



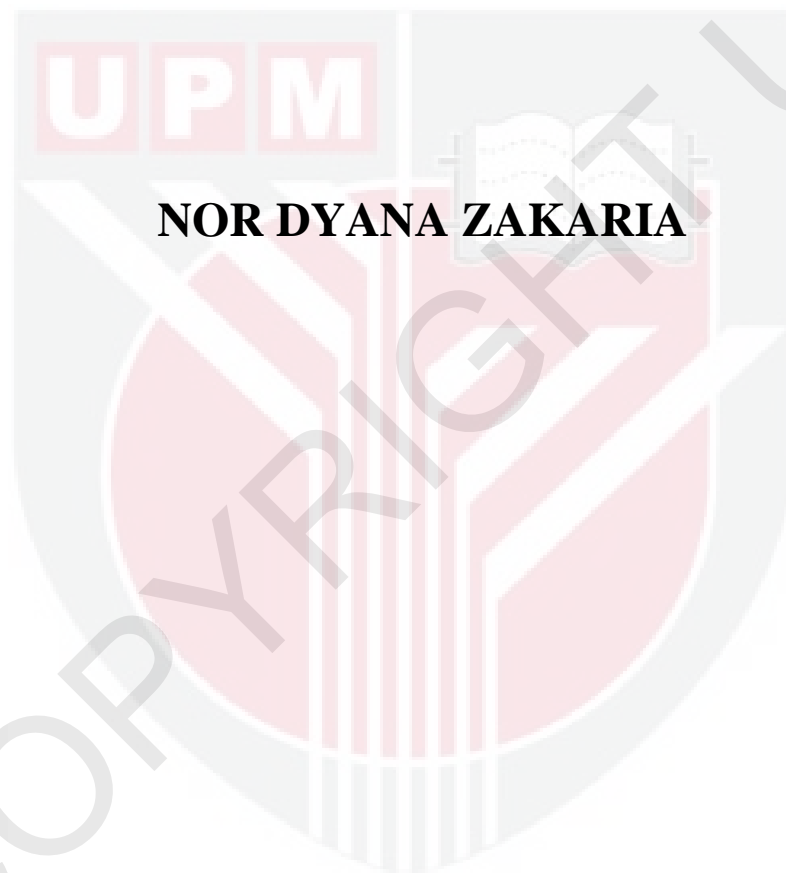
UNIVERSITI PUTRA MALAYSIA

***SYNTHESIS AND CHARACTERIZATION OF MOLECULARLY
IMPRINTED POLYMER FOR REMOVAL OF 2,4-DINITROPHENOL***

NOR DYANA ZAKARIA

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**MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA**

2010

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IMPRINTED POLYMER FOR REMOVAL OF 2,4-DINITROPHENOL**

By

NOR DYANA ZAKARIA

**Thesis Submitted to the School of Graduate Studies, Universiti Putra
Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science**

May 2010

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science.

SYNTHESIS AND CHARACTERIZATION OF MOLECULARLY IMPRINTED POLYMER FOR REMOVAL OF 2,4-DINITROPHENOL

By

NOR DYANA ZAKARIA

May 2010

Chairman : Nor Azah Yusof, PhD

Faculty : Science

In this work, molecular imprinted polymers (MIPs) were prepared by bulk polymerization method in acetonitrile using 2,4-dinitrophenol, acrylamide, ethylene glycol dimethacrylate, and benzoyl peroxide as template, functional monomer, cross-linker and initiator, respectively. The functional monomer and the cross linker (molar ratio of functional monomer to cross linker 1:3) and 1.6 mmol of the initiator BPO were used. Then, the polymer were crushed, ground and sieved to obtain regularly sized particles between 80-100 μm . The polymer obtained is then washed to remove the template using methanol/ acetic acid in 2:1 (v/v) ratio for 3 times. Membrane MIP was prepared by hybridization of MIP particle with cellulose acetate (CA) and polystyrene (PS), respectively. Sorption process for the removal of 2,4-dinitrophenol using the fabricated MIP was evaluated under various pH and time conditions. Parameters studied for the removal of 2,4-dinitrophenol include sorption kinetics, sorption isotherm, selectivity and reusability of the MIP and membrane MIP. The concentration of 2,4-dinitrophenol was

analyzed using UV-Vis Spectrophotometer. The prepared MIP was characterized using Fourier transformed infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), thermo gravimetric analysis (TGA), particle size analyzer (PSA) and Brunauer, Emmett Teller (BET) adsorption isotherm analysis.

The FTIR spectra showed a broadening at 3400 cm^{-1} indicating that a hydrogen bond interaction takes place between the phenolic hydroxyl group and the carbonyl from the amide group. From the surface morphology of SEM image, MIP could be seen to exhibit a more porous and rough structure than MIP before extraction and NIP. The surface area of the MIP is $103.65\text{ m}^2/\text{g}$ and the NIP is $8.99\text{ m}^2/\text{g}$. The results showed a type IV adsorption-desorption isotherm, which is typically characteristic of mesoporous materials. The size of the MIP particles was in the range of 130.00 nm and the particles size of non imprinted polymer (NIP) was in the range 400.00 nm .

The maximum sorption of 2,4-dinitrophenol by MIP was found to be 2.88 mg/g under acidic conditions at pH 6.0. The maximum sorption of 2,4-nitrophenol by the fabricated cellulose acetate membrane with molecular imprinted polymer (CA-MIP) and polystyrene membrane with molecular imprinted polymer (PS-MIP) were found at pH 7.0 and pH 5.0, respectively. Sorption data for MIP, CA-MIP and PS-MIP were described well at the Langmuir isotherm model equilibrium. The sorption of MIP, CA-MIP and PS-MIP towards 2,4-DNP reaches equilibrium in 1 h and 2 h, respectively.

The sorption of the 2,4-DNP by the MIP, CA-MIP and PS-MIP were found a better model at pseudo-second-order kinetic equation compared to first-order equation. For selectivity study, 2,4-dichlorophenol (2,4-DCP), 3-chlorophenol (3-CP) and phenol were selected as potential interferences. The sorption abilities of MIP, CA-MIP and PS-MIP for 2,4-DNP were far stronger than that of 2,4-DCP, 3-CP and phenol. The MIP could be reused after extraction with methanol: acetic acid in 2:1 (v/v) ratio and was stable for up to five sorption cycles without obvious decrease in the sorption capacity for 2,4-DNP.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains.

**SINTESIS DAN PENCIRIAN POLIMER CETAKAN MOLIKUL BAGI
PENYINGKIRAN 2,4-DINITROFENOL**

Oleh

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Polimer cetakan molikul (MIP) disediakan dengan pempolimeran pukal dan radikal, dalam asetonitril sebagai pelarut, 2,4-dinitrofenol, 4-vinylbenzoik asid, etilin glikol dimetaakrilat, dan benzil peroksida (BPO) masing-masing sebagai pencontoh molekul, monomer berfungsi, penggabung dan permula. Monomer berfungsi dan penggabung dengan nisbah 1:3 dan permula (BPO) telah digunakan untuk menghasilkan MIP. Polimer cetakan molikul kemudian di pecahkan dan di ayak untuk dijadikan butiran halus. Polimer kemudiannya dibasuh dengan methanol : asetik asid dengan nisbah 2:1 adalah untuk mengeluarkan pencontoh molekul. Membran MIP disediakan dengan cara hibrid menggunakan MIP partikel bersama selulosa asetat (CA) dan polistirena (PS). Parameter yang mempengaruhi erapan 2,4-dinitrofenol yang dikaji termasuklah kesan pH, penyerapan kinetik, isoterma, selektif dan guna semula untuk setiap MIP dan memberan MIP. Kepekatan 2,4-dinitrofenol telah dianalisis dengan menggunakan UV-VIS Spektrometer. MIP yang terhasil telah dicirikan dengan spektroskopi inframerah transformasi

Fourier (FTIR), analisa morfologi menggunakan mikroskopi elektron pengimbasan (SEM), analisis thermogravimetrik (TGA), analisa partikel saiz dan analisa penyerapan isoterma (BET).

Serapan FTIR menunjukkan puncak tajam pada 3400 cm^{-1} adalah ikatan hidrogen antara kumpulan hidroksil fenol dan karbonil yang dihasilkan daripada kumpulan amido. Keputusan daripada analisis morfologi menggunakan mikroskopi elektron pengimbasan (SEM), MIP kelihatan lebih berongga dan kasar pada permukaan berbanding dengan keputusan MIP sebelum dikeluarkan acuan dan tiada cetakan polimer molekul (NIP). Bagi analisis penyerapan isoterma (BET), kawasan permukaan bagi MIP adalah $103.6502\text{m}^2/\text{g}$ dan NIP adalah $8.9948\text{m}^2/\text{g}$. Keputusan menunjukkan penyerapan dan nyahpenyerapan isoterma adalah jenis IV dimana iainya bercirikan meso berongga. Saiz untuk MIP partikel adalah 130.00 nm manakala saiz untuk NIP adalah 400.00 nm .

MIP bagi penyerapan 2,4-dinitrofenol paling berkesan pada keadaan berasid pH 6.0 dengan nilai tertinggi bagi proses penyerapan 2,4-dinitrofenol ialah 2.88 mg/g . Muatan penyerapan maksima bagi CA-MIP dan PS-MIP berlaku pada pH 7 dan pH5. Muatan penyerapan bagi MIP, CA-MIP dan PS-MIP meningkat dengan kepekatan awal 2,4-dinitrofenol dan mematuhi model isoterma Langmuir. Penyerapan bagi 2,4-dinitrofenol oleh MIP, CA-MIP dan PS-MIP berlaku dengan keseimbangan pada masa 1 jam dan 2 jam, masing-masing. Tertib tindak balas bagi penyerapan 2,4-dinitrofenol ialah tertib kedua. Bagi kajian untuk selektif, 2,4-diklorofenol, 3-klorofenol dan fenol

digunakan sebagai gangguan. Penyerapan MIP, CA-MIP dan PS-MIP terhadap 2,4-dinitrofenol adalah sangat kuat dan jauh lebih kuat daripada penyerapan terhadap 2,4-diklorofenol, 3-klorofenol dan fenol. Selain itu, MIP juga boleh digunakan semula setelah dikeluarkan acuannya iaitu 2,4-dinitrofenol, dengan menggunakan pelarut methanol: asetik asid dengan nisbah 2:1 (v/v) dan iainya sangat stabil kepada 5 kali proses mengeluarkan acuan.



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I certify that a Thesis Examination Committee has met on 10 May 2010 to conduct the final examination of Nor Dyana Zakaria on her thesis entitled "**Synthesis and Characterization of Molecularly Imprinted Polymer for Removal of 2,4-Dinitrophenol**" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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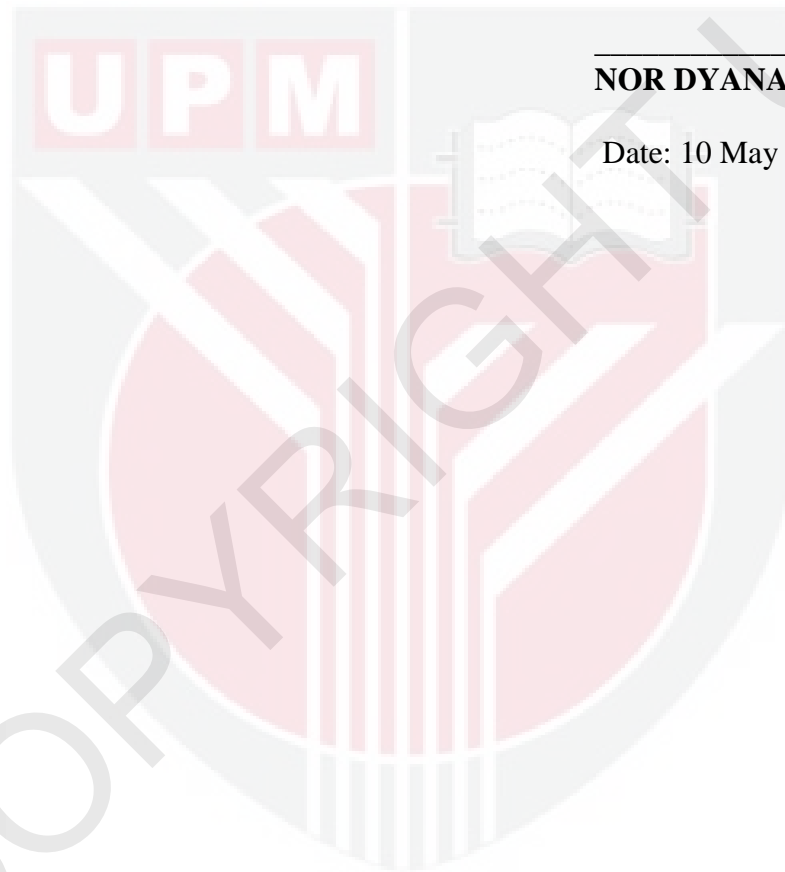
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Date: 12 August 2010

DECLARATION

I declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institutions.



NOR DYANA ZAKARIA

Date: 10 May 2010

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