Adsorption of betasitosterol on MIP

by Paulina Taba

FILE	5.PDF (261.14K)		
TIME SUBMITTED	04-NOV-2020 02:11PM (UTC+0700)	WORD COUNT	2281
SUBMISSION ID	1435744823	CHARACTER COUNT	12212

IOP Conf. Series: Materials Science and Engineering **188** (2017) 012048 doi:10.1088/1757-899X/188/1/012048

Adsorption of β-sitosterol on molecularly imprinted polymer

N H Soekamto[1], St Fauziah[2], P Taba[2] and M B Amran[3]

[1]Organic Chemistry Laboratory, Universitas Hasanuddin, Jl. Perintis Kemerdekaan, Km 10, Tamalanrea, Makassar 90245, Indonesia
[2]Physical Chemistry Laboratory, Universitas Hasanuddin, Jl. Perintis Kemerdekaan, Km 10, Tamalanrea, Makassar 90245, Indonesia
[3]Analitical Chemistry Laboratory, Institute Technology of Bandung, Jl. Ganesa No.10, Bandung 40132, Indonesia

Corresponding author's e-mail: noek_1512@yahoo.com

Abstract. Molecularly Imprinted Polymer (MIP) has been synthesized using methacrylate acid (MAA) as a monomer with hydroxyl and carbonyl functional groups that can react with ethylene glycol dimethacrylate (EGDMA) as a cross-linking agent, and β-sitosterol as a template molecule. After the template was removed from the polymer, MIP_TFMAA was obtained. The MIP was used to adsorb β-sitosterol. The amount of β-sitosterol in solution after the adsorption was determined by HPLC. The results showed that the MIP was able to adsorb well the β-sitosterol at a pH 7 and the contact time of 90 min. The kinetic adsorption data obtained for β-sitosterol followed the pseudo-second-order model and consistent with the model of Feundlich isothermal with the adsorption capacity of 1.05 mg/g. The MIP was selective on β-sitosterol because it was able to adsorb β-sitosterol better than cholesterol.

1. Introduction

Molecularly imprinted polymers (MIPs) are polymers synthesized using a template molecule to create cavities after removing the template [1]. Main materials that have to be considered in synthesis of MIP are monomers, template molecules, crosslinking agents (cross-linkers, porogen solvents and initiators. Selection of monomer is very important to produce the appropriate interaction with the template molecule [2] and to determine the stability of the polymer formed during the polymerization process [3]. Methacrylic acid (MAA) can be used as monomer in the synthesis of MIP because it is acidic and it can interact with the template molecules through acid-base interactions and hydrogen bonding. Several studies showed that the MIPs synthesized using the MAA monomer and the β-sitosterol template have high affinity and selectivity against β-sitosterol [3, 4]. Cross-linkers are required to control the polymer matrices, to stabilize binding sites, and to maintain mechanical stability of polymers [3]. They can affect approximately 70% to 98% of the MIP final result [4] and also affect the adsorption selectivity [5]. Among the cross-linkers, EGDMA is widely used because its functional groups can easily interact with functional groups of monomers to produce a polymer with a high degree of rigidity [4]. Porogen solvents must have the ability to dissolve the template molecule, initiator, monomer and cross-linking agents to form the cavity [6]. They must have a relative low polarity to reduce interference when interactions occur between the template molecules and monomers to produce the high selectivity MIP [5]. In the polymerization process, the role of initiator is very important in the formation of free radicals by heating (thermolysis) and radiation (photolysis) [7]. One initiator that mainly used in the radical polymerization is 2-2'-azobis isobutyronitrile (AIBN) because it is available in the market and it can produce radicals at the low temperature.

In this study, a MIP was synthesized using MAA as a monomer, β-sitosterol as a template molecule, EDGMA as a cross-linker, AIBN as an initiator, and toluene as the porogen solvent. The use of β-sitosterol as a template molecule was conducted to find a material that is selective to the molecule that frequently interfere in the isolation and purification process of natural product compounds. The MIP produced was evaluated through the optimization test and determination of adsorption capacity before being used in the solid phase extraction (SPE). Parameters that influence the optimization i.e. time, pH and concentration were studied.

2. Materials and methods

2.1. Materials

The materials used in this study were β-sitosterol 97% (Sigma-Aldrich), methacrylic acid 99% (MAA) (Sigma_Aldrich) as a monomer, ethyleneglycol dimethacrylate (EGDMA) (Sigma-Aldrich) as a crosslinking agent (cross-linker), 2,2'-azobisisobutyronitrile (AIBN) as initiator, toluene as porogen, aquabidest, methanol (HPLC grade), tetrahydrofuran grade (THF), acetic acid industrial grade as the washing solvent, NaOH, HCl, and nitrogen gas.

The equipments used included glassware, analytical balance, shaker, water bath, sonication apparatus, oven, mini peristaltic pump (Gilson), mini glass column (length 3 cm), bottles, micropipette (), 100, 1000 mL (Eppendorff), pH meter, 41 Whatman paper No. 41, aluminum foil, and paper towels. High Pressure Liquid Chromatography (HPLC) Agilent 1260 infinity using Cronus RP column type E18 C with the column length and diameter of 12.5 cm and 0.4 cm, Ultra violet-visible Spectrophotometer (UV-Vis) Agilent 8453, and Shimadzu.

2.2. Synthesis of MIP_MAA-co-EGDMA

A total of 50 mg β-sitosterol, 2 mL monomer MAA, and 3 mL EGDMA were dissolved with 5 mL toluene in a round bottom flask. The mixture was stirred slowly, and then added with 1.5 mL of AIBN. The solution was sonicated and purged with nitrogen. The polymerization was conducted by adjusting the temperature to 55°C in a water bath for 24 hours. The polymer formed was crushed, sieved, and washed with THF tetrahydrofuran, methanol: acetic acid (90:10% v / v) mixture, and methanol to release the β-sitosterol and porogen solvent [1]. Polymer or MIP was dried in an oven at a temperature of 50°C.

2.3. The pH influence on MIP_MAA-co-EGDMA adsorption

A total of 20 mg of MIP was put in four vial bottle then added with 3 mL of 10 ppm β-sitosterol that has been adjusted to the specified pH into each vial. The pH of solution was set at the pH of 4, 5, 6, and 7. The solution was mixed at room temperature for 6 hours. The solution was filtered and then β-sitosterol concentrations in the filtrate was analyzed by UV at a wavelength of 202 nm.

2.4. The effect of contact time influence on adsorption of MIP_MAA-co-EGDMA

A total of 20 mg MIP_MAA-co-EGDMA was put into five vials, 3 mL of 10 ppm β-sitosterol that has been set according to the optimum pH was added to the vial. The mixture was stirred with a shaker for 30, 60, 120, 180, 240 minutes at room temperature and filtered. The concentration of β-sitosterol in the filtrate was analyzed by the UV spectrophotometer at a wavelength of 202 nm.

2.5. The effect of concentration influence on adsorption of MIP_MAA-co-EGDMA

To determine the amount of β-sitosterol adsorbed by MIP, 3 mL of β-sitosterol with various concentrations of 2, 4, 6, 8, and 10 ppm at the optimum pH was put in a vial containing 20 mg of MIP_MAA-co-EGDMA. The mixture was then shaken at room temperature and at the optimum time. The solution was then filtered and the concentration of β-sitosterol in the filtrate was analyzed by the UV spectrophotometer at a wavelength of 202 nm. The adsorption capacity was determined by using Langmuir and Freundlich isotherms.

3. Results and discussion

3.1. The synthesis result of MIP_MAA-co-EGDMA

The polymer of MIP_MAA-co-EGDMA synthesized was obtained as white solid with the weight of 2.1352 g. The MIP was washed using THF, methanol:acetic acid mixture, and methanol, successively. The filtrate was tested with a solution of Liebermann Burchard and it was shown that β-sitosterol has been removed from the polymer.

3.2. The pH influence on adsorption of MIP_MAA-co-EGDMA.

The effect of pH on adsorption of β-sitosterol on MIP_MAA-co-EGDMA can be seen in figure 1. Figure 1 shows that the amount of β-sitosterol adsorbed on MIP_MAA-co-EGDMA gradually increases with the increasing pH. It is clear that the optimum pH in the range of studied pH for the adsorption of β-sitosterol was 7. The adsorption of MIP β-sitosterol at the low pH was very low. Yusof *et al*. [8] reported that at pH 3-5, a compound containing a particular functional group will be protonated so that it can affect the interaction with the active site of the MIP. Conversely, the increase of pH causes the reducing concentration of H^+ ions in the solution, resulting in the decrease of protonated functional groups on MIP and β-sitosterol, generating the formation of hydrogen bonds between -OH on β-sitosterol with functional groups on the active side of MIP. Thus, the best adsorption of β-sitosterol on MIP_MAA-co-EGDMA was achieved at the pH 7 with the adsorbed amount of 1.90 mg/g. The obtained data showed that the MIP's ability to adsorb a target molecule was strongly influenced by the pH. They also reported that adsorption of 2,4-dichlorophenol on MIP_acrylamide-co-EDGMA using 2,4-dichlorophenol as a template molecule decreased at the pH of 8.

3.3. Determination of the optimum time

The effect of time on the adsorption of β-sitosterol on MIP is given in figure 2. The amount of β-sitosterol adsorbed increases with the increasing contact time until achieves the maximum adsorbed amount at an equilibrium step. Further increase of time slightly decreases the amount adsorbed. The optimum time of MIP_MAA-co-EGDMA to adsorb β-sitosterol was 120 minutes and the amount of β-sitosterol adsorbed was 2.08 mg/g. The kinetic study of adsorption was evaluated using pseudo-first order and pseudo-second order equations [9]. Figure 3 shows the curve of log (q_e-q_t) vs time for the former order and the curve of t/qt vs t for latter order.

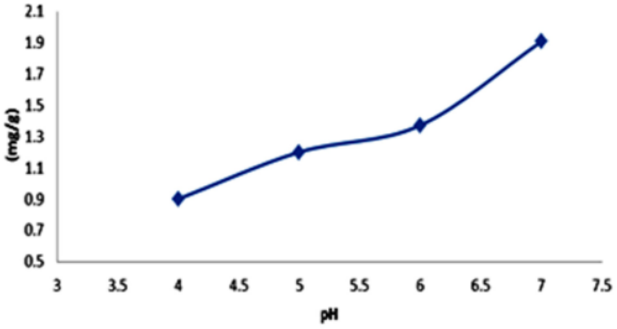


Figure 1. The amount of β-sitosterol adsorbed on MIP_MAA-co-EGDMA as a function of pH

The parameter suitability of adsorption kinetic model of first pseudo order and second pseudo order determined by linear regression correlation coefficient (R^2) of the curve obtained. The kinetic data for the adsorption of β-sitosterol are shown in table 1.

3.4. Determination of adsorption capacity of β-sitosterol on MIP

The adsorption isotherms of β-sitosterol on MIP_MAA-co-EGDMA are given in figure 4. The amount of β-sitosterol adsorbed increases with the increase of initial concentration of β-sitosterol solution. From figure 4, it is clear that the amount of β-sitosterol adsorbed continues to increase at the measured concentration. Therefore, Langmuir and Freundlich models were utilized to find the capacity of adsorption. Table 2 summarizes the constants of Langmuir and Freundlich for the adsorption of

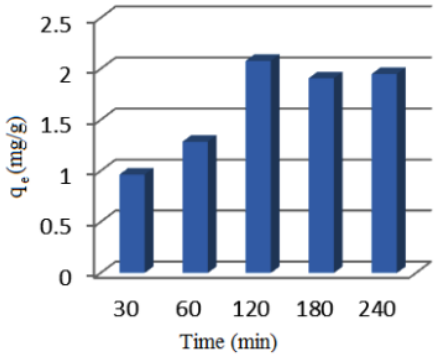
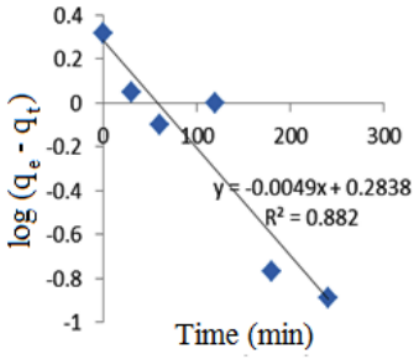
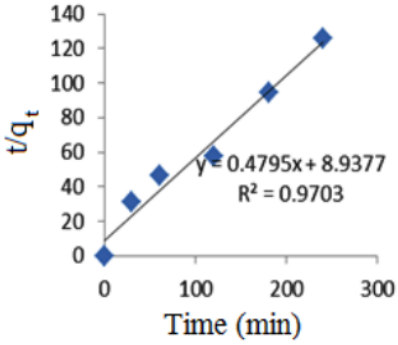


Figure 2. The influence of time on the β-sitosterol adsorption on MIP_MAA-co-EGDMA



(a)



(b)

Figure 3. (a) Kinetic curve of first pseudo order and (b) Kinetic curve of second pseudo order for β-sitosterol adsorption on MIP_MAA-co-EGDMA

Table 1. Kinetic data for adsorption of β-sitosterol by MIP

q_e Calculation		q_e	k_1	k_2	R^2	R^2
1st order	2nd order	Experiment			1st order	2nd order
1.92	2.09	2.08	0.0092	0.0257	0.882	0.970

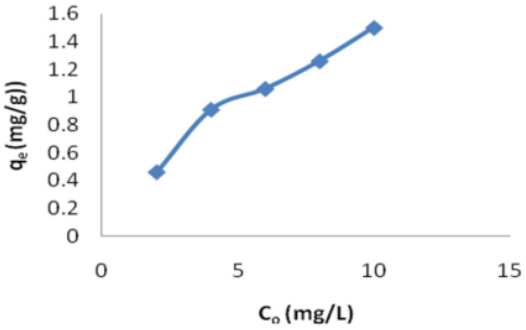


Figure 4. Adsorption isotherm of β-sitosterol on MIP_MAA-co_EGDMA

Table 2. Langmuir and Freundlich constant for the adsorption of β-sitosterol on MIP_MAA-co-EGDMA

Langmuir model			Freundlich model		
Q_o	b	R^2	k	n	R^2
2.03	1.07	0.966	1.05	1.89	0.967

β-sitosterol. Based on table 2, it can be stated that the adsorption of β-sitosterol on MIP_MAA-co-EGDMA followed both models with the adsorption capacity 2.03 and 1.05 mg/g for Langmuir and Freundlich models, respectively.

4. Conclusions

From the results above, it can be concluded that white solid of MIP_MAA-co-EGDMA has been synthesized. The obtained MIP was adsorbed well the β-sitosterol at pH 7. In addition, the optimum time for the adsorption of β-sitosterol was 120 min. Furthermore, the adsorption of β-sitosterol on MIP_MAA-co_EGDMA fitted the kinetic model of pseudo-second order with the rate constant of 0.0257 g $min^{-1}mg^{-1}$. The adsorption of β-sitosterol on MIP_MAA-co_EGDMA followed the Langmuir and Freundlich isotherm with the adsorption capacity of 2.03 and 1.05 mg/g for Langmuir and Freundlich models, respectively.

Acknowledgements

We thank the Directorate of Higher Education-Indonesia for the financial support and Universitas Hasanuddin for all facilities.

References

[1] Zhu T, Yoon C and Row K H 2011 *Chin. J. Chem.* **29** 1246-50
[2] Kim H, Spivak D A 2003 *J. Am. Chem. Soc.* **125** 11269-75
[3] Beltran A, Borrull F, Cormack P A G and Marcé R M 2010 *Trend in Analytical Chemistry* **29** 1363-75
[4] Mayes A G and Whitcombe M J 2005 *Adv. Drug Deliv. Rev.* **57** 1742-78
[5] Yan H Y and Row K H 2006 *Int. J. Mol. Sci.* **7** 155-78
[6] Holland N 2008 *An Investigation into the Role of Morphology on the Performance of Molecularly Imprinted Polymers* PhD thesis (Waterford: Waterford Institute of Technology Ireland)
[7] Walsh R 2010 *Development and Characterization of Molecularly Imprinted Suspension Polymers* PhD thesis (Waterford: Waterford Institute of Technology Ireland)
[8] Yusof N A, Rahman S K, Hussein M Z and Ibrahim N A 2013 *Polymers* **5** 1215-28
[9] Esmaeilian A, Mazdeh A M, Ghaforian H and Liaghat A M 2015 *Desalination and Water Treatment* **53** 2235-48

Adsorption of betasitosterol on MIP

ORIGINALITY REPORT

%5	%3	%3	%0
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	Touaibia, D.. "Removal of mercury (II) from aqueous solution by adsorption on keratin powder prepared from Algerian sheep hooves", Desalination, 20051230 Publication	%1
2	www.huwelijk-feest.nl Internet Source	%1
3	S. K. Bajpai, Shatrudhan Jhariya. "Selective Removal of Amikacin From Simulated Polluted Water Using Molecularly Imprinting Polymer (MIP)", Journal of Macromolecular Science, Part A, 2015 Publication	<%1
4	www.tandfonline.com Internet Source	<%1
5	A. El Nemr, A. El Sikaily, A. Khaled, O. Abdelwahab. " Removal of toxic chromium(VI) from aqueous solution by activated carbon using ", Chemistry and Ecology, 2007 Publication	<%1

6	iugg.org Internet Source	<%1
7	pubs.rsc.org Internet Source	<%1
8	B Benguella. "Cadmium removal from aqueous solutions by chitin: kinetic and equilibrium studies", Water Research, 2002 Publication	<%1
9	Y.C. Sharma, V. Srivastava, V.K. Singh, S.N. Kaul, C.H. Weng. "Nano-adsorbents for the removal of metallic pollutants from water and wastewater", Environmental Technology, 2009 Publication	<%1
10	www.jmst.org Internet Source	<%1
11	dspace.uevora.pt Internet Source	<%1

EXCLUDE QUOTES	ON	EXCLUDE MATCHES	< 5 WORDS
EXCLUDE BIBLIOGRAPHY	ON		