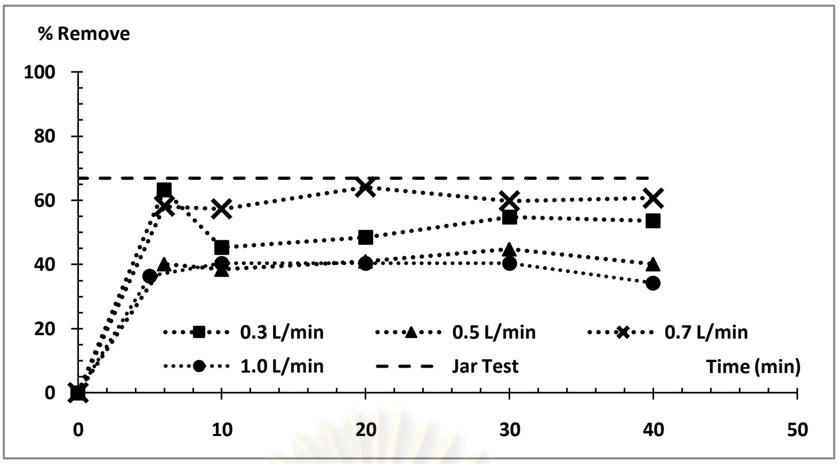
Figure 4.10 Removal efficiency versus alum concentration for optimal pH values

In conclusion, the crucial parameters, which affect on the obtained removal efficiencies, are 1) pH value which control complex ion species form after adding alum into water and 2) alum dosage which involves amount of generated positive ion present in wastewater. Again, the suitable condition for coagulation (Jar-Test) of 1.0 g/L cutting-oily emulsion was present at initial pH 7 with 150 mg/L alum concentration.

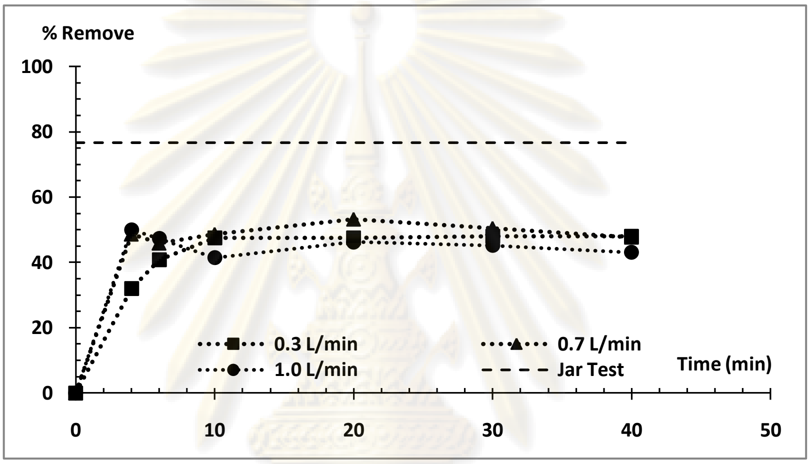
According to the comparison of the performance obtained between IAF process and coagulation-flocculation process from jar test, it can be observed that the treatment efficiencies obtained with coagulation process are obviously greater than those obtained with the IAF process. Additionally, it can be stated that the obtained removal efficiencies related with the oil-droplet size and also some chemical contaminants presence cutting oily-wastewater: this causes some limitation on the application of IAF process that is only based on the physical separation mechanism by modifying Stoke"s law concept. However, the disadvantage of the chemical process is long operation time requirement (rapid/slow mixing and sedimentation) and restriction of the optimum dosage of alum and pH value. Therefore, process performance improvement by using IAF incorporated with coagulation called MIAF process was included in the next part. Note that this optimal condition from jar test was applied further in MIAF study.

4.4 Treatment of cutting-oily wastewater by Modified Induced Air Flotation (MIAF) process

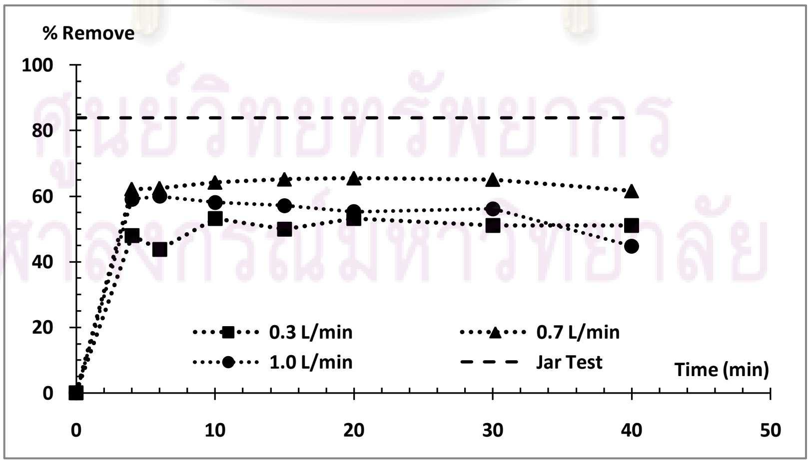
The objectives of this part were to determine the optimal air flow rate, aeration time (operating time) and chemical dosage in order to obtain the highest treatment efficiency. Note that the influence of diameter of flotation column was also investigated for providing a better understanding on the relation of associated bubble generation phenomena and overall treatment efficiency. The air flow rate varied between 0.3-1.0 L/min for small column and 0.3-2.0 L/min for large column. In this part, the operating time 0-40 min and 0-60 min were observed in small and large columns, respectively. Due to the previous experiments, the alum dosage was thus chosen and varied in range 75 – 175 mg/L and 100-225 mg/L for small and large columns, respectively. The removal efficiencies obtained experimentally of cutting-oily wastewater by MIAF process at different air flow rates were shown in **Figure 4.11 and Figure 4.12.** These tests were carried out in small and large flotation columns. Note that, an initial pH was adjusted to the optimum value obtained previously from jar test experiments and the effect of chemical dosage was also analyzed.



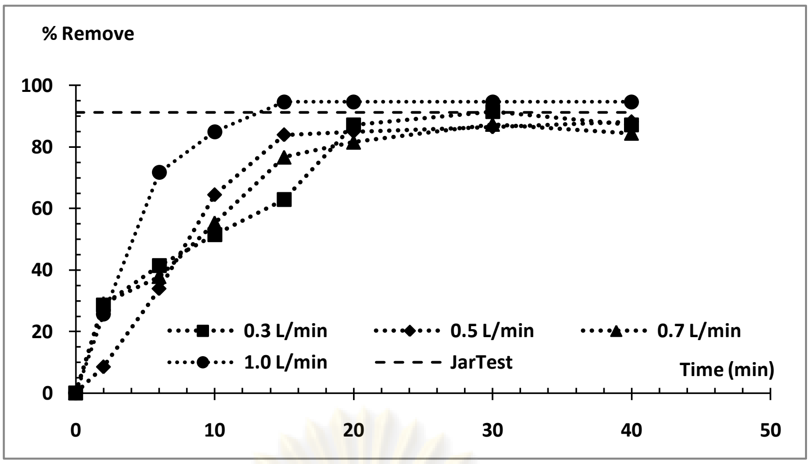
(a) Small column: 75 mg/L alum



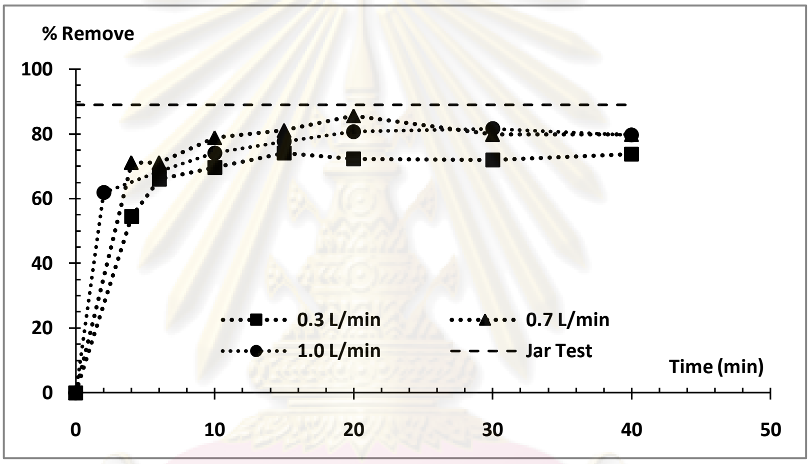
(b) Small column: 100 mg/L alum



(c) Small column: 125 mg/L alum

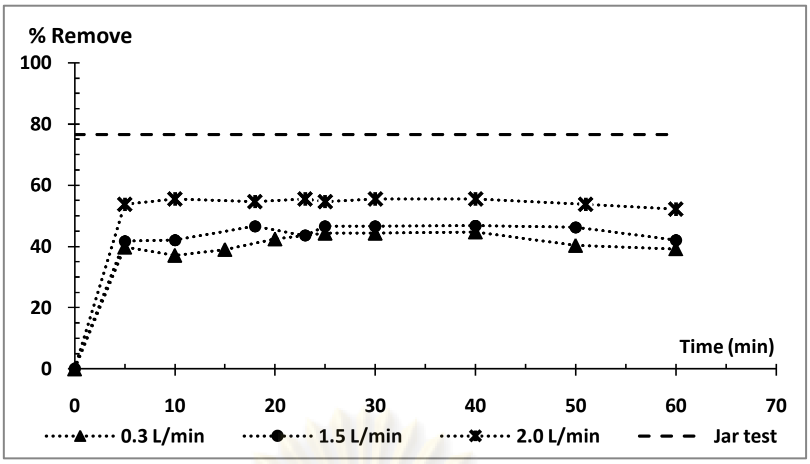


(d) Small column: 150 mg/L alum

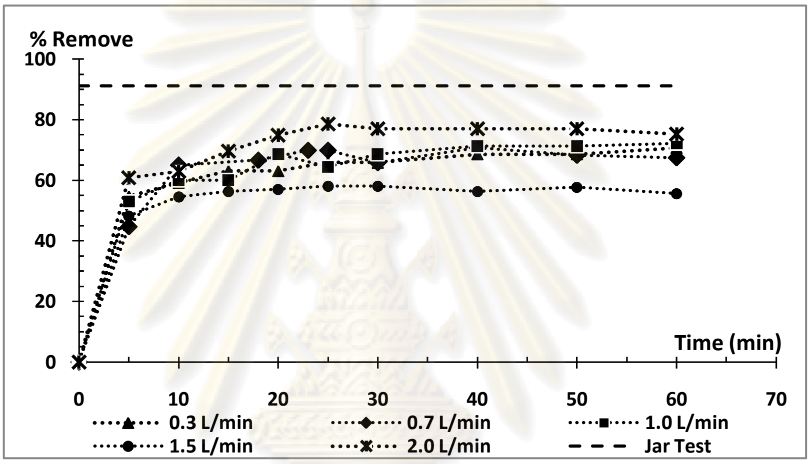


(e) Small column: 175 mg/L alum

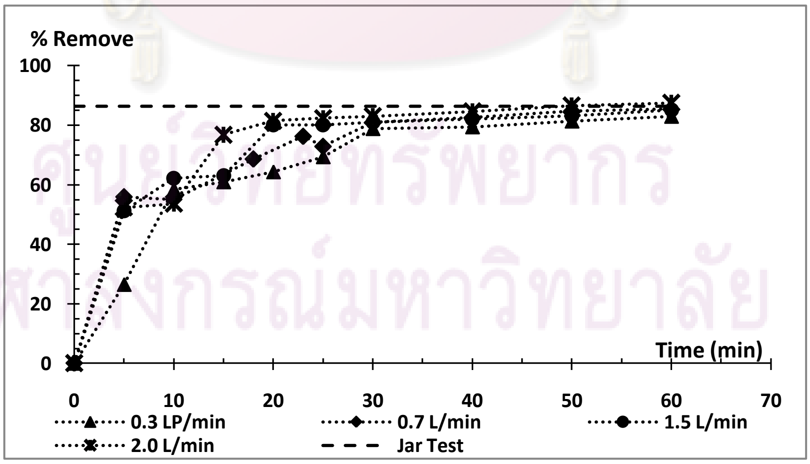
Figure 4.11 Treatment efficiency versus operating time of small column for different gas flow rates and alum concentration: (a) 75mg/L, (b)100 mg/L, (c)125 mg/L, (d) 150 mg/L, and (e) 175 mg/L



(a) Large column: 100 mg/L alum



(b) Large column: 150 mg/L alum



(c) Large column: 225 mg/L alum

Figure 4.12 Treatment efficiency of different gas flow rate versus operating time of large column for different alum concentration: (a) 100 mg/L, (b) 150 mg/L, (c) 225 mg/L

According to **Figure 4.11** and **Figure 4.12**, it can be noted that, the removal efficiencies, obtained with MIAF process in both small and large columns, were greater that those obtained with the decantation and IAF processes. The treatment efficiencies increased rapidly with time in the beginning (within first 10 min), then slightly increased, and finally reached to steady state due to the presence of three variation zones as illustrated in **Figure 4.13**.

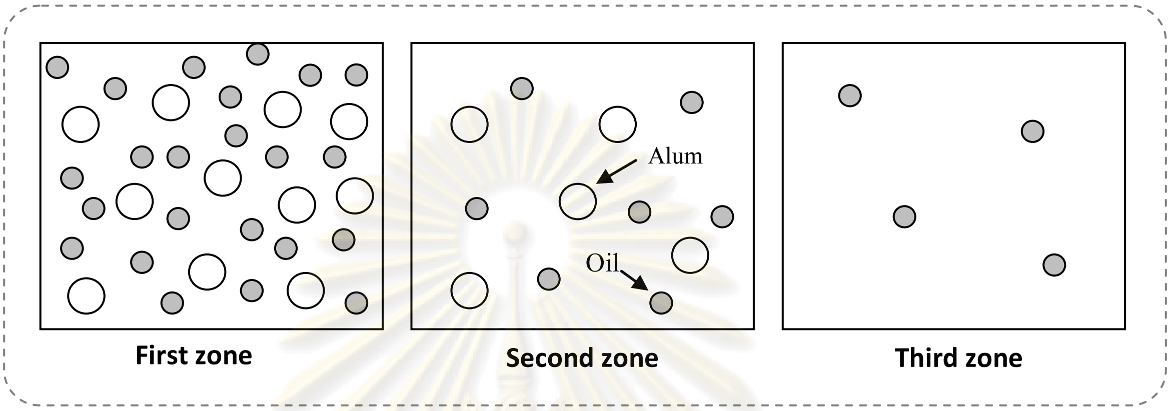


Figure 4.13 Three zones occurred in MIAF process depending on operating time

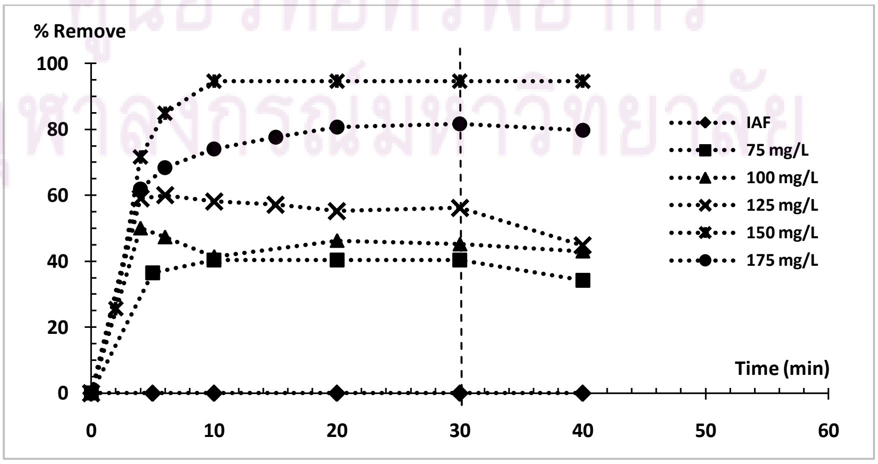
First zone: at the beginning, most oil content can be separated rapidly within first 10 minutes for all applied alum doses: this is due to the high available free surface of oil droplet present in liquid phase and alum dosage. Consequently, the rapid mixing (destabilization) of oil droplets and slow mixing (flocculation) can occur in order to form the lager oil-droplet aggregates, and then separated by the generated bubbles.

Second zone: the oil- removal rate was slightly increased due to the low amount of alum remained in liquid phase for low interacting and destabilizing the suspended oil droplets. Moreover, it can be observed that, for large flotation column, this second zone was longer than that for small flotation column. These results can be possibly related with the complicated fluid-flow regime occurred in large column. It can negatively affect on destabilizing mechanism between alum doses and cutting oil droplets occurred slowly and thus longer aggregated particle formation time.

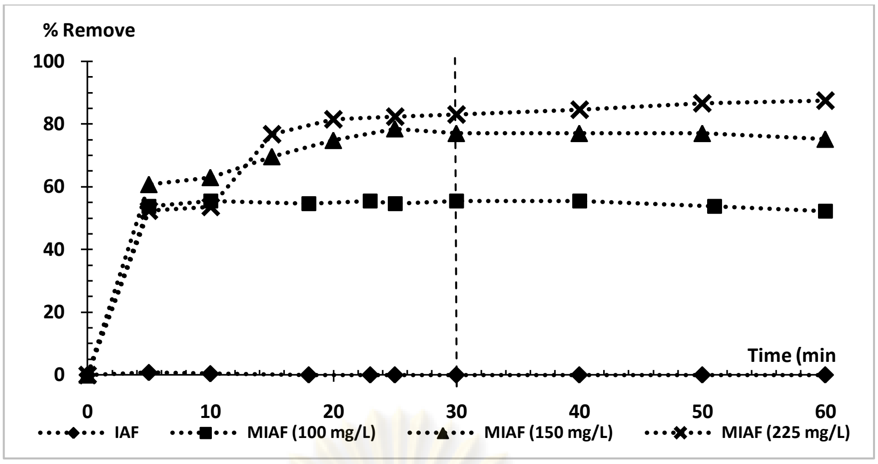
Third zone: in this zone, the treatment efficiencies reached to the steady state of treatment operation, or there were very small amount of remained alum for interacting oil droplet in liquid phase at the end of experiments. Therefore, some cutting-oily droplets remain in liquid phase and thus result on the roughly constant values of COD and turbidity in this zone. However, at the high gas flow rate, the longer operation time can cause floc breaking phenomena which serve the particle re-dispersion (Al-Shamrani, 2002: Meysaaami and Kasaeian, 2005). Moreover, there were some cases that the generated bubbles can support and carry this breaking floc up to the surface again. Thus, the final removal efficiencies were roughly stable, especially in case of large flotation column. It can be stated that column dimension and bubble distribution system should be responsible for these results. Note that this complex should be discussed, in detail, for next part.

Moreover, the highest removal efficiencies obtained with MIAF processes from both small and large flotation columns were closed to those obtained with jar test experiments. These results confirm that bubbles can perform either rapid mixing for destabilization or slow mixing for floc formation mechanisms. Moreover, the gas flow rate was proven to be less important than the chemical dosage (destabilization mechanism) for very small oil droplet size as cutting oily-droplet particle presence in wastewater. Due to the influence of chemical dosage, bubble hydrodynamic and fluid flow regime on the overall treatment efficiency, these parameters should be well considered in order to provide a better understanding on the treatment and scale-up design of cutting oily-wastewater by MIAF process.

As shown in **Figure 4.14**, the optimal condition was summarized be considering within 30 min, even if the actual highest efficiencies were achieved at longer operating time. Because the removal efficiencies obtained by operating MIAF process for only 30 min can be kept treatment efficiency at high performance (> 80 % for best value). Additionally, the selection of 30 min for MIAF operation was based on the concept for avoiding floc breaking phenomena that occurs when operate process for long time as discussed previously. Therefore, the operating time at 30 minutes will be applied, in further study, for calculating the overall treatment efficiency and also for carrying on the continuous system in this research.



(a) Small column



(b) Large column

Figure 4.14 Treatment efficiency of MIAF processes at optimal gas flow rate of (a) small column: 1.0 L/min (b) large column: 2.0 L/min for all alum concentration

Regarding to the chosen operating time at 30 min, **Figure 4.15** and **Figure 4.16** confirm that increasing alum concentration can affect the chemical destabilization and the treatment efficiencies of very small oil-droplet size with both columns compared with the conventional IAF process. The highest removal efficiencies obtained with small columns by using alum dose 75, 100, 125, 150, and 175 mg/L were 60%, 50%, 64%, 95%, and 82% respectively. The maximum values were found at high gas flow rate varied between 0.7-1.0 L/min. For large column, the highest removal efficiencies obtained at 2.0 L/min gas flow rate were 55%, 77%, and 83% approximately by applying alum dosage at 100, 150, and 225 mg/L respectively. Note that under the increase of gas flow rates, the mixing degree was reaching to turbulent condition which accelerates the oil and alum collision phenomena and thus provide not only the rapid floc-formation but also the oil/bubble attachment and separation by flotation (Lersjintanakarn, 2008). However, higher gas flow rates were not also necessary, in practice, due to the associated operating cost and reduction-tendency of the overall treatment efficiency, especially in case of small flotation column operated with lower alum concentration compared with large column: floc-particle stability obtained with this small coagulants should be responsible for these results.

In case of higher alum concentration required in large column experiments, it can be noted that the overall treatment efficiencies were lower than those obtained with small column. Therefore, column dimension was one of the important factors for flotation operation: higher gas flow rate is necessary for distributing or interacting completely among the oil-droplets, bubbles and alum dosage presence in large flotation column. Nevertheless, due to this high gas flow rates injected through flexible membrane, the bubble dispersion, turbulent condition and flow regime can be significantly difference. In addition, the bulk liquid located in large cross section area was more affected by the up-flow of bubble dispersions, and then exposed in different momentums which lead to water and floc circulation stream (Pareek et al, 2001) as illustrated in **Figure 4.17**. Note that these phenomena can probably relate with the unsuitable flocculation condition, breaking of floc size, and thus increase of small oil-droplets presence in liquid phase. Therefore, from this limitation of bubble dispersion regime, 225 mg/L alum dose was thus required instead 150 mg/L in large column to achieve nearly treatment efficiency obtained with small flotation column.

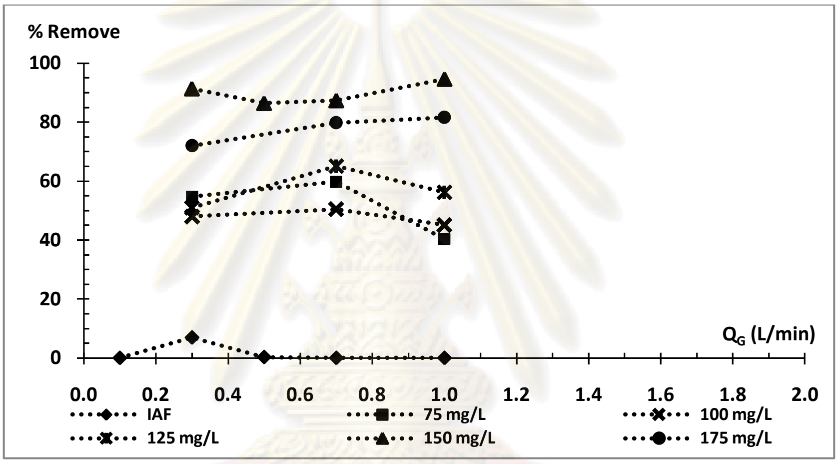


Figure 4.15 Treatment efficiencies of IAF and MIAF processes at 30 min with 0.1-1.0 L/min gas flow rate of small column

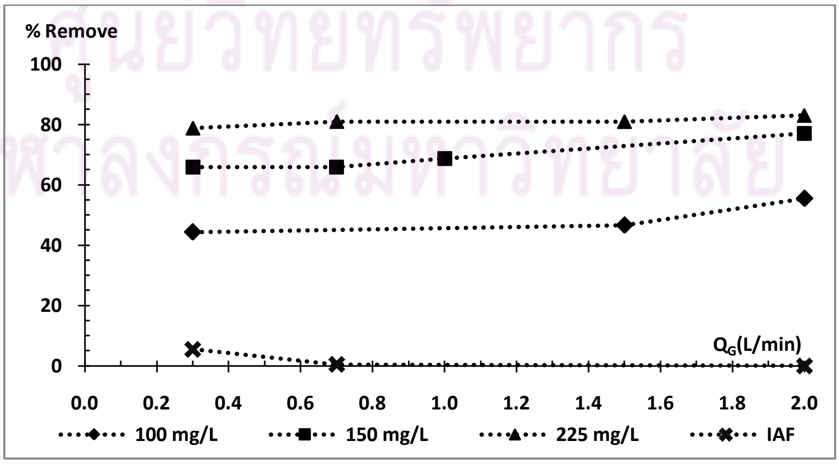


Figure 4.16 Treatment efficiencies of IAF and MIAF processes at 30 min with 0.3- 2.0 L/min gas flow rate of large column

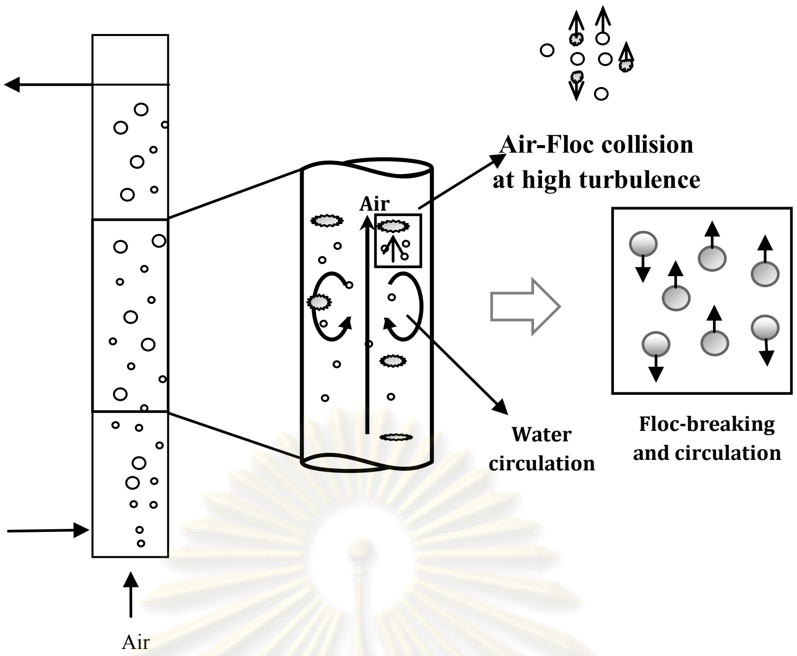


Figure 4.17 Water recirculation and floc breakage occurred in large flotation column

The results in **Figure 4.18** show the removal efficiencies obtained with MIAF process for different types of oily wastewater at suitable conditions (Sastravet, 2008 and Lersjintanakarn, 2008). According to various amounts of alum doses required for different types of oily wastewater, this confirms the influence of chemical destabilization (adsorption or charge neutralization) on the treatment of very small oil-droplet size of cutting oil-droplets presence in cutting oily wastewater, whereas sweep-floc coagulation mechanism corresponds with the others. The highest removal efficiencies obtained with both IAF and MIAF processes were found at 0.3 L/min of air flow rate. The optimal chemical dosage and associated removal efficiencies were 150 mg/L – 91.43%, 300 mg/L - 75.68% and 800 mg/L – 89.38% for cutting oil, lubricant and palm oil, respectively.

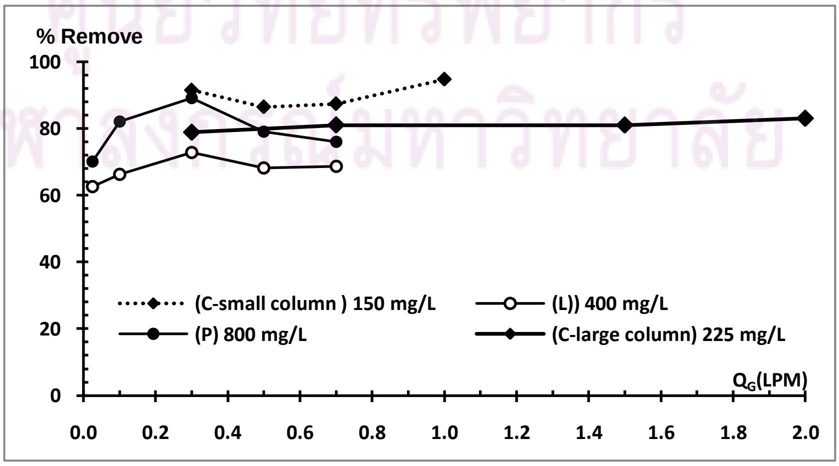


Figure 4.18 Treatment efficiency of MIAF versus gas flow rate for different types of oily wastewater

The optimal conditions of MIAF process that provide most attractive performance are summarized in **Table 4.2**.

Table 4.2 Summary of optimal operating conditions of MIAF process for small and large columns

Parameter	**Small column**	**Large column**
Air flow rate (L/min)	1.0	2.0
Alum dose (mg/L)	150	225
Operating time (min)	30	30
Treatment efficiency (%)	94.69	82.97

Note that, in practice, the lower dosage obtained from the jar test experiments can be possibly applied in order to achieve the reasonable removal efficiencies. In addition, the operation time for the MIAF process (< 30 min) was shorter than that for the chemical treatment process (40–60 min). Apart from shorter process time, MIAF process has also the advantages of lower mixing energy and smaller equipments size. It can be concluded that treatment efficiency of MIAF process in this study depends on gas flow rate, chemical dose, operating time, and also column dimension as describe below.

- **Gas flow rate**: Treatment efficiencies increase with the given flow rate (0.3-2.0 L/min) due to the suitable chemical mixing, floc formation and floc/bubble attachment conditions. However, too high value of air flow rate can not only break the aggregated floc (oil become re-disperse in solution), but also relate directly to operating cost.
- **Chemical condition**: In this work, the chemical destabilization was investigated as the main mechanism for cutting oily wastewater treatment (very small oil droplet presence). The coagulant concentration has to restrict for controlling amount coagulant species, and pH value is another factor involving particular coagulant species formed. In addition, this also associates with the flow behavior occurred in reactor: for the complex or fluctuate flow pattern, the chemical dosage may be added more than usual.
- **Operating time**: Removal efficiencies increase with time until they reach to steady state, then fall down. Because of floc breaking phenomena can occur at long operating time.
- **Column dimensions (ø)**: The turbulent condition and bubble dispersion strongly influence on fluid flow behavior depending on velocity variation in different column dimension. Water and also floc circulation easily take place in large column with large cross section area due to there is the greater stream of fluid.

For more understanding of treatment mechanisms and also flow behavior occurred during MIAF operation, the bubble hydrodynamic and mixing condition parameters were studied in next section. Note that, even the chemical destabilization was proven as the main cutting oily wastewater treatment mechanism; the proper bubble generation and mixing condition should be also investigated in order to understand and operate the flotation process with reasonable concept in terms of removal efficiency and operation cost.

4.5 Bubble hydrodynamic and mixing condition parameters

4.5.1 Bubble size, formation frequency, rising velocity, interfacial area

For providing a better understanding on variation of removal efficiencies with different gas flow rates, the bubble hydrodynamic parameters and mixing condition obtained with IAF and MIAF process were analyzed in this part. The bubble size, bubble formation frequency and rising velocity, and thus interfacial area (a) were determined as bubble hydrodynamic parameters, whereas, velocity gradient (G) as mixing condition parameter. Note that the presence of alum for MIAF process, even in the large quantities, has small effects on the bubble size generated in the flotation process (Painmanakul et al, 2009).

As shown in **Figure 4.19** the bubble diameters varied between 1.2 to 1.5 mm while gas flow rate were changed between 0.3 to 1.0 L/min for small column. For large column, bubble diameter varied between 0.8 to 1.5 mm while gas flow rate change between 0.3 to 2.0 L/min for large column. At the low gas flow rate, bubble size was regulated by gas distributor characteristics providing the controlling size is approximately 0.9 mm and 1.2 mm for rigid and flexible diffuser (Painmanakul et al. 2005). Either D_B values detached from rigid gas diffuser equipped in small column or flexible membrane installed in large column increased with gas flow rate applied in this study. Although gas flow rate is increased, the liquid phase properties and turbulence are still the same in both columns. Therefore, the generated bubble sizes obtained at higher gas flow rate is the consequence of bubble break up and coalescence phenomena (Painmanakul, 2009): the trend of bubble size variation occurred in large column is more obviously found than small column ($D_B \approx 1.4$ mm).

It can be stated that, the larger cross section area may receive smaller affect from turbulence due to larger volume operated at the same gas flow rate values compared to the smaller one. Consequently, lower bubble breaking-up and total increasing size of bubble are obviously presented. Additionally, different gas diffuser characteristic generates different detached bubble sizes. Moreover, the rigid gas diffuser is used for general bubbling proposes such as using in fish-aquarium tank while the flexible membrane is especially produced for aeration propose in wastewater treatment processes. Therefore, the selection of gas distributor is not only very affect to the bubble size but also other bubble hydrodynamic parameters.

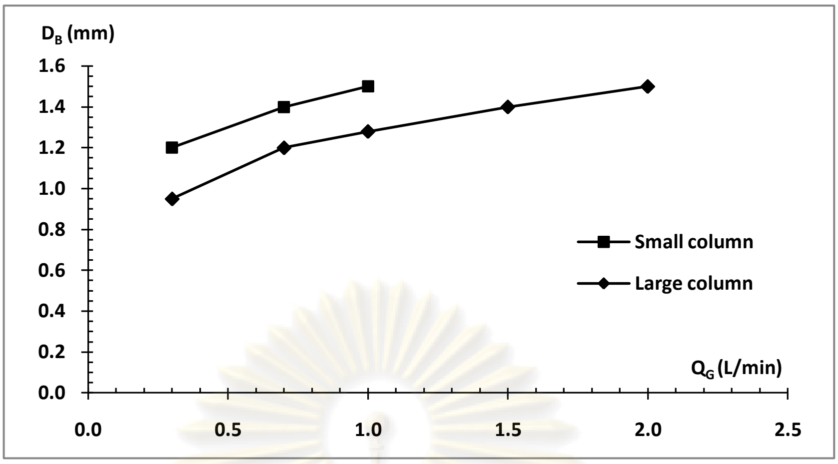


Figure 4.19 The variation of the detached bubble diameter (D_B) with respect to gas flow rate for the IAF and MIAF processes for cutting oily wastewater

According to **Figure 4.20**, the small difference observed on comparison of this result to other oily wastewater types was the D_B values detached from rigid gas diffuser passing through lubricating oil and palm oil were roughly constant, especially at low gas flow rates before increase at the high gas flow rate. However, at low gas flow rate, bubble diameter from rigid gas diffuser is directly associate the force balance between surface tension and buoyancy forces during bubbles growth and detachment (Painmanakul et al, 2009).

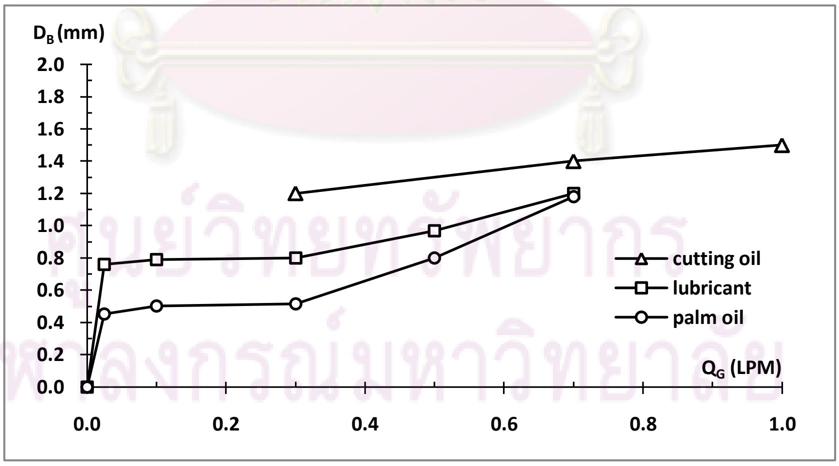


Figure 4.20 The variation of the detached bubble diameter (D_B) with respect to gas flow rate for the IAF and MIAF processes for different types of oily wastewater studied in small column.

Moreover, due to Laplace„s equation (Painmanakul et al, 2005), the bubble diameter, especially at low Q_G values, was related to surface tension as presented in **Table 4.1**. By comparing with the experimental data obtained from various studies concerning to the effect of liquid phase viscosity, the bubble size formed in low-viscosity liquids (μ from 1 to 20 cps) are dependent on gas flow rate under certain critical values (Q_{CR}) (Bondarev and Romanov, 1973). Therefore, in this study, it can be stated that the influence of surface tension of liquid phase has more pronounced than that of viscosity of liquid phase on the generated bubble size.

Due to the measured bubble size, the bubble formation frequency (f_B) and their rising velocity (U_B) can be then determined by the analytical technique as previously described in chapter 3. Therefore, the highest f_B value can be obtained with the lowest gas flow rate which corresponds to the smallest bubble size and thus volumes generated in bubble column. Moreover, over entire range of bubble diameter obtained in this study, the bubble terminal rising velocities (obtained experimentally) were increasing due to bubble enlarged at higher air flow rate and present correspondingly within the range of the U_B values of the contaminated systems of Grace and Wairegi (1986). Then, by using the **Eq. 2.7**, the values of D_B, f_B and U_B were applied for calculating the interfacial area (a) as shown in **Figure 4.21**. Noted that the obtained a values correspond with the number of generated bubble and thus the surface is available for interacting with oil droplets in water phase.

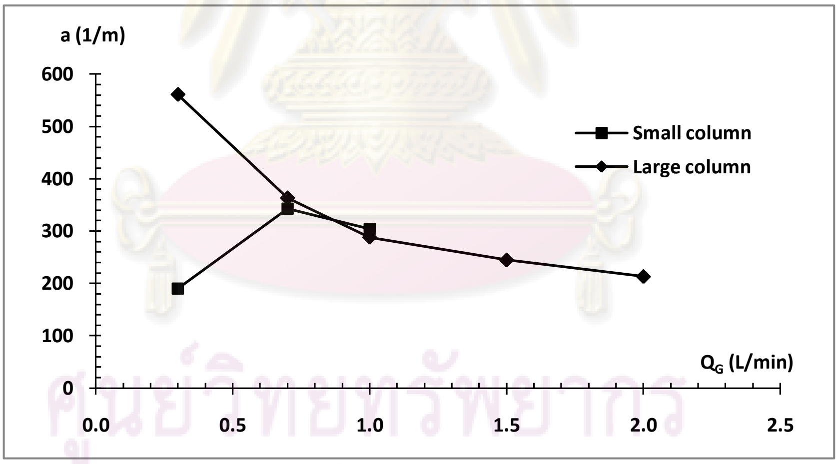


Figure 4.21 The variation of interfacial area a with respect to gas flow rate for the IAF and MIAF processes for cutting oily wastewater

In this study, the values of vary between 190-340 m^{-1} for gas flow rates varying between 0.3 – 1.0 L/min for small column while the values between 310 - 560 m^{-1} obtained from large column under 0.3-2.0 L/min of gas flow rate. It can be noted that the values of a in cutting oily wastewater study conducted in small column equipped with rigid gas diffuser increase linearly with the gas flow rates and then become slowly increase at higher gas flow rate. Additionally, gas flow rate defied in an interfacial area equation (**Eq.2.7**) presents as crucial controlling variable on consistent a values of both columns equal to 290 m^{-1} at the high gas flow rate This result of cutting oil as shown in **Figure 4.22** is similar to the lubricating oily wastewater studied in small column.

However, the decreasing trend line was clearly shown in case of palm oily-wastewater: the associated D_B values, which increase sharply at higher gas flow rates as presented in **Figure 4.20**, should be responsible for these results. Moreover, for a given gas flow rate, the interfacial areas obtained with palm oily-wastewater was greater than those obtained with other liquid phases. Conversely, a values exponential decrease with gas flow rate passing through flexible membrane present in large column. The difference was less pronounced at high Q_G values due to the sharp increased bubble size and thus lower bubble formation frequency from bubble break up and coalescence phenomena occurred in large column as shown in **Figure 4.19**.

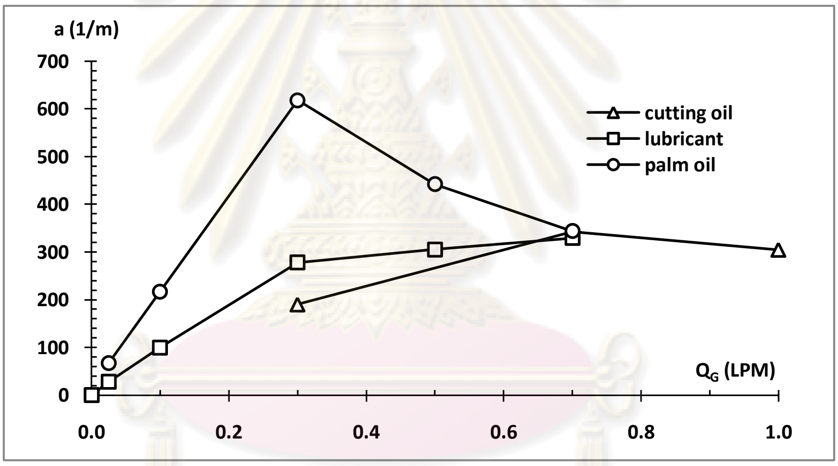


Figure 4.22 The variation of interfacial area a with respect to gas flow rate for the IAF and MIAF processes for different types of oily wastewater studied in small column.

4.5.2 Mixing parameters (G) and ratio between interfacial area and velocity gradient (a/G)

The calculated velocity gradient (G) at various different gas flow rate of cutting oil by using **Eq. 3.2** was shown in **Figure 4.23**. The values of G herein directly depends on gas flow rate and working volume increase linearly with gas flow rate leading to turbulent mixing condition occurred in flotation column. For large column, the velocity gradient slowly increases with gas flow rate. Since the larger working volume was used but small increased gas flow rate was injected in large column so that G obtained with small column has greater values than obtained with the large one.

This result is similar to the results obtained from lubricating oil and palm oil also (**Figure. 4.24**). It can be stated that, due to the lowest viscosity of cutting oily wastewater, the highest G values can be thus obtained: this result affects not only the mixing condition occurred in liquid phase, but also the interaction between the generated bubbles and oil droplet particles. This fact conforms to the lowest removal efficiency obtained with IAF process for treating the cutting oily wastewater (**Figure 4.3**).

Due to the liquid phase properties in both columns are the same, the turbulence causing from enhanced gas flow rate in large column over the value used with small column still gives lower mixing power (lower G). Thus, alum dosage required for destabilization in large column have to be much more than used in small column to compensate this lower mixing power input.

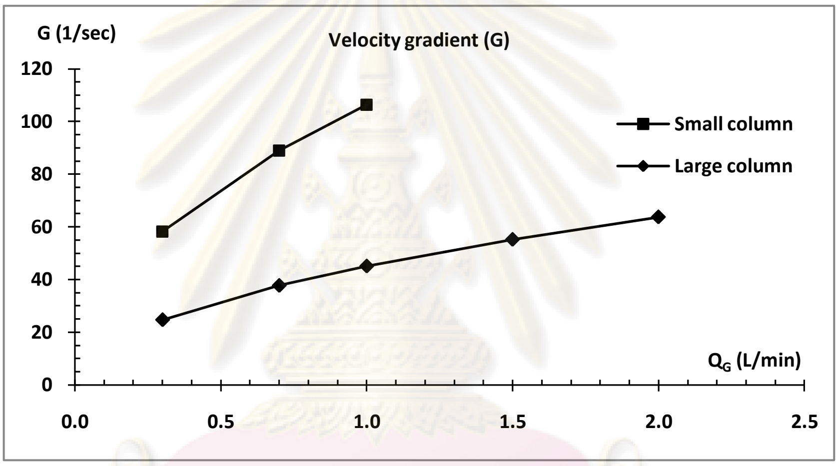


Figure 4.23 Velocity gradient (G) versus gas flow rate for cutting oily wastewater

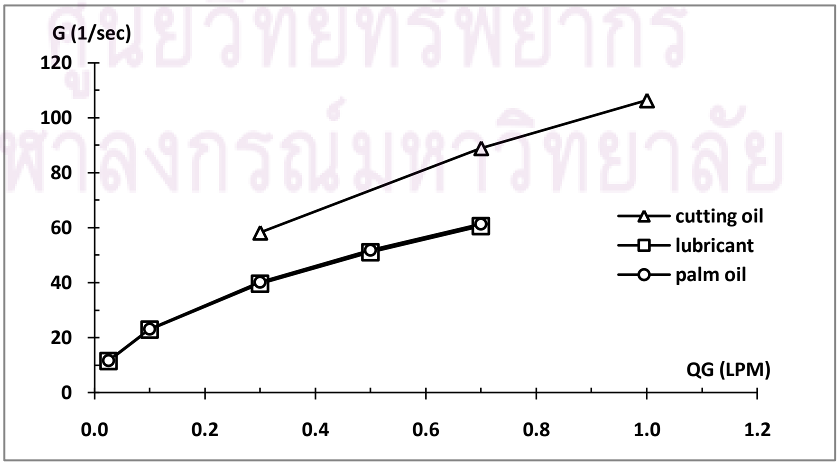


Figure 4.24 Velocity gradient (G) versus gas flow rate for different types of oily wastewaters

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 4.25 and 4.26.** It can be found that the maximum of the a/G values can be found at the gas flow rate equal to 0.3 L/min which correspond to the Q_G value that provides the highest removal efficiency obtained with both IAF and MIAF processes as shown in **Figure 4.15 and 4.18**. Therefore, the a/G ratio can be used as one of important parameter in order to select the optimal operating condition of the flotation process. Note that, the optimal chosen a/G ratio will relate to the gas 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 wastewater treatment efficiency.

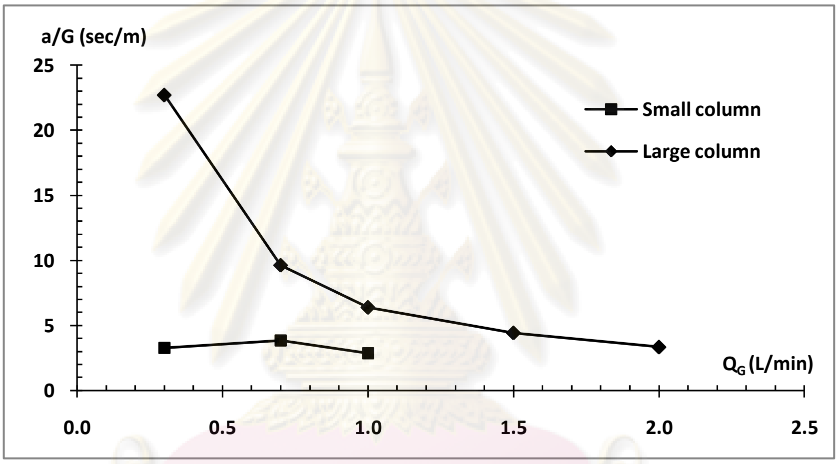


Figure 4.25 Ratio of interfacial area and gradient velocity (a/G) versus gas flow rate for cutting oily wastewater

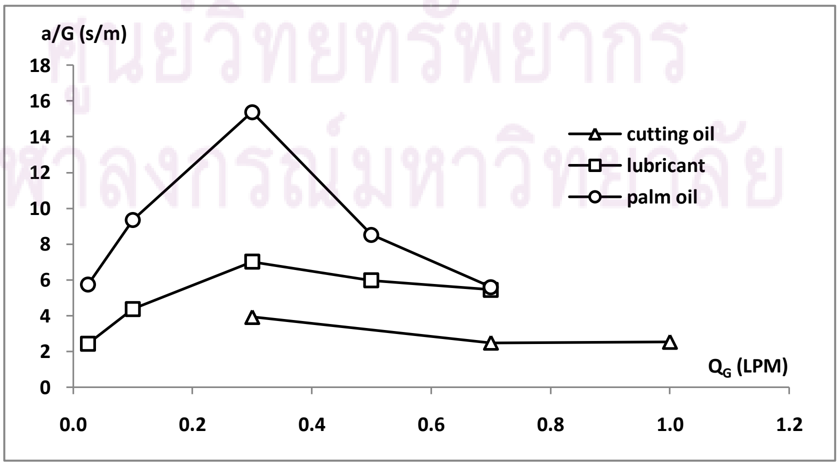
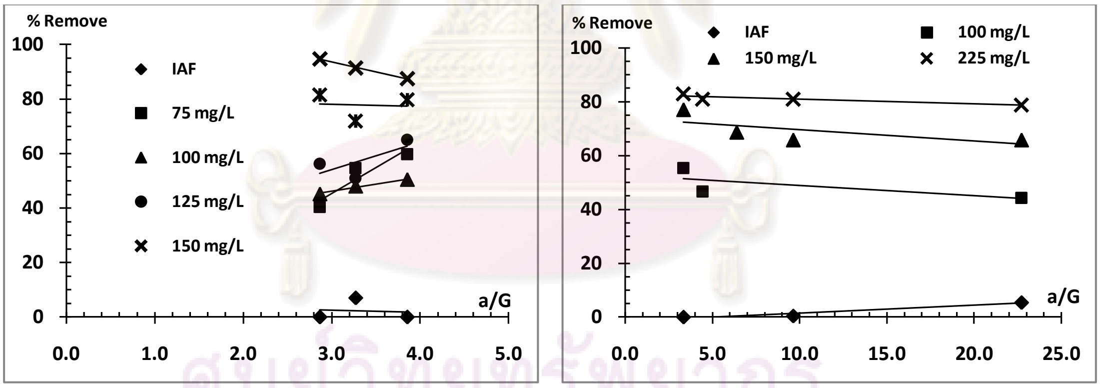


Figure 4.26 Ratio of interfacial area and gradient velocity (a/G) versus gas flow rate for different types of oily wastewaters

The **Figure 4.27** are confirmed that MIAF process for treatment of cutting oily wastewater is independent on a/G ratio or physical parameters such as bubble hydrodynamics and velocity gradient due to the limitation on the interaction between oil droplets and generate bubbles, but depends on chemical destabilization. In contrasted to the results obtained from larger oil droplet sizes of lubricating oil and palm oil that a/G ratio has been proved to be the important parameters for wastewaters treatment by IAF and MIAF processes as present in **Figure 4.28**.

However, even highest and lowest a/G values in case of palm and cutting oily-wastewaters respectively, the highest removal efficiency can be observed with cutting oily-wastewaters by using MIAF process. Thus, chemical destabilization mechanism related with different oil droplet properties should be also taken in account together with the bubble hydrodynamic and mixing condition in order to obtain the optimal operating condition for treating each stabilized oily-wastewater. Moreover, consideration of **Figure 4.25** on large flotation column, a/G ratio clearly presents higher values than small column especially at low gas flow rate. Therefore, it is very interesting for applying this process to other oily wastewaters that has larger oil drop than cutting oil because greater a/G values at low gas flow rate offer very high overall removal efficiency and cost saving. Another benefit from operation at low gas flow rate is that floc breakage at water surface is avoided.



(a) Small column (b) Large column

Figure 4.27 Treatment efficiency of cutting oily wastewater versus a/G ratio

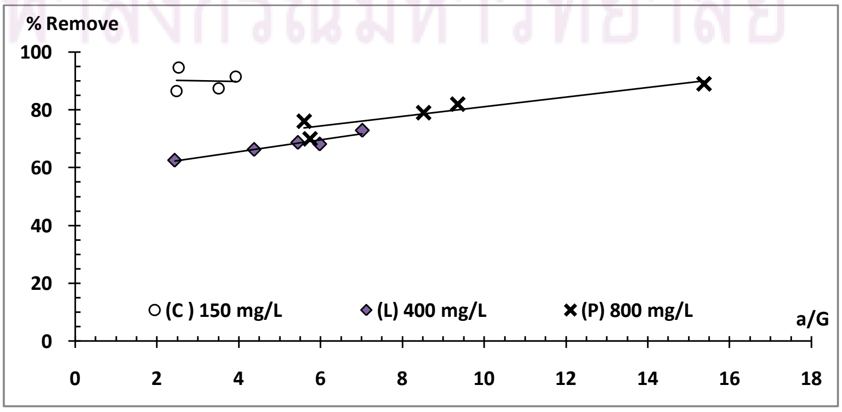


Figure 4.28 Treatment efficiency of different types of oily wastewater versus a/G ratio

In accordance with the preliminary study, except the chemical destabilization mechanism, the column dimension affect especially on an interfacial area, velocity gradient and turbulence at the high gas flow rate, and then treatment efficiency. Besides, the complex flow regime as mentioned before is another important factor that should be taken into an account for MIAF operation in the future. However, the study of continuous process in the next section is performed for adaptation in the real world and also provides better understanding on the effect of the different flow regime within the two different column dimensions in term of both process performance and residence time distribution function.

4.6 Continuous MIAF process study

In practice, the continuous process is typical used for wastewater treatment of large volume generated from industrial sectors. In order to extend operating condition of MIAF process, the continuous MIAF system should be performed for providing the information related with process scale-up in future. Note that the operating conditions performed in this section was applied from batch MIAF process (1.0 L/min gas flow rate with 150 mg/L alum dose and 2.0 L/min gas flow rate with 225 mg/L alum dose for small and large columns, respectively). The wastewater feed rate was varied at 5 and 11 L/hr for small column and 15, 30, 45 L/hr for large column. Under these associated ranges of liquid flow rates, the theoretical residence time (time material spent in reactor, τ= working volume/water flow rate) were 36 min and 16.36 min for small column and 62 min, 31min and 20.67 min for large column. In this work, feed rates were chosen due to the kinetic test results as described previously in batch system and also the available value of the pump equipment in practice.

For results obtained with small column (**Figure 4.29**), the average removal efficiencies of both 5 and 11 L/hr of influent feed rates were up to 76% and 80% approximately. This is due to the excess amount of oil content injected into small column with higher velocity providing the well mixing condition. Moreover, at higher feed rate (11 L/hr), the shorter operating time spent for achieving maximum efficiency was also remarked. However, the greater collision frequency between increased amount of oil droplets and excess alum at initial operating time (high loading of oil and chemical dosage) should be considered as the important factor on rapid destabilization mechanism. In opposite to the results obtained with large column, the overall oil removal efficiencies were 45%, 24% and 31% for wastewater feed rate at 15L/hr, 30 L/hr and 45 L/hr, respectively. It can be noted that the increase of oil and chemical loading cannot enhance the treatment efficiencies: floc-breaking phenomena, bubble dispersion and water recirculation occurred in large column should be responsible for these results. In comparison to batch MIAF results, the continuously fed water has been proven to affect the different momentum or force field, and thus cause the higher possibility of water circulation occurred in large cross section area. Therefore, in practice, the effect of column dimension should be well considered.

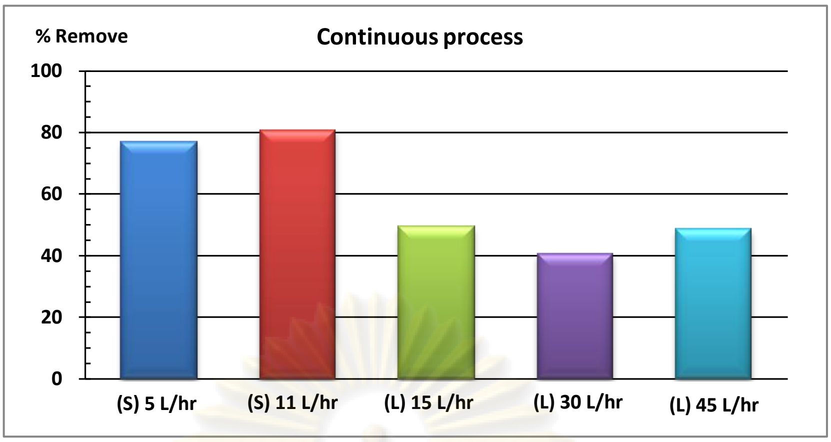


Figure 4.29 Treatment efficiency at steady state of continuous MIAF processes

As mention in previous section, for more understanding about the effect of flow regime on floc breaking phenomena, water circulation and eventual obtained treatment efficiency, the study of RTD was analyzed in the next step.

4.7 Study of Residence Time Distribution (RTD)

The objective of the RTD experiment was to characterize the fluid dynamic behavior of small and large flotation cells for more understanding of mechanism occurring during operation. The experiments were performed by pulse injection method using 10 ml of 5N NaOH as a tracer. The effect of aeration (bubbling) was included to investigate the variation of flow dynamic. The operating condition (feed rate) used in RTD experiment was the same as the conditions of continuous MIAF process. Tap water was used instead of oily wastewater to avoid interference during conductivity measurement.

Firstly, the conductivity profile obtained experimentally is converted to RTD function (E-curve) by using **Eq. 4.1**. (Fogler, 1992).

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)dt} \qquad \textbf{Eq. 4.1}$$

where E(t) is the fraction of tracer amount with residence time between t and t+dt whereas C(t) is tracer concentration measured at effluent stream at time t. The mean residence time $(\bar{t})$ and variance can be calculated from E(t) by using **Eq. 4.2** and **Eq**.**4.3** below.

$$\bar{t} = \int_0^\infty tE(t)dt \qquad \textbf{Eq. 4.2}$$

$$\sigma_t^{\ 2} = \int_0^\infty t^2 E(t)dt \qquad \textbf{Eq. 4.3}$$

However, the function E(t) is normally presented in term of the normalized RTD (dimensionless function: E(θ)) which can defined from **Eq.4.4**.

$$E(\theta) \equiv \bar{t}E(t)$$ **Eq. 4.4**

The variable t (time) can be transformed into the dimensionless (θ) by divided by mean residence time $\bar{t}$ as given by

$$\theta = \frac{t}{\bar{t}}$$ **Eq. 4.5**

Even if using dimensionless time (θ) instead of the actual time, the E(t)dt is still referred to the same meaning. This normalized distribution function aids in compared the performance of the different sizes of reactor.

Mostly, the real equipment is designed base on 2 ideal fluid flow models which are very different behavior, plug flow and completely mixed flow. However, the real flows of the equipment always deviate from these ideal patterns. To diagnosis the real flow that deviates from the two ideal flow models, plug flow and completely mix, models with one parameter are adequate to represent this system. The single parameter model used to fit the experimental RTD data in this study is Tanks-In-Series-Model which based on a series of perfectly mixed tanks and can be used to represent the deviations from plug flow and also represent the real stir tanks (C.G.C.C. Guitierrez, 2010). The E (θ) function for the model used in this parted are summarized as followed;

CSTR: $$E(\theta) = e^{\theta}$$ **Eq. 4.6**

Tanks-In-Series: $$E(\theta) = \frac{n(n\theta)^{n-1}}{(n-1)!}e^{-n\theta}$$ **Eq. 4.7**

The n represents the number of tanks in series determined from **Eq. 4.7.** As the number or series (n) become very large, the behavior of the system approaches of plug flow.

$$n = \frac{\tau^2}{\sigma^2}$$ **Eq. 4.8**

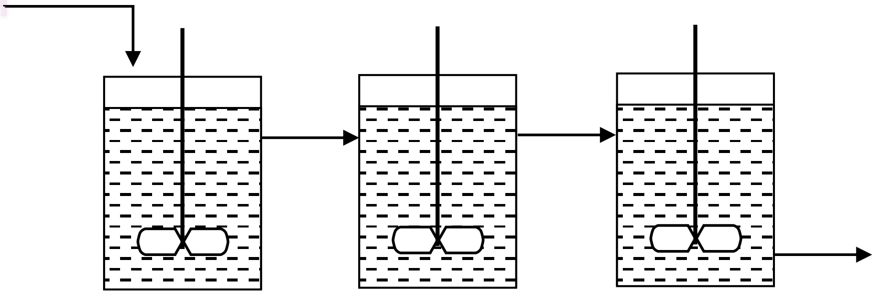


Figure 4.30 Tanks-In-Series

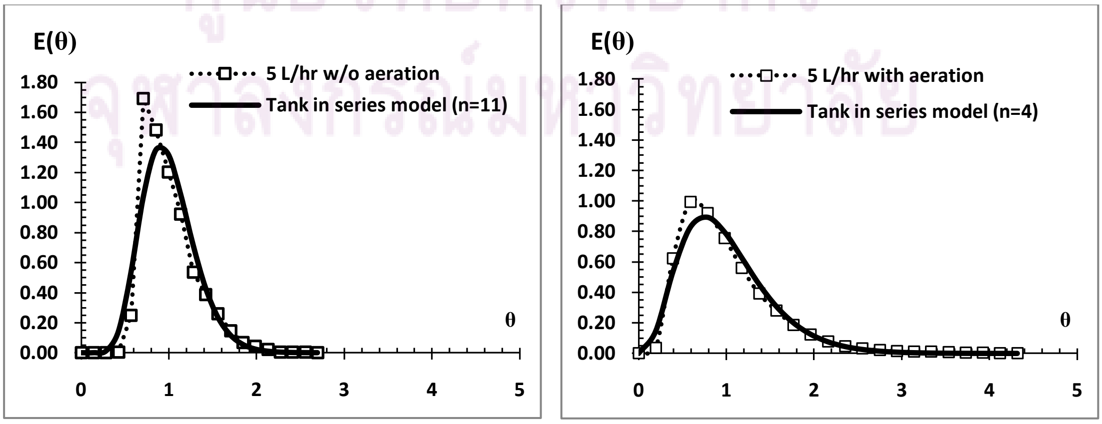
If the m tanks are connected to n more tanks (all of the same size), then the means are additive, or

$$\bar{t}_{m+n} = \bar{t}_m + \bar{t}_n \qquad \textbf{Eq. 4.9}$$

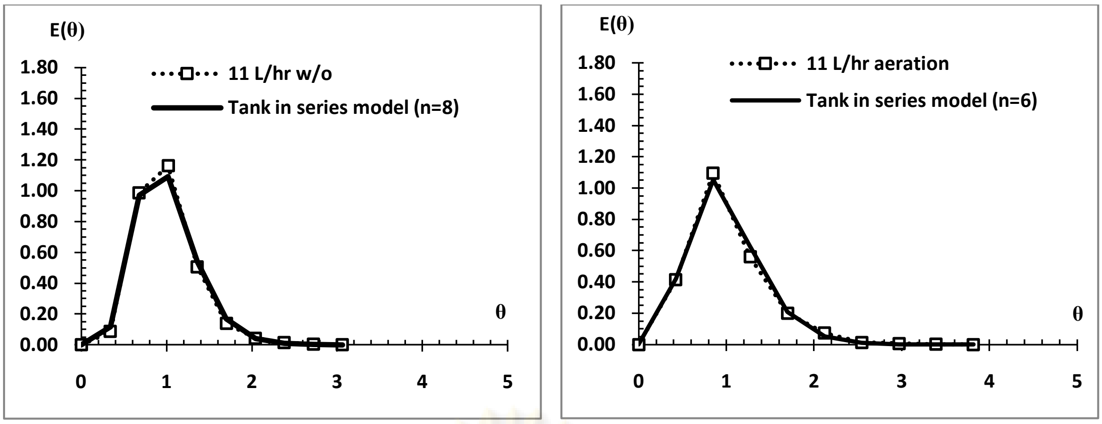
Because of this property we can join the streams with recycle streams. Thus, this model becomes useful for treating recirculation systems. The series of n tank present in **Figure. 4.30** show independence of stages.

As shown in **Figure 4.30**, the Tanks-In-Series Model shows reasonably good fit to RTD results for whatever condition performed in small column. The deviation on RTD data at the low feed rate 5 L/hr to this model was observed. Number of series (n) decrease when flow rate of liquid phase increases. Concerning to the flow through tanks in series in **Figure 4.30**, less n tanks inferred to low recirculation and the fluid flow tends to be close ideal CSTR. Furthermore, the effect of aeration increases n parameter resulting in liquid circulation which the flow pattern change closely to plug flow regime and thus high treatment efficiency (**Figure 4.31**).

This parabolic velocity profile of lamina flow may response to this result hindering sign of the stagnant backwaters. Although there was stagnant region occurred during operation, this becomes the beneficial for MIAF process by supporting available space and adequate contact time for floc aggregation along 2 m height of column before exit the reactor. Additionally, this proposed model corresponds to very attractive performance of MIAF process as described in previous section **(Figure 4.29)**.



(a) 5 L/hr without aeration (b) 5 L/hr with aeration



(c) 11 L/hr without aeration

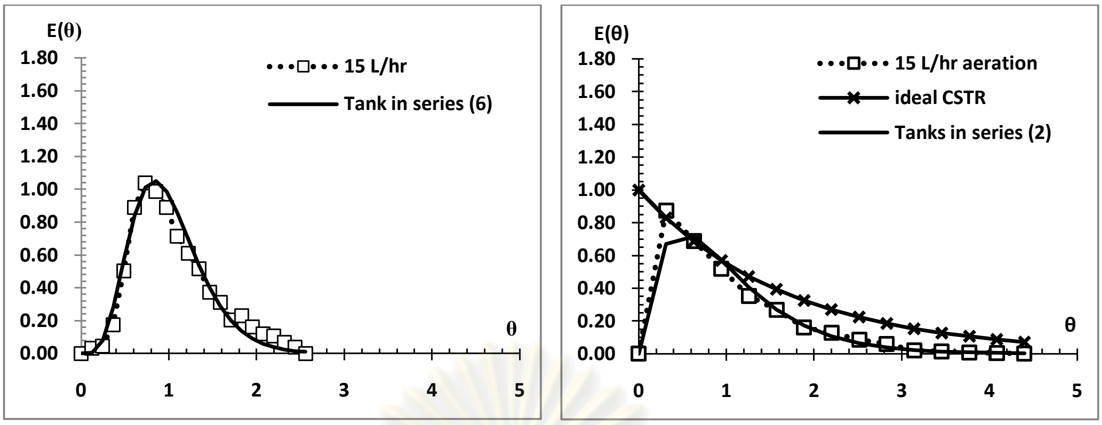
(d) 11 L/hr with aeration

Figure 4.31 RTD curves of small column at different feed rates

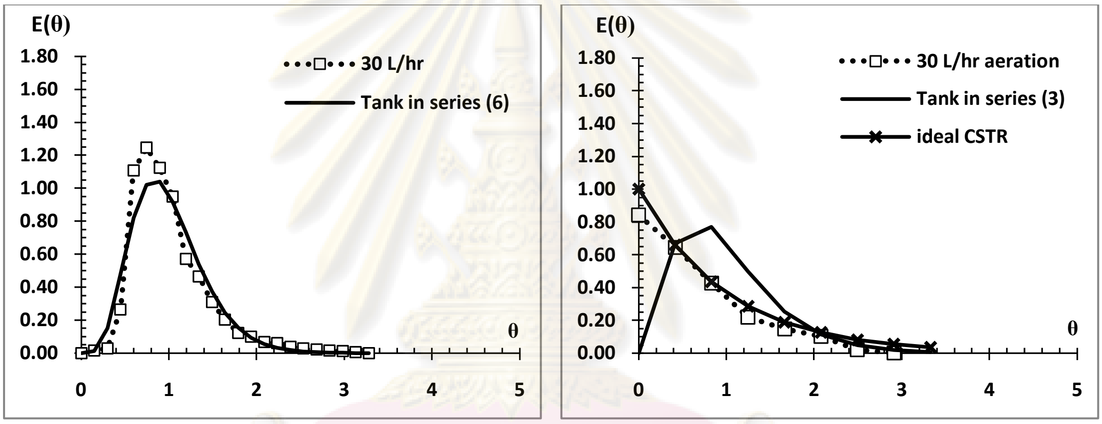
For large column in absent of aeration, the Tanks-In-Series Model still the best fits for 15 L/hr and 30 L/hr feed rates as shown in **Figure 4.31** (a), (c). Series (n) was reducing due to the liquid flow rate changing from 15L/hr to 30 L/hr. Also increasing of gas velocity in small column reduces conformation of plug flow behavior and tends to close ideal CSTR. Then, particle separating zone was indistinguishable present in less treatment efficiency attained in **Figure 4.32.**

Increasing of feed rate up to 45 L/hr, it cannot be identifying accurately flow model which are intermediate between ideal CSTR and tanks-in-series models as present in the **Figure 4.31** (e). On the other hand, flow behavior obviously presents closely to ideal CSTR in the presence of aeration for feed for whatever as seen in **Figure 4.31** (b), (d), (f). It can be stated that the effect of aeration shifts the flow behavior change closely to ideal CSTR. As a result, the perfect mixing occurred throughout the large column corresponding to the floc breaking phenomena. Because there is no area allowing for aggregation for destabilized oil droplet, and thus lower treatment efficiencies as shown in **Figure 4.32.**

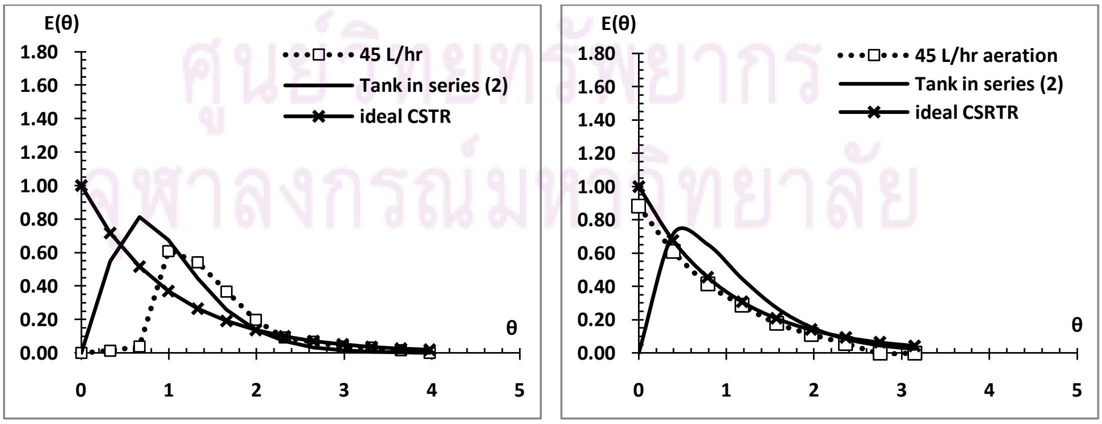
Additionally, the random fashion of bubble dispersion through large bulk fluid in cylindrical column seems to provide the flow regime closely to air lift reactor; water circulation around draft tube. Due to the geometry and dimension of reactor used in this study is cylindrical and water flow condition is laminar; Re varied from 4.6 to 17.4 is indicated in lamina flow. There is variation of velocity from axial to the wall of pipe so that the central of fluid moves with greater velocity than the fluid near the wall as shown in **Figure 4.33**. In present of aeration, bubble population is one factor aid in fluid movement upward and then liquid circulation in column center and the downward circulation near column wall (Kantarci et al, 2005).



(a) 15 L/hr Without aeration (b) 15 L/hr With aeration



(c) 30 L/hr Without aeration (d) 30 L/hr With aeration



(e) 45 L/hr Without aeration (f) 45 L/hr With aeration

Figure 4.32 RTD curves of large column at different feed rate

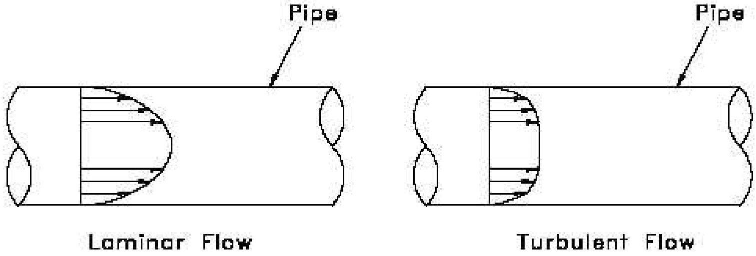


Figure 4.33 Velocity profile of fluid flow through pipe
(Laminar: Re < 2000; Re = ρvd/μ)

With respect to fluid dynamic, the RTD experiments can be applied in order to describe the different MIAF process performances obtained from both small and large column. The experimental RTD results of small flotation column are well described by a number of perfect mixers in series for whatever operating conditions, whereas the three different flow models was found in large column flotation consisted of tanks-in-series mpodel, intermediate configuration between ideal CSTR and tanks-in-series models, and very close ideal CSTR model. This directly associates with the floc breaking phenomena and water recirculation which are critical drawback or limitation of MIAF process and lacking of suitable flocculating area. To carry out this limitation, the settling stage should be considered and performed in the next section. Note that, the inaccurate data collection can cause from the peristaltic pump used in this work and also induces a weak pulse injection and broad tracer detecting time interval (5 min). This should be taken into an account to attain more accurate data, in future.

Table 4.3 Summary RTD data of small column study

Feed rate : Q_L (L/hr)	**Experimental mean residence time:** $\bar{t}$ **(min)** $\bar{t} = \int_0^\infty tE(t)dt$	**Theoretical mean residence time:** τ **(min)** $\tau = \frac{V}{Q_L}$	**Flow Model**	**n**
5 L/hr (w/o aeration)	35.23	36	Tanks in series	11
5 L/hr (with aeration)	25.38	36	Tanks in series	4
11 L/hr (w/o aeration)	14.75	16.36	Tanks in series	8
11 L/hr (with aeration)	11.71	16.36	Tanks in series	6

Table 4.4 Summary RTD data of large column study

Feed rate : Q_L (L/hr)	**Experimental mean residence time:** $\bar{t}$ **(min)** $\bar{t} = \int_0^\infty tE(t)dt$	**Calculated mean residence time:** τ **(min)** $\tau = \frac{V}{Q_L}$	**Flow Model**	**n**
15 L/hr (w/o aeration)	43.05	62.00	Tanks in series	6
15 L/hr (with aeration)	15.91	62.00	Tanks in series	2
30 L/hr (w/o aeration)	33.90	31.00	Tanks in series	6
30 L/hr (with aeration)	12.02	31.00	CSTR	-
45 L/hr (w/o aeration)	15.09	20.67	Tanks in series	2
45 L/hr (with aeration)	12.71	20.67	CSTR	-

4. 8 Continuous MIAF – Settling process

Due to several problems occurred in large flotation column as described previously, the modified concept by adding continuous MIAF process with flocculation-settling step was chosen in order to enhance MIAF continuous process. To prevent floc breaking phenomena occurred in continuous MIAF process of large column, the settling step was required for floc formation after rapid mixing. Then, floc was separated by reverse gravitational force due to its less density than water. Moreover, due to the influence of chemical treatment mechanism on very small size of cutting oily-droplet, the feasibility study for reducing the physical flotation time was investigated. Note that, the removal efficiencies were determined in a function of time. Therefore, the operating time (mixing time) of continuous process was varied from 1 hr to 10 minutes, and then 2 hrs allowing for floc aggregation.

Flocculent-settling (Flocculent-sedimentation)

Flocculent Settling is one of the various way particles can settle from suspension. Particle sizes tend to increase as particles settle and hence, settling velocity increases. This mechanism occurs when there is a greater solid and chemical alter particle surfaces to enhance attachment. In flocculent-settling, individual particles agglomerate themselves and formed floc tends to grow in size while settling. Therefore, the flocculent-settling the velocity is not constant, but tends to increase. Since the flocculation occurs, there is greater chance to contact another particle and agglomerate during travel through the column as seen in **Figure 4.34.** Consequently, the removal efficiency of flocculent settling is enhanced with the depth/height and time (Marcos, 2007).

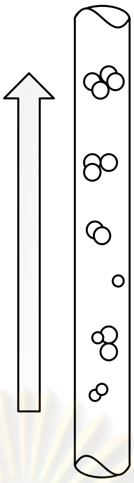


Figure 4.34 Flocculent–Settling

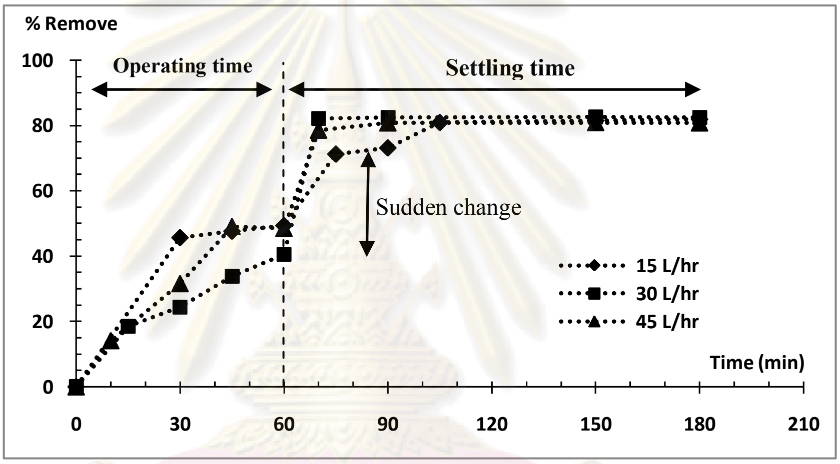


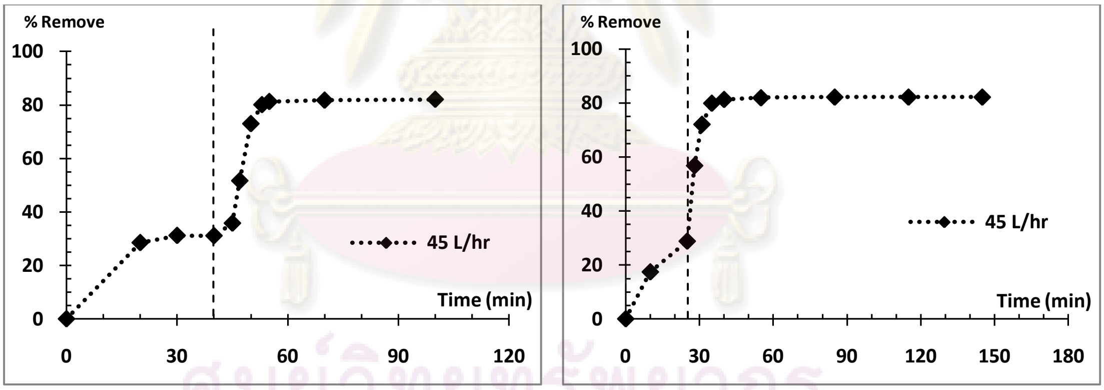
Figure 4.35 Treatment efficiency of combined settling time to continuous MIAF process for 1 hr mixing time

(a) (b)

Figure 4.36 (a) floc formation during settling time (b) floc accumulations at the water surface

According to **Figure 4.35 - 4.37,** the positive effect of increased settling time can be observed on the overall treatment efficiency for whatever the experiments. For 1 hr continuous operation, the highest removal efficiency was increased from 50 % up to 80% approximately within first 5 min of settling time as shown in **Figure 4.35**. This may be described that the floc aggregation was allowed when there was reduced the turbulent condition from hydrodynamic interaction. This is referred to the dissipation of interfere by mixing mechanism was occurred and also the slow stirring intensity acts on less shear rate (NAN Jun et al, 2009). This supports floc formation whereby the balance of floc aggregation and floc breakage (Jarvis et al, 2005). Thus, the increase of aggregated size was possibly occurred spontaneously due to the remaining energy from aeration, and then separated by flocculent settling mechanism.

In this study, the floc attribute as shown in the **Figure 4.36** (a) formed after the few minutes of setting time was allowed. In case of the oily floc, the reversed settling occurred and floc accumulated at the water surface finally as shown in **Figure 4.36** (b). This result clearly showed the severe effect of water circulation on floc breaking phenomena at the surface of flotation column and finally on the overall efficiencies. However, 1 hr of operation time is quite long in order to obtain 80% oil removal efficiency. Therefore, an attempt to reduce operating time with kept high removal efficiency was performed by studying the effect of mixing duration time varied between 25 min and 40 min with 45 L/hr of feed rate. **Figure 4.36** (a) and (b) present the results of continuous combined with flocculation-setting at mixing time duration at 40 min and 25 min, respectively.



(a) 40 min mixing duration time (b) 25 min mixing duration time

Figure 4.37 Performance of combined settling time to continuous MIAF process for mixing time

According to **Figure 4.37,** the result of feasibility study on mixing time reduction showed the similar treatment efficiencies. This indicated that long mixing time was not necessary for 80% removal efficiencies achievement, even the efficiencies before settling stage was different values. Moreover, these results will be confirmed again by using 10 min of mixing time for whatever influent feed rates as presented in **Figure 4.38** in order to ensure that only 10 minutes continuous mixing time was sufficient for well mixing mechanism including confirmation of the essential of settling tank for continuous MIAF process.

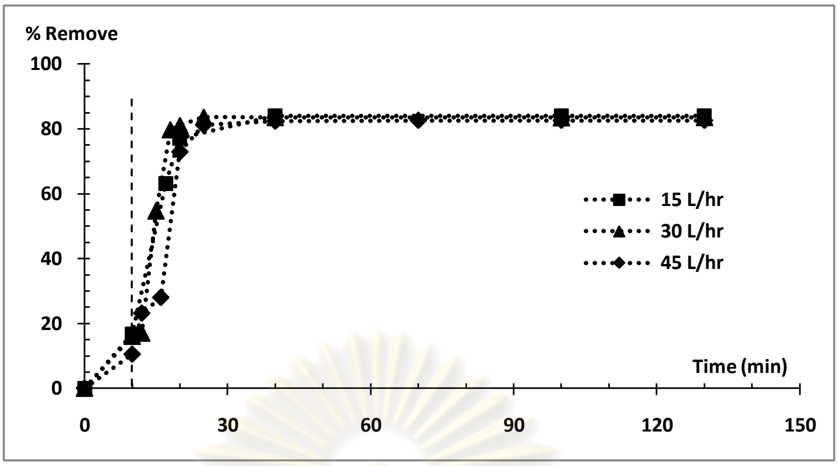


Figure 4.38 Performance of combined settling time to continuous MIAF process for 10 min mixing time

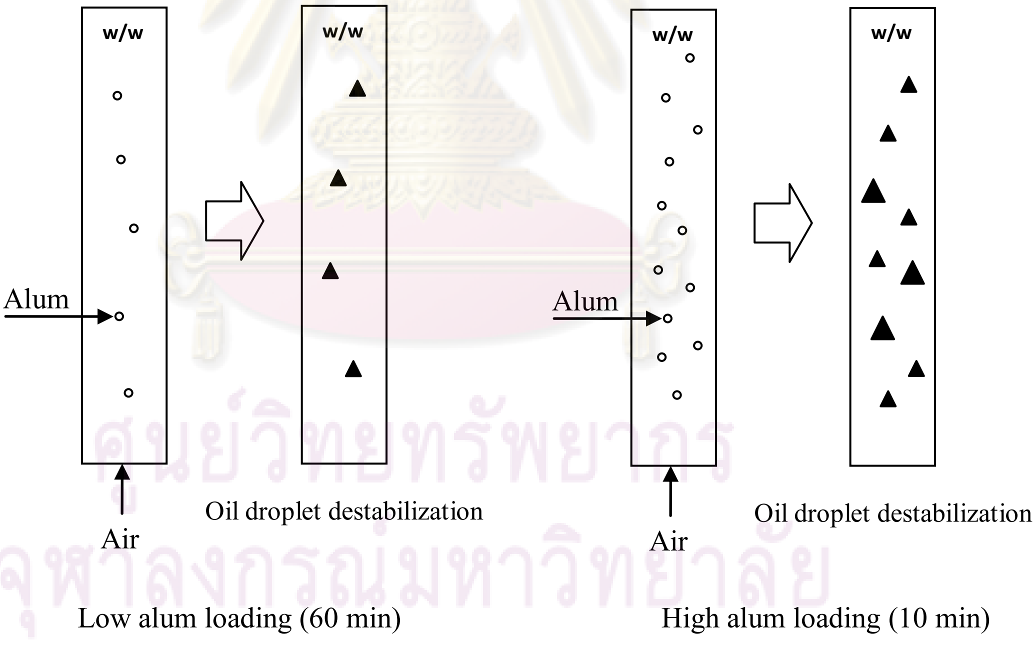


Figure 4.39 Comparison of different alum loading at long and short operating time; (▲: destabilized oil droplet), (∘ : alum)

From the results in **Figure 4.38**, it can be observed that only 10 min of continuous operation (mixing) time was enough for destabilizing and forming the floc of oil-droplet particles: high loading of cutting-oil and alum feeds within this short period should be one of the main reasons for these results. **Figure 4.39** presents the comparison of different loadings of cutting-oil and alum obtained with long and short operation (mixing) time. Another way it can be state that used the same alum concentration but different injected period creates different alum loading for each operating time resulting in effective treatment efficiency is possible.

Moreover, according to **Figure 4.35 - 4.38**, it can be observed that the settling time required for flocculation and floc separation was around 5 minutes for whatever feed rate: this can provide same treatment efficiencies as obtained with small column. It can be stated that the short settling time relates with increasing size of floc due to the aggregation with another floc along the height of column. Additionally, floc rising velocity increases with time which is corresponding to flocculent settling mechanism as described previously.

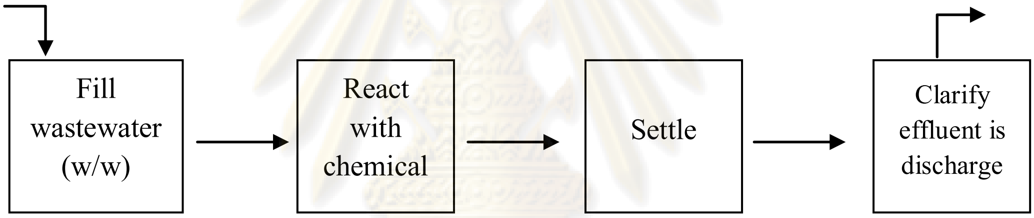


Figure 4.40 Schematic of Batch Sequencing Reactor Process

In conclusion, suitable amounts of oil-droplet and coagulant dose (loading) were more important than the other physical parameters, like liquid flow rate or detention time, bubble hydrodynamic and turbulent conditions, column dimension, etc. Therefore, in order to promote the overall treatment efficiency of cutting oily-wastewater in large column, Sequencing Batch Reactor (SBR) or Completely Mixed Stirred Tank (CSTR) combined with settling tank was recommended in this study. Note that, wastewater treatment is achieved by a timed sequence of operations which occur in the same SBR Tank, consisting of filling, reaction (aeration), settling, decanting, idling, and sludge wasting (**Figure 4.40**).

CHAPTER V

CONCLUSIONS

The induced air flotation (IAF) process combined with coagulation process called modified induced air flotation (MIAF) was studied and focused on determination of optimal condition for coagulation and flotation processes by Jar test, performance study of cutting oily wastewater treatment by IAF and MIAF processes, bubble hydrodynamics parameters, feasibility study of reactive oily bubble for cutting oily wastewater treatment, and continuous process study and also residence time distribution (RTD) analysis. Optimal conditions of individual treatment process were summarized in **Table 5.1**.

1. Oily wastewater Analysis and IAF Process

- Characteristic of the cutting oil-droplet size presence causes some limitation on the application of decantation and IAF process due to oil droplet has very small size (≈ 1.3 μm) and small affect by gravity force.

2. Reactive oily bubble flotations

- An attempt to treat cutting oily-wastewater by bubble coated with thin film of kerosene in reactive oily flotation process was unsuccessfully. Since kerosene properties can partial dissolve in cutting oily wastewater phase and mixing causes dispersed oil droplet break up into smaller size resulting in turbidity increased.
- Besides, using of kerosene coated bubble also recovered shortcomings such as giving strong bad characteristic odor and rubber part destruction on equipment, like membrane sparger, pipeline for inlet and chemical feed.

3. Treatment of oily wastewater by coagulation process (Jar Test)

- The crucial parameters, which affect on the obtained removal efficiencies in coagulation process, are 1) pH value which control complex ion species form after adding alum into water and 2) alum dosage which involves amount of generated positive ion present in wastewater.
- The treatment efficiencies obtained with coagulation process are obviously greater than those obtained with the IAF process. The suitable condition for coagulation (Jar-Test) of 1.0 g/L cutting-oily emulsion was present at initial pH 7 with 150 mg/L alum concentration.
- However, the disadvantage of the chemical process is long operation time requirement (rapid/slow mixing and sedimentation) and restriction of the optimum dosage of alum and pH value (chemical condition).

4. Treatment of cutting-oily wastewater by Modified Induced Air Flotation (MIAF) process

- The investigated parameters directly influence on treatment efficiency of MIAF process and thus flow regime in this study were gas flow rate, chemical condition, operating time, and also column dimension.
- The effect of column dimension obviously showed negatively effect of floc breaking phenomena and water circulation
- Nevertheless, due to this high gas flow rates injected through flexible membrane, the bubble dispersion, turbulent condition and flow regime can be significantly difference.

5. Bubble hydrodynamic and mixing condition parameters

- The average bubble size is controlled by physical characteristic and properties of gas distributor at low gas flow rate (gas velocity approximately less than 5 cm/s) while bubble break up and coalescence become predominant factors at the high gas flow rate instead.
- Lower power dissipation rate in large column can be well compensated by greater alum loading consumption.

6. Continuous MIAF process study

- The continuous MIAF process is only attractive for cutting oily wastewater treatment operated in small column. However for large flotation column, the limitation of floc breaking phenomena and water circulated similar to batch process still remains.
- The column dimension effect to treatment performance causes the different flow regime at the same gas velocity. Therefore, in practice, the effect of column dimension should be well considered.

7. Study of Residence Time Distribution (RTD)

- For small flotation column, the experimental RTD data of are well described by a number of tanks in series model for whatever operating conditions while three different flow models was found in large column flotation consisted of tanks-in-series model, intermediate configuration between ideal CSTR and tanks-in-series models, and very close ideal CSTR model.
- The tanks in series model and very close ideal CSTR experimentally obtained in this study revealed the strong incidence of limitations of floc breaking phenomena and water circulation.

8. Continuous MIAF – Settling process

- Operation of continuous MIAF process by using large column is not attractive due to much more intense bubble dispersion throughout column.

- The suitable amounts of oil-droplet and coagulant dose (loading) were more important than the other physical parameters, like liquid flow rate or detention time, bubble hydrodynamic and turbulent conditions, column dimension, etc.

Table 5.1 Summary of the best operating conditions for given treatment methods in this study

Process/Condition	**Small column**	**Large column**
Decantation		
Operating time (min)	60	60
Treatment efficiency (%)	**0**	**0**
IAF		
Gas flow rate (L/min)	0.3	0.3
Operating time (min)	30	20
Treatment efficiency (%)	**7.0**	**5.4**
Reactive oily bubble flotation		
Gas flow rate (L/min)	-	0.3
Treatment efficiency (%)	-	**2.76**
Coagulation		
Initial pH	7	
Alum dose (mg/L)	150	
Treatment efficiency (%)	**91.23**	
Batch MIAF*		
Alum dose (mg/L)	150	225
Gas flow rate (L/min)	1.0	2.0
Bubble size (mm)	1.5	1.5
Interfacial area: a (m^{-1})	304.527	213.168
Velocity gradient: G (s^{-1})	106.27	63.76
a/G	2.528	3.343
Treatment efficiency (%)	**94.69**	**82.97**
Continuous MIAF**		
Influent feed rate (L/hr)	11	45
Alum dose (mg/L)	150	225
Gas flow rate (L/min)	1.0	2.0
Flow model (RTD)	Tanks-In-Series	(close to ideal) CSTR
Treatment efficiency (%)	**80.65**	**48.52**
Continuous-Settling		
(Improvement of Large column)		
Influent feed rate (L/hr)	-	45
Alum dose (mg/L)	-	225
Gas flow rate (L/min)	-	2.0
Mixing time (min)	-	10
Settling time (min)	-	30
Treatment efficiency (%)	**-**	**82.33**

(*considered at 30 min operating time; **considered at 60 min operating time)

9. Recommendations

Due to the objective of this research was to studied performance of MIAF process for cutting oily wastewater treatment. Regarding to some limitations such as the braking phenomena, water circulation appeared in this study, the flocculent-setting, Sequencing Batch Reactor (SBR) or Completely Mixed Stirred Tank Reactor (CSTR) combined with settling tank, is recommended as the alternative choices response for the purpose of overall treatment efficiency improvement.

In future, the different types of coagulants and gas diffusers should be studied in order to extend operating condition ranges. a/G ratio found in large flotation column clearly presents higher values than small column especially at low gas flow rate (0.3 L/min). Therefore, it is very interesting for applying this process to other oily wastewaters, which oil droplet size presence is larger than cutting oily wastewater, and various oil concentrations. This will be very useful for proposing the predicting model for removal efficiency with a/G ratio. Additionally, MIAF process may offer a good potency to removal others substance which their size varied in similar range.

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APPENDICES

APPENDIX A

CUTTING OILY WASTEWATER

1. Droplets size distribution of 1.0 g/L cutting oily wastewater

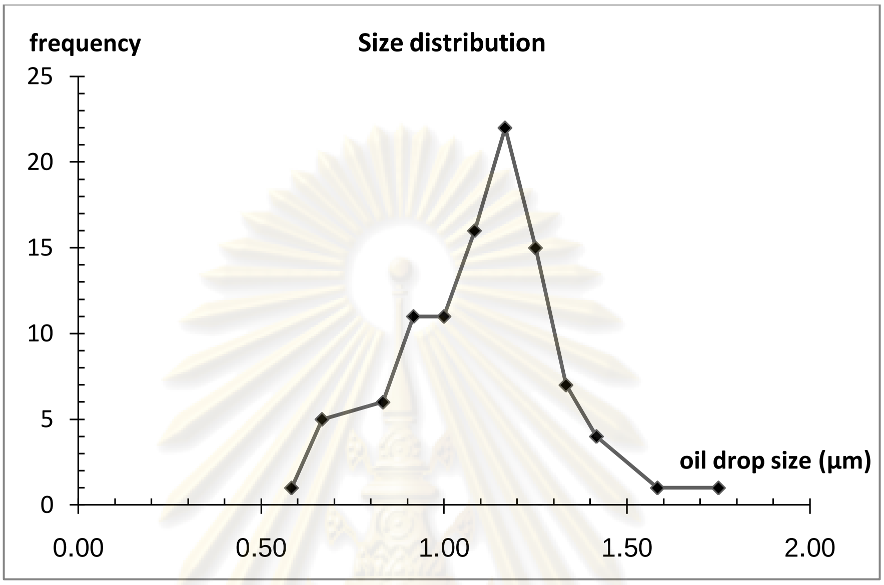

Figure A1 Size distribution of oil droplet (average size ≈ 1.3 µm)

2. Standard curve of oil concentration and COD values

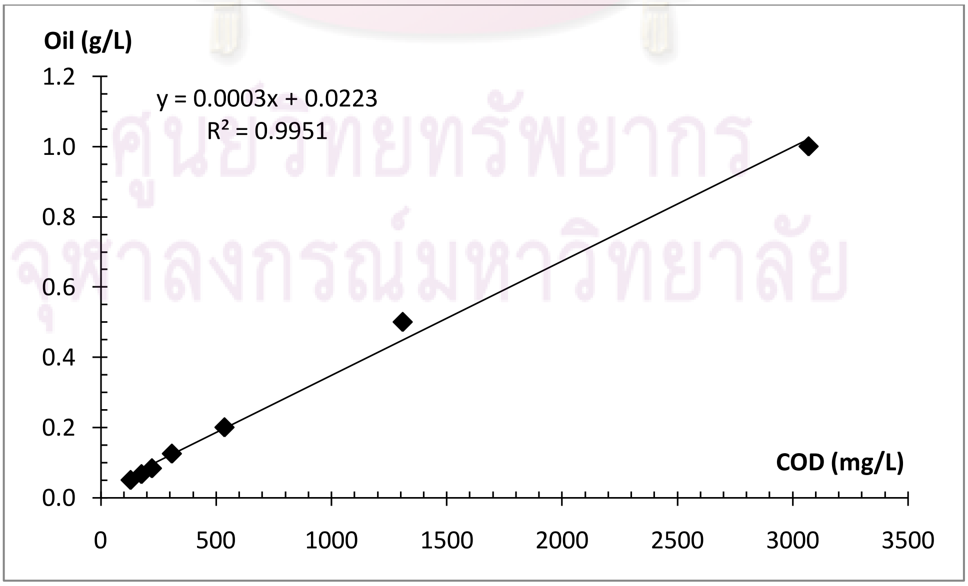

Figure A2 Standard curve of oil concentration and COD value

APPENDIX B

REACTIVE OILY BUBBLE FLOTATION

Table B1 Treatment efficiency of reactive oily bubble flotation (Large column only)

Turbidity (NTU)			
Q_G (L/min)	**0 min**	**Turbidity (NTU)**	**% Remove**
0.3	1195	1162	2.76
0.5	1249	1200	3.92
1.0	1213	1313	-8.24
2.0	1200	1310	-9.17

APPENDIX C

COAGULATION PROCESS

1. Optimal initial pH

Table C1: Removal efficiency at different initial pH with 50, 100, and 150 mg/L alum

	Alum concentration					
pH	**50 mg/L**		**100 mg/L**		**150 mg/L**	
	COD	**% Removal**	**COD**	**% Removal**	**COD**	**% Removal**
4	2474.0	7.88	2319.8	0.00	2748.9	0.00
6	2231.6	30.26	2242.1	0.00	2431.6	0.00
7	1510.3	57.31	827.6	76.61	310.3	91.23
8	2348.1	13.74	2846.8	0.00	561.0	79.39
10	2576.1	34.27	2201.8	43.82	2400.0	38.76

2. Optimal dosage of Alum at optimal initial pH

Table C2: Removal efficiency of alum dosage varied between 25-450 mg/L at an initial pH 7

Alum dose (mg/L)	**COD**	**Treatment efficiency (%)**
25	2772.4	21.64
50	1510.3	57.31
100	827.6	76.61
150	310.3	91.23
250	341.3	86.61
300	496.6	85.96
350	457.1	82.95
400	2410.4	10.08
450	2576.6	0.00

APPENDIX D

IAF AND MIAF PROCESSES

1. Removal efficiency of IAF processes at different gas flow rate

Table D1-1: Treatment efficiency of IAF process of small column

Qg	**0.3 L/min**			**0.5 L/min**			**0.7 L/min**		
Time (min)	**Turbidity**	**COD**	**% Remove**	**Turbidity**	**COD**	**% Remove**	**Turbidity**	**COD**	**% Remove**
0	1235	2150.4	0.00	1560.0	2870.4	0.00	1369.0	2721.6	0.00
2	1229	2150.4	0.00	1564.5	3036.8	0.00	1374.0	2678.4	1.59
6	1231	2150.4	0.00	1566.5	3016.0	0.00	1370.0	2678.4	1.59
8	1225	2150.4	0.00	1557.0	2891.2	0.00	1379.0	3024.0	1.60
10	1224	2240.0	0.00	1567.0	2953.6	0.00	1373.0	2678.4	1.59
15	1220	2240.0	0.00	1566.0	3010.2	0.00	1359.0	2721.6	0.00
20	1222	2150.4	0.00	1567.0	2849.6	0.72	1367.5	2851.2	0.00
30	1222	1702.4	7.00	1558.0	2828.8	1.45	1361.5	2721.6	0.00
40	1216	1344.0	5.00	1555.0	2912.0	0.00	1357.0	2635.2	0.00

Table D1-2: Treatment efficiency of IAF process of large column

Qg	0.3 L/min			0.5 L/min			2.0 L/min		
Time (min)	**Turbidity**	**COD**	**% Remove**	**Turbidity**	**COD**	**% Remove**	**Turbidity**	**COD**	**% Remove**
0	1254.0	2715.84	0.00	1205	2549.04	0.00	1253	2567.6	0.00
2	1250.0	2646.96	2.53	1210	2549.04	0.20	1229	2548.0	0.76
6	1249.0	2587.92	4.71	1210	2549.04	0.20	1228	2557.8	0.38
8	1250.0	2558.4	5.80	1210	2549.04	0.20	1227	2567.6	0.00
10	1248.0	2528.88	6.88	1210	2549.04	0.20	1234	2567.6	0.00
15	1247.0	2538.72	6.52	1210	2549.04	0.30	1239	2528.4	0.00
20	1245.0	2568.24	5.43	1215	2549.04	0.40	1243	2567.6	0.00
30	1243.0	2568.24	5.43	1216	2549.04	2.00	1253	2567.6	0.00
40	1242.0	2568.24	5.43	1216	2549.04	0.00	1254	2567.6	0.00

2. Removal efficiency of MIAF processes of small column

Table D2-1: Treatment efficiency of MIAF at 75 mg/L alum dosage

Qg	**0.3 L/min**			**0.5 L/min**			**0.7 L/min**		
Time (min)	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**
0	1212.0	2204.00	0.00	1183	2433.6	0.00	1151.5	2808	0.00
2	724.0	812.00	40.00	755	1456.0	40.17	582.0	1176	58.12
6	751.0	928.00	53.89	786	1497.6	38.46	597.0	1200	57.26
8	779.5	1206.40	48.26	814	1497.6	38.46	603.5	1200	57.26
10	788.5	1136.80	50.42	826	1435.2	41.03	603.5	1008	64.10
15	772.5	881.60	60.00	826	1331.2	45.30	606.5	1104	60.68
20	772.5	997.60	54.74	827	1643.2	32.48	611.0	1128	59.83
30	781.5	1020.80	53.68	818	1456.0	40.17	614.0	1104	60.68
40	1212.0	2204.00	0.00	1183	2433.6	0.00	1151.5	2808	0.00

Table D2-2: Treatment efficiency of MIAF at 100 mg/L alum dosage

Qg	0.3 L/min			0.7 L/min			1.0 L/min		
Time (min)	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**
0	1157.5	2142.4	0.00	1163.0	2267.2	0.00	1133.6	1934.4	0.00
2	966.0	1206.4	43.69	714.5	1185.6	47.71	616.7	1008.8	47.85
6	918.0	1268.8	40.78	665.5	1227.2	45.87	636.5	1019.2	47.31
8	889.0	1123.2	47.57	686.0	1164.8	48.62	606.7	1133.6	41.40
10	893.0	1393.6	34.95	699.0	1248.0	44.95	646.5	1071.2	44.62
15	893.0	1456.0	32.04	691.0	1060.8	53.21	557.0	1040.0	46.24
20	889.5	1414.4	33.98	688.0	1123.2	50.46	586.8	1060.8	45.16
30	879.5	1414.4	33.98	686.0	1123.2	50.46	586.8	1060.8	45.16
40	875.0	1331.2	37.86	688.5	1185.6	47.71	616.7	1102.4	43.01

Table D2-3: Treatment efficiency of MIAF at 125 mg/L alum dosage

Qg	**0.3 L/min**			**0.7 L/min**			**1.0 L/min**		
Time (min)	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**
0	1146.5	1996.8	0.00	1069.0	2381.6	0.00	1241.0	2184.0	0.00
2	953.0	1040.0	47.92	590.0	800.8	66.38	568.0	894.4	59.05
6	844.5	1123.2	43.75	531.0	894.4	62.45	586.0	873.6	60.00
8	745.0	1102.4	44.79	545.0	834.0	64.98	596.0	977.6	55.24
10	707.0	936.0	53.13	550.0	832.0	65.07	588.0	915.2	58.10
15	690.0	998.4	50.00	548.0	1123.2	52.84	591.5	936.0	57.14
20	671.0	977.6	51.04	548.5	852.8	64.19	597.0	956.8	56.19
30	664.5	977.6	51.04	560.0	915.2	61.57	605.0	1206.4	44.76
40	1146.5	1996.8	0.00	1069.0	2381.6	0.00	1241.0	2184.0	0.00

Table D2-4: Treatment efficiency of MIAF at 150 mg/L alum dosage

Qg	**0.3 L/min**			**0.5 L/min**			**0.5 L/min**			**1.0 L/min**		
Time (min)	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**
0	1554.0	3024	0.00	1329	2454.4	0.00	1369	2224.8	0.00	1303	2440.8	0.00
2	1795.0	2160	28.57	611	2246.4	8.47	665	1576.8	29.13	1182	1814.4	25.66
6	-	-	-	601	1892.8	22.88	634.5	1209.6	45.63	924	1166.4	52.21
8	1604.0	1771.2	41.43	438	1622.4	33.90	554	1382.4	37.86	568	691.2	71.68
10	1400.0	1684.8	44.29	391	1040.0	57.63	354.5	885.6	60.19	364	280.8	88.50
15	962.0	1468.8	51.43	291	873.6	64.41	286.5	993.6	55.34	264	367.2	84.96
20	506.0	1123.2	62.86	180	395.2	83.90	246.5	518.4	76.70	170	129.6	94.69
30	297.0	388.8	87.14	147	748.8	69.49	232	410.4	81.55	134	237.6	90.27
40	249.0	259.2	**91.43**	119	332.8	86.44	192	280.8	87.38	132	129.6	94.69

Table D2-5: Treatment efficiency of MIAF at 175 mg/L alum dosage

Qg	**0.3 L/min**			**0.7 L/min**			**1.0 L/min**		
Time (min)	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**
0	1265.0	2329.60	0.00	1453	2246.4	0.00	1204.0	2371.20	0.00
2	1414.0	2215.20	4.91	1067	1382.4	38.46	762.0	1050.40	55.70
6	857.0	1060.80	54.46	682.5	648.0	71.15	500.0	904.80	61.84
8	719.0	790.40	66.07	611.5	648.0	71.15	379.0	748.80	68.42
10	617.0	758.05	67.46	424	604.8	73.08	321.0	582.40	75.44
15	473.0	707.20	69.64	343	475.2	78.85	301.0	613.60	74.12
20	373.0	603.20	74.11	321	496.2	77.91	286.0	530.40	77.63
30	350.0	644.80	72.32	301	324.0	85.58	282.0	457.60	80.70
40	329.0	852.80	63.39	296	453.6	79.81	283.0	436.80	81.58

3. Removal efficiency of MIAF processes of large column

Table D3-1: Treatment efficiency of MIAF at 100 mg/L alum dosage

Qg	**0.3 L/min**			**1.5 L/min**				**2.0 L/min**			
Time (min)	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**	**Time (min)**	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**	**Time (min)**	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**
0	1207	2481.6	0.00	0	1226	2481.6	0.00	0	1201	2480.0	0.00
5	1067.0	1494.6	39.77	5	932	1447.6	41.67	5	825	1145.4	53.81
10	995	1560.4	37.12	10	874	1438.2	42.05	10	788	1105.6	55.42
15	966.0	1513.4	39.02	18	856	1325.4	46.59	18	781	1125.5	54.62
20	942.0	1428.8	42.42	23	852	1400.6	43.56	23	786	1105.6	55.42
25	932.0	1381.8	44.32	25	847	1325.4	46.59	25	786	1125.5	54.62
30	920.0	1381.8	44.32	30	848	1325.4	46.59	30	783	1105.6	55.42
40	907.0	1372.4	44.70	40	848	1320.7	46.78	40	796	1105.6	55.42
50	900.0	1480.5	40.34	50	850	1334.8	46.21	*51*	807	1145.4	53.81
60	898.0	1508.7	39.20	60	853	1438.2	42.05	60	812.5	1185.2	52.21

Table D3-2: Treatment efficiency of MIAF at 150 mg/L alum dosage

Qg	**0.3 L/min**			**0.7 L/min**				**1.0 L/min**				**2.0 L/min**			
Time (min)	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**	**Time (min)**	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**	**Time (min)**	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**	**Time (min)**	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**
0	1258.0	2697.8	0.00	0	1250	2460	0.00	0	1235	2392.0	0.00	**0**	1205	2570.4	0.00
5	950.0	1222	54.70	5	746	1360	44.72	5	856	1123.2	53.04	**5**	772	1009.1	60.74
10	716	1099.8	59.23	10	587	860	65.04	10	634	956.8	60.00	**10**	517	952.0	62.96
15	641.0	996.4	63.07	18	482	820	66.67	15	574	956.8	60.00	**15**	416	780.6	69.63
20	599.0	996.4	63.07	23	457	740	69.92	20	532	748.8	68.70	**20**	373	647.4	74.81
25	574.0	921.2	65.85	25	452	740	69.92	25	495	852.8	64.35	**25**	365	552.2	78.52
30	551.0	921.2	65.85	30	431	840	65.85	30	481	748.8	68.70	**30**	363	590.2	77.04
40	522.0	846	68.64	40	412	720	70.73	40	464	686.4	71.30	**40**	364	590.2	77.04
50	508.0	846	68.64	50	411	780	68.29	50	462	686.4	71.30	**50**	372	590.2	77.04
60	495.0	789.6	70.73	60	405	800	67.48	60	465.5	665.6	72.17	**60**	377	637.8	75.19

Table D3-3: Treatment efficiency of MIAF at 225 mg/L alum dosage

Qg	0.3 L/min			0.7 L/min				1.5 L/min				2.0 L/min			
Time (min)	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**	**Time (min)**	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**	**Time (min)**	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**	**Time (min)**	**Turbidity (NTU)**	**COD (mg/L)**	**% Remove**
0	1258.0	2697.8	0.00	0	1250	2460	0.00	0	1235	2392.0	0.00	**0**	1205	2570.4	0.00
5	950.0	1222	54.70	5	746	1360	44.72	5	856	1123.2	53.04	**5**	772	1009.1	60.74
10	716	1099.8	59.23	10	587	860	65.04	10	634	956.8	60.00	**10**	517	952.0	62.96
15	641.0	996.4	63.07	18	482	820	66.67	15	574	956.8	60.00	**15**	416	780.6	69.63
20	599.0	996.4	63.07	23	457	740	69.92	20	532	748.8	68.70	**20**	373	647.4	74.81
25	574.0	921.2	65.85	25	452	740	69.92	25	495	852.8	64.35	**25**	365	552.2	78.52
30	551.0	921.2	65.85	30	431	840	65.85	30	481	748.8	68.70	**30**	363	590.2	77.04
40	522.0	846	68.64	40	412	720	70.73	40	464	686.4	71.30	**40**	364	590.2	77.04
50	508.0	846	68.64	50	411	780	68.29	50	462	686.4	71.30	**50**	372	590.2	77.04
60	495.0	789.6	70.73	60	405	800	67.48	60	465.5	665.6	72.17	**60**	377	637.8	75.19

APPENDIX E

BUBBLE HYDRODYNAMIC PARAMETERS

1. Bubble hydrodynamic parameters of small column

Table E1 Bubble hydrodynamic parameters of small column

Q_G (L/min)	D_B (mm)	f_B	U_B (mm/sec)	a (1/m)	G (1/sec)	a/G (m/sec)
0.3	1.2	9554	90	190.329	58.21	3.924
0.7	1.4	8124	110	342.593	88.91	2.480
1.0	1.5	6482	150	304.527	106.27	2.528

2. Bubble hydrodynamic parameters of large column

Table E2 Bubble hydrodynamic parameters of large column

Q_G (L/min)	D_B (mm)	f_B	U_B (mm/sec)	a (1/m)	G (1/sec)	a/G (m/sec)
0.3	0.95	26001	90	560.970	24.695	22.715
0.7	1.2	12901	110	363.355	37.723	9.632
1.0	1.28	10630	130	288.239	45.087	6.393
1.5	1.4	8124	140	244.709	55.221	4.431
2.0	1.5	6605	150	213.168	63.763	3.343

APPENDIX F

CONTINUOUS MAF PROCESS

1. Continuous process of small column

Table F1-1 Treatment efficiency of continuous MIAF process at for 1 hr operating time

5 L/hr			**11**		
Time	**Turbidity**	**% Remove**	**Time**	**Turbidity**	**% Remove**
0	1204	0	**0**	1080	0.00
2	632	47.51	**1**	622	42.41
5	553	54.07	**3**	351	67.50
10	550	54.32	**10**	229	78.80
20	429	64.37	**21**	227	78.98
30	294	75.58	**31**	226	79.07
45	268	77.74	**45**	234	78.33
60	234	80.56	**60**	223	79.35

2. Continuous MIAF process of large column

Table F-1 Treatment efficiency of continuous MIAF process for1 hr operating time

Feed rate (Q_L)	**15 L/hr**			**30 L/hr**			**45 L/hr**		
Process	**Time (min)**	**Turbidity(NTU)**	**% Remove**	**Time (min)**	**Turbidity (NTU)**	**% Remove**	**Time (min)**	**Turbidity (NTU)**	**% Remove**
Continuous (1hr)	**0**	1220	0.00	**0**	1177	0.00	**0**	1082	0.00
	15	418	65.74	**15**	890	18.52	**10**	929	14.14
	30	663	45.66	**30**	778	24.38	**30**	740	31.61
	45	639	47.62	**45**	700	33.90	**45**	551	49.08
	60	618	49.34	**60**	270	40.53	**60**	557	48.52

3. Continuous-settling (Large column only)

Table E3-2 Treatment efficiency of continuous MIAF–settling process with 1 hr operating time and 225 mg/L alum

Feed rate (Q_L)	**15 L/hr**			**30 L/hr**			**45 L/hr**		
Process	**Time (min)**	**Turbidity(NTU)**	**% Remove**	**Time (min)**	**Turbidity (NTU)**	**% Remove**	**Time (min)**	**Turbidity (NTU)**	**% Remove**
Continuous (1hr)	**0**	1220	0.00	**0**	1177	0.00	**0**	1082	0.00
	30	663	45.66	**15**	890	18.52	**10**	929	14.14
	45	639	47.62	**30**	778	24.38	**30**	740	31.61
	60	618	49.34	**45**	700	33.90	**45**	551	49.08
	15	351	71.23	**60**	270	40.53	**60**	557	48.52
Settling (2 hrs)	**30**	328	73.11	**10**	210	82.16	**10**	232	78.56
	45	233	80.90	**30**	204	82.50	**30**	208	80.78
	90	226	81.48	**90**	206	82.58	**90**	207	80.87
	120	221	81.89	**120**	205	82.50	**120**	208	80.78

Table E3-2 Treatment efficiency of continuous MIAF–settling process with 10 min operating time and 225 mg/L alum

Feed rate (Q_L)	**15 L/hr**			**30 L/hr**			**45 L/hr**		
Process	**Time (min)**	**Turbidity (NTU)**	**% Remove**	**Time (min)**	**Turbidity (NTU)**	**% Remove**	**Time (min)**	**Turbidity (NTU)**	**% Remove**
Continuous (10 min)	**0**	1254	0	**0**	1247	0.00	**0**	1194	0.00
	10	1043	16.83	**10**	1047	16.04	**10**	1069	10.47
Settling (2 hrs)	**7**	462	63.16	**8**	252	79.79	**6**	860	27.97
	10	286	77.19	**10**	236	81.07	**10**	324	72.86
	30	217	84.05	**30**	205	83.56	**30**	211	82.33
	90	201	84.05	**90**	205	83.48	**90**	208	82.58
	120	200	84.05	**120**	205	83.56	**120**	208	82.58

APPENDIX G

RESIDENCE TIME DSTRIBUTION

1. RTD data for small column

Table G1-1 Feed rate (Q_L): 5 L/hr without aeration

Time (min)	Time θ	E(t) Experiment	E(θ) Experiment	E(θ) Tank in series
0	0.000	0.000	0.000	0.000
5	0.142	0.000	0.000	0.000
10	0.284	0.000	0.000	0.012
15	0.426	0.000	0.005	0.142
20	0.568	0.007	0.251	0.531
25	0.710	0.048	1.694	1.037
30	0.852	0.042	1.485	1.348
35	0.993	0.034	1.204	1.321
40	1.135	0.026	0.924	1.054
45	1.277	0.015	0.538	0.719
50	1.419	0.011	0.387	0.433
55	1.561	0.007	0.259	0.235
60	1.703	0.004	0.146	0.118
65	1.845	0.002	0.069	0.055
70	1.987	0.001	0.045	0.024
75	2.129	0.001	0.024	0.010
80	2.271	0.000	0.005	0.004
85	2.413	0.000	0.005	0.002
90	2.555	0.000	0.004	0.001
95	2.697	0.000	0.000	0.000

Table G1-2 Feed rate (Q_L): 5 L/hr with aeration

Time (min)	**Time θ**	**E(t) Experiment**	**E(θ) Experiment**	**E(θ) Tank in series**
0	0.000	0.000	0.000	0.000
5	0.196	0.001	0.034	0.147
10	0.393	0.025	0.624	0.537
15	0.589	0.039	0.995	0.826
20	0.785	0.036	0.920	0.893
25	0.982	0.030	0.755	0.796
30	1.178	0.022	0.559	0.627
35	1.374	0.015	0.392	0.454
40	1.570	0.011	0.281	0.309
45	1.767	0.007	0.185	0.201
50	1.963	0.005	0.122	0.126
55	2.159	0.003	0.076	0.076
60	2.356	0.002	0.045	0.045
65	2.552	0.001	0.030	0.026
70	2.748	0.001	0.021	0.015
75	2.945	0.001	0.015	0.008
80	3.141	0.000	0.012	0.005
85	3.337	0.000	0.010	0.003
90	3.534	0.000	0.008	0.001
95	3.730	0.000	0.006	0.001
100	3.926	0.000	0.004	0.000
105	4.122	0.000	0.002	0.000
110	4.319	0.000	0.000	0.000

Table G1-3 Feed rate (Q_L): 11 L/hr without aeration

Time (min)	Time θ	E(t) Experiment	E(θ) Experiment	E(θ) Tank in series
0	0.000	0.000	0.000	0.000
5	0.340	0.006	0.086	0.115
10	0.680	0.067	0.988	0.972
15	1.020	0.079	1.162	1.093
20	1.361	0.034	0.506	0.539
25	1.701	0.009	0.137	0.169
30	2.041	0.003	0.043	0.040
35	2.381	0.001	0.014	0.008
40	2.721	0.000	0.004	0.001
45	3.061	0.000	0.000	0.000

Table G1-4 Feed rate (Q_L): 11 L/hr with aeration

Time (min)	Time θ	E(t) Experiment	E(θ) Experiment	E(θ) Tank in series
0	0.000	0.000	0.000	0.000
5	0.424	0.035	0.412	0.419
10	0.848	0.093	1.096	1.052
15	1.272	0.047	0.559	0.627
20	1.696	0.017	0.200	0.207
25	2.120	0.006	0.072	0.050
30	2.545	0.001	0.013	0.010
35	2.969	0.000	0.005	0.002
40	3.393	0.000	0.001	0.000
45	3.817	0.000	0.000	0.000

2. RTD data for large column

Table G2-1 Feed rate (Q_L): 15 L/hr without aeration

Time	Time	E(t)	E(θ)	E(θ)
(min)	θ	Experiment	Experiment	Tank in series
0	0.000	0.000	0.000	0.000
5	0.122	0.001	0.031	0.005
10	0.244	0.001	0.044	0.077
15	0.366	0.004	0.174	0.283
20	0.487	0.013	0.503	0.574
25	0.609	0.022	0.889	0.844
30	0.731	0.026	1.038	1.011
35	0.853	0.025	0.988	1.051
40	0.975	0.022	0.889	0.987
45	1.097	0.018	0.715	0.856
50	1.219	0.015	0.609	0.698
55	1.340	0.013	0.516	0.541
60	1.462	0.009	0.373	0.402
65	1.584	0.008	0.311	0.289
70	1.706	0.005	0.205	0.201
75	1.828	0.006	0.230	0.137
80	1.950	0.004	0.162	0.091
85	2.072	0.003	0.118	0.059
90	2.194	0.003	0.106	0.038
95	2.315	0.002	0.068	0.024
100	2.437	0.001	0.037	0.015
105	2.559	0.000	0.000	0.009

Table G2-2 Feed rate (Q_L): 15 L/hr with aeration

Time	**Time**	**E(t)**	**E(θ)**	**E(θ)**
(min)	**θ**	**Experiment**	**Experiment**	**Tank in series**
0	0.000	0.000	0.000	0.000
5	0.314	0.092	0.873	0.670
10	0.629	0.073	0.688	0.715
15	0.943	0.055	0.519	0.572
20	1.257	0.037	0.354	0.407
25	1.571	0.028	0.268	0.271
30	1.886	0.017	0.162	0.174
35	2.200	0.014	0.129	0.108
40	2.514	0.009	0.086	0.066
45	2.828	0.006	0.060	0.040
50	3.143	0.002	0.020	0.023
55	3.457	0.001	0.013	0.014
60	3.771	0.001	0.007	0.008
65	4.085	0.000	0.003	0.005
70	4.400	0.000	0.000	0.003

Table G2-3 Feed rate (Q_L): 30 L/hr without aeration

Time	Time	E(t)	E(θ)	E(θ)
(min)	**θ**	**Experiment**	**Experiment**	**Tank in series**
0	0.000	0.000	0.000	0.000
5	0.149	0.001	0.017	0.012
10	0.298	0.001	0.028	0.153
15	0.447	0.008	0.264	0.475
20	0.596	0.033	1.106	0.819
25	0.745	0.037	1.247	1.022
30	0.894	0.033	1.123	1.039
35	1.044	0.028	0.949	0.918
40	1.193	0.017	0.573	0.732
45	1.342	0.014	0.466	0.539
50	1.491	0.009	0.309	0.373
55	1.640	0.006	0.202	0.246
60	1.789	0.004	0.124	0.155
65	1.938	0.003	0.101	0.095
70	2.087	0.002	0.067	0.056
75	2.236	0.002	0.062	0.032
80	2.385	0.001	0.039	0.018
85	2.534	0.001	0.028	0.010
90	2.683	0.001	0.022	0.006
95	2.832	0.001	0.017	0.003
100	2.982	0.000	0.011	0.002
105	3.131	0.000	0.006	0.001
110	3.280	0.000	0.000	0.000

Table G2-4 Feed rate (Q_L): 30 L/hr with aeration

Time	Time	E(t)	E(θ)	E(θ)
(min)	**θ**	**Experiment**	**Experiment**	**Tank in series**
0	0.000	0.000	0.000	0.000
5	0.416	0.070	0.843	0.671
10	0.832	0.054	0.646	0.770
15	1.248	0.036	0.428	0.498
20	1.664	0.018	0.218	0.254
25	2.080	0.012	0.147	0.114
30	2.496	0.008	0.101	0.047
35	2.912	0.002	0.021	0.018
40	3.328	0.000	0.000	0.007

Table G2-5 Feed rate (Q_L): 45 L/hr without aeration

Time	Time	E(t)	E(θ)	E(θ)
(min)	**θ**	**Experiment**	**Experiment**	**Tank in series**
0	0.000	0.000	0.000	0.000
5	0.331	0.001	0.015	0.549
10	0.663	0.002	0.037	0.812
15	0.994	0.040	0.609	0.676
20	1.325	0.036	0.543	0.445
25	1.657	0.024	0.368	0.257
30	1.988	0.013	0.198	0.137
35	2.319	0.006	0.092	0.069
40	2.651	0.004	0.067	0.033
45	2.982	0.002	0.037	0.016
50	3.313	0.002	0.031	0.007
55	3.645	0.001	0.016	0.003
60	3.976	0.000	0.000	0.001

Table G2-6 Feed rate (Q_L): 45 L/hr with aeration

Time	Time	E(t)	E(θ)	E(θ)
(min)	θ	Experiment	Experiment	Tank in series
0	0.000	0.000	0.882	0.000
5	0.393	0.069	0.611	0.716
10	0.787	0.048	0.414	0.652
15	1.180	0.033	0.287	0.446
20	1.574	0.023	0.178	0.270
25	1.967	0.014	0.112	0.154
30	2.360	0.009	0.058	0.084
35	2.754	0.005	0.000	0.045
40	3.147	0.000	0.000	0.023

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