BIODEGRADATION OF ALKANOLAMINES IN BATCH AND PACKED-BED REACTORS USING FREE LACCASE AND SOL-GEL LACCASE

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This thesis is dedicated to Allah swt, prophet Muhammad saw, my beloved husband, parents and grandparents

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ABSTRACT

Alkanolamine is commonly used in natural gas processing plant for carbon dioxide removal from natural gas. Alkanolamine may incidentally release and contaminate the surrounding soil and water due to plant operational failure or irresponsible related activities. Thus, the application of laccase for biodegradation of alkanolamine, which has not been reported so far, carried out in batch (shake flask) and continuous (packed-bed) reactors was investigated. Though, biodegradation using laccase may offer many advantages, the free laccase (FL) itself is unstable, cannot be reused and poor of thermal and storage stability. The sol-gel laccase (SGL), i.e. SOLAC04 was therefore synthesized by manipulating triethylamine (TEA) concentration (which was used as a gelating agent), laccase loading (L_L), agitation conditions (with or without sonication), and experimental procedures (one-step or two-step) towards obtaining a higher laccase catalytic activity and stability. The SOLAC04 synthesized using two-step procedure, TEA (0.1 mL), laccase loading, L_L (5 mg/mL) and without sonication had the highest laccase catalytic activity and stability as compared to other synthesized by SGL samples. This result suggested that the entrapment in silica matrix provided an additional framework for the preservation of an active laccase conformation at higher temperature and long storage duration. The biodegradation of alkanolamines: diethanolamine (DEA), ethanolamine and N-methylethanolamine was carried out in batch reactor using both FL and SGL; and optimized using response surface methodology. The results showed that the biodegradation efficiency (μ) and biodegradation rate of DEA using SOLAC04 was higher than other alkanolamines and observed to be higher compared to FL. The μ of DEA in batch reactor using FL and SOLAC04, respectively reached an optimum value at 50 °C and 40 °C. The μ of DEA increased with increasing dosage (D_s) of FL and SOLAC04. It was also revealed that the SOLAC04 are fairly stable and can be used many times. The μ of DEA remained constant at almost the same level after being reused for 5 times. The biodegradation performance and μ of DEA using FL under optimum pH of 5.8, temperature of 45.71°C, D_s of 37.14 mg, and reaction time of 42.66 minutes were 84.8 % and 0.077 mg^{-1}, while for SGL obtained under the optimum pH of 5, temperature of 41°C, D_s of 34.01 mg, and reaction time of 57.59 minutes were 66 % and 1.11 mg^{-1}, respectively. The μ of DEA in packed-bed reactor using SOLAC04 was optimum at pH 6, 250 mL/h and 500 ppm. The μ of DEA increased with increasing D_s of SOLAC04. These experimental results demonstrated the advantages gained from entrapment of laccase in silica matrix and the biodegradation superiority of the SGL over FL for the removal of alkanolamines. Thus, the potential of laccase especially SGL for biodegradation of the alkanolamine was finally demonstrated.

ABSTRAK

Alkanolamina lazimya digunakan dalam loji pemprosesan gas asli untuk penyingkiran karbon dioksida daripada gas asli. Alkanolamina secara tidak sengaja boleh terbebas dan mencemarkan tanah dan air yang berada di persekitaran yang berpunca daripada kegagalan operasi atau berkaitan kecuaian aktiviti. Oleh yang demikian, penggunaan lakase untuk biodegradasi, yang mana belum dilaporkan setakat ini telah dilaksanakan dalam reaktor kelompok (kelalang goncang) dan reaktor berterusan (turus terpadat). Walaupun biodegradasi menggunakan lakase boleh memberikan banyak manfaat, lakase bebas (FL) sendiri tidak stabil, tidak dapat diguna semula, dan kurang kestabilan terma dan penyimpanan. Dengan sebab itu, lakase sol-gel (SGL) seperti SOLAC04 telah disintesis dengan memanipulasi kepekatan trietilamina (TEA) (yang mana digunakan sebagai bahan gelatin), muatan lakase (L_L), keadaan pengadukan (bersama atau tanpa sonikasi), dan tatacara eksperimen (satu langkah atau dua langkah) ke arah mendapatkan peningkatan aktiviti bermangkin dan kestabilan. SOLAC04 disintesis menggunakan tatacara dua langkah, TEA (0.1 mL), muatan lakase, L_L (5 mg/mL) dan tanpa sonikasi mempunyai lakase aktiviti bermangkin dan kestabilan paling tinggi jika dibandingkan dengan yang disintesis oleh sampel SGL yang lain. Keputusan ini menunjukkan bahawa pemerangkapan dalam matriks silika memberikan rangka tambahan untuk pemeliharaan bentuk lakase aktif pada suhu yang lebih tinggi dan tempoh penyimpanan yang panjang. Biodegradasi alkanolamina: dietanolamina (DEA), etanolamina dan N-metiletanolamina telah dijalankan dalam reaktor kelompok menggunakan kedua-dua FL dan SGL, dan dioptimumkan menggunakan kaedah permukaan tindak balas. Keputusan menunjukkan bahawa kecekapan biodegradasi (μ) dan kadar biodegradasi untuk DEA menggunakan SOLAC04 lebih tinggi berbanding dengan alkanolamina lain, dan juga lebih tinggi berbanding dengan FL. Nilai μ untuk DEA dalam reaktor kelompok menggunakan FL dan SOLAC04 masing-masingnya mencapai optimum pada 50 °C dan 40 °C. Manakala nilai μ untuk DEA meningkat dengan peningkatan muatan (D_s) untuk FL dan SOLAC04. Ianya telah ditunjukkan bahawa SOLAC04 adalah sangat stabil dan boleh digunakan berulang kali, iaitu nilai μ untuk DEA kekal malar pada aras hampir sama selepas digunakan sebanyak 5 kali. Perolehan biodegradasi dan nilai μ untuk DEA menggunakan FL pada pH optimum 5.8, suhu 45.71°C, D_s 37.14 mg, dan masa tindak balas 42.66 minit masing-masing adalah 84.8 % dan 0.077 mg^{-1}, sementara untuk SGL yang telah didapati optimum pada pH 5, suhu pada 41°C, D_s 34.01 mg, dan masa tindak balas 57.59 minit masing-masing adalah 66 % dan 1.11 mg^{-1}. Nilai μ untuk DEA dalam reaktor turus terpadat menggunakan SOLAC04 memiliki tahap optimum pada pH 6, 250 mL/h dan 500 ppm. Nilai μ untuk DEA meningkat dengan peningkatan D_s untuk SOLAC04. Keputusan eksperimen ini telah membuktikan kemanfaatan yang diperolehi daripada pemerangkapan lakase dalam matriks silika dan keunggulan SGL berbanding FL bagi penyingkiran alkanolamina. Oleh yang demikian, akhirnya potensi lakase terutama SGL untuk biodegradasi alkanolamina telah akhirnya dibuktikan.

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2,6-DMP	-	2,6- dimethoxyphenol
BET	-	Brunauer, Emmett and Teller
BJH	-	Barrett–Joyner–Halenda
CO_2	-	Carbon dioxide
DEA	-	Diethanolamine
DMAMP	-	2-dimethylamino-2-methyl-1-propanol
EA	-	Ethanolamine
FL	-	Free Laccase
FTIR	-	Fourier Transform Infrared Spectrum
H_2S	-	Hydrogen sulfide
HCl	-	Hydrochloric acid
K_2HPO_4	-	di-potassium hydrogen phosphate
KBr	-	Potassium bromine
KH_2PO_4	-	Potassium dihydrogen phosphate
MEA	-	N-methyl ethanolamine
PEG	-	Polyethylene gylcol
PVA	-	Poly (vinyl alcohol)
RSM	-	Response Surface Methodology
SEM	-	Scanning Electron Microscopy
SGL	-	Sol-Gel Laccase
TEA	-	Triethylamine
TEOS	-	Tetraethoxysilane
TMOS	-	Tetramethoxysilane
UV/VIS	-	Ultraviolet/visible light
ANOVA	-	Analysis of Variance

LIST OF SYMBOLS

%	-	Percentage
A	-	Absorbance
D_s	-	Dosage
k_a	-	Linear coefficients
k_{aa}	-	Quadratic coefficients
k_{ab}	-	Quadratic coefficients
k_{ac}	-	Quadratic coefficients
k_{ad}	-	Quadratic coefficients
k_b	-	Linear coefficients
k_{bb}	-	Quadratic coefficients
k_{bc}	-	Quadratic coefficients
k_{bd}	-	Quadratic coefficients
k_c	-	Linear coefficients
k_{cc}	-	Quadratic coefficients
k_{cd}	-	Quadratic coefficients
k_d	-	Linear coefficients
k_{dd}	-	Quadratic coefficients
k_o	-	Constants
L_L	-	Laccase Loadings
L_m	-	Actual Laccase
mg	-	milligram
mL	-	millimetre
^oC	-	Degree Celsius
pH	-	Potential of Hydrogen
ppm	-	Part per million
SOLAC	-	Sol-gel laccase

T	-	Temperature
v	-	Volume
x	-	Multiple
Y	-	Process response or output
Y'	-	Biodegradation performance of alkanolamine

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CHAPTER 1

INTRODUCTION

1.1.1 Research Background

Alkanolamine solutions have been extensively studied during the last 25 years because of their industrial importance in natural gas processing plants, synthetic ammonia plants, fossil-fuel-fired power plants, chemical synthesis, petrochemical, cosmetic formulations, agriculture, and pharmaceutical (Chen *et al.*, 2011; Hansen *et al.*, 2010; Xi *et al.*, 2012; Zurita *et al.*, 2005). Alkanolamines are also used in industrial processing plants for acid gas impurities removal such as carbon dioxide (CO_2), hydrogen sulfide (H_2S), and sulfur dioxide (SO_2) from gas streams (Mundhwa and Henni, 2007).

The main problems associated with alkanolamine gas treatment plants is corrosion that occurs on the cross exchanger rich side, rich-amine piping after cross exchanger, still, and reboiler, where free acid gas and higher temperature are the main driving forces for corrosion (Vaidya and Kenig, 2009). This may result in loss of alkanolamine solution to surrounding soil and groundwater due to the rich-amine piping leakage. Other alkanolamine wastes include from the spillage and spent alkanolamine solution generated during plant shut-down. It was reported that alkanolamine, such as N-methylethanolamine (MEA), diethanolamine (DEA), and triethanolamine, are compounds with potential acute, sub-chronic, and chronic toxicity effects towards aquatic species (Libralato *et al.*, 2010).

One of the approaches that can be used to remediate if spillage and leakage of alkanolamine solutions into soil and underground water system or to dispose of the spent alkanolamine solutions is by using biological method (Grace Liu *et al.*, 2011). Enzyme-assisted reaction was investigated in recent years for its advantages in easy operation, high efficiency, economic, versatile, and environmentally sound solution. It can simulate natural processes and result in the complete destruction of hazardous compounds into innocuous products. The use of bioremediation to remove pollutants is typically less expensive than the equivalent physical/chemical methods (Fernández-Fernández *et al.*, 2013).

Laccases enzymes have great biotechnological potential due to their capabilities and potential in various applications, such as in juice manufacturing (Berka *et al.*, 1998), chemical synthesis, and wine stabilization (Fernández-Fernández *et al.*, 2013), dye decolonization (Bayramoğlu *et al.*, 2003; Champagne and Ramsay, 2010), bioleaching (Widsten and Kandelbauer, 2008), enzymatic fuel cells (Cardoso *et al.*, 2013), wastewater treatment (Georgieva *et al.*, 2008), biosensors in nanobiotechnology (Rodríguez Couto and Toca Herrera, 2006), and biopulping have recently attracted considerable research interests.

All laccase applications mentioned above, of especially on an industrial scale, have increased the demand for high amounts of isolated or immobilized laccase production (Birhanli *et al.*, 2013). Meanwhile biodegradation using enzyme has many advantages, the isolated enzymes themselves are unstable, difficult to handle under non-conventional conditions, easily denatured in non-conventional solvents, inhibited by substrates and products, and it can only work well on natural substrates and under physiological conditions. However, it can be improved by enzyme immobilization (Birhanli *et al.*, 2013).

Currently, the stability increase of laccase catalytic activity could be achieved through immobilisation, which has been investigated by researchers ranging from methods of adsorption (Rekuć *et al.*, 2010; Salis *et al.*, 2009) and covalent attachment (Bayramoğlu and Arıca, 2008; Quan and Shin, 2004; Rekuć *et al.*, 2009)

on various supports, cross-linking (Jordaan *et al.*, 2009; Matijošytė *et al.*, 2010; Rasera *et al.*, 2009), and encapsulation in reverse micelles and emulsions (Michizoe *et al.*, 2001; Okazaki *et al.*, 2002), organic polymers such as polyallylamine (Rasera *et al.*, 2009) and inorganic polymers such as sol-gel silicas (Mansor *et al.*, 2016; Mohidem and Mat, 2012b; Nogala *et al.*, 2010).

The common sol-gel materials used in biomolecules encapsulation are silica, aluminum, titanium, zirconium, tin, vanadium, and molybdenum oxides (Debecker *et al.*, 2013; Owens *et al.*, 2016). Among them, the use of silica as precursors, such as tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS), in synthesizing sol-gel could offer numerous advantages, for example improving the mechanical strength and stability. It does not swell in aqueous or organic solvent, thus preventing leaching of encapsulated biomolecules. Silica is not a food source for microorganisms and it is biologically inert. Besides, the organically modified silica, such as TEOS and TMOS, offer tolerable hydrophilic, hydrophobic, and H-bonding capacities, as well as electrochemical activities and display good porosities (Alvarez *et al.*, 2007; Owens *et al.*, 2016; Vera-Avila *et al.*, 2004).

1.2 Problem Statement

The present research investigates the use of potential laccase as an enzyme to degrade alkanolamine solutions such as diethanolamine (DEA), ethanolamine (EA) and N-methylethanolamine (MEA) in batch (shake flask) and continuous (packed-bed) reactors. It was reported that alkanolamines, such as diethanolamine (DEA), ethanolamine (EA) and N-methylethanolamine (MEA) are compounds with potential acute, sub-chronic, and chronic toxicity effects towards aquatic species. Generally, alkanolamine is widely used in natural gas processing plant for carbon dioxide removal from natural gas. However, it may incidentally release and contaminate the surrounding soil and water due to the operational plant failure or amine piping leakage. (Libralato *et al.*, 2010). It has been reported that other oxidoreductase

enzyme such as ethanolamine oxidase and myeloperoxidase appear to be specific for the oxidative deamination of ethanolamine (Lepaumier *et al.,* 2011).

Although biodegradation by using enzyme has many advantages, the free enzyme themselves are unstable, cannot be reused, poor of thermal and storage stability. However, the catalytic activity, stability, and reusability can be improved by enzyme immobilisation (Brena *et al.*, 2013; Sassolas *et al.*, 2013). One major substantial advantage of immobilization is reusability which drastically cut cost of laccase in treatment plant. Nevertheless, the experimental conditions of the sol-gel technique of immobilisation still require some optimisation to preserve the conformation of the most delicate biomolecule during immobilisation and to recover a high fraction of their catalytic activity (Owens *et al.*, 2016).

Consequently, in the present doctoral research, the sol-gel laccase (SGL) was synthesized by manipulating TEA concentration as a gelating agent, laccase loading (L_L), agitation conditions (with or without ultrasonic), and experimental procedures (one-step or two-step) in order to acquire a higher laccase catalytic activity and stability. TEA is widely used as chelating agents in organic synthesis such as the formation of cobalt ions based catalyst with TEA (Xu *et al.*, 2012) and new magnetic bromochromate hybrid nanomaterial with TEA surface modified iron oxide nanoparticles (Rahimi *et al.*, 2014).

1.3 Objectives of Research

The objectives of current research include:

a) To synthesize and characterize the sol-gel laccase (SGL);

b) To evaluate the biodegradation performance and biodegradation efficiency of alkanolamines using free laccase (FL) and SGL in batch reactors;

c) To optimise the biodegradation performance of alkanolamines using FL and SGL in batch reactors using Response Surface methodology (RSM);

d) To evaluate the biodegradation performance and biodegradation efficiency of alkanolamines using SGL in PBR.

1.4 Research Scope

The research scope is divided into three main parts:

a) Synthesis and characterisation of the SGL.

The SGL was synthesized by manipulating TEA concentration as a gelating agent, laccase loading (L_L), agitation conditions (with or without ultrasonic), and experimental procedures (one-step or two-step). The characterisation of SGL included particle morphology, Brunauer, Emmett and Teller (BET) surface areas, functional group, effect of pH, effect of temperature and effect of storage durations.

b) To evaluate the biodegradation process (i.e. biodegradation performance and biodegradation efficiency) of alkanolamines using FL and SGL in batch reactors;

In order to evaluate the biodegradation efficiency and biodegradation performance of alkanolamines in a batch reactor, several parameters were explored. These include the effect of reaction time, effect of pH, effect of temperature, effect of substrate concentration, effect of FL and SGL dosage (D_s) and reusability.

c) To optimise the biodegradation performance of alkanolamines using FL and SGL in batch reactors using Response Surface methodology (RSM);

In order to evaluate the biodegradation performance of alkanolamine by FL and SGL and its optimisation by using RSM, the Box–Behnken design was selected. The four parameters such as pH, temperature, reaction time, and FL or SGL dosage (D_s) were chosen based on the produced results.

d) To evaluate the biodegradation performance and biodegradation efficiency of alkanolamines using SGL in PBR.

In order to evaluate the biodegradation performance and biodegradation efficiency of alkanolamines in a PBR, several parameters were investigated. These include the effect of reaction time, effect of pH, effect of substrate concentration, effect of SGL dosage (D_s) and effect of flowrate.

1.5 Novelty Statement

The novelties of the present research are:

(a) A synthesis method of sol-gel laccase which resulted in high laccase catalytic activity and stability.

(b) The application of sol-gel laccase for removal of alkanolamines pollutants which is commonly found in the contaminated water from the natural gas processing plant. The alkanolamines are commonly used in removal process of carbon dioxide from natural gas.

1.6 Thesis Outline

This thesis consists of five chapters. Chapter 1 introduces the problem statements and clarified the objectives and scope of research. Chapter 2 provides a review of past research related to enzyme immobilisation and biodegradation of

alkanolamines. The materials and methods used in the present research are presented in Chapter 3 while the results and discussion of this research are described in Chapter 4. Conclusion and recommendations of research are presented in Chapter 5.

1.7 Summary

The enzymes immobilisation in the sol-gel matrix have been reported by many researchers to improve their functional characteristics to a large extent. Due to the need for enhancing the catalytic activity and stability of laccase enzyme for wide industrial applications, the synthesis of immobilised laccase in sol-gel silica matrix and its applications was studied. In present research, the SGL was obtained by simple precipitation of TEOS solution by using TEA as a gelating agent in order to degrade alkanolamine in a batch reactor and PBR. Thus the research background, objectives, scope and thesis outline were clearly elaborated in this chapter.

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