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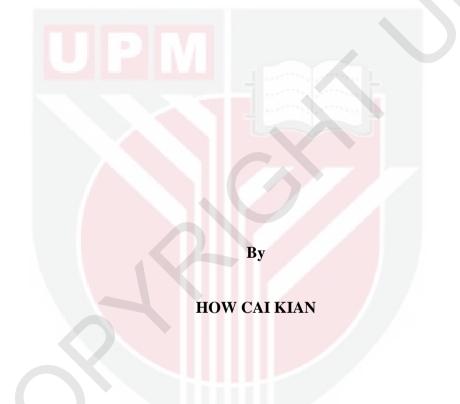
FABRICATION OF MODIFIED MESOPOROUS CARBONS-COATED MONOLITH SYNTHESIZED VIA EVAPORATION-INDUCED SELF-ASSEMBLY APPROACH FOR B-CAROTENE ADSORPTION

HOW CAI KIAN

FK 2015 193



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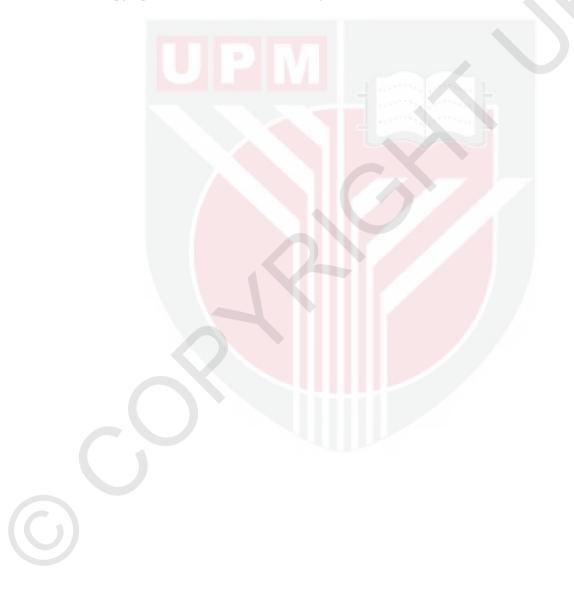
Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillments of the Requirement for the Degree of Master of Science

July 2014

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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

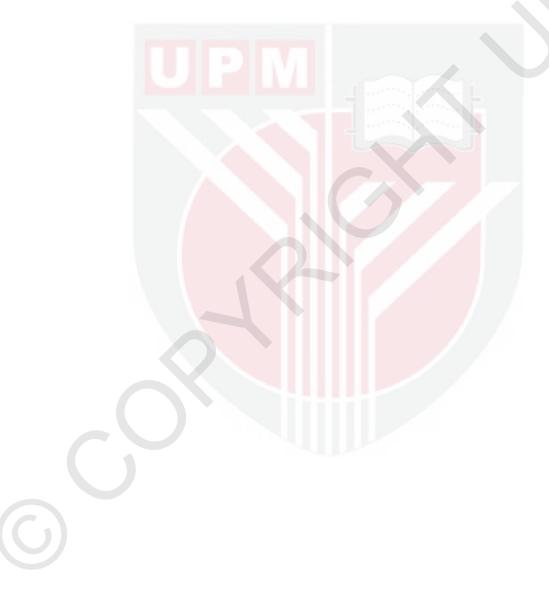


Chairman: Professor Ir. Thomas Choong Shean Yaw, PhDFaculty: Engineering

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 selfassembly 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/ HNO₃/ 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-

limiting step. Two adsorption isotherm namely Langmuir and Freundlich models were used to establish the adsorption equilibrium data at temperature of 30 to 50 °C. 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 °C. 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.



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

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Julai 2014

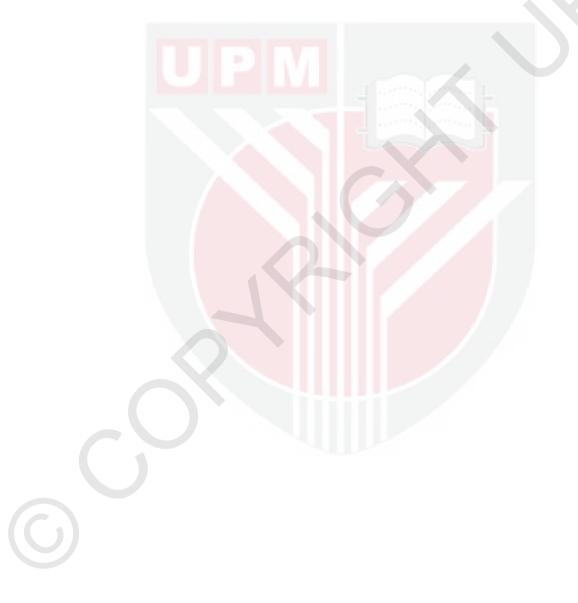
Pengerusi : Profesor Ir. Thomas Choong Shean Yaw, PhD Fakulti : Kejuruteraan

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/HNO₃/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

penjerapan pada suhu 30 hingga 50°C. 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 °C. Kebolehgunaan MCCM selepas proses penjerapan telah disiasat dalam sistem kelompok. Kapasiti penjerapan telah berkurangan selepas tiga penjanaan semula beturut-turutan.



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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.

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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:

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Date:

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.

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Name of Member	
of Supervisory	
Committee:	Professor Dr. Luqman Chuah Abdullah

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LIST OF ABBREVIATIONS / NOTATIONS / SYMBOLS

$a_{ m L}$	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
$C_{ m e}$	liquid phase concentration at the equilibrium	mg/L
C_{i}	initial concentration of β -carotene in solution	mg/L
$C_{ m o}$	initial β-carotene concentration	mg/L
Ct	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
$k_{ m id}$	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
$K_{ m L}$	Langmuir constant related to the affinity of the binding sites or net enthalpy of adsorption	L/mg
т	mass of adsorbent	g
n	Freundlich exponent (heterogeneity factor)	
$q_{ m e}$	solid phase concentration at the equilibrium phase	mg/g
$q_{ m i}$	initial solid phase β -carotene concentration	mg/g
$q_{ m t}$	amount of β -carotene adsorbed per g of adsorbent at any time	mg/g
R	universal gas constant (8.314)	J/mol K
$R_{\rm L}$	dimensionless equilibrium parameter defined by equation	
Т	temperature	°C or K
t	time	min
V	volume of liquid	L

 $\overline{\mathbf{G}}$

LIST OF ABBREVIATIONS

Brunauer, Emmett, Teller		
Fourier transform infrared spectroscopy		
furfuryl alcohol		
isopropyl alcohol		
scanning electron microscopy		
international centre diffraction data		
international union of pure and applied chemistry		
mesporous carbon coated monolith		
dichloromethane		
activated carbon		
mesporous carbon coated monolith		
dichloromethane		
activated carbon		

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).

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 acidactivated 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 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.

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