Journal of Applied Sciences

ISSN 1812-5654

science alert

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Journal of Applied Sciences 14 (13): 1455-1459, 2014
ISSN 1812-5654 / DOI: 10.3923/jas.2014.1455.1459

Characterization of Bisphenol a MIP (BPA-MIP) Synthesizing

S. Shahaidah, Che Ku M. Faizal and M.S. Shareena
Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang,
Lebuhraya Tun Razak, 26300 Gambang, Pahang, Malaysia

Abstract: Molecular Imprinted Polymer (MIP) has caught the attention of many researches in recent years as a great tool for molecule recognition and other applications. But the main issue in the synthesis of MIP nanoparticles is the identification and optimization of the main factors affecting the material structure and size. This study describe an experimental design approach to synthesis bisphenol A molecular imprinted polymer nanoparticles (BPA-MIP NPs) aimed at analysis of the relationship of four selected parameters: the polymerisation temperature, agitation rate, cross-linker to solvent ratio and percentage of initiator. The results presented demonstrate the importance of keeping the right balance between these various parameters of polymerisation conditions. Generally, it can be concluded that MIPs should be synthesized using enough heating, adequate agitation, low concentration of initiator and with a considerably higher amount of solvent. Such procedure is proven as time and cost effective and also can be used as a general tool in the preparation of MIPs for many different target molecules.

Key words: Molecular imprinted polymer, synthesis, copolymerization, binding capacity

INTRODUCTION

Scientific researches and developed technologies over the past decade has grown to release more chemicals that are prone to be toxics such as estradiol, nonylphenol, pharmaceuticals compound and also some pesticides, also known as Endocrine Disruptor Compound (EDC) mostly end up interfering the normal functioning endocrine system in living bodies (Zhang *et al*., 2006).

Molecular Imprinting Polymer (MIP), which is a newly preferred adsorbent material, is prepared using synthetics polymers with the ability to specifically recognize any target molecule. It is reported as adequately stable at moderately any given pH, pressure and temperature and also less expensive than antibodies. Attempts have been made to prepare BPA MIP bulk copolymers (Takeda and Kobayashi, 2005).

The polymers were ground in stages to form powders and the limitations on this procedure are irregular shape and ununiform size of particles after grinding. The advantage of smaller size polymer, it also possesses higher surface area-to-volume ratios (Tokonami *et al*., 2009). Thus, imprinted pores are highly accessible by templates and binding performances are improved (Gao *et al*., 2007).

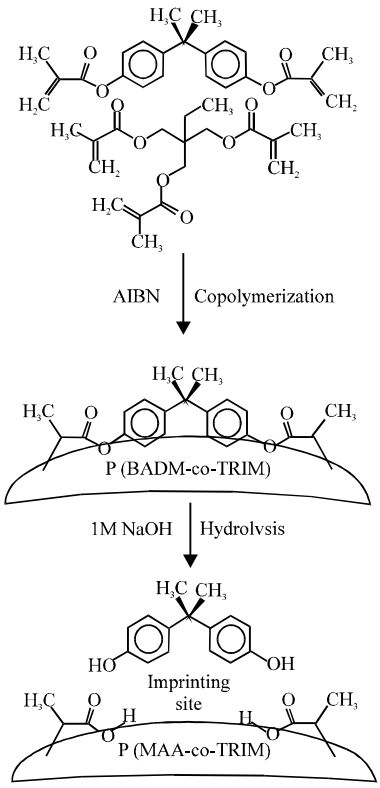
Previously, MIP nanoparticles were synthesized by various polymerizations involving stabilizers, surfactants and additions that can contaminate the final products (Haginaka and Sakai, 2000).

In the present study, a simple surfactant-free precipitation polymer was employed (Yoshimatsu *et al*., 2007) with a novel approach through the application of an experimental design and multivariate analysis methodology considering four selected parameters. Studying polymerization in the high and low range of each parameter, we were able to synthesize different sizes and dispersion of MIP spheres. As shown in Scheme 1, BPA imprinted spheres were formed by copolymerization of bisphenol A dimethacrylate (BADM) and trimethylolpropane trimethacrylate (TRIM). The spheres were then hydrolyzed before investigating their binding performance. The resultant copolymers were characterized by Fourier Transform Infra-Red (FTIR), Scanning Electron Microscopy (SEM) and Mastersizer. Binding analysis confirmed the successful template adsorbent.

MATERIALS AND METHODS

Materials: Bisphenol A dimethacrylate (BADM) as the functional monomer, 2,2'-Azobis(2-methylpropionitrile) (AIBN) as the initiator and trimethylolpropane trimethacrylate (TRIM) as cross-linker were purchased from Aldrich. Tetrahydrofuran (THF) a seluant and acetonitrile (ACN) as polar solvent were of HPLC grade.

Corresponding Author: S. Shahaidah, Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Pahang, Malaysia



Scheme 1: Formulation of BPA imprinted copolymer

Table 1: The range and levels of the variables in MIP synthesis

	Values of independent variables			
Run	Temperature (°C)	Agitation (rpm)	Solvent to crosslinker ratio (%)	Initiator (%)
1	80.00	100.00	50.00	1.00
2	80.00	0.00	80.00	1.00
3	45.00	100.00	80.00	1.00
4	80.00	0.00	80.00	3.00
5	80.00	100.00	80.00	3.00
6	80.00	0.00	50.00	1.00
7	45.00	0.00	50.00	3.00
8	45.00	100.00	50.00	3.00
9	45.00	0.00	80.00	1.00
10	80.00	100.00	50.00	3.00
11	62.50	50.00	65.00	2.00
12	45.00	100.00	80.00	3.00
13	45.00	100.00	50.00	1.00
14	45.00	0.00	80.00	3.00
15	45.00	0.00	50.00	1.00
16	80.00	0.00	50.00	3.00
17	80.00	100.00	80.00	1.00
18	62.50	50.00	65.00	2.00
19	62.50	50.00	65.00	2.00

Procedure of copolymerization: In this study, several sets of MIP runs were conducted using thermal initiation copolymerization with variation on four selected factors which were temperature, agitation, cross-linker to solvent ratios and initiator percentage, as listed in Table 1. Other factors such as monomer to cross-linker ratio and copolymerization time were fixed throughout the experiments.

The monomer solution was prepared by introducing BADM and TRIM (1:10 mol ratio) (Takeda and Kobayashi, 2005) into 250 mL three-neck flask in the presence of AIBN under nitrogen atmosphere. Samples were allowed to copolymerize in ACN following the sequence in Table 1 for 12 h. 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. Finally, they were filtered under vacuum and store in desiccator for further use.

Template removal was carried out via hydrolysis reaction in aqueous solution containing 1 M Sodium Hydroxide (NaOH) at 50°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. Bulk copolymers were prepared with the exemption of agitation. Non-imprinted polymer P(TRIM) were prepared following the same condition but without the functional monomer.

To examine the copolymers characteristics, FTIR spectra and SEM images were measured using FTIR, thermo Nicolet and SEM microscope (ZEIZZ), respectively. Particle distribution was analyzed using Mastersizer 2000 (Malvern).

Binding experiments: Batch BPA binding experiments were done as follows. 20 mg of MIP was dispersed in 20 mL aqueous BPA solution with 100 μm concentration. The mixed solution was shaken in a glass flask at 30°C and it was let incubated to a saturated binding process for 24 h. The final BPA concentration in the solution was determined using UV-Vis (Hitachi) at 278 nm. The binding S (μ mol g^{-1}) of BPA was calculated using:

$$[S] = \frac{(C_o - C_t)\,V}{W} \quad (1)$$

where, C_o and C_t represent the initial and final BPA concentration, respectively, V in the volume of BPA solution and W is the weight of MIP.

RESULTS AND DISCUSSION

Characteristics of MIP: The IR spectrum of obtained MIP particles was measured using FTIR where hydrolyzed ($P(BADM\text{-}co\text{-}TRIM)_H$) MIP is compared with the unhydrolyzed ($P(BADM\text{-}co\text{-}TRIM)_B$) one as shown in

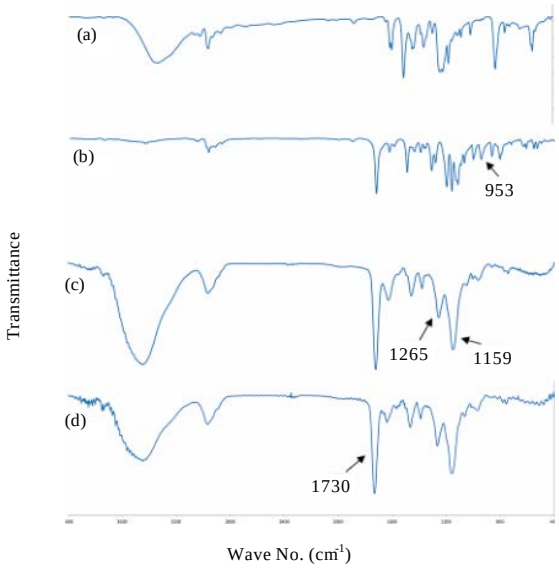


Fig. 1(a-d): FT-IR spectra of (a) BPA, (b) BADM, (c) $P(BADM\text{-}co\text{-}TRIM)_H$, (d) $P(BADM\text{-}co\text{-}TRIM)_B$ by KBr pellet method

Fig. 1. Strong peak of C = O group occurred at 1730 cm^{-1} showed that BADM segments exist in the copolymer. Symmetric and asymmetric C = O stretch ester bands at 1265 and 1159 cm^{-1} is well observed represents the TRIM segments in the copolymers.

To explain BADM IR spectrum in comparison with the resultant MIPs, it is observed that peak near 953 cm^{-1} was decreasing due to the out-of-plane alkene C-H bending vibration and noticed the loss of C-O stretching peaks in conjugated ester at 1292 and 1321 cm^{-1}. It is also noted in the FTIR data between hydrolyzed and unhydrolyzed MIP that the band near 3450 cm^{-1} for OH stretch show changes, signifying the formation of -COOH group in the copolymers after hydrolysis.

Figure 2 shows the TEM image of Run 12 and SEM image of Run 16 where sizes of MIP that were formed in powder showed 0.12 μm and 5 μm, respectively. From these images, it can be observed that Run 12 with parameters 45°C, 100 rpm, 80% solvent and 3% initiator, despite the small size, the polymer yield is less than Run 16 which parameters were 80°C, no agitation, 50% solvent and 3% initiator. This is the result of low temperature (45°C), which proved to contribute most in MIP synthesis.

Binding capacity: Figure 3 showed the amount of binding capacity of selected MIP runs It is reported that high concentration of initiator added into the monomer mixture, would generate heat and thus, increasing the temperature and polymerization rate (Carraher, 2000) but be cautious

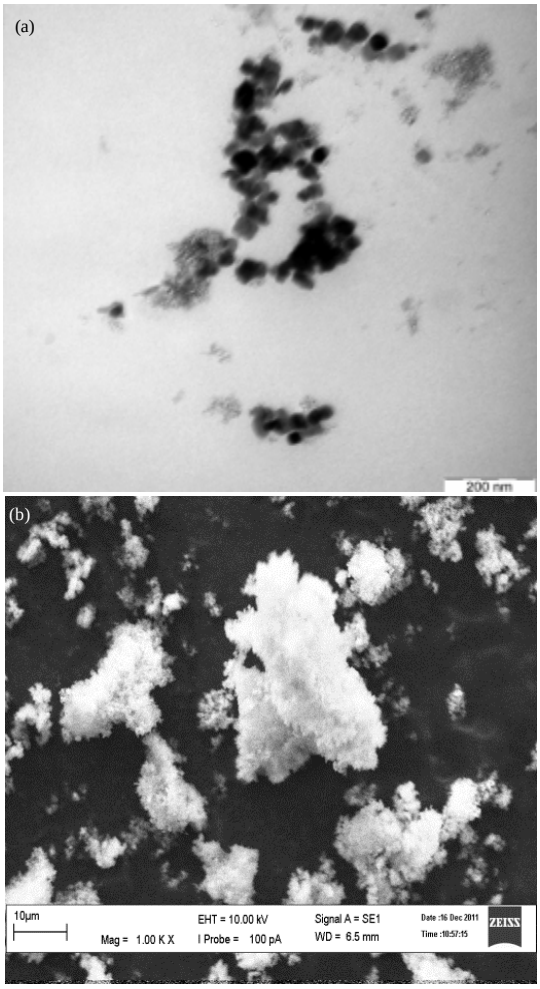


Fig. 2(a-b): (a) TEM image of Run 12 and (b) SEM image of Run 16

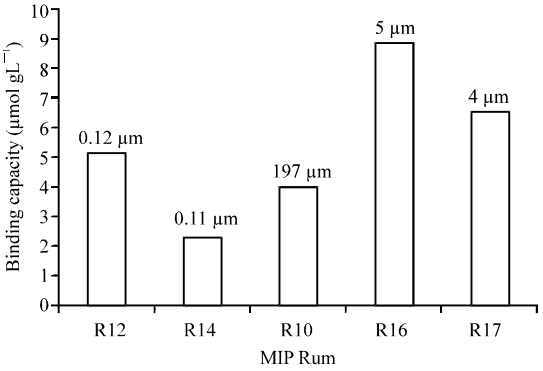


Fig. 3: Binding capacity of selected MIP Runs and its particle size

if too much heat were used, it would disrupt the complex formed between the monomers and reduce the affinity and

selectivity of MIPs. Nevertheless, high concentration of initiator added into the mixture would lead to the formation of a high amount of free radicals and thus generating large number of growing nuclei and globules which would result to smaller in particle size. These small sized globules would then produce a large number of small pores into the MIP spheres and possessed a large surface area all at once . This behavior can be explained by monitoring MIP Run 12 and Run 14 which holds small submicron size polymer. These MIPs were produced at low temperature but high concentration of initiator. Moreover, the variation of average pores diameter and total pore volume was probably due to the porogenic ability of the solvent vapors released during the exothermic reaction (Piletsky *et al*., 2004).

Additionally, in order to control the average diameter of MIP produced, the used of agitation would caused an efficient dispersion of monomers in the solution mixture. The speeding mixture would cause decreasing of the complex polymer length chain and thus increasing the number of polymer particles because of the nuclei aggregation (Ku *et al*., 2009). Because of this, smaller particle size with evenly distributed uniformity is produced. This phenomenon can also be observed in MIP Run 12 and Run 14. Both hold submicron size particles but have different value of binding capacity where Run 12 was higher than Run 14, probably due to uniformity and better dispersion of Run 12 particles acquired by utilization of agitation parameter during polymerization. Other researches also reported a similar result (Son *et al*., 2011).

Furthermore, Koohpaei *et al*. (2008a), reported that the morphology was influenced by the properties of the porogen, since the swelling of the polymers is dependent on the surrounding medium (Koohpaei *et al*., 2008b). This swelling behavior most probably would cause in the alteration of the three dimensional configuration of the functional groups, taking part in the unique sites recognition resulting in poorer biding capacity. The binding efficiencies of the template in the diverse range forms if imprinted polymer were found to be very dependent on the type of solvent used, which indicative of hydrophobic and hydrogen bonding interactions aggregation (Ku *et al*., 2009). Low binding amount observed could be probably due to the hydrogen bonding ability of acetonitrile. It can be said that some of the MIPs generate low binding capacity suggested that hydrophobic interactions were responsible for the adsorption of the solute in polar solution.

CONCLUSION

In this study, many factors and interaction of factors affected the synthesis and performance of the resultant MIP. It can be said that polymerisation temperature, agitation rate, cross-linker to solvent ratio and percentage of initiator was influenced synthesizing.

ACKNOWLEDGMENTS

Authors acknowledge financial supports from the Faculty of Chemical and Natural Resources Engineering of University Malaysia Pahang. The authors would like to thank everyone on the technical department and they who involved directly or indirectly throughout the research study.

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