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The Impact of Template Types on Polyeugenol to the Adsorption Selectivity of Ionic Imprinted Polymer (IIP) Fe Metal Ion

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Abstract. The synthesis of IIP was carried out by variation of Fe(III) ion templates from $Fe(NO_3)_3$, $K_3[Fe(CN)_6]$ and $NH_4Fe(SO_4)_2$ compounds which then tested IIP selectivity to the Fe metal ions through adsorption process. Ionic Imprinted Polymer (IIP) is a method of printing metal ions bound in a polymer, subsequently released from the polymer matrix to produce a suitable imprint for the target ion. The purposes of this study were to produce IIP from $Fe(NO_3)_3$, $K_3[Fe(CN)_6]$ and $NH_4Fe(SO_4)_2$ templates, to know the effect of templates on adsorption selectivity of IIP involving imprint cavity, and to know the impact of metal competitor on the selectivity adsorption of IIP to the Fe metals. The results obtained showed that IIP synthesized by variations of $Fe(NO_3)_3$, $K_3[Fe(CN)_6]$ and $NH_4Fe(SO_4)_2$ templates were successfully synthesized. The adsorption selectivity of Fe (III) metal ion in the $Fe(NO_3)_3$ template was greater than that of in the $K_3[Fe(CN)_6]$ and $NH_4Fe(SO_4)_2$ templates. The adsorption selectivity of Fe was greater on Fe-Cr compared to on Fe-Cd and Fe-Pb.

1 Introduction

Heavy metal pollution has become a global problem along with the increasing of industrialization, mining, laboratory and daily activities. Heavy metals have detrimental effects on the environment even in very low concentration. High level of Fe (iron) contained in the water influences its use, for example, concentrations of Fe content in water exceeding 1 mg/L will cause the color of the water becomes reddish, stains on the equipment and materials becomes white. World Health Organization, WHO (World Health Organization) limits the content of Fe in drinking water 0.3 mg/L [1].

One of the latest techniques developed for the preparation of highly effective adsorbents is the use of Ionic Imprinted Polymer (IIP), in which the synthesis material contains very specific receptor sites to the target compounds [2]. The advantages of IIP are easy and effective preparations for making polymer media having a specific molecular identifier for target compounds [3]. IIP can recognize and bind the desired target ions with high affinity and selectivity, due to the high cross-linking properties of the polymer in IIP material, it is stable and robust. The selectivity of IIP is determined by several factors, namely, the presence of template ion and crosslinking agent [4].

Eugenol as a natural ingredient of Indonesia has been utilized for the separation of metal ions. Eugenol can also be used as a starting material for the synthesis of a compound because of the presence of three functional groups attached to it, i.e., alkyl groups, hydroxy and methoxy. Through the allyl group, eugenol can be polymerized into polyeugenol which is the starting material for the synthesis of IIP [5-8].

In this research, the synthesis of IIP was conducted by using polyeugenol with variation of sources of Fe (III) template, namely, $Fe(NO_3)_3$, $K_3[Fe(CN)_6]$ and $NH_4Fe(SO_4)_2$, which was then crosslinked with PEGDE (Polyethylene glycol diglycidyl either) for selectivity test to Fe metal.

2 Experimental Method

The first stage of the research was the synthesis of polyeugenol from eugenol. Furthermore, IIP synthesis with Fe (III) ion templates from $Fe(NO_3)_3$, $K_3[Fe(CN)_6]$ and $NH_4Fe(SO_4)_2$ cross-linked using PEGDE. Subsequently, Fe ion contained was then released from the polymer formed using acid, the acid filtrate was added KSCN complexing agent which then tested using UV-Vis spectrophotometer. The final stage was the adsorption test of the product in which the adsorbent had been contacted with the binary Fe metal mixtures for 24 hours. The adsorption filtrate was analyzed by Atomic Absorption Spectrometer (AAS).

*Tools***:** Laboratory glassware, reflux apparatus, analytical balance, magnetic stirrer, spatula, pH meter, fine filter paper, UV-Vis Spectrophotometer, Atomic Absorption Spectroscopy (AAS), and FTIR.

*Materials***:** Eugenol p.a. (SIGMA Aldrich), anhydrous Na_2SO_4 technical grade (Merck), BF_3-diethyl ether (SIGMA Aldrich), HCl (Merck), NaOH p.a. (Merck), chloroform p.a. (Merck), methanol p.a. (SIGMA Aldrich), Poly Ethylene Glycol Diglycidyl Ether (PEGDE) (SIGMA Aldrich), KSCN (Merck), Aquabidest, $K_3[Fe(CN)_6$ (Merck), $NH_4Fe(SO_4)_2$ (Merck), $Fe(NO_3)_3$ (Merck), $Cr(NO_3)_3$ (Merck), $Pb(NO_3)_2$ (Merck), $Cd(NO_3)_2$ (Merck).

Experimental procedures

Material Preparation

Preparation of 50 ppm Fe (III) solution from 1000 ppm $Fe(NO_3)_3$ solution. 5 ml of $Fe(NO_3)_3$ 1000 ppm was diluted in 100 mL measuring flask with distilled water up to meniscus. The preparation of 50 ppm Fe (III) solution from $K_3[Fe(CN)_6]$ that was 29.4 mg of $K_3[Fe(CN)_6]$ was dissolved in 100 mL of distilled water. The preparation of 50 ppm Fe (III) solution from $NH_4Fe(SO_4)_2$ that was 43.05 mg of $NH_4Fe(SO_4)_2$ was dissolved in 100 mL of distilled water.

Synthesis of Polyeugenol [5-8].

Synthesis of IIP with Template Variation

0.5 g (0.003 mol) of poly eugenol was stirred with 50 ppm of Fe (III) ion which was conditioned at pH 3 for 24 h, then the result was filtered with filter paper and dried at room temperature. At this stage, the Fe (III) templates used were from $Fe(NO_3)_3$, $K_3[Fe(CN)_6]$ and $NH_4Fe(SO_4)_2$. After forming of Polyeugenol-Fe powder then each was crosslinked with 0.96 g (1 mol) of PEGDE and catalyzed using 20 mL of NaOH 1 M. The mixture had been refluxed at 80-90 °C for 15 minutes, the results were filtered and neutralized with aquabidest. The results in the form of precipitate (resin) were then heated at 110 ºC for 6 hours. The resulting resin was then added HCl to release Fe (III) ion bound for 24 hours and the acid filtrate was subsequently added by KSCN complexing agent and then tested using UV-Vis spectrophotometer. After the filtrate did not form red color (6 days) when KSCN was added, it was filtered, and the result (IIP) was dried.

NIP Synthesis

NIP was synthesized in the same procedure as IIP; however, without the binding of Fe (III) ions. Characterization of IIP and NIP was undertaken using FTIR.

Synthesis of NIP Acid

The procedure of the NIP acid preparation was the same as NIP preparation, but at the end of the procedure, the polymer was immersed in 0.5 M HCl and stirred for 24 hours by 6 days.

Adsorption Experiment
50 mg of adsorbent was contacted with a mixture of 10 ml of 10 ppm Fe (III) ion and 10 ppm of competitor ion for 24 hours at a constant velocity. The mixture was filtered through fine filter paper, and the Fe (III) concentration in the filtrate was determined using AAS.

Adsorption Selectivity Test
It was performed on competitive adsorption of binary solution consisting of Fe (III)/Cd (II), Fe (III)/Cr (III), Fe (III)/Pb (II) and compared with NIP.

3 Results and discussion

3.1 Synthesis of Polyeugenol [5-8]
The mechanism of formation of polyeugenol and characterization was published by Djunaidi *et al*. 2015)

3.2 Synthesis of IIP with Template Variation
The synthesized polyeugenol was bound to 50 ppm of Fe (III) ion (pH 3) using contacting them for 24 hours through stirring. The templates used were variation of $Fe(NO_3)_3$, $K_3[Fe(CN)_6]$ and $NH_4Fe(SO_4)_2$. The resulting polyeugenol-Fe was filtered and dried, then crosslinked with 0.96 g (1 mol) of PEGDE (Polyethylene glycol diglycidylether) (Mr 500); the resulting product was Polyeugenol-Fe-PEGDE. Further, the bounded Fe (III) ion was released by washing using acid (HCl) to produce imprint cavity. The binding reaction of Fe (III) template (in this case $Fe(NO_3)_3$ in example) to polyeugenol is shown in Figure 1a-d.

The test of Fe content released was carried out by adding KSCN as a complexing agent, the filtrate changed color to red indicating the presence of Fe metal that was released from the polymer. The reaction is [9]:

$$3SCN^- + Fe^{3+} \rightleftharpoons Fe(SCN)_3$$

The test was undertaken until the filtrate did not form a red complex when KSCN was added. The washing filtrate was analyzed using UV-Vis spectrophotometer at a wavelength of 460 nm for 6 days. The graph of Fe template release was shown in Figure 2.

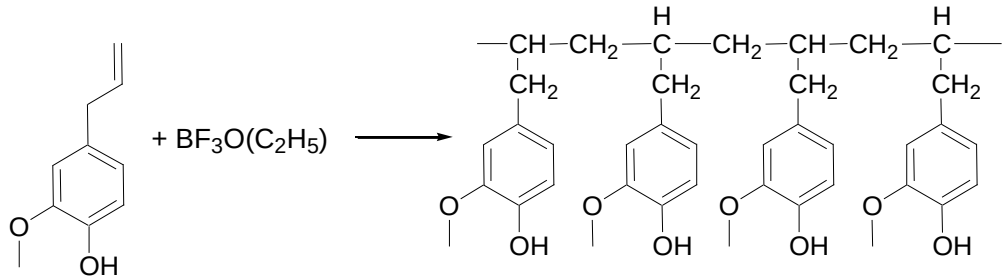


Figure 1a. IIP Synthesis: Polyeugenol Polymerization

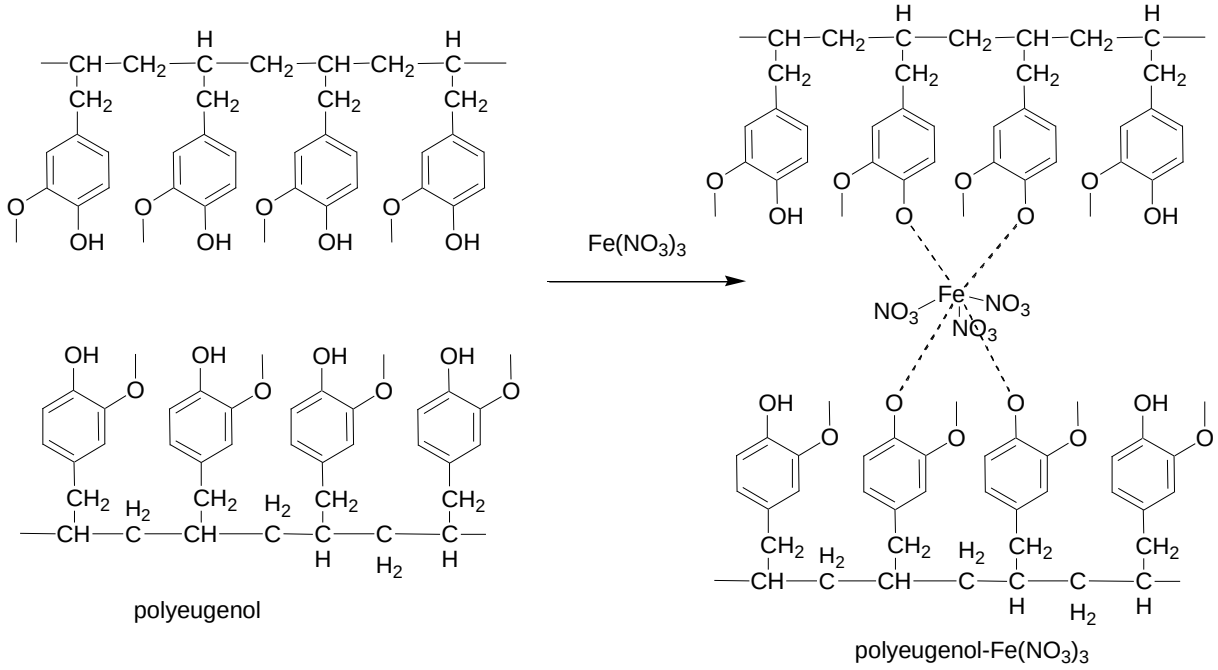


Figure 1b. IIP Synthesis: Binding of Ion Imprint, Fe (III)

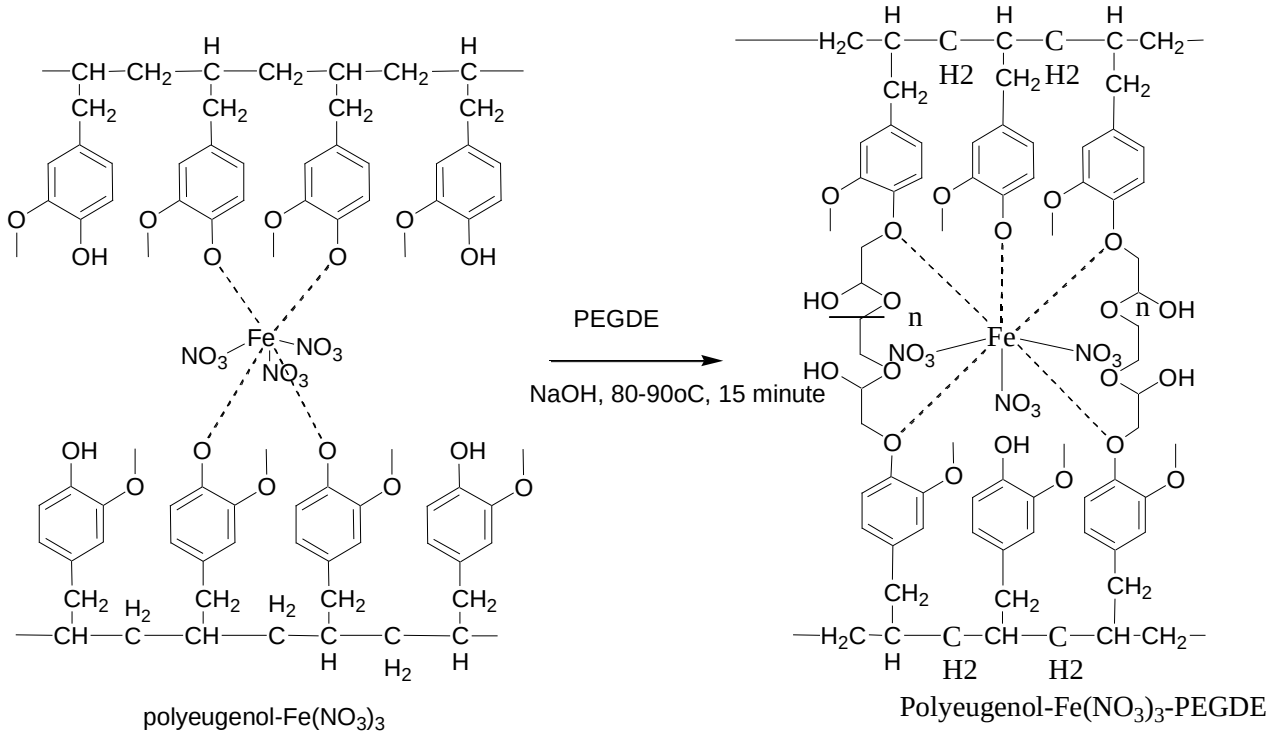


Figure 1c. IIP Synthesis: Crosslinker, PEGDE

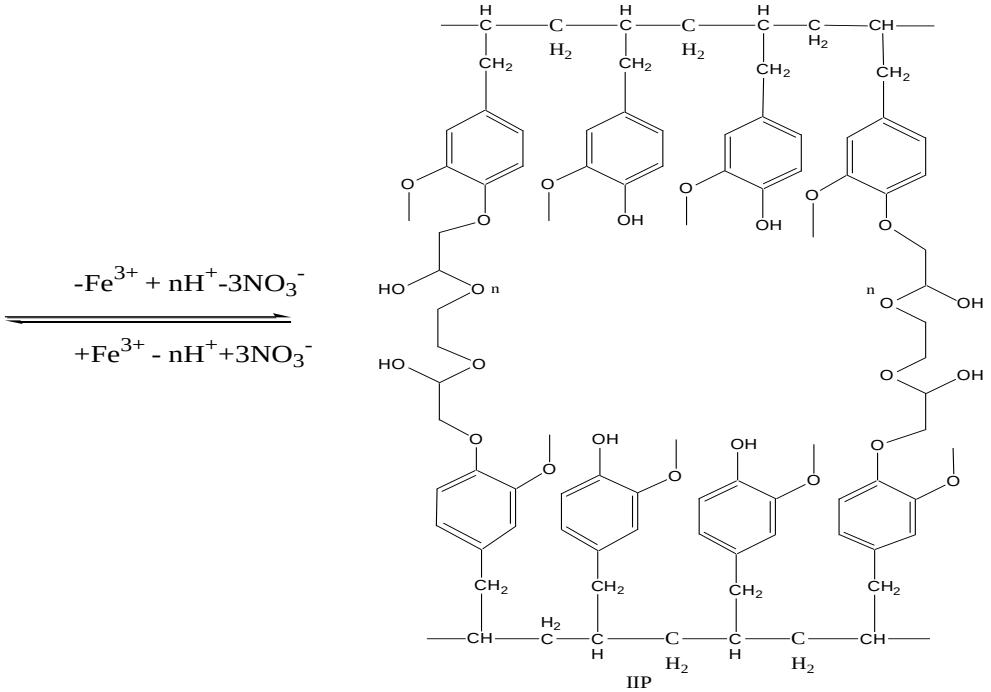


Figure 1d. IIP Synthesis: $Fe(NO_3)_3$ release

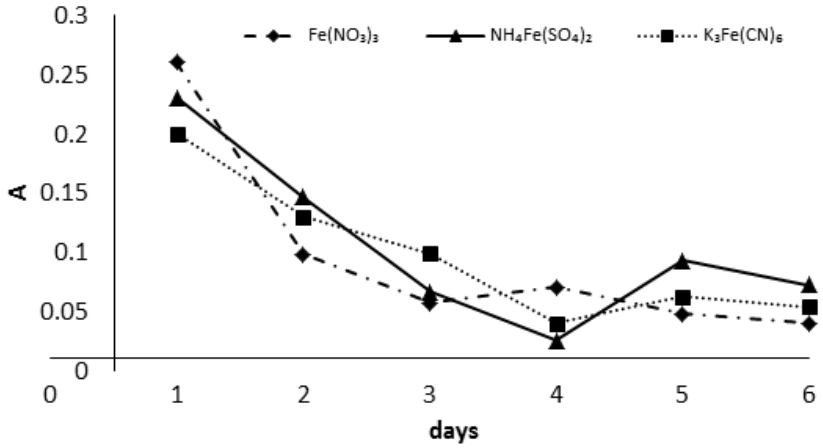


Figure 2. The graph of Fe template release

Polyeugenol synthesized using $Fe(NO_3)_3$ as template was able to bind Fe (III) higher than that of other templates; this was proved by generating high absorbance value in the acid release process. The resin which has been removed from the template is then dried and can be used as an adsorbent to adsorb metals.

3.3 Synthesis of NIP (Non-Imprinted Polymer)

The procedure of the NIP synthesis was similar to that of IIP synthesis but without binding of Fe (III) ion. Here is the reaction of NIP formation (Figure 3):

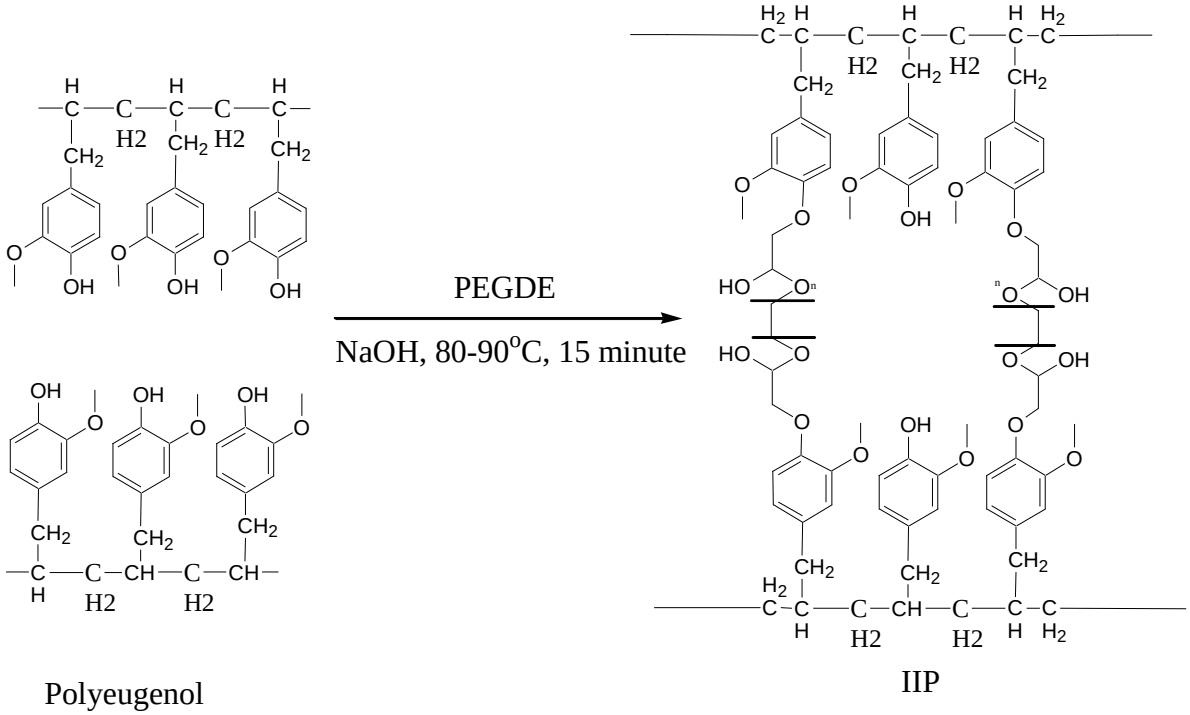


Figure 3. NIP Synthesis

The result obtained was further used as an adsorbent for metal adsorption to be compared with the IIP adsorbent.

3.4 FTIR analysis

From the analysis using FTIR, it can be seen that the -OH spectrum in polyeugenol decreased in intensity when Fe (III) was added because it bound Fe (III) and the intensity decreased when it was cross-linked using PEGDE (Polyeugenol-Fe-PEGDE). This intensity then rose again after the Polyeugenol-Fe-PEGDE polymer released Fe-containing ion using acid (HCl) to produce IIP. The IIP spectrum is sharper than NIP and NIP acid, indicating the role of -OH in IIP work. This can be seen in Figure 4 until 7. FTIR analysis results can be seen in the Figures 3-5, and The comparison of FTIR spectra of template variation can be seen in Figure 6.:

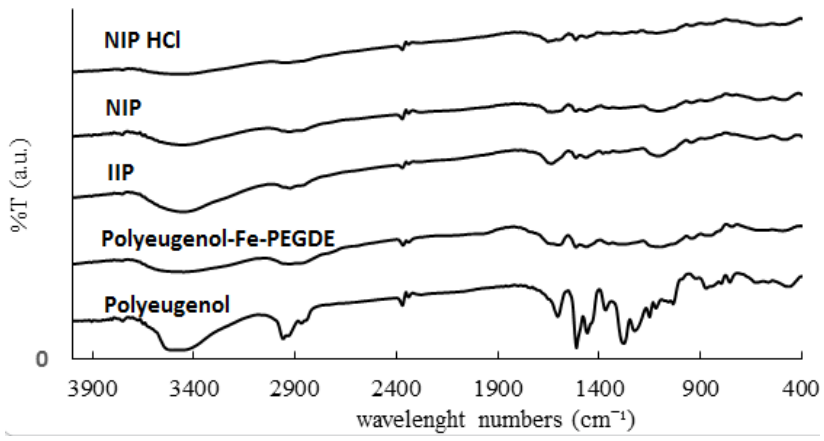


Figure 4. The graph comparison of FTIR spectra of $Fe(NO_3)_3$ template

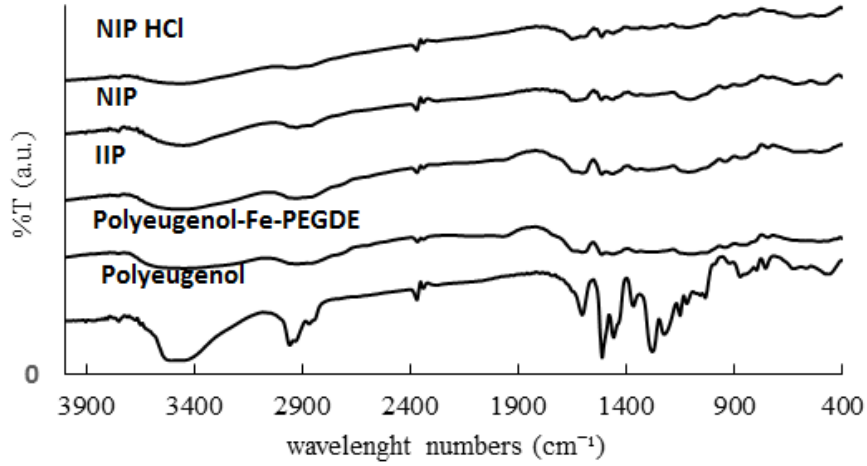


Figure 5. The graph comparison of FTIR spectra of $K_3[Fe(CN)_6]$ template

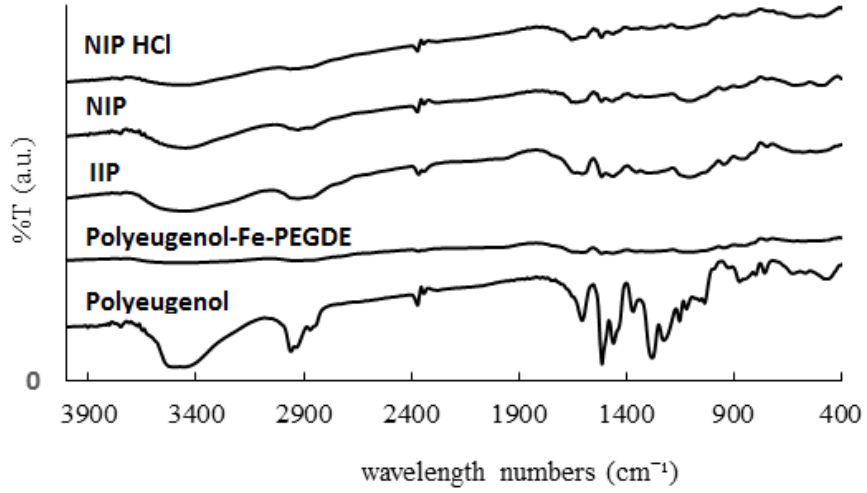


Figure 6. The graph comparison of FTIR spectra of $NH_4Fe(SO_4)_2$

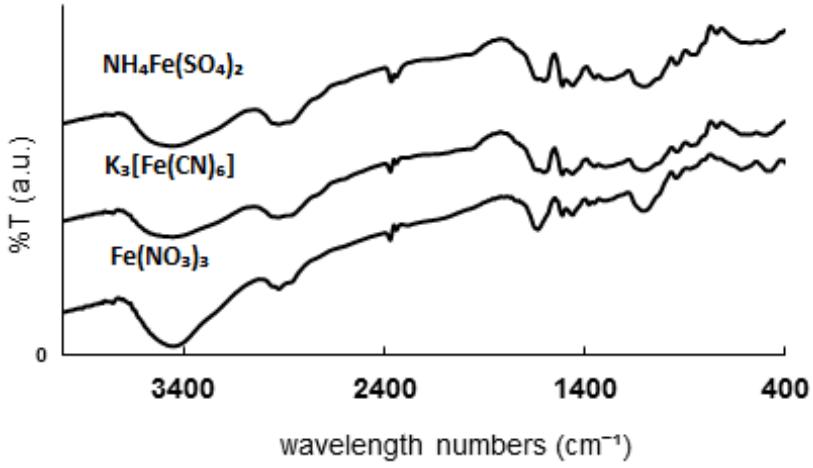
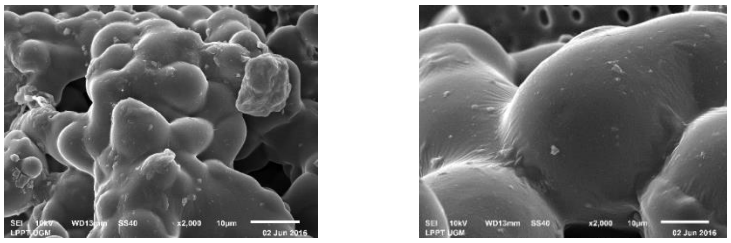


Figure 7. The comparison of FTIR spectra of template variation

3.5 SEM (Scanning Electron Microscopy) Analysis



Polyeugenol-Fe-PEGDE IIP

Figure 8. SEM analysis

Analysis of the products using SEM as presented in Figure 8 shows that the pores of Polyeugenol-Fe-PEGDE are bigger relative than that of IIP. It may be due to the presence of Fe (III) bound while IIP is fairly free from Fe, it could be due to the role of Fe bound and then released from the adsorbent. Djunaidi *et al*. 2015 were found the same phenomena.

3.6 Adsorption Selectivity of Metal Ion

The selectivity of Fe metal ion adsorption based on template variation can be seen in Table 1.

Table 1. Selectivity of Fe metal ion adsorption based on template

Selectivity	IIP of $Fe(NO_3)_3$	IIP of $K_3[Fe(CN)_6]$	IIP of $NH_4Fe(SO_4)_2$	NIP	NIP of acid
Fe-Cr	2.51	1.08	0	0	0
Fe-Cd	1.47	1.51	0.78	0.38	0.07
Fe-Pb	0.75	1.24	1.32	1.31	0

Based on Table 1 it shows that the IIP using $Fe(NO_3)_3$ template produced the greatest selectivity compared to other templates. This is because the Fe (III) solution used for adsorption contained nitrate. so that the adsorption of binary Fe metal was more easily bound to IIP synthesized using the same template. i.e. $Fe(NO_3)_3$. The result of the highest Fe selectivity on Fe-Cr shows that the imprint appropriate with the template was formed. that is the adsorbent was more suitable for Fe metal. although Fe and Cr are in the same group which have similar properties; however. the imprint of the adsorbent was highly selective to Fe metal.

The adsorption selectivity of Fe metal on Fe-Cd binary metal mixture was greater than Fe-Pb since Fe is categorized as a hard acid with small hydrated atomic radius compared to Cd in the soft acid group and Pb in the medium acid group (borderline) which has the greater hydrated atomic radius [10]. The greater the size of the hydrated radius of the competitor metal. the lower of the selectivity of the adsorbent for Fe metal because it inhibited Fe metal to enter the imprint of the template. The template-based selectivity sequence on polyeugenol is $Fe(NO_3)_3 > K_3[Fe(CN)_6] > NH_4Fe(SO_4)_2$.

4 Conclusion

IIP synthesized from polyeugenol with variation of Fe (III) templates $Fe(NO_3)_3$. $K_3[Fe(CN)_6]$ and $NH_4Fe(SO_4)_2$ were successfully synthesized. The adsorption selectivity of Fe (III) metal ion in the $Fe(NO_3)_3$ template was greater than that of in the $K_3[Fe(CN)_6)$ and $NH_4Fe(SO_4)_2$ templates.The adsorption selectivity of Fe was greater in Fe-Cr binary metal compared to in the Fe-Cd and Fe-Pb.

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