OIL PALM LEAVES ASH SILICA-MAGNETITE-*Candida rugosa* LIPASE NANOCONJUGATES FOR SYNTHESIS OF BUTYL BUTYRATE

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Specially dedicated to:

My lovely wife and children for their endless support and prayers.

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ABSTRACT

Although modern technologies have successfully converted a certain percentage of the oil palm biomass into useful bio-products, potentials of the largest oil palm biomass, that is oil palm fronds, have not been fully explored. In this study, a comprehensive physicochemical characterization of the Malaysian oil palm leaves (OPL) was carried out to establish suitability of its composition for industrial applications. Ultimate analysis revealed that the untreated OPL contained carbon (46.98 %), hydrogen (6.50 %), nitrogen (1.81 %) and sulfur (0.15 %) with a moderately high calorific value of 19.21 MJ/kg. Thermal gravimetric analysis indicated that OPL is a lignocellulosic material whereas X-ray fluorescence spectroscopy revealed Si (95.30 %) as the predominant element for acid treated OPL sample. Nanosilica extracted from OPL ash was coated on magnetite and was modified with APTES and glutaraldehyde. Suitability of protocol to immobilize *Candida rugosa* lipase (CRL) onto modified OPL-silica were assessed at different concentrations of glutaraldehyde and CRL solutions, as well as time and temperature. Data on surface topography and morphology obtained by Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetry analysis-differential thermogravimetry (TGA-DTG), atomic force microscopy (AFM), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) showed that CRL was present on the surface of the support (Gl-A-SiO_2-MNPs) as CRL/Gl-A-SiO_2-MNPs. Immobilization parameters showed that approximately 80 % of CRL initially available was covalently bound onto the Gl-A-SiO_2-MNP. Maximum protein loading and specific activity of 67.50 mg/g and 320.80 ± 0.42 U/g were obtained, respectively. Optimal conditions that gave the highest yield of butyl butyrate (94 %) by OVAT and Box-Behnken design were 3.50 mg/mL protein loading, incubated for 3 h at 45 ℃ using 1-butanol:n-butyric acid ratio 2:1. CRL/Gl-A-SiO_2-MNPs showed an extended operational stability, attaining 50 % of its initial activity after 17 of consecutive esterification cycles. CRL/Gl-A-SiO_2-MNPs catalyzed the esterification synthesis to produce butyl butyrate according to the Ping Pong bi-bi mechanism with inhibition by both substrates. The estimated kinetic values that corresponded to V_{max} of 0.29 mM/min, as well as K_M for substrates, n-butyric acid (K_M^a) and 1-butanol (K_M^b) were 17.27 and 13.78 mM, respectively. Values for K_{cat}, K_{eff} and K_i^b for the CRL/Gl-A-SiO_2-MNPs-catalyzed esterification were 5.11 /min, 0.37 /min/mM and 288.18 mM, respectively. CRL/Gl-A-SiO_2-MNPs exhibited higher thermal-stability than free CRL, based on the values of half-life (45.89 min), D-value (152.45 min), E_d (125.50 kJ/mol), ΔH_d° (122.64 kJ/mol) and ΔG_d° (11.96 kJ/mol) at 70℃. The results indicated that OPL-nanosilica coated on magnetite can potentially be employed as a support for lipase immobilization.

ABSTRAK

Walaupun teknologi moden telah berjaya mengolah peratusan tertentu biojisim kelapa sawit menjadi bio-produk yang berguna, potensi biojisim terbesar iaitu daun kelapa sawit, masih belum diterokai sepenuhnya. Dalam kajian ini, pencirian fizikokimia secara komprehensif ke atas daun kelapa sawit Malaysia (OPL) telah dijalankan untuk mengesahkan kesesuaian komposisinya bagi kegunaan industri. Analisis muktamad menunjukkan bahawa OPL yang tidak dirawat mengandungi karbon (46.98 %), hidrogen (6.50 %), nitrogen (1.81 %) dan sulfur (0.15 %) dengan nilai kalori yang agak tinggi iaitu 19.21 MJ/kg. Analisis gravimetri terma menunjukkan bahawa OPL adalah bahan lignoselulosa manakala spektroskopi pendarfluor sinar-X menunjukkan Si (95.30 %) merupakan unsur utama sampel OPL yang terawat asid. Nanosilika yang diekstrak daripada abu OPL telah disalut pada magnetit dan diubahsuai dengan APTES dan glutaraldehid. Kesesuaian protokol untuk memegunkan lipase *Candida rugosa* (CRL) kepada OPL-silika yang terubahsuai telah dinilai pada kepekatan glutaraldehid dan kepekatan CRL yang berlainan, begitu juga masa dan suhu. Data topografi permukaan dan morfologi yang diperoleh dengan spektroskopi Raman, spektroskopi inframerah transformasi Fourier (FTIR), pembelauan sinar-X (XRD), analisis termogravimetri-termogravimetri pembezaan (TGA-DTG), mikroskopi daya atom (AFM), mikroskopi elektron pengimbas pemancaran (FESEM) dan mikroskopi elektron penghantaran (TEM) menunjukkan kewujudan CRL di atas permukaan penyokong (Gl-A-SiO_2-MNPs) sebagai CRL/Gl-A-SiO_2-MNPs. Parameter pegun menunjukkan bahawa lebih kurang 80 % daripada CRL tersedia pada mulanya adalah terikat secara kovalen kepada permukaan Gl-A-SiO_2-MNP. Pemuatan protein maksimum dan aktiviti khusus yang diperolehi masing-masing adalah 67.50 mg/g dan 320.80 ± 0.42 U/g. Keadaan optimum yang memberikan hasil butil butirat tertinggi (94 %) dengan OVAT dan Box-Behnken ialah muatan protein 3.50 mg/mL yang diinkubasi selama 3 jam pada 45 ℃ menggunakan nisbah 1-butanol:asid n-butirik 2:1. CRL/Gl-A-SiO_2-MNPs menunjukkan kestabilan operasi yang panjang, mencapai 50 % daripada aktiviti awal selepas 17 kitaran pengesteran berturut-turut. CRL/Gl-A-SiO_2-MNPs memangkinkan tindak balas sintesis pengesteran untuk menghasilkan butil butirat menurut mekanisma Ping Pong bi-bi dengan perencatan oleh kedua-dua substrat. Nilai kinetik anggaran yang bersamaan dengan V_{max} 0.29 mM/min, serta K_M substrat, asid n-butirik (K_M^a) dan 1-butanol (K_M^b) masing-masing ialah 17.27 dan 13.78 mM. Nilai K_{cat}, K_{eff} dan K_i^b bagi pengesteran bermangkinkan CRL/Gl-A-SiO_2-MNPs masing-masing ialah 5.11 /min, 0.37 /min/mM dan 288.18 mM. CRL/Gl-A-SiO_2-MNPs menunjukkan kestabilan terma yang lebih tinggi daripada CRL bebas, berasaskan kepada nilai-nilai separuh hayat (45.89 min), nilai D (152.45 min), E_d (125.50 kJ/mol), ΔH_d° (122.64 kJ/mol) dan ΔG_d° (11.96 kJ/mol) pada suhu 70℃. Keputusan menunjukkan bahawa nanosilika OPL- yang tersalut pada magnetit berpotensi untuk digunakan sebagai bahan penyokong bagi memegunkan lipase.

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LIST OF ABBREVIATIONS

AAEMs	-	Alkali and alkaline earth metals
Adj. R^2	-	Adjusted coefficient of determination
AFM	-	Atomic force microscopy
ANOVA	-	Analysis of variance
APTES	-	3-aminopropyltriethoxysilane
BBD	-	Box-Behnken Design
Bi-	-	Two
BSA	-	Bovine serum albumin
CCD	-	Central Composite Design
CHNS	-	Carbon, Hydrogen, Nitrogen and Sulphure
CRL	-	*Candida rugosa* lipase
E_a	-	Activation energy
E_d	-	Deactivation energy
EDS	-	Energy disperse spectroscopy
EFB	-	Empty fruit bunches
$FeCl_2.4H_2O$	-	Iron(II) chloride tetrahydrate
$FeCl_3.6H_2O$	-	Iron(III) chloride hexahydrate
$FeSO_4.7H_2O$	-	Iron(II) sulphate heptahydrate
FFB	-	Fresh fruit bunch
FTIR	-	Fourier transform infrared spectroscopy
Gl	-	Glutaraldehyde
^1H NMR	-	Proton nuclear magnetic resonance
H_2SO_4	-	Sulphuric acid

HCl	-	Hydrochloric acid
I_c	-	Crystallinity index
K_2HPO_4	-	Dipotassium hydrogen phosphate
KH_2PO_4	-	Potassium dihydrogen phosphate
K_a	-	Activation constant
K_{cat}	-	Turnover number/catalytic constant
K_d	-	Deactivation constant
K_{eff}	-	Catalytic efficiency
K_i^A	-	Inhibitory constant of acid
K_i^B	-	Inhibitory constant of alcohol
K_M^B	-	Michaelis-Menten constant for alcohol
MF	-	Mesocarp fibres
NaOH	-	Sodium hydroxide
$-NH_2$	-	Amine group
NH_4OH	-	Ammonium hydroxide
OPF	-	Oil palm fronds
OPFL	-	Oil palm frond leaves
OPL	-	Oil palm leaves
OPLAT	-	Oil palm leaves ash treated
OPLAU	-	Oil palm leaves ash untreated
OPT	-	Oil palm trunks
OVAT	-	One-variable-at-a-time
PKS	-	Palm kernel shell
POME	-	Palm oil mill effluent
R	-	Molar gas constant
R^2	-	Coefficient of determination
RSM	-	Response surface methodology
-SH	-	Thio group
SiO_2	-	Silica

T	-	Absolute temperature
TEM	-	Transmission electron microscopy
TEOS	-	Tetraethyl orthosilane
Tetra-	-	Four
TMOS	-	Tetra methyl orthosilane
Tri-	-	Three
Uni-	-	One
Uv-vis	-	UV-visible spectroscopy
V_{max}		Maximum rate of reaction
XRD	-	X-ray diffraction
XPS	-	X-ray photoelectron spectroscopy
XRF	-	X-ray fluorescence

LIST OF SYMBOLS/UNITS

℃	-	Degree Celsius
g	-	Gram
H	-	Hour
J/mol	-	Joules per mole
L	-	Litre
K	-	Kelvin
kDa	-	Kilo Dalton
kJ/mol	-	Kilo Joules per mole
Mg	-	Milligram
Min	-	Minute
MJ/kg	-	Mega Joules per kilogram
mL	-	Millilitre
mM	-	Millimolar
mg/g	-	Milligram per gram
Rpm	-	Rotation per minutes
S	-	Second
s/v	-	Surface per volume
U	-	Units
μmol	-	Micro mole
v/v	-	Volume per volume
w/v	-	Weight per volume
w/w	-	Weight per weight

%	-	Percentage
ΔH_d°	-	Standard energy of deactivation
ΔG_d°	-	Standard free energy of deactivation
ΔS_d°	-	Standard entropy of deactivation

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

For several decades, the Malaysian economy has been positively enhanced by the oil palm industry, with Malaysia being one of the world's largest exporter of the commodity and its associated products (Agensi Innovasi Malaysia, 2013). Malaysian oil palm industry has experienced rapid growth, so much so that, the total oil palm plantations have grown from ~54 000 hectares in the 1960s, (Abdullah and Sulaiman, 2013) to a whopping ~5.39 million hectares in 2014 (Awalludin *et al.*, 2015). The consequent increase in the number of plantations invariably generate huge quantities of oil palm biomass, amounting to well over 190 million tonnes in 2015 (Awalludin *et al.*, 2015). Continuous pruning, harvesting and replanting of oil palm trees further adds between 44−47 million tonnes of dry weight oil palm fronds (OPF) to the existing annually produced biomass (Agensi Innovasi Malaysia, 2013; Awalludin *et al.*, 2015).

It is known that only an insignificant percentage of oil palm biomass has been converted into useful bio-products for various industrial applications. These include; nanocellulose (Elias *et al.*, 2017), biogas (Chaikitkaew *et al.*, 2015), cellulose nanocrystal (Chieng *et al.*, 2017), bio-composite (Abdulrazik *et al.*, 2017) and biofuel (Kurnia *et al.*, 2016). Despite development of various biotechnological, mechanical and thermochemical processes, in the efforts to convert oil palm biomass into value-added products viz. adsorbents, fillers, anti-caking, biofuels, bio-fertilizers, etc, (Abdul Khalil *et al.*, 2010; Abdulrazik *et al.*, 2017), the full economic and technological benefits of oil palm leaves (OPL) remains unexploited.

In view of the circumstances, it is evident that natural polymers present in large quantities in OPL are highly underutilised. According to literature, OPL is a rich source of cellulose, hemicellulose and lignin with substantial quantity of ash that is rich in SiO_2 (Abnisa *et al.*, 2013; Abdul Rahman *et al.*, 2014; Samiran *et al.*, 2015). Likewise, a recent study reported on the extraction of nanocellulose as well as SiO_2 from OPL (Roslan *et al.*, 2014). Some studies have claimed that palm oil fuel ash is a good source of renewable SiO_2 and can contain as much as 65 % of the compound (Chindaprasirt *et al.*, 2008; Foo and Hameed, 2009). From the industrial and biotechnological perspectives, OPL ash appears to be a promising renewable source of silica. It is a versatile material that can be converted into secondary raw materials or composites useful for manufacturing purposes. In view of this, scientific researches that explore the inexpensive and renewable SiO_2 present in OPL as intermediates for preparing value-added products, appears relevant. Moreover, the present study is supportive of the “Zero Waste Initiatives” proposed by the Malaysian government (Haslenda and Jamaludin, 2011). The direction which focuses on biomass waste utilisation is in accordance with the policy of the Malaysian government to promoting green technologies. It also serves as a source of encouragement to industry players and other stakeholders to participate in the conversion of biomass to value-added products (Agensi Innovasi Malaysia, 2013).

Most importantly, silica (SiO_2) has been rated high amongst the available inorganic support materials used for enzyme immobilisation. The compound has found technological importance for a myriad of applications due to its high thermal and mechanical stability and rigidity (Hartmann and Kostrov, 2013). This has somewhat to do with the abundance of surface polar groups on SiO_2 i.e. silanols (Si–OH) and siloxanes (Si–O–Si). These functional groups are easily converted into functional biomaterials for lipase immobilisation, hence one of the few reasons for SiO_2 being a popular choice of support (Arjmandi *et al.*, 2015; Hung *et al.*, 2015; Kato *et al.*, 2014).

So far, studies on SiO_2 have largely resorted to using SiO_2 sourced from tetraethyl orthosilica (TEOS) as adsorbent for biomaterials, filler in polymer industry (Arjmandi *et al.*, 2015) and support for the immobilisation of enzymes (Kato *et al.*, 2014; Hung *et al.*, 2015). Nonetheless, concerted efforts focusing on acquiring greener and sustainable source of SiO_2 from bio-based materials i.e. agricultural biomass have significantly gained momentum over the past decade. This development has focused on the use of agricultural wastes as renewable sources of SiO_2. This is a conceivable feat as a myriad of agricultural biomass sources are available all year round and, contribute to low carbon dioxide release (de Souza Rodrigues *et al.*, 2010; Ghani *et al.*, 2010).

Lipase (triacylglycerol ester hydrolase EC 3.1.1.3) is one of the several technologically relevant enzymes owing to its broad specificity and high activity. Specifically, this study used *Candida rugosa* lipase (CRL), a versatile enzyme known for its general ability to catalyse a number of important reactions. Among the reactions that CRL catalyses are hydrolysis, transesterification, esterification and interesterification (Che Marzuki *et al.*, 2015; Elias *et al.*, 2017; Manan *et al.*, 2018). Considering the wide commercial utilisation of CRL, its physical modification may prove useful, as the free form of CRL is rapidly deactivated under extreme industrial settings (Sheldon and van Pelt, 2013). Interestingly, the focus on immobilising CRL on a SiO_2-based support, followed a well-reported compatibility for supporting proteins or enzymes. Past studies have mostly resorted to using mesoporous SiO_2-based matrices for supporting enzymes, prepared from the hydrolysis of tetraethyl orthosilicate (TEOS) (Meléndez-Ortiz *et al.*, 2013). In this milieu, for this study to feasibly consider the use of renewable SiO_2 sourced from agricultural biomass as CRL support, innovative techniques of extracting SiO_2 from OPL at quantities exceeding 90% must, therefore, be established.

Correspondingly, the study hypothesised that employment of nanosized silica as support, to improve CRL activity would be more attractive. Aside from offering a higher surface area for CRL attachment, the approach also permits a high enzyme loading capability (Magner, 2013). Additionally, a well-executed immobilisation protocol would heighten the structural stability of CRL and enhance its lipase activity, while prolonging the half-life of CRL. The technique would be greener, too, as it allows the repeated use of the biocatalysts, hence an avenue for possible cost reduction. Reduced enzyme inhibition and the ability for high repeated use of CRL for successive esterification or hydrolytic reactions would be highly advantageous. In fact, these are among the key considerations in devising appropriate enzyme immobilisation protocol (Rodrigues *et al.*, 2013). Meeting these requirements can favourably result in higher interests of manufacturers into adopting newer and greener technology for large-scale manufacturing activities.

1.2 Problem Statement

Although, OPL is the most abundant agricultural biomass in Malaysia (Awalludin *et al.*, 2015), its full economic benefits remains unexploited. Despite implementation of policies, the industrial utilisation level for this biomass is still at its nascent stage as the rate of oil palm biomass conversion to value-added products remains rather low (Agensi Innovasi Malaysia, 2013). Herein, the present study proposed the use of a renewable source of SiO_2 nanoparticles extracted from OPL ash, to develop a new nanosupport material for immobilisation of CRL. In this study, the SiO_2 nanoparticles were covalently coated over magnetite (MNPs) to give the SiO_2-MNPs nanoparticles. The coating of MNPs with SiO_2 is crucial to facilitate easy recovery of CRL from the reaction mixture while extending its operational stability, productivity and catalytic efficacy. The study hypothesised that coating of the MNPs with SiO_2 prior to covalent attachment of CRL can potentially boost stability and catalytic properties of the lipase. This can be inferred from the previously reported biocompatibility of SiO_2 (Hung *et al.*, 2015) in supporting and activating enzymes, as well as its excellent biodegradability (Kwietniewska and Tys, 2014).

Imperatively, studies detailing the use of OPL-nanosilica to prepare SiO_2-MNPs support matrix for CRL immobilisation remains unreported. To test the catalytic efficacy of CRL immobilised onto SiO_2-MNPs, the study used the problematic esterification synthesis of butyl butyrate as the model reaction. The ester was chosen for this study considering its problematic low yields (~50 %), in addition to several other drawbacks from the current commercial Fisher-Speier reaction. In retrospect, the current synthetic method to produce butyl butyrate may be further improve by the biotechnological route. Hence, this study which evaluates the feasibility of enzymatic synthesis of this ester using CRL supported on magnetised SiO_2 from OPL becomes imperative.

1.3 Aim of Study

This research work is aimed at preparing a novel green biocatalyst using OPL-MNPs as highly functional support matrix to enhance activity of CRL to catalyse the high yield synthesis of butyl butyrate.

1.4 Objectives of Research

The study highlights four main objectives:

1. To characterise the physicochemical properties of the untreated and treated Malaysian OPL and ashes, as well as the extracted silica (SiO_2) from treated OPL.
2. To prepare and characterise the morphology of the synthesised SiO_2-MNPs, Gl-A-SiO_2-MNPs and CRL/Gl-A-SiO_2-MNPs.
3. To optimise the protocol for covalent immobilisation of CRL onto SiO_2-MNPs nanosupports.
4. To optimise the CRL/Gl-A-SiO_2-MNPs catalysed synthesis of butyl butyrate.

1.5 Scopes of the Study

This study collected OPL from Universiti Teknologi Malaysia (UTM) oil palm plantation. The OPL was washed and divided into two samples. The first sample was not subjected to acid treatment while the second sample was treated with hydrochloric acid (HCl). Both samples were subjected to thermal treatment to produce SiO_2-rich ash. Physicochemical characterisation of both untreated and treated OPL and their ashes were achieved by the study, using Thermo gravimetric analysis (TGA), Elemental analyzer (CHNS), X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier transform infrared (FTIR) and Nitrogen sorption (N_2).

The study also extracted SiO_2 from the ash of the acid treated oil palm leaves and the silica was coated over the MNPs prepared in the laboratory by co-precipitation of two hydrated iron salts to produce SiO_2-MNPs nanosupport. Activation of SiO_2-MNPs was achieved by treatment with 3-aminopropyltriethoxysilane (APTES) and glutaraldehyde to give a biocompatible nanosupport (Gl-A-SiO_2-MNPs), followed by immobilisation of CRL onto Gl-A-SiO_2-MNPs to produce the biocatalyst (CRL/Gl-A-SiO_2-MNPs). Optimisation of the immobilisation protocol was performed to predict the optimal conditions required for the highest yield of butyl butyrate displaying good catalytic activity.

The morphology and topography of SiO_2-MNPs, Gl-A-SiO_2-MNPs and CRL/Gl-A-SiO_2-MNPs were characterised by FTIR, XRD, TGA, Transmission electron microscopy (TEM), Field emission scanning electron microscopy (FESEM), N_2-sorption, X-ray photon spectroscopy (XPS) and Raman spectroscopy.

To examine efficacy of the CRL immobilisation protocol, the study used the prepared CRL/Gl-A-SiO_2-MNPs to catalyse the esterification synthesis of butyl butyrate as the model study. The study proceeded further to optimise the various esterification parameters to predict the optimal conditions that would give the highest yield of butyl butyrate, using CRL/Gl-A-SiO_2-MNPs as the biocatalyst. The two optimisation techniques used in this study were one-variable-at-a-time (OVAT) and

Response Surface Methodology (RSM) by the Box-Behnken Design (BBD). While seven parameters were optimised by OVAT, four parameters (enzyme loading, time, temperature and substrate molar ratio) were further optimised by RSM.

Kinetic and thermodynamic studies were also investigated to propose mechanism for the esterification reaction of 1-butanol and n-butyric acid. The study established bi-bi Ping-Pong with inhibition by both substrates as the mechanism for the synthesis of butyl butyrate using CRL/Gl-A-SiO_2-MNPs. Thermodynamic parameters such as activation energy of denaturation (E_d), half-life ($t_{1/2}$), $D - value$, standard enthalpy of denaturation (ΔH_d^o), standard free energy of denaturation (ΔG_d^o) as well as standard entropy of denaturation (ΔS_d^o) were also assessed in the study. Finally, the product of esterification was characterised by proton Nuclear magnetic resonance (^{1}H NMR), FTIR and GC-FID.

1.6 Significance of the Study

In line with this initiative, a novel sustainable and green CRL/Gl-A-SiO_2-MNPs nanobiocatalyst having OPL as silica source was prepared while adhering to the philosophy of green chemistry as well as sustainability. Interestingly, the study would concurrently solve environmental issues associated with open burning and active dumping of large quantities of OPL into the ecosystem, by turning it into a support matrix. Most importantly, the approach of using OPL to develop the CRL/Gl-A-SiO_2-MNPs biocatalysts may alleviate the prevailing drawbacks of the chemical synthetic route to manufacture commercial esters. SiO_2 from OPL is relatively cheap, hence, can be used for such purpose rather than the expensive conventional SiO_2 sources i.e. tetraethyl orthosilicate (TEOS) and tetramethyl orthosilicate (TMOS).

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