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M. Cholid Djunaidi, Arifatul Azizah, and Gunawan



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Synthesis of Molecularly Imprinted Polymer Urea Based on Polyeugenol with Ethylene Glycol Dimethacrylate As Crosslinking Agent

M Cholid Djunaidi^{1,a)}, Arifatul Azizah¹, Gunawan¹

¹*Analytical Chemistry Laboratory, Department of Chemistry, Faculty of Science and Mathematics, Diponegoro University, Jl. Prof. Soedharto SH., Tembalang, Semarang 50275, Indonesia*

^{a)}Corresponding author: choliddjunaidi@live.undip.ac.id

Abstract. In this research, the synthesis of molecularly imprinted polymer (MIP), Polyeugenol was used as a base polymer with EGDMA as the crosslinker. This research aims to produce a urea selective adsorbent. Polyeugenol produced from eugenol was bind with urea templates and cross-linked with EGDMA in a chloroform solvent and initiator 2, 2' azo-bis (2-methylpropionitril) (AIBN) producing a MIP. A non imprinted polymer (NIP) is also used in this study for comparison. Analysis of polymers and adsorbent characterized by FTIR spectrophotometer and SEM followed by adsorption test. MIP has higher adsorption results than the NIP. Besides, the size of urea, creatinine and vitamin B12 also affects the adsorption process. MIP and NIP adsorbent have adsorption percentages of urea > creatinine > vitamin B12 which are 32.51, 26.17, and 2.85% for MIP and 15.70, 9.40 and 1.90% for NIP respectively.

INTRODUCTION

Urea is a chemical compound that can be formed biologically in the body of living beings, whether human, animal or plant [1]. Urea is a metabolic waste compound that excreted from the body through urine. Excreted urea amount varied depending on the amount of urea in the blood. Urea levels in the blood reflect the balance between production and excretion. Normal urea levels in the blood (serum) ranged from 6-20 mg/dL or equal to 9.99×10^{-4} – 3.33×10^{-3} M. In women, normal levels of urea ranges from 6-20 mg/dL; in men ranged from 8-20 mg/dL. Whereas in children are ranged from 5-18 mg/dL [2].

Adsorption or entrapment is a process that occurs when a fluid, liquid or gas, is bound to a solid or a liquid and eventually formed a thin coat or film on the surface. Material that could adsorb substance is called adsorbent while the adsorbed substance is called adsorbate [3]. One method of producing a selective adsorbent is trough the molecularly imprinted polymer (MIP) method. MIP is a synthesis method of a polymer that has a recognizing ability for a targeted ion. Eugenol may also be used as a starting material for the synthesis of a new compound because of the three functional groups that were attached to it, namely allyl, hydroxyl, and methoxy group [4].

Research that has been conducted by [5] produced MIP using polyethylene glycol diglycid ether (PEGDE) as a cross-linking agent. Phenol selective MIP was synthesized and proved to adsorb phenol far more than compounds with similar structures like vanillin. Besides involving functional groups, MIP phenols also tend to works by involving imprinted molecular bonding. In this research, synthesis of molecularly imprinted particles (MIP) was done using eugenol derivates in the form of polyeugenol and using ethylene glycol dimethacrylate (EGDMA) as a crosslinker. The synthesized MIP with urea template is expected to show an increase in adsorption towards urea.

EXPERIMENTAL

The materials used in this study are eugenol p.a. (4-allyl-2-methoxyphenol) (SIGMA Aldrich), trifluoroborane ($\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$) (SIGMA Aldrich), methyl alcohol p.a. (CH_3OH) (Merck), distilled water, trichloromethane p.a. (CH_2Cl) (Merck), ethylene glycol dimethacrylate (EGDMA) (2-(2-methylprop-2-enoyloxy)ethyl 2-methylprop-2-enoate) (SIGMA Aldrich), AIBN (2,2', azobis (2-methylpropionitril) (SIGMA Aldrich), and technical anhydrous Na_2SO_4 (Merck).

The equipment used in this study is a set of reflux tools, a set of chemical glassware, analytical balance (OHAUS), pH meter (TRANS Instruments), Whatman filter paper (GE Healthcare), stirrer (Lab Tech), Ubbelohde viscometer, 100 mesh sieve, UV-Vis spectrophotometer (LW-V-200-RS), FTIR (Shimadzu prestige 21) and SEM (pro phenom X desktop SEM with EDX).

Synthesis of Polyeugenol

Five grams of eugenol were put in a three-neck flask and then added with 1 mL of trifluoroborane. The mixture is stirred using a stirrer for 4 hours with the addition of trifluoroborane as much as 0.25 mL every 1 hour. The reaction was carried in room temperature. After the reaction lasted 4 hours, the polymerization was stopped by adding 1 mL of methanol. The gel is formed and then diluted with diethyl ether and washed with distilled water until a neutral pH. The solution is then dried by adding anhydrous Na_2SO_4 . After totally free of water, the solution is evaporated at room temperature. The precipitate was dissolved with distilled water, dried and weighed. The results were analyzed by FTIR.

Synthesis of Molecularly Imprinted Polymer (MIP)

Polyeugenol (0.5 g) was stirred with a solution of 1000 ppm urea for 24 hours. The mixture was filtered with filter paper and dried. The resulted polyeugenol-urea were used as much as 0.222 grams and crosslinked with 0.4 mL EGDMA, mixed with 1.67 mL of chloroform and added with 0.48 mL of AIBN initiator. The mixture was refluxed until the temperature reached 110 °C. The resulted precipitate was then dried and sieved using 100 mesh sieve. A total of 0.5 g of the resulting resin-bound urea were removed during a 24-hour aquabidest produce resin MIP 100 mesh. The release of urea in the analysis using a UV-Vis spectrophotometer. MIP characterization was done by FTIR and SEM-EDX.

Synthesis of Non- Imprinted Polymer (NIP)

NIP synthesis is done in the same way with the MIM but without being contacted with urea solution. NIP characterization was done by FTIR and SEM-EDX.

Urea Adsorption

Adsorbent (0.125 g) was used to adsorb 10 mL of urea 200 ppm. The process was done while being stirred for 8 hours. Followed by filtration using Whatman filter paper and then the filtrate was analyzed using a UV-Vis spectrophotometer. This test is performed on the MIP and NIP as a comparison.

Creatinine Adsorption

Adsorbent (0.125 g) was used to adsorb 10 mL of creatinine 25 ppm. The process was done while being stirred for 8 hours. Followed by filtration using Whatman filter paper and then the filtrate was analyzed using a UV-Vis spectrophotometer. This test is performed on the MIP and NIP as a comparison.

Vitamin B12 Adsorption

Adsorbent (0.125 g) was used to adsorb 10 mL of vitamin B12 35 ppm. The process was done while being stirred for 8 hours. Followed by filtration using Whatman filter paper and then the filtrate was analysed using a UV-Vis spectrophotometer. This test is performed on the MIP and NIP as a comparison.

RESULTS AND DISCUSSION

Synthesis and Characterization of Polyeugenol

Polymerization of eugenol produced a solid form of orange powder with a yield of 95.37% with a molecular weight of 6127.16 Daltons ($n = 37$). Characterization of polyeugenol was done using FTIR and the result can be seen in Fig. 1.

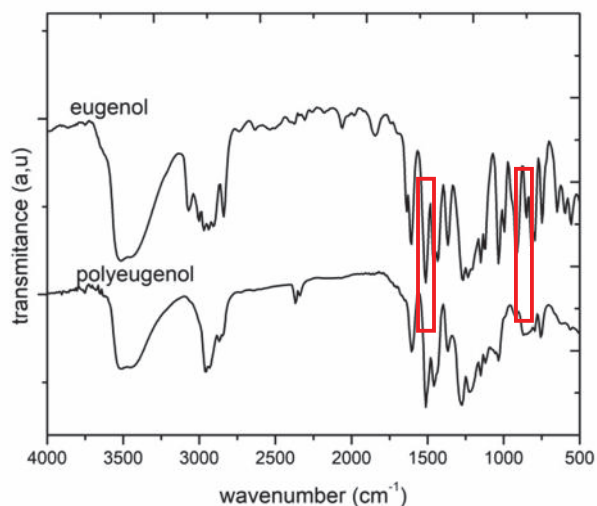


FIGURE 1. Comparison of eugenol and polyeugenol FTIR results

Figure 1 showed that the loss of group C=C on the wavelength range of $1648-1638\text{ cm}^{-1}$ for spectra of eugenol and were strengthened by the disappearance of the vinyl group at wavelength 915 cm^{-1} , 997 cm^{-1} . This indicates the possibility that polymerization has occurred.

Synthesis of MIP and NIP

Urea was contacted with polyeugenol to create a urea-form cavity in the polyeugenol membrane by releasing urea afterwards, which will give the membrane the ability to identify or bind a specific target molecule (urea) in related compounds. A successful polyeugenol contacting with urea can be seen from the results of the analysis of the concentration of urea solution before and after contacting procedure with UV-Vis spectrophotometer. The result calculated from determining the before and after value of UV-Vis spectrophotometry analysis showed that about 16-18% of urea is in contact with polyeugenol. Characterization of polyeugenol with urea was done by FTIR and the result was as seen in Fig 2.

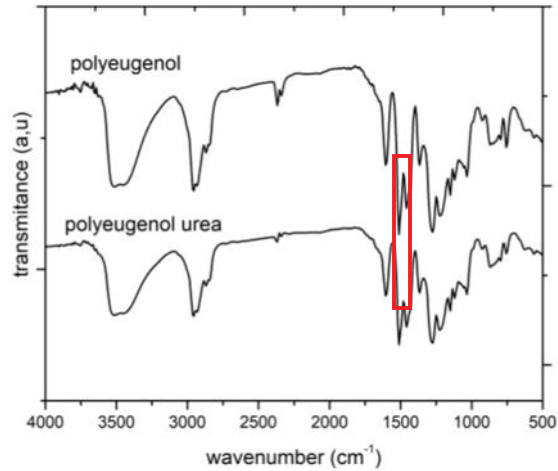


FIGURE 2. FTIR comparison result of polyeugenol and polyeugenol-urea compound

Based on the results of the functional group's spectral graph using FTIR, N-H bending was possible to be present in the Polyeugenol-urea spectra [6, 7], so it is possible for a shift to happen in the absorption range of 1660-1560 cm^{-1} . The absorption area can be further explained by the analysis using Fityk software as seen in Fig. 3 and Fig. 4.

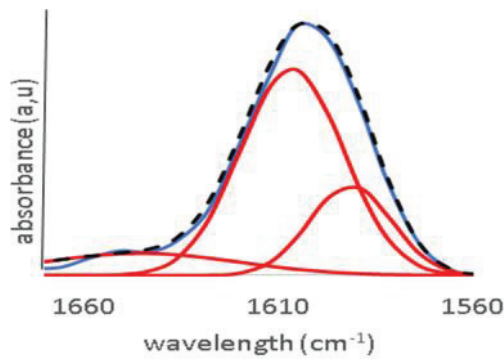


FIGURE 3. Polyeugenol absorption spectra at 1660 to 1560 cm^{-1}

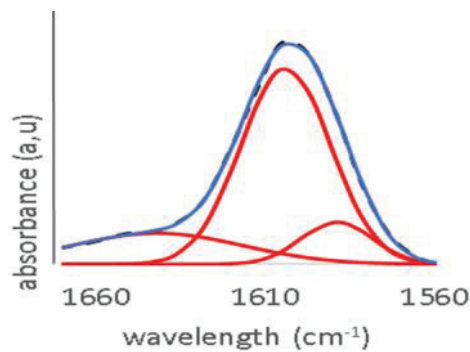


FIGURE 4. Polyeugenol-urea absorption spectra at 1660-1560 cm^{-1}

Based on the results of the FTIR spectra graph as seen in Fig.5, the emergence of carbonyl (C=O) peak at wave numbers around 1700 cm^{-1} indicates the presence of a crosslink agent (EGDMA) which have carbonyl acid group. In the MIP spectra, the -OH group is sharper than the NIP. This is because of the template that has been released by the distilled water. This showed the role of the -OH working in the MIP [8].

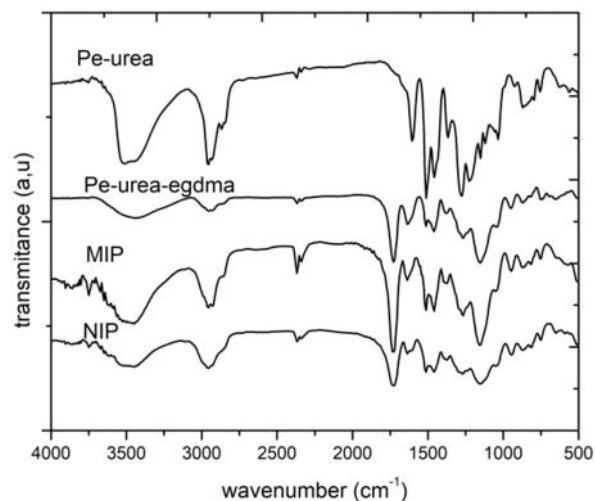


FIGURE 5. Comparison of MIP and NIP FTIR results

Analysis of SEM-EDX MIP and NIP

Figure 6 shows the surface morphology of the adsorbent. MIP has a pore size of 4.10 μm pore while NIP is 3.17 μm . MIP pores are bigger possibly because of the space that was used for template molecule that has been released from the membrane, leaving a cavity. EDX analysis of the results shown in Table 1 showed that the composition of C, N and O were random and irregular, so it cannot be assumed that the urea that was bound is already released.

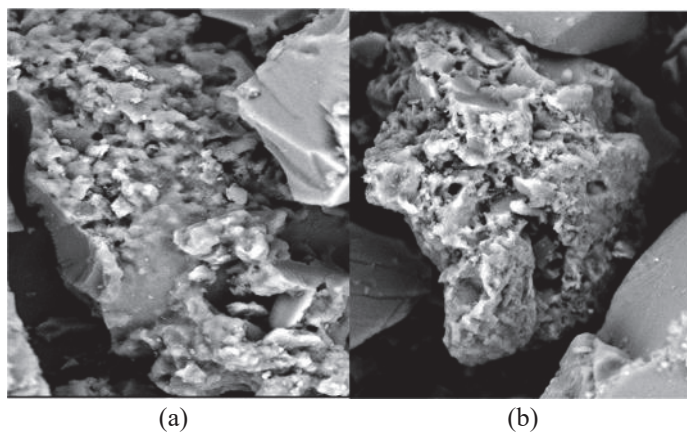


FIGURE 6. SEM results of the surface morphology form with 2000x magnification for a) MIP b) NIP

TABLE 1. Elements mass percentage in adsorbent

Elements	Mass (%)	
	MIP	NIP
C	40.3	39.8
O	25	27.6
N	34.7	32.6

Adsorption of MIP and NIP

Results showed that MIP adsorption is greater than the NIP. The MIP urea adsorbent performs better than the NIP one (non-imprinted). Besides, the size of urea, creatinine and vitamin B12 also affects the adsorption process. It is caused by the size difference. Urea and creatinine have the size of 60 and 113 Daltons respectively [9] while

vitamin B12 has a size of 8.5 Å or 1.35 kDa [10]. In Fig 7, it indicates the MIP and NIP adsorbents have adsorption percentage of urea > creatinine > vitamin B12. The adsorbed percentage for urea, creatinine and vitamin B12 in sequence are: 32.51, 26.17, and 2.85% for MIP, while with NIP: 15.70, 9.40, and 1.90%.

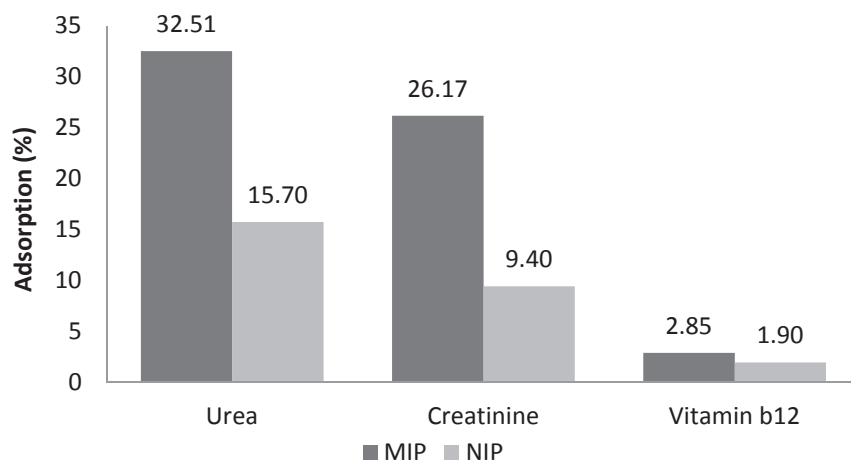


FIGURE 7. Adsorption comparison of the MIP and NIP for urea, creatinine, and vitamin B12

CONCLUSIONS

MIP showed better adsorption towards urea compared to its competitor with adsorption percentage of 32.51, 26.17 and 2.85% for urea, creatine and vitamin B12 respectively. MIP showed better adsorption towards urea compared to NIP.

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