CHAPTER I
INTRODUCTION

1.1 State of Problem

The conservation of water resource is an increasing concern around the world including in Thailand. In many regions, industrial development causes the increasing contamination, breaking the balance in ecological systems as well as leading to the deterioration of water qualities. Among the contaminants generated by chemical industry, oils and petroleum products are commonly found in industrial discharges as well as domestic wastewaters. Oils and petroleum products are considerably hazardous to the environment at all stages of their use and existence. In addition, they can commonly leak from storages. The leakage does not only cause the soil contamination but also leads to the contamination of underground water and nearly surface water because of the migration of the oils. Hence, it is of interest to develop a high efficiency process with low cost and simplicity in operation for removing contaminated oils from wastewaters before discharging into the environment. Froth flotation is a surfactant-based separation process (Somasundaran and Ananthapadmanabhan, 1987; Scamehorn and Harwell, 1989; Scamehorn and Harwell, 2000). It was first used in ore processing, and it has been pointed out to be a promising technique for oily wastewater treatment (Somasundaran and Ananthapadmanabhan, 1987; Scamehorn and Harwell, 1989; Yorar, 1997; Aplan, 1997; Pondstabodee *et al.*, 1998; Scamehorn and Harwell, 2000; Chavadej *et al.*, 2004a; Chavadej *et al.*, 2004b; Yanatatsaneejit *et al.* 2005a, Yanatatsaneejit *et al.* 2005b).

Froth flotation process is suitable for treating wastewaters containing suspended solids as well as oils in both emulsion and undissolved forms since it has several advantages including rapid operation, low space requirement for equipment set-up, high efficiency of removal, flexibility of application to various pollutants at various scales, and low cost of operation (Choi and Choi, 1996). Consequently, froth flotation has been increasingly used to solve many wastewater treatment problems (Leu *et al.*, 1994; Zouboulis *et al.*, 1994; Choi and Choi, 1996; Wungrattanasopon *et* *al.*, 1996) including selective separation of minerals (Benn and Cornell, 1993; Kabil and Ghazy, 1994), removing ink from pulp paper in paper recycling (Costa and Rubio, 2005; Beneventi *et al.*, 2003), and emulsified oil removal from wastewater (Pondstabodee *et al.*, 1998; Feng and Aldrich, 2000). The presence of emulsified oils, like diesel oil, cutting oil, and motor oil in water is a critical problem for wastewater treatment because these substances are non-biodegradable. Based upon our previous research (Pondstabodee *et al.*, 1998), the maximum oil removal was achieved when the system was in the Winsor's type III microemulsion region. Later, Chavadej *et al.* (2004b) found that the most oil removed during the froth flotation operation came from the excess oil phase rather than the middle phase in the Winsor's type III microemulsion system. This proves that it is the ultralow IFT corresponding to the Winsor's type III microemulsion which is responsible for efficient flotation; the formation of a third phase (middle phase) under this condition is coincidental to oil removal. Recently, Yanatatsaneejit *et al.* (2005a) found that ethylbenzene removal from water by froth flotation was efficient only when both low IFT and good frothing are obtained. Moreover, they proposed the four sequential steps in the mechanism of oil removal by froth flotation. Firstly, air bubbles are generated through the liquid solution and oil droplets adhere on the surface of the air bubbles. The second step is the formation of oil films on the surfaces of the air bubbles while the air bubbles are rising through the solution. The third step is the rising of the air bubbles with attached oil films to the top of the solution. The fourth step is the emerging of air bubbles from the liquid phase to form froth. In both third and fourth steps, high stability of the air bubbles covered by oil films is necessary. For a successful separation, high stability of the froth is needed to yield dry foam with a high oil content. Foamability or foam formation and foam stability influences the foam production rate which needs to be sufficient for a good separation, no matter how well the oil attaches to air bubbles rising through solution. Yanatatsaneejit (2004) correlated the performance of batch froth flotation to remove diesel from water with the system IFT, foam characteristics, and coalescence time between oil droplets.

As mentioned before, most studies of froth flotation were operated in a batch mode whereas large quantities of industrial wastewaters are more efficiently and economically treated by continuous, steady-state processes. Hence, in this work, a continuous froth flotation process was developed for treating oily wastewaters in order to obtain a better understanding of the mechanism of froth flotation process as well as to be applicable for treating industrial wastewaters.

1.2 Objectives

The main objective of this study was to assess the operational parameters affecting the process performance and to elucidate the process mechanism of continuous froth flotation for oily wastewater treatment under microemulsion conditions. The overall objectives of this work were as follows:

1. To study phase diagrams of microemulsions to form Winsor's type I-III-II with diesel oil, motor oil, and cutting oil.
2. To study the effects of operational parameters of the continuous froth flotation on the removal efficiency of different oils under microemulsion conditions and/or low system IFT.
3. To correlate foam formation and foam stability with the performance of continuous froth flotation.
4. To investigate the relationship between the froth characteristics, the system interfacial tension (IFT), and the efficiency of diesel removal by batch froth flotation under colloidal gas aphron (CGA) conditions.
5. To correlate the bubble characteristics and interfacial area of bubbles in the continuous flotation column with the removal efficiency of different oils under microemulsion conditions.

1.3 Scope of Work

In this work, three types of studied oils were diesel oil, motor oil, and cutting oil. Diesel oil was selected to form microemulsions with branch alcohol propoxylate sulfate sodium salt ($C_{14-15}(PO)_5SO_4Na$), an extended surfactant, as a single surfactant system and $C_{14-15}(PO)_5SO_4Na$ with sodium dodecyl sulfate (SDS) as a mixed surfactant system, then the interfacial tension (IFT) of each system was measured. The surfactant and NaCl concentrations were varied to construct the microemulsion diagram (fish diagram) of diesel oil. This diagram was used for selecting the optimum concentrations of NaCl and surfactant for running the continuous froth flotation experiments and foam characteristics experiments. The separation performance of the continuous froth flotation was investigated under various operational parameters: surfactant concentration, NaCl concentration, oil-to-water ratio, foam height, air flow rate, and hydraulic retention time (HRT). The foam characteristics experiments of diesel oil system were studied in order to correlate with the oil removal efficiency and to obtain a better understanding of the continuous froth flotation process.

In order to enhance the stability of foam, colloidal gas aphron (CGA) under microemulsion conditions was applied in a froth flotation column in batch mode of operation for investigating the feasibility the CGA in froth flotation operation before applying this technique to a continuous froth flotation system.

To obtain a better understanding about froth flotation process, the bubble characteristics (a bubble size distribution and a bubble rising velocity profile of air bubbles in the froth flotation column) were studied by using photographic method as a function of surfactant concentration and axial location of flotation column under the microemulsion conditions in order to correlate with the oil removal efficiency in the continuous froth flotation operation. In this studied part, motor oil was selected as a model oil. The effects of surfactant concentration and HRT were investigated to correlate with the bubble size distribution and bubble velocity profile. Moreover, several parameters about the bubble characteristics were calculated; for example, the average bubble diameter, the Suater mean diameter (d_{32}), the bubble surface area flux, and the bubble number flux.

In this studied part, cutting oil was selected as the model oil because of the need from industry. $C_{14-15}(PO)_5SO_4Na$ was again used to form microemulsions with the cutting oil. The condition providing the ultralow IFT was found to produce unstable froth in froth flotation experiments. Therefore, sodium dodecyl sulfate (SDS), an anionic surfactant was used to enhance the foam stability. The foam characteristics experiments of the cutting oil system were studied in order to correlate with the performance of the continuous froth flotation. In order to gain a better understand about the froth flotation process, the dynamic surface tension was measured to elucidate how fast the foam forming was. Moreover, the entering, bridging, and spreading coefficients were determined to correlate with the foam stability of the system.