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Screening of polymer precursors for preparation of nitrate imprinted polymer

Noorhidayah Ishak[1], Mohd Noor Ahmad[2], A K M Shafiqul Islam[1], Azalina Mohamed Nasir[1], Muhammad Syafie Ahmad[2] and Siti Fatimah Kamaruddin[2]

[1] Faculty of Engineering Technology, Universiti Malaysia Perlis, 02100 Sungai Chuchuh, Padang Besar, Perlis, Malaysia
[2] School of Material Engineering, Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 2, Taman Muhibbah, 02600 Jejawi, Arau, Perlis, Malaysia

Abstract. The molecular imprinting technique (MIT) has received considerable attention in the development of anion recognition materials which can be used in different applications. Major difficulty in molecular imprinting polymer is the selection of suitable polymer precursor such as template, type of monomer, amount of monomer and crosslinker that may influence the nitrate imprinted polymer (IIP) preparation. The main purpose of this study is to evaluate the optimum parameters (type of template, type of monomer, amount monomer and crosslinker) during polymerization process. The optimum polymer particles were prepared by bulk polymerization using sodium nitrate as a template, allylthiourea as functional monomer, ethylene glycol dimethacrylate (EGDMA) as a cross linker and acetonitrile and dimethylsulfoxide as solvent by heating in an oil bath at 60 °C for 20 hour. The non imprinted polymer (NIP) was synthesized using the same method but without template molecule. The optimal condition of nitrate imprinted polymer synthesis was 3 mmol of monomer, 20 mmol of cross linker and 6 ml of solvent used with adsorption capacity of 14.06 mg/g and 1.27 imprinting factor. The IIP and NIP were characterized using Fourier transform infrared (FTIR) spectroscopy. The FTIR analysis were showed that IIP and NIP were successfully synthesized. As conclusion from this research shows that the IIP produced has potential in to be used as nitrate adsorption in aqueous water.

1. Introduction

Nitrate is a highly soluble inorganic anion in water. This anionis chemically unreactive and occurs naturally within the nitrogen cycle. An excessive amount of nitrate ion in drinking water might cause the ‘blue baby syndrome’ or methaemoglobinemia illness among newborn children. This illness influences the capacity of blood cells to carry oxygen. Complication of pregnancy is another consequence towards high exposure of nitrate ion [1]. Nitrate require a host that has capability to selectively bind with itself due to its unique geometry configuration [2]. Therefore it is important to design a selective host that is compatible in size and shape of nitrate. In concern of the nitrate is ubiquitous in environment system and it is widely used in agricultural sector. Incessant application of this ion has raised concern on its potential toxicity towards human health. Therefore, controlling and monitoring the level of nitrate ion in water body is vital.

In order to produce a tailor-made adsorbent that has high selectivity towards the specific analytes, a common technique called Molecular imprinting technology can be applied. Throughout this technique, an ion imprinted polymer is synthesized with template, functional monomer, crosslinker, solvent and initiator that act as main component during polymerization process. A cavity with a complement shape and chemical functionality of the target analyte is formed through the polymerization process [3]. The template and functional monomer were surrounded by excess cross-linking monomers forming a pre-complex network of polymer before the polymerization begin. Once the polymerization completed, the template molecule located in the middle of three-dimensional polymer network was removed and form a complement shape of template. Therefore, it is important to highlight the crucial step of designing process which involve selection of chemical components in molecular imprinted polymer such as template, monomers and crosslinker. In fact, the binding capability, imprinting factor and selectivity performance are also affected by the amount of each chemical components [4].

In this research, type of templates, type of monomers, different ratio of template:monomers and different amount of crosslinker were studied using one factor at once (OFAT) method. All of these polymerization parameters were optimized and the performance of resultant polymers were compared in term of binding capacities and imprinting factor. The polymers were characterized with FT-IR and TGA in order to confirm the functionality of chemical components in the polymers for both IIP and NIP.

2. Experimental section

2.1 Material

Methacrylic acid (MAA), isobutylnitrate (IBN), acrylic acid (AA) and ethylene glycol dimethacrylate (EGDMA), were purchased from Sigma-Aldrich. Acetonitrile (ACN), acrylamide (AM) and 2,2'-azobisisobutylnitrile (AIBN) were purchased from Fisher Scientific, R&M Chemicals and Acros Organic respectively. Allylthiourea (AT) and dimethylsulfoxide (DMSO) were purchased from Merck. Sodium nitrate ($NaNO_3$) and ammonia solution were purchased from HmbG Chemicals. All chemicals used were analytical reagent grade.

2.2 Instrumentation

UV spectroscopy (Varian Cary 50) was used to quantify the concentration of nitrate solution. The FTIR (Perkin Elmer) spectroscope and TGA (Perkin Elmer pyris diamond TGA/DTA) were used to characterize the functional group presence in the imprinted polymer. Thermo Heraeus Megafuge 16R centrifuge was used to centrifuge during binding test. Shaker-Daihan Scientific: SHO-1D was used during binding analysis.

2.3 Screening of different template and monomer for polymer preparation

The IIPs were prepared separately for two set different templates with different monomers as stated in Table 1. First the template was dissolved in specified solvent containing functional monomers. Then EGDMA that act as crosslinker (20mmol) and initiator, AIBN were added into mixture. The solution was then sonicated and purged with nitrogen gas for 10 minutes to remove oxygen. It was then heated in oil bath for 22 hour at 60 ^{o}C for the polymerization process. The resultant polymer obtained was ground with a mechanical mortar and sieved to yield a powder particle size between ranges of 25µm - 75µm. A mixture of 500 ml of methanol: (1.0M) ammonia solution (4:1, v/v) was used to remove the template and methanol solution was used to rinse any residue in the polymer particle. Nitrate removal was controlled by UV-Vis spectroscopy. Preparation of NIP for both polymers were also made using the same synthesis procedure except no template was added during the polymerization process.

Table 1. Preparation of imprinted polymer with different functional monomer and template

Polymer	Template	Functional monomer	Solvent

		(3mmol)	
IIP1	IBN	MAA	ACN
IIP2		AA	
IIP3		AM	
IIP4		AT	
IIP5	$NaNO_3$	MAA	ACN:DMSO
IIP6		AA	
IIP7		AM	
IIP8		AT	

2.5 Screening of different template:monomer ratio for polymer preparation

The IIPs were prepared by applying the same method except different amount of allylthiourea (functional monomer) were varied for each polymer as stated in Table 2. The NIPs were synthesized along using the same procedure but without template being added during polymerization process.

Table 2. Preparation of imprinted polymer with different template-monomer ratio

Polymer	**Template**	**Functional monomer**	**Solvent**
IIP9	$NaNO_3$	AT (1mmol)	ACN:DMSO
IIP10		AT (2mmol)	
IIP11		AT (3mmol)	
IIP12		AT (4mmol)	

2.6 Screening of different template:crosslinker ratio for polymer preparation

The IIPs were prepared by applying the same method except different amount of ethylene glycol dimethacrylate (EDGMA) were varied for each polymer as stated in Table 3. The NIPs were synthesized along using the same procedure but without template being added during polymerization process.

Table 3. Preparation of imprinted polymer with different template: crosslinker ratio

Polymer	**Template**	**Functional monomer**	**Crosslinker**	**Solvent**
IIP17	$NaNO_3$	AT(4mmol)	EGDMA (10mmol)	ACN:DMSO
IIP18			EGDMA (20mmol)	
IIP19			EGDMA (30mmol)	

2.7 Characterization of IIP and NIP

FTIR spectra of imprinted and non-imprinted polymer were obtained by using FTIR spectrophotometer. The polymer particles (about 0.1 g) were thoroughly mixed with KBr and pressed into a pellet and FTIR spectrum was recorded.

2.8 Binding capacity analysis

The adsorption of NO_3^- ion in aqueous solution was investigated by batch experiment. 20mg of polymer with 5ml of known concentration of standard nitrate ion in aqueous solution were added into 15ml centrifuge tube. Then, the tube was oscillated for 1 hour with speed 130rpm at room temperature using Shaker-Daihan Scientific. In order to analyse the remaining concentration of nitrate, the solution was centrifuged for 5 minutes at 5000rpm to separate the mixture. UV-vis spectroscopy was used to determine the absorbance of nitrate at 301nm [5]. The amount of binding capacity was calculated using the following equation:

$$Q = \frac{V(C_i - C_f)}{m} \quad (1)$$

where *V* represent volume of standard solution (ml), C_i represents initial concentration of nitrate, C_f represent final concentration of nitrate solution and m is mass of polymer particle [6]. The binding capacities of ion imprinted polymers were compared with those non imprinted polymers to determine the imprinting factor (IF) according to equation below [7]:

$$IF = \frac{Q_{IIP}}{Q_{NIP}} \quad (2)$$

3. Results and discussion

3.1 Screening template and functional monomer

Table 4 shows complex of polymer that used isobutylnitrate as template, it can be seen that two polymers with the highest binding capacities (**IIP1** and **IIP3**) have lack of selectivity and their imprinting factors are below than one. The polymer of **IIP4** shows both high capacity and selectivity toward nitrate ion in aqueous solution**.** Meanwhile, all four polymers (**IIP5-IIP8**) that used sodium nitrate as template, show selectivity towards nitrate ion with high binding capacity. The amount of binding capacities for IIP4 and IIP8 show that sodium nitrate has higher value as compared to isobutylnitrate. This due to the same template has been used during the binding process, thus sodium nitrate was chosen for the further analysis. It can be seen that functional monomer of allylthiourea give a good result of binding capacity and imprinting factor. This can be supported with previous research reported by Herges.R that developed a thiourea macrocylic ionophore that has high capability to bind with nitrate ion in polar solvents. The study indicated that the thiourea unit provide the correct hydrogen bond angels toward nitrate molecule [8]. Based on the result, the allythiourea was selected as functional monomer for the further analysis.

Table 4. Imprinting factor of different functional monomers of nitrate imprinted polymer

Polymer	Template	Functional monomer	Binding capacities ±S.D (mg/g) IIP	NIP	Imprinting factor
IIP1	IBN	AM	22.50±0.22	24.22±0.22	0.93
IIP2	IBN	AA	5.73 ± 0.66	5.31±0.90	1.09
IIP3	IBN	MAA	16.35±0.44	18.59±0.22	0.88
IIP4	IBN	AT	22.81±0.88	14.84±1.10	1.54
IIP5	$NaNO_3$	AM	21.41±0.66	21.25±0.66	1.01
IIP6	$NaNO_3$	AA	24.38±1.55	24.22±0.66	1.01
IIP7	$NaNO_3$	MAA	23.44±1.10	22.50±0.88	1.04
IIP8	$NaNO_3$	AT	25.31±0.88	22.50±1.10	1.13

3.2 Screening of different template-monomer ratio

Based on data in table 5, IIP12 polymer with template–monomer ratio 1:3 exhibited high binding capability but less imprinting effect. However, IIP13 with template-monomer ratio 1:4 parameter was chosen for further examination using synthetic and analytical procedures. As the imprinting factor of IIP 13 was much higher than IIP 12 thus indicated higher selectivity. There are about six potential hydrogen bonding sites in nitrate ion. The interaction of template with allylthiourea was maximized and the quality of the imprinted sites in the polymer improved by adding sufficient amount of monomer to interact with all of those location [9].

Table 5. Imprinting factor of different ratio template: functional monomers of nitrate imprinted polymer

Polymer	**Template**	**Ratio (template: monomer)**	**Binding capacities ±S.D (mg/g)**		**Imprinting factor**
			IIP	**NIP**	
IIP10	$NaNO_3$	1:1	10.16±0.44	10.70±0.66	0.95
IIP11	$NaNO_3$	1:2	1.46±0.65	1.56±0.44	0.93
IIP12	$NaNO_3$	1:3	15.23±0.88	14.61±1.10	1.04
IIP13	$NaNO_3$	1:4	14.06±0.44	11.67±0.66	1.27

3.3 Screening of different template:crosslinker ratio

The formation of the cavity within the polymer network is influenced by the ratio of template-crosslinker as the crosslinker contribute toward the rigidity of the cavity shape formed. From the result in table 6 it can be observed a lower volume of EGDMA reduced the imprinting effect and binding capacity of the polymer probably due to less rigidity of the cavity. While excess amount of EGDMA would possibly non covalently interact with allylthiourea as well as sodium nitrate which contain functional group that could form hydrogen bond with EGDMA [10]. As a consequence, the interaction between template and monomer may reduce thus lower the volume of the cavities and affect the binding site of the polymers.

Table 6. Imprinting factor of different ratio template:crosslinker of nitrate imprinted polymer

Polymer	**Template**	**Ratio (template:crosslinker)**	**Binding capacities ±S.D (mg/g)**		**Imprinting factor**
			IIP	**NIP**	
IIP14	$NaNO_3$	1:10	5.63±0.63	5.00±0.36	1.13
IIP15	$NaNO_3$	1:20	14.06±0.44	11.09±0.66	1.27
IIP16	$NaNO_3$	1:30	10.21±1.33	9.06±0.94	1.13

3.4 Characterization of IIP and NIP

Figure 1 indicates that both leached IIP (the imprinted polymer has been washed with elution solvent and considered free from template molecule) and NIP have similar spectra backbones due to the same chemical functional group. Several functional groups can be seen in both spectra such as at 3454 cm^{-1} can be assigned to NH group contributed from allythiourea chemical functional. The hydrogen bonding caused a broad adsorption of this peak. While at 1150 cm^{-1}, the peak is contributed from O-C-C saturated ester stretching vibration. This suggests that copolymerization of EDGMA and AT due to the presence of EDGMA characteristic in the IR spectra. Other significant peaks were also observed, carbonyl group stretch (~1730 cm-1), and C-H vibrations (948.79 cm-1and 2989cm-1) implied that these polymers were successfully synthesized [11].

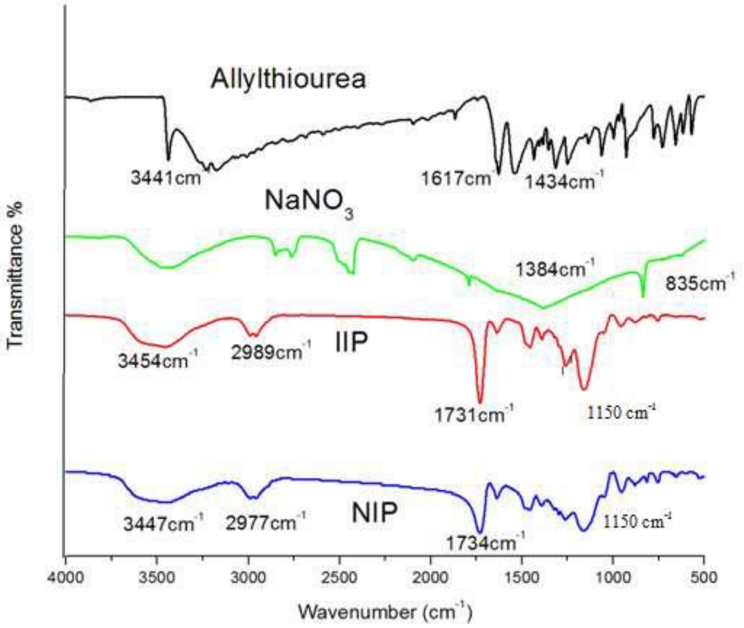

Figure 1: FTIR spectrum for four different polymers allylthiourea, sodium nitrate, IIP and NIP

4. Conclusions

The experimental shows allythiourea as functional monomer and sodium nitrate as template with 1:4:20 ratio templates:monomer:crosslinker gave higher imprinting factor and binding capability. The synthesized imprinted polymers exhibit capability to specifically recognize nitrate ions in aqueous solution with binding energy 14.06±0.44 mg.g and 1.27 imprinting factor. Generally, the results in this study have suggested that the proposed nitrate ion-imprinted polymer (IIP), has the potential to be further developed for exploitation in the wide field of anion synthetic receptor.

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