ABSORPTION STUDY OF BIS PHENOL A USING MOLECULAR IMPRINTED MEMBRANE

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ABSTRACT

Endocrine disruptors component (EDCs) are environmental chemicals that affect the function of the endocrine system, the system relating the glands and hormones of the body. In this study, Bisphenol A (BPA) has selected for evaluation because it has acknowledged significant consideration in recent years due to widespread human exposures and concern for reproductive and developmental effects toward health. There is some evidence that endocrine disruptors may not only impact the individual directly exposed, but also future generations. So, the removal of BPA must be efficient to protect our new generation and environment. In this study, Molecular Imprinted polymer (MIP) has been chosen because of their advantages such as MIPs possess excellent selective adsorption for templates due to the stereoscopic shape of specific cavity and interactions. Thus, this research is aims to practice the removal of BPA from aqueous solution by adsorption using an effective, reusable and low cost method like molecular Imprinted membrane that have highly selective factor. The MIP was synthesis by using bulk polymerization process and imprinted membrane were prepared by using phase inversion method. The adsorption kinetics was studied by stirring BPA-MIP, NIM and BPA-MIM in BPA aqueous solution for different times. The adsorption isotherms were studied by stirring BPA-MIP, NIM and BPA-MIM in BPA solution at different concentration. The maximum adsorption capacity of BPA ions for the NIM, BPA-MIM, and BPA-MIP was 0.1268 mmol/g, 0.1328 mmol/g, 0.1149 mmol/g respectively. In this study, it can be conclude that the MIP in membrane can absorb the BPA more than BPA-MIP powder, and membrane alone.

ABSTRAK

Komponen pengacau Endokrin (EDCs) adalah bahan kimia alam sekitar yang memberi kesan kepada fungsi sistem endokrin, sistem yang berhubungan kelenjar dan hormon badan. Dalam kajian ini, BPA telah dipilih untuk penilaian kerana ia telah diakui terdapat peningkatan yang ketara dan pendedahan yang meluas terhadap manusia dan alam sekitar dalam tahun-tahun kebelakangan dan terdapat kebimbangan untuk kesan pembiakan dan pembangunan ke arah kesihatan. Terdapat beberapa bukti bahawa EDCs bukan sahaja boleh memberi kesan kepada individu yang terdedah secara langsung, tetapi juga generasi akan datang. Jadi, penyingkiran BPA perlu cekap untuk melindungi generasi baru akan dating dan alam sekitar. Dalam kajian ini, polymer molecul bercetak (MIP) telah dipilih kerana MIP mempunyai penjerapan terpilih yang cekap kerana bentuk stereoskopik rongga dan interaksi tertentu. Oleh itu, kajian ini bertujuan untuk menyerap BPA ion daripada BPA larutan akueus oleh penjerapan menggunakan, kaedah kos rendah yang boleh diguna semula dan berkesan seperti membran dicetak molekul yang mempunyai faktor yang sangat selektif. MIP disintesis menggunakan proses pempolimeran pukal dan membran dicetak dengan menggunakan kaedah penyongsangan fasa. Kajian mengenai kinetik penjerapan terhadap membrane, BPA-MIP dan BPA-MIM dilakukan dalam masa yang berlainan untuk 24 jam. Kajian mengenai isotermal penjerapan dilakukan terhadap membrane BPA-MIP, dan BPA-MIM dalam larutan BPA pada kepekatan yang berbeza. Keupayaan penjerapan maksimum ion BPA untuk membran , BPA-MIM, dan BPA-MIP adalah 0.1268 mmol/g, 0.1328 mmol/g, 0.1149 mmol/g masing-masing. Dalam kajian ini, ia boleh membuat kesimpulan bahawa MIP dalam membran boleh menyerap lebih banyak BPA daripada serbuk BPA-MIP, dan membran sahaja.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

ED	Endocrine Disruptor
EDC	Endocrine Disruptor Component
BPA	Bis Phenol A
WW	Waste Water
WWS	Waste Water Sludge
MIP	Molecular Imprinted Polymer (In powder form)
BPA-MIP	Molecular Imprinted Polymer with BPA template (In powder form)
MIM	Molecular Imprinted Membrane
BPA-MIM	Molecular Imprinted Membrane with BPA template
NIP	Non Imprinted Membrane
SEM	Scanning electron microscope
FTIR	Fourier Transform Infrared
IR	Infrared
BADM	Bisphenol A dimethacrylate
NMP	N-methyl pyrorolidone
THF	Tetrahydofuron
AIBN	Azobibidobutyronitrile
TRIM	Trimehylolpropane trimethacrylate
Psf	Polysulfone
ACN	Acetonenitrile

1 INTRODUCTION

1.1 Motivation and statement of problem

Endocrine disruptors (EDs) are environmental chemicals that affect the function of the endocrine system, the system relating the glands and hormones of the body. The endocrine system coordinates the functions of various organs and systems in the body. EDs may interrupt the endocrine system in some ways: they may act as "imposters" of naturally occurring hormones, block the action of hormones, modify the chemical message sent by hormones, and disrupt the production of hormones or hormone receptors (Vanderberg *et al.*, 2007).

Most EDs act like naturally occurring estrogens in the body. The theory of endocrine disruptors gained credibility from a number of studies demonstrating reproductive problems in wildlife exposed to certain environmental chemicals. EDs are a different class of chemicals. They include: certain pesticides, industrial chemicals like PCBs, and dioxins, phthalates, phenols like bisphenol A, and alkylphenol, and plant hormones like phytoestrogens (Vanderberg *et al*., 2007).Endocrine disrupting compounds (EDCs) have caused various adverse health effects which have been reported in recent years. The EDCs has been as a social, environmental and global issue (Mohapatra *et al.*, 2010). Due to this, an effective treatment and disposal of Bisphenol A (BPA) in waste water (WW) or waste water sewage (WWS) has been one of the major concerns in wastewater treatment processes to degrade organic pollutants including BPA. There are several kinds of pre-treatment methods studied so far which involve chemical treatment, mechanical treatment, oxidative treatment, biological hydrolysis or combination of any two of these methods. One of the latest technologies in BPA extraction is using molecular recognition (Kryscio and Peppas., 2012).

Molecular recognition is a fundamental biological mechanism ubiquitous in nature. This elegant, yet simple, mechanism is found in a variety of biological processes, including antibody/antigen recognition in the immune system, enzymatic catalysis, signal transduction, and nucleic acid interactions such as replication, transcription, and translation. Molecular imprinting is a promising field in which a polymer network is

formed with specific recognition for a desired template molecule. This technique has been successfully applied to small molecule templates in the areas of separations, artificial enzymes, chemical sensors, and pharmaceuticals which will be discussed on chapter 2 .The imprinting of small molecules is well developed, and tailor-made molecular imprints are now available commercially (Mohapatra *et al.*, 2010).

According to the Toxics Release Inventory database, total environmental release of bisphenol A in 2004 was 181,768 pounds, with releases of 132,256 pounds to air, 3533 pounds to water, 172 pounds to underground injection, and 45,807 pounds to land. There is extensive evidence that many consumer products contain and release BPA and many of these products leach BPA under normal conditions of use. BPA has been detected in baby bottles, epoxy resins, and other consumer plastics and also been detected in a wide range of foods stored in cans with epoxy resins. There is very good evidence to indicate that BPA can be detected in environmental samples, including air, dust and water. Evidence for this is supported by studies of landfill leachates which indicate substantial release of BPA from landfills (Vandenberg *et al.*, 2007). Hence, the detection of BPA is very important in maintaining an awareness of pollutants in our immediate environments. Recently, various methods have been employed for the determination of BPA. Most use methods are adsorption method using activated carbon or clay as absorber. However, these methods are expensive, and require pre-treatment.

In this study, MIP has been chosen because of their advantages such as MIPs possess excellent selective adsorption for templates due to the stereoscopic shape of specific cavity and interactions. In addition to this property, they are reusable and durable against chemical conditions.

1.2 Objectives

The aims of this research are to study the adsorption of BPA-MIM toward BPA.

1.3 Scope of this research

The following are the scope of this research:

i) The synthesis of MIM

ii) To study the characterization of BPA-MIP and BPA-MIM

iii) To study the adsorption/absorption performance of BPA-MIP and BPA-MIM towards BPA.

1.4 Main contribution of this work

In this study, BPA has selected for evaluation because it has acknowledged significant consideration in recent years due to widespread human exposures and concern for reproductive and developmental effects toward health. BPA is most commonly described as being "weakly" estrogenic; however, an emerging body of molecular and cellular studies indicate the potential for a number of additional biological activities (Shelby. M. D., 2007). There is some evidence that endocrine disruptors may not only impact the individual directly exposed, but also future generations. So, the removal of BPA must be efficient to protect our new generation and environment.

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description of the applications and general design features of imprinted polymer. General description BPA properties are presented. This chapter also provides a brief discussion of the advanced experimental techniques available for MIP and MIM synthesis and mentioning their applications. A summary of the previous experimental work on MIP is also presented.

Chapter 3 gives a review of the approach applied for synthesis of BPA-MIM and BPA-MIP and experimental procedures. The performances of three different polymers, the imprinted powder, imprinted membrane and NIM were compared with batch binding capacity experimental data.

Chapter 4 is devoted to discuss on the results of the experiment that was done in order to determine which Polymer between BPA-MIP, BPA-MIM and NIM is more effective in absorption process in term of binding capacity of BPA in mg Polymer. The

characterization of BPA-MIP and BPA-MIM using SEM and FTIR is also presented, a brief review of the kinetic and adsorption isotherm result is also outlined.

Chapter 5 draws together a summary of the thesis and outlines the future work which might be derived from the model developed in this work.

2 LITERATURE REVIEW

2.1 Overview

A literature review was introduced to classified studies that related to the topic. There are five theme in this literature review which is overview of BPA include characteristic of BPA, sources of BPA, and effect of BPA towards our health. This chapter also provide overview of Molecular imprinted polymer (MIP), which is the special molecular recognition effecting factors like monomer, template, cross linking and etc, preparation method of MIP and adsorption isotherms.

2.2 Introduction

Endocrine disruptors are naturally occurring compounds or human made chemicals that may obstruct with the production or activity of hormones of the endocrine system leading to undesirable health effects. Several of these chemicals have been connected with developmental, neural, reproductive, immune, and other problems in flora and fauna and laboratory animals. A few scientists think these chemicals also are adversely affecting human health in similar ways resulting in declined fertility and increased incidences or progression of some diseases including endometriosis and cancers (Endocrine disruptors., 2007)

Endocrine disruptors can mimic or partly mimic naturally taking place hormones in the body like estrogens (the female sex hormone) and androgens (the male sex hormone) and thyroid hormones, potentially producing overstimulation. It also can attach to a receptor contained by a cell and block the endogenous hormone from binding. The typical signal then fails to occur and the body fails to respond properly. Examples of chemicals that block or antagonize hormones are anti-estrogens or anti-androgens. The ED also can interfere or block the way natural hormones or their receptors are made or controlled, for example by blocking their metabolism in the liver (Endocrine disruptors., 2007). Chemicals that are known endocrine disruptors include diethylstilbestrol (the drug DES), dioxin and dioxin like compounds, PCBs, DDT, and some other pesticides. This study pays more attention to BPA because of its widely application in industry.

2.3 Previous work on BPA-MIP

In the past few years molecular imprinting has entered many areas of chemistry, biochemistry and biotechnology. Nowadays polymers imprinted with different templates like drugs, herbicides, sugars, nucleotides, amino acids and proteins are more and more applied in analytics, as well as in catalysis or for synthetic processes (Huang *et al.*, 2012).

Molecular imprinting technology plays an important role in constructing molecule recognition sites into some polymer matrix (Zhao *et al.*, 2008). The current opinion about molecular imprinting is a technology in which specific recognition sites are formed in a polymer matrix by synthesis in the presence of the template molecule, or 'imprinting' molecule which results in the formation of specific recognition cavities complementary to the template in shape and chemical functionality (Yang *et al,*. 2005).

Molecular imprinting is a method for producing chemically selective binding sites, which distinguish a particular molecule, in a macro porous polymer matrix (Mayes & Mosbach., 1997). The current opinion about the MIP is that their peculiar molecular recognition properties are due to the presence of nanocavities formed during a polymerization process developed in the presence of a template molecule and of suitable functional monomers. According to the key-lock principle by Kryscio and Peppas, (2012); the shape of the nanocavities is complementary to that of the template. The non-covalent interactions which govern the molecular recognition mechanism are established between the binding site and a single, isolated template molecule.). Extraction of the template leaves sites in the polymer with specific shape and functional group complementarily to the original template (Zhang *et al.*, 2009). Moreover, as regards a polymer obtained by the non-covalent imprinting technique, the key-lock principle should be intended as effectively operating not in materials possessing a single, well-defined class of binding site but in a complex environment constituted by a multiplicity of binding sites with a wide and perhaps continuous distribution of affinities for the template (Bagiani *et al.*, 2004).

Intermolecular forces that develop during polymerization between the template molecules (T), functional monomer (M) and developing polymer matrix are responsible for creating a polymer microenvironment for the template or imprint molecule. The

process called imprinting polymerization consists of polymerizing a functional monomer, mixed with a template, in the presence of a very big portion of cross-linker. After the pre-arrangement between functional monomers and the template, the template-functional monomers and cross-linkers are co-polymerized. The extraction of template from Imprinted binding site is done by extensive washing using solvent. Thus, the binding sites are left, which are complementary to the template in size, shape, and functional groups (Batra and Shea., 2003).

Many variables of the imprinting process influence the selectivity and capacity of a MIP. First, complementary interactions between the template and the functional a cross linking monomers are necessary to create short-range molecular organization at the receptor site in presence of a initiator. These interactions include hydrogen bonding, electrostatic and/or van der Waals forces. Second, the stoichiometry and concentration of the template and monomers influences both polymer morphology and MIP selectivity. Third, the solvent used in the polymerization process and finally, the temperature of polymerization influences the timing of phase separation. Also, the temperature dependence of the equilibrium between the functional monomers and template affects MIP selectivity and capacity (Batra and Shea., 2003).

Basically, two types of molecular imprinting strategies have been established based on covalent bonds or non-covalent interactions between the template and functional monomers as shown in Figure 2.1. In both cases, the functional monomers, chosen so as to allow interactions with the functional groups of the imprinted molecule, are polymerized in the existence of the imprinted molecule. The special binding sites are formed by covalent or, more commonly, non-covalent interaction between the functional group of imprint template and the monomer, followed by a cross linked co-polymerization (Takeda & Kobayashi., 2005).

During the non-covalent approach, the special binding sites are formed by the self-assembly between the template and monomer, followed by a crosslinked co-polymerization (Svenson *et al.*, 2004 & Ekberg and Mosbach., 1989). The imprint molecules interact, during both the imprinting procedure and the rebinding, with the polymer via non-covalent interactions, like ionic, hydrophobic and hydrogen bonding. The non-covalent imprinting approach seems to hold more potential for the future of

molecular imprinting due to the vast number of compounds, including biological compounds, which are capable of non-covalent interactions with functional monomers (Sellergen *et al.*, 1993 & Michael *et al.*, 1997)

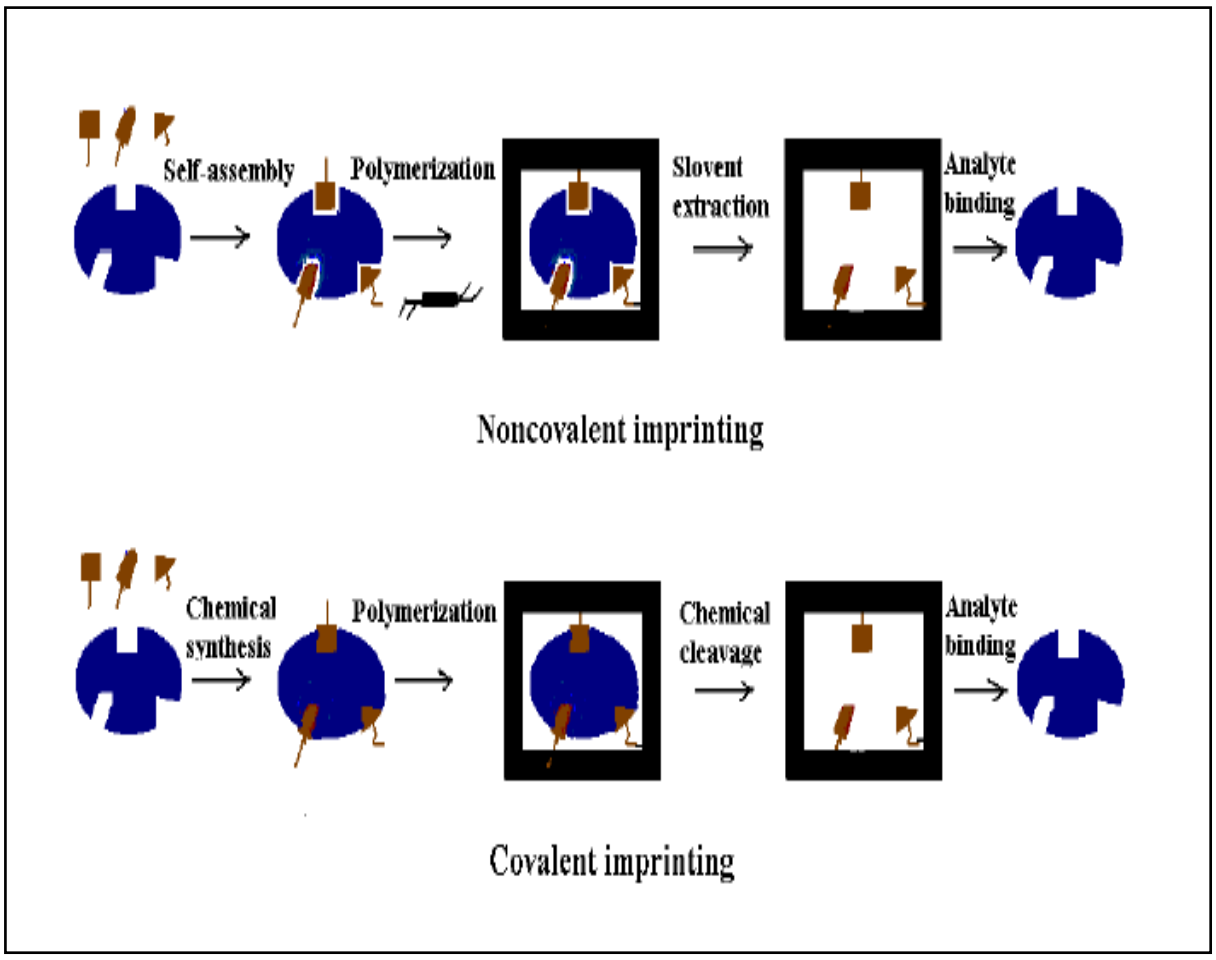

Figure 2-1: Schematic representation of covalent and non-covalent molecular imprinting procedures.

2.4 Evaluation of the BPA-MIP Using Adsorption Models

The discrete Langmuir and bi-Langmuir models are mostly simple to implement via Scatchard plots and generate the corresponding binding parameters: binding affinity (K) and number of binding sites (N). In the Scatchard analysis, the experimental binding isotherm is plotted in q/C versus q format (where q is the concentration of the analyte bound to a polymer in mol g−1 and C is the concentration of free analyte remaining in the solution in mol L−1). In homogeneous systems that contain only one type of binding site, the Satchard plot falls on a straight line with a slope equal to the negative of the

binding affinity (−K) and an x-intercept equal to the number of binding sites (N) as show in equation 2.1.

$$q/C = KN - Kq \quad (2.1)$$

In contrast, the Scatchard plots for most MIPs are curved. This curvature has been cited as evidence for binding site heterogeneity. Heterogeneity can still be accommodated using the Scatchard analysis by modelling the curved isotherm as two separate straight lines (bi-Langmuir model). This limiting slopes method yields two separate sets of binding parameters (K_1, N_1 and K_2, N_2) for two classes of sites. To predict the favourability of the adsorption system, the Langmuir equation may also be expressed in terms of a dimensionless separation factor RL defined as equation 2.2 where C_0 is the initial BPA concentration (mol L^{-1}) and K is the Langmuir adsorption equilibrium constant (L mol^{-1}). The parameter RL > 1, RL = 1, 0 < RL < 1, RL = 0, indicates the isotherm shape according to unfavourable, linear, favourable and irreversible, respectively (Pereza *et al.,* 2011 & Zakaria. *et al*., 2009).

$$R_L = 1/(1 + KC_0) \quad (2.2)$$

Zakaria *et al.,* 2009 have studies the adsorption of 2,4-dinitrophenol by MIP. According to the study, the equation is frequently used in the linear form by taking the logarithm of both sides as:

$$\text{Log qe} = \log K_f + 1/n \log Ce \quad (2.3)$$

Where K_f and n are isotherm constant, respectively. The applicability of the Freundlich sorption is also analyzed by plotting log qe versus log Ce. To determine the constant K_f and n, the linear form of equation, Eq 2.3 can be used. Compared to Freudlich, the Langmuir plots have a higher correlation coefficient of 0.985. It can be confirmed that 2,4-dinitrophenol adsorption by MIP follow the Langmuir (Yusof *et al.,* 2010 & Yusof *et al.,* 2009).

2.5 Review on MIP Membrane

A membrane is an interphase involving two adjacent phases acting as a selective barrier, at the mean time organizes a system into compartments and regulating the transport between the two compartments. The most important advantages of membrane technology as compared with other unit operations in biochemical engineering are associated to the unique separation principle, like the transport selectivity of the membrane. In addition, separations with membranes do not require additives, and they can be performed isothermally and at very competitive energy consumption (Ulbricht., 2004). Membrane technology has been already applied in many industrial fields like food, energy, environment, and artificial organs but, the possibility to introduce specific recognition sites in a synthetic membrane plays an important role for the transport of specific substances. An imprinted membrane is able to discriminate between target molecules and others, thus improving the separation process (Tasselli *et al*., 2008).

To develop molecularly imprinted membranes, which have become a latest category of membrane-absorbent materials, various challenges have acknowledged much attention and certain successes have been achieved. A MIM is a membrane either composed of a MIP or containing a MIP (Ulbricht., 2004 and Son *et al*., 2011). A high membrane performance depends on well-defined membrane morphology with respect to barrier pore size and layer topology, especially the thickness of the barrier layer (Ulbricht., 2004). First studies on molecularly imprinted polymer membranes were performed by Piletsky *et al*., in 1999 via in situ bulk polymerization of acrylate monomers. Since then, further researchers prepared successfully imprinted membranes using the similar method and try to approach another method (Tasselli., 2008). Dry phase separation, wet phase inversion, and surface imprinting have been investigated as possible methods to prepare imprinted membranes. In 1996, Kobayashi and friends have developed a method to prepare imprinted membranes, through phase inversion via non-solvent induced phase separation from a viscous solution of the membrane-forming polymer and the imprinted molecule. The washing of the membrane leaves in the structure free cavities that are able to bind the print molecule better than nonimprinted membrane and selectively with respect to molecules of similar structure as, theophylline with respect to caffeine (Silvestri *et al*., 2006).

In the first work on that MIM preparation, Ulbricht., (2004) had used polystyrene resins with peptide recognition groups, in a blend with a matrix polymer, for the MIM formation via a "dry PI" process, the polymer solidification was achieved by solvent evaporation. Remarkably, the permeability was much higher for the MIM as compared with the blank membranes. On the other hand, Takeda and Kobayashi., (2005) had used functional acrylate copolymers for a "wet PI" process yielding asymmetric porous MIM. In that case, the polymer solidification was achieved through a precipitation induced by contact with a non-solvent. The copolymer material and methodology had recently successfully been adapted by another group. In the meantime, the polymer selection for phase inversion imprinting had been extended to mainly of the frequently used membrane materials, example cellulose acetate, polyamide, polyacrylonitrile and polysulfone. The formation of porous MIM from a compatible blend of a matrix polymer for adjusting a permanent pore structure and a functional polymer for providing binding groups could provide even more alternatives. Furthermore, polyethyleneglycol as pore former in the polymer blend casting solution had been successfully used to increase the membrane permeability (Ulbricht., 2004).

It is remarkable, that most MIM prepared via phase inversion imprinting had at least acceptable binding performance in aqueous media. However, such MIM lost their "template memory" when exposed to a too organic environment where swelling and chain rearrangement seemed to "erase" the imprinted information .However, it should be noted, that even if the phase inversion should be most suited for the preparation of separation membranes, the adaptation of the process to the preparation of MIM is complicated because the conditions required for an optimal formation of MIP sites may not be compatible with the ones for obtaining an optimal pore structure (Ulbricht., 2004).

2.6 Summary

This literature review is the information of mass transfer study of MIP on BPA removal. MIP membrane has been chosen because of the highest selectivity and for the preparation of MIP, bulk polymerization is chosen. This chapter also have discussed about the adsorption isotherm and kinetics study about MIP.

3 MATERIALS AND METHODS

3.1 Overview

This section covers a method for BPA-MIP and BPA-MIM synthesis process. The resultant polymer was used to study their characterization using FTIR and SEM. This section provides scheme used in kinetic and adsorption study on BPA removal from BPA aqueous solution. The absorption of BPA is study in term of binding capacity of the BPA in polymer. Figure 3.1 summarizes the overview of this study.

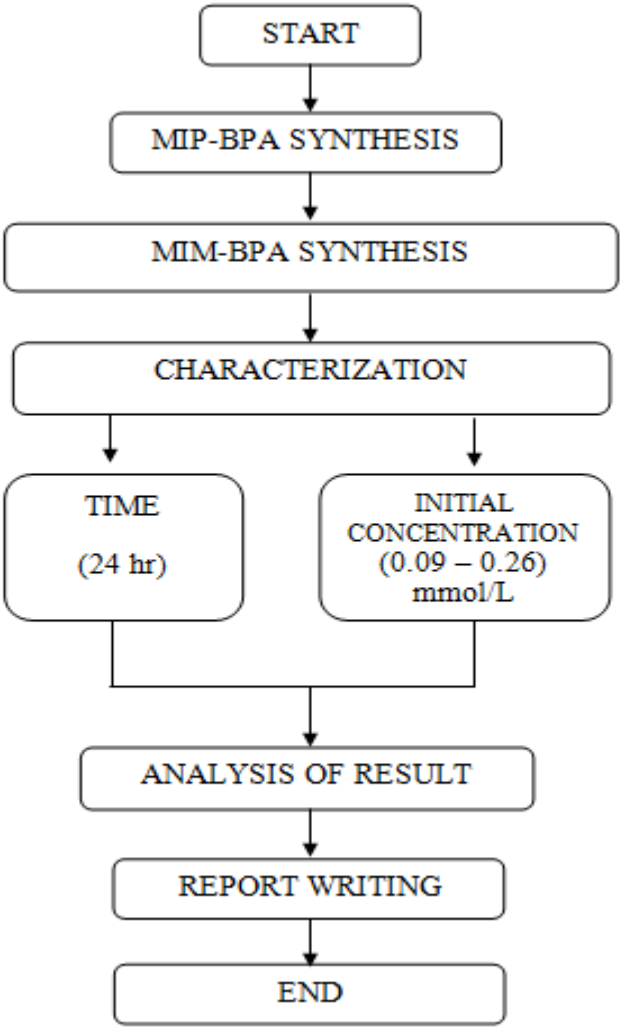

Figure 3.1 Overview of methodology

3.2 Chemicals and Equipment

The chemicals and equipment used in this study is of analytical grades, and they are summarizes in Table 3.1 and Table 3.2.

Table 3.1 List of equipment used

Equipment	Brand	Principal Used
Incubator Shaker	BS-21	Experiment
UV-Vis Spectrophotometer	U-1800	Analysis
FTIR	Thermo Nicolet	Characterization
SEM	Zeiss	Characterization

Table 3.2 List of chemical used

Chemical	Principal used
Bis Phenol A (BPA)	Analysis
Bisphenol A dimethacrylate (BADM)	MIP synthesis
N-methyl pyrorolidone (NMP)	MIM synthesis
Polysulfone	MIM synthesis
Trimehylolpropane trimethacrylate (TRIM)	MIP synthesis
Acetonenitrile	MIP synthesis
Azobibidobutyronitrile (AIBN)	MIP synthesis
Tetrahydofuron (THF)	Hydrolysis
Sodium Hydroxide(NaOH)	Hydrolysis

3.3 Synthesis of BPA-MIP and BPA-MIM

Synthesis of MIP is done by using the Bulk polymerization process. The formulations of BPA imprinted copolymer were showed in figure 3.2. The templates (BPA) were mixed with the functional monomer (BADM), the cross-linker (TRIM) in 1:10 mol ratio and ACN as a solvent. AIBN was applied as initiator of the polymerization solution. The glass tube was sealed and placed under after purging with nitrogen gas for 5 min to completely evacuate the air, thus avoiding the polymerization inhibition. Finally, the polymerization was carried out at 80 ◦C for 12 h at 200 rpm.

Then, the resulting precipitate was centrifuged and the supernatant was filtered under vacuum/was crushed with pestle and mortar. These copolymers were washed with ACN and then in THF. Then the polymer obtained was dry in desiccators until the constant weight obtained. Template removal was carried out via hydrolysis reaction in aqueous solution containing 1M Sodium Hydroxide (NaOH) at 50 ^{o}C with agitation until BPA concentration reached constant which the concentration reading were taken using UV-Visible Spectrophotometer (UV-Vis). The hydrolyzed polymers were washed with excess water until neutral pH.

Phase inversion techniques were selected in synthesis of BPA-MIM. Psf were used for hybridization with BPA-MIP powder. Phase inversion process of the polymer and the BPA-MIP powder was taken place as following. The BPA-MIP powder was mixed with 70% of NMP solution by stirring overnight at 50°C. The resultant viscous solution was spread on glass plate with thickness controlled by polyester film used as spacer at 50°C.Then spread polymer was immediately coagulated in 2L of water at 25 $^{\circ}$C and kept overnight in order to remove the solvent. After solidification, the resultant membrane was washed with excess of water. As references, membrane were prepared by similar phase inversion phase but not adding the BPA-MIP powder.

The characterization of BPA-MIM and BPA-MIP were conducted using Scanning electron microscope (SEM) and Fourier Transform Infrared (FTIR) Spectrometry. A Scanning electron microscope (SEM) ZEISS EVO 50 with EDX was used for the morphology observation of the BPA-MIM cross-sections. The FTIR Model Thermo Nicolet spectra equipment was used to measure the IR spectra of MIP to confirm the complete removal of BPA from the template.

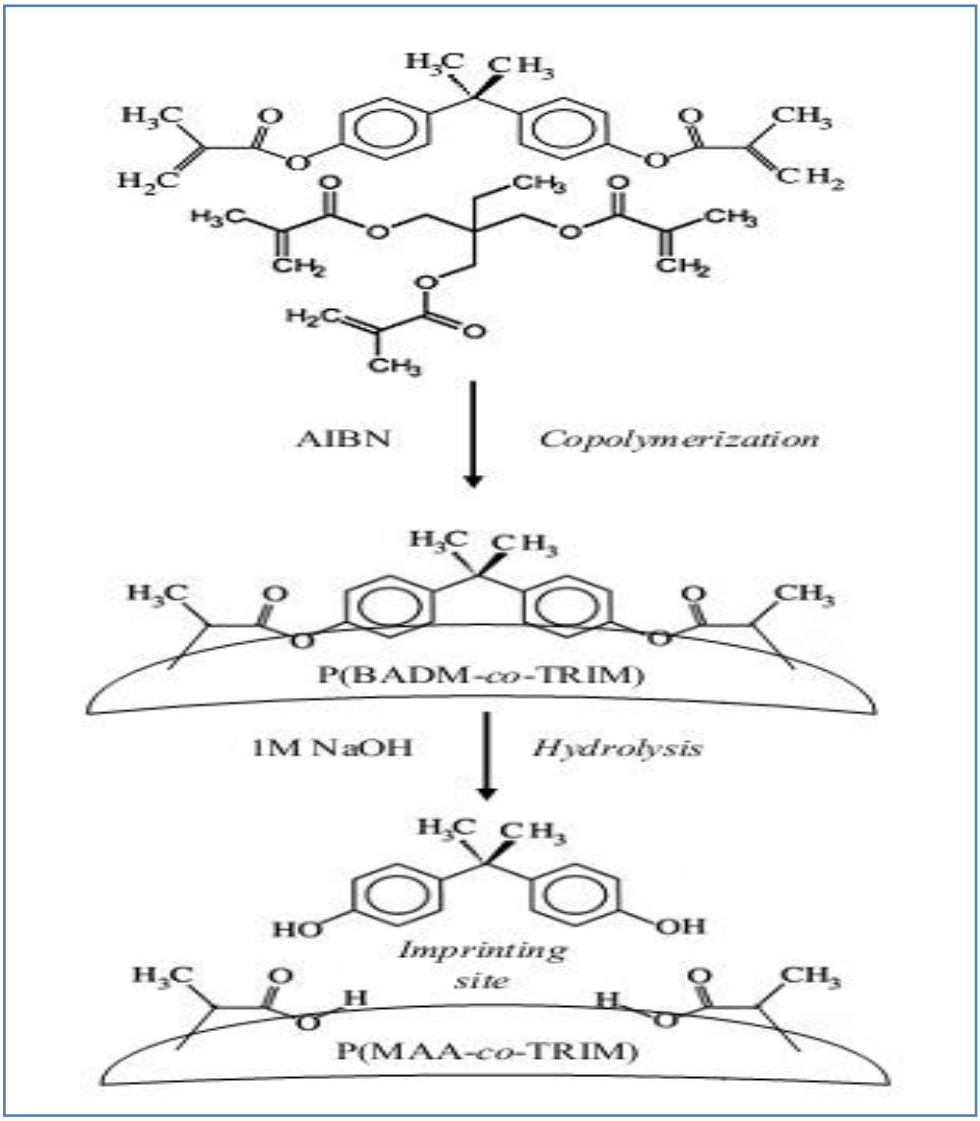

Figure 3.2: Formulation of BPA imprinted copolymer

3.4 Kinetic and Adsorption study

Batch binding tests were carried out to evaluate the binding properties of the BPA-MIP and BPA-MIM. The rate of the adsorption of BPA by the BPA-MIP, BPA-MIM and NIM from BPA aqueous solutions was investigated as a function of time. The adsorption kinetics for BPA-MIP was studied by stirring BPA-MIP, NIM and BPA-MIM (0.05 g) in 30 mg/ml BPA aqueous solution (50 mL) for different times in 24 hours. Immediately after mixing, the suspension was allowed to bind BPA by shaking at 150 rpm and 25^{o}C. During this period samples were collected at fixed intervals times. The adsorption isotherms were studied by stirring the polymer (0.05 g) in BPA aqueous solution (50 mL) at different concentration from 0.09 mmol/L to 0.28 mmol/L. The

concentration of the BPA compounds after treatment was measured by UV-Vis Spectroscopy at 276 nm.

The binding capacity was calculated as below:

$$q = \frac{(C_O - C_f)V}{M} \tag{3.1}$$

Where q (umol BPA/mg Polymer) is the amount of total adsorption of BPA, C_O and C_F are initial and final concentration of BPA in solution (umol/mL), respectively. V is the volume of the solution in mL and M is the weight of Polymer in mg.

During the batch experiments, adsorption isotherms were used to evaluate adsorption properties. For the systems considered, the Langmuir model was found to be applicable in interpreting BPA adsorption on the BPA imprinted polymer. The Langmuir isotherm is based on the assumption that the solid surface presents a finite number of identical sites which are energetically uniform, there is no interaction between sorbed species, meaning that the amount of sorbate molecules sorbed has no influence on sorption rate; and monolayer is formed when the solid surface reaches saturation.

The Langmuir model is probably the best known and most widely applied sorption isotherm. It has produced good agreement with a wide variety of experiment data and may be represented as follows (Liu *et al*. 2010):

$$q_e = \frac{q_m b\, C_e}{1 + C_e} \tag{3.2}$$

The above equation can be rearranged to the following linear form

$$\frac{C_e}{q_e} = \frac{C_e}{q_e} + \frac{1}{bq_m} \tag{3.3}$$

Where *Ce* is the equilibrium concentration, *qe* the amount of BPA adsorbed at equilibrium, *qm* is amount of BPA adsorbed for a complete monolayer, *b* is a constant

related to the energy or net enthalpy of sorption. The sorption data were analysed using the linear form Eq. (3.3) of the Langmuir isotherm.

3.5 Summary

This section consists of synthesizing of BPA-MIP and BPA-MIM technique. It also covers the study of adsorption isotherm and kinetic study of adsorption of BPA-MIP and BPA-MIM towards BPA solution. The resultant polymer was also characterized using FTIR and SEM.