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Characterization molecularly imprinted polymers as a selective adsorbent in the solid-phase extraction method

Characterization molecularly imprinted polymers as a selective adsorbent in the solid-phase extraction method

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Abstract. The Molecularly Imprinted Polymers (MIP) synthesis with the precipitation method uses more porogen solvent volume has been carried out. The purpose of this study was to obtain MIP which would be applied as a selective adsorbent against β-Sitosterol. The structural characteristics of MIP were carried out using FTIR, SEM, EDS, BET, and TGA. FTIR spectrum shows that functional groups that play a role in the formation of MIP are functional groups of OH, C=C, and C=O. The surface morphology of the MIP was analyzed by SEM and the analysis of very important elements in the formation of MIP was analyzed by EDS. Surface area, pore-volume, and pore diameter were analyzed by BET, and TG analyzed MIP resistance to heat. MIP is a white polymer granule and has better adsorption ability than NIP. The morphology of the rough and porous surface of MIP based on SEM data and EDS data shows that there is a loss of % carbon atoms and % mass respectively 1.88 % and 2.28 % after extraction of β-sitosterol as a printing molecule. BET data show that the pore diameter of MIP is 3.4 nm which includes mesoporous material. Based on the adsorption ability and structural characterization of MIP_MAA-co-TRIM β-sitosterol it is very good to be applied as an adsorbent in the SPE method and chromatography.

1. Introduction

The process of separating a compound from a sample of natural materials still has problems for researchers, because it requires a long process sequence and requires a lot of solvents, so it requires a large cost. The technique that is very developed at this time and is widely used for the process of separation and purification of compounds is Solid Phase Extraction (SPE). This technique is more efficient and the extraction process is simple [1] but also has disadvantages because the solid phase or adsorbent used is not selective towards the target molecule [2].

Currently, polymeric materials that have high selectivity and are used as selective adsorbents are known as intelligent materials because they can selectively identify target compounds. These polymers are high molecularly imprinted polymers (MIP), which can be stored for a long time at room temperature without losing the memory effect and can be reused [3]. MIP can be synthesized through several polymerization methods. In this study, precipitation polymerization methods are used because this polymerization method is simpler and easier to do than other polymerization methods, such as bulk polymerization. Precipitation polymerization is done by mixing printing molecules, monomers, and crosslinkers using more porogen solvents [4]. After synthesis, the resulting polymer is in the form of microspheres and does not need to be crushed as in the bulk polymerization method, so that the binding structure and sides of the polymer are not damaged [4] and [5].

Preliminary research was conducted by [6], the combination of MAA monomer and TRIM crosslinking using the β-sitosterol printing molecule was used to synthesize MIP through the bulk polymerization method. The results showed that the MIP produced had good adsorption ability against β-sitosterol. This is because of the influence of crosslinking and the monomers used. Therefore, the monomer chosen in this study is methyl acrylate acid (MAA), because it is acidic [7] and is highly reactive so that it can interact through hydrogen bonds and ionic bonds with printing molecules [8]. Whereas TRIM as a crosslink was chosen in this study because it has many vinyl groups so that the contribution of binding with more monomers, so that the resulting MIP is more stable and has a high degree of rigidity [9]. However, synthesis using bulk method still has problems because the resulting MIP needs to be crushed so that the structure and binding site of the polymer can be damaged [4] and [5]. Based on this, research was conducted to synthesize MIP through precipitation polymerization method using β-sitosterol as a printing molecule so that more selective polymers can be obtained against β-sitosterol. MIP produced is an adsorbent that can be used on SPE or as a stationary phase in column chromatography. The synthesis of MIP used β-sitosterol as a printing molecule, MAA monomer, and crosslinker TRIM with the precipitation polymerization method had never been done before. This is a novelty in this study.

2. Material and methods

2.1. Material and equipment

The materials used for synthesis in this study were β-sitosterol 96% (Sigma-Aldrich), and 99% cholesterol (Sigma_Aldrich) 99% methacrylate acid (MAA) (Sigma_Aldrich), trimethylolpropane trimethachrylate (TRIM) (Sigma-Aldrich), 2, 2' – azobisisobutyronitrile (AIBN), toluene pa, nitrogen gas. Aquades, aquabidest, methanol, tetrahydrofuran p.a. (THF), acetic acid p.a., pH Buffers 4, 7 and 10.

The equipment used included glassware, analytic balance, shaker, water bath, sonicator, oven, gas cylinder, vial bottle, 10, 100 micropipettes, 1000 µL (Eppendorf), pH meter, Whatman paper No. 41, aluminum foil and tissue. The instrument used by FTIR (Shimadzu: IRPrestige-21), UV-Vis (Agilent 8453), Scanning Electron Microscope (SEM-EDS), BET and TGA.

2.2. Procedure

2.2.1. MIP and NIP synthesis. The stages in MIP Synthesis using precipitation polymerization techniques are as follows: as much as 0.103 gr (0.25 mmol) β-sitosterol mixed with MAA monomer 0.339 mL (4 mmol) in round bottom flask and left for 15 minutes, then TRIM crosslinking 6,385 mL (20 mmol) is mixed and porogen solvent is toluene as much as 75 mL while stirring slowly, then 2.5 mL (0.5 mmol) AIBN is added. The solution is sonicated for 5 minutes and run with nitrogen for 15 minutes to remove oxygen. The next step is polymerization in a water bath at 55 oC for 24 hours. The polymer formed is then filtered and washed with distilled water. After that, the printing molecules were removed by Soxhlet extraction using THF solvents and a mixture of methanol: acetic acid (90:20% v /v) for 12 hours to release β-sitosterol and porogen solvents. Then MIP is washed with methanol and aqua bikes, then dried and stored. Non imprinted polymers (NIP) are made without using printing molecules in the same way without the extraction process. The same procedure is used to make MIP and NIP use stigmasterol as a printing molecule.

2.2.2. Characterization of NIP and MIPA. Structural Characterization NIP and MIP were carried out using FTIR, SEM-EDS, BET and TGA instruments.

2.2.3. MIP and NIP adsorption ability. The standard solution of sit-sitosterol is made with a concentration of 10 ppm as much as 5 mL. Then the solution was put into six vial bottles each filled

with 50 mg MIP. Then stirred for 60 minutes at room temperature. After adsorption at a predetermined time, the solution was filtered and analyzed by UV-Vis.

3. Results and discussion

3.1. Synthesis of NIP_MAA-co-TRIM and MIP_MAA-co-TRIM β-sitosterol

The NIP and MIP synthesized using the precipitation polymerization method through free radical polymerization reactions were produced in this study. MIP was obtained as white granules and Non-Imprinted Polymers (NIP) synthesized by the same procedure without using the beta-sitosterol printing molecule also produced in the form of white granules. The amount of NIP and MIP obtained from the synthesis results can be seen in table 1.

Table 1. Results of the Synthesis of NIP and MIP using the beta-sitosterol printing molecule

Monomer	crosslinker	Template	Porogen solvent volume	The weight of NIP (gr)	Polimer shape	The weight of MIP (gr)	Polimer shape
MAA	TRIM	Beta-sitosterol	Toluene	10.3791	Solid white	7.7852	Solid white

Table 1 data shows that the amount of NIP obtained from the synthesis results is more than the number of MIP. This can be caused by the monomers that can only bind to crosslinkers and are not disturbed by the presence of printing molecules that can also bind to monomers or crosslinking.

The beta-sitosterol printing molecules contained in the polymer were extracted using THF solvents, methanol: acetic acid (80:20) V / V, 100% methanol and aqua bikes to produce a molecular-printed polymer (MIP) ready to be used as an adsorbent. The synthesized polymers, namely NIP, MIP Before Extraction (BE) and MIP After Extraction (AE), are characterized by functional groups using FTIR to view the spectrum and shift the wave number data.

3.2. The adsorption capability study of NIP and MIP

MIP synthesized using β-sitosterol as a printing molecule and NIP synthesized without using β-sitosterol were tested for its adsorption ability. MIP which has the best ability to adsorb β-sitosterol can be known from the comparison of the highest qe (Δqe) difference between MIP and NIP. The value of qe from the four types of MIP based on the calculations obtained can be seen in Table 2.

Table 2. Value data of adsorption ability (qe) and value of the difference in adsorption (Δqe) ability between NIP and MIP_MAA-co-TRIM β-sitosterol (AE)

Volume of porogen solvent (mL)	Polymer type	The amount of β-sitosterol adsorbed (q_e) (mg/g)	Δq_e (mg/g)
100	MIP_MAA-co-TRIM	0.6931	0.3039
	NIP_MAA-co-TRIM	0.3892	

MIP_MAA-co-TRIM β-sitosterol (AE) with a solvent volume of 100 mL has the 0.3039 mg/g Δqe value. Quantitative calculation data of the adsorption ability of a NIP and MIP at various volumes of

solvents based on the precipitation method prove that using more solvents has better adsorption ability than other MIPs. The value of adsorption (qe) ability of MIP_MAA-co-TRIM β-sitosterol (AE) using a 100 ml solvent is 0.6931 mg / g. The amount of data on the adsorption ability of MIP synthesized using 100 mL solvent is expected to be related to the% mass lost after extraction (Table 4) and produces a large number of printing cavities in MIP (AE). Therefore the structural characterization data from MIP can be known using FTIR, SEM-EDS, and BET instruments.

3.3. Characterization of MIP and NIP

3.3.1. FTIR analysis. Characterization with FTIR aims to obtain information about the success of synthesis from NIP and MIP because of the interaction between functional groups shown by the shift of wave numbers after polymerization reactions. The polymer obtained is in the form of NIP and MIP has a group of functions that affect the formation of the polymer matrix. The monomers used in the synthesis were also characterized by a functional group with FTIR to explain that wave culture shifts and functional group absorption intensity in the monomers after interacting with crosslinkers to form a NIP matrix and monomers after interacting with printing molecules and crosslinking to form the MIP matrix. The spectrum of MAA, NIP and MIP_MAA monomers can be seen in Figure 1,

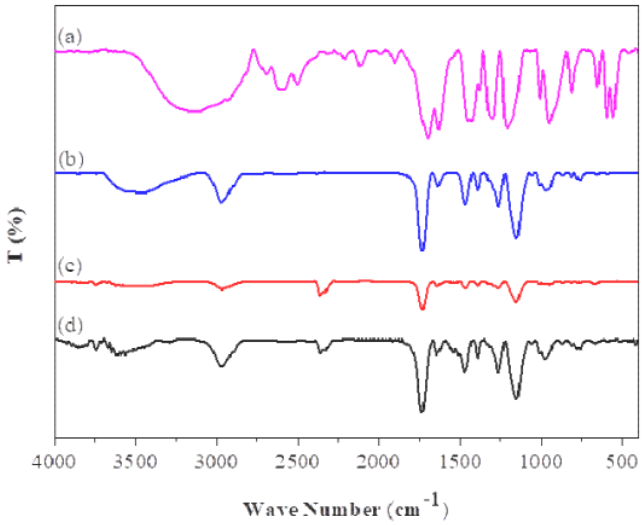

Figure 1. Spectrum: a).MAA, NIP, b). NIP MAA-co-TRIM, c). MIP_β-sitosterol-co-MAA-co-TRIM$_{(BE)}$, and d). MIP_β-sitosterol-co-MAA-co-TRIM$_{(AE)}$

Based on the FTIR spectrum obtained wavenumber data (cm-1) for MAA, NIP, MIP $_{(BE)}$, and MIP $_{(AE)}$ which can be seen in Table 3. The image of the spectrum and wavenumber data shows that, the absorption peak in the spectrum NIP_MAA-co -TRIM and MIP_MAA-co-TRIM have not extracted the changing printing molecules when compared with the MAA monomer spectrum, it is assumed that there is an interaction between the -OH, -C=O, and -C=C functional groups in the monomers with functional groups -C=O and -C=C, -CO in crosslinking.

The FTIR spectrum images are shown in the NIP_MAA-co-TRIM and MIP_MAA-co-TRIM spectra of synthesized Beta-sitosterol show that the OH stretching absorption intensity looks very weak compared to the OH stretching group absorption intensity on MAA monomers and printing molecules. It is assumed that the hydrogen bond formed between the monomers and the printing molecules in the polymerization reaction is not much.

Table 3. Data shifting functional group wavenumbers from MAA, NIP, MIP (BE), MIP (AE)

Functional groups	Wave numbers cm^{-1}			
	MAA	NIP	MIP (Before Extraction)	MIP (After Extraction)
-O-H *stretching*	3115.04	3456.44	3442.29	3572.47
C=O *stretching*	1697.36	1732.63	1730.15	1735.93
C=C *stretching*	1631.78	1635.64	1641.42	1643.35
-C-O *stretching*	1209.37	1151.50	1153.43	1151.50

The data in Table 3 shows that interactions can also occur between groups of functions -C=O in MAA and -OH monomers in β-sitosterol, causing a shift in the wavenumber of the function group -C=O and amplified by the group -CO at NIP_MAA- co-TRIM and MIP_MAA-co-TRIM β-sitosterol. Likewise, the function group -C=C in the MAA monomer appears to be shifting very small wave numbers after the NIP and MIP are formed as if no interaction occurred. But the spectrum image shows that the -C=C stretching functional group on the MAA monomer also experiences interaction because there is a change in the peak absorption intensity of the functional group -C=C in the MAA spectrum from strong intensity to weak and sharp uptake becomes not sharp after NIP_MAA-co-TRIM, and MIP-b-sitosterol-co-MAA-co-TRIM

Based on the image spectrum and wavenumber data show that the functional group influences the NIP_MAA-co-TRIM and MIP_MAA-co-TRIM beta-sitosterol situ -OH, -C=O, and -C=C.

3.3.2. SEM analysis. Surface morphology characterization of NIP and MIP can be analyzed using SEM. The surface morphology of NIP_MAA-co-TRIM MIP_MAA-co-TRIM β-sitosterol yet and has been extracted can be seen in Figure 2.

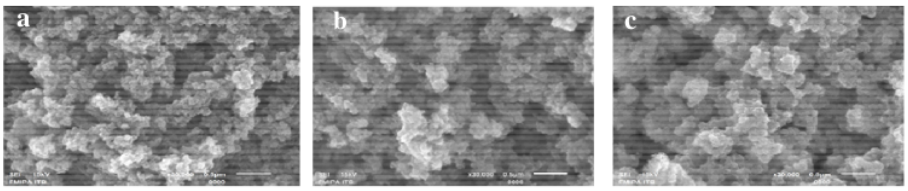

Figure 2. 30000x magnification surface morphology using SEM from (a) NIP_MAA-co-TRIM (b) MIP_MAA-co-TRIMβ-sitosterol (BE), and (c) MIP_MAA-co-TRIM β-sitosterol (TE)

The surface morphology of NIP_MAA-co-TRIM and MIP_MAA-co-TRIM β-sitosterol before and after extraction is composed of a collection of grains that are integrated with the others. The surface

morphology of NIP_MAA-co-TRIM and MIP_MAA-co-TRIM β-sitosterol before and after extraction are almost identical and appear irregular with a rough and porous surface.

3.3.3. EDS analysis. EDS analysis data is used to show the composition of the main constituents of the polymer material that has been synthesized. The images for EDS analysis data and the data in Table 4 show the composition of the main constituents in NIP_MAA-co-TRIM, MIP_MAA-co-TRIM β-sitosterol (BE), MIP_MAA-co-TRIM β-sitosterol (AE).

Table 4. EDS data from NIP, MIP_MAA-co-TRIM β-sitosterol (BE), MIP_MAA-co-TRIM β-sitosterol (AE).

Element	% Mass			Δ% Mass	% Atom			Δ% Atom
	NIP	$MIP_{(BE)}$	$MIP_{(TE)}$		NIP	$MIP_{(BE)}$	$MIP_{(TE)}$	
Carbon (C)	79.55	82.37	80,09	2.28	83.83	86.15	84.27	1.88

The shift of wavenumber from the -OH group in the MIP_MAA-co-TRIM spectrum (AE) shows that the hydrogen bond between the functional groups in the polymer and β-sitosterol has been broken. This is evidenced by the decrease in the atomic% value of C from MIP_MAA-co-TRIM (AE) and compared to MIP_MAA-co-TRIM (AE) that is equal to 1.88%, this decrease in value is significant with a decrease in% mass at MIP_MAA-co-TRIM (BE) compared to MIP_MAA-co-TRIM (AE) which is 2.28%.

3.3.4. BET analysis. Determination of pore surface area, pore-volume, and pore size of a specific sample can be analyzed using the BET method (Brunauer, Emmett, Teller. Based on the results of EDS analysis which explains the decrease in mass% of polymer and reduction in% carbon at MIP, it can be explained that the possibility of forming pores and cavities in MIP_MAA-co-TRIM β-sitosterol after extraction can be proven by analyzing using BET to determine the pore properties specifics such as pore surface area, pore-volume, and diameter. Data on the pore properties of MIP_MAA-co-TRIM β-sitosterol can be seen in Table 5.

Table 5. Surface Area Data, volume, and pore diameter of MIP_MAA-co-TRIM β-sitosterol

Type of Polymer	Surface area (m^2/g)	Total Pore Volume (cc/g)	Pore diameter (Å)
MIP_MAA-co-TRIM β-sitosterol	335.411	0.5707	34.03

Data analysis using BET shows pore surface area, pore volume and pore diameter of MIP_MAA-co-TRIM β-sitosterol. The pore diameter in both MIP is greater than 20 Å (> 2 nm) so that it is classified into the type of mesoporous polymer material.

3.3.5. TGA analysis. Data analysis using BET shows pore surface area, pore volume and pore diameter of MIP_MAA-co-TRIM β-sitosterol. The pore diameter in both MIP is greater than 20 Å (> 2 nm) so that it is classified into the type of mesoporous polymer material.

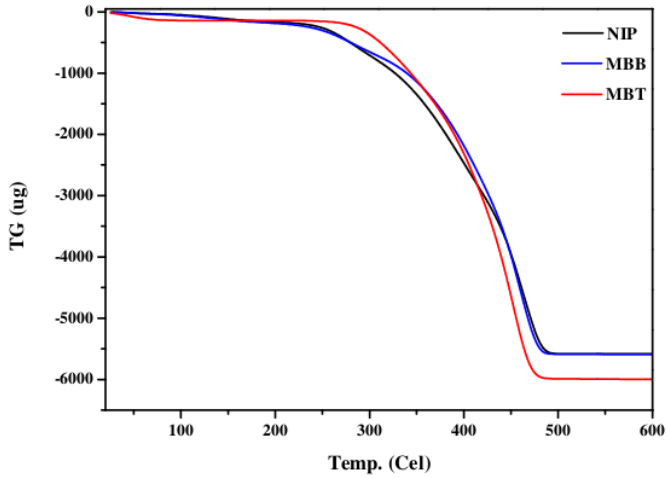

Figure 3. TGA thermograms of (a). NIP_MAA-co-TRIM$_{(Black)}$ and (b). MIP_MAA-co-TRIM β-sitosterol$_{(BE)\ (red),}$ (c). MIP_MAA-co-TRIM β-sitosterol$_{(AE)(blue)}$

Figure 3 shows that TG thermograms of NIP_MAA-co-TRIM have a pattern similar to MIP_MAA-co-TRIM β-sitosterol (AE) which uses solvents. This occurs because MIP_MAA-co-TRIM β-sitosterol (AE) no longer has β-sitosterol. The thermogram TG in NIP_MAA-co-TRIM and MIP_MAA-co-TRIM β-sitosterol (AE) shown in Figure 4 experienced several mass losses. NIP begins to lose mass at temperatures around 26.8 ^{o}C to temperatures of 562.1 ^{o}C and MIP_MAA-co-TRIM β-sitosterol (AE) begins to lose mass at temperatures around 25.14 ^{o}C to temperatures of 598.9^{o}C, initial mass loss from MIP_MAA-co-EGDMA allegedly is water. Very large mass losses occur at temperatures around 304.2 ^{o}C to 492.6 ^{o}C for NIP_MAA-co-TRIM and temperatures around 316.4 ^{o}C to around 479.93 ^{o}C for MIP_MAA-co-TRIM β-sitosterol (AE). At this temperature, MIP is predicted to be degraded so that CO and CO_2 are formed. Higher temperatures cause the bonds between the monomers and crosslinkers to break and leave carbon. The high final temperature of NIP and MIP degradation indicates that the polymer is stable to temperature.

4. Conclusion

The conclusions from the results of this study are:

1. NIP_MAA-co-TRIM, MIP_MAA-co-TRIM beta-sitosterol has been successfully synthesized using the precipitation method through free radical polymerization reactions. The resulting polymer is white solid.
2. MIP_MAA-co-TRIM β-sitosterol with a volume of the solvent of 100 mL has a high adsorption ability.
3. Functional groups that influence the formation of NIP_MAA-co-TRIM and MIP_MAA-co-TRIM beta-sitosterol namely -OH, -C=O, and -C=C.
4. The surface morphology of NIP_MAA-co-TRIM before and after extraction appears irregular with a rough surface.

5. The composition of the main constituents of MIP_MAA-co-TRIM is Carbon and the presence of β-sitosterol causes % C atoms and % mass to increase in MIP¬-_MAA-co-TRIM (BE) and % carbon atoms and % mass decreases at MIP_MAA extracted -co-TRIM was analyzed by EDS.
6. Pore surface area, pore volume and pore diameter of MIP_MAA-co-TRIM β-sitosterol are classified into the type of mesoporous polymer material with a pore diameter of 34.03 Å (3.403 nm).
7. The high final temperature of NIP and MIP degradation indicates that the polymer is stable to temperature.

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