



Synthesis of Molecularly Imprinted Polymers using Methacrylic Acid and Ethylene Glycol Dimethacrylate by Precipitation Polymerization Method

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Received: 18 September 2020;

Accepted: 19 January 2021;

Published online: 20 March 2021;

AJC-20283

The synthesis of molecularly imprinted polymers (MIPs) was carried out by using methacrylic acid as a monomer, ethylene glycol dimethacrylate as a crosslink and dibutyl phthalate as a mold through the precipitation polymerization method. The MIP was characterized with FTIR, surface area analyzer, SEM-EDS and ultraviolet-visible spectrophotometer. The MIP adsorption ability test variables for dibutyl phthalate were time and concentration. The FTIR indicates that the functional groups $-OH$, $-C=O$ and $-C=C$ contribute to the formation of MIP and the SEM-EDS analysis showed that the prepared MIP resembles as beads. The MIP's ability to adsorb dibutyl phthalate is better than NIP and the optimum time to adsorb dibutyl phthalate is 60 min.

Keywords: Monomer, Dibutyl phthalate, Molecularly imprinted polymer, Crosslinker.

INTRODUCTION

Dibutyl phthalate is one of the organic compounds from the phthalate group which is widely contained in carcinogenic food or beverage product packaging. The presence of phthalates in packaging can be identified and analyzed through the solid phase extraction (SPE) method because of its simpler and more selective action [1]. The important factor needed in the SPE extraction method is the selection of the right adsorbent. Molecular-imprinted polymers are the right adsorbent choices in the SPE extraction method [2,3].

Molecularly imprinted polymers (MIP) is a technique where the active site can be made in synthetic polymers, so that it can selectively recognize target molecules. This occurs due to the formation of a crosslinking polymer matrix and the interacting monomers [4]. MIP can be said to be an intelligent material because of its ability to recognize target molecules well [5]. MIP has the advantage of having high selectivity and affinity for the target molecules used in the printing process.

Printed polymers have physical resistance and resistance to increase the temperature and pressure and also MIP is

cheaper to synthesize [3]. In addition, MIP is widely applied in the process of extraction, purification, as a chemical sensor material [2,3]. Based on this, it is necessary to synthesize printed MIP with dibutyl phthalate molecules, which are useful for various applications, especially for the extraction method. The precipitation polymerization methods in MIP synthesis are the most widely used method to produce spherical particles [6], micro and nano-sized spherical beads [7]. Based on the description above, a study on the synthesis and characterization of dibutyl phthalate-printed polymers using methacrylic acid monomers and ethylene glycol dimethacrylate as crosslinking agents through the precipitation polymerization method was carried out to obtain DBP-printed polymers as adsorbents.

EXPERIMENTAL

The materials used for the synthesis in this study were 99.5% dibutyl phthalate (DBP), 99% methacrylic acid (MAA), ethylene glycol methacrylate (EGDMA), 2,2'-azobisisobutyronitrile (AIBN), toluene, acetone, methanol (HPLC grade), acetic acid, etc. All these were procured from the commercial sources.

Synthesis of MIP and NIP: Dibutyl phthalate (1 mmol) was mixed with methacrylic acid monomer (4 mmol) in a round bottom flask, then added 1 mL of EGDMA as crosslinker and dissolved in 50 mL of toluene as porogen solvent. The solution was sonicated for 10 min, then passed through nitrogen gas for 10 min to remove oxygen, then added 5 mL of 1 mmol AIBN. The solution was sonicated again for 15 min and then through with nitrogen gas for 15 min. The next step is polymerization by stirring in a reflux device at a temperature of 60 °C for 24 h. The polymer formed was then filtered and washed with toluene, acetone, methanol and distilled water, respectively. After that, the mold molecules were removed by washing with acetone, methanol and distilled water sequentially and then sonicated using a mixed solvent of methanol:acetic acid (9: 1 v/v) for 30 min to release dibutyl phthalate from MIP. Th MIP was then dried and stored. Non-imprinted polymers (NIP) were also prepared without using mold molecules in the same way [8,9].

Preparation of 100 mg L⁻¹ DBP standard solution: A total of 0.960 mL of DBP was mixed with methanol in a 10 mL volumetric flask and homogenized. Then the standard solution was varied in concentration to 1, 5, 10, 15 and 20 ppm.

MIP and NIP adsorption ability test: A total of 30 mg of each MIP and NIP were put into a different vial, then 5 mL of 10 mg L⁻¹ DBP solution was added. The mixture was shaken with a shaker vigorously for 1 h at room temperature, filtered and then the concentration of DBP in the filtrate was analyzed using a UV spectrophotometer with the maximum wavelength and then amount of DBP adsorbed in each gram of MIP was determined.

Effect of time on MIP adsorption ability: The standard solution of DBP 10 mg L⁻¹ as much as 5 mL and 30 mg MIP was put into 7 vials. The mixture was shaken using a shaker with a time variation of 30, 60, 90, 120, 150 and 180 min at room temperature. After adsorption at these time variations, the solution was filtered and analyzed using a UV spectrophotometer [10].

Effect of concentration on MIP adsorption ability: Each 5 mL of DBP solution with 5 variations in concentration, namely 6, 9, 12, 15, 18 and 21 ppm according to the optimum pH was added into a vial, which contains 30 mg of MIP each. The mixture was stirred with a shaker at the optimum time and room temperature, then the solution was filtered and analyzed by a UV spectrophotometer.

RESULTS AND DISCUSSION

Synthesis of MIP and NIP: MIP and NIP were synthesized using the precipitation polymerization method. The dibutyl phthalate used as a printing molecule still present in the polymer. Therefore, the polymer was extracted using organic solvents, namely methanol and acetone, then sonicated for 30 min with methanol: acetic acid (90:10% v/v) solvent to obtain a molecular printed polymer (MIP). Dibutyl phthalate which has been extracted from polymer was tested qualitatively using a UV spectrophotometer at 262.5 nm (for methanol solvent) and 287 nm (for methanol:acetic acid (9:1)).

The results indicated a decrease in the concentration of DBP, which had been extracted four times, as indicated by a decrease in the adsorption value until it reached a value of 0.041 (Table-1). This indicates that dibutyl phthalate had been extracted from MIP.

Extracts	Adsorbance
Extract I	1.009
Extract II	0.330
Extract III	0.093
Extract IV	0.041

The interaction process between monomer and DBP occurs in the pre-polymerization stage in toluene solvent due to the hydrogen bonding. The process of forming a polymer matrix between the EGDMA cross-linker and the MAA monomer with the help of an initiator occurs in the polymerization stage. The initiation, propagation and termination stages occur in the polymerization stage. The next step is the releasing of dibutyl phthalate in order to obtain a suitable mold for dibutyl phthalate. Polymerization process was initiated by AIBN, which was decomposed by UV or thermal process to a monomers through radicals [11].

FTIR studies: The FTIR spectra of the prepared beads *viz.* NIP and MIPs (before and after extraction) are shown in Fig. 1. The key IR data are shown in Table-2. It was observed that the -OH functional groups in both MIPs (before and after extraction) do not have a significant shift however, a stronger intensity was observed for MIPs (after extraction) compared to MIPs (before extraction). The reason is attributed due to the breaking of hydrogen bonds between -OH functional groups on the mold molecule.

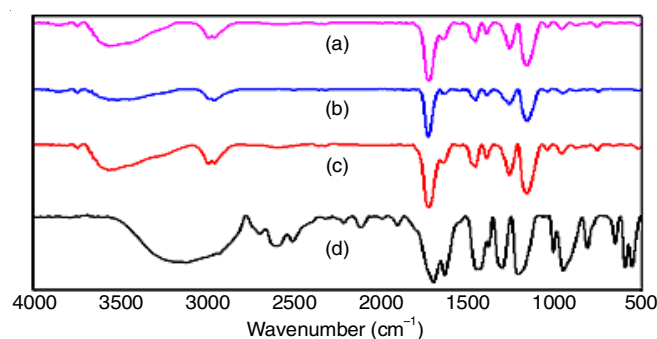


Fig. 1. FTIR spectrum (a) MIP (after extraction); (b) (before extraction); (c) NIP and (d) MAA

Functional groups	Monomer MAA	NIP	MIP	
			Before extraction	After extraction
-OH <i>str.</i>	3400-3200	3562.92	3523.95	3562.52
-CH <i>str.</i>	2929.87	2989.66	2985.81	2987.74
-C=O <i>str.</i>	1697.36	1643.35	1635.64	1643.35
-C=C <i>str.</i>	1631.78	1541.12	1541.12	1541.12

TABLE-3
EDS DATA OF NIP AND MIPs

Elements	Mass (%)			Atom (%)		
	NIP	MIP		NIP	MIP	
		Before extraction	After extraction		Before extraction	After extraction
C	79.37	82.3	77.97	83.67	86.1	82.5
O	20.63	17.7	22.03	16.33	13.9	17.5

The -CH absorption peaks in the NIP and MIPs (before and after extraction) appeared to have strong sharpness and intensity when compared to MAA. The interaction that occurs between the -C=O functional groups present in MAA and -OH group in DBP forms hydrogen bonds as a shift in wavenumbers for the -C=O group in NIP and MIPs (before extraction).

No shift in the wavenumber of -C=C- was observed (Table-2). However, the intensity of -C=C- in NIP and MIPs is weaker than MAA monomer. This occurs due to the breaking of the double bond by the initiator through a polymerization reaction on the monomer and crosslinker and this affects the formation of NIP and MIPs. The bands sorption in the region stretching C-H, O-H, C=C (aromatic rings) and C=O were also observed in the spectrum of MIP with a phthalate as template molecule in the polymer matrix during polymerization [12,13].

EDS analysis: EDS analysis was carried out to determine the C and O elements in all the three polymers *viz.* NIP and MIPs (before and after extraction) and the EDS data is shown in Table-3.

It is found that the mass percent carbon and atomic percent carbon from MIP (before extraction) decreased while the atomic and mass percent oxygen values increased. This is because the number of carbon atoms in DBP is higher than the number of oxygen atoms when DBP is released from the MIP, then the number of carbon atoms will decrease while the oxygen atom will increase. Reduction of the mass percent value of carbon by 4.33% and the atomic percent of carbon by 3.6% in MIP, thus indicating the release of dibutyl phthalate (DBP).

SEM analysis: The SEM images of NIP and MIPs (before and after extraction) is shown in Fig. 2. The surface morphology of NIP contains grains, which appeared as coarse with irregular sizes and are joined to one another. Meanwhile, the polymer surface morphology of both MIPs (before and after extraction) exhibited the granules which appear smooth with a more regular size and do not blend with each other.

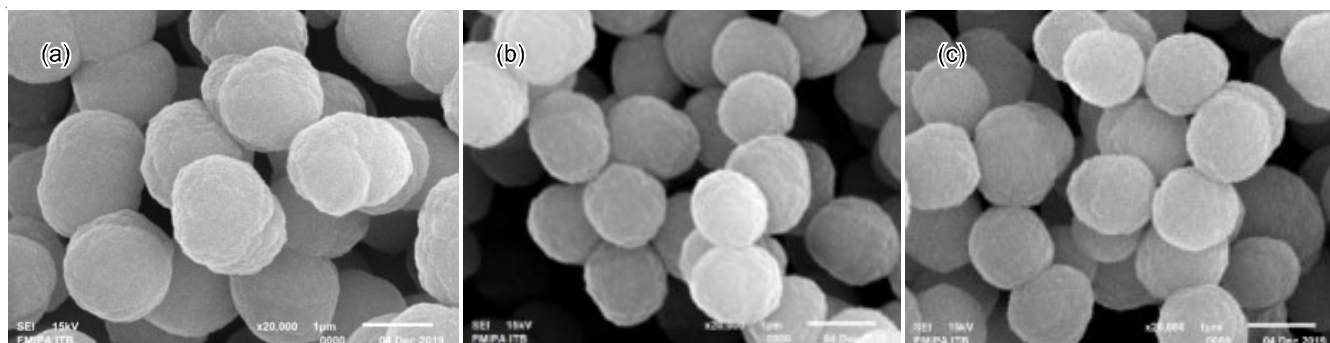


Fig. 2. SEM images of (a) NIP 20,000x magnification, (b) MIP (after extraction) 20,000x magnification, (c) MIP (before extraction) 20,000x magnification

Characterization of MIP using surface area analyzer:

The characterization of pore diameter and volume in MIP was determined by the Barret-Joyner-Hallenda (BJH) method. The measurements were made on the basis of adsorption data at 77.35 K. The pore diameter and volume can be determined from the amount of adsorbed N₂ as a function of pressure [11]. The results of measurements of pore area, volume and diameter are shown in Table-4. Based on the pore diameter size, the synthesized MIP (after extraction) is considered to be as mesopore since the average pore radius size was found to be 23.93 Å.

TABLE-4
MIP USING SURFACE AREA ANALYZER

Sample	Surface area (m ² /g)	Total pore volume (cc/g)	Average pore radius (Å)
MIP_DBP_MAA-co-EGDMA(AE)	105.509	0.1262	23.93

The Barrett-Joyner-Halenda (BJH) plot for the pore size distribution in the synthesized MIP is shown in Fig. 3. The blue curve indicates that an adsorption process increases with the

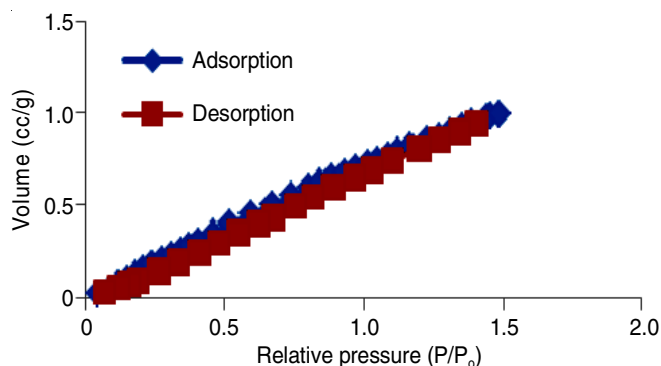


Fig. 3. Relation of pressure relative to the volume of N₂ adsorbed in MIP (after extraction)

increasing relative pressure, while the desorption process is marked by a red curve. The ability to absorb N_2 gas by synthesized MIP was found to be 1.4855 cc/g at the maximum pressure of 0.99 atm. The pore diameter size of 15.2832 Å adsorbs N_2 of 0.0078 cc/g, while a diameter of 888.1237 Å adsorbed 0.1248 cc/g of N_2 .

MIP and NIP adsorption ability: The adsorption ability of synthesized MIP for dibutyl phthalate (DBP) as a mold molecule was investigated. Fig. 4 shows that MIP has a better adsorption ability than NIP with a difference of 0.893 mg/g.

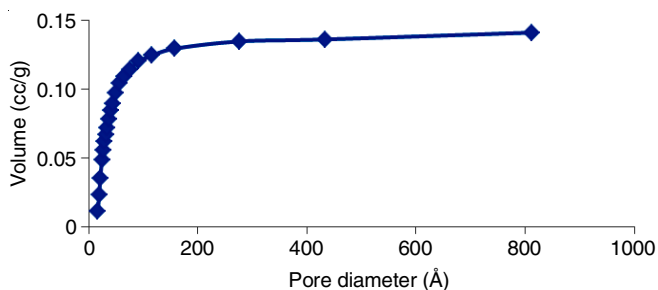


Fig. 4. Relationship of pore diameter to the volume of N_2 adsorbed on MIP (after extraction)

Effect of time on DBP adsorption by MIP: The effect of time on the adsorption ability of DBP by MIP is shown in Fig. 5. An increase in the adsorption of DBP is directly proportional to the increase in contact time. When the maximum adsorption is reached, then the additional time causes a decrease in the adsorption ability. Thus, the optimum time for the synthesized MIP to adsorb DBP is 60 min, which was found to be 1.1746 mg/g of adsorbed DBP.

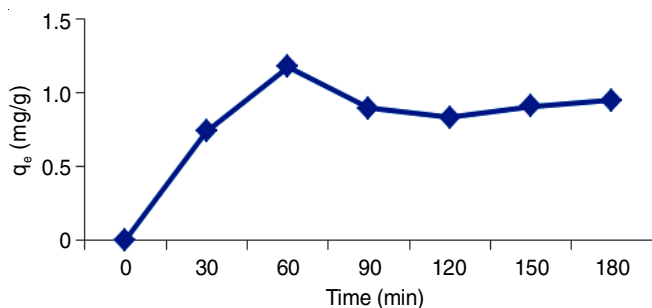


Fig. 5. Effect of time on the amount of DBP adsorbed by MIP (after extraction)

Effect of concentration on MIP adsorption: It is found that more DBP can be adsorbed by MIP as compared to NIP. However, if the maximum limit exceed its adsorption equilibrium, the adsorption capacity of MIP (after extraction) will tend to be constant even though the concentration is increased.

Conclusion

The molecularly imprinted polymers *viz.* NIP and MIPs (before and after extraction) were synthesized by the precipitation polymerization method. The surface morphology of the MIP beads of a similar size to a rough and rigid looking surface. The EDS characterization showed a decrease in mass percent C and atomic percent C, which indicates the release of dibutyl phthalate (DBP) molecules from MIP. The optimal time needed to adsorb dibutyl phthalate by MIP was 60 min, which was found to be 1.1746 mg/g of adsorbed DBP.

ACKNOWLEDGEMENTS

The authors thank to the Directorate of Higher Education Indonesia for funding support and also thanks to Hasanuddin University for providing all the research facilities.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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