UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF PHENOLIC ELECTROCHEMICAL BIOSENSORS USING ZrO_2, CeO_2 AND IONIC LIQUIDS-TYROSINASE NANOCOMPOSITES

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By

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Chairman : Jaafar Abdullah, PhD
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Phenolic compounds are one of the types of pollution that is present in water sources due to the effluents of a various industries such manufacturing, pharmaceutical, resin paint and textile wood. They are included by the Environmental Protection Agency's (EPA) as part of the priority pollutants due to its persistency and toxicity to the environment. In this study, three biosensors were developed to detect phenolic compounds which is practical to be used for sample in the environment with fast response, high selectivity, cost-effectiveness and simplicity of operation. The development of the phenolic biosensor was carried out by using screen printed carbon electrode (SPCE), hexadecyltrimethylammonium bromide (CTAB) and polyethylene glycol (PEG), zirconium oxide (ZrO_2), cerium oxide (CeO_2) and 1-butyl-3-methylimidazolium nitrate ($BMIMNO_3$).

These biosensors were named as ZrO_2/Tyr, ZrO_2/$BMIMNO_3$/Tyr and CeO_2/$BMIMNO_3$/Tyr. They were similar in the approach of electrode modification and enzyme immobilisation except in the used of different metal oxide and addition of ionic liquid on the electrode surface. The modified electrode was analysed using Scanning Electron Microscope- Energy-dispersive X-ray spectroscopy (SEM-EDX), Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV). The optimisation for the biosensors were enzyme loading, applied potential, pH, percentage of modifier and volume of nanocomposite that deposited onto the electrode. The biosensors required 10 mg/mL enzyme loading, pH range from 6 – 7, potential range from – 0.10 V until – 0.20 V, 2.0 – 3.0 percent of modifier and 2.0 – 2.5 μL of nanocomposite deposited. These biosensors operated at different potential versus Ag/AgCl which was – 0.20 V and – 0.10 V for ZrO_2/Tyr, ZrO_2/$BMIMNO_3$/Tyr and CeO_2/$BMIMNO_3$/Tyr, respectively. The fastest response

time was in the following order: ZrO_2/Tyr (10 s) > ZrO_2/$BMIMNO_3$/Tyr (15 s) > CeO_2/$BMIMNO_3$/Tyr (30 s). The limit of detection (LOD) of the 3 biosensors was found comparable 0.11 μM for ZrO_2/Tyr, ZrO_2/$BMIMNO_3$/Tyr and CeO_2/$BMIMNO_3$/Tyr respectively. The linearity of the biosensor was 0.075 – 55 μM, 0.25 – 30 μM and 0.25 – 40 μM for ZrO_2/Tyr, ZrO_2/$BMIMNO_3$/Tyr and CeO_2/$BMIMNO_3$/Tyr respectively. Sensitivity of the biosensors was found highest for ZrO_2/Tyr (219.5 nA/μM followed ZrO_2/$BMIMNO_3$/Tyr (133.79 nA/μM) and CeO_2/$BMIMNO_3$/Tyr (80.86 nA/μM).

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PEMBANGUNAN BIOSENSOR ELEKTROKIMIA FENOLIK MENGGUNAKAN ZIRKONIUM OKSIDA, CERIUM OKSIDA DAN CECAIR IONIK-TYROSINASE CAMPURAN NANO

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Sebatian fenolik merupakan salah satu pencemaran yang wujud dalam sumber air disebabkan kumbahan dari pelbagai industry seperti pembuatan, farmaseutikal, cat resin dan tekstil perkayuan. Mereka telah dimasukkan dalam senarai keutamaan pencemar 'Environmental Protection Agency' disebabkan oleh kedegilan dan ketoksikan kepada persekitaran. Dalam kajian ini, biosensor mengesan sebatian fenolik telah dibangunkan di mana ia adalah praktikal untuk digunakan kepada sampel persekitaran dengan tindakbalas pantas, selektiviti tinggi, keberkesanan kos dan operasi yang mudah. Pembinaan fenolik biosensor telah dijalankan menggunakan karbon elektrod cetak skrin (SPCE), heksadeciltrimethylammonium bromide (CTAB) and polietilena glikol (PEG), zirkonium oksida (ZrO_2), cerium oksida (CeO_2) and 1-butil-3-metilimidazolium nitrat ($BMIMNO_3$).

Biosensor-biosensor ini dinamakan sebagai ZrO_2/Tyr, ZrO_2/$BMIMNO_3$/Tyr and CeO_2/$BMIMNO_3$/Tyr. Biosensor-biosensor ini adalah serupa dari pendekatan yang digunakan untuk mengubah elektrod dan memegun enzim kecuali pengunaan logam oksida yang berbeza dan penambahan cecair ion pada permukaan elektrod. Elektrod yang diubahsuai telah dianalisa menggunakan pengimbas mikroskop elektron-spectroskopi x-ray penyebaran tenaga (SEM-EDX), Spektroskopi rintangan elektrokimia (EIS) and kitaran voltammetri (CV). Pengoptimum biosensor ini adalah kemasukan enzim, potensi yang digunakan, pH, peratusan pengubahsuai dan jumlah campuran-nano yang didepositkan ke atas elektrod. Biosensor ini memerlukan 10 mg/mL enzim, pH dari julat 6 – 7, potensi digunakan dari – 0.10 V sehingga – 0.20 V, peratus pengubahsuai sebanyak 2.0 – 3.0 peratus dan 2.0 – 2.5µL campuran nano didepositkan. Berdasarkan pengoptimum, biosensor-biosensor ini beroperasi di potensi terhadap Ag/AgCl yang berbeza iaitu – 0.20 V dan – 0.10 V untuk ZrO_2/Tyr,

ZrO_2/BMIMNO$_3$/Tyr and CeO_2/BMIMNO$_3$/Tyr masing-masing. Masa pengesanan terpantas adalah mengikut turutan berikut : ZrO_2/Tyr (10 s) > ZrO_2/BMIMNO$_3$/Tyr (15 s) > CeO_2/BMIMNO$_3$/Tyr (30 s). Had pengesanan 3 biosensor didapati sebanding 0.11 µM untuk ZrO_2/Tyr, ZrO_2/BMIMNO$_3$/Tyr and CeO_2/BMIMNO$_3$/Tyr masing-masing. Julat lurus biosensor adalah 0.075 – 55 µM, 0.25 – 30 µM dan 0.25 – 40 µM untuk ZrO_2/Tyr, ZrO_2/BMIMNO$_3$/Tyr dan CeO_2/BMIMNO$_3$/Tyr, masing-masing. Sensitiviti untuk biosensor didapati paling tinggi pada ZrO_2/Tyr (219.5 nA/µM) diikuti ZrO_2/BMIMNO$_3$/Tyr (133.79 nA/µM) dan CeO_2/BMIMNO$_3$/Tyr (80.86 nA/µM).

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the supervisory committee were as follows:

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This is to confirm that:

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LIST OF ABBREVIATIONS

PEG	Polyethylene glycol
ZrO_2	Zirconium oxide
CeO_2	Cerium oxide
CTAB	Hexadecyltrimethylammonium bromide
Tyr	Tyrosinase
SPCE	Screen printed carbon electrode
FTIR	Fourier-transform infrared spectroscopy
SEM-EDX	Scanning Electron Microscope- Energy-dispersive X-ray spectroscopy
CV	Cyclic voltammogram
DPV	Differential pulse voltammetry
A	Surface area
I	Current
A	Electroactive surface area
RSD	Relative standard deviation
Vs^{-1}	Voltmeter per second
mg/mL	Miligram per mililitre
Γ *	Surface coverage
n	number of electron
F	Faraday constant
R	gas constant
T	Temperature
µM	Micro molar
s	second
R^2	Correlation coefficient
σ	Standard deviation of blank measurement
b	Slope
LOD	Limit of detection
mA/M	Miliampere per molarity

K_M^{app}	Apparent michelis menten
$BMIMNO_3$	1-butyl-3-methylimidazolium nitrate
IL	Ionic liquid
XRD	X-ray Powder Diffraction
$Fe[(CN)_6]^{4-/3-}$	Ferrocyanide
ΔE	Potential difference
EIS	Electrochemical Impedance Spectroscopy
R_{CT}	electron transfer resistance
Rs	Ohmic resistance
Cdl	Double layer capacitance
Zw	Warburg impedance
μL	microliter
π-π	Pi to pi
Si	Silica
mol^1cm^{-2}	Mol per centrimetre square

CHAPTER 1

INTRODUCTION

1.1 Research Background

Water pollution contains harmful materials that are produced from domestic, industrial, commercial or agricultural activities (Ejeian *et al*., 2018; Mülazımoğlu & Yılmaz Selçuk *et al*., 2010; Rodríguez-Delgado *et al*., 2015). One of the major sources are organic pollution from phenolic compound such as cresol, bisphenol A, catechol and chlorophenol that are present in food, water, and plastic container. Most of them are extremely harmful to human health if they exceed the permitted level (Han *et al*., 2015; Li *et al*., 2006; Nazari *et al*., 2015).

The monitoring of water pollution in over the world requires attention of the development of new technique for measurement using inexpensive and simpler approach (Michael-Kordatou *et al*., 2015; Rehman *et al*., 2015). Typical laboratory techniques however require various chemical reagents, high skilled personnel to handle the instruments and tedious sample preparation. These factors motivate the needs to develop a new technique that is simple, sensitive, portable and efficient for in-situ detection (Asadnia *et al*., 2016; Biswas *et al*., 2017).

Biosensor has been known as one of the recent method that involves optical and electrochemical techniques (Abdullah *et al*., 2008; Soni *et al*., 2018; Khansili *et al*., 2018; Pino *et al*., 2016; Wang *et al*., 2018). Electrochemical biosensors are based on selective interaction between target analyte and recognition element such as enzyme, protein or DNA. The technique involves potentiometric, voltammetric, amperometric and electrochemical impedance spectroscopy which produce electrical signal proportional or inversely to the concentration of the analyte. Optical biosensors use optical transducers that respond to the analyte that has a change in their optical properties, such as absorption, reflectance, fluorescence emission (Wang *et al*., 2014).

Development of biosensors for the detection of phenolic compound has received considerable attention in the recent years. Many phenolic sensors were successfully developed for the detection at minimal level of analyte (Vicentinni *et al*., 2013; Zhang *et al*., 2009; Caetano *et al*., 2018; Han *et al*., 2015; Nazari *et al*., 2015; Shan *et al*., 2009).

Many attempts have been made to improve the developed phenolic biosensor for environmental monitoring using various types of smart material. In the recent years, the use of metal oxide nanoparticles and ionic liquid has attracted great interest in several applications such as sensors, biosensors and catalysts due to their unique physical, catalytic and chemical properties (Soltani *et al*., 2016; Najafi *et al*., 2014). They are promising materials for the immobilisation of biomolecules in biosensing applications due to the biocompatible nature and strong adsorption capability.

In this study, three (3) different types of phenolic biosensor using electrochemical techniques were developed based on zirconium oxide/tyrosinase, zirconium oxide/ionic liquid/tyrosinase and cerium oxide/ionic liquid/tyrosinase. In addition to the satisfactory performances, the proposed method is also simple, easy and less expensive without surface functionalisation and mediator.

1.2 Problem statement

Phenol is a major source of pollutants and could threaten human health. Maximum concentration limit of phenol in water permitted by EPA is 3.5 μgL^{-1} (Stoytcheva *et al*.,2014). Exceeding the amount of phenol may cause environmental pollution (Nazari *et al*., 2015). The typical analytical techniques used for the determination of phenols include high performance liquid chromatography (HPLC) (Vrsaljk *et al*., 2012; Bartosova *et al*., 2014; Zhong *et al*., 2016), gas chromatography mass spectrometry (GC-MS) (Schettgen *et al*., 2015) and ultraviolet-visible spectrophotometry (UV-Vis) (Sofoniou *et al*., 2000). However, these methods involved very complicated sample pre-treatment, time consuming, and expensive instrumentation and require high amount of solvents and chemicals.

An electrochemical method was widely used as a direct measurement for phenol and has several advantages such as fast response, easy operation and high accuracy. Amperometric biosensors play an important role for simple, sensitive, specific, accurate and fast determination of phenolic compounds and have potential for miniaturisation (Singh *et al*., 2013). In this study, the modification of working electrode using zirconium oxide (ZrO_2) and cerium oxide (CeO_2) in combination with ionic liquid 1-butyl-3-methylimidazolium nitrate ($BMIMNO_3$) improves the performances of phenolic biosensor. Due to great catalytic character, high electrolyte accessible area, easy fabrication and many other interesting properties, metal oxide nanoparticles are extensively used in a variety of electroanalytical processes (Campbell & Compton, 2010). Cerium oxide (CeO_2), based on its biocompatibility, high isoelectric point (IEP), and excellent adsorption capability, is attractive with extensive applications for a variety of enzymes such as cholesterol oxidase, glucose oxidase, and horseradish peroxidase (Ansari *et al*., 2008; Saha *et al*., 2009; Ansari *et al*., 2009). Other than that, due to its high IEP (~9.0), CeO_2 is suitable for adsorption of enzymes with low IEP (e.g., tyrosinase with an IEP of 4-5) without any harsh chemical treatment (Zhang *et al*., 2013a). In general, cerium dioxide can have two different oxide forms which is CeO_2 (Ce^{4+}) or Ce_2O_3 (Ce^{3+}), which can enhance the electron transfer at electrode surface. Zirconium oxide (ZrO_2) nanoparticles are nontoxic due to their excellent chemical inertness and biocompatibility and, thus, are an ideal support for immobilisation of biomolecules

(Pundir *et al*., 2012). High isoelectric point (~9.5) of ZrO_2 allowed the interaction with low isoelectric point of tyrosinase (Solanki *et al*., 2009a).

Ionic liquid (IL) has known as a new kind of modifier for a modified electrode in the recent years. This material contains bulky ions and remain as a liquid at room temperature with good solubility and chemical stability. It has efficient optical and electrochemical properties, such as higher ionic conductivity and wider electrochemical windows (Pahlavan *et al*., 2014). Besides, due to the high solvation properties of IL, they act as a good dispersants to a nanocomposite which helps a formation of a uniform structure with well-distributed components on the electrode surface (Abo-Hamad *et al*., 2016).

1.3 Scope of Study

This study focuses on the development of a phenolic biosensor based on zirconium oxide, cerium oxide and ionic liquid as composite materials for modification of the electrode. The first biosensor was developed using a combination of zirconium/tyrosinase. The performances were comparable and satisfactory with the previous study. By using the same method, ionic liquid of 1-butyl-3-methyl-imidazolium nitrate was incorporated into the zirconium oxide to improve the performance of the developed biosensor. The comparison study was also done using another metal oxide namely cerium oxide. This material was incorporated into the ionic liquid 1-butyl-3-methyl-imidazolium nitrate for the sensor development.

1.4 Objectives of Study

The general objective is to develop a phenolic biosensor using ZrO_2, CeO_2 nanoparticles incorporated with $BMIMNO_3$.

The specific objectives are divided into four (4) as follows:

i. To characterise the modified electrode with zirconium oxide (ZrO_2) and cerium oxide (CeO_2) in combination with ionic liquid 1-butyl-3-methylimidazolium nitrate ($BMIMNO_3$) and tyrosinase (Tyr).
ii. To evaluate the sensing capabilities of the modified electrode using cyclic voltammetry technique.
iii. To evaluate the performances of the developed biosensors using chronoamperometry technique.
iv. To validate the developed biosensor with spectrophotometric method and chromatographic techniques for the determination of phenol in a real sample.

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LIST OF PUBLICATIONS

Ahmad, N.M., Abdullah, J., Yusof, N.A., Sulaiman, Y., Ab. Rashid, A.H., Rahman, S.A., Hanibah, H., Haron, N. (2017). Enhanced Electron Transfer of Amperometric Biosensor Based on Cerium Oxide/1-Butyl-3-Methylimidazolium Nitrate/Tyrosinase Biocomposite Film for the Detection of Phenolic Compounds. *Sensor Letters,* 15, 928-938.

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Award

Ahmad, N.M., Abdullah, J., Yusof, N.A., Ab. Rashid, A.H., Rahman. (2016). Construction of an amperometry phenolic biosensor based on immobilisation of tyrosinase on zirconium oxide nanoparticles/polyethylene glycol composite film on screen printed carbon electrode. **Gold award**.

Conference Attended

1. Biosensors 2016 Congress, Svanska Massan Gothernburg Sweeden, 25-27 May 2016. (Poster presenter)

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