Synthesis and characterization of stigmasterol imprinted polymers with precipitation polymerization method

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SUBMISSION ID	1424092193	CHARACTER COUNT	14598

IOP Conference Series: Earth and Environmental Science

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IOP Conf. Series: Earth and Environmental Science **473** (2020) 012149 doi:10.1088/1755-1315/473/1/012149

Synthesis and characterization of stigmasterol imprinted polymers with precipitation polymerization method

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Abstract. Molecularly imprinted polymers (MIP) are porous materials that have an active binding site and can recognize specific target molecules. MIP synthesis was carried out by precipitation polymerization method using toluene as a porogen solvent and stigmasterol molecule as a template molecule. The synthesized NIP and MIP were characterized using FTIR and SEM-EDS. The ability of MIP adsorption on Stigmasterol was determined by concentration measurements using UV-Vis. The results of the characterization using FTIR showed that the functional groups that influence the formation of NIP and MIP are -OH, -CH, C=C, and -C=O. Characterization using SEM shows that the surface morphology of MIP is rougher than NIP. Characterization using EDS showed that there was a decrease in mass% by 2.54% and C% atom by 2.08% in MIP after extracting the Stigmasterol molecule. The ability of MIP adsorption on stigmasterol was 0.204 mg /g, while the ability of NIP adsorption on stigmasterol was 0.040 mg / g. The ability of MIP adsorption to stigmasterol molecules is better than NIP. Therefore, MIP can be used as an adsorbent to adsorb stigmasterol in sample extracts.

1. Introduction

Isolation of secondary metabolites from natural materials conducted because these secondary metabolites have a very good function for life. One of the secondary metabolites is stigmasterol, which is a group of phytosterol compounds. Stigmasterol has pharmacological prospects such as anti osteoarthritis, anti-tumor, antimutagenic, cytotoxicity, antioxidant and anti-inflammatory [1].

Currently, a highly developed extraction method for the isolation and purification of natural material compositions is solid-phase extraction or Solid Phase Extraction (SPE). The method has advantages such as the use of fewer solvents. However, SPE also has disadvantages, especially in the stationary phase in the extraction or adsorbent process which will be used in the adsorption process. The extraction or adsorption process will be effective if the stationary phase or adsorbent used in the SPE method has a high selectivity [2].

Selective adsorbents could be obtained by making adsorbents from synthetic polymers by using molecular printing techniques to produce molecular-printed polymers or so-called Molecularly Imprinted Polymers (MIP). MIP is called smart material because it can selectively identify target molecules. MIP can be used as an adsorbent in the separation process using solid-phase extraction (SPE) techniques because it is stable to changes in pH, temperature and can be stored for a long time at room temperature [3].

MIP synthesis is carried out by using several variables, namely molecular molds, monomers, crosslinkers, initiators and porogen solvents. The use of mold molecules must be in according to

the target molecule [4], for example, the target molecule to be isolated is stigmasterol, then the mold molecule is stigmasterol.

Functional monomers as polymeric matrix formers will interact with the molding molecule. The mold molecule in the polymer matrix will be released to form a cavity with a specific active side according to the mold molecule or target molecule. This molecule developed because there is a functional group on the monomer, which complements the target molecule's functionality to interact with one another. The selection of functional monomers must be precise so that the functions of the monomers in interacting and bonding with the print molecules are more effective [5].

One monomer that is often used is methacrylic acid (MAA). MAA monomers are functional monomers that are often used in polymer printing techniques through non-covalent interactions because they have an excellent ability to interact with various functional groups [2].

Besides mold molecules and monomers, crosslinker selection must also be considered. According to [6], crosslinkers used in MIP syntheses have three main roles, namely controlling the matrix morphology of the polymer (gel type, macroporous or microgel), stabilizing the side binding of molds and providing mechanical stability to the polymer matrix.

[7], synthesized β-sitosterol mapped molecules using MAA monomers and TRIM crosslinkers. The results prove that MIP with a combination of MAA monomers and TRIM crosslinkers has a high adsorption capacity and selectivity to β-sitosterol compared to MIP synthesized by [8], using EGDMA crosslinkers combined with MAA monomers.

The polymerization method used in polymer synthesis is important, to obtain the desired polymer. One method of polymerization that is often used is the method of precipitation polymerization where the polymerization technique is based on the use of solvents in large quantities where the amount of monomers is usually <5% of the total volume of the solvent. This method is done by growing the polymer chains in the solvent so that the polymer chains that are formed become longer and more insoluble, causing polymer particles to settle in solution. The amount of polymer produced is more [9]. The particles are formed in the range of 0.3-10 µm, where additional stabilizers are not needed in their interactions [10].

Based on this description, a study was carried out to synthesize stigmasterol molecular-printed polymers with MAA monomers and TRIM crosslinkers through precipitation polymerization. Synthesized MIP was characterized and tested for its adsorption ability against stigmasterol.

2. Material and method

2.1. Material and equipment

The ingredients used are 95% stigmasterol (Aldrich-Sigma), 99% methacrylic acid (Aldrich-Sigma), trimethyl propane trimethacrylate 98% (Aldrich-Sigma), 2,2'-azobisisobutyronitrile (AIBN), toluene, methanol pro analysis, acetic acid pro analysis, nitrogen gas, tetrahydrofuran (THF), Whatman paper no. 41, aluminum foil, tissue, (aquabides, and aquades).

Equipment that will be used includes conventional glassware, analytical balance, shakers, water baths, sonicators, ovens, glass bottles, micro pipets 100 and 1000 µL, Fourier Transform Infrared (FTIR) spectrophotometers, Ultra Violet Visible (UV-Vis) spectrophotometers and UV-Vis scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDS).

2.2. Procedures

2.2.1. Synthesis of MIP and NIP. Stigmasterol of 0.1032 g (0.25 mmol) and MAA monomer of 0.339 mL (4 mmol) was mixed in a round bottom flask, allowed to stand for 15 minutes. The mixture was added with TRIM 6.385 mL (20 mmol) crosslinker and dissolved with 50 mL porogen solvent, allowed to stand for 15 minutes, then covered and then sonicated for 5 minutes and nitrogen flowed for 10 minutes. The solution was added 2.5 mL (0.5 mmol) AIBN then closed tightly, then flowed again with nitrogen gas for 15 minutes to remove oxygen. Polymerization was carried out in a water

bath at a temperature of 55-60 ° C for 24 hours. The obtained polymer then washed with tetrahydrofuran (THF), then extracted through the extraction of soxhlet with a mixture of methanol: acetic acid (80: 20% v/v) for 12 hours to remove the molding molecule (stigmasterol). Next, MIP was washed with methanol and aquabides to neutral pH, then dried. Non imprinted polymers (NIP) are made without using stigmasterol in the same way without the extraction process. Polymers are named NIP_MAA-co-TRIM.

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

2.2.3. MIP and NIP adsorption ability. MIP and NIP of 50 mg each were added to the different vials that had been prepared, then 5 mL of 10 mg / L stigmasterol solution was added to the vials. The mixture was shaken with a shaker for 60 minutes at room temperature, then filtered and then the concentration of stigmasterol in the filtrate was analyzed with a UV spectrophotometer.

3. Results and discussion

3.1. Synthesis of Non-Imprinted Polymers (NIP) Molecularly Imprinted Polymers (MIP)

The amount of NIP obtained from the synthesis is greater than that of MIP. Both the NIP and MIP polymers are white solids which are difficult to distinguish before characterization.Synthesis of polymers using MAA monomers, TRIM crosslinkers, stigmasterol mold molecules with a solvent volume of 50 mL to produce polymers. The mold molecule is removed from the Polymer agar Molecularly Imprinted Polymer (MIP). Whereas Non-Imprinted Polymer (NIP) is a polymer that is synthesized like MIP without using the molecular mold. The results of the MIP and NIP synthesis are shown in Table. 1.

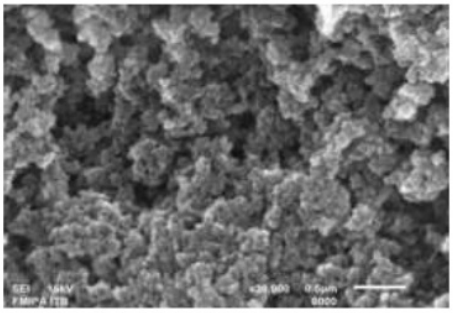
Table 1. Synthesis of NIP and MIP results using stigmasterol printed molecules

Monomer	crosslinker	Template	Porogensolvent volume(mL)	The weight of NIP (gr)	The weight of MIP (gr)	Polimer shape
MAA	TRIM	stigmasterol	50	11.5236	6.9809	Solid white

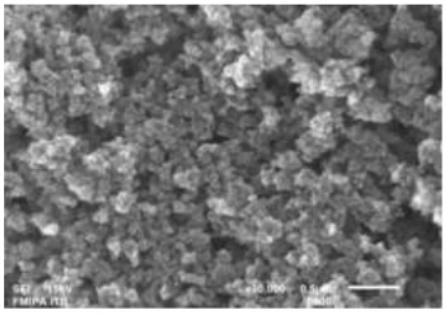
The amount of NIP obtained from the synthesis is more than MIP because the NIP monomer MAA is more bound to the TRIM crosslinker and other monomers without interference with the mold molecules. TRIM has a high density and more vinyl groups so that the binding contribution with the monomer is greater and causes the polymer (NIP) to form more and more from MIP.

3.2. Characterization of NIP and MIP

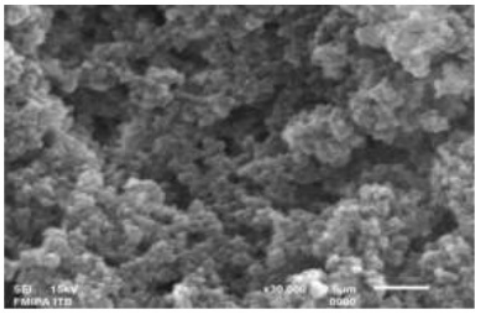
3.2.1. Characterization of NIP and MIP using SEM. The surface morphology of NIP and MIP is known from the results of the analysis using SEM. The surface morphology of the NIP and MIP is shown in Figure 1



(a.). NIP_MAA_co-TRIM



(b). MIP_stigmasterol_MAA-co-TRIM$_{(BE)}$



(c). MIP_stigmasterol_MAA-co-TRIM$_{(AE)}$

Figure 1. SEM characterization results with a magnification of 30,000x

The surface morphology of NIP and MIP is almost the same, in the form of solids composed of small granules of irregular size so that the surface of NIP and MIP looks rough. The surface morphology before extraction (BE) and after extraction (AE) at MIP_stigmasterol_MAA-co-TRIM (BE) which is composed of small beads on the surface looks denser. However, MIP_stigmasterol_MAA-co-TRIM (AE) looks more porous and is thought to have a larger cavity. This shows that the stigmasterol molding molecule has been released from the polymer matrix at the time of extraction.

3.2.2. Characterization of NIP and MIP using EDS. Characterization with EDS aims to determine the% atom and mass% of the main constituent elements of the polymer that is the element carbon. The results of the characterization can be seen in table 2.

Table 2. Characterization results using EDS

Solvent variation (mL)	% Carbon (C) Mass			% Carbon (C) element atom		
	MIP (BE)	MIP (AE)	Δ % Mass	MIP (BE)	MIP (AE)	Δ % element
50	84.04	81.50	2.54	87.52	85.44	2.08

Based on Table 2, the data show that there is a decrease in mass% C and % C atoms in the extracted polymer or MIP (AE) respectively by 2.54% and 2.08%. This proves that stigmasterol has been released from the polymer after extraction.

3.2.3. *Characterization of NIP and MIP using FTIR.* Characterization using Fourier Transform Infrared Spectroscopy (FTIR) was carried out to determine the influential bonds in the synthesis of NIP_MAA-co-TRIM polymers, MIP_stigmasterol_MAA-co-TRIM (BE) and MIP_stigmasterol_MAA-co-TRIM (AE) composed by MAA monomer. The FTIR spectrum of the monomer and the resulting polymer can be seen in Figure 2.

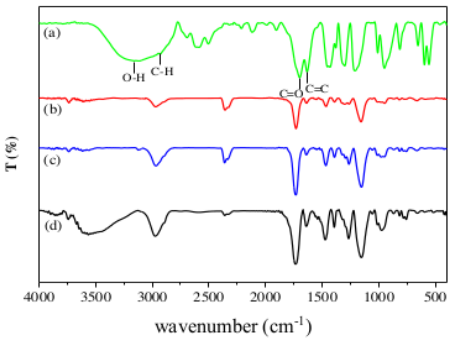


Figure 2. Spectrum of FTIR (a) MAA,(b) NIP_MAA-co-TRIM,(c)MIP_stigmasterol_MAA-co-TRIM$_{(BE)}$, (d)MIP_stigmasterol_MAA-co TRIM$_{(AE)}$

The FTIR spectrum shows the peak absorption of –OH, C = O and C = C from MAA monomers experiencing significant changes in intensity due to interactions with crosslinkers, mold molecules, and other monomers at the time of polymer formation. The -OH absorption peak in the MAA monomer spectrum appears to be widening due to the acidic nature of the MAA. The -OH intensity in the NIP_MAA-co-TRIM spectrum, MIP_stigmasterol _MAA-co-TRIM (BE),MIP_stigmasterol_MAA-co-TRIM (AE) becomes weaker because the acidity of the monomer decreases after forming the polymer. The -OH absorption peak of NIP_MAA-co-TRIM and MIP_stigmasterol_MAA-co-TRIM (BE), experienced a fairly large change in intensity compared to MAA monomers, due to the interaction of the -OH functional group on MAA monomers with MAA monomers themselves or -OH on stigmasterol forming hydrogen bonds so that when the polymer has formed its intensity is weaker than MIP_stigmasterol_MAA-co-TRIM (AE) intensity is stronger. This is because the hydrogen bonds formed with stigmasterol in the polymer matrix after extracting will break and leave free -OH on the polymer matrix.

The –C=O bonds found in MAA monomers and –OH found in stigmasterol can interact and form hydrogen bonds. It also causes a weak intensity in the functional group C=O when NIP_MAA-co-TRIM and MIP_stigmasterol_MAA-co-TRIM (BE) have been formed.A fairly weak intensity was seen for the peak absorption of –C=C in NIP_MAA-co-TRIM and MIP_stigmasterol_MAA-co-TRIM

(BE) compared to monomers (MAA). The intensity is stronger. This shows that the formation of polymers occurs when there is an interaction of –C=C bonds from the monomer because there is an initiator that causes the formation of free radicals in the –C=C bonds for monomers or crosslinkers. Radicals formed on monomers form new bonds with the C-C bond found in the crosslinker or on the monomer itself. Free radicals generated at certain positions from crosslinkers or monomers cause chain and polymer extension to form a polymer matrix.

3.3. NIP and MIP adsorption ability test on Stigmasterol

The NIP and MIP adsorption ability test on stigmasterol were carried out by quantitative analysis using a UV-Vis spectrophotometer at a wavelength of 203.5 nm. Based on the results of the analysis, the value of the ability of NIP to adsorb stigmasterol (qe NIP) is 0.040 mg / g and the MIP qe value is 0.204 mg / g, so the Δqe value is 0.164 mg / g. The Δqe value proves that MIP has better adsorption ability than NIP.

4. Conclusion

The synthesized polymer is a white solid called MIP and NIP. The MIP synthesized can adsorb stigmasterol with greater adsorption ability compared to NIP. The MIP was characterized using EDS and showed a mass reduction of% C and% C respectively by 2.54% and 2.08%. Surface morphology was characterized using SEM and the results showed a rough MIP surface. The functional groups that play a role in the synthesis process based on FTIR characterization results are -OH, C=C, and C=O.

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