

การแยกกรดปีตา-แคโรทีนจากปาล์มโอเลอิน โดยการดูดซับด้วยพอลิเมอร์
สังเคราะห์



นาย รัฐไท วีระชาติเทวีญ

สถาบันวิทยบริการ
วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
จุฬาลงกรณ์มหาวิทยาลัย
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2549

SEPARATION OF CRUDE β -CAROTENE FROM PALM OLEIN BY ADSORPTION
WITH SYNTHETIC POLYMER



Mr. Rutthai Veeracharttawan

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

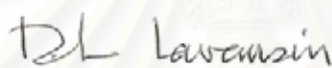
Faculty of Engineering

Chulalongkorn University

Academic Year 2006

Thesis Title SEPARATION OF CRUDE β -CAROTENE FROM
PALM OLEIN BY ADSORPTION WITH
SYNTHETIC POLYMER
By Mr. Rutthai Veeracharttawan
Field of Study Chemical Engineering
Thesis Advisor Associate Professor Chirakarn Muangnapoh, Dr.Ing.

Accepted by the Faculty of Engineering, Chulalongkorn University in
Partial Fulfillment of the Requirements for the Master's Degree



Dean of the Faculty of Engineering
(Professor Direk Lavansiri, Ph.D.)

THESIS COMMITTEE



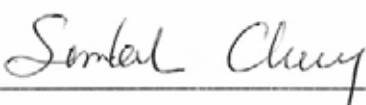
Chairman
(Associate Professor Tawatchai Charinpanitkul, Dr.Eng.)



Thesis Advisor
(Associate Professor Chirakarn Muangnapoh, Dr.Ing.)



Member
(Associate Professor Seeroong Prichanont, Ph.D.)



Member
(Sirikul Chunsawang, D.Eng.)

รัฐไท วีระชาติเทวัญ : การแยกครูดบีตา-แคโรทีนจากปาล์มโอเลอินโดยการดูดซับด้วยพอลิเมอร์สังเคราะห์ (SEPARATION OF CRUDE β -CAROTENE FROM PALM OLEIN BY ADSORPTION WITH SYNTHETIC POLYMER) อ. ที่ปรึกษา : รศ. ดร. จิรกานต์ เมืองนาโพธิ์, 67 หน้า.

งานวิจัยนี้มีจุดประสงค์เพื่อ หาสภาวะที่เหมาะสมสำหรับการแยกครูดบีตา-แคโรทีนจากปาล์มโอเลอินและปาล์มโอเลอินที่กำจัดกัมแล้ว โดยการดูดซับด้วยพอลิสไตรีน-โคไวนิลเบนซีนในระบบแบทช์ โดยทำการทดลองศึกษาผลของเวลาในการดูดซับ (15 30 60 และ 90 นาที) อัตราส่วนการเจือจางน้ำมัน (1:0 1:1 1:2 และ 1:3) และอุณหภูมิในการดูดซับ (35 และ 60 องศาเซลเซียส) ต่อการแยกครูดบีตา-แคโรทีน ออกจากปาล์มโอเลอินและปาล์มโอเลอินที่กำจัดกัมแล้ว จากผลการทดลอง พบว่า เวลาที่เหมาะสมในการดูดซับครูดบีตา-แคโรทีนทั้งจากปาล์มโอเลอินและปาล์มโอเลอินที่กำจัดกัมแล้ว คือ 60 นาที โดยเปอร์เซ็นต์คืนกลับของครูดบีตา-แคโรทีนจากปาล์มโอเลอินที่กำจัดกัมแล้วจะมากกว่าจากปาล์มโอเลอิน สำหรับผลของอัตราส่วนการเจือจางน้ำมัน พบว่า ที่ทุก ๆ อัตราส่วนการเจือจางน้ำมันเปอร์เซ็นต์การดูดซับจะเพิ่มขึ้นเมื่อเวลาการดูดซับเพิ่มมากขึ้น ซึ่งจะเริ่มคงที่เมื่อเวลา 60 นาที โดยเมื่ออัตราส่วนการเจือจางน้ำมันเพิ่มมากขึ้น เปอร์เซ็นต์การดูดซับและการคืนกลับจะเพิ่มมากขึ้นด้วย และเมื่อเปรียบเทียบระหว่างปาล์มโอเลอินและปาล์มโอเลอินที่กำจัดกัมแล้วที่เวลาการดูดซับ 60 นาที พบว่า มีค่าใกล้เคียงกัน ในส่วนของเปอร์เซ็นต์การปลดปล่อยครูดบีตา-แคโรทีน พบว่า ลดลงเมื่ออัตราส่วนการเจือจางน้ำมันเพิ่มมากขึ้น สำหรับผลของอุณหภูมิในการดูดซับ พบว่า เมื่ออุณหภูมิในการดูดซับเพิ่มมากขึ้น เปอร์เซ็นต์การดูดซับและการคืนกลับของครูดบีตา-แคโรทีนจะเพิ่มมากขึ้นด้วย และเมื่อเปรียบเทียบเปอร์เซ็นต์การคืนกลับของครูดบีตา-แคโรทีนระหว่างปาล์มโอเลอินและปาล์มโอเลอินที่กำจัดกัมแล้ว พบว่า มีค่าใกล้เคียงกัน โดยที่เวลาในการดูดซับ 60 นาที อุณหภูมิในการดูดซับ 60 องศาเซลเซียส จะได้เปอร์เซ็นต์การปลดปล่อยครูดบีตา-แคโรทีนจากปาล์มโอเลอินและปาล์มโอเลอินที่กำจัดกัมแล้ว คือ 28.67 และ 28.30 เปอร์เซ็นต์ ตามลำดับ จากงานวิจัย พบว่า สภาวะที่เหมาะสมสำหรับแยกครูดบีตา-แคโรทีน คือ ใช้ปาล์มโอเลอิน ทำการดูดซับที่อุณหภูมิ 35 องศาเซลเซียส เป็นเวลา 60 นาที

ภาควิชา วิศวกรรมเคมี
สาขาวิชา. วิศวกรรมเคมี
ปีการศึกษา 2549

ลายมือชื่อนิสิต รัฐไท วีระชาติเทวัญ
ลายมือชื่ออาจารย์ที่ปรึกษา จิรกานต์ เมืองนาโพธิ์

4670453821: MAJOR CHEMICAL ENGINEERING

KEY WORD : PALM OLEIN / CRUDE β -CAROTENE / SYNTHETIC POLYMER / ADSORPTION

RUTTHAI VEERACHARTTAWAN : SEPARATION OF CRUDE β -CAROTENE FROM PALM OLEIN BY ADSORPTION WITH SYNTHETIC POLYMER.
 THESIS ADVISOR : ASSOC. PROF. CHIRAKARN MUANGNAPOH, Dr.Ing.,
 67 pages.

The objective of this research was to investigate the suitable separation condition of crude β -carotene from palm olein and degummed palm olein using polystyrene-divinylbenzene (PSDVB) as adsorbent in batch system. The effects of adsorption time (15, 30 60 and 90 minutes), oil dilution (1:0, 1:1, 1:2 and 1:3 by wt.) and adsorption temperature (35 and 60 °C) on separation of crude β -carotene from palm olein and degummed palm olein were investigated to determine the suitable condition. Results shown that equilibrium adsorption time of both palm olein and degummed palm olein are at 60 minutes. The % recovery of crude β -carotene from degummed palm olein for all experiments gave higher values than palm olein. In case of oil dilution, at each oil dilutions, % adsorption of crude β -carotene increased with an increase of time until it was nearly constant at 60 minutes. The more oil was diluted, the higher % adsorption and % recovery were clearly obtained. Comparison of % adsorption and % recovery at 60 minutes from palm olein and degummed palm olein at different oil dilution, there were not significantly different from each other. % Desorption decreased as oil dilution increased. In case of adsorption temperature we found that the higher adsorption temperature, the higher % adsorption and % recovery were obtained. The results also showed that % recovery increased as adsorption temperature increased and there is not significantly different of % recovery between palm olein and degummed palm olein. % Recovery at 60 °C and 60 minutes were 28.67 % for palm olein and 28.30 % for degummed palm olein. For our work, we concluded in term of amount of β -carotene recover that the suitable condition was at 60 °C adsorption temperature for 60 minutes. Non diluted palm olein (in stead of degummed palm olein) is recommended.

Department Chemical Engineering
 Field of Study Chemical Engineering
 Academic Year 2006

Student's Signature Rutthai Veeracharttawan
 Advisor's Signature Chirakarn Muangnaphob

ACKNOWLEDGMENTS

I would like to express my earnest gratitude to my advisor, Assoc. Prof. Dr. Chirakarn Muangnapoh. for her encouragement, support, guidance, and unfailing faith all the way through my thesis work and study.

Thanks to all of my thesis committee, Assoc. Prof. Dr. Tawatchai Charinpanitkul, Assoc. Prof. Dr. Seeroong Prichanont and Dr. Sirikul Chunsawang for their kind advices and recommendations which are invaluable for improving my work.

Financial supports from the Department of Chemical Engineering, Chulalongkorn University for providing the partial scholarship for my master study is highly appreciated.

Sincere thanks are given to all members of the Biochemical Engineering Research Laboratory and all my friends and staffs in the Department of Chemical Engineering, Chulalongkorn University for their assistance, support, and warm collaborations.

Finally, I would like to express my highest gratitude to my parents for their affectionate support, blessings, inspiration, and love which guide me all the way throughout my life and study.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

CONTENTS

	Page
ABSTRACT IN THAI.....	iv
ABSTRACT IN ENGLISH.....	v
ACKNOWLEDGEMENTS.....	vi
CONTENTS.....	vii
LIST OF FIGURES.....	x
LIST OF TABLES.....	xiii
LIST OF SYMBOLS.....	xv
CHAPTER	
I Introduction.....	1
II Theoretical and Literature reviews	4
2.1 Palm oil	4
2.2 Carotenoids	4
2.2.1 The advantages of carotenoids.....	8
2.2.2 Analytical of carotenoids	10
2.3 The method of carotenoid recovery from palm oil	11
2.3.1 Adsorption.....	11
2.3.2 Gel permeation chromatography.....	11
2.3.3 Crystallization	14
2.3.4 Distillation.....	14
2.3.5 Supercritical CO ₂ extraction	15
2.3.6 Nanofiltration.....	15
2.4 Adsorption.....	16
2.4.1 Adsorbents and adsorption process	16
2.4.2 Equilibria; Adsorption Isotherms.....	17
2.5 Adsorbent.....	19
2.5.1 Activated carbon	19
2.5.2 Polystyrene-divinylbenzene (PSVDB)	20
III Materials and Method	22
3.1 Materials and chemicals.....	22

	Page
CHAPTER	
3.2 Instruments and apparatus.....	22
3.3 Experiment procedure.....	23
3.3.1 Separation of palm olein from crude palm oil.....	23
3.3.2 Preparation of adsorbent.....	23
3.3.3 Preparation of palm oil.....	23
3.3.4 Preparation of palm olein.....	23
3.3.5 Degumming investigation.....	23
3.3.6 Adsorption of crude β -carotene from palm olein on the adsorbent.....	24
3.3.7 The influence of parameters to adsorption.....	24
3.3.7.1 Effect of adsorption time.....	24
3.3.7.2 Effect of oil dilution.....	24
3.3.7.3 Effect of adsorption temperature.....	24
3.3.8 Quantitative analysis of β -carotene by UV-visible spectrometry.....	25
3.3.8.1 Adsorption maxima (λ_{\max}).....	25
3.3.8.2 Calibration Curve.....	26
3.3.9 Terminology.....	26
IV Results and Discussion	
4.1 Separation of palm olein from crude palm oil.....	27
4.2 Degumming.....	28
4.3 Effect of time on adsorption of crude β -carotene from palm olein and degummed palm olein.....	29
4.4 Effect of oil dilution on adsorption of crude β -carotene from palm olein and degummed palm olein.....	32
4.5 Effect of adsorption temperature on adsorption of crude β -carotene from palm olein and degummed palm olein.....	38
4.6 The adsorption isotherm of crude β -carotene from palm olein and degummed palm olein.....	45
4.7 Crude β -carotene recovery.....	47
V Conclusion and Suggestion.....	49

	Page
CHAPTER	
5.1 Conclusions.....	49
5.2 Recommendations.....	50
REFERENCES	51
APPENDICES	54
APPENDIX A.....	55
APPENDIX B	59
VITA.....	67



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF FIGURES

Figure	Page
2.1 Oil palm tree	4
2.2 Fresh fruit bunch	4
2.3 Fresh fruit.....	5
2.4 Structure of β -carotene	7
2.5 Adsorption isotherms	18
2.6 Structure of polystyrene-divinylbenzene (PSDVB).....	20
4.1 The gum content at various amounts of phosphoric acid	28
4.2 The concentration of crude β -carotene at various amounts of phosphoric acid.....	29
4.3 Effect of time on % adsorption of crude β -carotene from palm olein and degummed palm olein.....	30
4.4 Effect of time on % desorption of crude β -carotene from palm olein and degummed palm olein.....	31
4.5 Effect of time on % recovery of crude β -carotene from palm olein and degummed palm olein.....	32
4.6 Effect of oil dilution on % adsorption of crude β -carotene from palm olein at different adsorption time.....	33
4.7 Effect of oil dilution on % adsorption of crude β -carotene from degummed palm olein at different adsorption time.....	34
4.8 Effect of oil dilution on % adsorption of crude β -carotene from palm olein and degummed palm olein at 60 minutes.. ..	34
4.9 Effect of oil dilution on % desorption of crude β -carotene from palm olein at different adsorption time.....	35
4.10 Effect of oil dilution on % desorption of crude β -carotene from degummed palm olein at different adsorption time.....	36
4.11 Effect of oil dilution on % desorption of crude β -carotene from palm olein and degummed palm olein at 60 minutes	36
4.12 Effect of oil dilution on % recovery of crude β -carotene from palm olein at different adsorption time.....	37

Figure	Page
4.13 Effect of oil dilution on % recovery of crude β -carotene from degummed palm olein at different adsorption time	37
4.14 Effect of oil dilution on % recovery of crude β -carotene from palm olein and degummed palm olein at 60 minutes.	38
4.15 Effect of adsorption temperature on % adsorption of crude β -carotene from palm olein at different adsorption time	39
4.16 Effect of adsorption temperature on % adsorption of crude β -carotene from degummed palm olein at different adsorption time	39
4.17 Effect of adsorption temperature on % adsorption of crude β -carotene from palm olein and degummed palm olein at 60 minutes	40
4.18 Effect of adsorption temperature on % desorption of crude β -carotene from palm olein at different adsorption time	41
4.19 Effect of adsorption temperature on % desorption of crude β -carotene from degummed palm olein at different adsorption time	42
4.20 Effect of adsorption temperature on % desorption of crude β -carotene from palm olein and degummed palm olein at 60 minutes	42
4.21 Effect of adsorption temperature on % recovery of crude β -carotene from palm olein at different adsorption time	43
4.22 Effect of adsorption temperature on % recovery of crude β -carotene from degummed palm olein at different adsorption time	44
4.23 Effect of adsorption temperature on % recovery of crude β -carotene from palm olein and degummed palm olein at 60 minutes	44
4.24 Apparent adsorption isotherm of crude β -carotene from palm olein and degummed palm olein.....	45
4.25 Langmuir isotherm in its linear form for crude β -carotene from palm olein and degummed palm olein	46
A1 Calibration curve of Standard β -carotene in molar (UV-visible spectrometry)	49
A2 Calibration curve of Standard β -carotene in ppm (UV-visible spectrometry)	49
A3 UV-visible spectrum of standard β -carotene.	56
A4 UV-visible spectrum of palm olein.....	56

Figure	Page
A5 UV-visible spectrum of degummed palm olein.....	57
A6 UV-visible spectrum of crude β -carotene	57



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF TABLES

Table	Page
2.1 Fatty acid composition of palm oil and palm kernel oil	5
2.2 Minor components of crude palm oil.....	6
2.3 Carotenoids composition in palm oil	7
2.4 Retinol equivalents (RE) of red palm oil compared with other foods	8
2.5 Absorption maxima in different solvents of β -carotene	9
2.6 Physical properties of the synthetic adsorbents	21
3.1 The experimental conditions and number of experiments.....	25
4.1 % wt. and crude β -carotene of olein and stearin was separated from crude palm oil at different temperature and time.....	28
4.2 Viscosity of palm olein and degummed palm olein at different ratio of oil to Isopropanol	31
4.3 The viscosity of palm olein and degummed palm olein at different temperature.....	40
4.4 Crude β -carotene recovery of PSDVB compared with other researches.....	47
4.5 % Recovery and amount of crude β -carotene recovery from palm olein and degummed palm olein at 60 minutes	48
B1 Concentration of crude β -carotene after degumming	60
B2 The amount of gum from degumming	61
B3 % Adsorption, % desorption, % recovery of crude β -carotene and adsorption ability of PSDVB at 35 °C adsorption temperature, different adsorption time and ratio of palm olein to isopropanol was 1:0.....	61
B4 % Adsorption, % desorption, % recovery of crude β -carotene and adsorption ability of PSDVB at 35 °C adsorption temperature, different adsorption time and ratio of palm olein to isopropanol was 1:1	62
B5 % Adsorption, % desorption, % recovery of crude β -carotene and adsorption ability of PSDVB at 35 °C adsorption temperature, different adsorption time and ratio of palm olein to isopropanol was 1:2.....	62
B6 % Adsorption, % desorption, % recovery of crude β -carotene and adsorption ability of PSDVB at 35 °C adsorption temperature, different adsorption time and ratio of palm olein to isopropanol was 1:3.....	63

Table	Page
B7 % Adsorption, % desorption % recovery of crude β -carotene and adsorption ability of PSDVB at 35 °C adsorption temperature, different adsorption time and ratio of degummed palm olein to isopropanol was 1:0	63
B8 % Adsorption, % desorption, % recovery of crude β -carotene and adsorption ability of PSDVB at 35 °C adsorption temperature, different adsorption time and ratio of degummed palm olein to isopropanol was 1:1	64
B9 % Adsorption, % desorption, % recovery of crude β -carotene and adsorption ability of PSDVB at 35 °C adsorption temperature, different adsorption time and ratio of degummed palm olein to isopropanol was 1:2	64
B10 % Adsorption, % desorption, % recovery of crude β -carotene and adsorption ability of PSDVB at 35 °C adsorption temperature, different adsorption time and ratio of degummed palm olein to isopropanol was 1:3	65
B11 % Adsorption, % desorption, % recovery of crude β -carotene from palm olein and adsorption ability of PSDVB at 60 °C adsorption temperature and different adsorption time	65
B12 % Adsorption, % desorption, % recovery of crude β -carotene from degummed palm olein and adsorption ability of PSDVB at 60 °C adsorption temperature and different adsorption time	66

LIST OF SYMBOLS

β	Beta
λ_{\max}	Adsorption maxima
$^{\circ}\text{C}$	Degree Celsius
%	Percentage
UV	Ultraviolet
min.	Minute (s)
h	hour (s)
ml	Milliliter (s)
mg	milligram (s)
g	gram (s)
nm	Nanometer
ppm	Parts per million
rpm	Round per minute
wt.	weight
temp.	Temperature
CPO	Crude palm oil
PSVDB	Polystyrene-divinylbenzene
IPA	Isopropanol
THF	Tetrahydrofuran
Oil	Palm olein or Degummed palm olein

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Chapter I

Introduction

Due to the increase in the price of the petroleum based fuel, renewable energy sources are being considered seriously in Thailand. Biodiesel is promoted as a form of renewable energy that greatly reduces net emissions of carbon dioxide, oxide of nitrogen, and sulfur dioxide into the atmosphere. Therefore its use is being touted as a way to decrease the impact of the greenhouse effect and also the possibility of peak oil. In Thailand, feedstocks that have potential for biodiesel production are vegetable oil [1], such as: palm oil, coconut oil, soy bean oil, ground nut oil, castor oil, sesame oil, sunflower oil and jatropha oil.

The main feedstock for biodiesel production in Thailand is palm oil due to its lower production costs and being major marketing crop than the others.

The oil palm tree (*Elaeis guineensis*) originated from West Africa where it was growing wild and later developed into an agricultural crop. They are used in the production of edible palm oil. In its virgin form, the oil is bright orange-red due to the high content of carotene. Palm oil is nature's richest source of carotenoids as compared to the other vegetable oils, i.e. 15 times more than carrots, and 30 times more than tomatoes. The commercial palm oil contains about 500-700 ppm of carotenes of which alpha- and beta-carotene formed up to 91% of total carotenes. The β -carotene is a precursor of vitamin A. These are also widely used for applications in food, pharmaceutical and nutritional products. Moreover, the carotenes are also shown to inhibit tumor growth and associated with the prevention of cancer formation such as oral, pharyngeal, lung and stomach cancer [2, 3].

By the cabinet resolution in 2004 [4], there was a target on use biodiesel about 600,000 tons/year in 2011, so 300-420 tons/year of carotenes which are nutritional benefits remain available only in the palm oil, are discarded. If recovered, the value of carotene concentrated would be a chance of income. Various methods of carotenes recovery from palm oil have been reported. These include selective solvent extraction [5, 6], gel permeation chromatography [7], crystallization [8], supercritical CO₂ [9], nanofiltration [10] and transesterification, followed by both phase separation and distillation of ester [11-

12]. But these methods are not success for a commercial process due to inefficient, high production cost and high energy consumption.

Beside of those separation methods, adsorption is an interesting separation process which is simple and lower energy consumption. Adsorption process is widely used in industrial applications, especially for decolorization and deodorization. There were many studies about carotenes recovery from both crude palm oil and palm oil ester by adsorption process [13-22]. Good carotenes recovery comes from compatibility between carotenes and adsorbent. Many researchers have investigated adsorption and desorption ability using different kind of adsorbents, such as: bleaching earth, silica gel, alumina and activated carbon [17-22]. Only activated carbon was better performance than the others. However, toluene solution used in desorption carotene from activated carbon is harmful to human being and environment [17, 20].

Recently, highly porous polymeric adsorbent series are good to separate carotenes due to its larger surface area and pore radius than activated carbon [13-16, 18]. Hexane solution used in desorption carotene from these resins are less harmful than toluene and it is easily separated from oil phase by evaporation [13-16, 19]. Higher crude β -carotene recovery from palm oil using polymeric adsorbent is another advantage over activated carbon. The reason proposed by some researcher showed, by UV spectrum, that the oxidation of β -carotene on activated carbon surface would change the form of β -carotene and gave less recovery. [20, 23]

Crude palm oil (CPO) composes of two major compositions (olein and stearin) which appears in two phase co-exist at room temperature. At higher temperature CPO will be turn to single phase which is easier to manipulate but carotene separation became lower due to degradation of carotene [20]. Natural gum presented in crude palm oil may also have impact to carotene adsorption. From our reviews, there are not any reports shown about this aspect. Therefore, the objective of this study is to investigate the effect of gum on crude β -carotene recovery from palm olein and degummed palm olein using polystyrene-divinylbenzene (PSDVB) as an adsorbent in adsorption process.

1.1 Objective

To investigate the effect of gum on crude β -carotene recovery from palm olein and degummed palm olein using polystyrene-divinylbenzene (PSDVB) as an adsorbent in adsorption process.

1.2 Scope

1. Adsorbate is crude β -carotene in palm olein and degummed palm olein.
2. Adsorbent is polystyrene-divinylbenzene (PSDVB). Ratio of adsorbent to oil is fixed at 1:3 by wt.
3. Investigate the effect of gum on crude β -carotene adsorption in term of recovery at 2 adsorption temperatures, 4 different adsorption times and 4 different oil dilutions.
4. Desorption solvent is hexane.

1.3 Procedure

1. Prepare palm olein and degummed palm olein.
2. Prepare PSDVB by treated with isopropanol and dried at room temperature.
3. Do the experiment at different conditions.
4. Compare the experimental results from palm olein and degummed palm oil in term of adsorption, desorption and recovery.
5. Make discussion, conclusion and prepare thesis.

1.4 Benefits

Suitable condition for crude β -carotene separation from palm olein will be obtained.

Chapter II

Theoretical and Literatures Review

2.1 Palm oil

The oil palm *Elaeis guineensis* originated in West Africa (see figure 2.1-2.2). It produces two types of oils; crude palm oil from the fibrous mesocarp and crude palm kernel oil from the kernels (see figure 2.3). Although both oils originate from the same fruit, palm oil is chemically and nutritionally different from palm kernel oil (see table 2.1) [24]. It is one of the only two mesocarp oils available commercially, the other being olive oil.



Figure 2.1 Oil palm tree



Figure 2.2 Fresh fruit bunch

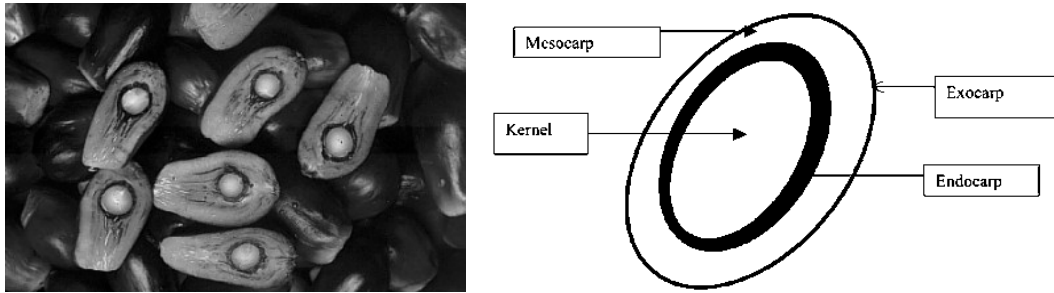


Figure 2.3 Fresh fruit

In conventional milling process, the fresh fruit are sterilized and the fruitlets stripped off. The loose fruitlets are then digested and pressed to extract the Crude palm oil. The kernels are separated from the fibrous mesocarp in the press cake and later cracked to obtain crude palm kernel oil.

Crude palm oil has a naturally semi solid characteristic at room temperature. It is deep orange red in color due to the high content of natural carotenes. Crude palm oil has a balanced ratio of unsaturated and saturated fatty acids. It contains 40% oleic acid (monounsaturated fatty acid), 10% linoleic acid (polyunsaturated fatty acid), 45% palmitic acid and 5% stearic acid (saturated fatty acid). This composition results in an edible oil that is suitable for use in a variety of food applications [2].

Table 2.1 Fatty acid composition of palm oil and palm kernel oil [24]

Acid	% of total acids	
	palm oil	palm kernel oil
Saturated		
Lauric	48.2	-
Myristic	16.2	1.0
Palmitic	8.4	44.3
Capric	3.4	-
Caprylic	3.3	-
Stearic	2.5	4.6
Monounsaturated		
Oleic	15.3	38.7
Polyunsaturated		
Linoleic	2.3	10.5

Crude palm oil is rich in natural chemical compounds important for health and nutrition. Approximately 1% of minor components contain carotenoids, vitamin E (tocopherols and tocotrienols), sterols, phospholipids, glycolipids, terpenic and aliphatic hydrocarbons, and other trace impurities (see table 2.2). The most important are carotenoids and vitamin E, both of which possess important physiological properties.

Table 2.2 Minor components of crude palm oil [2]

components	ppm
Carotenoids	500-700
Tocopherol and tocotrienols	600-1,000
Sterols	326-527
Phospholipids	5-130
Triterpene alcohol	40-80
Methyl sterols	40-80
Squalene	200-500
Aliphatic alcohols	100-200
Aliphatic hydrocarbon	50

2.2 Carotenoids

Carotenoids are a group of more than 700 compounds (e.g. alpha-carotene, beta-carotene) that produce the red, yellow, and orange colors found in many fruits and vegetables. The carotenoids pigment found largely in plants with chlorophyll are polyenes belonging to four principle groups given below [22]

1. The carotene, $C_{40}H_{56}$, which include α -carotene, β -carotene, γ -carotene and lycopenes (see figure 2.4).
2. The xanthophylls and oxo and hydroxy derivatives of carotenes which included among others, cryptoxanthin, and lutein
3. The xanthophylls esters, which are esters of xanthophylls with fatty acid.
4. The carotenoids, which are carboxyl derivatives of the carotenes.

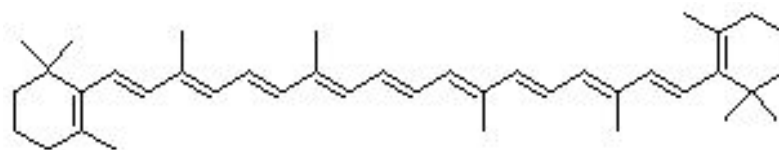


Figure 2.4 Structure of β -carotene

Crude palm oil is considered the richest natural source of carotenoids. The carotenoid content of crude palm oils varies between 500 and 700 ppm, the compounds contained within this portion of saponifiables contain α -carotene, β -carotene, γ -carotene, xanthophylls and lycopene. 91% of the fractions are α -carotene and β -carotene while the other components are represented more or less equally (see table 2.3).

Table 2.3 Carotenoids composition in palm oil

Compound	Quantity (%)
β -carotene	62
α -carotene	29
γ -carotene	4
Xanthophylls	3
Lycopene	2

Carotenes are the precursors of vitamin A, with β -carotene having the high provitamin A activity. Palm oil has the highest carotene-derived vitamin A activity. This is primarily due to β -carotene and secondarily, to α -carotene. For example, red palm oil has 15 times more vitamin A activity than carrots and 300 times more than tomatoes. Retinol equivalent of red palm oil compared with other foods, are illustrated in table 2.4.

Table 2.4 Retinol equivalents (RE) of red palm oil compared with other foods [2]

Fruits and vegetables	Retinol equivalents (RE ^a)	Relative quality ^b (< RPO)
Red palm oil	30,000	-
Carrots	2,000	15
Leafy vegetables	685	44
Apricots	250	120
Tomatoes	100	300
Bananas	30	1,000
Orange juice	8	3,750

a. Per 100 B edible portion (μg).

b. Times greater or less than red palm oil (RPO).

2.2.1 The advantages of carotenoids

There are many advantages of carotenoids given below [25]

- *Direct use in food coloration*

The main use of carotenoids is for the direct coloration of food. Natural extracts are used, but the major market is for synthetic carotenoids in either oil-based or water-dispersible formulation. β -carotene and 8-*apo*- β -carotene-8-*al* are the main carotenoids used in oil suspensions and solutions, and can provide yellow-orange and orange-red colors, respectively, depending on concentration. The solubility of canthaxanthin in triglyceride oils is too low for practical application. Although lycopene shows good coloration properties, its poor solubility and stability present serious difficulties for its practical application. The oil-based preparations, especially of β -carotene, are widely used for coloring butter, margarine, cheese, cooking fats, industrial egg products, bakery products, pasta, salad dressing, dairy product substitutes, pop-corn, potato products and many others. Water-dispersible forms of β -carotene, 8-*apo*- β -carotene-8-*al* canthaxanthin, and the water-soluble (norbixin) forms of annatto, are used extensively for coloring soft drinks (especially “orange juice”), ice-cream, desserts, sweets, soups and meat product.

- *Animal feeds*

Feeds for cattle, birds and fish will be considered

- Cattle

Natural pasture is very rich in β -carotene and provides sufficient of this compound to full fill the vitamin A requirement of the animals and also to give a desirable yellow color to the fat and rich cream color to cream and butter. Artificial diets must be supplemented with β -carotene to ensure adequate vitamin A levels and to maintain the required yellow color or dairy products and fat.

- Bird

Many ornamental birds owe their exotic yellow and red colors to the presence of carotenoids in the feathers. Adequate dietary supplied of carotenoid therefore need to be maintained in captive birds. A well-known example is the flamingo, which needs to be provided with substantial quantities of the oxocarotenoids that the wild birds obtain from their diet of crustaceans; otherwise the characteristic deep pink color is lost. Of far greater commercial importance is the poultry industry. Chicken adsorb and accumulate xanthophylls rather than carotenes and need substantial supplies of xanthophylls rather than carotenes and need substantial supplies of xanthophylls to ensure the required golden-yellow color of the egg yolk and also the yellow skin color demanded in many countries. The apocarotenoids and canthaxanthin can be used for yolk coloration, but the most natural colors of yolk and included in the diet in some countries.

- Fish

With the recent rapid development of farming methods for salmon and trout, it is essential that the products should have the same desired pink flesh coloration as the wild fish. This is now attained by the inclusion of astaxanthin (salmon) or canthaxanthin (trout) in the diet for several weeks before harvesting.

- *Medical and health products*

The beneficial role of β -carotene as provitamin A has long been known. β -Carotene is also now used successfully to alleviate the symptoms of light-sensitivity disease, especially erythropoietic protoporphyria, that are characterized by extreme irritation of the skin when exposed to strong light, because of the formation of singlet oxygen sensitized by the free porphyrins that accumulate in this condition. β -Carotene, administered at a high level (around 180 mg/day), is deposited in the skin and then quenches the triplet state of the sensitizer and prevents formation of singlet oxygen.

β -Carotene may be a useful antioxidant that can afford protection against cancer and other diseases have led to the appearance of a great number of β -carotene preparations on the health market, including crystalline carotene, extracts of natural sources such as carrots and algae, carotene drinks and even dried algal cells (*Dunaliella*). There seems little doubt that the demand for β -carotene and perhaps other carotenoids as beneficial health products will increase. Carotenoids are also used simply for coloration purposes in health products such as pills, capsules and suppositories.

2.2.2 Analytical of carotenoids

For UV-visible spectroscopy is the basic method used as a first identification criterion for carotenoids. Both the position of the absorption maxima (λ_{\max}) and the shape or fine structure of the spectrum are characteristic of the chromophore of the carotenoid molecule. A key feature of carotenoids is their long system of conjugated double bonds on their hydrocarbon “backbone”. These conjugated double bonds give rise to the yellow or red carotenoid color. Mostly, carotenoids exhibit three distinct absorption maxima between 400 and 500 nm which have been listed in Table 2.5. Usually, the carotenoid double bonds are in all-trans position, however, cis-isomers of individual carotenoids are also known. The adsorption spectra of the carotenoids are very much dependent on the solvent [26].

Table 2.5 Absorption maxima in different solvents of β -carotene [26]

Solvent	λ_{\max} (nm)
Acetone	428, 452, 477
Benzene	463, 492
Carbon disulfide	450, 485, 520
Chloroform	463, 493
Cyclohexane	457, 485
Ethanol	426, 451, 478
Hexane	425, 450, 478
Petroleum ether	426, 451, 477

2.3 The method of carotenoid recovery from palm oil

There are various methods of carotenoid recovery from palm oil have been reported, are the followings;

2.3.1 Adsorption

Barharin *et al.* [13] were desirable to develop a separation technique for carotene extraction from crude palm oil by adsorption chromatography with a synthetic polymer adsorbent. The adsorbent include HP-20 (styrene-divinyl benzene copolymer), alumina, and silica gel. The initial solvent was isopropanol and the second was n-hexane. The results show that the maximum adsorption capacity of HP-20 was about 10 times that of the other adsorbents. Carotene was concentrated to about 10^5 ppm solution, which is about 160 times the original concentration in crude palm oil. Carotene recovery varied from 40 to 65% depending upon chromatographic condition. The carotene composition was also almost the same as that in palm oil.

Latip *et al.* [14] studied different types of synthetic adsorbents, combinations of adsorbents, and adsorbent/crude palm oil (CPO) ratios for carotene extraction from CPO. The adsorbents include synthetic highly porous resin (HP 20), synthetic porous resins (SP 850, SP 825, and SP 207), and synthetic adsorbents (Relite Exa 31, Relite Exa 32, and Relite Exa 50). The results show that carotene was concentrated to about 15,000 ppm, which is about 25 times the original concentration in CPO. Carotene recovery varied from 30 to 62% depending on the process condition. SP 850 gave the highest percentage of carotene extracted compared to other adsorbents. Combinations of HP 20 and SP 850 slightly increased the percentage of carotene extracted. An adsorbent/CPO ratio of 4 was most suitable for this process for optimal recovery and concentration of carotene.

Latip *et al.* [15] studied effect of the adsorption times, isopropanol (IPA) extraction times, temperatures of the adsorption and solvent extraction processes (agitation during IPA extraction and adsorbent lifespan) on the percentage of carotene extracted from crude palm oil. The adsorbent in this experiment was HP-20 (styrene-divinyl benzene copolymer). The results show that carotene was concentrated to about 20,000 ppm or about 33.3 times the original concentration in CPO. Carotene recovery varied from 16 to 74% depending on the process conditions. The minimum adsorption time required was 0.5 h. However, an adsorption time of 1.5 h gave a significantly higher carotene concentration than adsorption times of 0.5, 1.0, and 2.0 h. The suitable temperature for adsorption and solvent extraction process was 40 °C. There was no significant difference in the percentage

of carotene extracted and carotene concentration between the IPA extraction process with and without agitation.

Barharin *et al.* [16] studied the effect of carotene extraction system on crude palm oil (CPO) quality, carotene composition, and carotene stability during storage. The adsorbent in this experiment was HP-20 (styrene-divinyl benzene copolymer). Evaluation of feed CPO and CPO which underwent the carotene extraction process was conducted. The quality of CPO after the extraction process was slightly deterioration in terms of free fatty acid, moisture content, impurities, peroxide value, anisidine value, discriminant function, and deterioration of bleach ability index. However, the CPO still can be refined to produce refined, bleached, deodorized palm oil that meets the Palm Oil Refiners Association of Malaysia specifications. No extra cost was incurred by refining this CPO as the dosage of bleaching earth used was vary similar to the refining of standard CPO. The triglyceride carbon number and fatty acid composition of CPO after going through the carotene extraction process were almost the same as CPO data. The major components of the carotene fraction were similar to CPO, which contains mainly α - and β - carotene. The carotene could be stored for at least 3 months.

Hussein *et al.* [17] studied kaolin-carbon adsorbents for carotene removal of red palm oil. The adsorbents were prepared with and without sulfuric acid pretreatment followed by activation-carbonization at 500 °C. The mixture of red palm oil and adsorbent was stirred for 40 minutes at room temperature. The adsorbent was extracted with soaking in toluene for 40 minutes. The results show that a maximum removal of carotene from red palm oil was obtained at 20% kaolin loading for both adsorbents were prepared with and without sulfuric acid pretreatment with about 45 and 65% carotene removal, respectively. About 3-4% of carotene adsorbed could be recovered from both types of adsorbents under optimum condition, in which the percentage recovered decreased with the increase in kaolin loading.

Thangwongjathroengit [20] studied extraction of β -carotene from palm oil using activated carbon in the batch and column system. The result show that the optimum condition in the batch system for carotene adsorption was carried out by using activated carbon treated with antioxidant at a ration of 1:4 by weight of palm oil to activated carbon, at 80 °C for 30 minutes. The suitable condition for elution was carried out 25 °C by using toluene as an eluent which yield 30%. In the 3 column system, the condition was carried out by using activated carbon treated with antioxidant at a ratio of 3:4 by weight of palm oil to activated carbon, 40 °C adsorption temperature and 25 °C elution temperature, 1.0

ml/min flow rate, and toluene as an eluent. The recovery yield was 60% with 61% adsorption and 98% elution.

Poopunpanich [21] studied the separation of carotenoids from palm oil was carried out by adsorption on six types of Thai clays. The clays include bentonite, diatomite, talcum, china clay (Lampang), china clay (Ranong), and ball clay. The efficiencies of acid activated clays, ion exchanged clays, adsorption temperature, ratio of clay to palm oil, adsorption time and types of eluting solvents were investigated to determine the effect on the percentage of β -carotene adsorption and β -carotene recovery, respectively. The results show that the optimum conditions for β -carotene adsorption on clays were carried out by using acid activated bentonite which was treated with antioxidant at a ration of 1:5 by weight of clay to palm oil, at 70 °C for 70 minutes could adsorb 99.78% β -carotene. The suitable condition for β -carotene desorption from clay was carried out at room temperature by using tetrahydrofuran as an eluting solvent resulted in 73.73% desorption. Overall β -carotene recovery from crude palm oil correspond to 73.56% by weight of carotenoids in crude palm oil.

Dechfoong [22] studied the separation of carotenoids from palm oil using Ag-treated clays. In this experiment, clays were bentonites originated from China and Japan. The Ag-treated clays were prepared at different Ag types and content in various forms (Ag^+ form, AgO form, AgCl form and Ag^0 form). The type of Ag-treated clays, adsorption time, ratio of clay to palm oil, type of eluting and desorption temperature were investigated to determine the optimum condition. The results show that the optimum condition for carotene adsorption on 0.5% AgCl-treated bentonite from China (2-steps) which was treated with antioxidant (BHT) at a ratio of 1:5 by weight of clay to palm oil, at 60 °C for 60 minutes could adsorb 86.82% carotene. The suitable condition for carotene desorption from clay was carried out at room temperature by using tetrahydrofuran as an eluting solvent resulted in 75.76% desorption. Overall carotene recovery from crude palm oil corresponds to 65.77% by weight of carotenoids in crude palm oil.

2.3.2 Gel permeation chromatography

Kunst *et al.* [6] showed preparation of concentrates of coloring agents such as carotene. A gel permeation chromatography column having a diameter of 25 mm. and fitted with a heating jacket was used. The column was packed with 75 g. resins which had been preswollen in ethyl acetate giving a column height of 50 cm. The resin was a

polystyrene polymer with divinylbenzene crosslinkages. The column was heated to 60 °C and 12 g. sample of a 1:1 mixture of ethyl acetate and crude palm oil was loaded on top of the column. The column was eluted with ethyl acetate at a linear flow rate of 0.65 cm/min. The crude palm oil was mainly in the form of tri-, di- and monoglycerides but also contains a number of minor ingredients including from 500 to 1000 ppm carotene. The eluted fraction contained 90% of the total carotenes. The ethyl acetate was removed from this fraction by distillation to yield a solution of at least 0.5%

2.3.3 Crystallization

Khachick [7] disclosed a process for purification of a mixture of carotenoids from palm oil, comprising, dissolving the palm oil which contains 2-30 wt% carotenes in an organic solvent such as tetrahydrofuran, tert-butylmethyl ester or similar ethers. First, saponifying the organic solution with about 10% potassium or sodium hydroxide in methanol or ethanol, and the separated carotenes are washed with an alcohol to obtain crystallized carotenes having a purity of about 49-55%. Then, crystallized carotenes are recrystallized from a mixture of organic solvent (acetone, tetrahydrofuran, chloroform, dichloromethane or 1, 2-dichloroethane) and an alcohol at low temperature (-15, -40 °C or lower) to obtain a crystalline mixture of carotenes having about 76-80% purity, and further subjecting the crystalline mixture of carotenes to a second recrystallization with a mixture of acetone and an alcohol to increase the purity of carotenes to 93% or greater.

2.3.4 Distillation

Nitsche *et al.* [12] showed the process for recovery of carotene from palm oil in five process steps in an economic industrial process. The process began with transesterifying the oil with an alkanol having up to 4 carbon atoms to form fatty acid alkyl ester and glycerol. The ester phase is subjected to distillation to remove the fatty acid alkyl ester. The distillation residue obtained in the second process step is saponified with alkali metal hydroxide. Carotene is extracted from the product obtained in the third process step and the extract phase is concentrated by evaporation. A yield of carotene at least about 80% is achieved.

Keat *et al.* [11] showed a process for the recovery of carotenes and the production of carotene concentrates from palm oil. 200 parts by weight of crude palm oil having a concentration of carotene of 645 ppm was transesterified with 79-120 parts by weight methanol and 0.5-1.0 parts by weight base catalyst. After, the ester was separated from the

glycerol, and washed with water until the washing was neutral. The ester was then dried using drying agents or vacuum. The dried ester was still orange red in color and had a carotene content of 700 ppm. 200 parts by weight of dried ester was then added with 20 parts by weight of refined and deodorized (RD) red palm oil. The resulting mixture was then passed through a vacuum distillation column at a pressure of 0.020-0.025 torr and a temperature of 90 °C. The concentration of carotene in the concentrate obtained after the distillation was 6570 ppm.

2.3.5 Supercritical CO₂ extraction

Chuang and Brunner [9] studied the enrichment of minor constituents from crude palm oil with supercritical CO₂. The beginning material is crude palm oil, which has a concentration of free fatty acid up to 4%, 600 ppm tocochromanols and 500 ppm carotene. The free fatty acid was first separated, and the crude palm oil was then transesterified to fatty ester methyl esters with methanol using base catalyst. Afterwards, the glycerol was separated and the product was washed with water to remove catalyst and methanol. In a pilot counter-current extraction apparatus, which was built according to the mixer-settler principle, fatty acid methyl esters were extracted at 60 °C and 140 bars. The apparatus was operated with a CO₂ flow rate of 20 kg/h. With three steps of extraction, an enrichment of 200-fold for carotenoids and 100-fold for tocochromanols was found.

2.3.6 Nanofiltration

Darnako and Cheryan [10] studied a novel approach for recovering carotenoids from red palm oil using membrane technology. Red palm oil is first transesterified to produce red palm methyl ester (RPME). Since the carotenes have an average M.W. of approximately 536, they fall into the pore size range of nanofiltration membranes. The results show that flux with a model RPME solution ranged from 0.5-10 Lm⁻²h⁻¹, and rejection of β-carotene was 60-80% at a transmembrane pressure of 2.7 MPa and 40 °C. A multistage membrane process was designed for continuous production of palm carotene concentrate and decolorized methyl esters. With a feed rate of 10 tons per hour of RPME containing 0.5 gL⁻¹β-carotene, the process could produce 3611 Lh⁻¹ of carotene concentrate containing 1.19 gL⁻¹carotene and 7500 Lh⁻¹ of decolorized methyl esters containing less than 0.gL⁻¹β-carotene.

2.4 Adsorption

Adsorption is a process that occurs when a gas or liquid or solute (called adsorbate) accumulates on the surface of a solid or more rarely a liquid (adsorbent), forming a molecular or atomic film (adsorbate). It is different from absorption, where a substance diffuses into a liquid or solid to form a "solution". The term *sorption* encompasses both processes, while desorption is the reverse process.

Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Adsorption, ion exchange and chromatography are sorption processes in which certain adsorptive are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column.

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favorable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption [27-28].

2.4.1 Adsorbents and adsorption process [27]

Most adsorbents are highly porous materials, and adsorption takes place primarily on the walls of the pores or at specific sites inside the particle. Because the pores are generally very small, the internal surface area is orders of magnitude greater than the external area and is often 500 to 1,000 m²/g. Separation occurs because differences in molecular weight, shape, or polarity cause some molecules to be held more strongly on the surface than others or because the pores are too small to admit the larger molecules. In many cases, the adsorbing component (or adsorbate) is held strongly enough to permit complete removal of that component from the fluid with very little adsorption of other components. Regeneration of the adsorbent can then be carried out to obtain the adsorbate in concentrated or nearly pure form.

Adsorption from the liquid phase is used to remove organic components from drinking water or aqueous wastes, colored impurities from sugar solutions and vegetable oils, and water from organic liquids. Adsorption can also be used to recover reaction products that are not easily separated by distillation or crystallization. Some of the same

types of solids are used for both vapor-phase and liquid-phase adsorption, though often adsorbents with larger pores are preferred for use with liquids.

2.4.2 Equilibria; Adsorption Isotherms

The adsorption isotherm is the equilibrium relationship between the concentration in the fluid phase and the concentration in the adsorbent particles at a given temperature. For gases, the concentration is usually given in mole percent or as a partial pressure. For liquid, the concentration is often expressed in mass units, such as mg/L (ppm) or $\mu\text{g/L}$ (ppb). The concentration of adsorbate on the solid is given as mass adsorbed per unit mass of original adsorbent

Some typical isotherm shapes are shown as arithmetic graphs in Figure 2.5. The *linear isotherm* goes through the origin, and the amount adsorbed is proportional to the concentration in the fluid. Isotherms that are convex upward are called *favorable*, because a relatively high solid loading can be obtained at low concentration in the fluid. The Langmuir isotherm is given by the relation;

$$W = W_{\max} \left[\frac{K * C}{1 + (K * C)} \right]$$

Where

W	is	the adsorbate loading
C	is	the concentration in the fluid
K	is	the adsorption constant

This isotherm is of the favorable type. When K is large and $K * C \gg 1$, the isotherm is strongly favorable; and when $K * C < 1$, the isotherm is nearly linear. The Langmuir isotherm is derived assuming a uniform surface (not a valid assumption) but the relation works fairly well for gases that are weakly adsorbed. For strongly favorable isotherms the empirical Freundlich equation;

$$W = b * C^m$$

Where

W	is	the adsorbate loading
C	is	the concentration in the fluid
b, m	are	the constants (and $m < 1$)

The empirical Freundlich equation is often a better fit, particularly for adsorption from liquids.

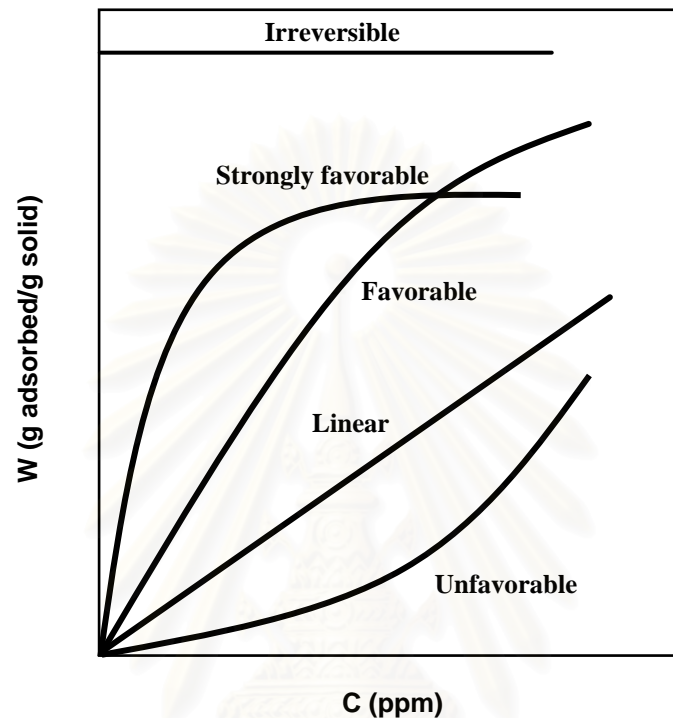


Figure 2.5 Adsorption isotherms

The limiting case of a very favorable isotherm is *irreversible adsorption*, where the amount adsorbed is independent of concentration down to very low values. All systems show a decrease in the amount adsorbed with an increase in temperature, and of course adsorbate can be removed by raising the temperature even for the cases labeled “irreversible”. However, desorption requires a much higher temperature when the adsorption is strongly favorable or irreversible than when the isotherms are linear.

An isotherm that is concave upward is called *unfavorable* because relatively low solid loadings are obtained and because it leads to quite long mass-transfer zones in the bed. Isotherms of this shape are rare, but they are worth studying to help understand the regeneration process. If the adsorption is favorable, mass transfer from the solid back to the fluid phase has characteristics similar to those for adsorption with an unfavorable isotherm.

2.5 Adsorbent

The adsorbents are used usually in the form of spherical pellets, rods, moldings or monoliths with hydrodynamic diameter between 0.5 and 10 mm. They must have high abrasion resistance, high thermal stability and small micropore diameter, which results in higher exposed surface area and hence high capacity of adsorption. The adsorbents must also have a distinct macropore structure which enables fast transport of the gaseous vapors. Different types of industrial adsorbents used are:

- Oxygen-containing compounds (hydrophilic/polar) such as silica gel and hydrophilic zeolites.
- Carbon-based compounds (hydrophobic/non-polar) such as activated carbon.
- Polymer-based compounds (polar/non-polar) functional groups in porous polymer matrix.

2.5.1 Activated carbon

Activated carbon is highly porous, amorphous solids consisting of microcrystallites with a graphite lattice. They are non-polar and cheap. One of their main drawbacks is that they are combustible.

Activated carbon can be manufactured from carbonaceous material, including coal (bituminous, subbituminous, and lignite), peat, wood, or nutshells (i.e., coconut). The manufacturing process consists of two phases, carbonization and activation. The carbonization process includes drying and then heating to separate by-products, including tars and other hydrocarbons, from the raw material, as well as to drive off any gases generated. The carbonization process is completed by heating the material at 400–600 °C in an oxygen-deficient atmosphere that cannot support combustion.

The unique surface property of activated carbon, in contrast to the other major sorbent, is that its surface is nonpolar or only slightly polar as a result of the surface oxide groups and inorganic impurities. This unique property gives activated carbon the following advantages [29]:

- It is the only commercial sorbent used to perform separation and purification processes without requiring prior stringent moisture removal.
- Because of its large, accessible internal surface and pore volume, it adsorbs more nonpolar and weakly polar organic molecules than other sorbents do.

- The heat of adsorption, or bond strength, is generally lower on activated carbon than on other sorbents. This is because only non-specific; van der Waals forces are available as the main forces for adsorption. Consequently, stripping of the adsorbed molecules is relatively easier and results in relatively lower energy requirements for regeneration of the sorbent.

2.5.2 Polystyrene-divinylbenzene (PSDVB) [29]

A broad range of synthetic, non-ionic polymer is available for use as sorbents, ion exchange and chromatographic column packing. Styrene and divinylbenzene react together to form the copolymer styrene-divinylbenzene (see figure 2.6). It acts as a cross-linking agent in ion exchange polymers. Over the years, these PSDVB has been produced with a wide range of porosities and macropore sizes.

The macroporous polymeric resins can be further reacted to attach functional groups to the benzene rings to generate functionalities for ion exchange. The resulting polymers are ion exchange resins.

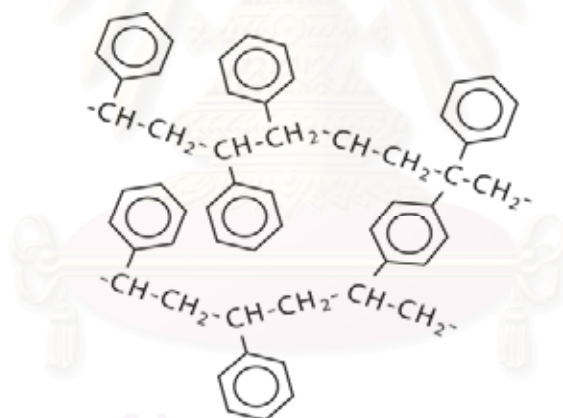


Figure 2.6 Structure of polystyrene-divinylbenzene (PSDVB)

The advantages and applications of polymeric resin given below,

- Carbonaceous polymeric sorbents have been developed by partially pyrolyzing the PSDVB and their sulfonated forms. These sorbents are particularly of interest for water purification because they have shown 5 to 10 times the capacity of granulated activated carbon (GAC) for low concentrations of some volatile organic compounds.

- Polymeric resins have been widely used for water treatment as well as other applications. More recently, there has been a surge in applications designed to remove organic compounds from water. The main advantage of polymeric resins lies in its ease of regeneration. An additional advantage is that the resins can be tailored for special

applications such as that in the pharmaceutical and semiconductor industries. The major use for both polymeric sorbents and ion exchange resins involves water treatment.

- The polymer resins are in the form of spherical beads, usually in the size range of 20-60 mesh. Each spherical bead consists of an agglomeration of a large number of very small “microspheres”. These microspheres are clusters of microgel particles ranging in size between 0.01 to 15 μm . Thus, the pore structure is comprised of inter-microsphere mesopores and the micropores within the microspheres. The latter depends directly on the degree of cross-linking, i.e., the amount DVB. Most of the resins have 5-20% cross-linking; although resins with a very high degree of cross-linking are also available. Cross-linking provides the high surface area as well as rigidity and mechanical strength.

- For a target solute from the aqueous solution, a resin with high selectivity is obtained by a special functionality that is attached on the surfaces of the resin. A number of selective resins designed for special applications are available. High purity and selective resins are being used for potable water purification as well as by the food and pharmaceutical industries, for example, for purification of antibiotics and vitamins, recovery of products from fermentation, and purification of food products.

The general properties of some representative commercial PSDVB are given in table 2.6 [14].

Table 2.6 Physical properties of the synthetic adsorbents

Synthetic adsorbent	Physical properties		
	Pore volume (mL/g)	Pore radius (\AA)	Surface area (m^2/g)
HP 20 ^a	1.30	260	511
SP 850 ^a	1.20	38	995
SP 825 ^a	1.39	57	977
SP 207 ^a	1.08	105	627
Relite Exa 31 ^b	1.20	175	470
Relite Exa 32 ^b	1.30	250	600
Relite Exa 50 ^b	1.40	70	950

a. Manufactured by Mitsubishi Chemical Corporation (Tokyo, Japan).

b. Manufactured by Resindion (Milano, Italy).

Chapter III

Materials and Methods

3.1 Materials and chemicals

1. Crude palm oil was supplied from Patum Vegetable Oil Co.,Ltd.
2. Polystyrene-divinylbenzene (PSDVB)
Sigma-Aldrich, USA
3. Standard β -carotene
Analytical grade; Sigma-Aldrich, USA
4. n-Hexane
Analytical grade; Fisher Scientific, UK
5. Isopropanol (IPA)
Analytical grade; Fisher Scientific, UK
6. Phosphoric acid (85%)
Analytical grade; Riedel-de Haën, Germany

3.2 Instruments and apparatus

1. UV-visible spectrophotometer
SHIMADZU UV 2450, Japan
2. Centrifuge
KUBOTA 7820, Japan
3. Incubator shaker
INNOVA 4000, UK
4. Vacuum oven
BINDER VD 23, Germany
5. Vacuum pump
EYELA ASPIRATOR A-3S, Japan
6. Magnetic stirrer
IKA, Germany
7. Viscometer
CANNON 150A, USA

3.3 Experiment procedure

3.3.1 Separation of palm olein from crude palm oil

Palm olein was separated from crude palm oil (CPO) by centrifuge at 6500 rpm 0 and 20 °C for 15 and 30 minutes. Then, the palm olein was separated from residual, as stearin, by pouring out. The palm olein and stearin was weighted and analyzed for crude β -carotene content by UV-visible spectrometry.

3.3.2 Preparation of adsorbent

Polystyrene-divinylbenzene were treated with isopropanol (IPA) for about 15 min with rapid agitation, separated from IPA and dried at 35 °C before use [13-16].

3.3.3 Preparation of palm olein

Palm olein was separated from crude palm oil (CPO) by centrifuge at 6500 rpm 20 °C for 30 minutes. The residual solution was analyzed for crude β -carotene content by UV-visible spectrometry.

3.3.4 Preparation of degummed palm olein

30 grams of palm olein was shaken with 0.03 ml of 85 % phosphoric acid at 60 °C for 30 minutes then, separated degummed palm olein by centrifuge at 6500 rpm for 30 minutes. The residual solution was analyzed for crude β -carotene content by UV-visible spectrometry.

3.3.5 Degumming investigation

30 grams of palm olein was shaken with 0.01, 0.02, 0.03, 0.04 and 0.05 ml of 85 % phosphoric acid at 60 °C for 30 minutes. The mixture was centrifuged at 6500 rpm for 30 minutes. Then, the mixture was filtrated. The precipitate was dried in vacuum oven at 50 °C for 6 hr. After dried, the precipitate was weighted. The residual solution was analyzed for crude β -carotene content by UV-visible spectrometry.

3.3.6 Adsorption and desorption of crude β -carotene from in adsorbent

The adsorbent from topic 3.3.1 was mixed with oil from topic 3.3.2 and 3.3.3 at weight ratio of adsorbent to oil as 1:3 in flask which well-lapped with aluminum foil for light protection. The mixture was shaken (120 rpm) at 35 °C for 30 minutes. The adsorbent was washed with IPA to remove residual oil. Then, the mixture solution was separated from the adsorbent by pouring out. The supernatant was determined for crude β -carotene content by UV-visible spectrometry. Then, the β -carotene in adsorbent was removed by soaking in hexane at 35 °C for 4 hours and then hexane solution was separated by pouring out. The crude β -carotene contents in hexane solution were determined by UV-visible spectrometry.

3.3.7 The influence of parameters to adsorption in palm oil and degummed palm olein

3.3.7.1 Effect of adsorption time

Adsorption process was conducted at 35 °C for 15, 30, 60 and 90 minutes. % Adsorption, % desorption and % recovery were calculated in order to study the effect of adsorption time.

3.3.7.2 Effect of oil dilution

Adsorption process was conducted at 35 °C by diluting oil with isopropanol. Oil to isopropanol ratio was 1:0, 1:1, 1:2 and 1:3 by wt. % Adsorption, % desorption and % recovery were calculated in order to study the effect of oil dilution.

3.3.7.3 Effect of adsorption temperature

Adsorption process was conducted at 35 and 60 °C for 15, 30, 60 and 90 minutes. % Adsorption, % desorption and % recovery were calculated in order to study the effect of adsorption temperature.

The experimental conditions and number of experiments were shown in Table 3.1.

Table 3.1 The experimental conditions and number of experiments

Conditions	Palm olein	Degummed palm olein
<u>Adsorption</u>		
Adsorbent : oil (by wt.)	1:3	1:3
Temperature (°C)	35, 60	35, 60
Shaker speed (rpm)	120	120
Adsorption time (min.)	15, 30, 60, 90	15, 30, 60, 90
Adsorption dilution (oil : IPA) by wt.	1:0, 1:1, 1:2, 1:3	1:0, 1:1, 1:2, 1:3
Number of experiments	16	16
<u>Oil removal from adsorbent</u>		
Reagent	IPA	IPA
Dosage (g oil/ml IPA)	0.075	0.075
<u>Desorption</u>		
Dosage (g oil/ml hexane)	0.3	0.3
Desorption time (h)	4	4
Desorption temperature (°C)	35	35
Shaker speed (rpm)	120	120

3.3.8 Quantitative analysis of crude β -carotene by UV-visible spectrometry

The crude β -carotene content was determined by diluting aliquot of each supernatant with hexane to the appropriate dilution and measuring absorbance in a UV-visible Spectrophotometer at λ_{\max} (450 nm). Standard β -carotene (> 99%) was used to prepare the calibration curve.

3.3.8.1 Adsorption maxima (λ_{\max})

From the experiment, λ_{\max} of standard β -carotene by using hexane as a blank and measuring in a UV-visible spectrophotometer was 450 nm.

3.3.8.2 Calibration Curve

Standard β -carotene at different concentrations were used for preparing calibration curve as shown in figure A1 and A2 (Appendix A). This calibration curve was used to calculate crude β -carotene content, % adsorption, % desorption and % recovery of crude β -carotene from palm olein and degummed palm olein.

Spectrum of standard β -carotene, palm olein, degummed palm olein and the extracted crude β -carotene by using UV-visible spectroscopy were shown in figure A3, A4, A5 and A6, respectively.

3.3.9 Terminology

$$\% \text{ Adsorption} = \frac{W_a}{W_i} * 100$$

$$\% \text{ Desorption} = \frac{W_d}{W_a} * 100$$

$$\% \text{ Recovery} = \frac{W_d}{W_i} * 100$$

Where W_i = Initial β -carotene content (g)

W_a = β -carotene adsorbed content (g)

W_d = β -carotene desorbed content (g)

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Chapter IV

Results and Discussion

Crude β -carotene recovery from palm olein and degummed palm olein was investigated under different conditions of adsorption on PSDVB.

The influence of parameters, *i.e.* adsorption time oil dilution and adsorption temperature for adsorption on PSDVB were studied. The results from the experimental procedures mentioned in chapter III were presented in the following tables and figures. The results were also discussed as in the followings.

4.1 Separation of palm olein from crude palm oil

Crude palm oil, naturally, consists of two main parts, olein and stearin. Separation of olein which is liquid form from stearin which is semi-solid form at room temperature is very difficult due to being well dispersion suspension. To reach high olein yield, many variable parameters have to involve. They are temperature, rate of cooling, cooling time and agitation speed in crude palm oil tank. Suitable condition from these parameters will create well crystal form of stearin which is easy to separate out by filtration [30]. However, the aim of this study is only to recover palm olein for use in this research, not to determine the suitable separation condition.

In our work, centrifugation (6,500 rpm) was used to separate olein from stearin at 0 and 20 °C for 15 and 30 minutes. Table 4.1 shows that olein separation at 20 °C for 30 minutes gave higher olein yield than the other conditions. Crude β -carotene presented in these two portions at each experiment is in the same range of crude palm oil [2].

Table 4.1 % wt. and crude β -carotene of olein and stearin was separated from crude palm oil at different temperature and time.

Temperature (°C)	Time (min.)	Olein		Stearin	
		% wt.	Crude β -carotene (ppm)	% wt.	Crude β -carotene (ppm)
0	15	46.06	620.80	53.94	535.73
	30	43.17	646.85	56.83	572.75
20	15	47.99	640.36	52.01	566.10
	30	48.64	616.84	51.36	532.98

4.2 Degumming

The effect of phosphoric acid content on amount of gum and concentration of crude β -carotene were shown in figure 4.1, figure 4.2, table B1 and table B2. They indicated that amount of gum increased with the increase of phosphoric acid content. The experimental result also found that an increasing of phosphoric acid content ranged from 0.0004 to 0.002 (ml of acid/g palm olein) does not affected to the concentration of crude β -carotene in palm olein. So we choose degummed palm olein at 0.001 ml of acid/g palm olein in order to avoid oil loss at high acid content [31]. This acid dosage is widely used in palm oil industry [32].

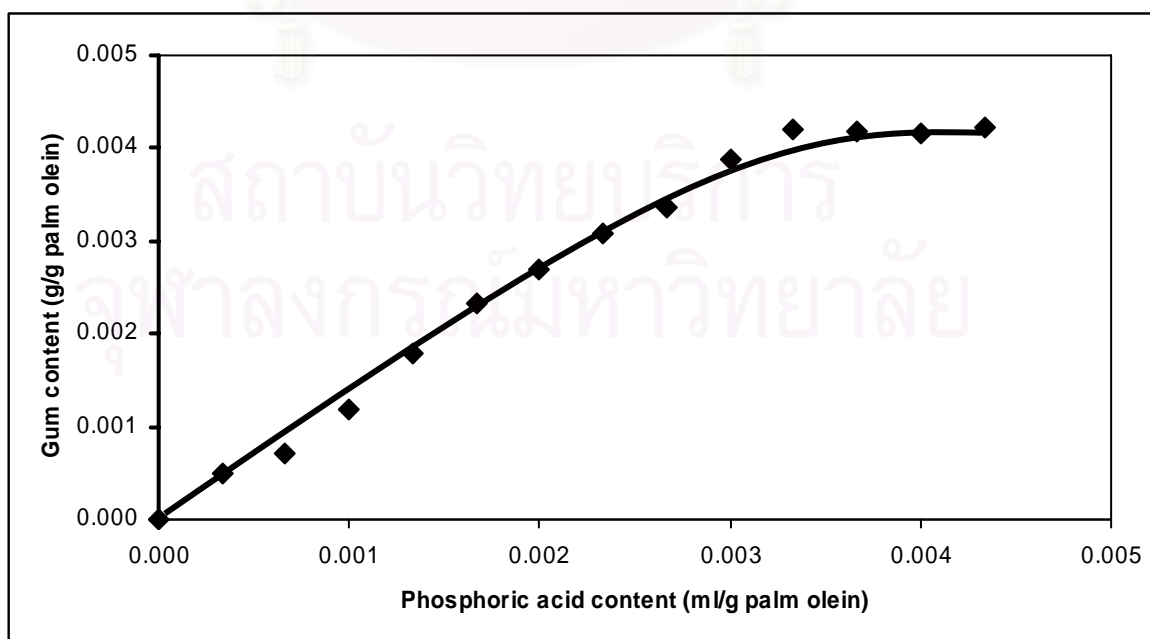


Figure 4.1 The gum content at various amounts of phosphoric acid

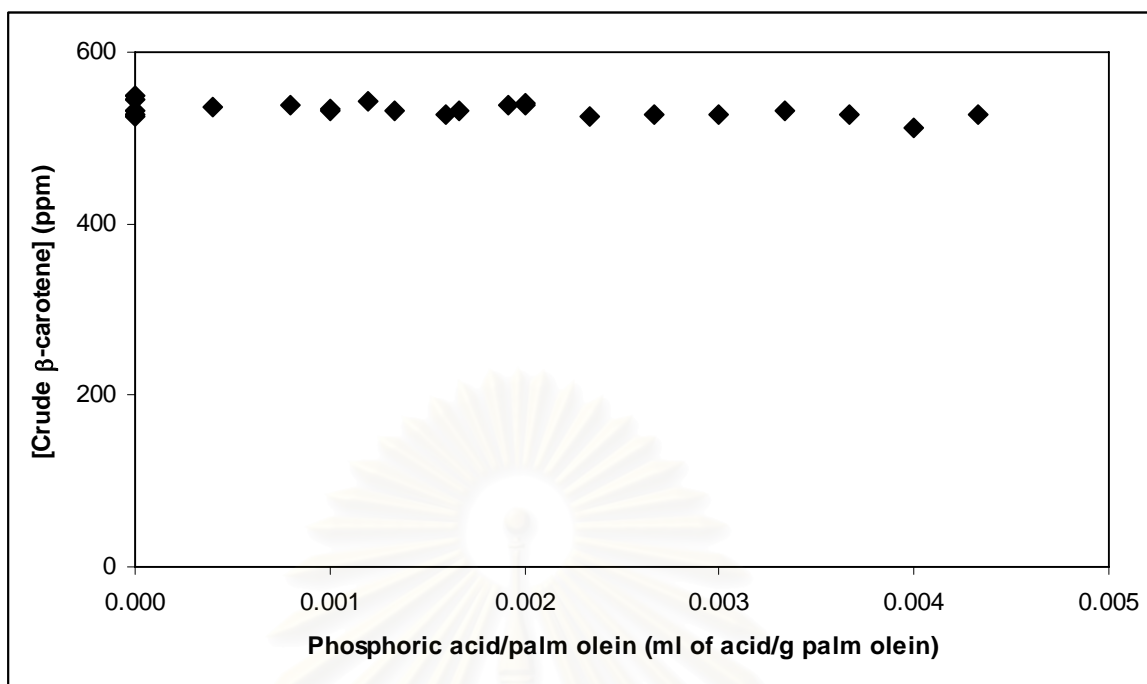


Figure 4.2 The concentration of crude β -carotene at various amounts of phosphoric acid

4.3 Effect of time on adsorption of crude β -carotene from palm olein and degummed palm olein

The aim of this study is to determine equilibrium adsorption time for crude β -carotene separation from palm olein and degummed palm olein. The adsorption experiments were carried out at 15, 30, 60 and 90 minutes. % Adsorption of crude β -carotene from palm olein and degummed palm olein are presented in figure 4.3, table B3 and table B7. Similar trend of % adsorption of palm olein and degummed palm olein with time were observed. With an increase in time, amount of crude β -carotene adsorbed on PSDVB also increased in the range of 24.29 to 32.29 % adsorption. Equilibrium adsorption time of both palm olein and degummed palm olein are at 60 minutes.

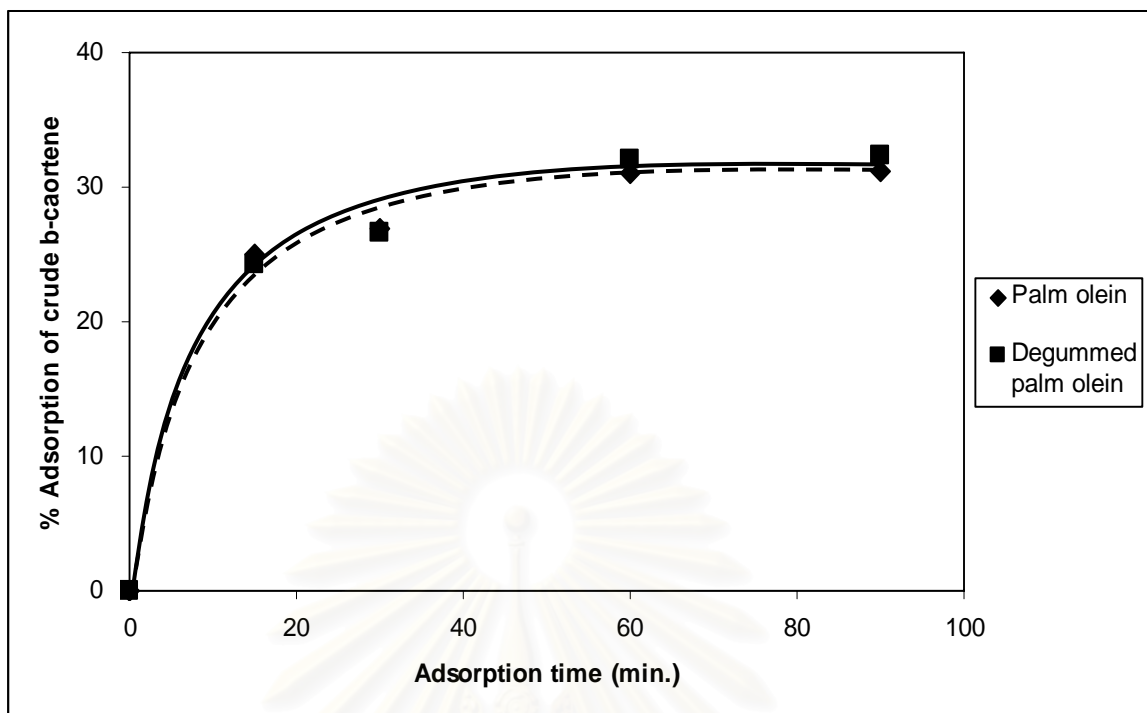


Figure 4.3 Effect of time on % adsorption of crude β -carotene from palm olein and degummed palm olein.

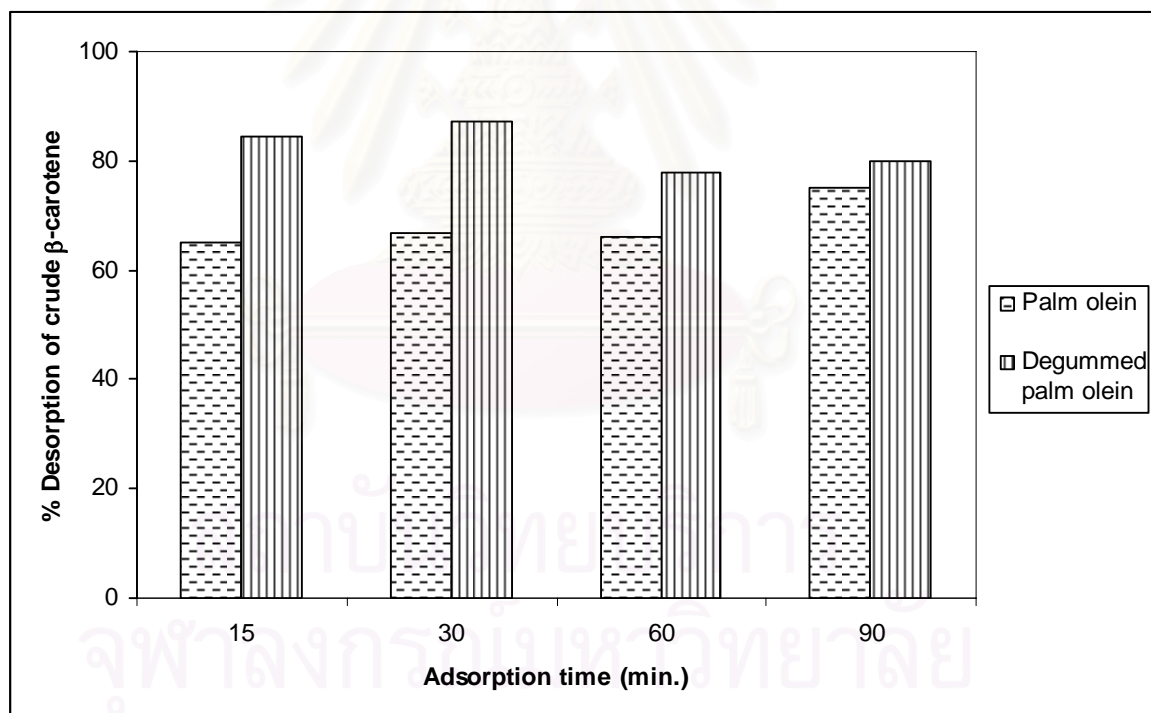
Desorption of crude β -carotene from PSDVB resins was done by soaking the resin in hexane solution for 4 hours. Figure 4.4 shows the results of crude β -carotene desorption from PSDVB resins in term of % desorption, both palm olein and degummed palm olein. From % desorption data, degummed palm olein give an average % desorption of 82.35 % while palm olein is at 68.19 %. Higher % desorption of degummed palm olein indicated that phospholipid in palm olein has the important role in desorption of crude β -carotene. Normally, phospholipids or also known as phosphatides are bonded with metal ions in oils [31]. The process of acid degumming will remove phospholipids from oils in form of solid precipitation, therefore, degummed palm olein contains less phospholipid than palm olein.

In crude β -carotene adsorption on PSDVB resins, oil will firstly penetrate into the pores of resins and then, crude β -carotene will be adsorbed on PSDVB surface due to the similarity of the molecular structures of crude β -carotene and adsorbent and also to hydrophobic interaction between the adsorbent and crude β -carotene. From the viscosity data shown in table 4.2 point out that degummed palm olein and palm olein had not much different in viscosity, resulting to get similar adsorption. In case of desorption using

hexane, phospholipids incorporated with oil in the pores of PSDVB resins may interfere the desorption of crude β -carotene.

Table 4.2 Viscosity of palm olein and degummed palm olein at different ratio of oil to isopropanol

Ratio of oil to isopropanol	viscosity of palm olein (cP)	viscosity of degummed palm olein (cP)
1:0	44.82	42.87
1:1	5.45	5.39
1:2	3.36	3.39
1:3	2.79	2.73



▨ Average % desorption = 68.19 %

▨ Average % desorption = 82.35 %

Figure 4.4 Effect of time on % desorption of crude β -carotene from palm olein and degummed palm olein.

% Recovery of crude β -carotene in adsorbed oil is shown in figure 4.5. The results suggest that % recovery of crude β -carotene from degummed palm olein of all experiments gave higher values than palm olein. % Recovery ranged from 16.24 to 23.50 % for palm olein and 20.53 to 25.77 % for degummed palm olein.

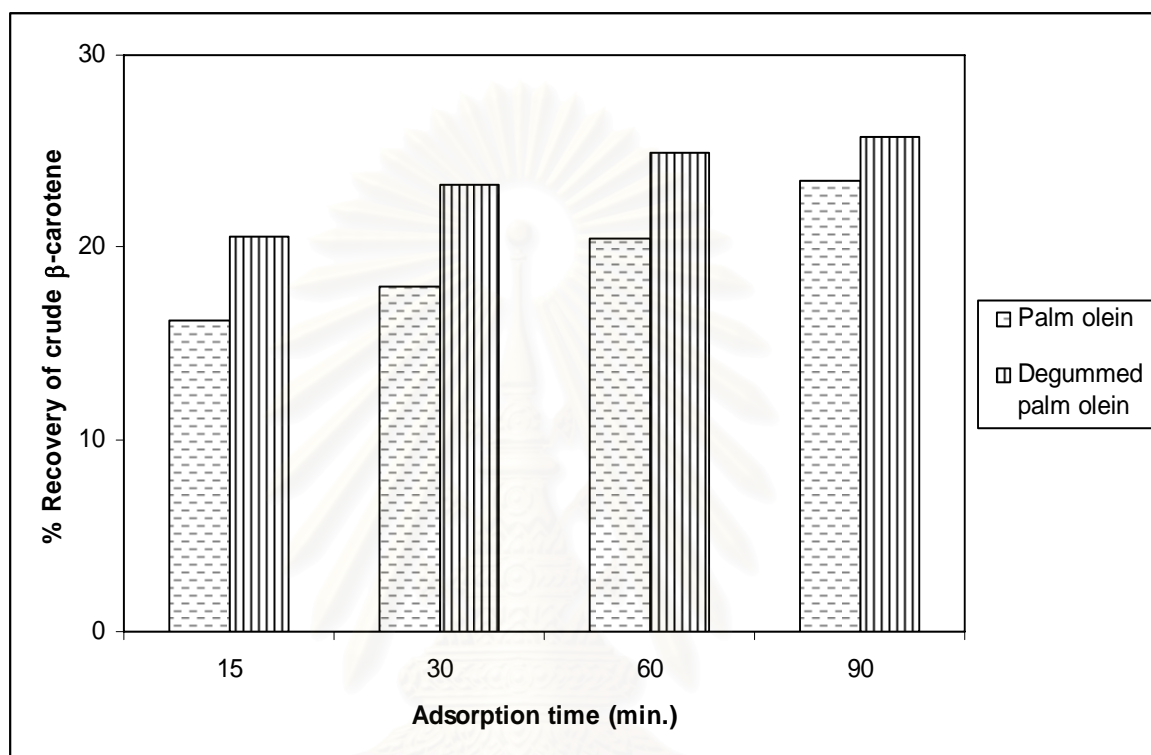


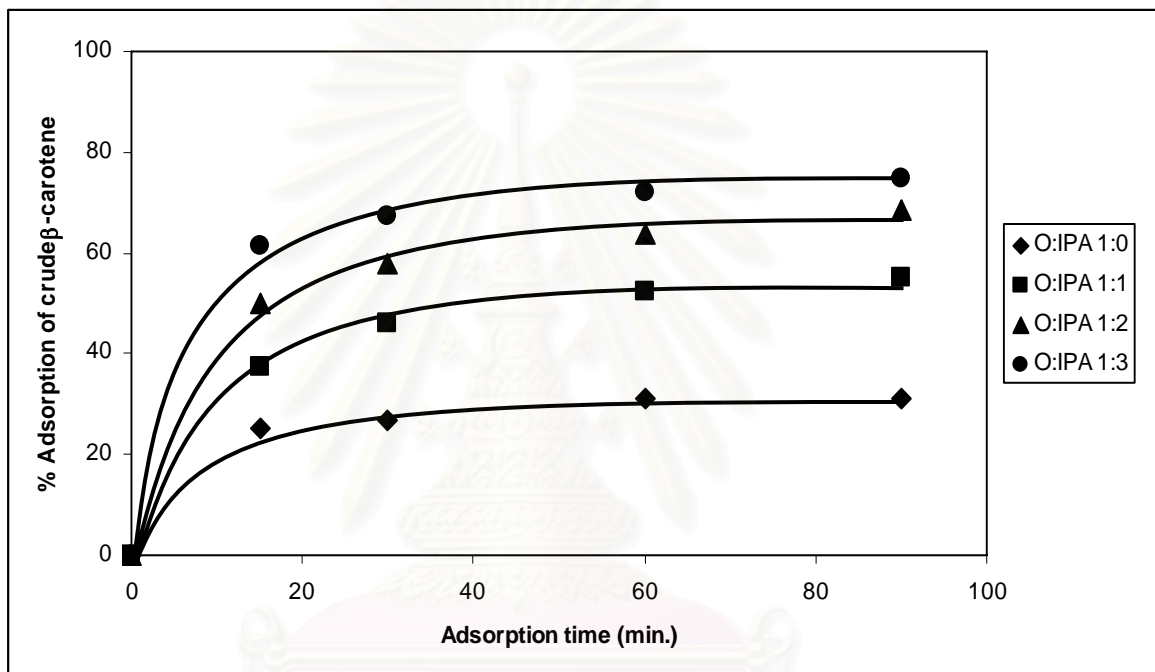
Figure 4.5 Effect of time on % recovery of crude β -carotene from palm olein and degummed palm olein

4.4 Effect of oil dilution on adsorption of crude β -carotene from palm olein and degummed palm olein.

In topic 4.3, the equilibrium adsorption time was investigated using non-diluted palm olein and degummed palm olein. The aim of this topic is to determine the effect of oil dilution with isopropanol on adsorption of crude β -carotene from palm olein and degummed palm olein using PSDVB resins. The ratios of oil to isopropanol were at 1:1, 1:2 and 1:3. Figure 4.6 (table B3-6) and figure 4.7 (table B7-10) shows the results of % adsorption at different oil dilutions and times from palm olein and degummed palm olein. At each oil dilutions, % adsorption of crude β -carotene increased with an increase of time until it was nearly constant at 60 minutes. We also found that the more oil was diluted, the higher % adsorption was clearly obtained. Theoretically, adsorbents with larger pores are

preferred for use with liquid than gas phase since liquid has higher viscosity than gas [27]. In our case, viscosity of oil to isopropanol ratio at 1:3 has 15 times less than those of 1:0 ratio (table 4.2). Therefore, low viscosity condition, oil can easily penetrate into the pores of PSDVB resins.

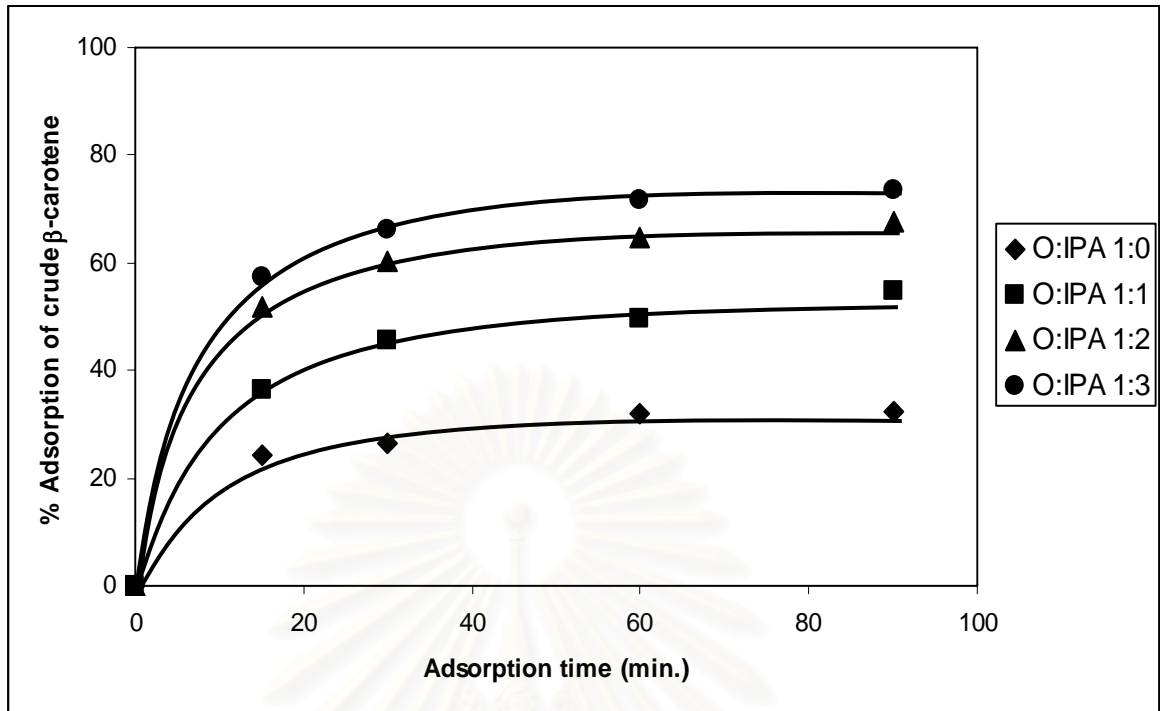
Comparison of % adsorption at 60 minutes from palm olein and degummed palm olein at different oil dilution was shown in figure 4.8. The result indicated that there were not significantly different from each other.



O = Palm olein

IPA = Isopropanol

Figure 4.6 Effect of oil dilution on % adsorption of crude β -carotene from palm olein at different adsorption time.



O = Degummed palm olein

IPA = Isopropanol

Figure 4.7 Effect of oil dilution on % adsorption of crude β -carotene from degummed palm olein at different adsorption time.

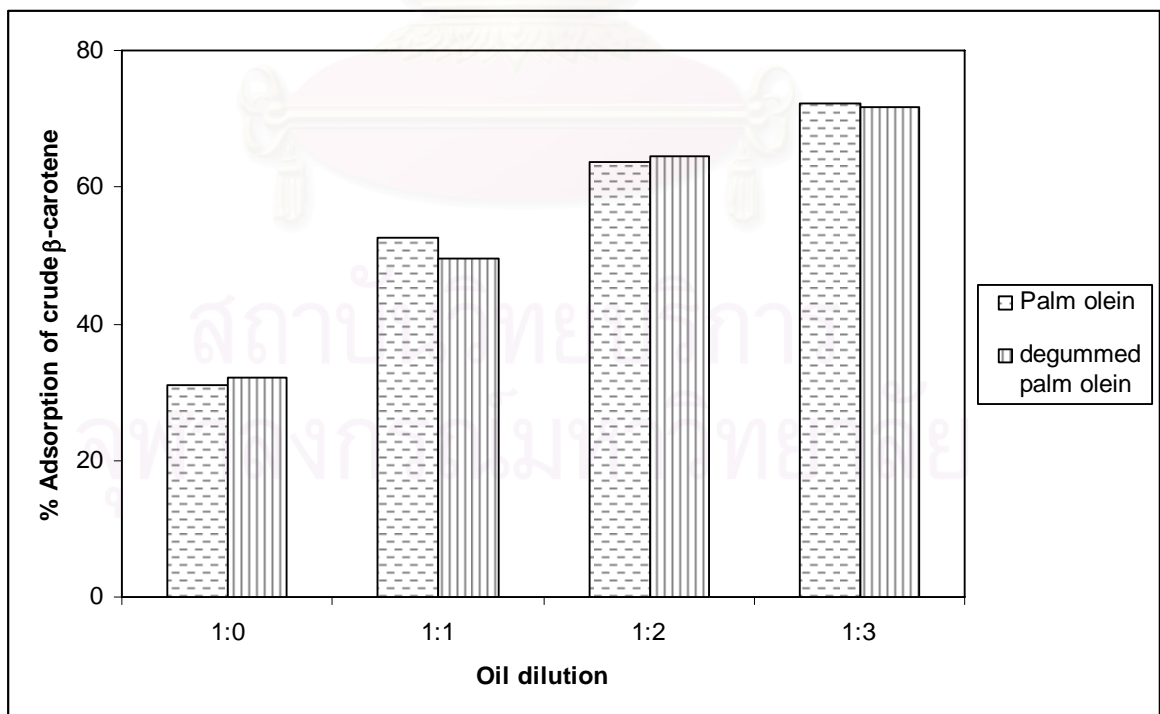
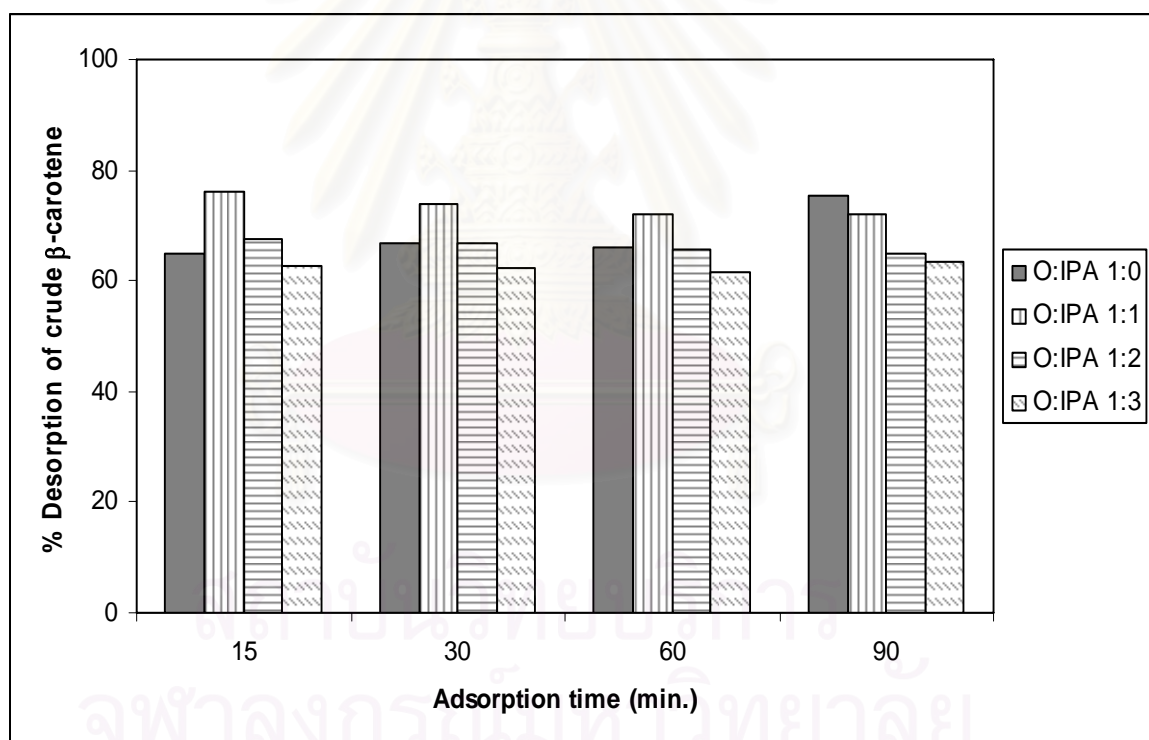


Figure 4.8 Effect of oil dilution on % adsorption of crude β -carotene from palm olein and degummed palm olein at 60 minutes.

In case of desorption of crude β -carotene from the resins with hexane, % desorption from degummed palm olein was slightly higher than palm olein (figure 4.9, 4.10 and 4.11) since oil containing phospholipid was diluted resulting that phospholipids in palm olein was also diluted. Low phospholipids content will create less interfering crude β -carotene desorption. We also found that % desorption decreased as oil dilution increased since there might be competitive adsorption between isopropanol and crude β -carotene on adsorbent surface [13].

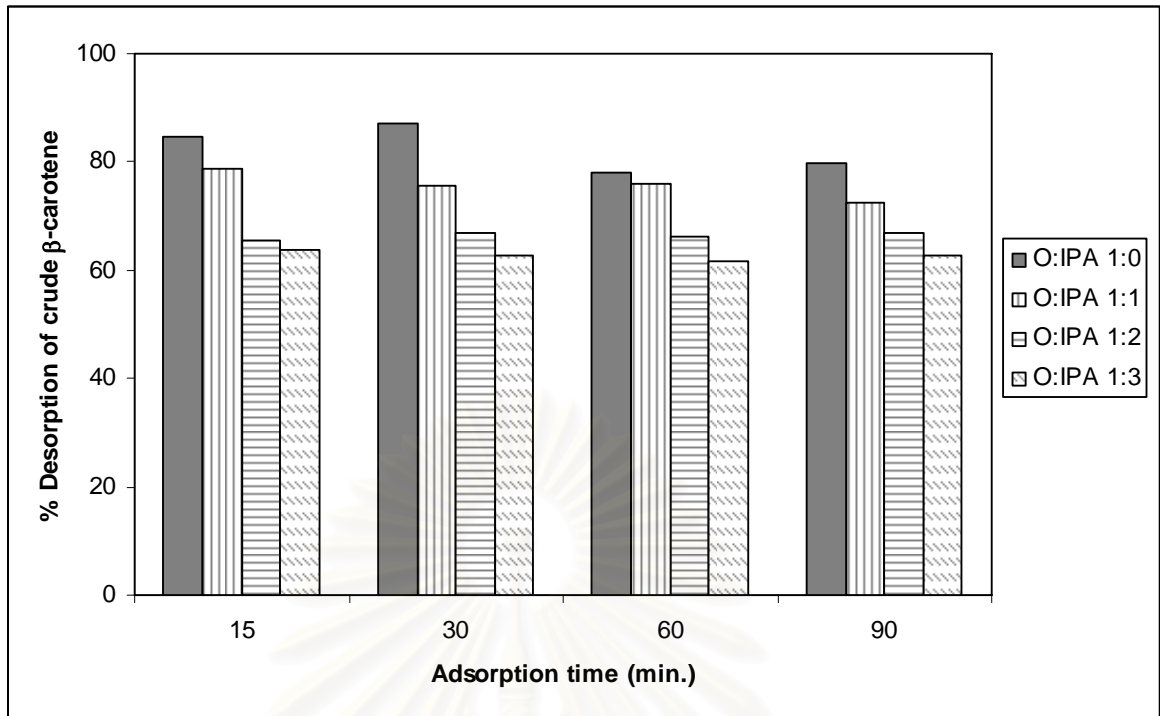
Figure 4.12, 4.13 and 4.14 showed % recovery of crude β -carotene from palm olein and degummed palm olein. The results indicated that % recovery increased as oil dilution increased and there is not significantly different of % recovery between palm olein and degummed palm olein since at diluted condition, the effect of gum is less impact than viscosity.



O = Palm olein

IPA = Isopropanol

Figure 4.9 Effect of oil dilution on % desorption of crude β -carotene from palm olein at different adsorption time.



O = Degummed palm olein
 IPA = Isopropanol

Figure 4.10 Effect of oil dilution on % desorption of crude β -carotene from degummed palm olein at different adsorption time.

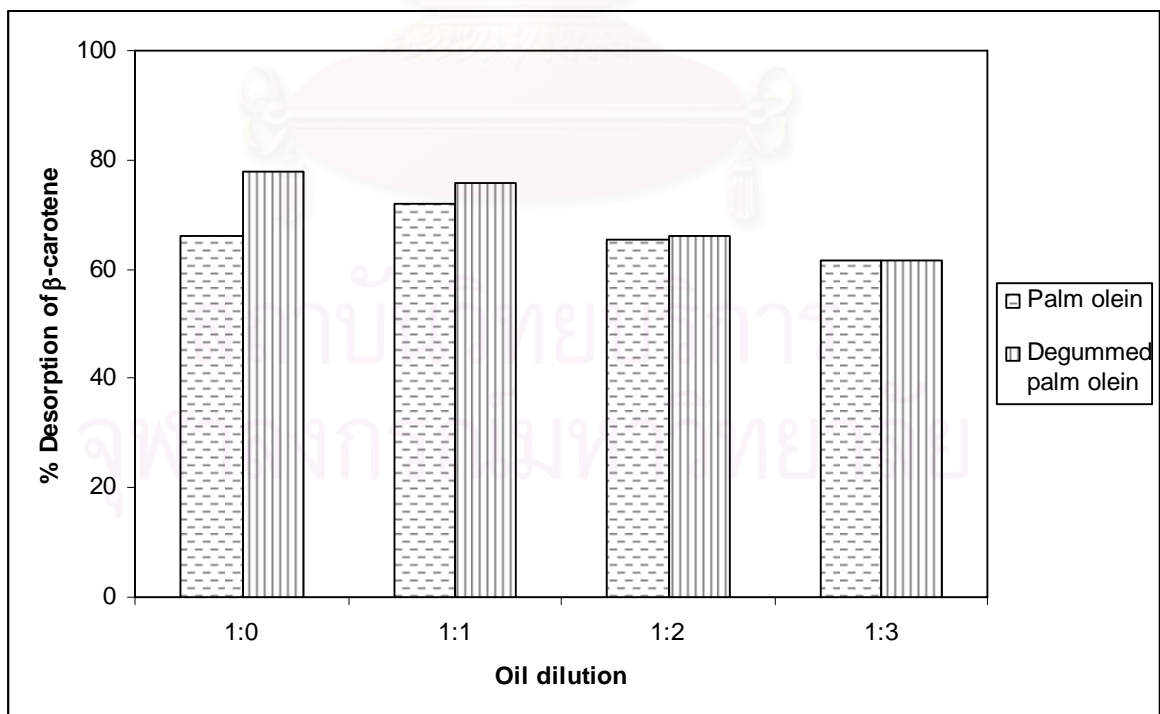
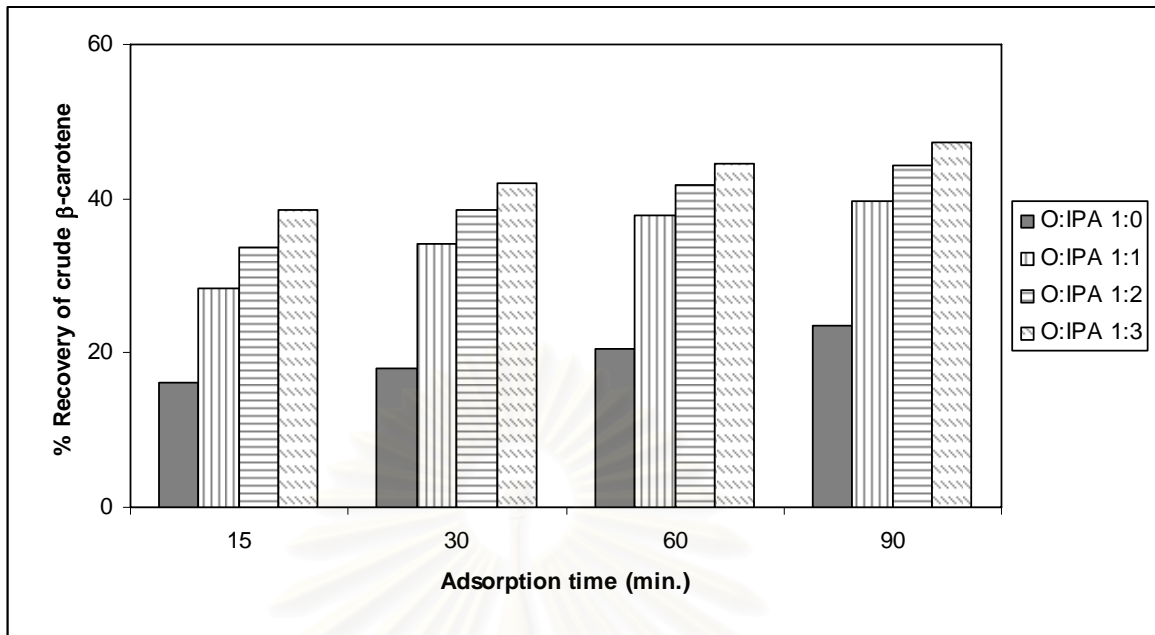


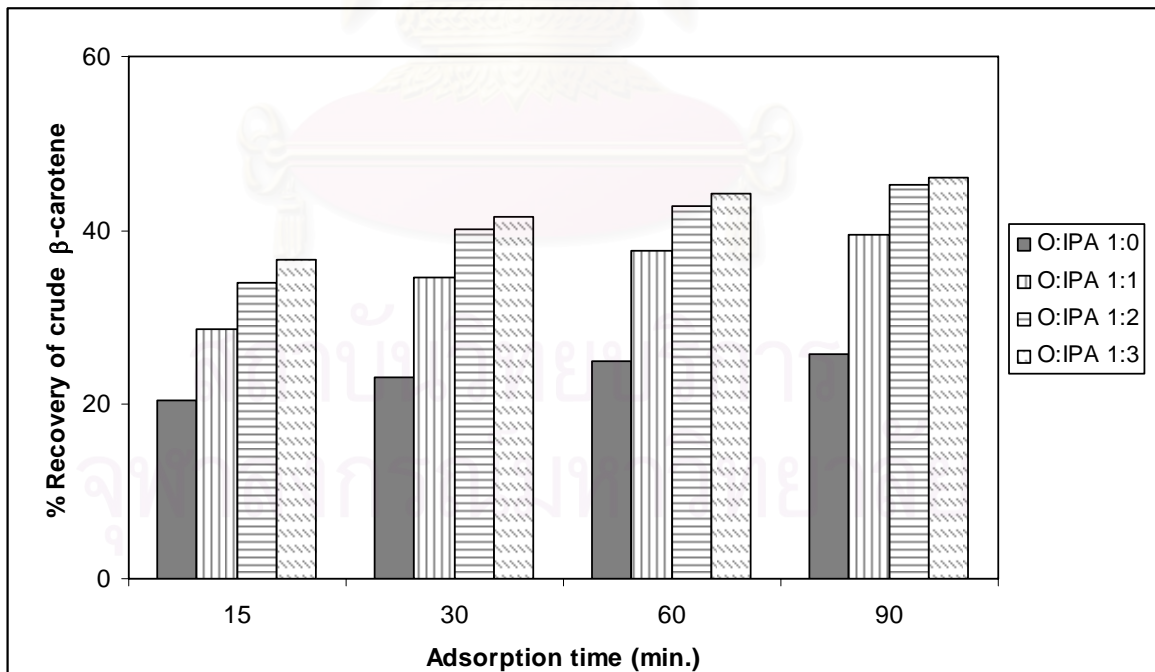
Figure 4.11 Effect of oil dilution on % desorption of crude β -carotene from palm olein and degummed palm olein at 60 minutes.



O = Palm olein

IPA = Isopropanol

Figure 4.12 Effect of oil dilution on % recovery of crude β -carotene from palm olein at different adsorption time.



O = Degummed palm olein

IPA = Isopropanol

Figure 4.13 Effect of oil dilution on % recovery of crude β -carotene from degummed palm olein at different adsorption time.

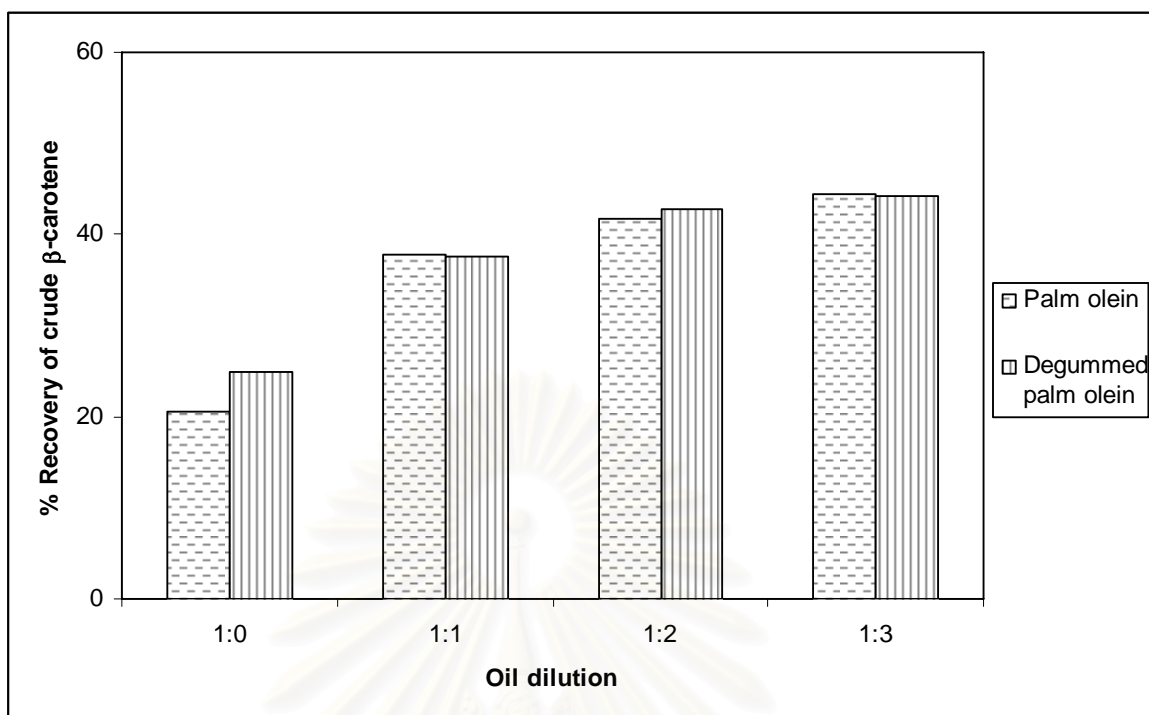


Figure 4.14 Effect of oil dilution on % recovery of crude β -carotene from palm olein and degummed palm olein at 60 minutes.

4.5 Effect of adsorption temperature on adsorption of crude β -carotene from palm olein and degummed palm olein.

From oil dilution experiments, although the reduction of oil viscosity can improve crude β -carotene adsorption, but the amount of crude β -carotene adsorbed in non diluted oil and diluted oil look similar. Therefore, an increase of adsorption temperature was another way for reducing oil viscosity. So, the aim of this topic is to determine the effect of adsorption temperature on adsorption of crude β -carotene from palm olein and degummed palm olein using PSDVB resins. The adsorption experiments were carried out at 35 and 60 °C for 15, 30, 60 and 90 minutes. % Adsorption of crude β -carotene from palm olein and degummed palm olein at different adsorption temperature are presented in figure 4.15 (table B3 and B11) and figure 4.16 (table B7 and B12). At each adsorption temperature, % adsorption of crude β -carotene increased with an increase of time until it was nearly constant at 60 minutes. We also found that the higher adsorption temperature, the higher % adsorption was clearly obtained. In our case, viscosity of oil at 60 °C has 2.2 times less than those of 35 °C (table 4.3). Therefore, at low viscosity condition, oil can easily penetrate into the pores of PSDVB resins.

Comparison of % adsorption at 60 minutes from palm olein and degummed palm olein at different adsorption temperature was shown in figure 4.17. The result indicated that at each temperature, % adsorption was not significantly different from each other. This suggests that an increase in temperature has more effect on viscosity than oil degumming.

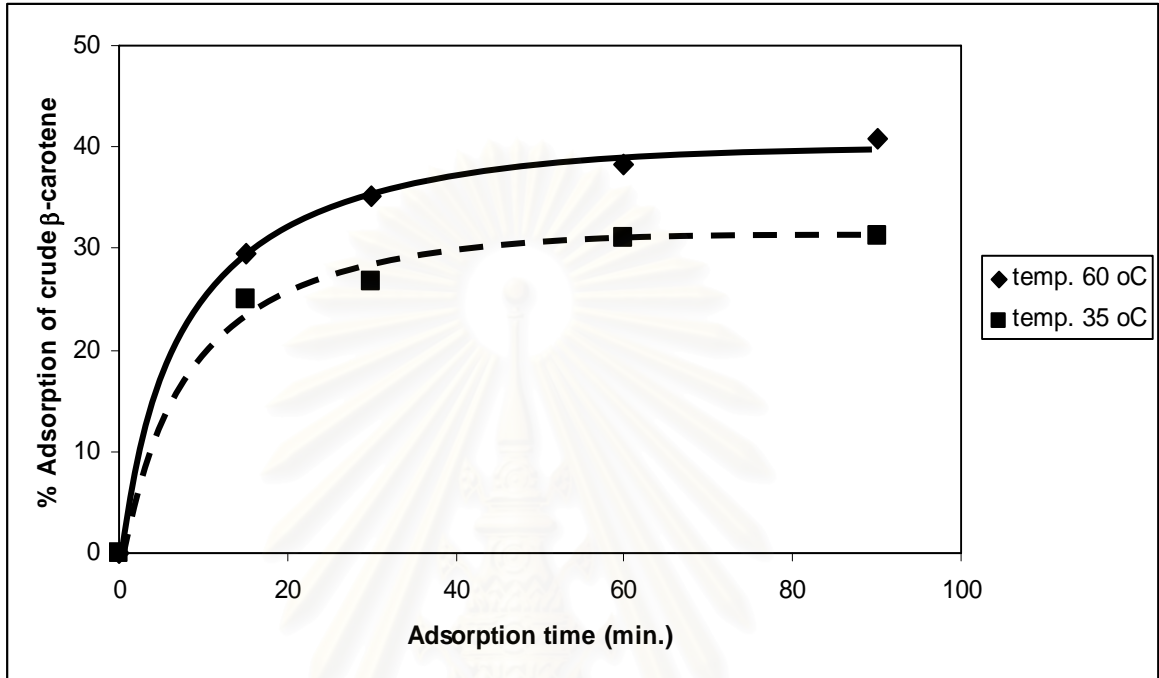


Figure 4.15 Effect of adsorption temperature on % adsorption of crude β -carotene from palm olein at different adsorption time.

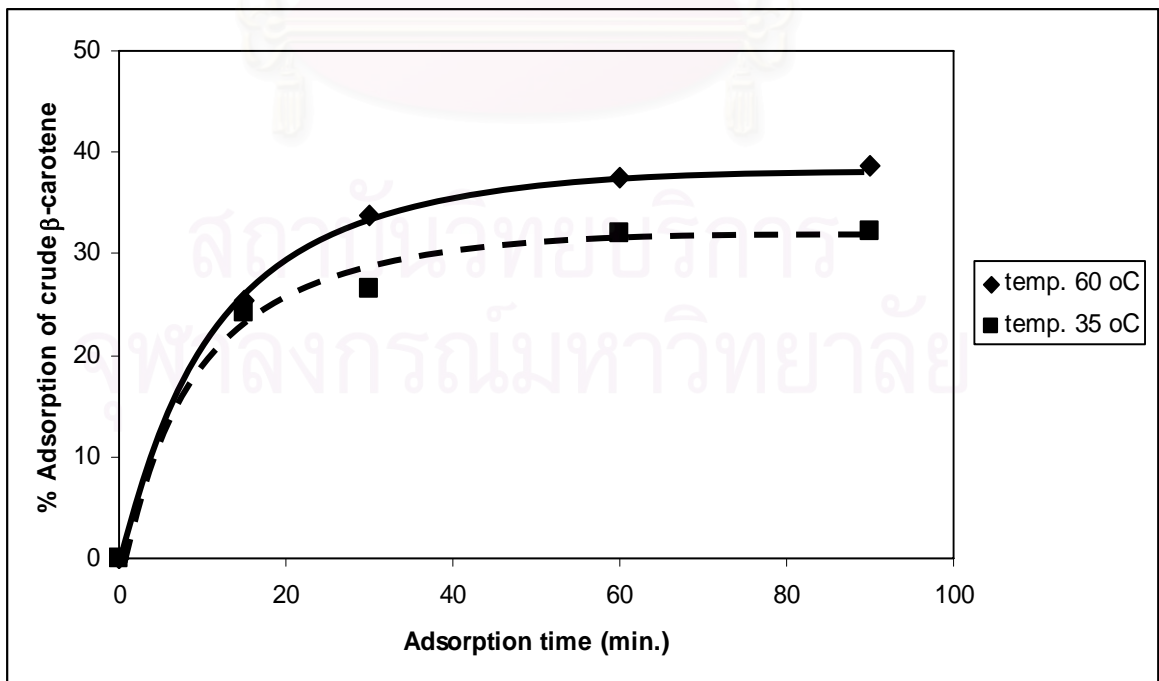


Figure 4.16 Effect of adsorption temperature on % adsorption of crude β -carotene from degummed palm olein at different adsorption time.

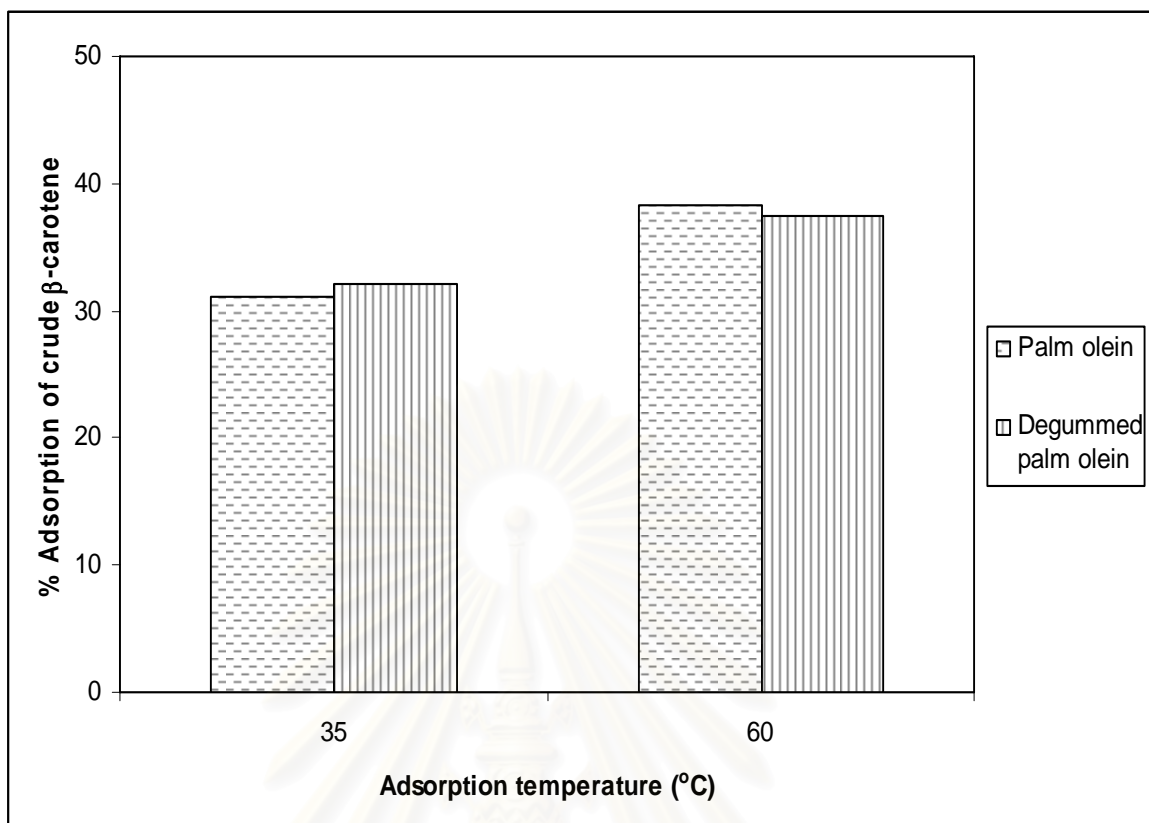


Figure 4.17 Effect of adsorption temperature on % adsorption of crude β -carotene from palm olein and degummed palm olein at 60 minutes.

Table 4.3 The viscosity of palm olein and degummed palm olein at different temperature

Sample	Temp. (°C)	viscosity (cP)
Palm olein	60	19.77
	35	44.82
Degummed palm olein	60	19.14
	35	42.87

In case of desorption of crude β -carotene from PSDVB resins with hexane, the results shown in figure 4.18, 4.19 and 4.20. From the results, adsorption temperature at 60 °C of degummed palm olein has closely % desorption to palm olein, while at 35 °C, degummed palm olein shows significantly higher % adsorption than palm olein. Higher % desorption of degummed palm olein indicates that phospholipid in palm olein has the important role in desorption of crude β -carotene as mentioned before.

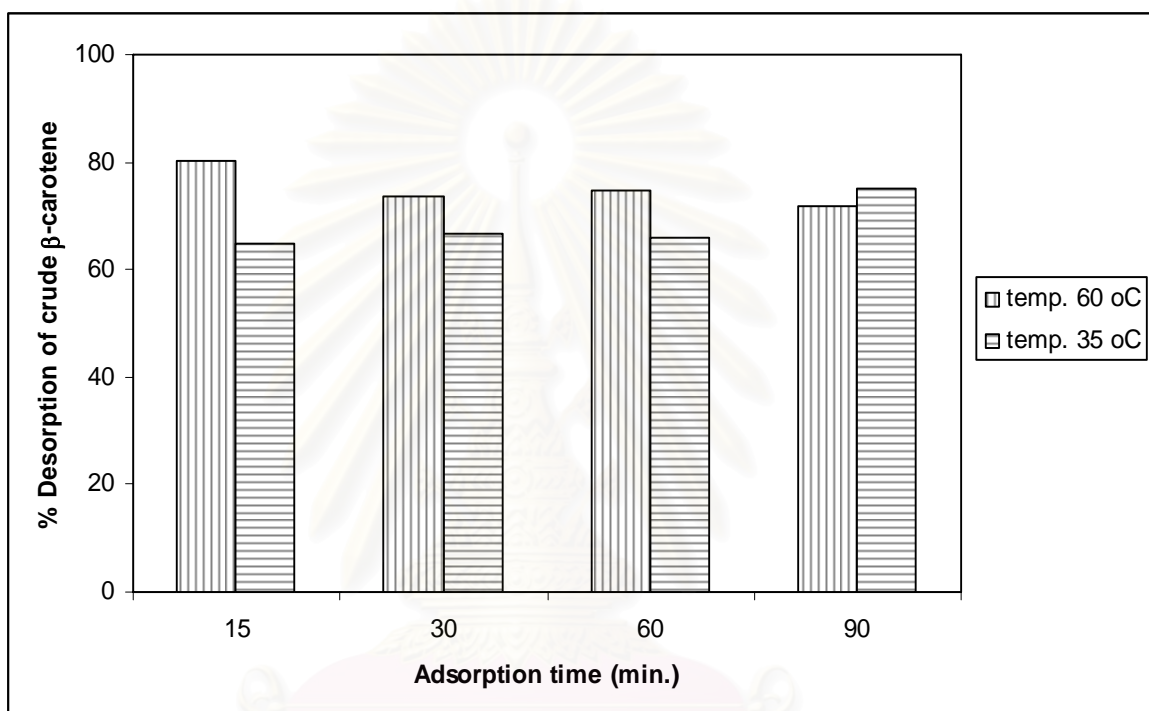


Figure 4.18 Effect of adsorption temperature on % desorption of crude β -carotene from palm olein at different adsorption time.

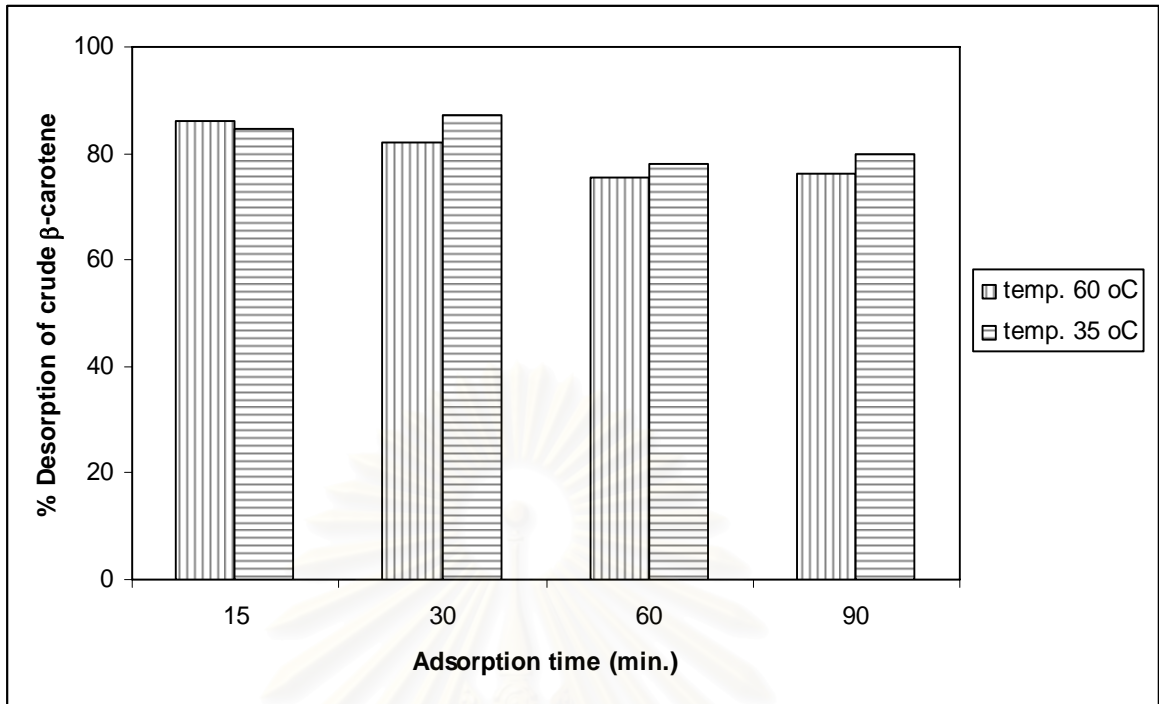


Figure 4.19 Effect of adsorption temperature on % desorption of crude β -carotene from degummed palm olein at different adsorption time.

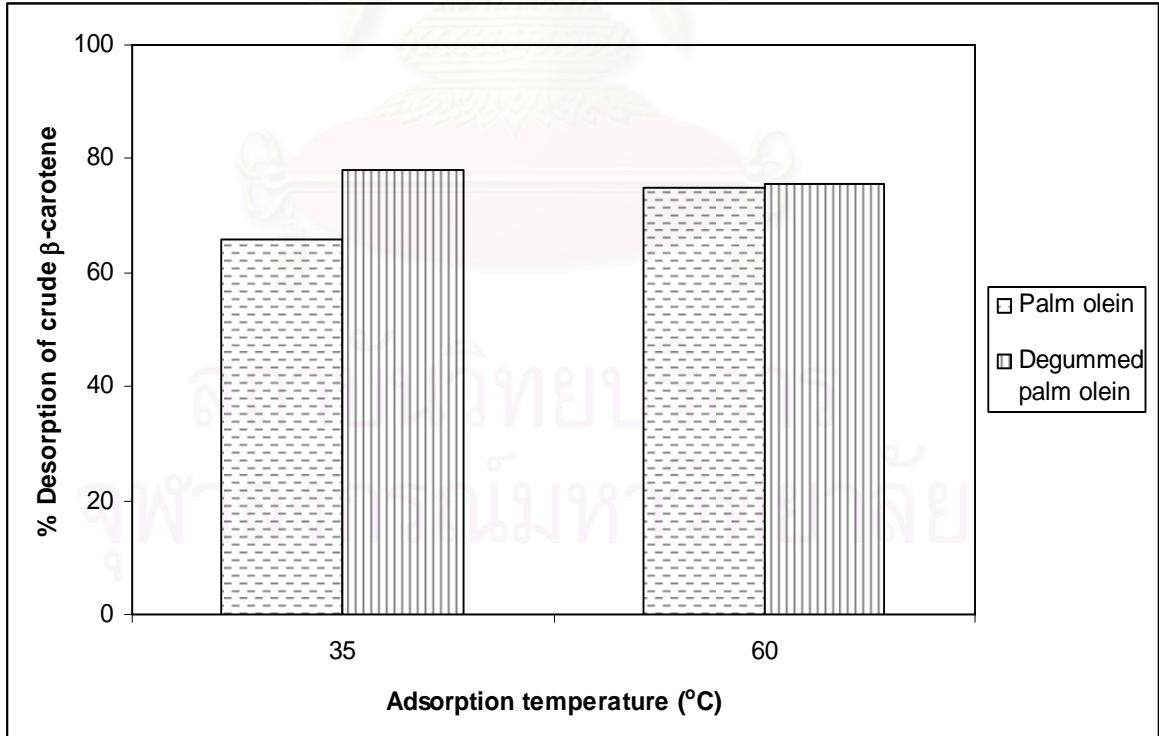


Figure 4.20 Effect of adsorption temperature on % desorption of crude β -carotene from palm olein and degummed palm olein at 60 minutes.

Figure 4.21, 4.22 and 4.23 showed % recovery of crude β -carotene from palm olein and degummed palm olein. The results indicated that % recovery increased as adsorption temperature increased and there is not significantly different of % recovery between palm olein and degummed palm olein at 60 °C. However, at 35 °C, % recovery of degummed palm olein is higher than palm olein because % desorption is higher as mentioned before.

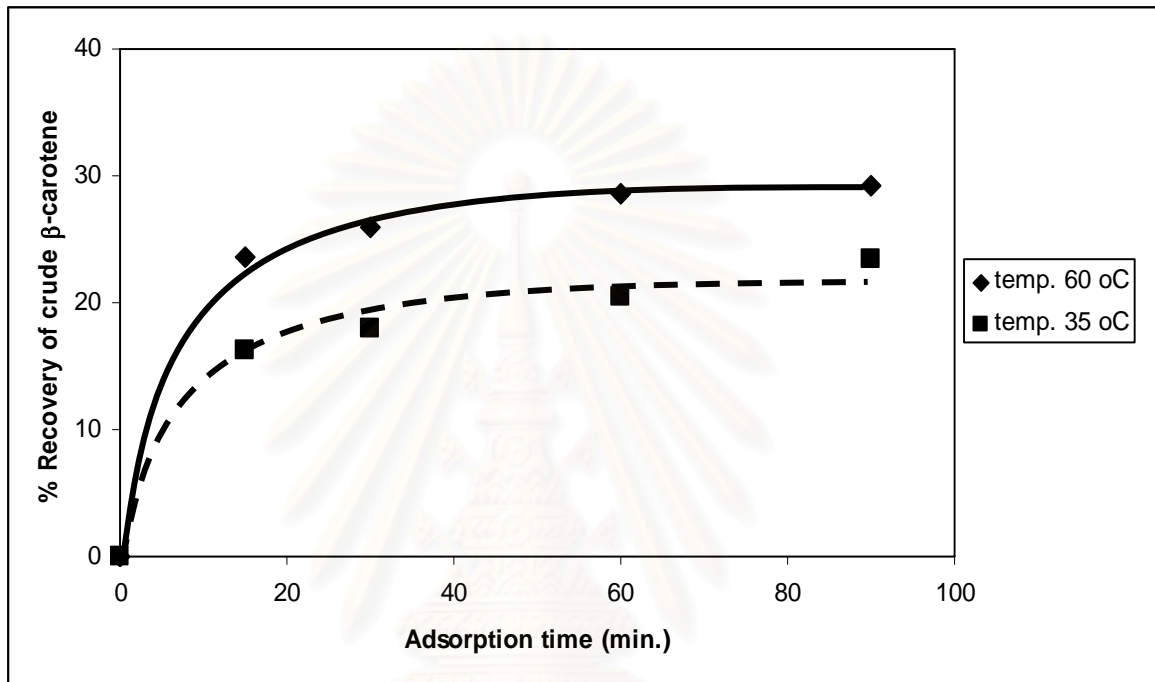


Figure 4.21 Effect of adsorption temperature on % recovery of crude β -carotene from palm olein at different adsorption time.

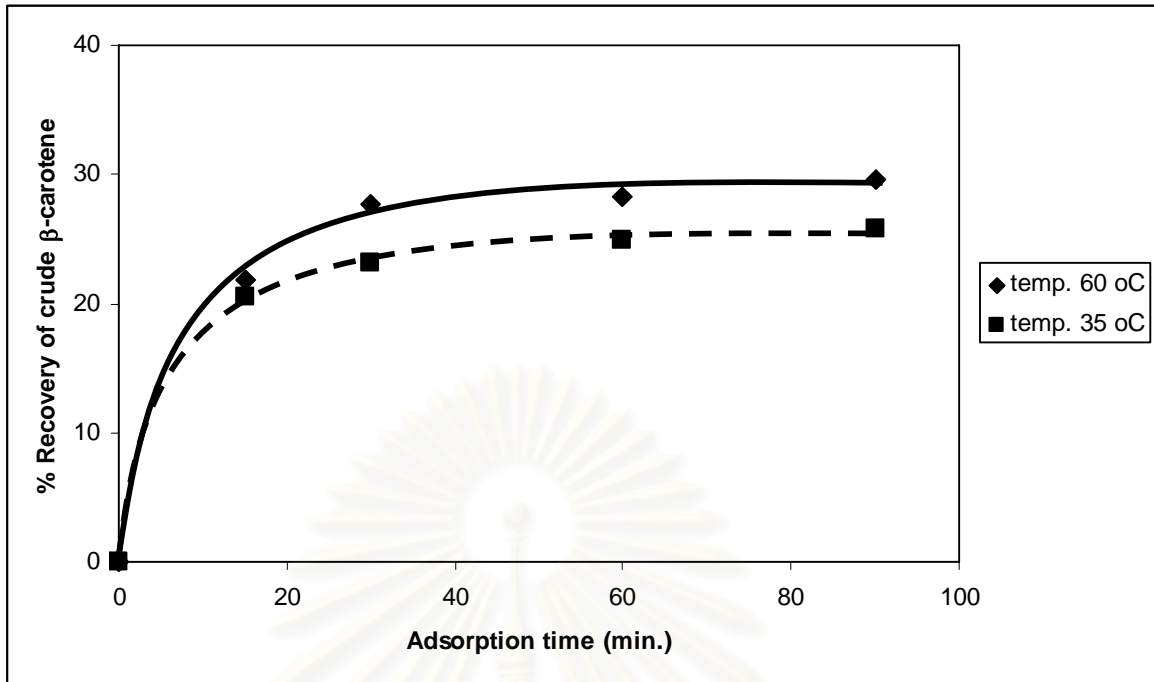


Figure 4.22 Effect of adsorption temperature on % recovery of crude β -carotene from degummed palm olein at different adsorption time.

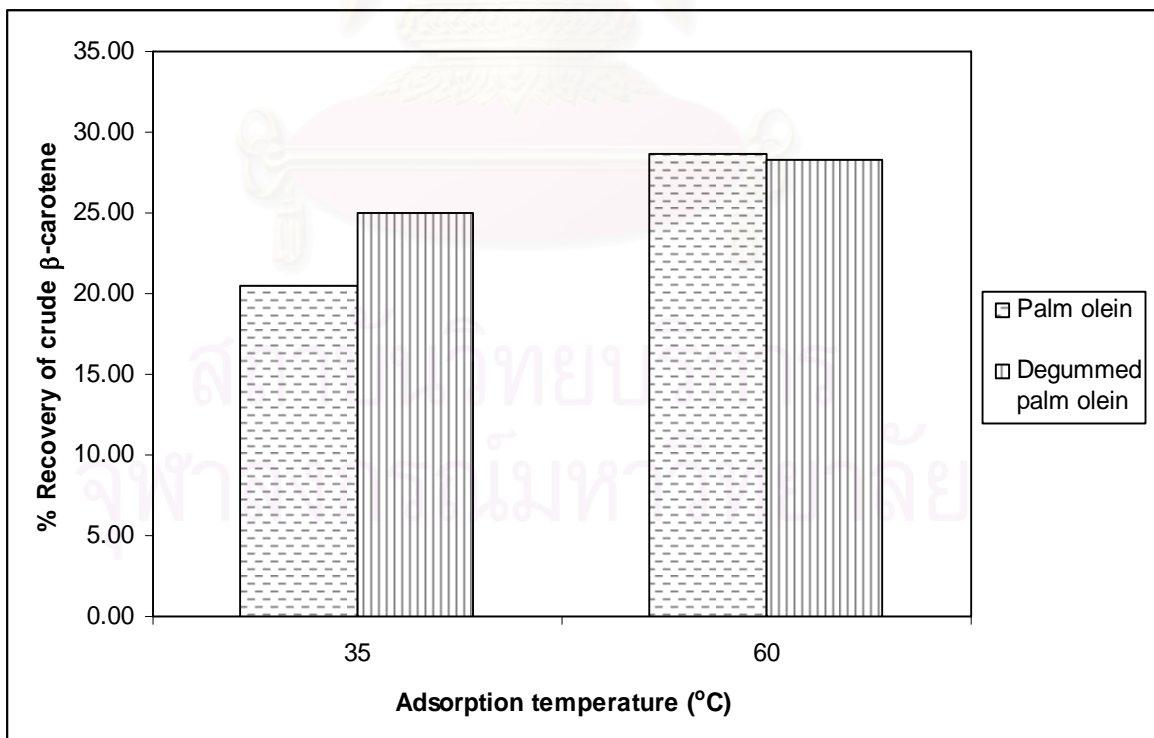


Figure 4.23 Effect of adsorption temperature on % recovery of crude β -carotene from palm olein and degummed palm olein at 60 minutes.

4.6 The adsorption isotherm of crude β -carotene from palm olein and degummed palm olein

Apparent adsorption isotherm of crude β -carotene from palm olein and degummed palm olein was obtained by plotting the mass of adsorbed crude β -carotene/mass of adsorbent (W) versus the concentration of crude β -carotene (C). Figure 4.24 shows the Langmuir isotherm of PSDVB of palm olein and degummed palm olein fitting with a Langmuir equation (1) of the form:

$$W = W_{\max} \left[\frac{K * C}{1 + (K * C)} \right] \dots\dots\dots(1)$$

- W is the mass of adsorbed crude β -carotene/mass of adsorbent (mg/g)
 C is the concentration of crude β -carotene (ppm)
 K is the adsorption constant

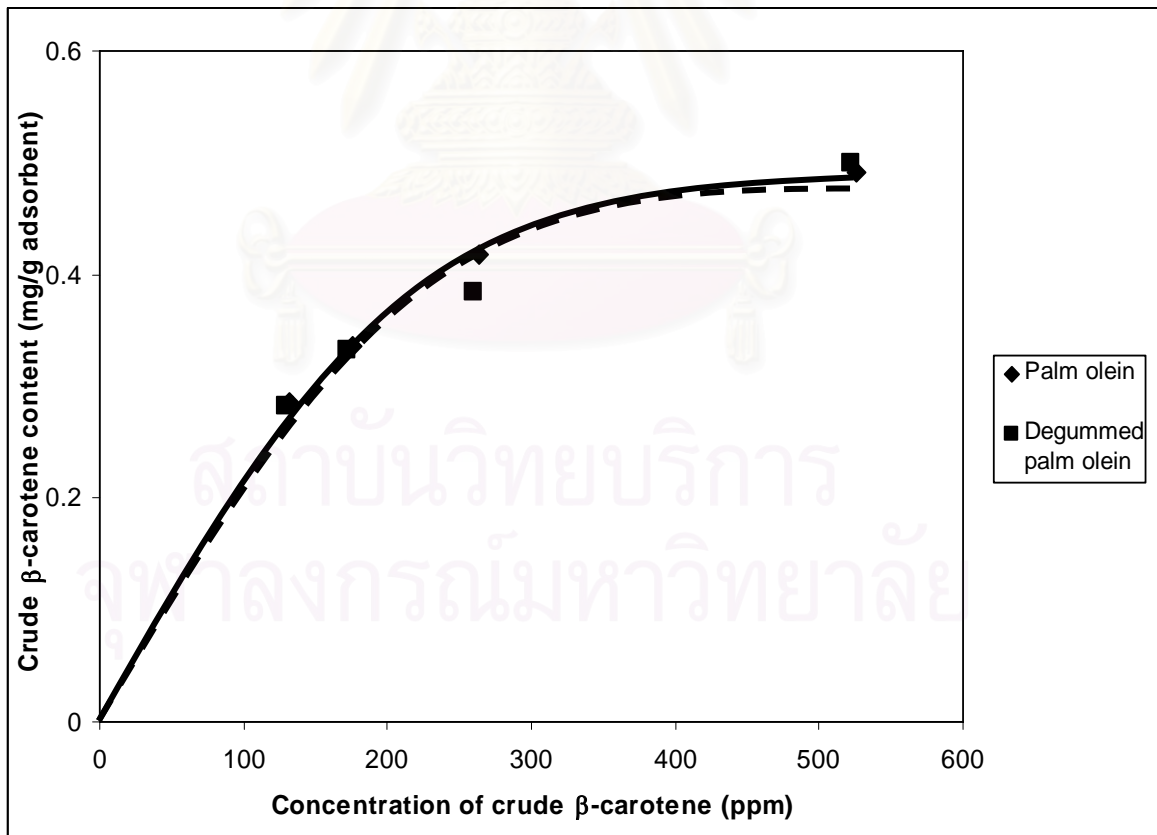


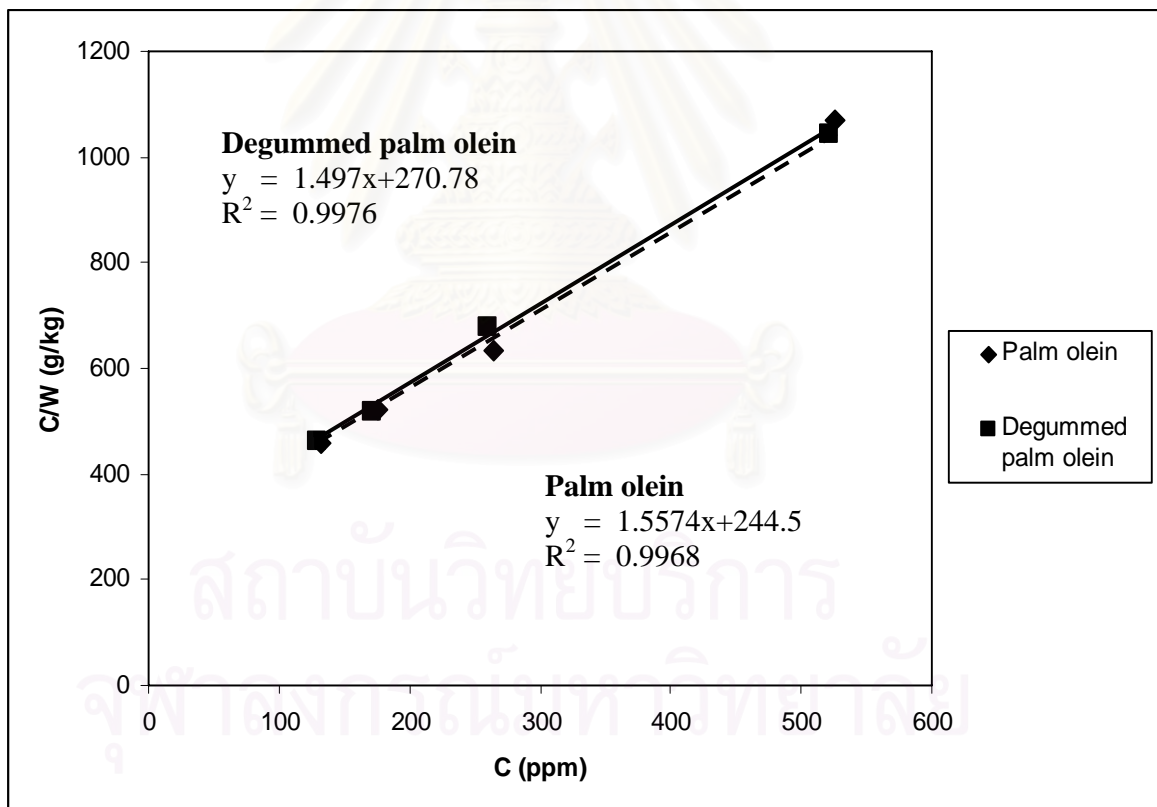
Figure 4.24 Apparent adsorption isotherm of crude β -carotene from palm olein and degummed palm olein.

The similar trend of adsorption isotherm of crude β -carotene from palm olein and degummed palm olein were observed.

At low concentration, the Langmuir isotherm may appear to be nearly linear. The non-linear form can be evaluated by transforming to the linear equation (2):

$$\frac{C}{W} = \frac{1}{(W_{\max} * K)} + \left(\frac{1}{W_{\max}}\right)C \dots\dots\dots(2)$$

Linear Langmuir plots which was obtained by plotting C/W versus C showed in figure 4.25 for crude β -carotene from palm olein and degummed palm olein, respectively. From the linear equation (2), W_{\max} and K constant can be calculated from slope and intercept in linear plots.



For palm olein, $W_{\max} = 0.6420$ and $K = 0.0064$

For degummed palm olein $W_{\max} = 0.6707$ and $K = 0.0055$

Figure 4.25 Langmuir isotherm in its linear form for crude β -carotene from palm olein and degummed palm olein.

The values for W_{\max} and K are inserted into the generic formula (1):

For palm olein,

$$W = \frac{0.0041 * C}{(1 + 0.0064 * C)} \dots\dots\dots(3)$$

For degummed palm olein,

$$W = \frac{0.0037 * C}{(1 + 0.0055 * C)} \dots\dots\dots(4)$$

In addition, the isotherm which is Langmuir type implied that crude β -carotene is adsorbed in the form of unimolecular layer since in our work, the value of $K < 1$.

4.6 Crude β -carotene recovery

Crude β -carotene recovery from palm olein depends on many factors, such as the kind of adsorbents, adsorption conditions, desorption solvent and conditions. Loading of oily materials per gram of resins has strongly impact to crude β -carotene recovery. Table 4.4 presents the % recovery of crude β -carotene comparisons from various researches.

Table 4.4 Crude β -carotene recovery of PSDVB compared with other researches

Palm oil	Adsorbent	Oil loading (g oil/g adsorbent)	Adsorption temp., desorption temp. ($^{\circ}$ C)	Eluting solvent	% Recovery	Ref.
CPO	PSVDB	0.25	50,60	Hexane	74	15
CPO	Ag-clay	5	60,25	THF	66	22
Palm olein	Activated carbon	4	80,25	Toluene	30	20
<u>Palm olein</u> at Oil:IPA 1:0	PDVB	2	35,35	Hexane	20.47	This study
at Oil:IPA 1:3	PDVB	2	35,35	Hexane	44.52	
<u>Degummed palm olein</u> at Oil:IPA 1:0	PDVB	2	35,35	Hexane	24.96	
at Oil:IPA 1:3	PDVB	2	35,35	Hexane	44.16	

From table 4.4, Ag-clay had the higher % crude β -carotene recovery than our work resins. However, we must also consider about toxicity of solvent and cost, clay must treat with antioxidant before used. Hexane is particular preferable from the standpoint of safety in the case where the recovered crude β -carotene are used for food, e.g. as edible coloring. Baharin's work [15] also had highest % crude β -carotene recovery since they performed at very low oil loading. In our work, we used higher oil loading since we considered that adsorbent cost is very expensive comparing to activated carbon.

However, we should consider the amount of crude β -carotene recovery from olein instead of high % recovery value. Table 4.5 showed the amount of crude β -carotene recovery at different conditions suggests that the suitable condition for crude β -carotene recovery from non diluted oil was at adsorption temperature and adsorption time of 60 °C and 60 minutes, respectively. We also found that degummed palm olein and palm olein gave similar amount of crude β -carotene recover at 0.1485 and 0.1545 mg β -carotene/gram of oil, respectively.

Table 4.5 % Recovery and amount of crude β -carotene recovery from palm olein and degummed palm olein at 60 minutes.

Condition	Palm olein		Degummed palm olein	
	% Recovery	Amount of crude β -carotene recovery (mg/initial weight of g oil)	% Recovery	Amount of crude β -carotene recovery (mg/initial weight of g oil)
Oil:IPA 1:0 (60 °C)	28.67	0.1545	28.30	0.1485
Oil:IPA 1:0 (35 °C)	20.47	0.1077	24.96	0.1303
Oil:IPA 1:1 (35 °C)	37.81	0.0997	37.65	0.0978
Oil:IPA 1:2 (35 °C)	41.78	0.0734	42.78	0.0735
Oil:IPA 1:3 (35 °C)	44.52	0.0586	44.16	0.0574

Chapter V

Conclusions and Recommendations

5.1 Conclusions

The aim of this research was to investigate crude β -carotene recovery from palm olein and degummed palm olein at various conditions of adsorption on PSDVB. The influence of parameters, *i.e.* adsorption time (15, 30, 60 and 90 minutes), oil dilution (1:0, 1:1, 1:2 and 1:3 by wt.) and adsorption temperature (35 and 60 °C) were studied. The results were also concluded as in the followings.

1. In degumming investigation, we found that amount of gum increased with the increase of phosphoric acid content. However, phosphoric acid content did not affect to the concentration of crude β -carotene in palm olein.

2. In case of different adsorption time experiments (15, 30, 60 and 90 minutes), similar trend of % adsorption of palm olein and degummed palm olein with time were observed. With an increase of adsorption time, amount of crude β -carotene adsorbed on PSDVB also increased in the range of 24.29 to 32.29 % adsorption. Equilibrium adsorption time of both palm olein and degummed palm olein are 60 minutes. The result of desorption of crude β -carotene from PSDVB resins indicated that degummed palm olein give an average % desorption of 82.35 % while palm olein is 68.19 %. The % recovery of crude β -carotene in adsorbed oil suggested that % recovery from degummed palm olein of all experiments gave higher values than palm olein. % Recovery ranged from 16.24 to 23.50 % for palm olein and 20.53 to 25.77 % for degummed palm olein.

3. In case of oil dilution experiments (1:0, 1:1, 1:2 and 1:3 by wt), the results of % adsorption at different oil dilutions and times from palm olein and degummed palm olein showed that at each oil dilutions, % adsorption of crude β -carotene increased with an increase of time until it was nearly constant at 60 minutes. We also found that the more oil was diluted, the higher % adsorption was clearly obtained. Comparison of % adsorption at 60 minutes from palm olein and degummed palm olein at different oil dilution, indicated that there were not significantly different from each other. In case of desorption of crude β -carotene from the resins with hexane, % desorption from degummed palm olein was

slightly higher than palm olein. We also found that % desorption decreased as oil dilution increased. For % recovery of crude β -carotene from palm olein and degummed palm olein, the results indicated that % recovery increased as oil dilution increased and there is not significantly different of % recovery between palm olein and degummed palm olein.

4. For the effect of adsorption temperature (35 and 60 °C), we found that at each adsorption temperature, % adsorption of crude β -carotene increased with an increase of time in the range of 24.29 to 40.78 until it was nearly constant at 60 minutes. The higher adsorption temperature, the higher % adsorption was obtained. There is not significantly different of % adsorption between palm olein and degummed palm olein. In case of desorption, adsorption temperature at 60 °C of degummed palm olein has closely % desorption to palm olein (degummed palm olein give an average % desorption of 79.98 % while palm olein is 75.11 %), while at 35 °C, degummed palm olein shows significantly higher % desorption than palm olein (degummed palm olein give an average % desorption of 82.35 % while palm olein is 68.19 %). For % recovery the results showed that % recovery increased as adsorption temperature increased and there is not significantly different of % recovery between palm olein and degummed palm olein. % Recovery at 60 °C and 60 minutes were 28.67 % for palm olein and 28.30 % for degummed palm olein.

5. For our work, we concluded in term of amount of β -carotene recover that the suitable condition was at 60 °C adsorption temperature for 60 minutes. Non diluted palm olein (in stead of degummed palm olein) is recommended.

5.2 Recommendations

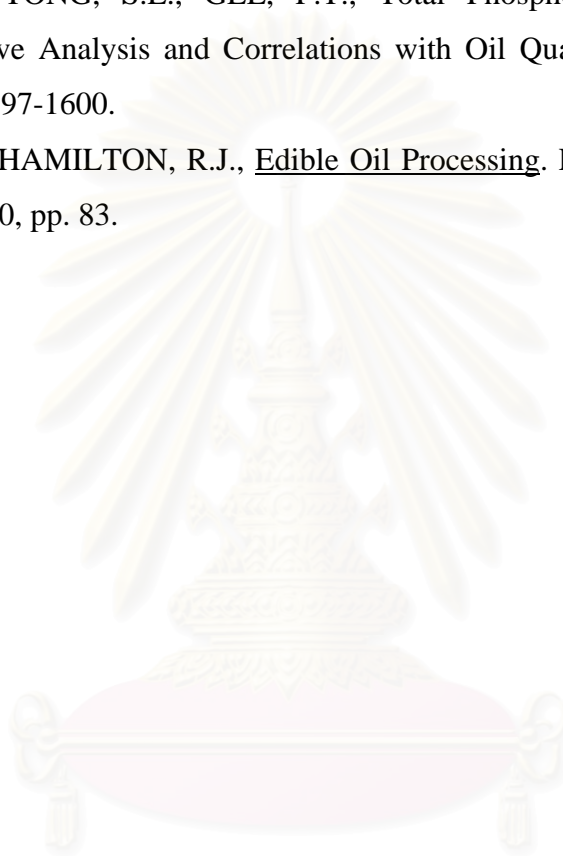
1. Should try 100 % degummed oil in stead of 28 % (in this study).
2. Concerning to high cost of PSDVB, life-span of PSDVB adsorption should be studied.

REFERENCES

- [1] Biodiesel [Online]. Available from: <http://www.dede.go.th>. [2006, January 5].
- [2] Choo, Yuen, May. Palm oil carotenoids. Food and Nutrition Bulletin. 15(1993/1994): 1-18
- [3] Ooi, C.K., Choo, Y.M., Ma, A.N., Yap, S. C. Recovery of carotenes. United States Patent. US 6,072,092, 2006.
- [4] <http://www.tistr.or.th/tistr2006/indexn.php?pages=home>
- [5] Heidlas, J., Huber, G., Cully, J., Kohlrausch, U., Process for the extraction of carotenes from natural sources. United States Patent. US 5,714,658, 1998.
- [6] Tan, B., Saleh, M.H., Integrated process for recovery of carotenoids and tocotrienols from oil. United States Patent. US 5,157,132, 1992.
- [7] Kunst, A., Hakkaart, M.J.J., Preparation of concentrates of coloring agents, United States Patent. US 5,246,722, 1993.
- [8] Khachik, F., Process for purification and crystallization of palm oil carotenoids. United States Patent. US 7,119,238, 2006.
- [9] Chuang, M.H., Brunner, G., Concentration of minor components in crude palm oil. J. of Supercritical Fluids. 37 (2006): 151-156.
- [10] Darnako, D., Cheryan, M., Carotenoids from red palm oil methyl esters by nanofiltration. JAOCs. 83 (2006): 365-370.
- [11] Keat, O.C., May, C.Y., Hock, A.O.S., Recovery of carotenoids. United States Patent. US 5,019,668, 1991.
- [12] Nitsche, M., Johannsbauer, W., Jordan, V. Process for obtaining carotene from palm oil. United States Patent. US 5,902,890, 1999.
- [13] Baharin, B.S., Rahman, A., Kawim., Oyaizu, T., Tanaka, Y., Takagi, S, Separation of Palm Carotene from Crude Palm Oil by Adsorption Chromatography with a Synthetic Polymer Adsorbent. JAOCs. 75 (1998): 399-404.
- [14] Latip, R.A., Baharin, B.S., Man, Y.B.C., Rahman, A., Evaluation of different types of synthetic adsorbents for carotene extraction from crude palm oil. JAOCs. 77 (2000): 1277-1281.

- [15] Latip, R.A., Baharin, B.S., Man, Y.B.C., Rahman, A., Effect of adsorption and solvent extract process on the percentage of carotene extracted from crude palm oil. JAOCS. 78 (2001): 83-78.
- [16] Latip, R.A., Baharin, B.S., Man, Y.B.C., Rahman, A., The effect of carotene extraction system on crude palm oil quality, carotene composition, and carotene stability during storage. JAOCS. 78 (2001): 851-855.
- [17] Hussein, M.Z.B., Kuang, D., Zainal, Z., Teck, T.K., Kaolin-carbon adsorbents for carotene removal of red palm oil. Journal of Colloid and Interface Science. 235 (2001): 93-100.
- [18] Hock, G.R.S., Seok, K.R.T., Recovery of carotenoids, tocopherols, tocotrienols and sterols from esterified. U.K. Patent. GB 2,218,989, 1989.
- [19] Yoshiro, T., Itsuo, H., Akira, O., Akio, O, A process for producing carotene from oils and fats. U.K. Patent. GB 2,160,874, 1986
- [20] Thangwongjathroengit, D., Extraction of β -carotene from palm oil using activated carbon. Master's Thesis, Program of Biotechnology, Faculty of Science, Chulalongkorn University, 1994.
- [21] Poopunpanich, W. Separation of carotenoids from palm oil by adsorption on clays. Master's Thesis, Program of Petrochemistry, Faculty of Science, Chulalongkorn University, 2003.
- [22] Dechfoog, P., Separation of carotenoids from palm oil using Ag-treated clays. Master's Thesis, Program of Petrochemistry, Faculty of Science, Chulalongkorn University, 2005.
- [23] Ong, A.H., Boey, P.L., Ching, H.S., Ooi, C.K., A Study on Carotene Extraction from Palm Oil. J. Palm Oil Prod. Technol. 1980: 505-519.
- [24] Palm oil [online]. Available from: http://en.wikipedia.org/wiki/Oil_palm [2006, January 5].
- [25] Hendry, G.A.F., Houghton, J.D., Natural Food Colorants. 2nd ed. London: Blackkei, 1996, pp. 197-200, 228-230.
- [26] Zweig, G., Aherrna, J., Handbook of Chromatography Volume 1. Florida: Boca Raton, 2000, pp. 4-5, 97.
- [27] McCabe, W.L., Smith, J.C., Harriott, P., Unit operation of chemical engineering. 6th ed. New York: McGraw-Hill, 2001, pp. 812-817.
- [28] Adsorption [Online]. Available from: <http://encyclopedia.the freedictionary.com/adsorption>. [2006, January 5].

- [29] Yang, R.T., Adsorbents Fundamentals and Applications. New Jersey: Haboken, pp. 79-84.
- [30] Kreulen, H.P., Fractionation and winterization of Edible Fats and Oil. JAOCS. 53(1993): 393-396.
- [31] Nasirullah, Physical Refining: Electrolyte Degumming of Nonhydratable Gums from Selected Vegetable Oils. Journal of Food Lipids. 12(2005): 103-111.
- [32] GOH, S.H., TONG, S.L., GEE, P.T., Total Phospholipids in Crude palm oil: Quantitative Analysis and Correlations with Oil Quality Parameters. JAOCS. 61 (1984): 1597-1600.
- [33] HAMM, W., HAMILTON, R.J., Edible Oil Processing. England: Sheffield Academic Press, 2000, pp. 83.

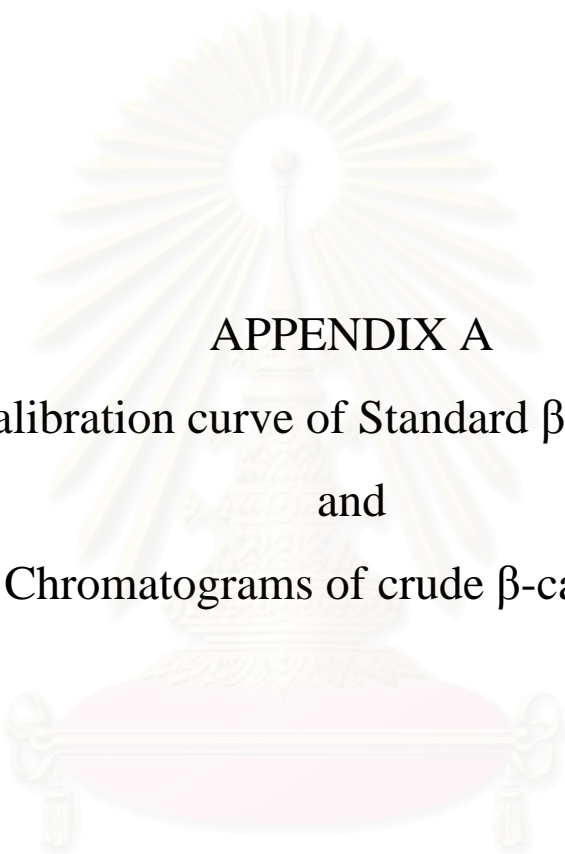


สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



APPENDICES

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



APPENDIX A
Calibration curve of Standard β -carotene
and
Chromatograms of crude β -carotene

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

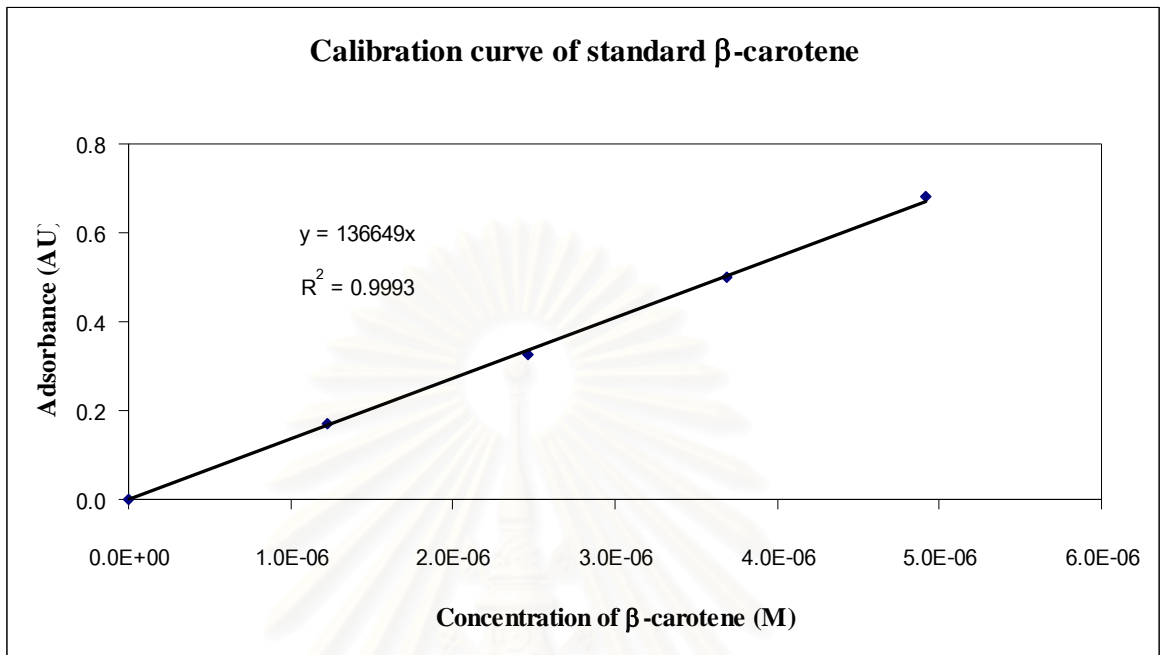


Figure A1 Calibration curve of Standard β -carotene in molar (UV-visible spectrometry).

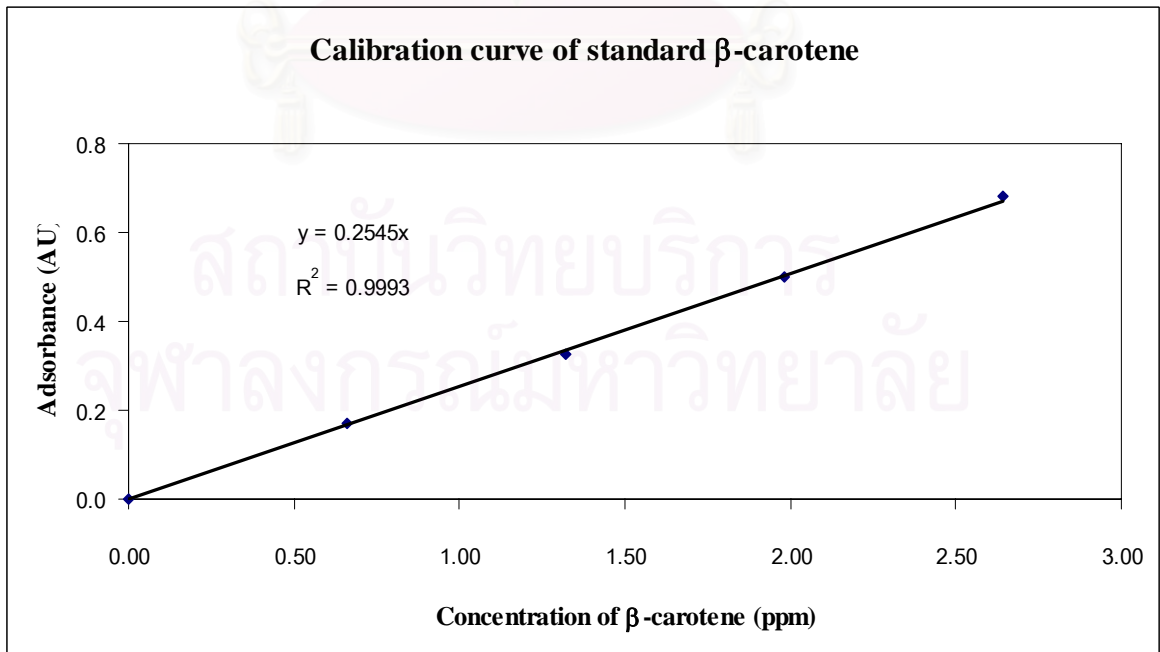


Figure A2 Calibration curve of Standard β -carotene in ppm (UV-visible spectrometry).

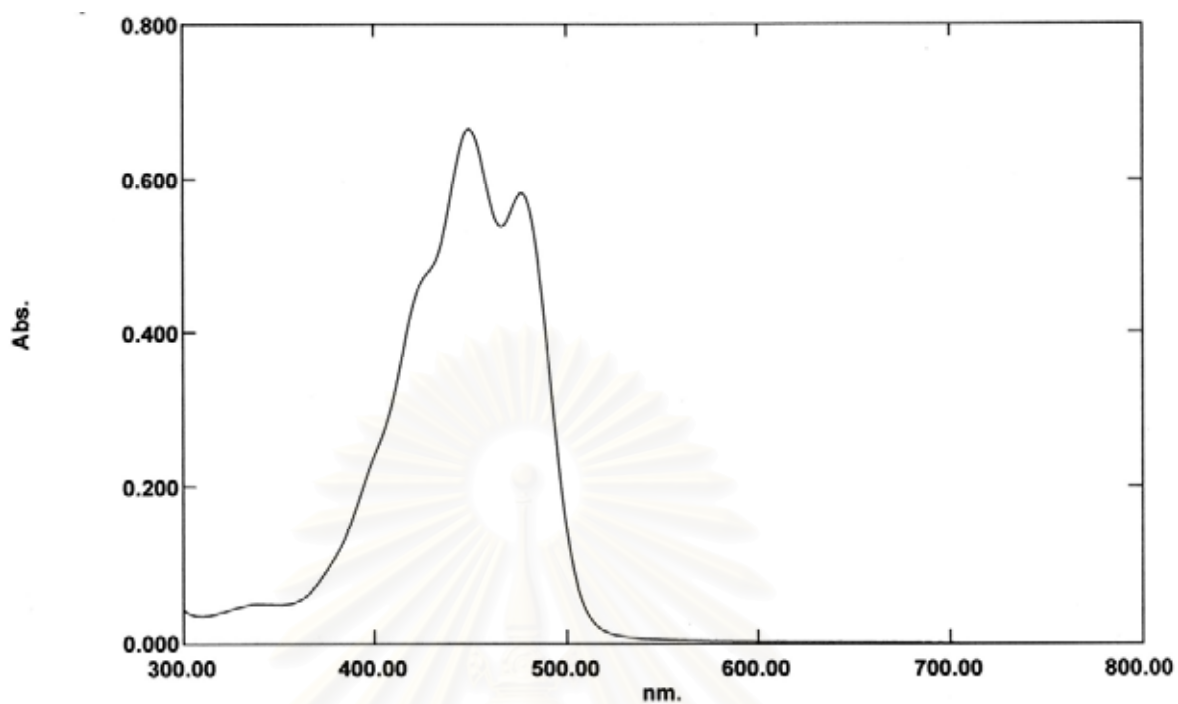


Figure A3 UV-visible spectrum of standard β -carotene.

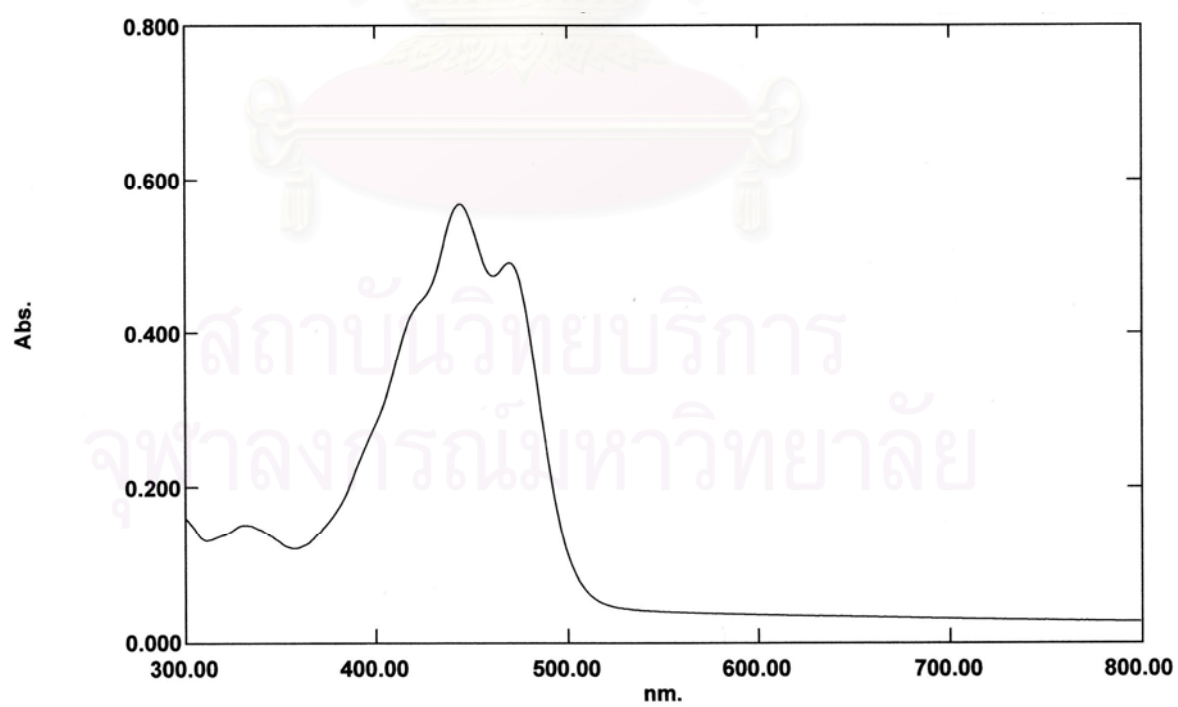


Figure A4 UV-visible spectrum of palm olein.

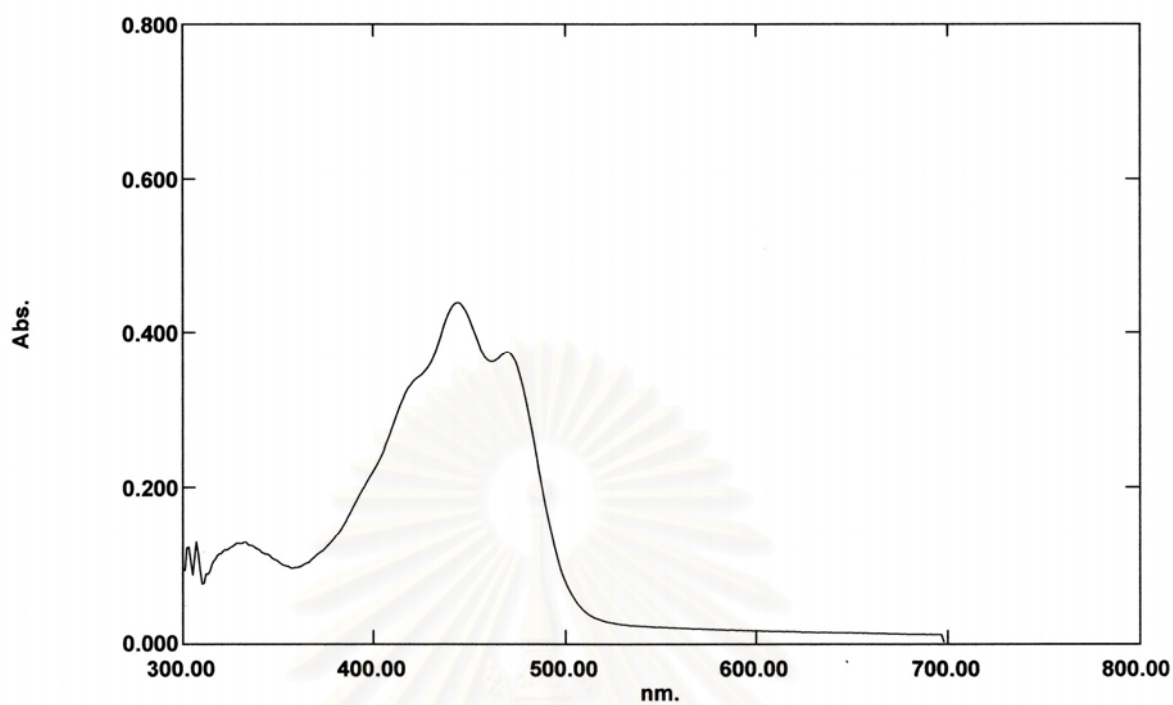


Figure A5 UV-visible spectrum of degummed palm olein.

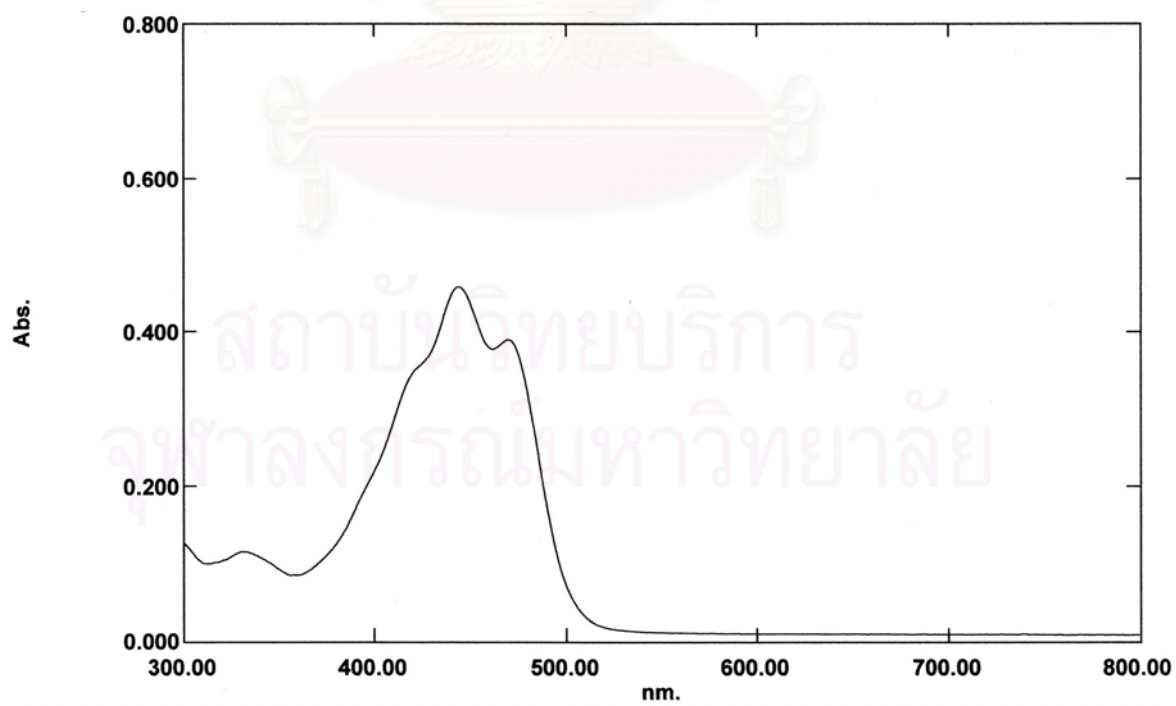
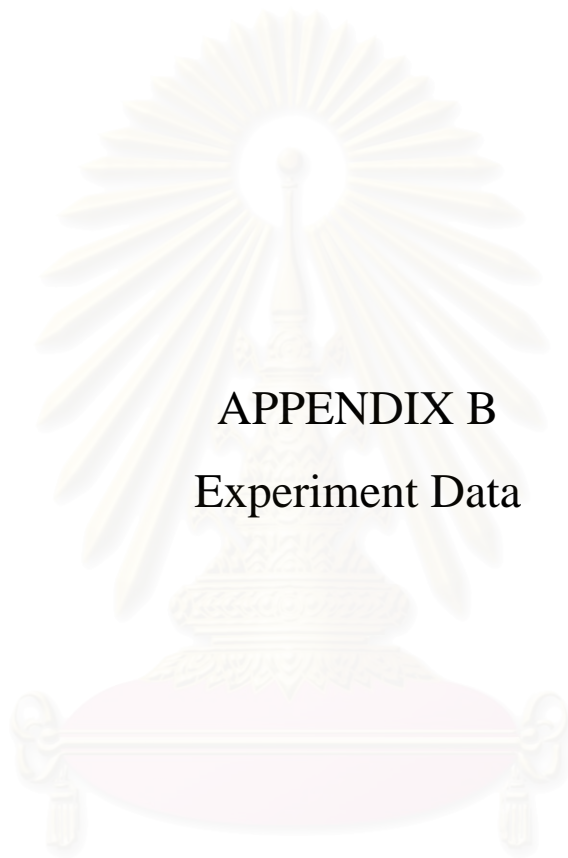


Figure A6 UV-visible spectrum of crude β -carotene



APPENDIX B
Experiment Data

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Table B1 Concentration of crude β -carotene after degumming

Phosphoric acid content (ml/g palm olein)	Concentration of crude β -carotene (ppm)
0.0000	548.2616
0.0000	545.6701
0.0000	530.6773
0.0000	525.6561
0.0004	536.9990
0.0008	538.6498
0.0010	531.2224
0.0010	533.0043
0.0012	542.2653
0.0013	531.4312
0.0016	527.9161
0.0017	531.0824
0.0019	538.3286
0.0020	538.8352
0.0020	540.6637
0.0023	525.5833
0.0027	526.3658
0.0030	527.0096
0.0033	530.5906
0.0037	526.8197
0.0040	511.0372
0.0043	526.5082

Table B2 The amount of gum from degumming

Phosphoric acid (ml/g palm olein)	Gum content (g/g palm olein)
0.00033	0.0005
0.00067	0.0007
0.00100	0.0012
0.00133	0.0018
0.00167	0.0023
0.00200	0.0027
0.00233	0.0031
0.00267	0.0034
0.00300	0.0039
0.00333	0.0042
0.00367	0.0042
0.00400	0.0042

Table B3 % Adsorption, % desorption, % recovery of crude β -carotene and adsorption ability of PSDVB at 35 °C adsorption temperature, different adsorption time and weight ratio of palm olein to isopropanol was 1:0.

Adsorption time (min.)	% Adsorption	% Desorption	% Recovery	Adsorption ability of PSDVB (mg crude β -carotene/g PSDVB)
15	25.02	64.92	16.24	0.40
30	26.85	66.71	17.91	0.43
60	31.06	65.92	20.47	0.49
90	31.24	75.20	23.50	0.49

Table B4 % Adsorption, % desorption, % recovery of crude β -carotene and adsorption ability of PSDVB at 35 °C adsorption temperature, different adsorption time and weight ratio of palm olein to isopropanol was 1:1.

Adsorption time (min.)	% Adsorption	% Desorption	% Recovery	Adsorption ability of PSDVB (mg crude β-carotene/g PSVDB)
15	37.36	76.26	28.49	0.30
30	46.15	73.77	34.04	0.37
60	52.52	71.98	37.81	0.42
90	55.16	72.13	39.79	0.44

Table B5 % Adsorption, % desorption, % recovery of crude β -carotene and adsorption ability of PSDVB at 35 °C adsorption temperature, different adsorption time and weight ratio of palm olein to isopropanol was 1:2.

Adsorption time (min.)	% Adsorption	% Desorption	% Recovery	Adsorption ability of PSDVB (mg crude β-carotene/g PSVDB)
15	49.88	67.66	33.74	0.26
30	57.89	66.63	38.57	0.31
60	63.76	65.52	41.78	0.34
90	68.43	64.89	44.40	0.36

Table B6 % Adsorption, % desorption, % recovery of crude β -carotene and adsorption ability of PSDVB at 35 °C adsorption temperature, different adsorption time and weight ratio of palm olein to isopropanol was 1:3..

Adsorption time (min.)	% Adsorption	% Desorption	% Recovery	Adsorption ability of PSDVB (mg crude β-carotene/g PSVDB)
15	61.35	62.79	38.52	0.24
30	67.24	62.45	41.99	0.26
60	72.24	61.62	44.52	0.29
90	74.61	63.33	47.25	0.29

Table B7 % Adsorption, % desorption, % recovery of crude β -carotene and adsorption ability of PSDVB at 35 °C adsorption temperature, different adsorption time and weight ratio of degummed palm olein to isopropanol was 1:0.

Adsorption time (min.)	% Adsorption	% Desorption	% Recovery	Adsorption ability of PSDVB (mg crude β-carotene/g PSVDB)
15	24.29	84.53	20.53	0.38
30	26.63	87.14	23.20	0.42
60	32.03	77.93	24.96	0.50
90	32.29	79.80	25.77	0.51

Table B8 % Adsorption, % desorption, % recovery of crude β -carotene and adsorption ability of PSDVB at 35 °C adsorption temperature, different adsorption time and weight ratio of degummed palm olein to isopropanol was 1:1.

Adsorption time (min.)	% Adsorption	% Desorption	% Recovery	Adsorption ability of PSDVB (mg crude β-carotene/g PSDVB)
15	36.51	78.79	28.77	0.29
30	45.76	75.53	34.57	0.36
60	49.63	75.87	37.65	0.38
90	54.63	72.43	39.56	0.42

Table B9 % Adsorption, % desorption, % recovery of crude β -carotene and adsorption ability of PSDVB at 35 °C adsorption temperature, different adsorption time and weight ratio of degummed palm olein to isopropanol was 1:2.

Adsorption time (min.)	% Adsorption	% Desorption	% Recovery	Adsorption ability of PSDVB (mg crude β-carotene/g PSDVB)
15	52.02	65.53	34.09	0.27
30	60.23	66.74	40.20	0.31
60	64.61	66.22	42.78	0.33
90	67.53	67.02	45.26	0.35

Table B10 % Adsorption, % desorption, % recovery of crude β -carotene and adsorption ability of PSDVB at 35 °C adsorption temperature, different adsorption time and weight ratio of degummed palm olein to isopropanol was 1:3.

Adsorption time (min.)	% Adsorption	% Desorption	% Recovery	Adsorption ability of PSDVB (mg crude β-carotene/g PSVDB)
15	57.41	63.77	36.61	0.23
30	66.34	62.58	41.52	0.26
60	71.70	61.59	44.16	0.28
90	73.40	62.66	45.99	0.28

Table B11 % Adsorption, % desorption, % recovery of crude β -carotene from palm olein and adsorption ability of PSDVB at 60 °C adsorption temperature and different adsorption time.

Adsorption time (min.)	% Adsorption	% Desorption	% Recovery	Adsorption ability of PSDVB (mg crude β-carotene/g PSVDB)
15	29.51	80.13	23.64	0.48
30	35.18	73.79	25.96	0.57
60	38.34	74.79	28.67	0.63
90	40.78	71.74	29.25	0.66

Table B11 % Adsorption, % desorption, % recovery of crude β -carotene from degummed palm olein and adsorption ability of PSDVB at 60 °C adsorption temperature and different adsorption time.

Adsorption time (min.)	% Adsorption	% Desorption	% Recovery	Adsorption ability of PSDVB (mg crude β-carotene/g PSDVB)
15	25.32	86.02	21.78	0.40
30	33.77	81.93	27.67	0.53
60	37.43	75.61	28.30	0.58
90	38.73	76.37	29.58	0.61

VITA

Mr. Rutthai Veeracharttawan was born on 27 September, 1981 in Bangkok, Thailand. He received a Bachelor's Degree of Industrial Chemistry from Faculty of Science, King Mongkut's Institute of Technology North Bangkok in 2002. After then he subsequently completed the requirements for a Master's Degree in Chemical Engineering at the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University in 2006.



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย