UNIVERSITI PUTRA MALAYSIA

FABRICATION OF MODIFIED MESOPOROUS CARBONS-COATED MONOLITH SYNTHESIZED VIA EVAPORATION-INDUCED SELF-ASSEMBLY APPROACH FOR B-CAROTENE ADSORPTION

HOW CAI KIAN

FK 2015 193

FABRICATION OF MODIFIED MESOPOROUS CARBONS-COATED MONOLITH SYNTHESIZED VIA EVAPORATIVE-INDUCED SELF-ASSEMBLY APPROACH FOR β-CAROTENE ADSORPTION

By

HOW CAI KIAN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillments of the Requirement for the Degree of Master of Science

July 2014

© COPYRIGHT UPM

COPYRIGHT

All material contained within the thesis, including without limitation text, logos, icons, photographs, and all other artwork, is copyright material of Universiti Putra Malaysia unless otherwise stated. Use may be made of any material contained within the thesis for non-commercial purposes from the copyright holder. Commercial use of material may only be made with the express, prior, written permission of Universiti Putra Malaysia.

Copyright © Universiti Putra Malaysia

© COPYRIGHT UPM

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the Degree of Master of Science

FABRICATION OF MODIFIED MESOPOROUS CARBONS-COATED MONOLITH SYNTHESIZED VIA EVAPORATIVE-INDUCED SELF-ASSEMBLY APPROACH FOR β-CAROTENE ADSORPTION

By

HOW CAI KIAN

July 2014

Chairman : Professor Ir. Thomas Choong Shean Yaw, PhD
Faculty : Engineering

A rapid synthesis procedure of mesoporous carbons coated monolith (MCCM) adsorbent have been accomplished by the mean of evaporative induced self-assembly (EISA) approach. Furfuryl alcohol acts as carbon precursor, triblock copolymer Pluronic F-127 as soft-template or pore-forming agent, pyrrole as binder for polymerization with nitric acid as catalyst and inorganic cordierite as substrate through dip-coating method. Boehm's acid-base titration experiment revealed dominance of acidic sites over surface of the adsorbents with majority of acidic active sites occupied by phenolic and carboxylic sites. The basicity remains unchanged after modification which is 0.0137mmol/g. Nitrogen adsorption isotherm indicated the representative Type IV isotherm which according to IUPAC classification, resemble mesoporous phase of carbonaceous materials. PSD curves showed bimodal pore sizes distribution of mesoporous carbon adsorbents with excessive acid catalyst and ethanol loading. Higher acid concentration yields fast condensation of polymeric resin during self-assembly process meanwhile excess of ethanol solvent detour the cross-linkage of polymeric materials thus leads to a decrease in adsorption capacities. The β-carotene adsorption capacity were varies between 179.60 (optimum) and 112.56 mg/g (lowest) under various experimental modification conditions. Therefore, adsorption properties: Isotherm, kinetics, and thermodynamics studies have been analyzed using MCCM adsorbent with composites of FA/ F-127/ HNO_3/ EtOH/ Py at molar mass of 3/2.5/ 0.2/ 5/1.

The adsorption kinetics of β-carotene onto MCCM adsorbent in isopropyl alcohol solution was investigated through two kinetic models, namely Largregren first-order and pseudo-second-order model. The adsorption kinetics exemplified the chemisorption of β-carotene onto MCCM adsorbent. Intra-particle diffusion featured the involvement in β-carotene adsorption mechanism however it is not the sole rate-

© COPYRIGHT UPM

limiting step. Two adsorption isotherm namely Langmuir and Freundlich models were used to establish the adsorption equilibrium data at temperature of 30 to 50 ºC. The adsorption experiments data were described better by Freundlich model which elucidated the heterogeneity of surface active sites over MCCM adsorbents with more effective adsorption process at higher temperature. The maximum adsorption capacity of β-carotene obtained was 192.64 mg/g at 50 ºC. The reusability of MCCM adsorbent after adsorption process have been conducted by several batch desorption process. A slight reduction in adsorption capacities have been observed after three consecutive regeneration cycles.

© COPYRIGHT UPM

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

FABRIKASI PENGUBAHSUAIAN MONOLIT DISALUT KARBON MESOLIANG MELALUI PENYEJATAN ARUHAN HIMPUNAN DIRI PENDEKATAN UNTUK PENJERAPAN β-KAROTEN

By

HOW CAI KIAN

Julai 2014

Pengerusi : Profesor Ir. Thomas Choong Shean Yaw, PhD
Fakulti : Kejuruteraan

Kaedah yang cepat untuk sintesis karbon mesoliang melapisi monolit (MCCM) telah dicapai melalui penyejatan aruhan himpunan diri (EISA). Furfuril alkohol bertindak sebagai pelopor karbon, tiga bongkah kopolimer Pluronic F-127 sebagai pembentuk liang, pyrole sebagai ejen pempolimeran dengan asid nitrik sebagai pemangkin dan monolit sebagai substrat melalui kaedah pencelupan. Pentitratan acid-bes eksperimen telah mendedahkan penguasaan keasidan di permukaan MCCM dengan majoriti aktif tapak dikelompoki oleh kumpulan fenolik diikuti oleh karboksilik dan lactonic. Tiada perubahan dalam kebesan, iaitu 0.0137mmol/g. Nitrogen isoterma bagi semua MCCM menunjukkan isoterma jenis IV berdasarkan IUPAC klasifikasi, menyerupai karbon mesoliang fasa. PSD menunjukkan bimodal taburan saiz liang dengan menggunakan asid mangkin dan kandungan etanol yang berlebihan. Kepekatan asid yang tinggi didapati menyebabkan pemeluwapan yang cepat semasa himpunan diri misel sementara itu kandungan etanol yang tinggi melarutkan kepekatan polimer resin dan menghalang proses bersilang-kait antara bahan polimer justeru mengurangkan penyerapan kapasiti. Kapasiti penjerapan β-karoten telah berubah antara 179.60 (optimum) dan 112.56 mg/g (paling rendah) di bawah pelbagai keadaan pengubahan parameter dalam eksperimen. Oleh itu, ciri-ciri penjerapan: Isoterma, kinetik dan kajian termodinamik telah dianalisis dengan menggunakan MCCM penjerapan dengan komposit FA/F-127/HNO_3/EtOH/Py pada jisim molar 3/2.5/0.2/5/1.

Kinetik penjerapan β-karoten ke atas MCCM dalam larutan isopropil alkohol disiasat melalui dua kinetik model, iaitu Largregren tertib pertama dan pseudo-tertib kedua model. Penjerapan β-karoten ke atas MCCM adalah berdasarkan kimia jerapan. Resapan intrapartikel juga terlibat dalam penjerapan mekanisme β-karoten bagaimanapun ia bukan langkah tunggal dalam proses penjerapan. Kesan suhu ke atas keupayaan penjerapan β-karoten telah dinilai melalui dua penjerapan isoterma model iaitu Langmuir dan Freundlich model bagi mewujudkan data keseimbangan

© COPYRIGHT UPM

penjerapan pada suhu 30 hingga 50ºC. Eksperimen penjerapan data yang baik telah diterangkan dengan menggunakan model Freundlich yang menggambarkan kepelbagaian laman permukaan aktif melalui MCCM dengan proses penjerapan lebih berkesan pada suhu yang tinggi. Maksimum kapasiti penjerapan β-karoten yang diperolehi ialah 192.64 mg/g pada 50 ºC. Kebolehgunaan MCCM selepas proses penjerapan telah disiasat dalam sistem kelompok. Kapasiti penjerapan telah berkurangan selepas tiga penjanaan semula beturut-turutan.

© COPYRIGHT UPM

ACKNOWLEDGEMENTS

Throughout my master degree, I learned and gained a lot of knowledge regarding the mesoporous carbon coated onto hierarchical monolith and its synthesized mechanism. Hence, I would like to take this opportunity to acknowledge those who helped me during my research studies at UPM.

First of all, I would like to express my sincere appreciation to my supervisor, Prof. Dr. Ir. Thomas Choong Shean Yaw for his enthusiasm, motivation, continuous guidance and invaluable suggestion throughout the duration of my research project. Special thanks also go to Prof. Dr. Luqman Chuah for his encouragement and insightful opinions. Besides that, I would like to acknowledge the laboratory assistants and technicians for their favorable assistance related to various problems at Laboratory of Environmental and Chemical Engineering, especially En. Joha and Puan Maslinda.

Besides that, heartiest thank is also extended to my post-doctoral senior, Dr. Soraya for her generous assistance, advices and immerse knowledge. I would like to express a deep sense of gratitude to my fellow lab mates: Meiyi, Willie, Terry, Nima and Yinshin for their cordial supports, valuable information and long-lasting friendship which helped me a lot in completing my research study.

Last but not least, I am exceptionally grateful to my parents for their spiritually and financially support. Without these, my research will not be completed successfully.

© COPYRIGHT UPM

This thesis was submitted to the Senate of the Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Thomas Choong Shean Yaw, PhD
Professor Ir.
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Luqman Chuah Abdullah, PhD
Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

ROBIAH BINTI YUNUS, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

© COPYRIGHT UPM

Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) were adhered to.

Signature:	_____
Name of Chairman of Supervisory Committee:	Professor Ir. Dr. Thomas Choong Shean Yaw
Signature:	_____
Name of Member of Supervisory Committee:	Professor Dr. Luqman Chuah Abdullah

© COPYRIGHT UPM

TABLE OF CONTENTS

© COPYRIGHT UPM

© COPYRIGHT UPM

LIST OF TABLES

© COPYRIGHT UPM

LIST OF FIGURES

© COPYRIGHT UPM

© COPYRIGHT UPM

© COPYRIGHT UPM

LIST OF ABBREVIATIONS / NOTATIONS / SYMBOLS

a_L	Langmuir constant related to the affinity of the binding sites or net enthalpy of adsorption	L/mg
b	monolayer capacity of the adsorbent	mg/g
C_e	liquid phase concentration at the equilibrium	mg/L
C_i	initial concentration of β-carotene in solution	mg/L
C_o	initial β-carotene concentration	mg/L
C_t	β-carotene concentration at any time in the liquid phase	mg/L
k_1	rate constant of pseudo first-order sorption	1/min
k_2	rate constant of pseudo second-order sorption	g/mg min
k_{id}	intra-particle diffusion rate constant	mg/g $min^{-0.5}$
K	Langmuir constant	L/g
K_F	Freundlich constant for a heterogeneous adsorbent	L/mg
K_L	Langmuir constant related to the affinity of the binding sites or net enthalpy of adsorption	L/mg
m	mass of adsorbent	g
n	Freundlich exponent (heterogeneity factor)	
q_e	solid phase concentration at the equilibrium phase	mg/g
q_i	initial solid phase β-carotene concentration	mg/g
q_t	amount of β-carotene adsorbed per g of adsorbent at any time	mg/g
R	universal gas constant (8.314)	J/mol K
R_L	dimensionless equilibrium parameter defined by equation	
T	temperature	°C or K
t	time	min
V	volume of liquid	L

© COPYRIGHT UPM

LIST OF ABBREVIATIONS

BET	Brunauer, Emmett, Teller
FTIR	Fourier transform infrared spectroscopy
FA	furfuryl alcohol
IPA	isopropyl alcohol
SEM	scanning electron microscopy
ICDD	international centre diffraction data
IUPAC	international union of pure and applied chemistry
MCCM	mesporous carbon coated monolith
DCM	dichloromethane
AC	activated carbon
MCCM	mesporous carbon coated monolith
DCM	dichloromethane
AC	activated carbon

© COPYRIGHT UPM

CHAPTER 1

INTRODUCTION

1.1 Introduction on Palm Carotene

Malaysia is the world's largest producer and exporter of palm oil which accounts for 51% of world palm oil production and 62% of world exports (Sumathi *et al*., 2008). In additional, crude palm oil (CPO) consists of 1% of minor valuable components, which among them are the carotenoids, vitamin E (tocopherols and tocotrienols) and sterols (Sundram *et al*., 2003) Crude palm oil naturally contains 500-700 ppm of carotenoids, mainly in the form of β-carotene. Recent studies have shown that carotenoids have anticancer activity against certain types of cancers such as oral, pharyngeal, lung and stomach cancers (Choo *et al*., 1997, Sundram *et al*., 2003).

However, the conventional refining of crude palm oil (either physical or chemical process) into lighter coloured oil may lead to the destruction of natural β-carotene (Gapor, 1990). During oil refining process, high temperature and vacuum have been applied during deodorization and deacidification reaction in which are necessary for the removal of all the undesirable components such as free fatty acids (FFA) and decomposition products (Nagendran *et al*., 2000). Consequently, various methods have been developed to recover and extract β-carotene from palm oil in order to prevent the loss of the natural products including saponification (Blaizot, 1953), adsorption using polymeric adsorbents (Tanaka *et al*., 1986, Chan *et al*., 2000), selective solvent extraction (Tanaka *et al*., 1986, Nitsche *et al*., 1999), transesterification followed by both phase separation and molecular distillation of the esters (Iwasaki and Murakoshi, 1992, Choo, 1995), nanofiltration membrane technology (Darnoko and Cheryan, 2006) and supercritical carbon dioxide (Lau *et al*., 2006).

However, transesterification is the only commercial viable process. This carotenoids recovery involves the interesterification of triglycerides (TG) with methanol to yield methyl esters, followed by phase separation, resulting in a carotene-rich layer and a decoloured methyl ester layer. The carotene-rich layer is then further concentrated by molecular distillation and chromatographic methods (Baharin *et al*., 1998). A similar process which involving transesterification of palm oil, followed by molecular distillation of the esters to recover the carotenoids has been reported (Ooi *et al*., 1994), however no edible oil was obtained. Commercial scale production of crude oil for carotenes recovery through chemical transformation of TG to methyl esters resulted in a loss of edible oil (Latip *et al*., 2001).

© COPYRIGHT UPM

Based on present oil refining process, most of the carotenoids in the edible oil are destroyed and discarded by thermal or catalytic process in order to fulfil the demand of light-colored edible oil (Goh *et al*., 1985). To obtain edible oil while separating and concentrating carotenes from crude palm oil, adsorption method have been developed by utilizing the synthetic polymer adsorbents for the extraction of carotenes (Baharin et al., 1998, Sabah and Çelik, 2005, Ahmad et al., 2009, Wu and Li, 2009, Tong et al., 2008, Muhammad et al., 2010). Through adsorption process, palm carotenes have been successfully extracted without undergoing chemical conversion of triglyceride to methyl ester while maintaining the edible-oil quality.

1.2 Carbon

Activated clays, activated carbon and silica-based products are adsorbents commonly used in the edible oil refining process. Fuller's earth-type activated clay such as acid-activated bentonite (AAB) or acid-activated montmorillonite is the most popular adsorbent among activated clays due to its cheapness price (Srasra *et al*., 1989, Kheok and Lim, 1982, Low *et al*., 1998, Falaras *et al*., 1999).

Decolourization or bleaching capacity of Fuller's earth and clay for crude edible oil is generally expressed as β-carotene adsorption (Boki *et al*., 1992, Christidis and Kosiari, 2003, Khoo *et al*., 1979, Kheok and Lim, 1982, Sarier and Güler, 1988). However, the adsorption capacity of β-carotene on Fuller's earth and clay is not as effective as activated carbon adsorbent. Furthermore, the carotenes were found to be suffering from oxidative or acid-catalyzed degradation reaction (Goh *et al*., 1985). Several studies for adsorption of β-carotene by using activated carbon adsorbent have been reported (Hussein *et al.*, 2001, Muhammad *et al.*, 2010, Ong and Boey, 1980).

Conventional porous carbons constitute variety of applications such as adsorption and filtration etc. due to their versatile properties. However in certain applications their properties are insufficient (Gupta, 2009). For example, surface area of macroporous carbon blacks is relatively low whereas micropore sizes in active carbons are too small to fulfil certain needs. Thus, a new class of porous carbon was introduced which exhibits bigger surface area and porosity larger than 2 nm. IUPAC defines these properties as mesopores which possess pores between 2 to 50 nm. (Sterk, 2010). Mesoporous carbons play a dominant role particularly in the adsorption of large molecules such as vitamins and polymers. The advantageous of the mesoporous carbon make them very attractive in variety applications, for instance chromatography, electrochemistry (double-layer capacitors and fuel cells) and adsorption of large biomolecules. Therefore, knowledge of how to control the mesoporosity is desirable and tailoring the carbons with such pores attracted much attention in nanomaterials science (Gierszal, 2008).

Mesoporous carbons can be synthesized through several methods: firstly, carbons material with non-uniform pores and broad pore sizes distribution while secondly, carbons with relatively uniform pores. The first group of carbons are the most common and rather easy to fabricate. One of distinct methods that allow one to develop

© COPYRIGHT UPM

mesoporosity is through carbonization of polymer blends with different degrees of thermal stability. These polymers are physically or molecularly mixed and then subjected to high temperature treatment. During this process, one of the polymers undergoes carbonization and becomes a matrix of porous carbon while the other polymer decomposes and, in turn, volatizes leaving behind voids in the form of irregularly located mesopores (Gierszal, 2008). An example of the pair of thermally unstable and carbonizing polymers employed in the synthesis of mesoporous carbons are poly(ethylene glycol)-poly(diphenylene pyromellitimide) and poly(vinyl butyral)-novolac phenol resin (Ozaki *et al.*, 1997). Additional information on the carbons with irregular mesopores can be found in the review published by Kyotani (Kyotani, 2000).

The second group of the carbons are characterized by uniform mesopores size which can be synthesized by mean of either hard-template (with assistance of mesoporous silica) or soft-template (with assistance of block copolymer) method. Preliminary studies revealed that the synthesis route via hard-template method was laborious (time-consuming) since multi-steps are required for nano-casting and removal (dissolution) of silica-based template (Lee *et al.*, 2004, Yang and Zhao, 2005, Gierszal and Jaroniec, 2006). Therefore, a new rapid synthesis procedure had been developed by employing evaporative induction self-assembly route in which supra molecular self-assembly carbon precursor and amphiphilic block copolymer as soft-template in presence of evaporative solvent, basically ethanol was used (Jaroniec, 2008, Jin *et al.*, 2009, Hao *et al.*, 2011).

However, the simplified mechanism of soft-templating method is based on the amphiphilic nature of surfactant which will be self-assembled to form hydrophilic micellar core-shell and hydrophobic micellar core in the presence of ethanol medium. Hydrophilic micellar core-shell nanostructures are hydrogen-bonded with carbon precursors, followed by pyrolysis to form mesoporous carbonaceous materials while hydrophobic micellar core tend to decompose to form pores which allowing the incorporation or adherence of other molecules (adsorption). One of the reports on mesoporous carbons synthesized via soft-template route was first published in 2004 by Dai (Liang *et al.*, 2004) . Dai and coworkers proposed that hexagonal cylindrical mesopores (p6mm symmetry) carbon films were accomplished by self-assembly of copolymerizable resorcinol and formaldehyde with the help of polystyrene-block-poly(4-vinylpyridine) as the soft-template.

In this dissertation, adsorption process of β-carotene was carried out by using mesoporous carbonaceous materials coated on honeycomb cordierite monolith, namely MCCM as adsorbent. The MCCM adsorbent was synthesized through evaporative induced self-assembly approach using furfuryl alcohol as carbon precursor, triblock copolymer Pluronic F-127 as soft-template or pore-forming agent, pyrrole as binder for polymerization with nitric acid as catalyst and inorganic cordierite as substrate by employed dip-coating method.

Adsorbent and catalyst coating on inorganic ceramics monoliths are of great significance for industry because of their favourable properties such as low pressure drop, high geometric surface area, short diffusion lengths, lack of attrition by vibration, thermal shock resistance, and convenient separation from media without assistance of outer magnetic field (Garcıa-Bordejé *et al*., 2002, Garcia-Bordeje *et al*., 2006, Pérez-Cadenas *et al*., 2006). Mesoporous carbons layer can be easily coated on cordierite monolith by dip-coating with polymer resin such as Novalac resin, Furan resin and polyfurfuryl alcohol. Several steps are necessary: first, dipping the ceramic monolith in the carbon precursor then flushing with pressurized air, followed by treatment at elevated temperature for curing purpose and finally carbonization process (Wan *et al*., 2011). Previous works on mesoporous carbons showed diversified architectures of mesostructure can be obtained by changing the composition of polymeric resin composites.

1.3 Problem Statement

The conventional oil refinery process into lighter coloured edible oil might destroy the natural occurring carotenoids in palm oil. To prevent such losses, palm carotenes in CPO are extracted and concentrated from transesterified methyl ester through subsequent washing steps using methanol solvent. However conventional carotenes extraction process caused two major problems: half the pigment is lost during the extraction process and environmental issues due to the high consumption of methanol. In this study, adsorption using synthetic adsorbent has been developed in order to extract and recover the palm carotenes. Previous development on MCCM adsorbent obtained maximum adsorption capacity of 62.12 and 48.78 mg/g using IPA and n-hexane, respectively (Muhammad *et al*., 2010). Therefore, modified MCCM adsorbents have been developed for example by alter the acid catalyst concentration and ethanol concentration to fabricate a desire mesopores of carbonaceous materials for a better adsorption of β-carotene molecules.

1.4 Objectives

a) To synthesize MCCM adsorbent by evaporative self-assembly of furfuryl alcohol (carbon precursor) with the assistance of triblock copolymer Pluronic F-127 as soft-template through dip-coating method.
b) To investigate the effect of nitric acid concentration and ethanol loading on the pore architecture and their corresponding adsorption properties.
c) To predict the β-carotene adsorption kinetic and mechanism by using Lagergren first-order, pseudo-second-order and intra-particle diffusion model.
d) To investigate the adsorption equilibrium of β-carotene onto MCCM adsorbent at temperature of 30 to 50°C. Thermodynamic parameters such as change in Gibb free energy (ΔG°), change in enthalpy (ΔH°) and change in entropy (ΔS°) were evaluated to check the spontaneity of the adsorption process.
e) To investigate the desorption efficiency of MCCM adsorbent by using three different kinds of desorbing agent and its reusability after three consecutive regeneration cycles.

© COPYRIGHT UPM

REFERENCES

Ahmad, A., Chan, C., Abd Shukor, S. and Mashitah, M. 2009. Adsorption kinetics and thermodynamics of β-carotene on silica-based adsorbent. *Chemical Engineering Journal* 148: 378-384.

Alcaniz-Monge, J.A., Cazorla-Amoros, D., Linares-SolanoI, A., Morallon, E. and Vazuez, J. 1998. Preparation of conductive carbon-ceramic composites from coal tar pitch and ceramic monoliths. *Carbon* 36: 1003-1009.

Alkan, M., Demirbaş, Ö. and Doğan, M. 2007. Adsorption kinetics and thermodynamics of an anionic dye onto sepiolite. *Microporous and Mesoporous Materials* 101**:** 388-396.

Argun, M. E., Dursun, S., Ozdemir, C. and Karatas, M. 2007. Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics. *Journal of Hazardous Materials* 141**:** 77-85.

Baharin, B., Rahman, K.A., Karim, M.A., Oyaizu, T., Tanaka, K., Tanaka, Y. and Takagi, S. 1998. Separation of palm carotene from crude palm oil by adsorption chromatography with a synthetic polymer adsorbent. *Journal of the American Oil Chemists' Society* 75**:** 399-404.

Biswas, A.K., Sahoo, J. and Chatli, M.K. 2011. A simple UV-Vis spectrophotometric method for determination of β-carotene content in raw carrot, sweet potato and supplemented chicken meat nuggets. *LWT - Food Science and Technology* 44**:** 1809-1813.

Blaizot, P. 1953. Method of Obtaining Carotene FKOM. Google Patents.

Blomberg, L., Demirbüker, M. and Andersson, M. 1998. Characterization of lipids by supercritical fluid chromatography and supercritical fluid extraction. *Lipid Analysis in Oils and Fats*, pp. 34-58. Springer.

Boki, K., Kubo, M., Kawasaki, N. and Mori, H. 1992. Adsorption isotherms of pigments from alkali-refined vegetable oils with clay minerals. *Journal of the American Oil Chemists' Society* 69**:** 372-378.

Boki, K., Mori, H. and Kawasaki, N. 1994. Bleaching rapeseed and soybean oils with synthetic adsorbents and attapulgites. *Journal of the American Oil Chemists' Society* 71**:** 595-601.

Brigante, M. and Schulz, P.C. 2012. Synthesis of mesoporous silicas in alkaline and acidic media using the systems cetyltrimethylammonium tosylate (CTAT)–Pluronic F127 triblock copolymer and CTAT–Pluronic F68 triblock copolymer as templates. *Journal of colloid and interface science* 369: 71-81.

© COPYRIGHT UPM

Britton, G. 1995. Structure and properties of carotenoids in relation to function. *The FASEB Journal* 9**:** 1551-1558.

Chan, K., Baharin, B., Man, Y.C. and Takagi, S. 2000. Adsorption isotherm studies of palm carotene extraction by synthetic polymer adsorbent. *Journal of Food Lipids* 7**:** 127-141.

Cheah, W., Hosseini, S., Khan, M.A., Chuah, T.G. and Choong, T.S.Y. 2013. Acid modified carbon coated monolith for methyl orange adsorption. *Chemical Engineering Journal* 215–216**:** 747-754.

Chen, Y., Chen, Q., Song, L., Li, H.P. and Hou, F.Z. 2009. Preparation and characterization of encapsulation of Europium complex into meso-structured silica monoliths using PEG as the template. *Microporous and Mesoporous Materials* 122**:** 7-12.

Choo, Y. 1995. Carotenoids from palm oil. *Palm Oil Developments* 22**:** 1-6.

Choo, Y., Ma, A. and Yap, S. 1997. Carotenes, vitamin E and sterols in oils from Elaeis guineensis, Elaeis oleifera and their hybrids. *Palm Oil Dev* 27**:** 1-9.

Choo, Y.M., Yap, S.C., Ooi, C.K., Ma, A.N., Goh, S.H. and Ong, A.S.H. 1996. Recovered oil from palm-pressed fiber: a good source of natural carotenoids,vitamin E, and sterols. *Journal of the American Oil Chemists' Society* 73**:** 599-602.

Choura, M., Belgacem, N.M. and Gandini, A. 1996. Acid-catalyzed polycondensation of furfuryl alcohol: mechanisms of chromophore formation and cross-linking. *Macromolecules* 29**:** 3839-3850.

Christidis, G.E. and Kosiari, S. 2003. Decolorization of vegetable oils: A study of the mechanism of adsorption of β-carotene by an acid-activated bentonite from Cyprus. *Clays and Clay Minerals* 51**:** 327-333.

Darnoko, D. and Cheryan, M. 2006. Carotenoids from red palm methyl esters by nanofiltration. *Journal of the American Oil Chemists' Society* 83**:** 365-370.

Falaras, P., Kovanis, I., Lezou, F. and Seiragakis, G. 1999. Cottonseed oil bleaching by acid-activated montmorillonite. *Clay Minerals* 34**:** 221-232.

Freundlich, H. 1906. Over the adsorption in solution. *J. Phys. Chem* 57**:** 292.

Fytianos, K., Voudrias, E. and Kokkalis, E. 2000. Sorption–desorption behaviour of 2,4-dichlorophenol by marine sediments. *Chemosphere* 40**:** 3-6.

Gadkaree, K. 1998. Carbon honeycomb structures for adsorption applications. *Carbon* 36**:** 981-989.

© COPYRIGHT UPM

Gapor, M. 1990 Effect of refining and fractionation on vitamin E in palm oil. In *Proceedings of 1989 PORIM International Palm Oil Development Conference*, pp 261-5. Kuala Lumpur, Malaysia: Palm Oil Research Institute of Malaysia.

Garcia-Bordeje, E., Lazaro, M., Moliner, R., Alvarez, P., Gómez-Serrano, V. and Fierro, J. 2006. Vanadium supported on carbon coated honeycomb monoliths for the selective catalytic reduction of NO at low temperatures: Influence of the oxidation pre-treatment. *Carbon* 44**:** 407-417.

Gierszal, K.P. 2008. *Synthesis, adsorption and structural properties of carbons with uniform and ordered mesopores*, PhD Thesis, Kent State University.

Gierszal, K.P. and Jaroniec, M. 2006. Carbons with extremely large volume of uniform mesopores synthesized by carbonization of phenolic resin film formed on colloidal silica template. *Journal of the American Chemical Society* 128**:** 10026-10027.

Goertzen, S.L., Thériault, K.D., Oickle, A.M., Tarasuk, A.C. and Andreas, H.A. 2010. Standardization of the Boehm titration. Part I. CO_2 expulsion and endpoint determination. *Carbon* 48**:** 1252-1261.

Goh, S., Choo, Y. and Ong, S. 1985. Minor constituents of palm oil. *Journal of the American Oil Chemists' Society* 62**:** 237-240.

Gonzalez-Pradas, E., Villafranca-Sanchez, M., Valverde-Garcia, A. and Villafranca-Sanchez, E. 1991. Adsorption of β-carotene from acetone solution on natural and chemically modified bentonite. *Materials Chemistry and Physics* 27**:** 307-319.

Gregg, S., Sing, K. and SW, A. 1982. Surface area and Porosity. *Academic Press Inc. Ltd., London*.

Güler, Ç. And Tunç, F. 1992. Chlorophyll adsorption on acid-activated clay. *Journal of the American Oil Chemists Society* 69**:** 948-950.

Gupta, V. 2009. Application of low-cost adsorbents for dye removal–A review. *Journal of environmental management* 90**:** 2313-2342.

Hao, N., Wang, H., Webley, P. A. and Zhao, D. 2010. Synthesis of uniform periodic mesoporous organosilica hollow spheres with large-pore size and efficient encapsulation capacity for toluene and the large biomolecule bovine serum albumin. *Microporous and Mesoporous Materials* 132**:** 543-551.

Hao, G.P., Li, W.C., Wang, S., Wang, G.H., Qi, L. and Lu, A.H. 2011. Lysine-assisted rapid synthesis of crack-free hierarchical carbon monoliths with a hexagonal array of mesopores. *Carbon* 49**:** 3762-3772.

Ho, Y.S. and Mckay, G. 2000. The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Research* 34**:** 735-742.

© COPYRIGHT UPM

Hosseini, S., Khan, M.A., Malekbala, M.R., Cheah, W. and Choong, T.S.Y. 2011. Carbon coated monolith, a mesoporous material for the removal of methyl orange from aqueous phase: Adsorption and desorption studies. *Chemical Engineering Journal* 171**:** 1124-1131.

Hussein, M.Z.B., Kuang, D., Zainal, Z. and Teck, T.K. 2001. Kaolin–carbon adsorbents for carotene removal of red palm oil. *Journal of colloid and interface science* 235**:** 93-100.

Iwasaki, R. and Murakoshi, M. 1992. Palm oil yields carotene for world markets. *International news on fats, oils and related materials,* pp. 3.

Jaroniec, M. 2008. Incorporation of inorganic nanoparticles into mesoporous carbons synthesized by soft templating. *The Journal of Physical Chemistry* 112**:** 11657-11660.

Jaroniec, M., Gorka, J., Choma, J. and Zawislak, A. 2009. Synthesis and properties of mesoporous carbons with high loadings of inorganic species. *Carbon* 47**:** 3034-3040.

Jia, Y. and Thomas, K. 2000. Adsorption of cadmium ions on oxygen surface sites in activated carbon. *Langmuir* 16**:** 1114-1122.

Jin, J., Nishiyama, N., Egashira, Y. and Ueyama, K. 2009. Vapor phase synthesis of ultrathin carbon films with a mesoporous monolayer by a soft-templating method. *Chemical Communications* 11: 1371-1373.

Kaynak, G., Ersoz, M. and Kara, H. 2004. Investigation of the properties of oil at the bleaching unit of an oil refinery. *Journal of colloid and interface science* 280**:** 131-138.

Kheok, S. and Lim, E. 1982. Mechanism of palm oil bleaching by montmorillonite clay activated at various acid concentrations. *Journal of the American Oil Chemists Society* 59**:** 129-131.

Khoo, L., Morsingh, F. and Liew, K. 1979. The Adsorption of β-Carotene by bleaching earths. *Journal of the American Oil Chemists Society* 56**:** 672-675.

Ko, Y.S., Koh, C.W., Lee, U. and Kwon, Y.U. 2011. Synthesis of mesoporous titania thin films with vertical pore channels and thick and crystalline walls. *Microporous and Mesoporous Materials* 145: 141-145.

Kresge, C., Leonowicz, M., Roth, W., Vartuli, J. and Beck, J. 1992. Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature* 359: 710-712.

Kruk, M., Jaroniec, M., Ko, C.H. and Ryoo, R. 2000. Characterization of the porous structure of SBA-15. *Chemistry of material* 12**:** 1961-1968.

© COPYRIGHT UPM

Kyotani, T. 2000. Control of pore structure in carbon. *Carbon* 38**:** 269-286.

Lagergren, S. 1898. About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademiens Handlingar* 24**:** 1-39.

Langmuir, I. 1916. The Constitution and Fundamental Properties of Solids and Liquids: Part I Solids. . *Journal of the American Chemical Society* 38**:** 2221-2295.

Latip, R., Baharin, B., Man, Y. C. and Rahman, R.A. 2000. Evaluation of different types of synthetic adsorbents for carotene extraction from crude palm oil. *Journal of the American Oil Chemists' Society* 77**:** 1277-1282.

Latip, R., Baharin, B., Man, Y.C. and Rahman, R.A. 2001. Effect of adsorption and solvent extraction process on the percentage of carotene extracted from crude palm oil. *Journal of the American Oil Chemists' Society* 78**:** 83-87.

Lau, H.L.N., Choo, Y.M., Ma, A.N. and Chuah, C.H. 2006. Characterization and supercritical carbon dioxide extraction of palm oil (Elaeis Guineensis). *Journal of Food Lipids* 13**:** 210-221.

Lee, J., Han, S. and Hyeon, T. 2004. Synthesis of new nanoporous carbon materials using nanostructured silica materials as templates. *Journal of Materials Chemistry* 14**:** 478-486.

Li, K., Zheng, Z., Huang, X., Zhao, G., Feng, J. and Zhang, J. 2009. Equilibrium, kinetic and thermodynamic studies on the adsorption of 2-nitroaniline onto activated carbon prepared from cotton stalk fibre. *Journal of Hazardous Materials* 166**:** 213-220.

Liang, C., Hong, K., Guiochon, G.A., Mays, J.W. and Dai, S. 2004. Synthesis of a Large-Scale Highly Ordered Porous Carbon Film by Self-Assembly of Block Copolymers. *Angewandte Chemie International Edition* 43**:** 5785-5789.

Liang, C., and Dai, S. 2006. Synthesis of mesoporous carbon materials via enhanced hydrogen-bonding interaction. *Journal of the American Chemical Society* 128(16): 5316-5317.

Liew, K., Yee, A. and Nordin, M. 1993. Adsorption of carotene from palm oil by acid-treated rice hull ash. *Journal of the American Oil Chemists' Society* 70**:** 539-541.

Long, D., Qiao, W., Zhan, L., Liang, X. and Ling, L. 2009. Effect of template and precursor chemistry on pore architectures of triblock copolymer-templated mesoporous carbons. *Microporous and Mesoporous Materials* 121: 58-66.

Low, K.S., Lee, C.K. and Kong, L.Y. 1998. Decolorisation of crude palm oil by acid-activated spent bleaching earth. *Journal of Chemical Technology and Biotechnology* 72**:** 67-73.

© COPYRIGHT UPM

Ma, M.H. and Lin, C.I. 2004. Adsorption kinetics of β-carotene from soy oil using regenerated clay. *Separation and Purification Technology* 39**:** 201-209.

Mckay, G., Bino, M. and Altameni, A. 1985. The adsorption of various pollutants from aqueous solutions on to activated carbon. *Water Research* 19**:** 491-495.

Meng, Y., Gu, D., Zhang, F., Shi, Y., Yang, H., Li, Z., Yu, C., Tu, B. and Zhao, D. 2005. Ordered mesoporous polymers and homologous carbon frameworks: amphiphilic surfactant templating and direct transformation. *Angewandte Chemie* 117: 7215-7221.

Muhammad, Choong, T.S.Y., Chuah, T.G., Yunus, R. and Yap, Y. 2010. Adsorption of β-carotene onto mesoporous carbon coated monolith in isopropyl alcohol and *n*-hexane solution: equilibrium and thermodynamic study. *Chemical Engineering Journal* 164**:** 178-182.

Muhammad, Khan, M.A., Choong, T.S.Y., Chuah, T. G., Yunus, R. and Yap, Y.H.T. 2011. Desorption of β-carotene from mesoporous carbon coated monolith: Isotherm, kinetics and regeneration studies. *Chemical Engineering Journal* 173**:** 474-479.

Nagendran, B., Unnithan, U., Choo, Y. and Sundram, K. 2000. Characteristics of red palm oil, a carotene-and vitamin Erich refined oil for food uses. *Food & Nutrition Bulletin* 21**:** 189-194.

Nitsche, M., Johannisbauer, W. and Jordan, V. 1999. Process for obtaining carotene from palm oil. Google Patents.

Ong, A. and Boey, P. 1980. An improved method for extraction of carotene. British Patent.

Ooi, C., Choo, Y., Yap, S., Basiron, Y. and Ong, A. 1994. Recovery of carotenoids from palm oil. *Journal of the American Oil Chemists' Society* 71**:** 423-426.

Ozaki, J., Endo, N., Ohizumi, W., Igarashi, K., Nakahara, M., Oya, A., Yoshida, S. and Iizuka, T. 1997. Novel preparation method for the production of mesoporous carbon fiber from a polymer blend. *Carbon* 35**:** 1031-1033.

Patterson, H.B.W. 1992. Bleaching and purifying fats and oils: theory and practice, American Oil Chemists' Society.

Pérez-Cadenas, A.F., Kapteijn, F., Moulijn, J.A., Maldonado-Hódar, F.J., Carrasco-Marín, F. and Moreno-Castilla, C. 2006. Pd and Pt catalysts supported on carbon-coated monoliths for low-temperature combustion of xylenes. *Carbon* 44**:** 2463-2468.

Ryoo, R., Joo, S.H., Kruk, M. and Jaroniec, M. 2001. Ordered mesoporous carbons. *Advanced Materials* 13**:** 677-681.

© COPYRIGHT UPM

Sabah, E. and Çelik, M.S. 2005. Sepiolite: An effective bleaching adsorbent for the physical refining of degummed rapeseed oil. *Journal of the American Oil Chemists' Society* 82**:** 911-916.

Sabah, E., Çinar, M. and Çelik, M. S. 2007. Decolorization of vegetable oils: Adsorption mechanism of β-carotene on acid-activated sepiolite. *Food Chemistry* 100**:** 1661-1668.

Sarier, N. and Güler, C. 1988. β-Carotene adsorption on acid-activated montmorillonite. *Journal of the American Oil Chemists Society* 65**:** 776-779.

Seo, J.S., Burri, B.J., Quan, Z. and Neidlinger, T.R. 2005. Extraction and chromatography of carotenoids from pumpkin. *Journal of Chromatography A* 1073**:** 371-375.

Silva, S.M., Sampaio, K.A., Ceriani, R., Verhé, R., Stevens, C., Greyt, W.D. and Meirelles, A.J. 2013. Adsorption of Carotenes and Phosphorus from Palm Oil onto Acid Activated Bleaching Earth: Equilibrium, kinetics and thermodynamics. *Journal of Food Engineering*.

Srasra, E., Bergaya, F., Van Damme, H. and Ariguib, N. 1989. Surface properties of an activated bentonite—Decolorisation of rape-seed oils. *Applied Clay Science* 4**:** 411-421.

Srivastava, V.C., Mall, I.D. and Mishra, I.M. 2006. Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA. *Journal of Hazardous Materials* 134**:** 257-267.

Sterk, L. J. 2010. *Soft-Templating Synthesis and Adsorption Properties of Phenolic Resin-based Mesoporous Carbons in the Presence of Metal Salts*, PhD Thesis, Kent State University.

Stratton, S.P., Schaefer, W.H. and Liebler, D. C. 1993. Isolation and identification of singlet oxygen oxidation products of. beta.-carotene. *Chemical research in toxicology* 6**:** 542-547.

Sumathi, S., Chai, S. and Mohamed, A. 2008. Utilization of oil palm as a source of renewable energy in Malaysia. *Renewable and Sustainable Energy Reviews* 12**:** 2404-2421.

Sundram, K., Sambanthamurthi, R. and Tan, Y.A. 2003. Palm fruit chemistry and nutrition. *Asia Pacific journal of clinical nutrition* 12**:** 355-362.

Tan, I., Ahmad, A. L. and Hameed, B. 2008. Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: Equilibrium, kinetic and thermodynamic studies. *Journal of Hazardous Materials* 154**:** 337-346.

© COPYRIGHT UPM

Tan, I., Hameed, B. and Ahmad, A. 2007. Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon. *Chemical Engineering Journal* 127**:** 111-119.

Tanaka, Y., Hama, I., Oishida, A. and Okabe, A. 1986. A process for producing carotene from oils and fats. British Patent, 2160874.

Tanaka, S., Nishiyama, N., Egashira, Y., & Ueyama, K. (2005). Synthesis of ordered mesoporous carbons with channel structure from an organic–organic nanocomposite. Chemical communications, (16), 2125-2127.

Temelli, F. and Güçlü-Üstündağ, Ö. 2005. Supercritical technologies for further processing of edible oils. *Bailey's industrial oil and fat products*.

Teoh, Y.P., Khan, M.A. & Choong, T.S.Y. 2013. Kinetic and isotherm studies for lead adsorption from aqueous phase on carbon coated monolith. *Chemical Engineering Journal* 217**:** 248-255.

Tong, J., Wu, Z., Sun, X., Xu, X. and Li, C. 2008. Adsorption Kinetics of β-Carotene and Chlorophyll onto Acid-activated Bentonite in Model Oil. *Chinese Journal of Chemical Engineering* 16**:** 270-276.

Vergunst, T., Kapteijn, F. and Moulijn, J.A. 1998. Carbon coating of ceramic monolithic substrates. *In:* B. DELMON, P.A.J.R.M.J.A.M.P.G. and PONCELET, G. eds. *Studies in Surface Science and Catalysis.* Elsevier.

Wan, Y. and Zhao, D. 2007. On the controllable soft-templating approach to mesoporous silicates. *Chemical reviews* 107: 2821-2860.

Wan, Y., Cui, X. and Wen, Z. 2011. Ordered mesoporous carbon coating on cordierite: Synthesis and application as an efficient adsorbent. *Journal of Hazardous Materials* 198**:** 216-223.

Wang, B.E., Hu, Y.Y., Xie, L. and Peng, K. 2008. Biosorption behavior of azo dye by inactive CMC immobilized Aspergillus fumigatus beads. *Bioresource Technology* 99**:** 794-800.

Weber, W. and Morris, J. 1963. Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div. Am. Soc. Civ. Eng* 89**:** 31-60.

Wu, C.H. 2007. Adsorption of reactive dye onto carbon nanotubes: equilibrium, kinetics and thermodynamics. *Journal of Hazardous Materials* 144**:** 93-100.

Wu, F.C., Tseng, R.L. and Juang, R.S. 2005. Comparisons of porous and adsorption properties of carbons activated by steam and KOH. *Journal of colloid and interface science* 283**:** 49-56.

© COPYRIGHT UPM

Wu, Z. and Li, C. 2009. Kinetics and thermodynamics of β-carotene and chlorophyll adsorption onto acid-activated bentonite from Xinjiang in xylene solution. *Journal of Hazardous Materials* 171**:** 582-587.

Yang, H. and Zhao, D. 2005. Synthesis of replica mesostructures by the nanocasting strategy. *Journal of Materials Chemistry* 15**:** 1217-1231.

Yao, J., Li, L., Song, H., Liu, C. and Chen, X. 2009. Synthesis of magnetically separable ordered mesoporous carbons from F127/$[Ni(H_2O)_6](NO_3)^2$/resorcinol-formaldehyde composites. *Carbon* 47: 436-444.

Zanatta, C.F. and Mercadante, A.Z. 2007. Carotenoid composition from the Brazilian tropical fruit camu–camu (Myrciaria dubia). *Food Chemistry* 101**:** 1526-1532.

Zhang, F., Meng, Y., Gu, D., Yan, Y., Yu, C., Tu, B., and Zhao, D. 2005. A facile aqueous route to synthesize highly ordered mesoporous polymers and carbon frameworks with Ia3d bicontinuous cubic structure. *Journal of the American Chemical Society* 127(39): 13508-13509.

Zhang, N., Qiu, H., Si, Y., Wang, W. and Gao, J. 2011. Fabrication of highly porous biodegradable monoliths strengthened by graphene oxide and their adsorption of metal ions. *Carbon* 49**:** 827-837.

Zhao, D., Huo, Q., Feng, J., Chmelka, B.F. and Stucky, G.D. 1998. Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures. *Journal of the American Chemical Society* 120**:** 6024-6036.

© COPYRIGHT UPM

PUBLICATION

How, C. K., Khan, M. A., Hosseini, S., Chuah, T. G., & Choong, T. S. (2014). Fabrication of mesoporous carbons coated monolith via evaporative induced self-assembly approach: Effect of solvent and acid concentration on pore architecture. *Journal of Industrial and Engineering Chemistry*, *20*(6), 4286-4292.

© COPYRIGHT UPM

UNIVERSITI PUTRA MALAYSIA

STATUS CONFIRMATION FOR THESIS / PROJECT REPORT AND COPYRIGHT

ACADEMIC SESSION : _____

TITLE OF THESIS / PROJECT REPORT :

FABRICATION OF MODIFIED MESOPOROUS CARBONS-COATED MONOLITH SYNTHESIZED VIA EVAPORATIVE-INDUCED SELF-ASSEMBLY APPROACH FOR β-CAROTENE ADSORPTION

NAME OF STUDENT: HOW CAI KIAN

I acknowledge that the copyright and other intellectual property in the thesis/project report belonged to Universiti Putra Malaysia and I agree to allow this thesis/project report to be placed at the library under the following terms:

1. This thesis/project report is the property of Universiti Putra Malaysia.
2. The library of Universiti Putra Malaysia has the right to make copies for educational purposes only.
3. The library of Universiti Putra Malaysia is allowed to make copies of this thesis for academic exchange.

I declare that this thesis is classified as :

*Please tick (√)

☐	**CONFIDENTIAL**	(Contain confidential information under Official Secret Act 1972).
☐	**RESTRICTED**	(Contains restricted information as specified by the organization/institution where research was done).
☐	**OPEN ACCESS**	I agree that my thesis/project report to be published as hard copy or online open access.

This thesis is submitted for :

☐	**PATENT**	Embargo from_____ until _____ (date) (date)

Approved by:

_____	_____
(Signature of Student)	(Signature of Chairman of Supervisory Committee)
New IC No/ Passport No.:	Name:
Date :	Date :

[Note : If the thesis is CONFIDENTIAL or RESTRICTED, please attach with the letter from the organization/institution with period and reasons for confidentially or restricted.]

© COPYRIGHT UPM