**Faculty of Resource Science and Technology**

# Synthesis and Characterization of Molecularly Imprinted Polymer for the Removal of Triazine Herbicides from Water Samples

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# Synthesis and Characterization of Molecularly Imprinted Polymer for the Removal of Triazine Herbicides from Water Samples

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A thesis submitted

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(Chemistry)

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## DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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Signature

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**ABSTRACT**

Cyanazine (CYZ), Ametryn (AME) and Atrazine (ATZ) are mostly utilized 1, 3, 5-triazine herbicides to control the growth of broadleaf grasses and weeds, however, their extensive usage has adverse effects on the environment, non-target organisms, and human health. Therefore, molecularly imprinted polymers (MIPs) were applied to remove triazine herbicides in the environment. In this study, MIPs of triazine herbicides were synthesized by precipitation polymerization in the presence of template molecules (CYZ, AME and ATZ), functional monomers (methacrylic acid, acrylamide, 2-vinylpyirdine, and 4-vinylpyridine), cross-linker (ethylene glycol dimethacrylate), initiator (azo-bis-isobutyronitrile), and solvent (toluene and acetonitrile). For comparison study, the non-imprinted polymers (NIPs) were synthesized without the addition of template molecule. The Fourier Transform Infra-Red (FTIR) analysis of MIPs of triazine herbicides indicated the presence of CYZ, AME and ATZ were observed at ~756 $cm^{-1}$, ~1450 $cm^{-1}$, and ~1389 $cm^{-1}$, respectively. MIP (AAm) of CYZ had its maximum adsorption efficiency in 6 ppm CYZ solution at pH 7, 0.1 g of polymer and 240 mins of contact time. MIP (MAA) of AME had its highest adsorption efficiency in 7 ppm AME solution at pH 7, 0.1 g of polymer and 210 mins of contact time. MIP (2VP) of ATZ exhibited its maximum adsorption efficiency in 8 ppm of ATZ solution at pH 7, 0.3 g of polymer and 15 mins of contact time. The thermogravimetric analysis (TGA) of MIPs of triazine herbicides depicted that the decomposition of polymers was between ~320 °C to ~500 °C. MIP (AAm) of CYZ, MIP (MAA) of AME and MIP (2VP) of ATZ were more selective towards their target compounds with relative selectivity coefficients of 2.36, 2.66 and 2.77, respectively. The synthesized MIP (AAm) of CYZ, MIP (MAA) of AME and MIP (2VP) of ATZ were successfully applied

to remove CYZ, AME and ATZ from different water samples (distilled water, tap water and river water) with removal efficiencies between ~84% to ~95%.

**Keywords:** Cyanazine, Ametryn, Atrazine, precipitation polymerization, molecularly imprinted polymers

***Sintesis dan Pencirian Molekul Polimer Tercetak untuk Penyingkiran Herbisida Triazin daripada Sampel Air***

## *ABSTRAK*

*Sianazin (CYZ), Ametrin (AME), dan Atrazin (ATZ) adalah herbisida triazin yang banyak digunakan untuk mengawal pertumbuhan rumput dan rumpai daun lebar. Namun, penggunaannya yang berleluasa memberikan kesan buruk kepada alam sekitar, organisma bukan sasaran, dan kesihatan manusia. Oleh itu, molekul polimer tercetak (MIPs) digunakan untuk menyingkirkan herbisida triazin daripada alam sekitar. Dalam kajian ini, MIPs herbisida triazin disintesis menggunakan pempolimeran pemendakan dengan menggunakan molekul templat (CYZ, AME dan ATZ), monomer berfungsi (metakrilik,, akrilamida, 2-vinilpiridin dan 4-vinilpiridin), penggabung silang (etilena glikol dimetakrilat), bahan pemula (azo-bis-isobutironitril) serta pelarut (toluen dan asetonitril). Sebagai perbandingan, molekul polimer tidak tercetak (NIPs) disintesis tanpa penambahan molekul templat. Analisa Spektrum Inframerah Transformasi Fourier (FTIR) menunjukkan bahawa kewujudan CYZ, AME dan ATZ dapat dikenalpasti di ~756 $cm^{-1}$, ~1450 $cm^{-1}$, dan ~1389 $cm^{-1}$. Kadar optimum penjerapan maksimum bagi MIP (AAm) CYZ diperolehi dalam larutan CYZ 6 ppm pada pH 7, 0.1 g polimer dengan jangka waktu penjerapan selama 240 mins. MIP (MAA) AME mempunyai kadar penjerapan tertinggi dicapai dalam larutan AME 7 ppm pada pH 7, 0.1 g polimer dengan jangka waktu penjerapan selama 210 mins. MIP (2VP) ATZ mencapai kadar penjerapan maksimum dalam larutan ATZ 8 ppm pada pH 7, 0.3 g polimer dengan jangka waktu penjerapan selama 15 mins. Analisa termogravimetrik (TGA) bagi MIP herbisida triazin menunjukkan penguraian polimer antara ~320 °C to ~500 °C. MIP (AAm) CYZ, MIP (MAA) AME, dan MIP (2VP) ATZ lebih selektif terhadap molekul sasaran dengan koefisien relatif selektif iaitu 2.36, 2.66, dan 2.77, masing-masingnya. MIP*

*(AAm) CYZ, MIP (MAA) AME dan MIP (2VP) ATZ telah berjaya menyingkirkan CYZ, AME dan ATZ dalam pelbagai sampel air (air suling, air paip dan air sungai) dengan kadar penyingkiran antara ~84% to ~95%.*

***Kata kunci:*** *Cyanazin, ametrin, atrazin, pempolimeran mendakan, molekul polimer tercetak*

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| | |
|---|---|
| % | Percentage |
| °C | Degree Celsius |
| µg/mL | Microgram Per Millilitre |
| 2VP | 2-Vinylpyridine |
| 4VP | 4-Vinylpyridine |
| AA | Acrylic Acid |
| AAm | Acrylamide |
| ABDV | Azobisdimethylvaleronitrile |
| Ace | Acetone |
| ACN | Acetonitrile |
| AcOH | Acetic Acid |
| AIBN | Azobisisobutyronitrile |
| AME | Ametryn |
| BET | Brunauer-Emmett-Teller |
| BIPB | Bis-(1-Tert-Butylperoxy)-1-Methylethyl)-Benzene |
| BPO | Bensoylperoxide |
| C | Another Kinetic Constant |
| $C_e$ | Analyte Concentration at Equilibrium |
| CEC | Capillary Electro Chromatography |
| $C_f$ | Final Concentration in the Solution After Binding |
| $C_i$ | Initial Concentration in the Solution Before Binding |
| cm | Centimetre |
| $cm^{-1}$ | Per Centimetre |

| | |
|---|---|
| CYZ | Cyanazine |
| DAD | Diode Array Detection |
| DCP | Dicumyl peroxide |
| DEA | Dielectric Thermal Analysis |
| DIPB | 1,3-Diisopropenylbenzene |
| DIW | Distilled Water |
| DMA | Dynamic Mechanical Analysis |
| DSC | Differential Scanning Calorimetry |
| DSPE | Dispersive Solid-Phase Extraction |
| DTA | Differential Thermal Analysis |
| DVB | Divinylbenzene |
| EDCs | Endocrine Disrupting Chemicals |
| EDX | Energy Dispersive X-Ray |
| EGDMA | Ethylene Glycol Dimethacrylate |
| EPA | Environmental Protection Agency |
| EtOH | Ethanol |
| FESEM | Field Emission Scanning Electron Microscopy |
| FRP | Free Radical Polymerization |
| FTIR | Fourier Transform Infra-Red |
| g | Gram |
| GC | Gas Chromatography |
| GC-MS | Gas Chromatograph-Mass Spectrometer |
| GPC | Gel Permeation Chromatography |
| h | Hour |
| HEMA | 2-Hydroethylmethacrylate |

| | |
|---|---|
| HPLC-UV | High Performance Liquid Chromatography-UltraViolet |
| IR | Infra-Red |
| ISEC | Inverse Size Exclusion Chromatography |
| K | Kelvin |
| k’ | Relative Selectivity Coefficient |
| $K_1$ | Pseudo-First-Order |
| $K_2$ | Pseudo-Second-Order |
| $K_D$ | Distribution Ratio |
| $K_{diff}$ | Pseudo-First-Order Equilibrium Rate Constant |
| $K_F$ | Maximum Adsorption Capacity of MIP |
| $K_L$ | Langmuir Constant |
| KPS | Potassium Persulfate |
| $K_{sel}$ | Selectivity Coefficient |
| m | Mass |
| MAA | Methacrylic Acid |
| MBAm | N, N-Methylenebisacrylamide |
| MeOH | Methanol |
| mg | Milligram |
| min | Minute |
| MIP | Molecularly Imprinted Polymer |
| MISPE | Molecular Imprinted Solid Phase Extraction |
| MIT | Molecular Imprinting Technology |
| mL | Millilitre |
| mmol | Millimoles |
| mol | Moles |

| | |
|---|---|
| MSPE | Magnetic Solid-Phase Extraction |
| n | Constant for the Intensity of Adsorption |
| NIP | Non-Imprinted Polymer |
| nm | Nanometre |
| NMR | Nuclear Magnetic Resonance |
| O/W | Oil-in-Water |
| PDMS | Diphenyldiethoxysilane |
| PhTMS | Phenyltrimethoxysilane |
| ppm | Parts Per Million |
| $q_e$ | Amount of Analyte Adsorbed at Equilibrium Time |
| $q_{max}$ | Maximum Adsorption Capacity of MIP |
| $q_t$ | Amount of Analyte Adsorbed at Any Given Time |
| $R_L$ | Parameter of Equilibrium |
| RP-HPLC | Reversed Phase-High Performance Liquid Chromatography |
| rpm | Round Per Minute |
| SBSE | Stir Bar Sorptive Extraction |
| SEM | Scanning Electron Microscopy |
| SERS | Surface-Enhanced Raman Scattering |
| SPE | Solid Phase Extraction |
| SPME | Solid-Phase Microextraction |
| t | Time |
| TAIC | Triallyl Isocyanurate |
| TEM | Transmission Electron Microscopy |
| TEOS | Tetrathoxysilane |
| TGA | Thermogravimetric Analysis |