



Synthesis and Characterization of Molecularly Imprinted Polymers of Di-(2-Ethylhexyl) Phthalate Using the Precipitation Polymerization Method



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Abstract

Molecularly Imprinted Polymers (MIP) is a synthetic functional material that can recognize target molecules selectively. This study aims to synthesize and characterize MIP and its performance by precipitation polymerization method using methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), and di-(2-Ethylhexyl) phthalate (DEHP). Characterization of MIP was conducted by FTIR, SEM-EDS, SAA, and UV-Vis spectrophotometer. The effect of concentration and time on MIP adsorption ability against DEHP was also determined. SEM shows that MIP_DEHP_MAA-co-EGDMA surface morphology is arranged from more uniform, less tight, and more fine granules than NIP_MAA-co-EGDMA. FTIR characterization of MIP and NIP (Non-Imprinted Polymers) shows absorption bands of functional groups were –OH, C-H, C=O, and –C=C. SAA characterization shows MIP surface area is 137.660 m²/g, total pore volume 0.1555 cc/g, and an average pore radius 22.59 Å that indicates as mesopore material. MIP_DEHP_MAA-co-EGDMA (AE) adsorbed DEHP better than NIP_MAA-co-EGDMA. The difference value of the adsorbed DEHP (Δq_e) was 0.212 mg/g.

Keywords: Synthesis; diethylhexyl phthalate; molecular imprinting polymer; precipitation.

1. Introduction

The use of plastic packaging for food and beverages has shifted cans and glass packaging significantly because plastic packaging is easy to produce, easy to obtain, lightweight to carry, and cheap. Drinking water stored in bottles of the polyethylene terephthalate (PET) type has become popular because it is easy to use and inexpensive [1]. Three types of phthalate esters (PAEs), dibutyl phthalate (DBP), diethyl phthalate (DEP), and di (2-Ethylhexyl) phthalate (DEHP), have been detected in bottled PET [1] [2] [3]. DEHP is most commonly used as a plastic material because it is strong and waterproof but can contaminate water when exposed to heat and stored for a long time [4]. DEHP are used as plasticizers to make plastic flexible in polymer products especially medical devices, furniture materials, cosmetics, and personal care products [4].

The DEHP threshold in drinking water is 0.006 mg L⁻¹ [5]. The method for detecting DEHP in plastic packaging products can be done using the Solid

Phase Extraction (SPE) method [6]. The selective adsorbent currently used in SPE is Molecularly Imprinted Polymer (MIP). MIP is applied in the process of extraction, purification, and chemical sensor material with the advantage that it is more resistant to conditions (temperature and pH) and can be used for a large number of samples [7] [8]. Based on this, it is necessary to synthesize a MIP imprinted DEHP molecule which is useful for re-extracting DEHP from plastic-packed samples.

MIP synthesis is carried out based on the principle of polymerization involving print molecules, functional monomers, crosslinkers, initiators, and porogen solvents [9]. The polymer will have a mold or cavity with functional groups that can bind to the target molecule selectively [10]. The use of appropriate functional monomers in MIP synthesis determines the selectivity of MIP to molecular targets. The most commonly used monomer is methacrylic acid (MAA) because this monomer can be accepted by printing molecules through hydrogen bonds and forming ion pairs. The selectivity and high

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adsorption capabilities also depend on the cross-linker used [11]. Cross-linkers used in this study were ethylene glycol dimethacrylate (EGDMA) which is reactive and can produce polymers with high stiffness so that it is more stable [12]. EGDMA has functional groups that easily interact with MAA functional groups so that it can produce MIP with a high degree of stiffness and stability [13] [12].

The polymerization method greatly determines the characteristics, adsorption ability and selectivity of an MIP. The synthesis of MIP imprinted with DEHP using bulk polymerization method showed that about 15% of the MIP produced had less adsorption ability [14]. Another polymerization method is the precipitation polymerization method to obtain MIP with a uniform particle size (about 0.3-10 μm), a high percentage of polymer yield, and a high affinity constant. The precipitation polymerization method can reduce damage and reduce polymer mass due to grinding and sieving such as bulk polymerization methods [15] [16].

The aim of the present work deals to synthesis and characterization of Molecularly Imprinted Polymers (MIP) imprinted with DEHP using MAA monomer and EGDMA cross-linker to be applied as adsorbent in the extraction process and as a DEHP sensor material. The resulting MIP was characterized using a Scanning Electron Microscope (SEM), Energy Dispersive Spectroscopy (EDS), Fourier Transform Infrared (FTIR), Surface Area Analyzer (SAA), as well as a qualitative and quantitative test of the adsorption capability of DEHP compounds.

2. Experimental

2.1 Material:

The ingredients used for the synthesis were di (2-Ethylhexyl) phthalate (DEHP) 99.5% (Sigma-Aldrich), methacrylic acid 99% (MAA) (Sigma-Aldrich), ethylene glycol dimethacrylate (EGDMA) (Sigma Aldrich), 2,2'-azobisisobutyronitrile (AIBN) (Sigma-Aldrich), toluene, acetone, methanol (Grade HPLC), acetic acid pa, nitrogen gas, filter paper Whatman no. 41, aluminum foil, tissue paper, and distilled water.

2.2 Tools:

The equipment used in this study includes glassware which is commonly used in laboratories, analytical balance, shakers, water baths, sonicators, ovens, bottles, 100 and 1000 μL micropipettes, Fourier Transform Infrared (FTIR) spectrophotometers (Shimadzu, IRPrestige 21), Ultra spectrophotometers Violet Visible (UV-Vis) (Shimadzu, UV-2600), Surface Area Analyzer (SAA) (NOVA, 1200e), Scanning Electron Microscope

(SEM, Tescan Vega 3SB) and Energy Dispersive Spectroscopy (EDS) (JEOL, JSM-6510 LA).

The procedure in this study was divided into several stages, such as the synthesis of MIP and NIP, MIP characterization, MIP optimization (the influence of time and the effect of concentration), determination of capacity and kinetics of adsorption.

2.3 General procedure:

Synthesis of MIP and NIP

The DEHP liquid was pipetted 0.3944 mL (1 mmol) into a round bottom flask and 0.3393 mL (4 mmol) MAA monomers were added and then allowed to stand for 5 minutes. Then the mixture was added with a cross-linker EGDMA 1.5087 mL (8 mmol) and dissolved with 50 mL of toluene porogen solvent after being allowed to stand for 5 minutes. The pre-polymerization solution was then sonicated for 10 minutes then the nitrogen gas was flowed for 10 minutes to remove oxygen. Then the solution was added with 5 mL of AIBN initiator (1 mmol), then sonicated 15 minutes and flowed with nitrogen gas for 15 minutes in a row. The next step is polymerization carried out into a water bath at a temperature of 60°C for 24 hours [17]. The formed polymers then washed with acetone, methanol, and aquadest in sequence. After that the template molecule (DEHP compound) is extracted out of the polymer by sonicated using a mixture of methanol: acetic acid (9: 1 v / v) for 30 minutes, then the MIP is taken. The polymer is named MIP_DEHP_MAA-co-EGDMA_(BE) and after extraction is named MIP_DEHP_MAA-co-EGDMA_(AE) [18]. The extract was then tested with a UV spectrophotometer at a maximum wavelength to detect DEHP compounds. This procedure is repeated until the absorbance value of the extract becomes zero. Next, MIP was washed with methanol and distilled water to neutral pH, then dried and further characterized. Non imprinted polymers (NIP) are made without the use of printed molecules in the same way without the extraction process. This polymer is named NIP_MAA-co-EGDMA.

Preparation of DEHP 100 mg L⁻¹ Standard Solution

The DEHP liquid was piped 1.010 mL into a 10 mL volumetric flask, then fill with methanol until the mark and homogenized. Then standard solutions with varieties in concentrations of 3, 6, 9, 15, and 18 mg L⁻¹ were made.

MIP and NIP Adsorption Capability Test

MIP and NIP solids of 30 mg were added to each of the different vials prepared, then 5 mL of DEHP solution of 10 mg L⁻¹ was added to the vial. The mixture was shaken with a shaker for 60 minutes

at room temperature, then filtered and then the DEHP concentration in the filtrate was analyzed with a UV spectrophotometer at maximum wavelength. The amount of DEHP adsorbed in each gram of MIP and NIP is determined by equation:

$$q_e = \frac{(C_o - C_e)V}{W}$$

3. Results and Discussion

3.1 Synthesis of Molecularly Imprinted Polymers (MIP)

The MIP material was synthesized using precipitation polymerization method through molecular printing technique. The MIP material obtained is in the form of a fine white solid. The DEHP compound contained in the polymer was washed using sequential acetone and methanol, and sonication extracted several times to obtain the molecular molded polymer MIP_DEHP and DEHP compounds. They were tested qualitatively using UV spectrophotometer instruments at wavelengths of 270.5 nm (for methanol: acetic acid (9:1) solvents) and 264 nm (for methanol solvents). A sample solution containing DEHP compound will give the absorbance value to the instrument. The results of the tests on the washing solvent and extracts obtained can be seen in Tables 1 and 2.

Table 1.

Qualitative test of DEHP compounds in washing solvents with a UV spectrophotometer at a wavelength of 264 nm

Washing solvent	Absorbance
Acetone	4.431
Methanol	4.436

Table 2.

Qualitative test of DEHP compounds in methanol: acetic acid (9:1) mixture solvent extracts with a UV spectrophotometer instrument at a wavelength of 270.5 nm

Extraction	Absorbance
Extract 1	4.354
Extract 2	2.850
Extract 3	0.749
Extract 4	0.326
Extract 5	0.219
Extract 6	0.192
Extract 7	0.121
Extract 8	-0.015

Table 1 shows the absorbance values of the washing solvent both acetone and methanol on the UV spectrophotometer instrument. This illustrates that there are DEHP compounds that come out from

the MIP during the washing process. Table 2 shows the decrease in absorbance or absorption value of each extraction repetition until it reaches -0.015. This indicates that all DEHP compounds in MIP have been extracted. When compared with research conducted by Tabarestani et al. [17], the extraction process was carried out 10 times, while the extraction process of this study was only carried out 8 times until it reached an absorbance value of -0.015.

According to Shaikh [14], the polymerization stage that occurred in MIP_DEHP_MAA-co-EGDMA synthesis consisted of the pre-polymerization, polymerization, and DEHP extraction stages of the MIP matrix. The description of the reaction at each polymerization stage can be seen in Figure 1.

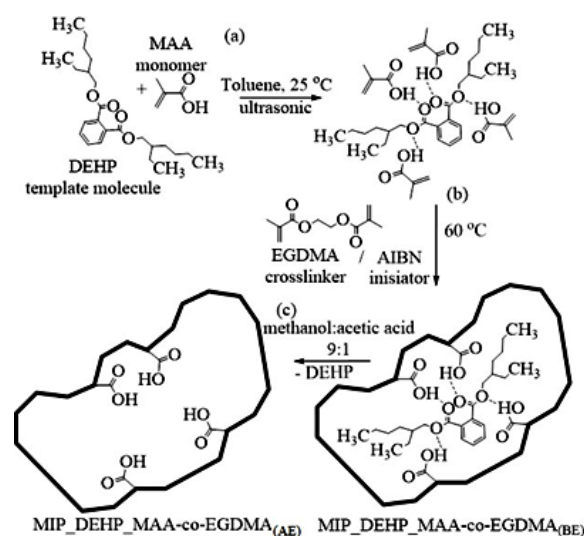


Fig. 1. Scheme of MIP_DEHP_MAA-co-EGDMA synthesis reaction, (a) pre-polymerization step, (b) polymerization step, and (c) extraction step

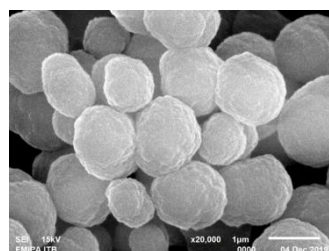
In the pre-polymerization step, monomers and DEHP firstly interact non-covalently through hydrogen bonds with the aid of toluene solvents. In the polymerization step, the EGDMA cross linker and the MAA monomer build the polymer matrix with the help of an initiator. This polymerization step consists of the initiation, propagation or extension of the chain and the termination stage. The next step is DEHP that contained in the polymer is released, to obtain an imprint with a functional group corresponding to DEHP as the target molecule. DEHP compounds can interact again non-covalently with the -COOH function groups found in the MIP through hydrogen bonds due to the suitability of shape, size, and functional groups. The success of MIP synthesis was evaluated through characterization with FTIR and EDS.

Characterization of NIP and MIP using EDS

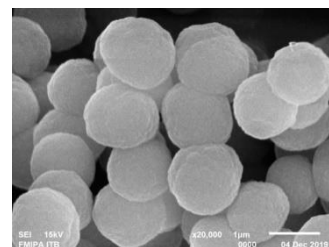
EDS analysis is carried out so that the composition of the main constituent atoms of each polymer can be known. The constituents of NIP_MAA-co-EGDMA, MIP_DEHP_MAA-co-EGDMA_(BE) and MIP_DEHP_MAA-co-EGDMA_(AE) atoms are C, O, and H, but the EDS data only displays percent C and O atoms because the mass of H atoms is very small, so it is difficult to detect by the instrument. The success of DEHP_MAA-co-EGDMA_(AE) MIP synthesis can be seen from the amount of atomic percent loss and carbon mass percent due to the release of DEHP from the polymer. EDS data on NIP_MAA-co-EGDMA, MIP_DEHP_MAA-co-EGDMA_(BE) and MIP_DEHP_MAA-co-EGDMA_(AE) can be seen in Table 3.

The percent C atom and percent mass C of MIP_DEHP_MAA-co-EGDMA_(BE) shown in Table 3 are higher than percent C atom and mass C percent of MIP_DEHP_MAA-co-EGDMA_(AE), while the value of atomic O and mass percent O is increased in MIP_DEHP_MAA-co-EGDMA_(AE) compared to MIP_DEHP_MAA-co-EGDMA_(BE). This is caused by the number of C atoms in DEHP which is far more than O atoms, so that when DEHP is still in the polymer the percent atom and percent mass C increase, whereas by the time DEHP has been released from the polymer the percent atom and mass percent O will increase and percent atom and percent C will decrease. The decrease in the value of percent C at MIP_DEHP_MAA-co-EGDMA (% C MIP_(BE) atom - % C MIP_(AE) atom) is 3.01% and the decrease in value of percent mass C in MIP_DEHP_MAA-co-EGDMA (% mass C MIP_(BE) - % mass C MIP_(AE)) is 2.52%, this proves that DEHP has escaped from the polymer. The small percent mass loss of C and percent of C atoms in the polymer is caused by the amount of DEHP as a template molecule contained in the polymer is very small compared to the mass percent of C and percent of the C atom in the polymer matrix formed from monomers and cross linkers.

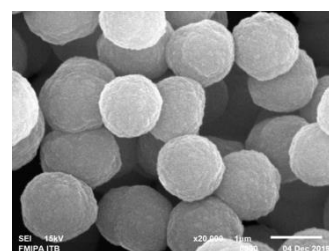
MIP_DEHP_MAA-co-EGDMA_(AE) which were characterized using SEM can be seen in Figure 2.



(a)



(b)



(c)

Fig. 2. Surface morphology (a) NIP_MAA-co-EGDMA 20,000x magnification, (b) MIP_DEHP_MAA-co-EGDMA_(BE) 20,000x magnification, (c) MIP_DEHP_MAA-co-EGDMA_(AE) 20,000x magnification

The surface morphology of the three produced polymers appears as a collection of small granules that having different grain sizes, densities, and textures. The surface morphology of the NIP_MAA-co-EGDMA appears to be composed of small grains whose shapes are not uniform, denser, and texture

Table 3.

EDS data from NIP_MAA-co-EGDMA, MIP_DEHP_MAA-co-EGDMA_(BE) and MIP_DEHP_MAA-co-EGDMA_(AE)

Element	% Mass			% Atom		
	NIP	MIP _(BE)	MIP _(AE)	NIP	MIP _(BE)	MIP _(AE)
C	78.33	80.14	77.13	82.80	84.31	81.79
O	21.67	19.86	22.87	17.20	15.69	18.21

Characterization of NIP and MIP using SEM

The surface morphology of NIP_MAA-co-EGDMA, MIP_DEHP_MAA-co-EGDMA_(BE), and

that looks rough. The surface morphology of MIP_DEHP_MAA-co-EGDMA_(BE) and MIP_DEHP_MAA-co-EGDMA_(AE) is composed of

round grains that tend to be uniform in size, less dense, and have a finer texture compared to NIP_MAA-co-EGDMA_(AE). The surface morphology of MIP and NIP using EGDMA cross linkers tends to be arranged relatively regularly when compared to using TRIM cross linkers [17], as well as using EGDMA cross linkers which are synthesized with a combination of silica gel [18].

Characterization of NIP and MIP using FTIR

The purpose of characterization using FTIR is that the success of synthesis based on functional groups that affect the formation of NIP and MIP can be known, based on changes in absorption intensity and shifting of wavenumbers in the FTIR spectrum. The FTIR spectrum of NIP_MAA-co-EGDMA, MIP_DEHP_MAA-co-EGDMA_(BE), and MIP_DEHP_MAA-co-EGDMA_(AE) are shown in Figure 3.

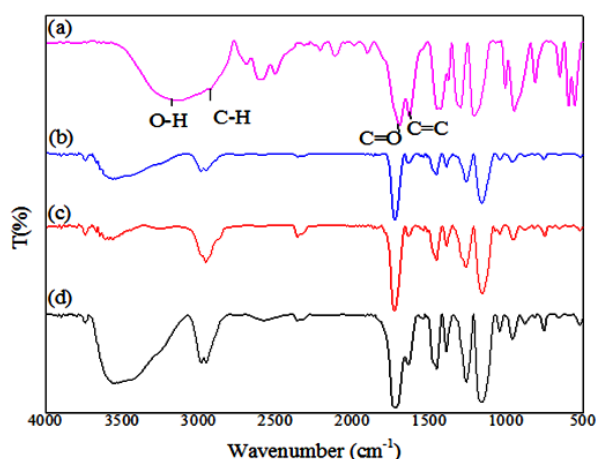


Fig. 3. FTIR Spectra (a) MAA, (b) NIP_MAA-co-EGDMA, (c) MIP_DEHP_MAA-co-EGDMA_(BE), (d) MIP_DEHP_MAA-co-EGDMA_(AE)

The polymer formation process involves the interaction between MAA and cross linkers causing the absorption peaks of the -OH, -CH, -C=O and -

shift in wave numbers and a change in intensity. The peak absorption of the -OH functional groups in the NIP_MAA-co-EGDMA spectrum, MIP_DEHP_MAA-co-EGDMA_(BE), and MIP_DEHP_MAA-co-EGDMA_(AE) changes compared to MAA monomers because the acidity of the monomer decreases after forming the polymer. Most of the stretch peaks in the MIP spectrum shift toward higher wave numbers after DEHP was printed and prove that DEHP has joined [19]. Based on data from Table 4, the -OH functional group in MIP_DEHP_MAA-co-EGDMA_(BE) and MIP_DEHP_MAA-co-EGDMA_(AE) experienced a very small wavenumber shift, but the absorption intensity of MIP_DEHP_MAA-co-EGDMA_(AE) is stronger than MIP_DEHP_MAA-co-EGDMA_(BE), it can be caused by the breaking of hydrogen bonds between the -OH functional groups on the polymer matrix with the imprinted molecule. The -OH functional group in NIP_MAA-co-EGDMA does not undergo a shift in wave numbers when compared to MIP_DEHP_MAA-co-EGDMA (TE) and has decreased in intensity due to lack of bonds or electrostatic bonds [20].

Table 4. Wavenumber data results of FTIR analysis for MAA, NIP_MAA-co-EGDMA, MIP_DEHP_MAA-co-EGDMA_(BE) and MIP_DEHP_MAA-co-EGDMA_(AE)

The FTIR spectrum of NIP_MAA-co-EGDMA, MIP_DEHP_MAA-co-EGDMA_(BE), and MIP_DEHP_MAA-co-EGDMA_(AE) shows sharp C-H absorption peaks and their intensity is strong compared to C-H absorption peaks in MAA. This can be caused by changes in carbon sp² to sp³ in NIP_MAA-co-EGDMA, MIP_DEHP_MAA-co-EGDMA_(BE), and MIP_DEHP_MAA-co-EGDMA_(AE) after the polymer is formed. The C-C=C function group on NIP_MAA-co-EGDMA, MIP_DEHP_MAA-co-EGDMA_(BE), and MIP_DEHP_MAA-co-EGDMA_(AE) experience a small wavenumber shift, as if there was no interaction. But the intensity of the functional group -C=C after the polymer is formed, namely NIP_MAA-co-EGDMA, MIP_DEHP_MAA-co-EGDMA_(BE)

Table 4.

Wavenumber data results of FTIR analysis for MAA, NIP_MAA-co-EGDMA, MIP_DEHP_MAA-co-EGDMA_(BE) and MIP_DEHP_MAA-co-EGDMA_(AE)

Functional Group	Wave number (cm ⁻¹)			
	Monomer MAA	NIP_MAA-co-EGDMA	MIP_DEHP_MAA-co-EGDMA _(BE)	MIP_DEHP_MAA-co-EGDMA _(AE)
-OH stretching	3400-3200	3562.52	3564.45	3562.52
-CH stretching	2929.87	2954.95	2956.87	2954.95
-C=O stretching	1697.36	1726.29	1728.22	1724.36
-C=C stretching	1631.78	1635.64	1637.56	1637.56

C=C functional groups of NIP and MIP undergoes a

and MIP_DEHP_MAA-co-EGDMA_(AE) is weaker

than MAA monomers. This proves that the initiation of the double bond is broken by the initiator through the reaction of radical polymerization on the monomer and the cross-linker forms the polymer matrix.

Interactions can also occur between the -OH functional groups contained in MAA monomers and the C-O groups found in DEHP to form hydrogen bonds so that the shift of the wavenumber of the functional groups C-O occurs in NIP_MAA-co-EGDMA, MIP_DEHP_MAA-co-EGDMA_(BE) and MIP_DEHP_MAA-co-EGDMA_(AE) although only slightly. Based on spectrum data, the bonds that play a role in the formation of NIP_MAA-co-EGDMA and MIP_DEHP_MAA-co-EGDMA are the same. The bonds are -OH, -CH, -C=O, and -C=C. The bands in region 2956.87 and 2954.95 cm⁻¹ were only observed in the spectrum of MIP with template molecule (Fig.3(c-d)). The O-H stretching of carboxylic acids from DEHP and C=C stretching in aromatic rings, respectively, which proves the presence of DEHP in the polymer matrix during polymerization [14]

Characterization of MIP using Surface Area Analyzer (SAA)

The Barret-Joyner-Hallenda (BJH) method is the basis for the characterization of pore diameters and volumes in MIP. This measurement is based on the results of isothermal adsorption at 77.35 K. The amount of N₂ gas adsorbed by the sample is the basis for calculating pore diameter and pore volume. The results of measurements of volume, surface area, and pore diameter are shown in Table 5.

Table 5. Results of analysis using SAA

Sample	Surface Area (m ² /g)	Total Pore Volume (cc/g)	Average Pore Radius (Å)
MIP_DEHP_MAA-co-EGDMA _(AE)	137.660	0.155	22.589

Based on the data in Table 5, the pore diameter in MIP_DEHP_MAA-co-EGDMA_(AE) is included in the mesoporous material because the average pore radius size is 22.589 Å. This is following the classification of pore size by IUPAC, which is: micro pore (pore radius <20 Å), mesoporous (20 <pore radius <500 Å) and macropore (pore radius > 500 Å). This mean pore radius is larger when compared to MIP synthesized using TRIM [17] and smaller than MIP synthesized with a combination of silica gel [18].

The surface area of MIP_DEHP_MAA-co-EGDMA_(AE) of 137.660 m²/g is smaller when compared to MIP synthesized using TRIM [17] and MIP synthesized with a combination of silica gel

[18]. Total pore volume for pores with a total diameter smaller than 1127.600 Å is 0.155cc/g. This volume is greater compared to MIP synthesized using TRIM [17] and smaller than MIP synthesized with a combination of silica gel [18]. BJH graphics showing pore distribution of MIP_DEHP_MAA-co-EGDMA_(AE) can be seen in Figure 4.

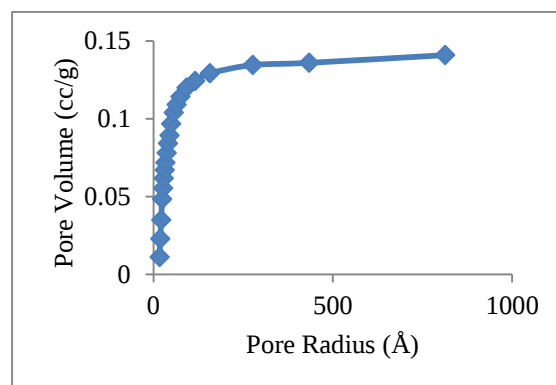


Fig 4. Relationship of pore diameter to the volume of N₂ adsorbed on MIP_DEHP_MAA-co-EGDMA_(AE)

The measured pore diameter range in MIP_DEHP_MAA-co-EGDMA_(AE) is between 17.014 Å to 812.991 Å where the pore size with a diameter of 17.014 Å adsorbs N₂ gas at 0.011 cc/g and diameter 813.990 Å to adsorb N₂ gas at most is 0.141 cc/g. Isothermal adsorption of N₂ on MIP_DEHP_MAA-co-EGDMA_(AE) can be seen in Figure 5.

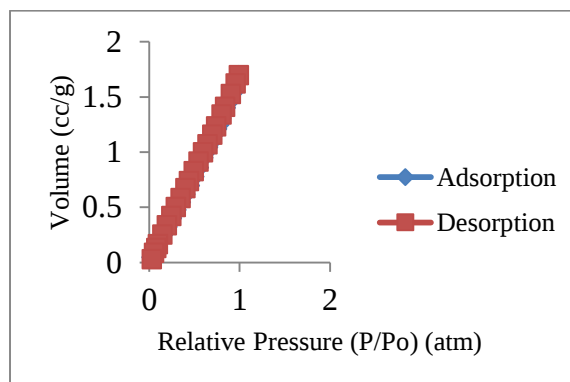


Fig 5. Relationship of relative pressure to the volume of N₂ absorbed in MIP_DEHP_MAA-co-EGDMA_(AE)

Figure 5 shows that the lower curve is the adsorption process where the volume increases with the increase in relative pressure, while the desorption process decreases in volume as the relative pressure decreases, the curve is shown at the top. MIP_DEHP_MAA-co-EGDMA_(AE) can absorb N₂

gas as much as 1.699 cc/g at a maximum pressure of 0.99 atm.

Characterization of MIP and NIP Adsorption Capabilities

MIP_DEHP_MAA-co-EGDMA_(AE) and NIP_MAA-co-EGDMA materials were tested for their adsorption capabilities. Polymers with good adsorption ability can be seen from the ratio of the amount of DEHP adsorbed by each MIP and NIP material. The amount of DEHP adsorbed on the polymer can be seen in Figure 6.

Figure 6 shows that MIP is better at adsorbing DEHP compared to NIP with a difference in the amount of DEHP adsorbed (Δq_e) of 0.212 mg/g. This is consistent the research reported by Shaikh [14] and [18] which also shows the superiority of MIP compared to NIP. Even though MIP adsorption performance is better than NIP, it is necessary to optimize various adsorption parameters such as contact time and concentration variations. This is intended to the known ability of the maximum adsorption capacity.

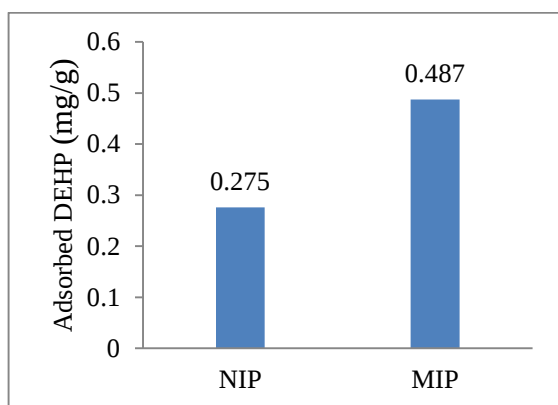


Fig. 6 The adsorption capability of MIP and NIP to diethylhexyl phthalate(DEHP)

4. Conclusions

It can be concluded that the functional material in the form of MIP_DEHP_MAA-co-EGDMA and NIP_MAA-co-EGDMA has been successfully synthesized using the precipitation polymerization method with the results in the form of white fine solids. SEM characterization results show the surface morphology of MIP_DEHP_MAA-co-EGDMA is composed of round grains that tend to be uniform in size, less dense, and have a smoother texture compared to NIP_MAA-co-EGDMA. The EDS characterization results showed a decrease in atomic percent and mass percent of C due to the extraction of DEHP in MIP_DEHP_MAA-co-EGDMA. The

results of the characterization with FTIR showed that the bonds that influenced the formation of polymers (NIP and MIP) were -OH, -CH, -C=O, and -C=C. The results of the SAA characterization showed a surface area of MIP 137.660 m²/g, a total pore volume of 0.155 cc/g, and an average pore radius of 22.589 Å which indicated MIP was a mesoporous material.

MIP_DEHP_MAA-co-EGDMA_(AE) adsorbed DEHP better than NIP_MAA-co-EGDMA. DEHP adsorbed (q_e) by MIP_DEHP_MAA-co-EGDMA_(AE) was 0.275 mg/g while NIP_MAA-co-EGDMA was only 0.487 mg/g. The difference value of the adsorbed DEHP (Δq_e) was 0.212 mg/g

5. Conflicts of interest

We as authors declare that there is no conflict of interest in the publication of the article.

6. Acknowledgments

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7. References

- [1] Xu X., Zhou G., Lei K., LeBlanc G.A., and An L., Phthalate Esters and Their Potential Risk in PET Bottled Water Stored under Common Conditions. *Int. J. Environ. Res. Public Health*, 17, 141 (2020), doi:10.3390/ijerph17010141.
- [2] Cao X.L., Determination of phthalates and adipate in bottled water by headspace solid phase microextraction and gas chromatography/mass spectrometry. *J. Chromatogr. A*, 1178, 231–238 (2008).
- [3] Montuori P., Jover E., Morgantini M., Bayona J.M., and Triassi M., Assessing human exposure to phthalic acid and phthalate esters from mineral water stored in polyethylene terephthalate and glass bottles. *Food Additive Contamination A*, 25(4):511-518 (2008)
- [4] Rowdhwal S.S.S., and Chen J., Toxic Effects of Di-2-ethylhexyl Phthalate: An Overview. *BioMed Research International*, Volume 2018 (2018).
- [5] United State Environmental Protection Agency (US EPA), Public Health Goal for Di(2-ethylhexyl)Phthalate (DEHP) in Drinking Water, *California Environmental Protection Agency*, California (1997).
- [6] Hennion M.C., 1999, Solid Phase Extraction: Method Development, Sorbents, and Coupling

- with Liquid Chromatography. *Journal Chromatography A*, **856**: 3-54.
- [7] Yang Y., Jianlong Y., Jie Y., Bing S., and Jing Z., Molecularly Imprinted Solid-Phase Extraction for Selective Extraction of Bisphenol Analogues in Beverages and Canned Food. *Journal of Agriculture and Food Chemistry*, **62**: 11130-11137 (2014).
- [8] Vasapollo G., Sole R.D., Margola L., Lazzoi M.R., Scardino A., Scoranno S., and Mele, G., Molecularly Imprinted Polymers: Present and Future Prospective, *International Journal of Molecular Science*, **12**: 5909-5945 (2011).
- [9] Kirsch N., Alexander C., Lubke M., Whitcombe M.J., and Vulfson E.N., Enhancement of Selectivity of Imprinted Polymers Via Post-Imprinting Modification of Recognition Sites. *Polymers*, **14**: 5583-5590 (2000).
- [10] Caro E., Marce R.M., Borrul F., Cormack P.A.G., and Sherrington D.C., Application of Molecularly Imprinted Polymer to Solid-Phase Extraction of Compounds from Environmental and Biological Samples. *Trends in Analytical Chemistry*, **25**: 143-154 (2006).
- [11] Fauziah S., Soekamto N.H., Taba P., and Amran M.B., Selectivity of β -Sitosterol Imprinted Polymers as Adsorbent. *Journal of Physics: Conf. Series* 979, 012059 doi :10.1088/1742-6596/979/1/012059 (2018)
- [12] Walsh R, Development and characterization of molecularly imprinted suspension polymers. Thesis. *Pharmaceutical and Molecular Biotechnology Research Centre Waterford Institute of Technology* (2010)
- [13] Mayes A.G., and Whitcombe M.J., Synthetic Strategies for the Generation of Molecularly Imprinted Organic Polymers. *Advanced Drug Delivery Review*, **57**: 1742-1778 (2005).
- [14] Shaikh H., Memon N ., Khan H., Bhanger M.I., and Nizamani S.M., Preparation and characterization of molecularly imprinted polymer for di(2-ethylhexyl) phthalate: Application to sample clean-up prior to gas chromatographic determination. *Journal of Chromatography A*, **1247**: 125-133 (2012).
- [15] Yan, H., dan Row, K.H., Characteristic and Synthetic Approach of Molecularly Imprinted Polymer. *International Journal of Molecular Science*, **7**: 155-178 (2006).
- [16] Cacho C., Turiel E., Martin A.E., Perez C.C., and Camara C., Characterisation and quality assessment of binding sites on a propazine-imprinted polymer prepared by precipitation polymerisation, *Journal of Chromatography B*, **802**: 347-353 (2004).
- [17] Tabarestani M.S., Rahnama K., Jahanshahi M., Nasrollanejad S., and Fatemi M.H., Synthesis of a Nanoporous Molecularly Imprinted Polymers for Dibutyl Phthalate Extracted from *Trichoderma harzianum*. *Journal Nanostructure*, **6**(3): 245-249 (2016).
- [18] Yang Z., Chen F., Tang Y., dan Li S., Selective Adsorption of Di(2-ethylhexyl) Phthalate by Surface Imprinted Polymers with Modified Silica Gel as Functional Support. *Journal of Chemistry Society Pak.*, **37**(5): 939-949 (2015).
- [19] Yusof N.F., Shimal F., Mehamod, and Suah F.B.M., Synthesis and Evaluation of Bis(2-Ethylhexyl) Phthalate-Imprinted Polymers in an Aqueous Medium. *Malaysian Journal of Chemistry*, **2019**, Vol. **21**(3), 50-58 (2019).
- [20] Jin Y.F., Zhang Y.J., Zhang Y.P., Chen J., Zhou X.M., and Bai L.Y., 2013, Synthesis and Evaluation of Molecularly Imprinted Polymer for the Determination of the Phthalate Esters in the Bottle Beverages by HPLC, *Journal of Chemistry*, **2013**: 1-9 (2013)