

**ATRAZINE-BASED MOLECULARLY
IMPRINTED POLYMER AS
ELECTROCHEMICAL SENSOR FOR PESTICIDE
DETECTION**

by

NUUR FAHANIS BINTI CHE LAH

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LIST OF SYMBOLS

B_e	Atrazine bound per gram of polymer
C	Capacitance
F_e	Unbound atrazine per volume of solution
IP	Peak Current
I_{pa}	Anodic current
I_{pc}	Cathodic current
K	Rate of adsorption
K_d	Equilibrium dissociation constant
M	Molar
n_F	Freundlich isotherm parameter
N_J	Binding site density
Q	Template bound
Q	Constant phase element
Q_{max}	Maximum template bound
R	Resistance
r^2	Coefficient of determination
R_{ct}	Charge transfer resistance
R_{Ω}	Ohmic Resistance
V	Voltage
α	Transfer coefficient
δ	Solubility parameter
δ_{MIP}	Solubility parameter for molecular imprinted polymer
v	Scan rate
E_{pa}	Anodic Peak Potential

E_{pc}	Cathodic Peak Potential
k_o	Heterogeneous electron transfer rate

LIST OF ABBREVIATIONS

ACN	Acetone
Atr	Atrazine
BET	Brunauer–Emmett–Teller
CA	Chronoamperometry
CH	Chloroform
CV	Cyclic Voltammetry
DEA	Deethylatrazine
DMSO	Dimethyl Sulfoxide
DVB	Divinylbenzene
ECBS	Electrochemical biosensors
EGDMA	Ethylene Glycol Dimethacrylate
EIS	Electrochemical Impedance Spectroscopy
EPA	Environmental Protection Agency
FESEM	Field Emission Scanning Electron Microscope
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
FRA	Frequency-Response Analyzer
FTIR	Fourier Transform Infrared
GC	Gas Chromatography
GFE	Graphite Felt Electrode
HPLC	High Performance Liquid Chromatography
IF	Imprinting Factor
LOD	Limit Of Detection
LSV	Linear Sweep Voltammetry
MA	Mercury Analyzer

MAA	Methacrylic Acid
MIP	Molecular Imprinted Polymer
MMA	Methyl Methacrylate
MS	Mass Spectrometry
na	Not Available
NaCl	Sodium Chloride
NIP	Non-imprinted Polymer
NMP	N-Methyl-2-pyrrolidone
NMR	Nuclear Magnetic Resonance Spectroscopy
OPP	Organophosphorus Pesticide
PCA	Principle Component Analysis
PVC	Polyvinyl Chloride
RE	Reference Electrode
RVC	Reticulated Vitrified Carbon
SCE	Saturated Calomel Electrode
SEE	Standard Error of Estimate
SEM	Scanning Electron Microscopy
SNE	Sum of Normalize Error
TOC	Total Organic Carbon
Tol	Toluene
TRIM	Trimethylolpropane trimethacrylate
WHO	World Health Organization
WQI	Water Quality Index

POLIMER CETAKAN MOLEKUL BERASASKAN ATRAZIN SEBAGAI PENGESAN ELEKTROKIMIA UNTUK RACUN PEROSAK

ABSTRAK

Penggunaan racun perosak dan racun serangga yang meluas meningkatkan tahap kebimbangan terhadap kesannya terhadap manusia dan kehidupan haiwan, yang secara langsung dan tidak langsung dihubungkan dengan sebatian berbahaya melalui pembentukan racun makhluk perosak dalam makanan dan air minuman. Oleh itu, tujuan kajian ini dijalankan adalah untuk mengetengahkan kaedah dan teknik pengesanan atrazin dalam larutan akueus. Polimer bersilang tinggi telah disediakan melalui proses pempolimeran yang menggunakan kepekatan monomer yang tinggi ($\geq 25 \text{ v / v\%}$) yang secara amnya membawa kepada monolit pukal. Perumusan polimer diubahsuai dengan mengubah nisbah Asid Metakrilik (MAA) sebagai monomer dan Etilen Glikol Dimetacrilat (EDGMA) sebagai pemautesilang serta menggunakan beberapa jenis pelarut porogenik. Perumusan optimum bagi polimer diperoleh apabila 1:15:40 (Atr:EDGMA:MAA) bersama 5% Dimetil Sulfoksida (DMSO) dan 95% toluena sebagai sebatian porogenik dapat meningkatkan efisiensi polymer cetakan molekul berbanding dengan formulasi dalam 100% toluena. Kapasiti pengikat meningkat sebanyak 18% berbanding formulasi original. Dua morfologi berbeza dapat dikenalpasti. Mikrosfera monosebaran diperoleh dengan menggunakan toluena manakala zarah-zarah tidak tersusun dibentuk dengan DMSO. Nisbah monomer, pemautesilang dan jenis campuran pelarut/porogenik telah dikenalpasti sebagai parameter berpengaruh pada morfologi zarah. Data keseimbangan penjerapan dikaitkan kepada empat model iaitu Linear, Langmuir, Freundlich, Jovanovic. Keputusan menunjukkan bahawa polimer yang dicetak mempunyai ralat yang

terendah untuk model isotherm Jovanovic. Penjerapan kinetik atrazin pada polimer yang dicetak turut dikaji dan didapati bersesuaian dengan model kinetik pertama Lagergen. Formulasi optimum polimer yang dicetak telah digabungkan dengan elektrod jalinan grafit sebagai transduksi untuk analisis elektrokimia. Kitaran voltammetrik (CV) dan spektrum impedans elektrokimia (EIS) digunakan untuk mencirikan sensor dan menyiasat tindak balas elektrokimia sensor. Pemalar pemindahan electron heterogen, k_0 dikira melalui CV menunjukkan bahawa sistem ini merupakan sistem kuasi boleh balik dengan nilainya adalah 0.0661 cm.s^{-1} bagi anodik dan 0.0195 cm.s^{-1} bagi katodik. Had pengesanan bagi sistem tersebut adalah pada 4.99 nM . Plot Nyquist menunjukkan bahawa impedans yang diperolehi dalam kajian ini dapat menggambarkan sistem sensor dengan baik. Litar yang sama diolah daripada plot Nyquist tersebut memberikan nilai kesesuaian χ^2 yang berada di antara 0.6298 dan 1.475 yang boleh menganalisis setiap komponen sistem sensor secara kuantitatif. Dengan metodologi yang dicadangkan, sensor elektrokimia polimer tercetak molekul berasaskan atrazin telah berjaya diformulasikan dalam kepekatan monomer yang tinggi dengan penambahbaikan dalam memanipulasi campuran porogen/pelarut.

ATRAZINE-BASED MOLECULARLY IMPRINTED POLYMER AS ELECTROCHEMICAL SENSOR FOR PESTICIDE DETECTION

ABSTRACT

The wide-ranging use of pesticides causes concern for their effect on human as well as animal life, which is in direct and indirect contact with hazardous compounds through pesticide build-up in food and drinking water. Therefore, this study aimed of the outmost importance to develop methods and techniques for atrazine detection in aqueous solutions. Highly crosslinked polymers have been prepared by precipitation polymerization using high monomer loadings (≥ 25 v/v %) which generally lead to bulk monolith. The formulation of the polymer was modified by varying the Methacrylic Acid (MAA) as the monomer and Ethylene Glycol Dimethacrylate (EDGMA) as the crosslinker ratio together with several types of porogenic solvent. It was observed that the formulation of 1:15:40 (Atr:EDGMA:MAA) with 5% of Dimethyl Sulfoxide (DMSO) and 95% of toluene as the porogen mixture improves the efficiency of the imprinted polymer compared to the formulation in 100% of toluene. The binding capacity increase for almost 18% from the original formulation. Two distinct morphologies were observed. Monodispersed microspheres were obtained using toluene whereas segmented irregular particles were formed with DMSO. The ratio of monomer, crosslinker and the type of solvent mixture were identified as influential parameters on the particle morphology. The adsorption equilibrium data showed that the imprinted polymer resulted in the lowers error for Jovanovic isotherm model. The adsorption kinetics of atrazine on MIPs was studied and found to fit the best with Lagergen first order kinetic model. The optimum formulation of imprinted polymer was assembled with graphite

felt electrode as the transduction for electrochemical analysis. Cyclic voltammetry (CV) and electrochemical impedance spectrum (EIS) were used to characterize the sensor and investigate the electrochemical response of the sensor. The heterogeneous electron transfer constant, k_0 that was calculated from CV indicates that the constant fall between the quasi reversible system with 0.0661 cm.s^{-1} for anodic and 0.0195 cm.s^{-1} for cathodic. The limit of detection (LOD) for the system was found to be at 4.99 nM . An equivalent circuit was suggested from the Nyquist plot that gives good fits with χ^2 value between 0.6298 and 1.475 interpret the process of molecule diffusion from the bulk solution onto the electrode surface by quantitatively analyse each component of the sensor system. With the proposed methodology, electrochemical atrazine-based molecular imprinted polymers (MIPs) sensor have been prepared successfully in high monomer concentration with the improvement by manipulating the porogen/solvent mixture.

CHAPTER ONE

INTRODUCTION

1.1 Overview

Water pollution is a global problem. Pollutants from agricultural resources, once dispersed, are spread throughout the entire stream. It is not just a phenomenon characteristic of large crops area and regions, it also affects small fields, although pollutants concentration does reach greater values in these areas. However, as the living standards expand, water pollution has emerged as a major nuisance. Thus, many national, regional, city administrators and individuals are challenged to cope with the demands for stricter controls over water pollution.

Unwanted constituents in the water can bring detrimental effects on human health, the health of other creatures, the value of properties, and the quality of life. There are many vivid evidences demonstrating that water pollution can seriously endanger public health. In National Transformation (TN50) dialogue session in Kota Samarahan, Deputy Energy, Green Technology and Water Minister Datuk Dr James Dawos Mamit said that there are many rivers in West Malaysia categorised as 'dead' due to pollution, which contributed to the reduction of dissolved oxygen (Povera 2017). Without dissolved oxygen, fishes cannot live, and the same fate awaits plants growing within the affected rivers. In India, from the northern Himalayas to the sandy, palm-fringed beaches in the south, 600 million people - nearly half India's population

- face acute water shortage, with close to 200,000 dying each year from polluted water (Foundation 2018).

The geographic distribution of pesticide concentrations generally follows regional patterns in agricultural use and the influence of urban areas, although this relation is stronger for streams than for groundwater. Compared with streams, the occurrence of pesticides in groundwater is more strongly governed by compound properties and hydrogeologic factors that affect transport from land surface to a well (Gilliom et al. 1999). In water that comes mainly from agricultural areas, the most commonly found pesticides are the major herbicides atrazine, metolachlor, cyanazine and alachlor. In water that comes mainly from urban areas, the most common pesticides are the herbicides simazine and prometon and the insecticides diazinon and carbaryl (Fuhrer 1999).

Pesticides can be carcinogenic and cytotoxic. They can cause bone marrow and nerve disorders, infertility, and immunological and respiratory disease (Audrey Sassolas 2012). There are many sources of exposure to pesticides. The three routes of exposure for pesticides are oral ingestion, dermal absorption, and inhalation. Pesticide can be tracked into homes or brought home from work on clothing and in vehicles, exposing family members as well. Pesticides used domestically or in agriculture run off into ground and surface water, thus becoming exposed to the entire population.

1.2 The monitoring methods of the pollutants

Water quality index (WQI) is useful in assessing the suitability of river waters for a variety of uses such as agriculture, aquaculture, and domestic use. WQI is used to relate a group of parameters to a common scale and combining them into a single number. In Malaysia, there is no specific regulation on the limit of atrazine in raw water quality. Most of the detection limit is based on the WHO regulation. Generally, the use of atrazine beyond maximum residue level (Maximum Contaminant Level Goals: 0.003mg/L) in agricultural sectors can cause contamination of groundwater and surface water resources due to leaching and runoff losses (Salman et al. 2011, Moh et al. 2013).

One of the primary goals of World Health Organization (WHO) and its member states is that “all people, whatever their stage of development and their social and economic conditions, have the right to have access to an adequate supply of safe drinking water.” An increasing effort is now being put into the environmental monitoring of pesticides that may pose a risk to the health of humans and the ecosystem. Earlier techniques used for pesticide detection were chromatographic methods like Gas Chromatography (GC), High Performance Liquid Chromatography (HPLC) along with Mass Spectrometry (MS). They were sensitive and reliable (Bhadekar et al. 2011). The time and expenses involved in classical analytical methods (i.e. sampling, sample preparation, and laboratory analysis) limit the number of samples that can be analysed in environmental surveys. There is a real need for developing fast, easy-to-use, robust, sensitive, cost-effective and field-analytical techniques (Hennion and Barcelo 1998).

In Western countries, pesticides, together with new and modified patterns of exposure to chemicals, have been implicated in the increasing prevalence of diseases associated with alterations of the immune response, such as hypersensitivity reactions, certain autoimmune diseases and cancers (Corsini et al. 2012). These persistent pollutants were primarily used for agriculture and vector control (Ibrahim 2007). Pesticides have been in use in Malaysia following the Second World War to control pests in agricultural plantations, namely rubber, oil palm, and cocoa (Li et al. 2011). The regulation on the importation and handling of these pesticides comes under the Pesticide Act 1974. Under the Act, all pesticides imported into and used in Malaysia have to be registered with the Pesticides Board Malaysia. Importers have to supply information such as trade names, active ingredients, amounts, and formulations. The Pesticides Board reviews the registration of these pesticides from time to time when toxicity and eco-toxicological data become available. The 1997 registration listed a total of 1767 formulations of pesticides and herbicides. Atrazine is one of the pesticides listed in the registration list.

Detection of pesticides at the levels established by the Environmental Protection Agency (EPA) remains a challenge. Chromatographic methods coupled with selective detectors have been traditionally used for pesticide analysis due to their sensitivity, reliability and efficiency. Nevertheless, they are time consuming and laborious, and require expensive equipment and highly trained technicians. To overcome this, over the past decade, considerable attention has been given to the development of biosensors for the detection of pesticides as a promising alternative. One of the types of biosensor is the electrochemical molecular imprinted polymer

(MIP) sensor that combines the characteristics of electrochemical technology with the highly selective recognition of the molecular imprinting technique.

This molecularly imprinted polymers (MIPs) have engrossed much attention due to their unique properties, such as simplicity, low cost, facile preparation, high selectivity and sensitivity. Typically, MIPs include template molecules, functional monomers and cross-linking reagents. Functional monomers interact with templates through non-covalent (hydrogen bond, ionic or hydrophobic) and covalent interactions to form a complex before cross-linking reaction between the network structure (Gui et al. 2018). A general procedure for MIPs synthesis comprises of: 1) template molecules assemble with functional monomers to fabricate a complex via covalent or non-covalent bonds in solution; 2) cross-linkers and initiators polymerize with the complex under photo-/thermal conditions; 3) embedded templates in polymers are removed through extraction that often uses solvent elution because the analyte has a higher solubility in the solvent. The three-dimensional structure of microcavities that complement the shape and chemical functionality of templates are generated after template removal. MIPs containing the microcavities have outstanding capabilities for specifically and sensitively rebinding targets with the near shape and microstructure of templates (Okutucu and Önal 2011).

Electrochemical techniques have undergone many important developments in terms of electrode's process and instrumentation improvement in recent years. Recently, numerous modern electrochemical or electroanalytical techniques have been established such as linear sweep voltammetry (LSV) (Herdman et al. 2018, Janakiraman et al. 2019), cyclic voltammetry (CV) (Valero Vidal and Igual Muñoz