



*Article*

## Enhancement of Crossflow Ultrafiltration for the Treatment of Stabilized Oily Emulsions

Thaksina Poyai<sup>1,2,a</sup>, Phuntharee Khiewpuckdee<sup>3</sup>, Aunnop Wongrueng<sup>2,4</sup>,  
Pisut Painmanakul<sup>2,3,5,6</sup>, and Nattawin Chawaloesphonsiya<sup>3,5,b,\*</sup>

<sup>1</sup> International Program in Hazardous Substance and Environmental Management, Graduate School, Chulalongkorn University, Bangkok 10330, Thailand

<sup>2</sup> Center of Excellence on Hazardous Substance Management (HSM), Chulalongkorn University, Bangkok 10330, Thailand

<sup>3</sup> Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

<sup>4</sup> Department of Environmental Engineering, Faculty of Engineering, Chiang Mai University, Chiang Mai 50200, Thailand

<sup>5</sup> Research Unit on Technology for Oil Spill and Contamination Management, Chulalongkorn University, Bangkok 10330, Thailand

<sup>6</sup> Research Program on Remediation Technologies for Petroleum Contamination, Center of Excellence on Hazardous Substance Management (HSM), Chulalongkorn University, Bangkok 10330, Thailand

E-mail: <sup>a</sup>mookthaksina@gmail.com, <sup>b</sup>nattawin\_ch@hotmail.com (Corresponding author)

**Abstract.** Separation of stabilized oil droplets was conducted via crossflow ultrafiltration (UF) in a laboratory scale. A plate-and-frame membrane module was operated with two commercial organic membranes: regenerated cellulose (RC) and polyethersulfone (PES). Cutting oil was used for preparing oil-in-water emulsions. Membrane fluxes were observed under varied oil concentrations and transmembrane pressures (TMP). It was found that UF provided oil rejection more than 97% for all operational cases. The optimal operating condition was found at the oil concentration less than 1 g/L and TMP of 2–3 bar. As predicted by Hermia's model, the dominant fouling mechanism was the cake formation upon the membrane surface. The fouled membrane was effectively regenerated by the sequential cleaning of 0.5N-SDS, 0.1N-NaOH, and 0.01N-EDTA, respectively. The cleaned membrane was acquired with 96% flux recovery (FR) and 55% resistance removal (RR). Additionally, an integration of UF and pretreatments (i.e., chemical destabilization and coalescence) could improve flux decline of the membrane, while satisfactory discharge quality was achieved.

**Keywords:** Stabilized oily emulsion, ultrafiltration, organic membrane, membrane fouling, membrane cleaning.

**ENGINEERING JOURNAL** Volume 23 Issue 4

Received 14 August 2018

Accepted 11 April 2019

Published 8 August 2019

Online at <http://www.engj.org/>

DOI:10.4186/ej.2019.23.4.15

## 1. Introduction

Oily wastewater is a serious environmental problem worldwide, particularly that generated from industrial sectors. Generally, the treatment of oily wastewater is required in order to meet the stringent environmental regulations. In most Asian countries, including Thailand, the maximum oil and grease (O&G) in water discharge should not exceed 10–15 mg/L [1, 2]. Whereas, more than 1000 mg/L O&G is mostly found in produced oily wastewater [3]. Cutting oil has been employed in most industries for serving as coolant and lubricant in machining work. Despite its beneficial properties, cutting oil has gained a great deal of concern due to its toxicity to ecology and human health [4-6]. Additionally, metal-working processes could generate wastewater containing O&G up to 4000–6000 mg/L [3]. In addition to cutting oil, global demand for palm oil has been rising since it plays a key role in food and energy production. In Thailand, biofuels have been extensively promoted and thus increasing the need for palm oil manufactures [7]. Wastewater generated from palm oil industries is commonly known as palm oil mill effluent (POME) [8]. POME is produced from various stages of production and it comprises O&G varying from 300–7000 mg/L [9]. Oily wastewater is usually found in the form of stabilized oil-in-water (O/W) emulsions. Surface-active agents, either from oil additives or cleaning chemicals, normally exist in the oily wastewater and thus lessening oil-water interfacial tension. Therefore, oil droplets become finely dispersed and highly stable, which are difficult to be treated via gravitational separation processes. Besides, if oil droplets are less than 5  $\mu\text{m}$  in size, they will undergo Brownian motions by which their rising velocity is considered negligible [10]. In Asia, especially in Thailand, oily wastewater is commonly contaminated with a wide range of oil concentrations. A major problem regarding its treatment and ultimate disposal is still unsolved. In most cases, a single treatment unit is inadequate to handle produced oily wastewater. Conventional technologies like decantation, coagulation, flotation, and coalescence might be effective only as the pre-treatment step, in which oil concentrations have been reduced to certain levels [11-15]. To achieve desired water quality, the oily waste stream must be subject to post-treatment afterwards.

Amongst physicochemical methods, ultrafiltration (UF) is considered a promising technology for oily wastewater both in terms of separation efficiency and discharge quality [16-21]. Despite its high efficiency, membrane fouling is still an inevitable limitation which results in permeate flux decline [22]. To overcome the problem, this work aims to provide optimum UF operation for oily wastewater treatment. Effects of membrane types, transmembrane pressure (TMP), and feed concentrations on water fluxes were studied in details. The UF performance was evaluated from flux decline rate and oil rejection efficiency. Since membrane fouling is a major drawback during filtration, membrane cleaning was then conducted to regenerate the fouled membrane. Prior to cleaning process, the fouling phenomena were predicted to imply the interaction between oil droplets and the membrane surface. The various types of washing reagents were studied, and the cleaning efficiency was determined through flux recovery (FR) and resistance removal (RR) of the membrane. Lastly, the UF process was validated with different oil types. The variation in oil droplet size during UF was also observed. Additionally, with the aim of process enhancement, an integration of UF with a pretreatment was proposed in terms of conceptual design and operational conditions.

## 2. Materials and Procedures

### 2.1. Experimental Setup

The crossflow UF system was installed as demonstrated in Fig. 1. The synthetic oily emulsion was prepared in a 2-L Pyrex® glass beaker, in which continuous mixing was provided. The UF cell (Nitto Denko C-10T test cell, Japan) was made of clear acrylic accompany with plate-and-frame membrane module, which contains the filtration area of 60  $\text{cm}^2$  (Figs. 1(a) and 1(b)). A 0.05 cm mesh-spacer was also placed within the UF cell for inducing turbulence on the membrane surface and thus lessening concentration polarization. The magnetic gear pump (Iwaki Co., Ltd., Japan) was connected to the UF cell to supply operating pressure and feed circulation. The UF system was also equipped with a globe valve and two pressure gauges for controlling pressure drop across the membrane. The permeate was collected in a graduated cylinder along time for flux analysis.

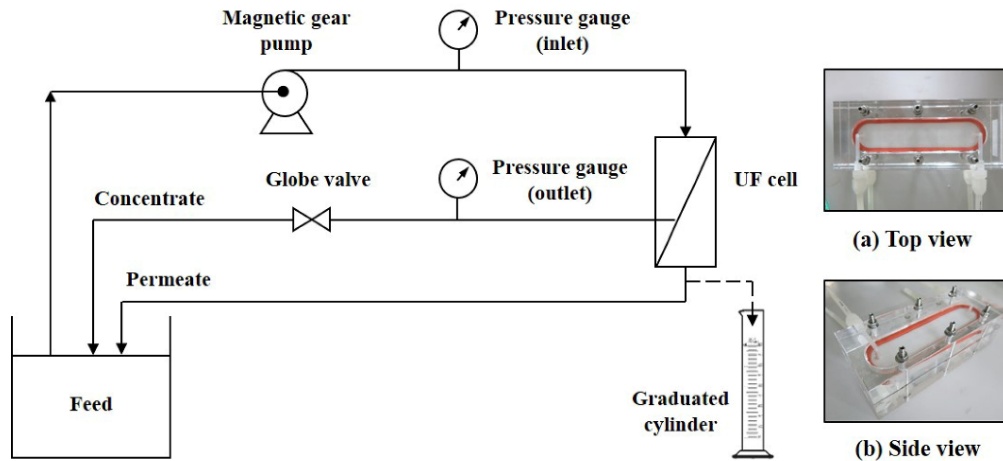


Fig. 1. A schematic of the crossflow UF setup.

## 2.2. Preparation of Oily Emulsions

A stabilized oil-in-water (O/W) emulsion was prepared from two different types of oil, including cutting oil (Castrol Cooledge BI, BP-Castrol Corp., Thailand) and palm oil (Morakot Industries Co., Ltd., Thailand). An oily emulsion was synthesized by blending the commercial oil with tap water at 200 rpm for 30 min. The various concentrations of cutting oil emulsions were prepared (0.5, 1, 5, 10 and 20 g/L), whereas the palm oil was blended at a sole concentration of 5 g/L [9]. It is worth noting that the palm oil was added with surfactants for promoting a stable emulsion. Since oil droplets are negatively charged, anionic surfactants should be selected for inducing the electrical barriers on a foulant layer and thus reducing membrane fouling. In this work, sodium dodecyl sulfate (SDS) was applied to the palm oil at its critical micelle concentration (CMC) [23]. Finally, the synthetic oily emulsions were studied for their characteristics, including COD, BOD, turbidity, pH, viscosity, and droplet size. Most parameters were examined by the procedures provided in the standard methods [24]. The oil droplet size was measured via the particle size analyzer (Malvern instrument, Ltd.). The oil concentration was analyzed using high performance liquid chromatography (HPLC) equipped with the evaporative light scattering detector (Shimadzu, Corp.). The isopropyl alcohol was used as a HPLC mobile phase under the flow velocity and injection volume of 0.5 mL/min and 20  $\mu$ L, respectively.

## 2.3. Membranes and UF Operation

Two commercially flat-sheet organic membranes were applied in this work: (1) regenerated cellulose (RC) with the pore size of 0.120  $\mu$ m (100 kDa) and (2) polyethersulfone (PES) with the pore size of 0.005  $\mu$ m (10 kDa). Both membranes held hydrophilic properties with the water contact angle of 55° and 74° respectively. Their desired operational ranges were pH of 2-12 and pressure of 1-10 bar. To maintain their properties, the membrane sheets were preserved in deionized water at 4 °C, and left under room temperature for 2 hours before the operation. It is worth noting that a new piece of membrane was employed for each experiment. Additionally, prior to oil separation, the membrane was operated with distilled water for 1 hour at a specific pressure to ensure its functional stability.

Effects of various transmembrane pressures (TMP) and cutting oil concentrations on flux decline were investigated. All experiments were conducted in duplicate under a pressure control mode. As the filtration proceeded, the crossflow velocity (CFV) of 0.1 m/s and the feed temperature of 25 $\pm$ 1 °C were maintained. The permeate volume was measured as a function of time, and the flux can be calculated from Eq. (1). Where  $J_p$  is the permeate flux (l/m<sup>2</sup>h),  $V_p$  is the permeate volume (L),  $A$  is the effective area of the membrane (m<sup>2</sup>), and  $\Delta t$  is the filtration time (h).

$$J_p = V_p / A \Delta t \quad (1)$$

The PES membrane was operated under the TMP of 2–4 bar and feed concentrations of 0.5, 1 and 5 g/L. Whereas, the RC membrane was studied with the TMP and oil concentrations ranging from 1–2.5 bar and

1–20 g/L, respectively. It should be noted that, due to a relatively large pore size, the RC membrane was performed with a lower range of pressure to avoid sudden irreversible fouling in the membrane pores. Both concentrate and permeate were returned to the feed tank for lessening the error that might occur from feed variation. The UF efficiency was determined via the removal of COD, BOD, turbidity, and oil and grease (O&G).

## 2.4. Fouling Mechanisms

To study the interaction between oil droplets and the membrane surface, the fouling mechanism of an individual operational condition was predicted using the Hermia's model as given in Eqs. (2–5) [25].

**Complete pore blocking**—this model assumed that each solute molecule approaches the membrane surface and causes pore sealing. Moreover, there is no molecule settling over another previously deposited molecule:

$$\ln(J) = \ln(J_0) - K_b t \quad (2)$$

**Standard pore blocking**—this model considers the fouling caused by solute molecules smaller than that of the membrane pores. Molecules are able to enter and block the membrane pores inside, decreasing the membrane's pore volume:

$$1/J^{0.5} = 1/J_0^{0.5} + K_s t \quad (3)$$

**Intermediate pore blocking**—this model assumes that some molecules may deposit onto other molecules. It happens when solutes hold the molecular size similar to that of the membrane pore. Therefore, the membrane pore might not be completely obstructed by solute molecules:

$$1/J = 1/J_0 + K_i t \quad (4)$$

**Cake (or gel layer) formation**—In this case, solute molecules are larger than the membrane pore size. Thus, they do not enter the membrane pores and form a cake layer over the membrane surface:

$$1/J^2 = 1/J_0^2 + K_c t \quad (5)$$

Where  $J$  is the permeate flux at a specific time ( $l/m^2h$ ),  $J_0$  is the initial permeate flux ( $l/m^2h$ ),  $K_b$  is the complete pore blocking constant ( $1/s$ ),  $K_s$  is the standard pore blocking constant ( $s^{-0.5}m^{-0.5}$ ),  $K_i$  is the intermediate pore blocking constant ( $1/m$ ), and  $K_c$  is the cake formation constant ( $s/m^2$ ). The most fitting model was identified by the highest determination coefficient ( $R^2$ ) obtained from each condition.

## 2.5. Membrane Cleaning

Prior to the filtration process, the initial water flux was determined and named  $J_{wi}$ . According to the results from section 2.3, the membrane was made fouled by the condition that fouling completely occurred. The chemicals applied for membrane cleaning are presented in Table 1.

Table 1. Chemical reagents used for membrane cleaning.

Chemical	Company	Concentrations (N)		
Sodium dodecyl sulfate (SDS)	Carlo Erba Co., Ltd	0.25	0.5	1
Sodium hydroxide (NaOH)	J.T. Baker	0.05	0.1	0.25
Ethylenediaminetetraacetic acid (EDTA)	J.T. Baker	0.005	0.05	0.01

The fouled membrane was initially washed with distilled water and the water flux,  $J_{ww}$ , was measured. After that, the membrane was soaked in the 50-mL cleaning solution for 30 min and then rinsed with distilled water. The water flux after cleaning is denoted as  $J_{wc}$ . Note that the cleaning procedure was adapted from that

reported by Regula et al. [26]. The cleaned membrane was subsequently operated for another 2 hours with the oily feed, and its performance was then compared to that of the initial state. The cleaning efficiency of each chemical was determined in terms of flux recovery (FR) and resistance removal (RR) as given in Eqs. (6) and (7), respectively. Where  $R_f$  is the resistance after fouling and  $R_c$  is the resistance after cleaning [27].

$$FR (\%) = [(J_{nc} - J_{nm}) / (J_{ni} - J_{nm})] \times 100 \quad (6)$$

$$RR (\%) = [(R_f - R_c) / R_f] \times 100 \quad (7)$$

### 3. Results and Discussion

#### 3.1. Analysis of Cutting Oil Emulsions

Properties of various cutting oil concentrations are presented in Table 2. All cutting oil emulsions held the viscosity of 0.005 Pa.s and the average droplet diameter of 1.50  $\mu\text{m}$ , which can be classified as the secondary emulsion [28].

Table 2. Characteristics of the synthetic cutting oil emulsions.

Parameter	Unit	Cutting oil (g/L)				
		0.5	1.0	5.0	10	20
COD	mg/L	1,889	3,081	16,154	35,765	51,789
BOD	mg/L	1,456	2,542	11,776	24,730	32,840
Turbidity	NTU	911	1,822	10,165	19,655	25,420
pH	-	8.1	8.5	8.7	8.9	9.3

Micro-sized oil droplets normally hold extremely low rising velocity, which is difficult for them to be removed by gravitational separation techniques. Figure 2 illustrates the efficacy of various conventional treatment processes on cutting oil removal, which was conducted during this study. Coalescer coupled with destabilization (i.e., 1-2 g/L  $\text{CaCl}_2$ ) seems to be most effective for a wide range of oil concentrations. The main mechanism is to provide particle enlargement and thus increasing the separation performance. Despite its high efficiency, oil remaining in the effluent still exceeded the required discharge quality. Therefore, treating oily emulsions by these techniques might be insufficient. In other words, conventional treatment may need further steps to serve as a post-treatment for effective oil separation.

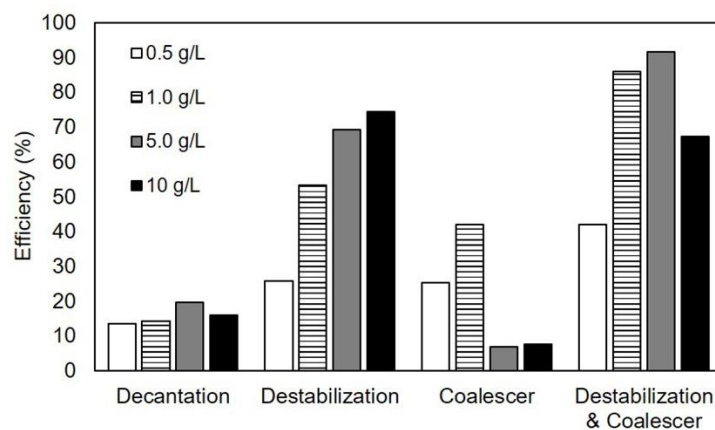


Fig. 2. Oil removal efficiency of different conventional treatment processes.

#### 3.2. UF for Oily Emulsion Separation

As confirmed by numerous previous studies, UF is considered a feasible treatment process for a wide range of oily wastewater [1, 17-18, 20, 29]. However, without optimal operation, membrane is normally subject to

severe fouling within the initial stage of filtration. The problem causes less throughput and the need for frequent membrane replacement, resulting in higher operating cost. Therefore, optimization of the UF process is required for minimizing the fouling problem, while the satisfactory yield is attained.

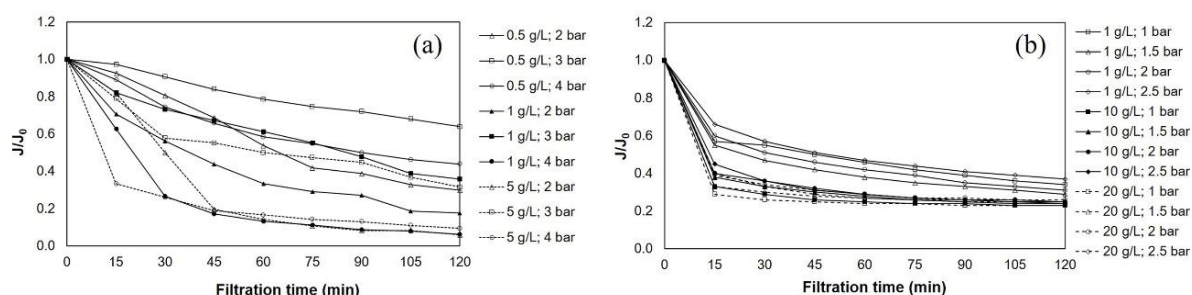


Fig. 3. Flux decline under different operating conditions of the (a) PES membrane and (b) RC membrane.

Figure 3 shows the changes in permeate flux as a function of time. As a result of concentration polarization [30], the membrane flux suddenly fell in the first transient stage (0–15 min) and gradually became consistent after 60-min filtration. Moreover, at the initial operating time, oil droplets rapidly penetrated to the membrane surface, causing immediate pore blocking and the sharp fall of permeate flux [31]. For all oil concentrations, the highest permeate flux was obtained at the TMP of 3 bar for PES and 2.5 bar for RC. The pure water fluxes from these conditions were 145 L/m<sup>2</sup>h and 150 L/m<sup>2</sup>h, respectively. The same trend was also found in the study of Abbasi et al. [32]. All operational conditions provided high effluent quality with oil rejection of more than 97%. The results were similar to those reported in literature data [18-19, 33], in which polysulfone (PSF, 30 kDa), regenerated cellulose (RC, 100 kDa), and polyacrylonitrile (PAN, 20 kDa) were applied.

Generally, an increase in TMP produces higher permeate flux due to the greater amount of driving force. Nevertheless, too high TMP (i.e., 4 bar) could lead to higher rate of particle accumulation, resulting in more hydraulic resistance on the membrane surface and lower attainable permeate flux [31, 33]. The membrane fluxes also declined as oil concentration increased since higher oil concentrations caused thicker oil layers built up on the membrane surface. As presented in Fig. 3, it can be concluded that UF was most effective with oil below 1 g/L. However, the oily feed less than 0.2 g/L might not be suitable for membrane filtration in terms of oil rejection [34].

The influence of membrane's properties on flux decline was also remarkable. Both RC and PES are polymeric hydrophilic membranes. Permeate fluxes of the PES membrane, however, gradually decreased over time compared to that of the RC. One influential factor was the membrane's pore size [35]. The RC membrane held the pore size much larger than that of the PES membrane. Therefore, the internal fouling could be greater at the beginning and thus causing a sudden fall to permeate fluxes. Membrane structure could be another potential parameter. Materials of which the membrane are made result in the degree of chemical resistance and mechanical strength of the membrane sheet. Since the PES membrane held strong alkaline resistance [30], its function to the basic oily emulsions could be more stable.

### 3.3. Membrane Fouling Mechanisms

In addition to concentration polarization, membrane fouling is another key factor causing the reduction of membrane flux. Generally, a deposit takes place either on the membrane surface (i.e., external fouling) or inside the porous structure (i.e., internal fouling). Therefore, UF fouling could occur through various mechanisms such as adsorption, pore blocking, and cake formation. A type of fouling depends on several factors such as operating conditions, membrane properties, and feed solution. The maximum  $R^2$  acquired from the Hermia's equation was used to indicate the dominant fouling model. As can be seen in Table 3, the membrane surface was dominantly fouled by cake layer formation followed by intermediate pore blocking. Whereas, complete pore blocking was least compatible with the experimental data compared to others. Since oil droplets were much larger than that of the membrane pores, most of them deposited upon the membrane surface and less internal fouling could occur. Similar results were observed from Noshadi et al. [36], who analyzed the fouling on UF caused by oily wastewater. They found that the fouling mechanism fitted well with the cake formation model ( $R^2 > 0.9$ ) for all conditions.

Table 3. Pore blocking model of different operational conditions.

	Condition		R <sup>2</sup> value of pore blocking model			
	Oil (g/L)	TMP (bar)	Complete blocking	Standard blocking	Intermediate blocking	Cake formation
PES	0.5	2	0.921	0.952	0.972	<b>0.974</b>
		3	0.978	0.987	0.992	<b>0.993</b>
		4	0.93	0.97	0.976	<b>0.995</b>
	1.0	2	0.891	0.892	0.963	<b>0.977</b>
		3	0.729	0.854	0.906	<b>0.944</b>
		4	0.772	0.856	0.973	<b>0.986</b>
	5.0	2	0.783	0.849	0.858	<b>0.955</b>
		3	0.847	0.933	0.955	<b>0.969</b>
		4	0.425	0.947	0.951	<b>0.951</b>
RC	1.0	1	0.972	0.988	0.995	<b>0.996</b>
		1.5	0.946	0.969	0.985	<b>0.998</b>
		2	0.948	0.972	0.988	<b>0.995</b>
		2.5	0.993	0.997	0.995	<b>0.999</b>
	10	1	0.821	0.854	0.884	<b>0.937</b>
		1.5	0.930	0.945	0.958	<b>0.978</b>
		2	0.929	0.946	0.960	<b>0.980</b>
		2.5	0.817	0.853	0.883	<b>0.932</b>
	20	1	0.927	0.939	0.950	<b>0.968</b>
		1.5	0.854	0.872	0.888	<b>0.917</b>
		2	0.890	0.906	0.921	<b>0.946</b>
		2.5	0.839	0.861	0.881	<b>0.917</b>

Filtration under a constant TMP results in three stages of flux behavior: (1) rapid cake layer formation and compaction; (2) slow cake layer growth and compaction; and (3) pseudo steady flux [37]. The built up oil layers led to an additional resistance on the membrane surface, thus decreasing the permeate flow. As the filtration proceeds, the membrane gradually becomes unavailable and eventually needs to be replaced or cleaned. The interaction between foulants and the membrane surface (i.e., fouling mechanism) defines the degree of fouling reversibility [38]. The study on membrane cleaning strategy was elucidated in the following section.

### 3.4. Membrane Cleaning

Fouling mechanism is a key factor involving the selection of an appropriate cleaning approach. As explained in the previous section, fouling through cake formation was found dominant for all conditions. To conduct the cleaning process, the membrane was introduced to the fouling condition by 10 g/L cutting oil under the TMP of 2.5 bar for 2 hours (75% flux decline). Since both organic membranes underwent the same fouling mechanism, only the RC membrane was selected to be applied in cleaning experiments.

As displayed in Fig. 4, 0.5N SDS provided the highest cleaning efficiency (41% FR; 37% RR) followed by 0.1N NaOH (36% FR; 22% RR) and 0.01N EDTA (31% FR; 8% RR). A combination of various chemicals was also studied for enhancing the membrane cleanliness. Considering from the optimal FR and RR, 0.5N SDS, 0.1N NaOH, and 0.01N EDTA were selected to investigate their abilities on the removal of accumulated oil droplets. The fouled membrane was governed by 30-min soaking in SDS, NaOH, and EDTA, respectively. It was found that the membrane sheet could be regenerated with the FR up to 96% and RR of 55%.



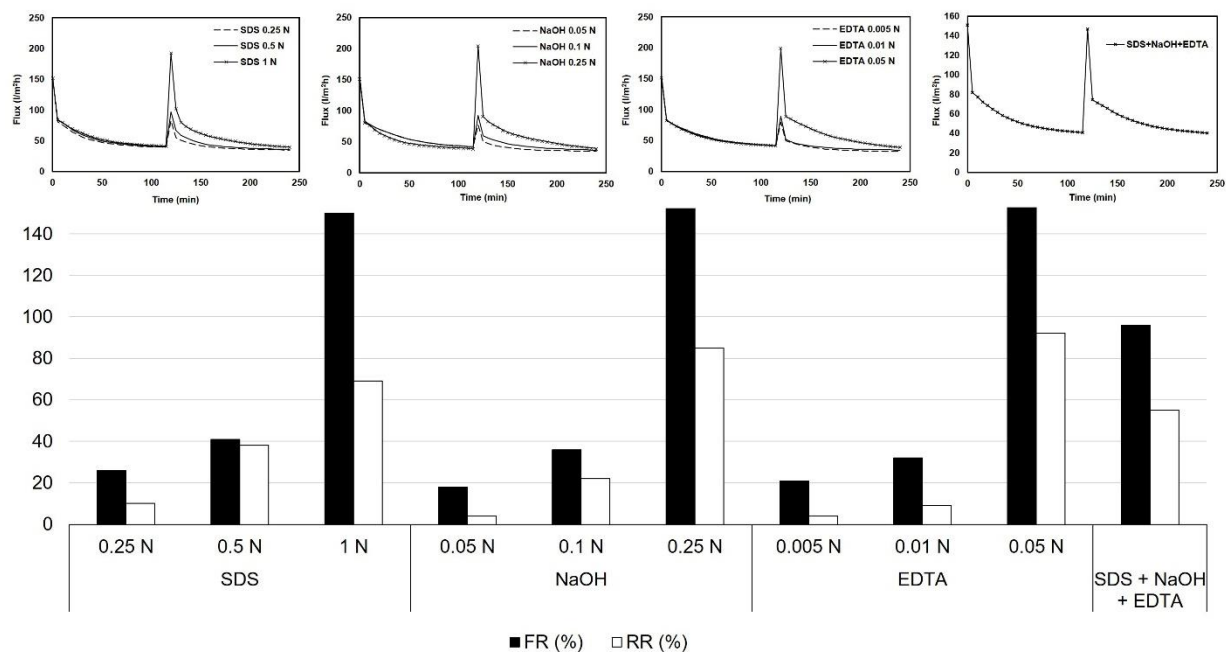


Fig. 4. Effects of different cleaning reagents on FR (%) and RR (%) of the membrane.

Once cleaning chemicals diffuse through the foulant, a number of chemical reactions could occur depending on the type of reagents used. Surfactants generally serve as the emulsifier reducing the surface tension of contaminant molecules. In addition to hydrophobic interactions with the oily layer, SDS was able to improve hydrophilicity of the membrane surface [39]. Therefore, the membrane was more permeable and less prone to fouling [40-42]. The alkali solution, NaOH, alter the pH in the system via negatively charged OH<sup>-</sup>. Due to the repulsive force between deposited oil droplets and the membrane surface, the oily cake layer could be detached more easily. In case of EDTA, it served as a chelating agent forming complex molecules with metals, which is a minor composition in cutting oil [27, 43]. Thus the fouled membrane could be treated more effectively. According to the outstanding function of each chemical (i.e., surfactant, alkali, and chelating agent), their combination could result in greater cleaning efficiency. It is worth noting that an increase in chemical concentrations causes the change in cake's permeability. The optimal level of cleaning reagents leads to the best condition for the deposit to be removed. When using too high chemical dosages (i.e., 1N SDS, 0.25 N NaOH, and 0.05N EDTA), the membrane structure could be impaired as indicated by the FR value above 100%.

### 3.5. Validation of the UF Practicality

#### 3.5.1. UF organic membrane for the treatment of palm oil emulsion

The RC membrane was chosen to apply with palm oil emulsion, and the result was compared to that conducted with 1 g/L cutting oil. The palm oil of analysis was prepared at the concentration of 5 g/L. The COD of 21,639 mg/L, BOD of 12,289 mg/L, turbidity of 2,938 NTU, viscosity of 0.0197 Pa·s, and mean diameter of 3.60  $\mu$ m were measured. Both cutting oil and palm oil emulsions were successfully treated by UF in terms of turbidity as well as O&G (removal eff.  $\approx$  100%). The removal of COD and BOD was more challenging for palm oil ( $\approx$ 80%) compared to that of the cutting oil ( $\approx$ 97%). Besides the higher concentration, palm oil held viscosity and mean diameter much greater than those of the cutting oil. Additionally, it might be the effect of SDS molecules added to the palm oil that penetrated through the membrane's pores with the permeate.



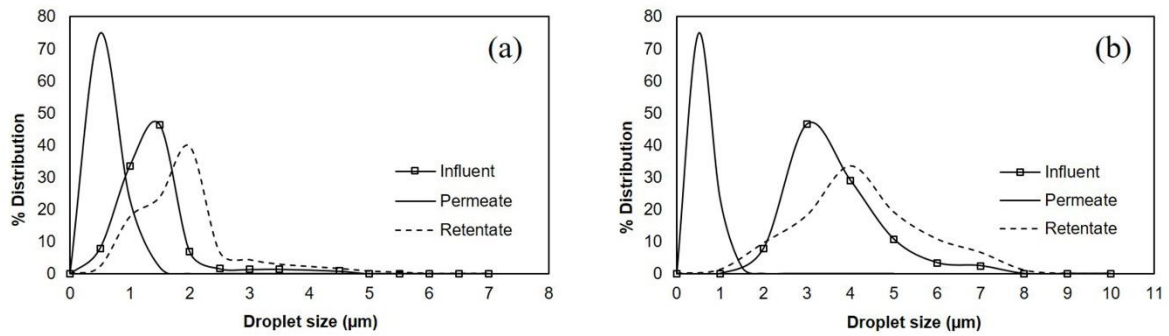


Fig. 5. Size distribution of (a) 1 g/L cutting oil and (b) 5 g/L palm oil during UF treatment.

In addition to treatment efficiency, a variation in oil size relating to UF applications was also studied. As illustrated in Fig. 5, the retentate contained oil droplets with a mean diameter of 2.0 μm and 4.0 μm for cutting oil and palm oil, respectively. These sizes were much greater than that of the membrane's pores and slightly increased from those of the influent. As aforementioned, the retentate was constantly circulated as the filtration proceeded. Thus, the deposited oil particles might agglomerate onto the membrane surface and formed larger droplet sizes. On the other hand, oil present in the permeate were smaller than those in the influent since only tiny droplets could penetrate through the membrane's pore.

### 3.5.2. Fouling mitigation via pretreatment

High oil loads in the influent could lead to rapid membrane fouling and sudden fall in the permeate fluxes. Pretreatment is one potential methodology for minimizing or impeding the fouling problem. As discussed in Jamaly et al. [44], a number of hybrid technologies have been found promising for oily wastewater treatment. Here, a suggested combined process is schematically demonstrated in Fig. 6.

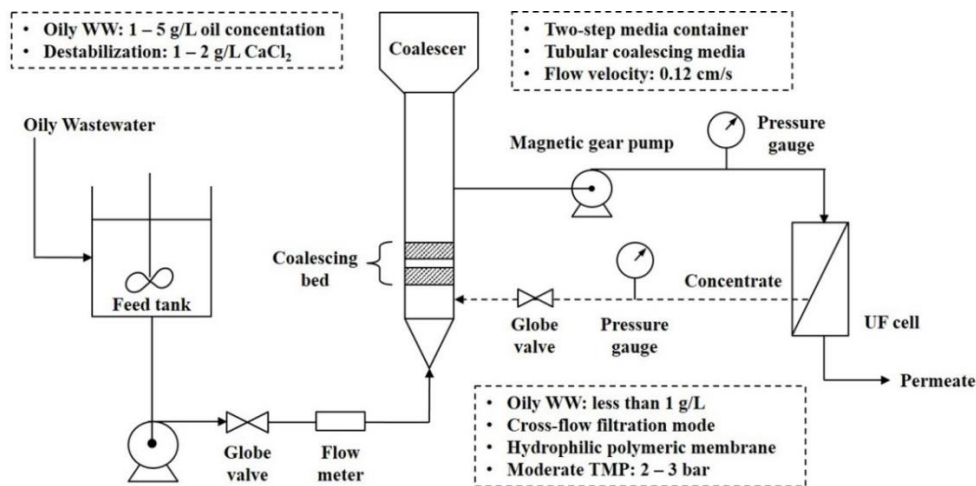


Fig. 6. An integrated system of UF and pretreatment.

According to the result displayed in Fig. 2, coalescer with chemical destabilization was selected as a pretreatment process due to its high efficiency. The system was connected to the crossflow UF, provided with a liquid recirculation. The principles of coalescer and chemical destabilization have been reported elsewhere [14, 45–48]. The addition of electrolyte (i.e., CaCl<sub>2</sub>) lessened the energy barriers surrounding oil particles, thus promoting instantaneous oil droplets' aggregation [49]. Under the conditions provided, an integration of destabilization and coalescence could enlarge oil droplet size up to 2–4 times compared to the coalescer itself (i.e., 0.42 → 0.88 μm for 1 g/L oil; 0.51 → 2.11 μm for 5 g/L oil). The pretreatment provided oil removal up to 90%, resulting in the residual oil of 150–450 mg/L. It is obvious that the oil content was greatly reduced before entering the UF membrane. Once completing the filtration process, the discharge

quality corresponded well with the regulatory standard (i.e., residual oil <10 mg/L [50]). Additionally, as can be seen from Fig. 7, the fouling rate could be retarded when coupling UF with the pretreatment. The membrane thus could be prolonged and be able to deal with higher effluent loads. However, the combined process could yield relatively low permeate volume (7–20 L/m<sup>2</sup>h) when compared to that of the sole UF (12–58 L/m<sup>2</sup>h).

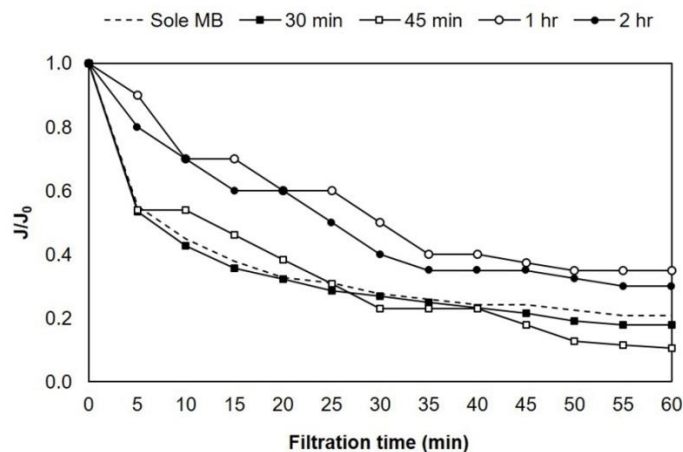


Fig. 7. Flux decline of a combined process at different decantation times compared to that of the sole membrane.

#### 4. Conclusions

The current paper encompasses a study on the UF technology for stabilized oily wastewater treatment. Information regarding operating conditions, membrane regeneration, and process optimization are offered. From the aforementioned data, the following conclusions can be drawn:

- Both hydrophilic organic membranes (i.e., RC and PES) could be applied with stabilized oily emulsions. The optimal operating conditions were obtained at oil concentrations less than 1 g/L, TMP of 2–3 bar, and CFV of 0.1 m/s.
- The membrane was dominantly fouled by a cake layer forming upon its surface. The successful membrane cleaning was achieved via the use of combined chemicals, including SDS, NaOH, and EDTA. Since each reagent played its own exceptional role on the cleaning mechanism, the fouled membrane could be regenerated with 96% FR and 55% RR.
- Under the optimal conditions, a stabilized palm oil emulsion could be treated by UF. Despite effective oil and turbidity removal, the effluent still contained a considerable COD and BOD contents. This could be the effect of high oil content as much as 5 g/L, which was far above the recommended values. Moreover, a partial of surfactant molecules (i.e., SDS) added to palm oil might penetrate through the membrane's pores and existed in the permeate.
- Coupling UF with a pretreatment seems to be plausible. The oil load upstream could be reduced before entrance the UF process, resulting in better effluent quality and less intensity of flux decline.

Further experiments should be operated under a continuous mode for representing the system in real practice. To accomplish higher throughput, a replacement of flat-sheet membranes by a hollow-fiber type may be helpful due to the larger filtration area. Moreover, the UF system should be conducted with authentic oily wastewater for validating the process applicability. Finally, the combined process should be studied in more aspects such as oil recovery and flux enhancement.

## Acknowledgement

The authors are thankful to Center of Excellence on Hazardous Substance Management and International Program in Hazardous Substance and Environmental Management, Graduate School, Chulalongkorn University for research grant and laboratory facilities. This work is also supported by Ratchadapisek Somphot Fund for Postdoctoral Fellowship and Research Unit on Technology for Oil Spill and Contamination Management, Chulalongkorn University.

## References

- [1] A. Salahi, T. Mohammadi, R. Mosayebi Behbahani, and M. Hemmati, "Asymmetric polyethersulfone ultrafiltration membranes for oily wastewater treatment: Synthesis, characterization, ANFIS modeling, and performance," *J Environ Chem Eng*, vol. 3, no. 1, pp. 170-178, 2015.
- [2] L. Y. Susan, S. Ismail, B. S. Ooi, and H. Mustapa, "Surface morphology of pvdf membrane and its fouling phenomenon by crude oil emulsion," *J Water Process Eng*, vol. 15, pp. 55-61, 2017.
- [3] M. Cheryan and N. Rajagopalan, "Membrane processing of oily streams. Wastewater treatment and waste reduction," *J Membr Sci*, vol. 151, no. 1, pp. 13-28, 1998.
- [4] M. A. El Baradie, "Cutting fluids: Part II. Recycling and clean machining," *J Mater Processing Technol*, vol. 56, pp. 798 - 806, 1996.
- [5] Occupational Safety & Health Administration. (1999). *Metalworking Fluids: Safety and Health Best Practices Manual* [Online]. Available: <https://www.osha.gov>, Accesses on: Oct. 29, 2017
- [6] M. Ii, H. Eda, T. Imai, M. Nishimura, T. Kawasaki, J. Shimizu, T. Yamamoto, and L. Zhou, "Development of high water-content cutting fluids with a new concept: Fire prevention and environmental protection," *Precis Eng*, vol. 24, no. 3, pp. 231-236, 2000.
- [7] K. Saswattecha, C. Kroeze, W. Jawjit, and L. Hein, "Options to reduce environmental impacts of palm oil production in Thailand," *J Clean Prod*, vol. 137, pp. 370-393, 2016.
- [8] M. Khemkhao, S. Techkarnjanaruk, and C. Phalakornkule, "Simultaneous treatment of raw palm oil mill effluent and biodegradation of palm fiber in a high-rate CSTR," *Bioresour Technol*, vol. 177, pp. 17-27, 2015.
- [9] W. L. Liew, M. A. Kassim, K. Muda, S. K. Loh, and A. C. Affam, "Conventional methods and emerging wastewater polishing technologies for palm oil mill effluent treatment: a review," *J Environ Manag*, vol. 149, pp. 222-235, 2015.
- [10] Y. Aurelle, "Treatment of oil-containing wastewater," Chulalongkorn University, Bangkok, Thailand, 1985.
- [11] K. Bensadok, M. Belkacem, and G. Nezzal, "Treatment of cutting oil/water emulsion by coupling coagulation and dissolved air flotation," *Desalination*, vol. 206, no. 1-3, pp. 440-448, 2007.
- [12] P. Cañizares, F. Martínez, C. Jiménez, C. Sáez, and M. A. Rodrigo, "Coagulation and electrocoagulation of oil-in-water emulsions," *J Hazard Mater*, vol. 151, no.1, pp. 44-51, 2008.
- [13] N. Chawaloeshphonsiya, "Enhancement of cutting oil wastewater treatment and separation by coalescer process," M.S. thesis, Env. Mngt., Chulalongkorn University, Bangkok, Thailand, 2009.
- [14] N. Chawaloeshphonsiya and P. Painmanakul, "Study of cutting-oil emulsion separation by coalescer process in terms of medium characteristics and bed packing," *Sep Sci and Technol*, vol. 49, no. 18, pp. 2960-2967, 2014.
- [15] N. Chawaloeshphosiya, J. Mongkolnauwarat, C. Prommajun, K. Wongwailikhit, and P. Painmanakul, "Treatment of cutting-oily wastewater by electrocoagulation-flotation (ECF) process: Modeling approach," *Environ Eng Res.*, vol. 20, no. 4, pp. 392-396, 2015.
- [16] J. M. Benito, S. Ebel, B. Gutiérrez, C. Pazos, and J. Coca, "Ultrafiltration of a waste emulsified cutting oil using organic membranes," *Water, Air and Soil Pollut*, vol. 128, no. 1, pp. 181-195, 2001.
- [17] M. Belkacem, M. Bahlouli, A. Mraoui, and K. Bensadok, "Treatment of oil-water emulsion by ultrafiltration: A numerical approach," *Desalination*, vol. 206, no. 1-3, pp. 433-439, 2007.
- [18] B. Chakrabarty, A. K. Ghoshal, and M. K. Purkait, "Ultrafiltration of stable oil-in-water emulsion by polysulfone membrane," *J Membr Sci*, vol. 325, no.1, pp. 427-437, 2008.
- [19] M. Hesampour, A. Krzyzaniak, and M. Nyström, "Treatment of wastewater from metal working by ultrafiltration, considering the effects of operating conditions," *Desalination*, vol. 222, no. 1-3, pp. 212-221, 2008.

- [20] M. Karhu, T. Kuokkanen, J. Ramo, M. Mikola, and J. Tanskanen, "Performance of a commercial industrial-scale UF-based process for treatment of oily wastewaters," *J Environ Manage*, vol. 128, pp. 413-420, 2013.
- [21] X. Zhu, A. Dudchenko, X. Gu, and D. Jassby, "Surfactant-stabilized oil separation from water using ultrafiltration and nanofiltration," *J Membr Sci.*, vol. 529, pp. 159-169, 2017.
- [22] T. Mohammadi, A. Kohpeyma, and M. Sadrzadeh, "Mathematical modeling of flux decline in ultrafiltration," *Desalination*, vol. 184, no.1-3, pp. 367-375, 2005.
- [23] E. Ceschia, J. R. Harjani, C. Liang, Z. Ghoshouni, T. Andrea, R. S. Brown, and P. G. Jessop, "Switchable anionic surfactants for the remediation of oil-contaminated sand by soil washing," *RSC Adv.*, vol. 4, no. 9, pp. 4638-4645, 2014.
- [24] APHA, *Standard Methods for the Examination of Water and Wastewater*. Washington, DC: American Public Health Association, 2005, vol. 21.
- [25] J. Hermia, "Constant Pressure Blocking Filtration Laws - Application Topower-Law Non-Newtonian Fluids," *Trans Inst Chem Eng.*, vol. 60, no.3, pp. 183-187, 1982.
- [26] C. Regula, E. Carretier, Y. Wyart, G. Gésan-Guiziou, A. Vincent, D. Boudot, and P. Moulin, "Chemical cleaning/disinfection and ageing of organic UF membranes: A review," *Water Res.*, vol. 56, pp. 325-365, 2014.
- [27] M. Kazemimoghadam and T. Mohammadi, "Chemical cleaning of ultrafiltration membranes in the milk industry," *Desalination*, vol. 204, no.1, pp. 213-218, 2007.
- [28] S. Rachu, "Computer Program Development for Oily Wastewater Treatment Process Selection, Design and Simulation," PhD thesis, INSA-Toulouse, 2005.
- [29] H. Falahati and A. Y. Tremblay, "Flux dependent oil permeation in the ultrafiltration of highly concentrated and unstable oil-in-water emulsions," *J Membr Sci.*, vol. 371, no. 1-2, pp. 239-247, 2011.
- [30] X. Shi, G. Tal, N. P. Hankins, and V. Gitis, "Fouling and cleaning of ultrafiltration membranes: A review," *J Water Process Eng.*, vol. 1, pp. 121-138, 2014.
- [31] S. Hong, R. S. Faibish, and M. Elimelech, "Kinetics of permeate flux decline in crossflow membrane filtration of colloidal suspensions," *J colloid and interface sci.*, vol. 196, no. 2, pp. 267-277, 1997.
- [32] M. Abbasi, M. Mirfendereski, M. Nikbakht, M. Golshenas, and T. Mohammadi, "Performance study of mullite and mullite-alumina ceramic MF membranes for oily wastewaters treatment," *Desalination*, vol. 259, no. 1, pp. 169-178, 2010.
- [33] A. Salahi, M. Abbasi, and T. Mohammadi, "Permeate flux decline during UF of oily wastewater: Experimental and modeling," *Desalination*, vol. 251, no. 1-3, pp. 153-160, 2010.
- [34] P. Mittal, S. Jana, and K. Mohanty, "Synthesis of low-cost hydrophilic ceramic-polymeric composite membrane for treatment of oily wastewater," *Desalination*, vol. 282, pp. 54-62, 2011.
- [35] H. Li and V. Chen, "Membrane fouling and cleaning in food and bioprocessing," in *Membrane Technology*. Oxford: Butterworth-Heinemann, 2010, ch. 10, pp. 213-254.
- [36] I. Noshadi, A. Salahi, M. Hemmati, F. Rekabdar, and T. Mohammadi, "Experimental and ANFIS modeling for fouling analysis of oily wastewater treatment using ultrafiltration," *Asia-Pacific J Chem Eng.*, vol. 8, no. 4, pp. 527-538, 2013.
- [37] S.-H. Yoon, "Membrane Fouling in Membrane Bioreactor," in *Membrane Bioreactor Processes*: CRC Press, 2015, pp. 197-252.
- [38] D. Jermann, W. Pronk, and M. Boller, "Mutual Influences between Natural Organic Matter and Inorganic Particles and Their Combined Effect on Ultrafiltration Membrane Fouling," *Environ Sci & Technol*, vol. 42, no. 24, pp. 9129-9136, 2008.
- [39] S. S. Madaeni, E. Rostami, and A. Rahimpour, "Surfactant cleaning of ultrafiltration membranes fouled by whey," *International J Dairy Technol*, vol. 63, no. 2, pp. 273-283, 2010.
- [40] A. N. Cherkasov, S. V. Tsareva, and A. E. Polotsky, "Selective properties of ultrafiltration membranes from the standpoint of concentration polarization and adsorption phenomena," *J Membr Sci.*, vol. 104, no. 1, pp. 157-164, 1995.
- [41] M. Kabsch-Korbutowicz, K. Majewska-Nowak, and T. Winnicki, "Analysis of membrane fouling in the treatment of water solutions containing humic acids and mineral salts," *Desalination*, vol. 126, no. 1, pp. 179-185, 1999.
- [42] S. C. Tu, V. Ravindran, W. Den, and M. Pirbazari, "Predictive membrane transport model for nanofiltration processes in water treatment," *AICHE J*, vol. 47, no. 6, pp. 1346-1362, 2001.
- [43] T. Mohammadi, S. S. Madaeni, and M. K. Moghadam, "Investigation of membrane fouling," *Desalination*, vol. 153, no. 1, pp. 155-160, 2003.

- [44] S. Jamaly, A. Giwa, and S. W. Hasan, "Recent improvements in oily wastewater treatment: Progress, challenges, and future opportunities," *J Environ Sci.*, vol. 37, pp. 15-30, 2015.
- [45] J. Li and Y. Gu, "Coalescence of oil-in-water emulsions in fibrous and granular beds," *Sep and Purif Technol*, vol. 42, no. 1, pp. 1-13, 2005.
- [46] S. Maiti, I. M. Mishra, S. D. Bhattacharya and J. K. Joshi, "Removal of oil from oil-in-water emulsion using a packed bed of commercial resin," *Colloids and Surfaces A: Physicochem and Eng Aspects*, vol. 389, no. 1, pp. 291-298, 2011.
- [47] N. Chawaloeshonsiya, P. Guiraud, and P. Painmanakul, "Analysis of cutting-oil emulsion destabilization by aluminum sulfate," *Environ Technol*, vol. 39, no. 11, pp. 1450-1460, 2018.
- [48] N. Chawaloeshonsiya, C. Prommajun, K. Wongwailikhit, and P. Painmanakul, "Comparison of cutting-oil emulsion treatment by electrocoagulation–flotation in bubble column and airlift reactors," *Environ Technol*, vol. 38, no. 10, pp. 1295-1304, 2017.
- [49] G. Rios, C. Pazos, and J. Coca, "Destabilization of cutting oil emulsions using inorganic salts as coagulants," *Colloids and Surfaces A: Physicochem and Eng Aspects*, vol. 138, no. 2–3, pp. 383-389, 1998.
- [50] Pollution Control Department (PCD). (2016). *Water Quality Standard for Industrial Discharge in Thailand* [Online]. Available: [http://www.pcd.go.th/info\\_serv/reg\\_std\\_water04.html#s1](http://www.pcd.go.th/info_serv/reg_std_water04.html#s1), Accessed on: Oct. 15, 2017.