The synthesis of magnetic molecularly imprinted polymer against di-(2-ethylhexyl)phthalate

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Abstract. Magnetic molecularly imprinted polymer (MMIP) was prepared against di-(2-ethylhexyl)phthalate, using methacrylic acid as a functional monomer, ethylene glycol dimethacrylate as a crosslinker and benzoyl peroxide as an initiator. MMIP was characterized using Scanning Electron Microscope and infrared spectrophotometer. IR spectrum shows successful preparation of MMIP. The peak at 586 cm\(^{-1}\) is a typical vibration of Fe-O. The strong peaks at 1728 cm\(^{-1}\), 1261 cm\(^{-1}\), and 1153 cm\(^{-1}\) are stretching vibration of C=O and C-O of methacrylic acid and DEHP. The peak at 1462 cm\(^{-1}\) due to C-C aromatic vibration of DEHP. A broad absorption band at 3468 cm\(^{-1}\) due to the stretching vibration of hydroxy bonds between target molecule and functional monomer. The MMIP has a spherical morphology and pores that important for adsorption process. Experimental results show the potential of magnetic molecularly imprinted polymer for recognition of di-(2-ethylhexyl) phthalate.

1. Introduction
Di(2-ethylhexyl)phthalate (DEHP) or dioctylphthalate is specified as phthalate esters group. This compound used as a plasticizers, an additive compound that added to improve the flexibility of plastic, especially for polyvinyl chloride. This compound also used in many products such as medical device, plastic furniture, baby clothes, vinyl flooring, some toys, shoes, shower curtains and packaging material [1]. DEHP is physically dispersed on the surface of polymer so it will leach out to the environment easily [2]. DEHP has harmful effects on animal and human health [3]. Earlier study by the US Environmental Protection Agency (USEPA) showed that this compound classified as a pollutant that act as endocrine disruptors compound (EDG) [4],[5]. DEHP also causes endometriosis in woman, and also gives effects on fetus, heart, kidneys, lungs, and liver [6].

Gas chromatography and liquid chromatography are the common method to analyze DEHP. Sometimes, another separation method is needed before chromatography analysis to concentrate the DEHP from a complex sample [7]. Adsorption is one of the common separation method for organic compounds because of its easy operation [8],[9],[10]. Some adsorbents such as chitosan [11], nanoporous gold polyethyleneimine [12], and graphene [13] were used to adsorbed DEHP. Unfortunately, these adsorption methods has poor selectivity for recognition of DEHP [2].

Recently, researchers were used molecularly imprinted polymer to improve the selectivity of the adsorbent. This polymer has a specific recognition sites towards the template [14]. The monomer could interact with the target molecule through covalent or non covalent interaction, resulting prepolymerization complexes[15]. Polymerization took place with the presence of initiator and crosslinker. The template (target molecule) were extracted from the polymers to form a recognition sites [16]. Bulk polymerization is a common synthetic method. However, MIPs synthesized by these methods
have an irregular shape, the polymer have heterogeneous binding sites, and the template were hard to completely removed [17]. These problems could be minimalized by surface molecularly imprinted polymer.

Magnetic molecularly imprinted polymers (MMIPs) is one of the surface imprinting technology. In this method, polymerization took place on the surface of magnetit. The MMIPs have advantages such as fast binding and separation due to the magnetic properties and have uniform shape so that the polymers doesn’t need to be ground [18]. In conventional method, polymer separated by filtration or centrifugation. In MMIPs, polymer separated from the solution easily using a magnetic field [19].

In this paper, a new magnetic molecularly imprinted polymers (MMIPs) were prepared using DEHP as a template, Fe₃O₄ particles as a core, ethylene glycol dimethacrylate as a crosslinker, methacrylic acid as a functional monomer, and benzoyl peroxide as an initiator. The MMIPs were characterized using Fourier transform infrared (FTIR) and scanning electron microscopy (SEM).

2. Materials and Methods

2.1. Chemicals
d(2-ethylhexyl) phthalate (DEHP) (>99.5%) were obtained from Sigma Aldrich. Methacrylic acid (MAA), benzoyl peroxide (BPO), acetonitrile, ethylene glycol dimethacrylate (EGDMA), iron (III) chloride (FeCl₃·6H₂O), iron (II) chloride (FeCl₂·4H₂O), polyvinylpyrrolidone (PVP), oleic acid, methanol, sodium hydroxide, acetic acid glacial, ethanol, , were analytical grade and obtained from Merck.

2.2. Synthesis of MMIPs
In the first step, the Fe₃O₄ particles was synthesized by the co-precipitation method [20]. Iron (II) and iron (III) were dissolved in 100 ml water with the comparation 1:2. The solution were then stirred with the presence of nitrogen gas in a hotplate at 80°C. Sodium hydroxide (2 M) were added dropwise to the mixture resulting a change of color solution from orange to black. The black precipitant is Fe₃O₄ particle that could separated from the solvent using external magnetic field. The Fe₃O₄ then washed with water and ethanol several times. The Fe₃O₄ were dried in the oven at 60°C. After that, 1 g of Fe₃O₄ mixed with 1 mL of oleic acid, then the mixture were sonicated for 15 min.

MMIPs were synthesized by mixing DEHP (1 mmol) and methacrylic acid (4 mmol) in acetonitrile (30 mL). In another glass, 20 mmol EGDMA mixed with 1 g Fe₃O₄- oleic acid. The complex solution of DEHP and MAA was added to this mixture and then sonicated for 30 minutes. This was a pre-polymerization solution. In another glass, 0.4 g PVP was dissolved in 100 ml ethanol (80%) then stirred with the presence of nitrogen gas at 400 rpm. This solution was added to the pre-polymerization solution. After that, BPO (150 mg) was added to the solution. The nitrogen gas was added to the solution for 10 min. Polymerization took place in an oil bath (70°C) with continuous stirring for 1 hour, resulting MMIPs that could separated from the solution using magnetic field. The template were removed by washing the polymer with a methanol:acetic acid solution (9:1, v/v) several times until no DEHP detected. Then, the MMIPs were dried in the oven at 60°C. The magnetic non-molecularly imprinted polymers (MNIPs) were prepared with the same procedure without the presence of DEHP.

2.3. Characterization
The morphology of MMIPs were observed by Scanning Electron Microscope (SEM JSM-6510A). FTIR spectra of MMIPs, MNIPs and Fe₃O₄ were obtained by Jasco FTIR-4200.

3. Results and Discussion
3.1. **Synthesis of MMIPs**

The MMIPs and MNIPs were synthesized by surface imprinting method. The polymerization took place on the surface of Fe$_3$O$_4$. Fe$_3$O$_4$ were obtained by reacting iron (II) and iron (III) in an alkaline conditions. The surface of Fe$_3$O$_4$ were modified using oleic acid. The hydroxy group on the surface of Fe$_3$O$_4$ would react with carboxylic group of oleic acid. The next step is polymerization using DEHP, MAA, and EGDMA with the mol ratio 1:4:20. The specific sites of the polymer were due to the non covalent interaction between DEHP and methacrylic acid. DEHP has four oxygen atoms that could interact with hydroxy functional group in methacrylic acid through hydrogen bond. Moreover, there could be a van der Waals forces between long alkyl chain of DEHP with the polymers. The DEHP were extracted from the polymers by eluting the MMIPs with MeOH: acetic acid (9:1, v/v) and dried in oven at 60°C. In this synthesis method, MMIPs doesn’t need to be grounded and sieved because the polymer was fabricated on the surface of magnetite and it expected to have more uniform particular size. This is one of the advantage of surface polymerization method over conventional method that time consuming. The separation of MMIPs from the solution was done by using external magnetic field while in conventional method polymers should be filtrated or centrifugated. **Figure 1** show the synthesis scheme of MMIPs.

![Synthesis scheme of MMIPs](image)

**Figure 1.** Synthesis scheme of MMIPs.

3.2. **SEM analysis**

The morphology of MMIPs were shown in **Figure 2**. The MMIPs have a pores and the particles were spherical. The pores on the surface of the polymers was useful in the adsorption process. In the synthesis process, DEHP interact with methacrylic acid by hydrogen bonding and van der Waals forces. After template removal, it will produce cavities due to the shape, size and functional group of DEHP. However, further study was needed to ensure the formation of a specific cavities of MMIP towards DEHP.
3.3. FTIR analysis

The prepared Fe$_3$O$_4$-oleic acid, MMIPs and MNIPs were characterized by FTIR. The IR spectra was shown in Figure 3. The presence of Fe$_3$O$_4$-oleic acid was confirmed from the peak 586 cm$^{-1}$ that was an absorption band of Fe-O bond. The Methacrylic acid as a monomer could be seen at peak 1728 cm$^{-1}$ confirmed the presenc of C=O from MAA. The peak at 1153 cm$^{-1}$ and 1261 cm$^{-1}$ were vibration of C-O in MAA. The C-H vibration at 2954 cm$^{-1}$ was atributed to oleic acid. The presence of DEHP was confirmed at 709 cm$^{-1}$. The presence of C=C aromatic shown at 1600 cm$^{-1}$ and 1462 cm$^{-1}$. The band at 3468 cm$^{-1}$ in the curve (c) atributed to the hidroxy bond interaction between DEHP and MAA.

![Figure 3. Infrared spectra of oleic acid-coated Fe$_3$O$_4$ (a), MNIPs (b), MMIPs (c) and DEHP (d).](image)

Nevertheless, there is still a challenge to ensure the formation of a specific pores of MMIP in molecular level. Further characterization such as Brunauer Emmet Teller could provide the differences of surface area beetween MMIP and MNIP. Furthermore, selectivity study using another compound that similar to DEHP in an adsorption process was needed to proves the succesful fabrication of specific pores of MMIP.
4. Conclusions
A new magnetic molecularly imprinted polymers were prepared against DEHP. The morphology and IR spectra of MMIPs were characterized. SEM image show that MMIPs have pores and a spherical morphology. The infrared peaks at 1153 cm\(^{-1}\), 586 cm\(^{-1}\), 1462 cm\(^{-1}\), 2358 cm\(^{-1}\), 709 cm\(^{-1}\), 3468 cm\(^{-1}\), 2954 cm\(^{-1}\) and 1728 cm\(^{-1}\) confirmed the presence of EGDMA co-MAA polymers, respectively. However, further study was needed to investigate the adsorption performance of MMIP towards DEHP.

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