

**SYNTHESIS, CHARACTERIZATION AND
METHOD DEVELOPMENT STUDIES OF A
MOLECULARLY IMPRINTED POLYMER FOR
THE EXTRACTION OF 2,4,6-TRINITROTOLUENE**

NORHAFIZA ILYANA BINTI YATIM

**MASTER OF SCIENCE
UNIVERSITI MALAYSIA TERENGGANU**

2013

**SYNTHESIS, CHARACTERIZATION AND METHOD DEVELOPMENT
STUDIES OF A MOLECULARLY IMPRINTED POLYMER FOR THE
EXTRACTION OF 2,4,6-TRINITROTOLUENE**

NORHAFIZA ILYANA BINTI YATIM

**A Thesis Submitted in Fulfillment of the Requirement for the Degree of Master of
Science in the School of Marine Science and Environment
Universiti Malaysia Terengganu**

2013

DEDICATION

This work is dedicated to

My lovely husband,
Mr. Mohd Yusof bin Samsudin

And my adorable daughters,
Adani Fathonah binti Mohd Yusof
&
Amina Syafiyya binti Mohd Yusof

Thanks for everything.

Abstract of thesis presented to the Senate of Universiti Malaysia Terengganu in fulfillment of the requirement for the degree of Master of Science

**SYNTHESIS, CHARACTERIZATION AND METHOD DEVELOPMENT
STUDIES OF A MOLECULARLY IMPRINTED POLYMER FOR THE
EXTRACTION OF 2,4,6-TRINITROTOLUENE**

NORHAFIZA ILYANA BINTI YATIM

2013

Main Supervisor : Assoc. Prof. Marinah binti Mohd Ariffin, Ph.D.
Co-Supervisor : Prof. Norhayati binti Mohd Tahir, Ph.D.
Mohd Aidil Adhha bin Abdullah, Ph.D.
School : Marine Science and Environment

A novel molecularly imprinted polymer (MIP) was synthesized to be used as a highly selective and specific sorbent for solid phase extraction (SPE) of 2,4,6-trinitrotoluene (TNT). TNT-MIP was prepared by using 2,4,6-trinitrotoluene (TNT) as template, methacrylic acid (MAA) as the functional monomer and ethylene glycol dimethylacrylate (EGDMA) as the cross-linker using the non-covalent approach. Non-imprinted polymer (NIP) was prepared under the similar approach but in the absence of a template as a reference for evaluating the performance of MIP. The resulting polymer monoliths were ground and sieved to obtain sizes in the range of 25-38 μm and incorporated as SPE sorbent. Their extraction performance were analysed using high performance liquid chromatography (HPLC) equipped with UV detector at 254 nm.

The proposed MISPE protocols provided good coefficient of correlation (r) of the calibration curves (≥ 0.993) for TNT and its metabolites. The limit of detection (LOD) and limit of quantitation (LOQ) range were 0.03-0.07 $\mu\text{g/mL}$ and 0.05-0.11 $\mu\text{g/mL}$,

respectively. The MIP showed excellent selectivity towards TNT with percentage recovery and RSD value, 94.1 ± 13.7 compared to 4-amino-2,6-dinitrotoluene (4-ADNT) and 2-amino-4,6-dinitrotoluene (2-ADNT), with 31.7 ± 27.2 and 41.2 ± 6.1 , respectively. The binding capacity of the MIP cartridge (20 mg/1 mL cartridge) approximately 0.15 $\mu\text{g}/\text{mg}$ of polymer. The physical imprinting effect of MIP and NIP was characterized by using scanning electron microscopy (SEM) and Brunauer, Emmett and Teller (BET). SEM micrographs showed that there were no obvious differences in the surface morphology when chloroform was used as a porogen solvent in the polymer synthesis. Further surface analysis was studied by BET analysis to verify the existence of the imprinted cavities.

This work was successfully applied to the analysis of TNT and its metabolites in soil samples. From the analysis of quarry samples it revealed the detection of TNT amounting to 0.06 $\mu\text{g}/\text{mL}$ and 0.07 $\mu\text{g}/\text{mL}$ by MISPE and commercial STRATA-X SPE, respectively, in 1 g of soil samples. The performance of the developed MISPE was good and comparable to the commercial STRATA-X SPE.

Abstrak tesis yang dikemukakan kepada Senat Universiti Malaysia Terengganu sebagai memenuhi keperluan untuk ijazah Sarjana Sains.

**SINTESIS, PERCIRIAN DAN PEMBANGUNAN KAEDAH BAGI POLIMER
MOLEKUL TERCETAK UNTUK PENGEKSTRAKAN 2,4,6-
TRINITROTOLUENA**

NORHAFIZA ILYANA BINTI YATIM

2013

Penyelia Utama : Prof. Madya. Marinah binti Mohd Ariffin, Ph.D.
Penyelia Bersama : Prof. Norhayati binti Mohd Tahir, Ph.D.
Mohd Aidil Adhha bin Abdullah, Ph.D.
Pusat : Sains Marin dan Sekitaran

Polimer molekul tercetak (MIP) yang berkepilihan tinggi telah disintesis sebagai bahan pengerap yang selektif untuk pengekstrakan fasa pepejal (SPE) untuk mengekstrak 2,4,6-trinitrotoluena (TNT). TNT-MIP telah disediakan dengan menggunakan 2,4,6-trinitrotoluena (TNT) sebagai templat, asid metilakrilik (MAA) sebagai monomer berfungsi dan etilena glikol dimetilakrilat (EGDMA) sebagai pemaut silang dengan menggunakan pendekatan tak-kovalen. Polimer molekul tidak-tercetak (NIP) telah disediakan seperti cara penyediaan MIP tetapi dengan ketiadaan templat bertujuan sebagai kawalan dalam penilaian prestasi MIP. Polimer molekul terhasil telah dikisar dan diayak untuk mendapatkan saiz molekul dalam julat 25-38 μm dan telah digunakan sebagai bahan pengerap SPE. Prestasi pengerap dianalisis dengan menggunakan kromatografi cecair berprestasi tinggi (HPLC) dilengkapi dengan pengesan UV pada 254 nm.

Protokol MISPE yang dicadangkan ini telah memberikan pekali korelasi (r) yang baik bagi lengkung penentukuran (≥ 0.993) bagi TNT dan metabolitnya. Had pengesanan (LOD) dan had kuantitatif (LOQ), masing-masing berada di dalam julat 0.03-0.07 $\mu\text{g/mL}$ and 0.05-0.11 $\mu\text{g/mL}$. MIP menunjukkan kepilhan yang tinggi terhadap TNT dengan peratus perolehan dan nilai sisihan piawai relatif (RSD), 94.1 ± 13.7 berbanding dengan 4-amino-2,6-dinitrotoluena (4-ADNT) dan 2-amino-4,6-dinitrotoluena (2-ADNT), masing-masing dengan nilai 31.7 ± 27.2 dan 41.2 ± 6.1 . Kapasiti keupayaan katrij MIP (20 mg/1 mL katrij) dianggarkan sebanyak 0.15 $\mu\text{g/mg}$ polimer. Kesan fizikal pencetakan MIP dan NIP telah dikaji dengan menggunakan mikroskopi imbasan elektron (SEM) dan Brunauer, Emmett dan Teller (BET). Mikrograf SEM yang diperolehi menunjukkan bahawa tiada perbezaan yang ketara dalam morfologi permukaan apabila klorofom digunakan sebagai pelarut semasa pempolimeran. Analisis lanjut ke atas permukaan telah dijalankan dengan menggunakan BET untuk mengesahkan kewujudan kaviti pencetakan.

Kajian ini telah berjaya dijalankan untuk menganalisis TNT dan metabolitnya ke atas sampel tanah. Analisis sampel dari sebuah kuari telah mendedahkan pengesanan TNT oleh MISPE dan STRATA-X SPE komersial, masing-masing sebanyak 0.06 $\mu\text{g/mL}$ dan 0.07 $\mu\text{g/mL}$ dalam 1 g sampel tanah. Prestasi pembangunan MISPE sangat baik dan mampu bersaing dengan STRATA-X SPE komersial.