

**REMOVAL OF EMULSIFIED OIL FROM WASTEWATER USING
FROTH FLOTATION**



Ms. Wisakha Phoochinda

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
And Case Western Reserve University

1999

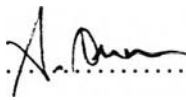
ISBN 974-331-913-1

21 ก.พ. 2550


1 19584994


Thesis Title : Removal of Emulsified Oil from Wastewater Using
Froth Flotation
By : Ms. Wisakha Phoochinda
Program : Petrochemical Technology
Thesis Advisors : Prof. John F. Scamehorn
Assoc. Prof. Sumaeth Chavadej

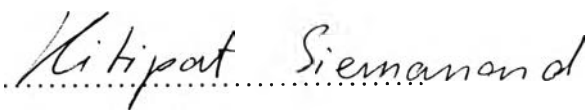
Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfillment of the requirements for the Degree of Master of Science.


..... College Director
(Prof. Somchai Osuwan)

Thesis Committee:


.....
(Prof. John F. Scamehorn)


.....
(Assoc. Prof. Sumaeth Chavadej)


.....
(Dr. Kitipat Siemanond)

ABSTRACT

#971027 : PETROCHEMICAL TECHNOLOGY PROGRAM

KEY WORD : Froth Flotation/Microemulsion/Ortho-Dichlorobenzene

Wisakha Phoochinda: Removal of Emulsified Oil from
Wastewater Using Froth Flotation. Thesis Advisors: Prof.

John F. Scamehorn and Assoc. Prof. Sumaeth Chavadej

75 pp ISBN 974-331-913-1

Froth flotation is a surfactant-based separation process which is applicable for removing oil from water. Ortho-dichlorobenzene (ODCB) which is commonly used in many industrial applications was used as the oil for studying the removal efficiency by batch froth flotation. Mixtures of sodium dodecyl sulphate (SDS) and nonylphenol ethoxylate (NP(EO)₁₀ or Teric 10) were used for studies of microemulsion formation of ODCB. It was found that small amounts of NaCl added to mixed surfactants could improve microemulsion formation. However, precipitation and liquid crystal that limit the solubilization capacity of solution appeared at high NaCl concentration. The mixed surfactants concentrations of 3 and 5 % by weight of mixed surfactants were selected for froth flotation experiment. The prepared solutions i.e. water and middle phase (w-m), water and oil phase (w-o) and water, middle and oil phase (w-m-o) were transferred to a flotation column to determine oil removal efficiency. The results showed that ODCB removal in the w-m-o system was much higher than the w-o and w-m systems. The effect of NaCl in the w-m-o system was studied and showed that adding 0.5 by weight of NaCl increased ODCB removal but adding more than 1.0 by weight of NaCl decreased ODCB removal. The effect of volume of each phase was also studied. The results showed that when volume of oil phase decreased and

volume of water phase increased in the w-o system, ODCB removal decreased. When volume of middle phase increased and volume of water phase decreased in the w-m system, ODCB removal increased.

บทคัดย่อ

วิชา ภาวูจันดา : การกำจัดอิมัลชันไฟต์ออยด์จากน้ำเสียโดยวิธีการทำให้ลอย (Removal of emulsified oil from wastewater using froth flotation) อ. ที่ปรึกษา : ศ. จอห์น เอฟ สเคิร์มมาฮอร์น และ รศ. สุเมธ ชวเดช

กระบวนการทำให้ลอย (froth flotation) เป็นกระบวนการแยกสารโดยใช้สารลดแรงตึงผิว ซึ่งสามารถนำไปประยุกต์ใช้ในการแยกน้ำมันออกจากน้ำเสีย ออร์โธ-ไดคลอโรเบนซีนเป็นสารทั่วไปที่นำมาใช้ประโยชน์ในอุตสาหกรรมและได้นำมาใช้เป็นน้ำมันในการศึกษาประสิทธิภาพของกระบวนการทำให้ลอยแบบกะ สารลดแรงตึงผิวผสมระหว่างโซเดียม-โดเดซิลซัลเฟต (SDS) กับโนนิลฟีนอลโพลีเอทิลีนออกไซด์ (NP(EO)₁₀) ได้นำมาใช้ในการศึกษาการเกิดไมโครอิมัลชันของน้ำและออร์โธ-ไดคลอโรเบนซีน(ODCB) จากผลการทดลองพบว่าการเติมเกลือ(NaCl) ในสารลดแรงตึงผิวผสมในปริมาณน้อยจะช่วยเพิ่มการเกิดไมโครอิมัลชัน แต่การเติมเกลือ(NaCl) ในปริมาณมากและการใช้สารลดแรงตึงผิวผสมที่มีความเข้มข้นสูงเกินไปจะทำให้เกิดการตกตะกอนและการเกิดผลึกของเหลว(liquid crystal)ของเกลือและสารลดแรงตึงผิว สารลดแรงตึงผิวเข้มข้น 3 และ 5 เปอร์เซ็นต์โดยน้ำหนักถูกนำมาใช้ในการศึกษาประสิทธิภาพของกระบวนการทำให้ลอยแบบกะ ในการทดลองนี้ได้เตรียมสารไมโครอิมัลชันระบบวินเซอร์ชนิดที่3 ซึ่งมี 3 ชั้น (น้ำ, สารละลายชั้นกลาง, น้ำมัน) ในปริมาณมากและนำมาแยกเป็น 3 ระบบคือระบบน้ำและสารละลายชั้นกลาง, ระบบน้ำและน้ำมัน และระบบน้ำ, สารละลายชั้นกลางและน้ำมัน เพื่อศึกษาความแตกต่างของทั้ง 3 ระบบที่มีต่อประสิทธิภาพของกระบวนการทำให้ลอย จากผลการทดลองพบว่าประสิทธิภาพของกระบวนการทำให้ลอยในระบบน้ำ, สารละลายชั้นกลางและน้ำมัน ดีกว่าระบบน้ำและน้ำมัน และระบบน้ำและสารละลายชั้นกลางตามลำดับ การเติมเกลือประมาณ 0.5 เปอร์เซ็นต์โดยน้ำหนักในระบบน้ำ, สารละลายชั้นกลางและน้ำมันจะช่วยเพิ่มประสิทธิภาพของกระบวนการทำให้ลอย แต่ถ้าปริมาณเกลือมากกว่า 1 เปอร์เซ็นต์โดยน้ำหนักจะไปลดประสิทธิภาพของกระบวนการทำให้ลอย ผลของความแตกต่างของปริมาณน้ำ, สารละลายชั้นกลาง, น้ำมัน ได้นำมาศึกษาประสิทธิภาพของกระบวนการทำให้ลอยในระบบน้ำและน้ำมันเพิ่มขึ้นเมื่อปริมาณของน้ำมันเพิ่มขึ้นและประสิทธิภาพของกระบวนการทำให้ลอยในระบบน้ำและสารละลายชั้นกลางเพิ่มขึ้นเมื่อปริมาณของสารละลายชั้นกลางเพิ่มขึ้น

ACKNOWLEDGEMENTS

This work gave me a lot of knowledge as well as a valuable experience. Without the assistance of many persons including organizations, it would not have succeeded. I would like to acknowledge all of them for their help in this work.

First of all, I would like to give my deep appreciation to Professor John F. Scamehorn who was my US thesis advisor for his guidance and encouragement throughout this work. Moreover, I would like to thank him especially for insightful discussions and professional suggestions as well.

My great appreciation also goes to Assoc. Prof. Sumaeth Chavadej who was my Thai thesis advisor for providing many necessary things throughout this work. I would like to thank him for his encouragement, constant advice and support. This work would never have been completed without his assistance.

I would like to give my deep appreciation to the Petroleum and Petrochemical College for providing a full scholarship.

Thanks is also extended to Dr. Kitipat Siemanond who acted as my thesis committee. I thank him for his guidance and assistance.

I would like to thank Dr. Pramoch Rangsunvigit and Ms. Jintana Chamnanmanoontham as well. Both of them help me regarding to a spinning drop tensiometer. I thank them for their encouragement and guidance.

I would like to extend thanks to all of the staff of the Petroleum and Petrochemical College for their nice help.

The East Asiatic (Thailand) Public Company Limited was very generous for supplying me chemicals for this work.

Finally, I would like to express deep appreciation to my parents and my brother who always encourage me and give their endless love as well as support throughout my life.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	v
Acknowledgements	vi
Table of Contents	vii
List of Tables	x
List of Figures	xiii
CHAPTER	
I INTRODUCTION	1
II LITERATURE SURVEY	
2.1 Natures of surfactants	3
2.2 Emulsion systems	6
2.2.1 Characteristics of microemulsion	6
2.2.2 Effect of electrolyte on micromulsion formation	9
2.2.3 Formation of liquid crystal	9
2.3 Principles of froth flotation	10
2.4 Chlorobenzene as a hazardous substance	15
III EXPERIMENTAL	
3.1 Chemicals	17
3.1.1 Surfactants	17
3.1.2 Studied oil	18

CHAPTER	PAGE
3.1.3 Water	18
3.1.4 Electrolyte	19
3.2 Experiment procedures	19
3.2.1 Study of phase behavior and formation of microemulsion	19
3.2.2 Froth flotation experiment	21
3.3 Analytical methods	23
IV RESULTS AND DISCUSSION	
4.1 Microemulsion formation	24
4.1.1 Effect of single surfactant concentration on microemulsion formation	24
4.1.2 Effect of mixed surfactants concentration on microemulsion formation	25
4.1.3 Effect of NaCl on microemulsion formation of mixed surfactants system	29
4.2 Froth flotation experiment	37
4.2.1 Effect of initial mixed surfactants concentration on ODCB removal	37
4.2.2 Effect of phases on ODCB removal	38
4.2.3 Effect of NaCl concentration on ODCB removal	42
4.2.4 Effect of the weight ratio of SDS on ODCB removal	43
4.2.5 Effect of phase volume on ODCB removal	44

CHAPTER	PAGE
V CONCLUSIONS AND RECOMMENDATIONS	
5.1 Conclusions	49
5.2 Recommendations	50
REFERENCES	51
APPENDICES	
APPENDIX A	54
APPENDIX B	68
CURRICULUM VITAE	75

LIST OF TABLES

TABLE	PAGE
3.1 Chemical properties of TERIC N10	17
3.2 Chemical and physical properties of ortho-dichlorobenzene	18
4.1 The foam volume of different systems having different Xsds	45
A-1 Volume fraction of water, middle and oil phases in microemulsion formation at different SDS concentrations and initial oil/water ratio =1/1	54
A-2 Volume fraction of water, middle and oil phases in microemulsion formation at different NP(EO) ₁₀ concentrations and initial oil/water ratio =1/1	54
A-3 Volume fraction of water, middle and oil phases in microemulsion formation at different mixed surfactant (SDS and NP(EO) ₁₀) concentrations and different Xsds with initial oil/water ratio =1/1	55
A-4 Volume fraction of water, middle and oil phases in microemulsion formation at 1 wt. % mixed surfactants (SDS and NP(EO) ₁₀) concentration and different NaCl concentrations and different Xsds with initial oil/water ratio =1/1	57
A-5 Volume fraction of water, middle and oil phases in microemulsion formation at 3 wt. % mixed surfactants (SDS and NP(EO) ₁₀) concentration and different NaCl concentrations and different Xsds with initial oil/water ratio =1/1	59

TABLE	PAGE
A-6 Volume fraction of water, middle and oil phases in microemulsion formation at 5 wt. % mixed surfactants (SDS and NP(EO) ₁₀) concentration and different NaCl concentrations and different Xsds with initial oil/water ratio =1/1	61
A-7 Volume fraction of water, middle and oil phases in microemulsion formation at 7 wt. % mixed surfactants (SDS and NP(EO) ₁₀) concentration and different NaCl concentrations and different Xsds with initial oil/water ratio =1/1	63
A-8 Volume fraction of water, middle and oil phases in microemulsion formation at 9 wt. % mixed surfactants (SDS and NP(EO) ₁₀) concentration and different NaCl concentrations and different Xsds with initial oil/water ratio =1/1	65
B-1 Removal efficiency of ODCB at different mixed surfactants concentrations with initial oil/water ratio = 1/1 in water, middle and oil phase system (w-m-o)	68
B-2 Removal efficiency of ODCB at different mixed surfactants concentrations with initial oil/water ratio = 1/1 in water and oil phase system (w-o)	69
B-3 Removal efficiency of ODCB at different mixed surfactants concentrations with initial oil/water ratio = 1/1 in water and middle phase system (w-m)	69

TABLE	PAGE
B-4 Removal efficiency of ODCB at 3 wt. % mixed surfactants with initial oil/water ratio = 1/1 at different systems: water, middle and oil phase (w-m-o), water and oil phase (w-o), water and middle phase (w-m)	70
B-5 Removal efficiency of ODCB at 5 wt. % mixed surfactants with initial oil/water ratio = 1/1 at different systems: water, middle and oil phase (w-m-o), water and oil phase (w-o), water and middle phase (w-m)	71
B-6 Removal efficiency of ODCB at 3 wt. % mixed surfactants, Xsds = 0.6 with initial oil/water ratio = 1/1 at different NaCl concentrations in water, middle and oil phase system	72
B-7 Removal efficiency of ODCB at 3 wt. % mixed surfactants with initial oil/water ratio = 1/1 at different volume of each phase in water and oil phase (w-o), water and middle phase (w-m) system	73
B-8 Removal efficiency of ODCB at 5 wt. % mixed surfactants with initial oil/water ratio = 1/1 at different volume of each phase in water and oil phase (w-o), water and middle phase (w-m) system	74

LIST OF FIGURES

FIGURE	PAGE
2.1 Schematic diagram of monomer, micelles and micellization	4
2.2 Schematic diagram of normal micelles and inverse micelles	5
2.3 Schematic diagram of types of microemulsions	7
2.4 Schematic diagram of lamellar liquid crystal	10
2.5 Schematic diagram of froth flotation column in batch mode and mechanism of oil removal	12
2.6 Experimental configurations for foam or froth separation	13
3.1 Schematic experiment of microemulsion formation	20
3.2 Schematic diagram of microemulsion solution in froth flotation experiment	22
3.3 Schematic diagram of the froth flotation apparatus	22
4.1 Volume fractions of water, middle and oil phases at different SDS concentrations with initial oil/water ratio = 1/1	24
4.2 Volume fractions of water, middle and oil phases at different NP(EO) ₁₀ concentrations with initial oil/water ratio = 1/1	25
4.3 Volume fraction of water, middle and oil phases at different mixed surfactants concentrations with initial oil/water ratio = 1/1	26

FIGURE	PAGE
4.4 Volume fraction of middle phase at different X_{sds} and mixed surfactants concentrations with initial oil/water ratio = 1/1	28
4.5 Average volume fraction of middle phase at mixed surfactants concentrations with initial oil/water ratio = 1/1	28
4.6 Volume fractions of water, middle and oil phases at 1 wt. % mixed surfactants concentration with initial oil/water ratio = 1/1 at different SDS fractions	30
4.7 Volume fractions of water, middle and oil phases at 3wt. % mixed surfactants concentration with initial oil/water ratio = 1/1 at different SDS fractions	31
4.8 Volume fractions of water, middle and oil phases at 5 wt. % mixed surfactants concentration with initial oil/water ratio = 1/1 at different SDS fractions	33
4.9 Volume fractions of water, middle and oil phases at 7 wt. % mixed surfactants concentration with initial oil/water ratio = 1/1 at different SDS fractions	34
4.10 Volume fractions of water, middle and oil phases at 9 wt. % mixed surfactants concentration with initial oil/water ratio = 1/1 at different SDS fractions	35
4.11 ODCB removal at two initial mixed surfactants concentrations and $X_{sds} = 0.2$ with initial oil/water ratio = 1/1	37
4.12 ODCB removal at 3 and 5wt. % mixed surfactants concentrations and $X_{sds} = 0.2$ with initial oil/water ratio = 1/1	39

FIGURE	PAGE
4.13 ODCB removal of three different systems at 3 wt. % mixed surfactants concentration and $X_{sds} = 0.4, 0.6,$ and 0.8 with initial oil/water ratio = 1/1	40
4.14 ODCB removal of three different systems at 5 wt. % mixed surfactants concentration and $X_{sds} = 0.4, 0.6,$ and 0.8 with initial oil/water ratio = 1/1	41
4.15 ODCB removal of w-m-o phase obtained from the microemulsion systems with 3 wt. % mixed surfactants concentration at different NaCl concentrations	42
4.16 ODCB removal of w-m, w-o and w-m-o phases as a function of SDS fraction in the system containing 3 wt. % mixed surfactants concentration	43
4.17 ODCB removal of different combination of two phases obtained from the microemulsion system under 3 and 5 wt. % mixed surfactants concentrations and at different SDS fractions ($f_w =$ volume fraction of water phase, $f_m =$ volume fraction of middle phase and $f_o =$ volume fraction of ODCB phase)	45